ADVANCES IN DESTRUCTIVE AND NON-DESTRUCTIVE ANALYSIS FOR ENVIRONMENTAL MONITORING AND NUCLEAR FORENSICS

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ADVANCES IN DESTRUCTIVE AND NON-DESTRUCTIVE ANALYSIS FOR ENVIRONMENTAL MONITORING AND NUCLEAR FORENSICS

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FOREWORD

The illicit trafficking of nuclear material has been an issue of concern since the first seizures in the early 1990s. This subject has gained increased attention in the context of the recent discussions on the possibilities of nuclear terrorism. In March 2002, the IAEA Board of Governors approved, in principle, a set of specific proposals, or a plan of action, for protection against nuclear terrorism. While the plan emphasizes prevention, it also recognizes that measures are required to detect and respond to malicious acts involving nuclear and other radioactive materials. The combating of illicit nuclear trafficking remains important in the plan of action.

The need for nuclear forensic science has emerged from the concern over the smuggling of nuclear materials. Its role is to determine the nature of seized material, its intended use and its origin. Much can be learned from the analysis of reported cases of illicit trafficking. What specifically could the material have been used for? Where was the material obtained — in stock, scrap, or waste? Was the small amount seized only a sample of a much more significant quantity? These and many other questions can be answered through detailed technical characterization of seized material samples. The scientific methods used for this purpose are normally referred to as *nuclear forensics,* an indispensable tool for use in law enforcement investigations of nuclear trafficking.

In international safeguards activities, some of these methods are used to analyse swipe samples from equipment or from the environs of nuclear facilities (referred to as 'environmental sampling'). The analysis may identify isotopes that reveal information about past nuclear activities. Nuclear material seized in trafficking can be identified, and a profile of its physical properties created. Such a profile may indicate the source of the material seized, as well as other characteristics that are essential in a criminal investigation. In order to identify the source of the material, comprehensive databases of known nuclear material sources are essential.

The aim of this conference — convened by the IAEA jointly with the Institute for Transuranium Elements, Joint Research Centre, European Commission — was to promote the further development of nuclear forensic methods and international co-operation among laboratories. Another aim was to facilitate access to such capabilities by national law enforcement authorities in investigating and prosecuting nuclear crimes. It is hoped that this conference provided important incentives to enhance co-operation and to bring nuclear forensic methodology to a broader audience and encourage greater use.

A total of 118 participants from 37 countries and 4 international organizations attended this conference, held in Karlsruhe, Germany. These proceedings include the keynote addresses, invited papers, poster presentations and summaries of the technical sessions. The conclusions and recommendations of the conference participants are given at the beginning of this volume.

The IAEA gratefully acknowledges the co-operation of the Institute for Transuranium Elements in convening this conference and the generous hospitality extended to the participants by the Government of Germany.

EDITORIAL NOTE

The Proceedings have been edited to the extent considered necessary for the reader's assistance. The views expressed remain, however, the responsibility of the named authors or participants. In addition, the views are not necessarily those of the governments of the nominating Member States or of the nominating organizations.

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EXECUTIVE SUMMARY

1. BACKGROUND

The scientific methods used for determining the nature of radioactive material seized during illicit trafficking incidents are normally referred to as *nuclear forensics*, and are an indispensable tool for use in law enforcement investigations of nuclear trafficking. The determination of radioisotopes, isotopic and mass ratios, material age, impurity content, chemical form and physical parameters may reveal a nuclear ‘fingerprint’ of the material. Radioactive material seized in nuclear trafficking can be identified, and a profile of the physical properties of the material created. Such a profile may indicate the source of the material, as well as other characteristics that are essential in a criminal investigation. In order to identify the source of the material seized, comprehensive databases of known nuclear material are also essential.

2. AIM OF THE CONFERENCE

The aim of this conference — convened by the IAEA jointly with the Institute for Transuranium Elements, Joint Research Centre, European Commission — was to promote the further development of nuclear forensic methods and international co-operation among laboratories, and to facilitate access to such capabilities for use by national law enforcement authorities in investigating and prosecuting crimes involving nuclear material. Another aim of the conference was to provide important incentives to enhance co-operation and to bring nuclear forensic methodology to a broader audience and encourage its greater use. A total of 118 participants from 37 countries and 4 international organizations attended the conference, which was held in Karlsruhe, Germany. The conference brought together eminent scientists to: exchange information on the contemporary state of the scientific methods in the field; discuss laboratory capabilities and the availability of laboratories with nuclear forensic analytical capability; and identify information on characterized nuclear material profiles.

3. CONFERENCE STATEMENTS

In summarizing the conference, the participants agreed on a number of statements about nuclear forensics and made several recommendations for consideration by the international community.

3.1. General considerations

- Co-operation between the scientific community and the law enforcement organizations must be enhanced and expanded.
- Sophisticated nuclear measurement technology exists that can be applied in nuclear forensics, environmental monitoring (verification) and in other applications.
- The development of nuclear forensics capabilities should consider its preventive dimension.
- There is a need to convey the existence and multipurpose use of these techniques to the international community beyond the non-proliferation and safeguards community.
- The continued development of these techniques as well as their applications need to be ensured.
- Much has been achieved in efforts to establish the basic concepts of nuclear forensics (inter alia through the work of the International Technical Working Group (ITWG)).
- The effective development of non-destructive and destructive methodologies for environmental monitoring and nuclear forensics requires the preservation of knowledge in the nuclear field, in areas such as nuclear engineering, reactor physics, nuclear physics and radiochemistry.

3.2. Legal considerations

- In the context of seizure of nuclear and radioactive material, forensic evidence needs to be preserved.
- Analysis results must meet the quality required in a court of law, including: (a) documented methods and processes; (b) sample management, including chain of custody and sample integrity; and (c) adequate quality assurance/quality control (QA/QC) procedures, including certified reference materials.

3.3. Operational considerations

- A model action plan, developed within the context of the ITWG, may provide a basis for a uniform approach for responding to the seizure of radioactive material.
- Nuclear forensics analyses and the associated training and international support must be made available to a larger number of States. The analyses employ sophisticated and expensive instruments and laboratories that

cannot be justified in most countries. However, all countries may need to have such analyses performed.

- There is a need for reference information on the characteristics of known material types. Several existing databases contain an extensive amount of such information. There is a need to consolidate and further upgrade this information, also when available from commercial companies.
- The need for a broad spectrum of training for both the scientific community and law enforcement was identified.
- All seizures of plutonium and high enriched uranium (HEU) have been made by accident or as a result of intelligence. The capability to detect and characterize these materials needs to be improved.

4. CONFERENCE RECOMMENDATIONS

- The continued development of advanced non-destructive and destructive analytical techniques should be encouraged through topical meetings, including within the IAEA Co-ordinated Research Project on Improvement of Measures to Detect and Respond to Illicit Trafficking of Nuclear and other Radioactive Material.
- Measures to promote closer co-operation between the scientific community, other forensic communities and the law enforcement community need to be put in place, including through the joint development of protocols, procedures and training curricula.
- To ensure a continued viable programme and to make the results available to a larger audience, the results of work performed by members of the ITWG should be integrated into the IAEA nuclear security programme.
- A global ‘network’ of laboratories with identified analytical capabilities to offer analysis for nuclear forensics purposes to countries in all regions should be considered.
- Means and ways to ensure QA/QC through, inter alia, accreditation, round robin tests and proficiency testing should be considered.
- A comprehensive set of reference information should be established. The potential for making information available from different existing databases should be explored, and areas in which additional information is needed should be identified, with due consideration given to the need to maintain the confidentiality of sensitive information and other practical needs.
- A well documented, internationally based QA/QC programme should be established to have a usable and legally defensible nuclear forensics programme.

THE ROLE OF NUCLEAR FORENSICS IN COMBATING ILLICIT TRAFFICKING AND NUCLEAR TERRORISM

(Session 1)

Chairperson

A. NILSSON
IAEA

Co-Chairperson

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European Commission

Keynote Address

THE ROLE OF NUCLEAR FORENSICS IN THE PREVENTION OF ACTS OF NUCLEAR TERRORISM

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Cases of illicit trafficking that involve nuclear and other radioactive materials continue to be reported. Over the past decade, about five hundred cases have been confirmed by States Points of Contact and another three hundred remain unconfirmed. Most of the confirmed cases have a criminal dimension, even if not for known terrorist purposes. Much can be learned from analysis of reported cases: What specifically could the material have been used for? Where was the material obtained, in stock, scrap or waste? Was the amount seized only a sample of a much more significant quantity? These and other questions can be answered through detailed technical characterization of the stolen material. The scientific methods used for this purpose are normally referred to as *nuclear forensics,* an indispensable tool in law enforcement investigations of nuclear trafficking.

The events of 11 September 2001 were a wake-up call for the need for protection against nuclear terrorism. In response to a resolution by the IAEA General Conference, the IAEA Director General has reviewed thoroughly the Agency's activities and programmes with a view to strengthening protection against acts of terrorism involving nuclear and other radioactive materials. A set of specific proposals for protection against nuclear terrorism, a *plan of action*, was approved, in principle, by the IAEA Board of Governors in March 2002. Although the plan emphasizes *prevention,* it also recognizes that measures are required to *detect* and *respond* to malicious acts involving nuclear and other radioactive materials. Combating illicit nuclear trafficking remains important in the plan of action. The implementation of the plan will be funded through Member States' extrabudgetary contributions.

The IAEA has adopted an integrated approach to protection against nuclear terrorism. This brings together IAEA activities concerned with physical protection of nuclear material and nuclear installations, nuclear material accountancy, detection and response to illicit nuclear trafficking, security and safety of radioactive sources, emergency-response measures including pre-emergency measures in Member States and at the IAEA, and the promotion of States' adherence to relevant international instruments.

Also, in the broad perspective of the IAEA's activities to protect against nuclear terrorism, the importance of nuclear forensic capability is recognized. While preventing theft of nuclear and radioactive materials remains the goal, there is always a risk that the prevention measures will be insufficient. Whenever trafficked material is intercepted, it is essential for authorities to learn all they can on the circumstances of the case. Such knowledge will provide important feedback to strengthen the protection of nuclear and other radioactive materials against new thefts or misuse.

Through this conference, the IAEA aims to promote further development of nuclear forensic methods and international co-operation among laboratories, and to facilitate access to such capabilities for use by national law enforcement authorities in investigating and prosecuting nuclear crimes. We are convinced that this conference will provide important incentives to enhance co-operation and to bring nuclear forensic methodology to a broader audience and use.

Keynote Address

FROM ILLICIT TRAFFICKING TO NUCLEAR TERRORISM — THE ROLE OF NUCLEAR FORENSIC SCIENCE

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Abstract

The events of 11 September 2001 reminded us of the importance of taking preventative action in the field of nuclear terrorism as well as measures to mitigate the effects of any such attack. We have seen, in the last 10 years, a new and potentially hazardous form of smuggling: that of nuclear and radioactive materials. The threat of terrorist activities involving nuclear materials has now become a matter of concern. Dispersion of such materials over urban areas, their introduction to the food chain or drinking-water system are examples of currently perceived risks to modern society. Following its early involvement in a large number of cases of illicit trafficking and environmental issues, the Institute for Transuranium Elements developed a new discipline to support Member State authorities to combat illicit trafficking and to deal with criminal environmental issues: nuclear forensic science. Significant expertise and experience have been gained in this area, ranging from scientific development work, actual investigation of a large number of seizures, tools for data interpretation, establishing contacts with competent authorities, and organizing training sessions and workshops in co-operation with the International Atomic Energy Agency, particularly with central and eastern European countries.

1. INTRODUCTION

The conclusions of the IAEA General Conference of September 2002 clearly stated that Member States were called upon “to improve nuclear security and prevent nuclear terrorism”. Furthermore, it was emphasized that the General Conference “welcomes activities in the physical protection of nuclear material and facilities and the prevention and detection of, and response to, illicit trafficking activities involving nuclear and other radioactive materials”. These explicit statements underline the attention that is directed at the issue of illicit trafficking and at the threat posed by nuclear terrorism.

The Institute for Transuranium Elements (ITU) has been involved in the analysis of seized nuclear materials and in combating illicit trafficking since the early 1990s. The activities described above are fully in line with ITU's mission "to protect the European citizenry against the risks associated with the handling and storage of highly radioactive elements to contribute to an effective safety and safeguards system for the nuclear fuel cycle". Based on experience with nuclear material that has been gained by ITU personnel over many years, the Institute can effectively handle seized materials and provide expertise in order to identify possible origin of material and to determine intended uses. This is achieved using the tools (scientific instrumentation, handling equipment, compilation of relevant information) and the skills available. The effectiveness of these efforts is fostered by close co-operation with national authorities (e.g. Bundesumweltministerium, Ministerium für Umwelt und Verkehr Baden-Württemberg, Landesanstalt für Umweltschutz, Bundeskriminalamt, Zollkriminalamt), and investigations resulting from seizures are carried out under contract or in co-operation with these authorities. Collaboration with international authorities (IAEA, International Technical Working Group (ITWG), Europol, Interpol) is also important. Close contacts with other services of the European Commission (DG TREN, DG Enlargement, DG Relex, DG AIDCO) are maintained to ensure optimum information flow and support at all levels. Co-operation with and support from the latter three DGs are of particular importance with respect to combating illicit trafficking in the central and eastern European States. Recent experience has shown that projects with these countries can be successfully implemented with improvements in detection and analytical capabilities and in the national response. Under the guidance of ITU, a national response plan has been implemented in the Ukraine, and similar activities are in progress in all co-operating countries; demonstration exercises are checking interactions among various authorities, and upgrades of measurement equipment have been achieved in Hungary and the Czech Republic. Forensic analytical capabilities are being upgraded in the Russian Federation and a nuclear materials database has been established jointly with the Bochvar Institute in Moscow.

In all of these projects, ITU personnel share their experience and know-how with the relevant authorities and scientists in analytical laboratories to effectively combat illicit trafficking and prevent nuclear terrorism.

2. NUCLEAR FORENSIC SCIENCE

In the event of a seizure of illicit nuclear material, the role of the nuclear forensic scientist can be defined in the following terms:

- To identify the nature of the seized material.
- To assess the immediate danger involved and advise law enforcement authorities on procedures to be followed.
- To confirm whether an offence has been committed under the appropriate nuclear regulations.
- To locate the original source of the material, if possible.
- To identify the possible route to the point of seizure.
- To give an opinion on intended use of the material and/or to advise on suitable decontamination procedures.

The ITU has broad experience in the examination of samples of seized nuclear materials. Cases that have been investigated include the Munich Airport seizure in 1994, in which a suitcase containing a mixture of plutonium and uranium oxides was confiscated by law-enforcement agencies following a tip-off, and, in the same year, the chance discovery of a quantity of high weapons-grade plutonium (99.7% ^{239}Pu) in Tengen on the German–Swiss border.

In addition to these cases, ITU investigated samples of contaminated scrap metal found during a spot-check at the Rheinhafen, Karlsruhe, in 1997. This material was contaminated with highly enriched uranium oxide, and the origin was traced back to the BN10 reactor at Obninsk in Russia. Trade in scrap metal is one of the biggest problems at the present time.

Investigations have also been made in cases where nuclear materials were released accidentally and no criminal intent was involved, such as the Dounreay radioactive particles found in the sea and on the foreshore [1]. These were identified as U–Al matrix fuel particles from the Dounreay Materials Testing Reactor, which had had been washed into the sea some 30 to 40 years before.

A total of twenty-four seizures have been investigated and the ITU has participated in two round robin tests organized by the International Technical Working Group (ITWG).

3. THE NUCLEAR FINGERPRINT

The materials are characterized by their so-called nuclear fingerprint, which consists of the following items:

- Macroscopic parameters (e.g. pellet diameter, height, inner hole).
- Isotopic composition (isotopic fingerprint).
- Elemental composition (major elements and impurities).

— Microscopic parameters (microstructural fingerprint [2]):
  - particle morphology
  - particle size and size distribution
  - grain size and size distribution
  - porosity size distribution and density
  - dislocation density and character
  - precipitation of other phases.

In the case of nuclear materials, chemical and isotopic compositions are the primary factors for determining the nature of a sample, its age and its possible source. However, a sample may consist of a mixture of components, or an attempt may have been made to disguise the nature of the material by deliberately adding substances of different chemical or isotopic composition. In these cases, the microstructural fingerprint becomes an invaluable tool, since the microstructure of a sample can be changed only by complete reprocessing.

Most of the seized samples that have been investigated to date have been in the form of pellets and, thus, relatively easy to identify from their form and dimensions by comparing with information in the nuclear materials database. For example, pellets of uranium oxide (Fig. 1), seized in Munich in 1994, were immediately identified as fuel intended for use in an RBMK type reactor.

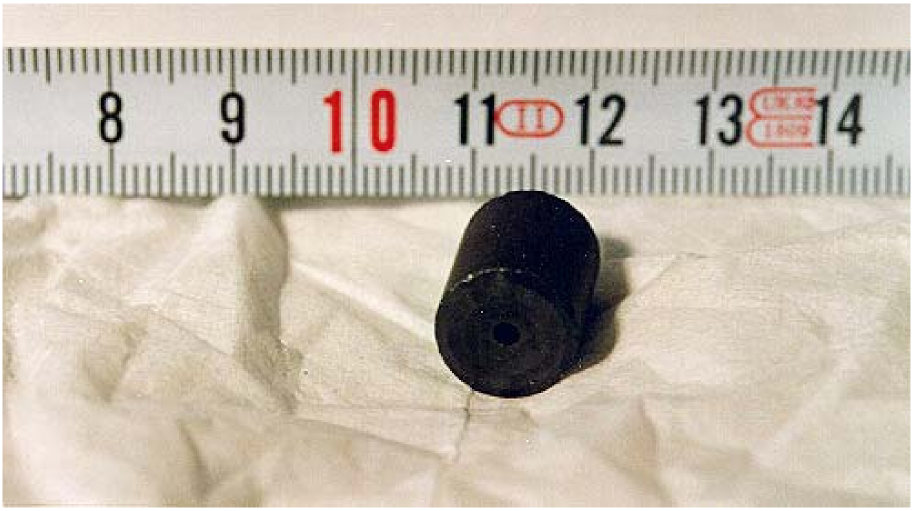

FIG. 1. A uranium oxide fuel pellet from a seizure of material in Munich in 1994 identified from its form, diameter and height, and the presence of a central hole, as a pellet intended for use as fuel in an RBMK reactor.

However, in some cases, the sample consists of a mixture of components that must be separated and analysed individually to obtain meaningful isotopic information. An example of this is the powder shown in the scanning electron micrograph (Fig. 2) of an illicit sample of plutonium and uranium oxides seized at Munich Airport in 1994. The powder can be seen in the scanning electron microscope to consist of three components: plutonium oxide (PuO_2) in the form of platelets (Fig. 2, red arrows), plutonium oxide in the form of rod shaped particles (yellow arrow), and uranium oxide (U_3O_8) as rods of a constant size and a very characteristic hexagonal cross-section (green arrow).

It is now possible to extract individual particles and mount them for analysis by mass spectrometry, using a micromanipulator inside the specimen chamber of a microscope while it is in operation.

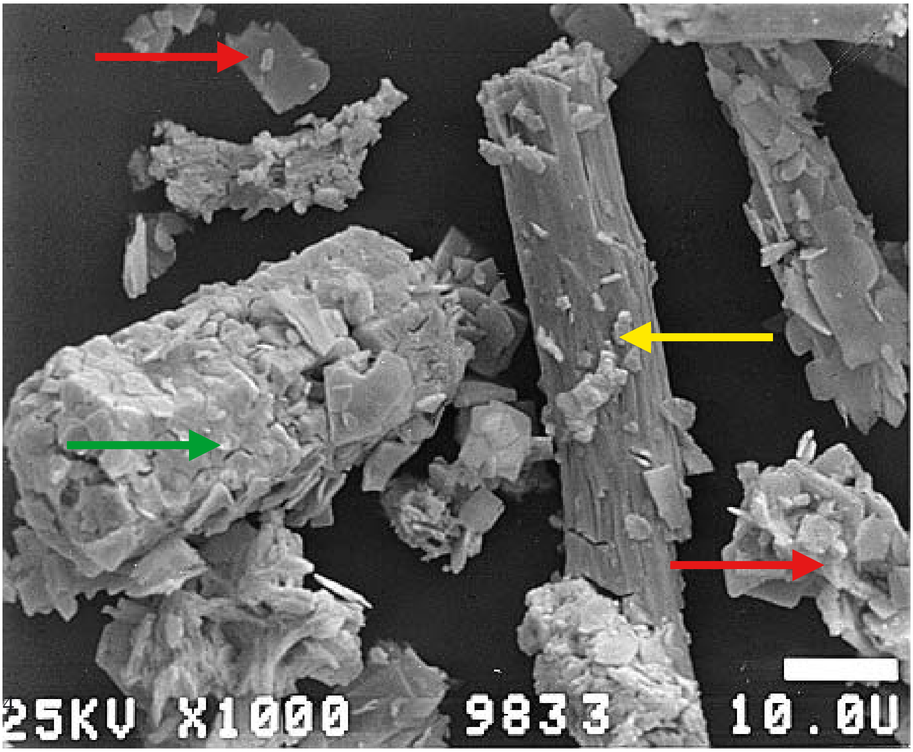

FIG. 2. A scanning electron micrograph of a powder sample seized at Munich Airport in 1994 showing the presence of three components.

As pointed out above, isotopic composition may provide useful information on mode of production and on the intended use of the material. The radioactive decay of the isotopes contained in the nuclear material leads to the build-up of daughter products, which can be used as a built-in chronometer, hence providing information on the age (time elapsed since the last chemical separation) of the material. Using the example given in Fig. 2 (Munich), the isotopic analysis of the plutonium particles showed that the material was of low burn-up and attributable (according to the Pu–isotope ratios) to an RBMK type reactor. From the measured ^{236}U/^{240}Pu ratio, an age of 20 years was calculated.

In a more recent case that involved the theft of radioactive material from a nuclear installation under decommissioning, accurate isotopic analysis of the plutonium contained in the stolen items, in contaminated materials and on the clothes of suspect individuals provided useful information for solving this case. Figure 3 shows in a multidimensional graph the plutonium–isotope abundances of different samples, expressed relative to the primary source of contamination (referred to as Q1). It clearly shows that all samples, with the exception of Q9,

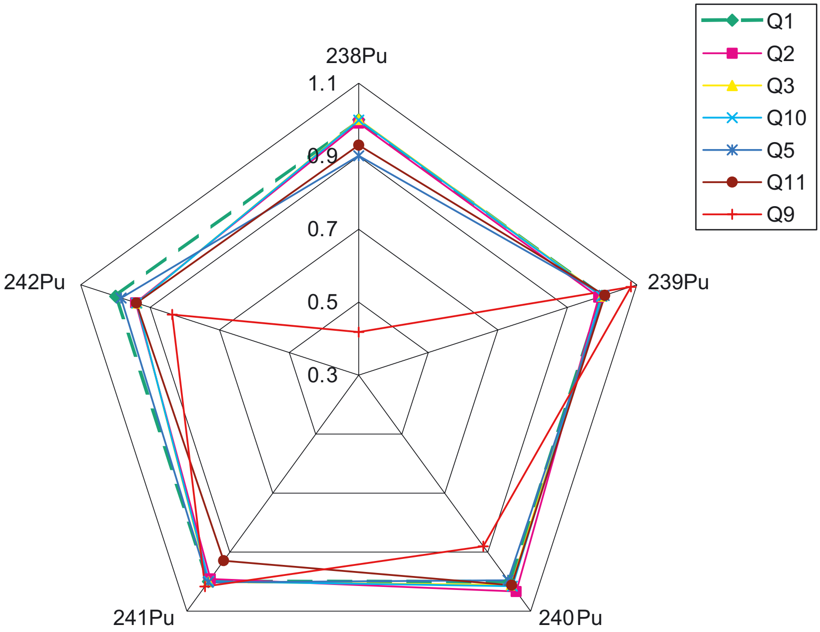

FIG. 3. Characteristic isotopic pattern of samples expressed relative to sample Q1. This multidimensional graph demonstrates that all samples except one had the same isotopic composition. Hence, it was concluded that all samples were contaminated by the same source (namely Q1).

showed very similar isotopic patterns, indicating that they were contaminated by Q1. The significantly different isotopic composition of Q9 may be explained by the extremely low Pu content of that sample. At low concentrations, the contribution of fall-out plutonium from atmospheric weapons tests in the early 1960s becomes a factor, altering isotopic composition.

On the other hand, the activity ratio of the nuclides ^{241}Am/^{137}Cs in the various samples helped to understand how the items were contaminated and which were subject to some kind of ‘treatment’ (e.g. machine washing, leaching through rain water). Different solubilities of the two elements lead to variations in the measured activity ratios.

4. CONCLUSIONS AND OUTLOOK

In order to effectively combat illicit trafficking of nuclear and radioactive materials, effort is needed to enhance detection capabilities, including installation of affordable detectors at a large number of border crossing stations and airports. Furthermore, the methodology for establishing a ‘nuclear fingerprint’ of seized material needs to be perfected, comprising aspects such as isotopic pattern, elemental composition, impurities, microstructural parameters and macroscopic dimensions. The interface with classical forensics needs to be optimized, ranging from the preservation of evidence to the application of fingerprinting, DNA analysis and collection of pollen from contaminated items. The nuclear-materials database needs to be extended.

Simulation and evaluation of nuclear-terrorist scenarios should be performed in order to ensure optimum emergency management. This would also allow the development of methodology that permits the early detection of some “critical” scenarios. Concepts should be developed for contamination measurement and evaluation after a potential terrorist act, in order to contribute to the criminalistic solution of the case.

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THE NUCLEAR SMUGGLING INTERNATIONAL TECHNICAL WORKING GROUP: MAKING A DIFFERENCE IN COMBATING ILLICIT TRAFFICKING

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The International Technical Working Group (ITWG) was first formed in 1995 for the purpose of fostering international co-operation for combating illicit trafficking of nuclear materials. The initial focus for the ITWG was on the development of nuclear forensics to help answer attribution questions regarding nuclear materials of unknown origin. More recently, the ITWG has expanded its focus to include detection of nuclear materials during transit. In this paper we present key developments and potential impact for combating nuclear smuggling.

The initial focus of the ITWG was to write a status report on international co-operation on nuclear smuggling forensic analysis. The twenty-six page report summarized work on nuclear forensics and gave an initial analysis on prioritizing techniques and methods for forensic analysis regarding source and route attribution. It was submitted to the G-8 countries, and, shortly thereafter, nuclear forensics was endorsed at the Moscow summit in April 1996, as part of an anti-illicit-trafficking programme. The work of the ITWG was noted also at subsequent summit declarations, e.g. Cologne.

The ITWG's primary goal is to develop a preferred approach for nuclear forensic investigations that is widely understood and accepted as credible. The technical elements include: (1) development of protocols for (a) collection and preservation of evidence, and (b) laboratory investigation, (2) prioritizing of techniques for forensic analysis, (3) development of forensic databanks to assist in interpretation, (4) executing inter-laboratory exercises, and (5) facilitating technical assistance to countries upon request.

Protocols have been developed jointly by law-enforcement officials and laboratory scientists. A major focus during much of the past six years has been the development of a model action plan for nuclear forensics. This action plan sets out necessary elements in the event of discovery of illicit nuclear material, e.g. incident response, crime scene analysis, collection of evidence (both radioactive and 'traditional' forensics, transportation to a nuclear facility, subsequent laboratory analyses) and then development of the case. The action plan recommends categorizing the special nuclear material (SNM) (i.e. weapons-grade, weapons usable, or reactor-grade) in the field when possible.

The ITWG meetings included reports from scientific studies that help to advance nuclear forensics. For example, at our meeting two years ago (ITWG-6 in Vienna) the following topics were presented: age-dating and source attribution for plutonium production, verification of assumptions in age-dating of nuclear materials, a follow-up study on the plutonium sample that was used in a round-robin experiment, the initial results of an investigation of the characteristics of nuclear materials that might be used to identify the location of fabrication plants, and the Illicit Trafficking and Radiation Assessment Programme (ITRAP) study by the IAEA on detection at border crossings.

Many potential forensic clues cannot currently be interpreted due to the lack of appropriate databases. Several years ago, this need led to a joint effort by the Russian Federation and the European Commission (at the Institute for Transuranium Elements (ITU)) to develop a forensics databank. They have developed a structure for the database that naturally complements questions that are raised during investigations. Some of the information in the databank is jointly shared, while other data entries are accessible only with appropriate authorization. In addition to such a formal databank, the ITWG recognizes a future need to develop a network of experts with appropriate access to databases in order to assist others in interpreting results from nuclear forensics investigations.

International exercises have been instrumental in helping the ITWG to assess the value of various experimental techniques for addressing attribution questions. Our first exercise involved a sample of Pu, and the second focused on a sample of highly enriched uranium (HEU). These exercises provide a concrete focus for discussions of the pros and cons of various forensics measurements and their interpretation. The goal is to share information on nuclear forensic investigations, rather than to foster competition between laboratories.

Numerous examples can be cited of how the ITWG has provided assistance to countries that are developing programmes for combating illicit trafficking. Again, using the ITWG-6 meeting as an example, reports were presented by representatives from Latvia, Hungary and Ukraine on recent progress that specifically drew upon earlier work by the ITWG. In the latter two countries, exercises were held that included a test and demonstration of the ITWG's model action plan for nuclear forensics. In another presentation, a case was reported from Bulgaria on intercepted HEU that was subsequently analysed in another country with the necessary specialized laboratory facilities.

Several years ago, the ITWG began to address the issue of detection of SNM during transit. This topic frequently arises due to the technical linkage between nuclear forensics and radiation detection. Furthermore, many of the ITWG participants are directly involved in detecting transit of nuclear materials. One product was an evaluation of a survey of border detection systems. This evaluation helped to summarize the information provided, and recommendations were made for possible future improvements.

Because the ITWG is a highly informal group, the annual meetings are the principle means of communication. Increasingly, however, it is using task groups to continue work between meetings. Examples of the subjects of recently formed task groups are: plutonium isotopics of reactors, HEU detection research needs, identification of databases and experts in nuclear forensics, and IAEA/ITWG co-operation.

FEDERAL BUREAU OF INVESTIGATION'S USE OF NUCLEAR FORENSICS IN COMBATING ILLICIT TRAFFICKING AND NUCLEAR TERRORISM*

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The paper outlines the role, responsibility and use of nuclear forensics analysis by the Federal Bureau of Investigation in combating illicit trafficking and nuclear terrorism. Nuclear forensics is defined and approached from a law enforcement perspective using the objectives of anticipation, prevention, attribution, and prosecution in a court of law. A sustained, systematic and integrated approach is discussed, utilizing established standard operating procedures and protocols between law-enforcement and scientific establishments, as well as challenges that still exist.

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* Only an abstract is given here as the full paper was not available.

ROLE OF EUROPOL IN THE FIELD OF COMBATING THE ILLICIT TRAFFICKING OF NUCLEAR MATERIAL AND RADIOACTIVE SUBSTANCES

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Presented by F. Zablot

Europol is the European Police Agency, based in The Hague, in the Netherlands. Our mandate is to provide the European Union States with support in various areas of investigation of serious crime, including illicit trafficking of nuclear material and radioactive substances.

Within Europol are liaison officers from several non-EU States: Norway, Poland, the Czech Republic and Estonia. We also have two permanent representatives in Washington, who liase with various US law enforcement agencies.

In the field of illicit trafficking, our current activities consist of:

- Acting as a central point of exchange of information between the Member and other States and scientific agencies.
- Analysing cases from a law enforcement perspective to discern recurring patterns, especially based on modus operandi or origin of the smuggled material.
- Developing awareness and knowledge of this rather technical subject among relevant law enforcement agencies through publications and training sessions.

For all of these activities, links need to be established or reinforced between the nuclear science and law enforcement communities, represented by members of the police, customs and/or intelligence services who have little or no understanding of the issues. We participate in conferences and various exercise and training programmes in order to disseminate knowledge.

Communication is the reason for the participation of Europol in this conference, the outcome of which will be summarized, as much as possible, in language accessible to officers with little previous scientific background. We hope to be able to provide them with a synthesis document on what to expect from nuclear forensics and sample analyses, how the analyses can be interpreted, what are the foreseeable delays and constraints, and what are the current and likely future developments.

It is important to mention the need to conduct, in parallel with detailed analysis of the nuclear material, “traditional” forensic analyses, especially on the packaging, shielding container, labels, etc., which can provide valuable information on origin, smuggling routes and individuals involved. The few past years have seen great improvements in this sphere of endeavour, but much remains to be done in terms of preserving traditional forensic evidence (fingerprints, DNA, dust, fibres, pollen) from the outset — usually the seizure of the material — when the first priority is often the radiation and/or the contamination of the sample. It should be kept in mind that the objective of any forensic analysis is to bring evidence to court in order to convict the perpetrators.

In the absence of legal constraints, we invite communication with other agencies on recent nuclear forensic analyses in order to explore similarities and possible links between cases.

FORENSIC RECOVERY WITHIN CONTAMINATED ENVIRONMENTS*

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The Exhibit Handling System, operated by the Anti-Terrorist Branch, has evolved from experience gained in dealing with long term domestic terrorism and subsequent prosecution of offenders. Stringent criminal laws in the United Kingdom in regard to exhibits and forensic evidence require a strict system in order to provide continuity and integrity to every item that comes into the possession of the police. This system also applies to items that are eventually deemed ‘unused’, as nearly all evidence is disclosed to the defence. I believe that if a system can withstand the close examination that British Criminal Law provides, it will probably be suitable in most countries.

The system relies on each item being supplied with a documented trail of all persons who have had possession of it, and who have opened the security packaging for examination purposes.

In contaminated environments, the initial process within the system has to be adapted to ensure strict monitoring of items during packaging. It is also recognized that access to many exhibits will be heavily restricted, therefore protocols are in place to examine the evidence at the packaging stage in order to avoid unnecessary spread of contamination. The protocols are similar for radiological and nuclear incidents as well as for chemical and biological incidents. Regardless of the type of incident, the system can be adapted on the advice of the relevant scientific authority. In the United Kingdom, the Atomic Weapons Establishment (AWE), Aldermaston, has authority for radiological and nuclear incidents.

The integrity and continuity regime should be continued within the laboratory in which a recovered exhibit is examined. It is also important that nuclear forensic laboratories do not overlook traditional evidence, such as DNA, fingerprints and fibre traces. Good record photography of items that are unlikely to be released by the laboratory is essential.

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* Only an abstract is given here as the full paper was not available.

Finally, every effort should be made to avoid cross-contamination, which has, in the past, been a major issue in terrorist trials. This requires adherence to strict protocols at all stages of a forensic investigation, particularly at recovery and at subsequent examination.

DEVELOPMENT OF AN ELECTRONIC ARCHIVE ON NON-CONVENTIONAL FUELS AS AN INTEGRAL PART OF A NUCLEAR FORENSICS LABORATORY

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Abstract

The development of a database on nuclear-fuel materials is described, for use in a nuclear forensics laboratory. It is designed for analytical evaluation of laboratory-generated data. Along with two existing modules, one on fuel-fabrication data and one on analytical techniques, the database is now complemented with an electronic archive containing non-conventional literature information on nuclear materials. The development of this third module is necessary to extend identification beyond fuel used in commercial or typical research reactors. A pilot project on setting up such an archive was completed a contract between the Institute for Transuranium Elements (Karlsruhe) and the A.A. Bochvar Research Institute of Inorganic Materials (Moscow, Russian Federation). The specific purposes, organizational method and main results of the project are described. A preliminary analysis of the information contained in the relevant documents is presented and a possible approach for integrating the literature archive into the nuclear forensics laboratory is discussed.

1. INTRODUCTION

In order to combat illicit trafficking of nuclear materials, an analytical centre comprising three research laboratories was set up at the A.A. Bochvar Research Institute of Inorganic Materials (VNIINM). The centre includes a nuclear forensics laboratory in which the following are performed:

- Identification of fissile materials of unknown origin;

- Installation and maintenance of the database (DB) on nomenclature, properties, characteristics of fissile materials, and on fuel suppliers and consumers;
- Checks and comparisons of data from different laboratories internationally to ensure uniformity of measurements.

A conceptual plan of the laboratory was developed under a contract with the European Commission's Joint Research Centre. Accordingly, several activities are under way for methodology improvement, equipment delivery and training of personnel.

Here we describe the development of the DB on nuclear-fuel materials as an integral part of the nuclear forensics laboratory, designed for analytical evaluation of results generated in the laboratory.

2. COMMON DATABASE

In most cases, seized nuclear materials are in the form of fuel pellets of uranium dioxide, of various initial enrichments, that are typically used in commercial reactors [1–5]. These pellets are produced according to certain specifications and are subject to random inspection for conformity with quality-control parameters that can be easily formalized and tabulated. Thus, a material's origin can be identified from a common DB on nuclear-fuel materials that includes nominal values and limits of supplier-specific quality-control parameters [2, 3]. The successive exclusion method gradually reduces the number of possible sources, and, eventually, the DB elucidates the producer as well as the legal user of the material.

Comparison between results of analyses and parameter values stored in the DB allows the optimization of subsequent analyses. Thus, the importance of the existing DB lies in elucidating systematic methods and the use of equipment at VNIINM and the Institute for Transuranium Elements (ITU) for the analysis of seized nuclear materials. The number of analytical methods used varies from four to thirteen depending on the sample type. In some cases, however, it is sufficient to determine only two or three characteristic parameters in a manner that simplifies the typical flow chart of the analysis [6]. Hence, the general approach is flexible to enable rapid adaptation for each specific case of an illicit nuclear-material incident [7].

Mean grain size of the nuclear fuel is a typical characteristic parameter. Figure 1 shows distributions of mean grain size for two suppliers of WWER-1000 fuel pellets [3]; for the first supplier it was 7 to 14 μm, whereas for the second it was mainly in the 15 to 19 μm range. The most probable values for mean grain size were appreciably different. These differences can be explained in terms of production process characteristics.

One main goal of the DB development was the selection of parameters that characterize basic phases of a nuclear-fuel cycle: enrichment, fresh fuel fabrication, in-pile irradiation and reprocessing. At the same time, the parameters should be such that they can be linked with a specific supplier or user of the material. These data:

— must be amenable to tabulation, and
— are, in part, proprietary.

In order to implement a consistent tabular structure, the Oracle Relational Database Management System was chosen as a platform for database installation. A graphical user interface that is based on a successive-exclusion algorithm and uses client applications linked dynamically to data sources, has been developed to simplify the retrieval procedure [2, 3].

Due to the sensitivity of the information stored in the common sector of the DB, an agreement on confidentiality was signed. Thereafter, ITU and VNIINM exchanged representative packages of data containing information on macroscopic parameters, chemical and isotopic compositions and impurity contents. The shared sector of the DB is now in operation and is regularly updated at both institutes.

The existing shared DB ensures the identification of nuclear material originating from a fuel fabrication plant. However, illicit trafficking in nuclear material has resulted in cases in which the sample was not a standard fuel

FIG. 1. Distributions of mean grain size for WWER-1000 fuel pellets of various origins.

pellet. Such samples may have large amounts of additives, may be of non-conventional isotopic content, and may be mixtures of components of varied morphology and chemical composition. Waste, generated during R&D, is of potential danger, since it is difficult to reprocess in small amounts and because of lack of value as compared to the nuclear material prior to use. Such materials are stored in a wide range of nuclear laboratories and research institutes where they were manufactured, handled and studied.

In order to link investigation results with a definite source — a fuel cycle facility, a research institute or a nuclear reactor — a broad understanding is required of production processes and intended uses; appropriate technological and analytical parameters should be known. Although these data are, to a certain extent, freely available in the literature, only a limited number of publications describe material microstructure or content of impurities introduced at particular stages of fabrication. Therefore, a decision was made to set up a historical literature archive to complement the existing DB and to systematize information from diverse text documents.

For such a wide range of materials, it has been difficult to adapt some characteristic parameters into the tabular structure. Hence, the next phase of DB development will be the creation of an additional text module. The structure of the DB will then include:

- A fuel fabrication module containing data from commercial reactor-fuel suppliers.
- An analytical module containing information on methods and equipment for nuclear material characterization.
- A text module comprising a electronic archive of information from non-conventional literature on nuclear material.

3. HISTORICAL LITERATURE ARCHIVE

3.1. Purpose

The main goal is the creation of an archive of literature — containing data on nuclear material used in research and in the nuclear industry — that was published in the Russian Federation or the former Soviet Union. These literature sources are not directly accessible in Western Europe. Such a system will help trace nuclear material and extend possibilities of identification beyond fuels used in commercial and typical research reactors. Moreover, it will prevent eventual loss of such relevant information.

Specific purposes:

- To link the results of an investigation with a specific fuel cycle facility or research institute;
- To systematize information from diverse text documents on materials:
  - Produced for non-conventional nuclear reactors;
  - Not used for batch production;
  - No longer produced;
- To archive corresponding information about the producer, location and date of manufacture of the material.

3.2. Organization and method

The pilot project, to set up an electronic archive, completed in 2002 under a contract between ITU and VNIINM, involved the following activities.

Phase 1 was devoted to analysis of information contained in literature sources and to the preparation of a list of documents of potential interest for identification of seized nuclear materials. A search profile for each literature source was formalized and keywords were defined for information retrieval in card-files and a bibliography. The preliminary selected relevant documents were categorized into common and separate sectors. The common sector of the archive includes documents from sources difficult to access in Western Europe (Russian and Soviet conference reports, preprints, reviews, low circulation journals, etc.). The separate sector covers mainly reports from institutes and facilities of the Ministry for Atomic Energy of the Russian Federation (Minatom).

During Phase 2 of the project, literature sources published between 1972 and 2001 were processed digitally. Each document entry was provided with keywords and an abstract. Full-text documents that are of interest for identification purposes have been transformed into electronic format.

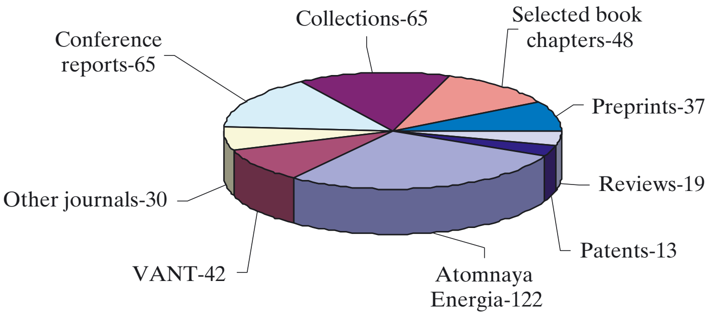
3.3. Volume and categories of relevant documents

Table I shows the relative abundance of special terms in Russian literature sources dispatched to the International Nuclear Information System (INIS) over the past 30 years. Taking into account possible cross-referencing of the terms, the number of sources was probably not more than a thousand.

The new electronic archive mainly comprises sources not covered by INIS. Figure 2 shows the categories of the documents already inserted, or are prepared for insertion, into the archive. Although the number of documents is small so far, it can be correlated with the volume of the corresponding Russian sources dispatched to INIS. The distinctive feature of the archive is that it contains full-text electronic versions of documents, most of which are very difficult to access.

TABLE I. ABUNDANCE OF SPECIAL TERMS IN THE RUSSIAN DOCUMENTS DISPATCHED TO INIS

Term	Abundance
Highly enriched uranium	94
Highly enriched plutonium	11
Uranium alloys	991
Plutonium alloys	109
Uranium carbides	177
Plutonium carbides	45
Uranium nitrides	72
Plutonium nitrides	22
Uranium silicides	20
Plutonium silicides	4
Total	**1545**



Total documents selected to date: 441

FIG. 2. Distribution of the archive documents by publication category.

Low circulation journals, preprints, and Russian and Soviet conference reports and patents have been proposed for insertion into the common sector of the archive as information sources not covered by INIS. Nine categories of publications have been delineated. Articles from Atomnaya Energia, Questions of Nuclear Science and Technology (VANT) and other specialized scientific journals published in Russian constitute the major portion of the archive.

Additionally are conference reports, collections of scientific papers, selected book chapters, preprints, reviews and patents arranged in descending numerical order. Preprints are “press proofs”, self-published by Minatom institutes, that contain the results of R&D on material properties. The distribution of preprints selected to date from various organizations is shown in Fig. 3. The list of organizations may be enlarged on completing a systematic search in the library and electronic catalogues.

3.4. Publication date and circulation

Accessibility of a literature source is determined largely by the time passed since its publication date. Moreover, it is unlikely that nuclear material produced more than 30 years ago is still in existence. That information on fuel materials has become more readily available is indicated by increases in publication numbers with time (Fig. 4).

As is evident from Fig. 5, a large number of the analysed documents belong to publications that are difficult to access and/or are of low circulation: reviews, preprints and collections of scientific papers with circulations of 50 to 200. Compendium volumes of the Atomnaya Energia and Cosmonautics News have maximum circulations of 3000 to 5000.

3.5. Analysis of the information contained in the documents

A preliminary analysis of document contents shows that the data cover a wide range of nuclear materials (Fig. 6). First, there are potential fuel compositions under development and pilot nuclear materials, which were studied intensively at different times. The list presented below is not complete and the comments are illustrative.

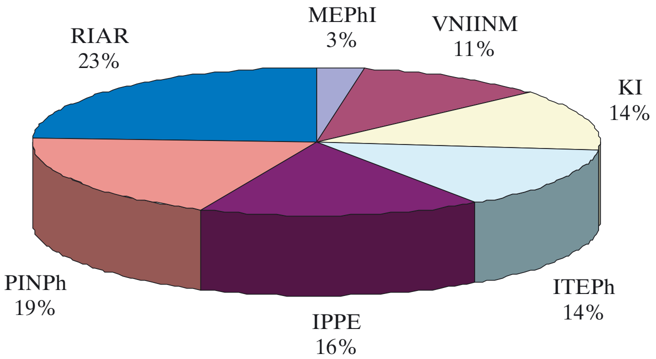


FIG. 3. Distribution of preprints by organization.

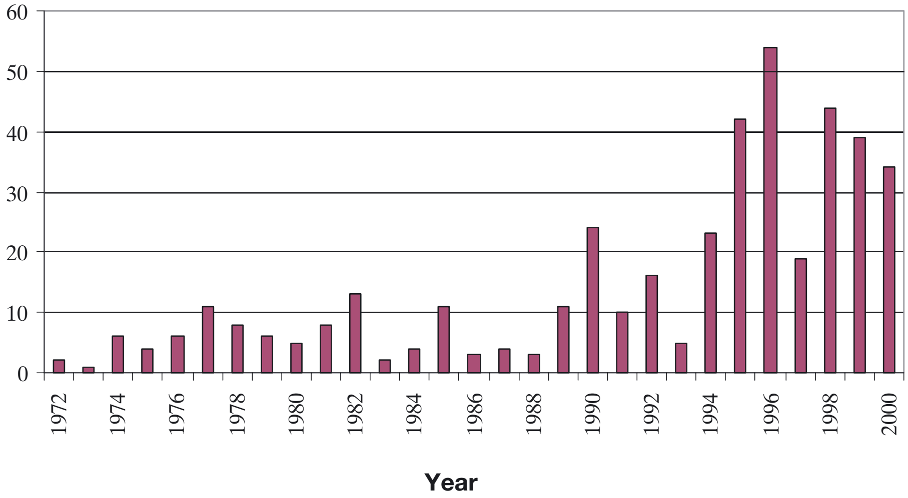


FIG. 4. Distribution of documents by imprint date.

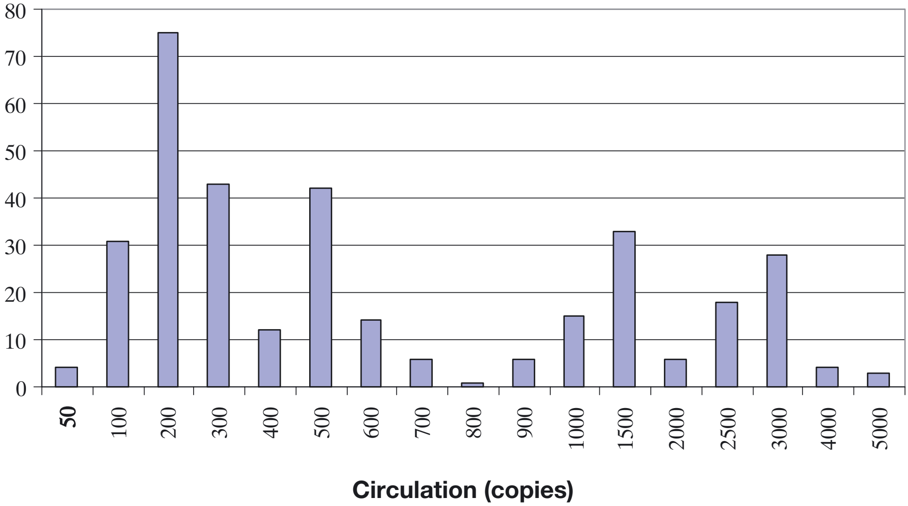


FIG. 5. Distribution of documents by circulation.

Dispersed fuel most widely described in the archive represents plate, annular, cylindrical and variously shaped elements for research and commercial reactors, as well as spherical and hexagonal fuel elements for high-temperature gas reactors (HTGRs). The variety of designs, nuclear materials used and availability of elements of complex geometry make their systematization difficult.

Non-standard oxide fuel differs from batch production in that it may have non-standard geometrical dimensions and enrichment, or may contain alloying additives. Non-standard oxide fuel can also be of non-conventional chemical composition. For example, plutonium dioxide fuel has been produced for the BR-5 fast prototype reactor and the IBR-2 burst research reactor.

Metallic fuel represents uranium-, plutonium, and thorium based alloys treated with various additives in order to achieve required properties.

Studies of **carbide, nitride and carbonitride fuels** (mostly nitrides) are performed with the aim of finding application in fast commercial reactors with liquid metal coolants.

Potential fuel is described in projects in the design–development phase, or in conceptual studies. Proposed designs of a fuel element or a fuel assembly are considered in some publications. Most such projects are far from implementation and describe rather hypothetical material. Although experimental studies of pilot fuel batches were described in one document, no detailed information was presented.

Mixed oxide (MOX) fuel is widely used for thermal commercial reactors in France, Great Britain, Belgium, and Germany, and for fast breeder reactors with sodium coolant in the Russian Federation. It can be vibrocompacted or pelletized and may contain weapons grade plutonium.

Thermionic fuel elements and fuel for nuclear rocket engines are combined due to their space applications. Thermionic nuclear power units are being considered for spacecraft. Serviceability of such units has been demonstrated by the results of the TOPAZ programme. Basic development work on nuclear rocket engines was done in the 1960s, with emphasis on ground tests and irradiation tests of individual units in specially designed IGR, IVG-1 and IGRIT reactors.

Fuels and targets for minor actinide (MA) transmutation are special types of fuel and targets developed for conversion of ^{239}Pu and MAs, ^{237}Np, ^{241}Am, ^{244}Cm, in fast research reactors or accelerator driven systems. The ultimate objective is to remove these highly radiotoxic nuclides from spent fuel by separation and their transmutation to stable or less harmful products. Publications on basic actinide research also fall into this category.

Radionuclide sources and radioisotopic thermoelectric generators (RITEGs) are various radioisotopic products for industrial, research and medical applications. Most are alpha and gamma-sources, radionuclide thermogenerators that may include plutonium isotopes and other transuranium elements.

Spherical coated fuel particles are generally used in HTGRs. There are alternative concepts for implementation of coated fuel particles in light water reactors: filling into a specially designed fuel assembly with water coolant crossflow, and packing into a graphite matrix inside a fuel rod of cylindrical design.

Publications on nuclear materials used in **test facilities and critical assemblies** aid the identification of sites where pilot fuel batches might be tested.

A relation between production process and properties of the produced nuclear material can be found in many documents. Of interest are publications that provide data on effects of process parameters on quality of finished products. However, the number of such documents published in open literature is limited.

Literature sources covering data on a wide spectrum of nuclear fuel materials have been considered, from pilot batches of oxide fuel for commercial reactors to electro-generating channels for nuclear power units used for space exploration, fuel for nuclear rocket engines and targets for MA transmutation. It is an open question as to which of these materials will be of interest for identification purposes. However, at this point, it is clear that the archive under study provides broad understanding of nuclear material production and application methods and may extend the existing common DB. More detailed analysis of the information contained in the documents will be possible after adaptation of the retrieval system to be compatible with the special features of the literature archive.

3.6. Proposals on the integration of the electronic archive

Alternative methods are under consideration for integration of the electronic archive into the existing DB.

(1) Full integration using the Oracle *inter*Media Text software that is already installed in our system platform. The newly developed archive would be an integral part of the existing DB. Text queries would be possible from most Oracle interfaces, e.g. Oracle Forms, Oracle Graphics, SQL*Plus.

In the case of separate storage of information, a classical client server model, based on distributed Internet application or one of the universal systems for document processing, e.g. Lotus Domino or Evfrat Office, can be considered. Such systems have built-in features for full-text search or field search based on abstract contents or other informative fields of the list of documents.

4. CONCLUSIONS

The common DB on nuclear materials is now extended to include an electronic literature archive containing data on non-conventional fuels. As part of the project, the search profile of the relevant literature source was formalized. Keywords were defined for information retrieval in card-files and a bibliography. The preliminary selected relevant documents were categorized into two storage sectors. During the final phase of the project, the literature sources were processed digitally. Full-text documents that are of interest for identification have been transformed into an electronic format.

Preliminary analysis of the information contained in the documents demonstrates that this literature archive — in combination with an up-to-date retrieval system — can be used as an efficient tool for the identification of nuclear materials originating from research centres.

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CURRENT CAPABILITIES AND PAST EXPERIENCES

(Session 2)

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INTERNATIONAL TECHNICAL WORKING GROUP ROUND ROBIN TESTS

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Abstract

The goal of nuclear forensics is to develop a preferred approach to support illicit-trafficking investigations. This approach must be widely understood and accepted as credible. The principal objectives of round robin tests conducted by the Round-Robin Task Group within the Nuclear Smuggling International Technical Working Group are to prioritize forensic techniques and methods, evaluate attribution capabilities and examine the utility of the database for attribution. The HEU (high enriched uranium) Round Robin and the previous Plutonium Round Robin have made significant contributions to fulfilling these goals through a collaborative learning experience that resulted from the outstanding efforts of members of eleven participating laboratories in ten countries. A prioritized list of techniques and methods has been developed based on these exercises. Current work is focused on the extent to which the techniques and methods can be generalized. The HEU Round Robin demonstrated a rather high level of capability to determine important characteristics of the materials and processes using analytical methods. When this capability is combined with the appropriate knowledge/data base, it results in significant capability to attribute the source of a material to a specific process or facility. Shortfalls were also identified in current capabilities, including procedures for non-nuclear forensics and lack of a comprehensive network of data/knowledge bases. The results of the round robin will be used to develop guidelines or a "recommended protocol" to be made available to interested authorities and countries for investigative use.

1. INTRODUCTION

A Nuclear Smuggling International Technical Working Group (ITWG) was created in 1996 to combat illicit trafficking in nuclear materials and radioactive substances under the auspices of the P-8 Non-Proliferation Experts

Group (NPEG). The primary purpose of the ITWG is to provide technical co-operation and collaboration on the development of nuclear forensics. Participants in the ITWG are from a broad range of backgrounds including law enforcement agencies, safeguard authorities, customs, non-proliferation organizations and the scientific community.

The goal with nuclear forensics is to develop a **preferred approach** to support investigations of illicit trafficking. The approach, which must be widely understood and accepted as credible, will evolve and improve with acquired experience and technical developments. The description of the preferred approach should include a listing of technologies along with a specified means of interpreting data. Success in meeting this goal would provide the basis for the international community speaking with one voice regarding technical evaluation of illicit trafficking cases.

Technical elements for the ITWG's work on nuclear forensics currently include:

- **Developing protocols** for collecting and preserving evidence that meet requirements of specialized laboratories; in addition, developing protocols for laboratory investigations;
- **Prioritizing techniques and methods** for forensic analyses of nuclear and non-nuclear materials associated with illicit nuclear-materials trafficking to address questions regarding source attribution, route attribution and intended use of the materials;
- **Developing forensic databanks** to assist in the interpretation of analytical results.

To support these elements, the ITWG has formulated recommendations and has executed two international interlaboratory exercises to evaluate and improve the effectiveness of forensic techniques and methods. To this end, the techniques and methods of forensic analysis of seized nuclear materials are assessed and compared. This paper describes the major achievements of the two exercises, and focuses on results from the HEU Round Robin.

2. OBJECTIVES OF THE ITWG ROUND ROBIN TESTS

The principal objectives of the round robins were to prioritize forensic techniques and methods, evaluate attribution capabilities (i.e., determine the sources of the materials) and examine the utility of existing databases. The round robin exercises are intended to be a collaborative learning experience for the scientific, safeguards and law enforcement communities, and not a performance evaluation of individual laboratory participants.

Members of six laboratories participated in the analysis phase of the Plutonium Round-Robin Test performed in 1999 to 2000, and of nine laboratories in the HEU Round Robin (2000–mid-2002). The laboratories participating were:

- Austrian Research Centre, Seibersdorf, Austria;
- AWE Aldermaston, United Kingdom;
- CEA Valduc, France;
- Cekmece Nuclear Research and Training Center, Istanbul, Turkey;
- Institute for Transuranium Elements, Karlsruhe, European Union;
- Institut für Radiochemie, Munich, Germany;
- Institute of Nuclear Chemistry and Technology, Warsaw, Poland;
- Institute of Isotope and Surface Chemistry, Hungary;
- Lawrence Livermore National Laboratory, United States of America;
- Lithuania Institute of Physics, Vilnius, Lithuania;
- Nuclear Research Institute, Rež, Czech Republic.

The authors accepted responsibility for the organization, co-ordination and evaluation of the exercises on behalf of the ITWG Task Group. Attendees of the HEU Round-Robin Task Group Meeting in Luxembourg in June 2002 are shown in Fig. 1.

Two types of material were selected for the exercises: (1) **plutonium oxide** originating from the civil cycle within the European Union, which is no longer proprietary; and (2) **high enriched uranium oxide** of undeclared history, which was provided by the Czech Nuclear Research Institute in Rež. The oxide forms of the materials were selected because transportation requirements were less restrictive; nevertheless, transportation presented a major obstacle for timely prosecution of the exercise.

The reprocessed plutonium oxide originated from a batch of three pressurized water reactor (PWR) fuel elements irradiated in a 1890 MW(th) (ca 600 MW(e)) European reactor with an initial ^{235}U fuel enrichment of 3.28 w%.

The Nuclear Research Institute in the Czech Republic provided the high enriched uranium oxide (90% ^{235}U) powder for the exercise. The history of the material was not declared, but it was reported to be similar to materials seized in Prague in 1994. Non-nuclear forensic evidence (i.e., fingerprints, seeds, plastic shopping bags, and a handwritten map on a beer coaster) was added to the sample and incorporated in the scenario in recognition of the importance of standard forensic evidence in such cases.

3. TEST ELEMENTS AND PROCEDURES

The ITWG organized the interlaboratory comparison (round robin) exercises to have the broadest possible participation by encouraging all ITWG members to contribute, even if they were unable to participate in the sample analysis itself. Considering the wide variation in expertise of the ITWG participants, one of the purposes of the round robin was to provide a common problem set from which to compare nuclear forensic techniques and methods. Obviously, a large variety of forensic techniques could be applied, depending on the type of package, the physical/chemical form and quantity of the material, the technologies available in the laboratories, etc.

These round robin exercises were performed in two distinct phases:

(1) Sample analysis at **the individual participating laboratories**,
(2) Prioritization of the techniques and methods, evaluation of the forensic capabilities, and examination of the utility of existing databases, **as a group**.

The first phase of the round robins included the development of analytical data and interpretation of results generated at individual laboratories in the context of available information. Some interpretation of the data could be done based on general principles and a basic knowledge of methods and practices for producing nuclear materials. Other, more specific interpretations

FIG. 1. Round-Robin Task Group, Luxembourg, June 2002.

relied on specific production knowledge, records, and access to process and safeguard databases.

During the second phase, the Round-Robin Task Group participants discussed the value of, and prioritized, techniques and methods.

The following general scenario was developed to help focus the investigations:

Police seized materials that appear to be, or are declared by the smugglers as being, nuclear. Therefore, the competent authority decides to send the apprehended items, with the appropriate precautions and without delay, to a laboratory for forensic analysis.

The HEU exercise encompassed a more sophisticated scenario, similar to real cases, that included people, places and organizations that were consistent with the presence of common forensic elements of fingerprints, seeds, a plastic shopping bag, and a drawing on a beer coaster.

The participants were asked to address some specific questions that were intended to help elucidate on the attribution of the samples. Similar questions were asked by law enforcement authorities in actual cases in Europe in the 1990s:

- What is the material?
- Does it represent a hazard or threat?
- Do legal provisions govern the material?
- What are its potential uses?
- What is the source?

In the light of experience with real cases, it also appeared important to identify what information could be made available to answer the questions of investigators, prosecutors and decision makers in (1) **24 hours,** for a first assessment, (2) **1 week,** for more precise information, and (3) **2 months,** for a comprehensive report.

The first assessment (24 hours) focused on issues associated with the safety of responders and law enforcement personnel, public health and safety, and determining if there was criminal activity or immediate threat. In real cases, it is necessary to provide certain information within a very short timespan to enable prosecutors to decide how to address the case and decide whether suspected smugglers should be detained.

The second assessment (1 week) was focused on issues associated with the preliminary forensic analyses and collection of evidence to develop leads for the investigators. It is necessary to provide investigators with the results of analyses for confirmation of information to guide the investigation. Timely transmission of the second report to the police and legal authorities, even at the political level, is of great importance and, in practice, should occur within 1 week of receipt of the seized material.

The third assessment (2 months) was focused on issues associated with comprehensive forensic analysis and attribution of the materials, to provide new leads for investigation and evidence for prosecution. In real cases, it is necessary to provide investigators with as much forensic data as possible to support the investigation and to provide prosecutors with the evidence necessary to prosecute the crime.

Variations in arrival time of samples and start of the analyses were unavoidable due to transport constraints. Therefore, each laboratory was asked to identify a start time ("time zero") at receipt. Thereafter, a 2 month period was allocated for analyses and attribution. Each laboratory was asked to communicate its time zero as a part of the 24 hour report. Special report forms included specific questions to be addressed for each reporting period. Moreover, it was suggested that each group introduce a sequential approach by recording techniques used and results obtained after the first 24 hour period. The same information was again requested after 1 week and 2 months. This information was important in determining what techniques were the most useful and the most available.

Confidentiality of data and the laboratory's anonymity were granted, as is the case for other round robin tests. The organizing committee assigned each laboratory a code name, either a volcano (plutonium) or an island (HEU). The code names were used throughout the tests and in all correspondence concerning results and their evaluation.

4. HEU ROUND ROBIN RESULTS

The intent of the HEU Round Robin exercise was to:

(1) Evaluate and improve the effectiveness of nuclear forensic techniques and methods by:
    (a) prioritizing techniques and methods,
    (b) evaluating attribution capabilities,
    (c) examining utility of databases and knowledge bases;
(2) Assess capability of employing non-nuclear forensic techniques and methods;
(3) Provide the agencies dealing with illicit trafficking of nuclear materials and the scientific community recommendations and guidelines **that could be part of a model action plan**.

The results from the HEU Round Robin are based on a set of written questions for a given reporting period, the organizers' expectations of responses and the participants' actual responses. As a result of the information provided in the HEU scenario and the questions provided, each laboratory investigation was initiated, guided and focused. Subsequent laboratory findings augmented the investigation, directing the laboratory scientists towards specific technologies and methods to resolve questions in a particular reporting period.

Within the first **24 hour reporting period**, the scientists were able to address health and safety concerns, and took precautions to preserve and collect fingerprint evidence, note that the material in question was HEU, and in some laboratories they were able to obtain initial indications of relative abundances of other uranium isotopics. In all of the laboratories it was noted that the material in question constituted a hazard.

Within the **first week**, participants in most of the laboratories were able to locate fingerprints (which, in all cases, were deemed unsuitable and insufficient for identification); determine accurate (final) isotopic and elemental analyses of the sample material; characterize the material as weapons-useable; and describe potential applications and end uses for HEU of the quality and characteristics seen in the samples.

Within the **2 month reporting period**, confirmatory measurements were made with efforts to determine attribution of the samples. Participants were unable to identify the fingerprints introduced in the HEU Round Robin exercise, and in many cases they did not detect seed or plant material evidence. Contrary to the rather homogeneous responses in the Plutonium Round Robin, multiple nuclear processes were cited and attributed to the HEU, as summarized in Table I. In many cases, no attempt was made to provide a country of origin because of insufficient knowledge and/or databases with which to compare their nuclear forensic findings. In four laboratories, age dating data for the uranium (date since last purification or processing) were reported: February to July 1979. Uncertainty in the four age dates overlapped, indicating good agreement.

The reported uranium isotopic abundances and the methods of analysis are shown in Table II. It is noteworthy that the TIMS results from ^{235}U analysis were within 0.1%, and that the multi-collector ICP-MS results were within the TIMS values.

The methods and techniques that provided the best results for a given reporting period were discussed at length by the participants at the HEU Round-Robin Task Group meeting in June 2002 in Luxembourg, the results of which are in Table III. The binning of these technologies was similar to the resultant binned technologies for the Plutonium Round Robin, but completion was generally more timely.

TABLE I. HEU ATTRIBUTION — NUCLEAR PROCESS

Laboratory	Nuclear process
Azores	Reprocessed fuel/enrichment plant
Barbados	Enrichment convert to U_3O_8
Borneo	Material test reactor, submarine reactor
Chatham	Special enrichment plant
Galapagos	Gas diffusion plant
Mindanao	Sol–gel precipitation
Tobago	Secondary enrichment after reprocessing
Tonga	Reprocessed fuel
Trinidad	Chemically reprocessed U metal

A number of shortfalls were noted by the participants in, and the organizers of, the HEU Round Robin. These are binned into two categories: procedural and technical.

From a **procedural standpoint**, of predominant concern was the trace contamination that several laboratories identified from the preparation of the samples for the exercise. Contamination control was, obviously, of critical concern. Another feature of running a "legitimate" blind experiment was the

TABLE II. HEU ISOTOPIC ANALYSIS RESULTS

Laboratory	U-234	U-235	U-236	U-238	Method
Azores	0.97	89.99	0.68	8.37	LEGS HRGS ICP-MS TIMS
Barbados		85.6 +/– 3.8 U-235			HPGe
Borneo	0.85 +/– 0.15	86.7 +/–1.5	0.57 +/– 0.08	11.9 +/– 0.9	ICP-MS
Chatham	0.960 +/– 0.001	89.94 +/– 0.06	0.643 +/– 0.003	8.462 +/– 0.006	TIMS
Galapagos	0.96	89.89	0.68	8.47	TIMS
Mindanao	0.96 +/– 0.40	89.91 +/– 0.11	0.678 +/– 0.23	8.443 +/– 1.29	TIMS
Tobago	1.05 +/– 0.07	89.37 +/– 1.8	0.69 +/– 0.05	8.88 +/– 0.2	ICP-MS
Tonga	0.967 +/– 0.001	89.99 +/– 0.02	0.679 +/– 0.001	8.362 +/– 0.005	TIMS
Trinidad	0.955 +/– 0.075	90.01 +/– 0.35	0.673 +/– 0.030	8.365 +/– 0.033	MC ICP-MS

TABLE III. TECHNIQUE AND METHOD PRIORITIZATION FOR THE HEU ROUND ROBIN

Techniques/methods	24 hour	1 week	2 months
Radiological	Dose rate (α, γ, neutron) Surface contamination Radiography		
Physical characterization	Visual inspection Photography Weight Dimension Optical microscopy Density	SEM (EDX) XRD	TEM (EDX)
Classical forensics	e.g., Fingerprints		
Isotope analysis	γspectroscopy αspectroscopy	MS(SIMS, TIMS, MCMS)	
Elemental/Chemical		ICP-MS XRF IDMS	Ion chromatography

transport and receipt of "unknown" samples, when most shipping requirements entail disclosure of what is being shipped. Finally, the specific material used in this exercise was of unknown origin and pedigree so that feedback to the laboratories could not be reasonably and readily applied.

From a **technical standpoint**, the results from this exercise demonstrate the importance, and lack of a comprehensive network, of data and knowledge bases to assist in the interpretation of information in terms of nuclear processes and country of origin. Also, from a classical forensic technologies standpoint, it was obvious that closer relationships with law enforcement agencies are needed to integrate nuclear forensics into the overall scheme of application of forensic techniques and methods to the investigation of crime scenes. Scientists need to be generally sensitive to standard forensic methods to avoid contamination of evidence for application of other techniques. Also, effort is needed to develop, compile, and share data and knowledge bases associated with the characteristics of nuclear processes in various countries.

5. CONCLUSIONS AND RECOMMENDATIONS

The intent of the round robin exercises is to develop a preferred approach to nuclear forensic investigations in support of illicit-trafficking investigations. We have described the approach of the ITWG Round-Robin Task Group in establishing a series of round robin exercises to discuss protocols that can be widely understood and are technically credible so as to support the law enforcement aspects of attribution of interdicted samples. Specifically, we discussed the role of the HEU Round Robin Exercise and its findings in this broader context.

The members of the nuclear forensics laboratories participating in the ITWG and its Task Groups are self-managed and realize that attribution assessment of nuclear forensic materials from a seizure requires a network of knowledge and databases to adequately digest the resulting information. Two facets of the attribution analysis are key: (1) the interpretation of the results of a technical assay of the seized material, which requires a database of countries and the characteristic properties of their nuclear materials, and (2) QA/QC standardization that extends to development of defensible protocols, timely reporting, validation of procedures, and calibration efforts woven together with the common attribution goal.

The HEU Round Robin built upon the findings of a previous round robin exercise (the Plutonium Round Robin). Questions for a reporting period and suggested technologies from the Plutonium Round Robin were vetted in the HEU Round Robin and a new aspect was added: a scenario incorporating standard forensic signatures that include fingerprints and seeds/plant material. The reporting period questions proved to be appropriate for guiding the assessment, but much work needs to be done to coordinate with law enforcement and other forensic science disciplines to develop databases and knowledge bases for the attribution aspect of the problem. A prioritized listing was developed for techniques and methods for the HEU Round Robin.

The next steps for the ITWG Round-Robin Task Group include: documentation of the results of the round robins and the protocols, a confirmatory round robin exercise in which “unknown” samples are assayed, a protocol/illustration developed in which authentic samples can be used on a periodic basis to exercise the capabilities in the laboratories, and expansion of the network of laboratories associated with the ITWG.

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REPORT ON RECENT PROGRESS AT THE CENTRAL ANALYTICAL LABORATORY (NRI ŘEŽ plc) FOR UPGRADING CAPABILITIES FOR IDENTIFICATION OF ILLICIT NUCLEAR MATERIALS

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Abstract

The Central Analytical Laboratory is the main Czech institution working in the field of chemical analysis of nuclear material. Special methods have been introduced for determination of uranium content, isotopic composition, swipe sample analysis and determination of age of nuclear materials. Results from analyses of various materials are presented.

In the first half of the 1990s, the State Office for Nuclear Safety (SONS) — in close co-operation with other State organizations and following the IAEA's extended safeguards system — strengthened its procedures for the characterization of unknown nuclear materials. This problem became important in the context of increasing danger from illicit trafficking of nuclear materials that occurred after political changes in former "Comecon" countries during the late 1980s and 1990s. Particular attention has been paid to upgrading counting potential in possible transit countries in Central Europe. The Central Analytical Laboratory (CAL), the main Czech institution for chemical analysis of nuclear material, participated in the development and upgrading of analytical procedures for detailed identification and characterization of samples of nuclear material. Special methods were developed for determinations of uranium content, isotopic composition, and age of long-lived radioisotopes, and for swipe-sample analysis.

In the second half of the 1990s, under the auspices of the IAEA project entitled "Special analytical methods for determination of traces of radioactivity and detection of undeclared nuclear activities", basic procedures were prepared for determination of:

- Selected isotopes of the natural disintegration series in samples of water, sediments and industrial waste solutions after termination of uranium ore mining;

- Age of uranium and plutonium materials based on the ^{230}Th/^{234}Th, ^{226}Ra/^{234}U and ^{241}Am/^{241}Pu pairs (and studies on the application of the ^{231}Pa/^{235}U pair were initiated).

Results for various analyses are presented in Tables I to V, and hot-cell swipe-sample data are shown in Table VI.

In 1998, the PHARE PH5.01/95 project "Assistance in setting up special analytical services including a data bank for analysis of radioactive substances and nuclear materials of unknown origin" was begun. Funded by the European Commission's Phare Programme, the project was based at the Nuclear Research Institute (NRI), Řež plc, of which the CAL is part, and was co-ordinated by scientists at the Institute for Transuranium Elements (ITU), in Karlsruhe, Germany, a component of the European Commission Joint Research Centre.

As part of this project, appropriate analytical capabilities of the CAL were substantially upgraded. In cases of requested analyses of nuclear material of unknown origin seized in the Czech Republic, it is now possible — after categorization by standard isotopic measurements — to perform rapid precision measurements of impurity contents.

After the upgrade, complementary measurements were made on nuclear materials previously seized in the Czech Republic. Determinations of selected impurities found in pellets of HEU and LEU, UO_2 type, are presented in Tables VII and VIII. These results were included in a compilation of data characteristic of nuclear materials used in Czech research facilities. The complete set has been added to the nuclear material database available at ITU.

In order to develop a common scheme for complementary analyses of nuclear materials of unknown origin in respective EU institutions — upon request of a partner State's nuclear regulatory authority — selected samples were shipped to ITU and corresponding analyses were performed. The experience gained thereby can be used as a model for interface procedures that, in cases of necessity, can be invoked at short notice.

These activities provided an excellent basis for co-operation of SONS and NRI with the Joint Research Centre of the European Commission in terms of:

- Elaboration of State-response procedures following seizure of illicit nuclear material,
- Choice of analytical procedures for nuclear safeguards.

In 2001, CAL participated in the second interlaboratory comparison (round robin) exercise, organized by the Nuclear Smuggling International Technical Working Group (ITWG), the focus of which was forensic analysis of selected HEU samples. The CAL data are presented in Tables IX to XI.

TABLE I. ISOTOPIC CONTENT OF U SAMPLES

Sample	Isotope	Content [%]	SD [%]	RSD [$\%_r$]
MPDF-X1	U-232	≤ 0,000002	-	-
	U-233	≤ 0,000002	-	-
	U-234	0,9608	± 0,0003	0,03
	U-235	89,9974	± 0,0035	0,00
	U-236	0,5405	± 0,0003	0,06
	U-238	8,5013	± 0,0035	0,00
SQ-5-A	U-232	≤ 0,000001	-	-
	U-233	≤ 0,000001	-	-
	U-234	0,0544	± 0,0001	0,10
	U-235	6,4132	± 0,0012	0,02
	U-236	0,0456	± 0,0001	0,11
	U-238	93,4868	± 0,0012	0,00
SQ-5-B	U-232	≤ 0,000001	-	-
	U-233	≤ 0,000001	-	-
	U-234	0,3525	± 0,0001	0,03
	U-235	35,8266	± 0,0040	0,01
	U-236	0,1537	± 0,0002	0,13
	U-238	63,6672	± 0,0040	0,00
SQ-5-C	U-232	≤ 0,000002	-	-
	U-233	≤ 0,000002	-	-
	U-234	0,9912	± 0,0003	0,02
	U-235	89,9041	± 0,0054	0,00
	U-236	0,1841	± 0,0003	0,17
	U-238	8,9206	± 0,0067	0,07
U-B-4	U-232	≤ 0,000002	-	-
	U-233	≤ 0,000002	-	-
	U-234	0,5127	± 0,0005	0,10
	U-235	49,3821	± 0,0029	0,01
	U-236	0,0753	± 0,0002	0,26
	U-238	50,0299	± 0,0029	0,01
URAN-A	U-232	≤ 0,00002	-	-
	U-233	≤ 0,00002	-	-
	U-234	1,0781	± 0,0003	0,03
	U-235	87,7314	± 0,0042	0,00
	U-236	0,2108	± 0,0001	0,05
	U-238	10,9797	± 0,0042	0,04

TABLE II. ACTIVITIES OF THE ^{234}U AND ^{230}Th ISOTOPES AND CALCULATED AGE OF URANIUM MATERIALS

Sample	Activity ^{234}U ($Bq{\cdot}g^{-1}$)	Activity ^{230}Th ($Bq{\cdot}g^{-1}$)	Age of the material (year)
SQ-5-A	1.241E5	47.348	29.5 (SD ± 1.1, RSD = 3.9 %)
SQ-5-B	8.045E5	397.008	36.9 (SD ± 1.2, RSD = 3.1 %)
SQ-5-C	2.261E6	922.664	31.3 (SD ± 1.2, RSD = 3.8 %)
U-B-4	1.170E6	319.805	22.1 (SD ± 0.9, RSD = 4.0 %)
MPDFX-1		irrelevant data	irrelevant data
URAN-A	2.459E6	1 280.96	38.6 (SD ± 1.6, RSD = 4.1 %)

TABLE III. ACTIVITIES OF THE ^{234}U AND ^{226}Ra ISOTOPES AND CALCULATED AGE OF URANIUM MATERIALS

Sample	Activity ^{234}U ($Bq{\cdot}g^{-1}$)	Activity ^{226}Ra ($Bq{\cdot}g^{-1}$)	Age of the material (year)
SQ-5-C	2.261E6	2.7588	28.9 (SD ± 1.5, RSD = 5.1 %)

TABLE IV. ACTIVITIES OF THE ^{235}U AND ^{231}Pa ISOTOPES AND CALCULATED AGE OF URANIUM MATERIALS

Sample	Activity ^{235}U ($Bq{\cdot}g^{-1}$)	Activity ^{231}Pa ($Bq{\cdot}g^{-1}$)	Age of the material (year)
SQ-5-A	5.1074E3	1.0156	8.9
SQ-5-B	2.8549E4	11.8131	20.4
SQ-5-C	7.1632E4	18.4625	12.7
U-B-4	3.9347E4	20.5489	25.8
URAN-A	6.9903E4	40.5134	28.4

TABLE V. ACTIVITIES OF THE ^{241}PU AND ^{241}AM ISOTOPES AND CALCULATED AGE OF PLUTONIUM MATERIALS

Sample	Activity ^{241}Pu ($Bq{\cdot}g^{-1}$)	Activity ^{241}Am ($Bq{\cdot}g^{-1}$)	Age of the material (year)
Pu 949f	0.476 ± 0.004	0.0399 ± 0.0012	26.6 ± 0.8
Pu 947	45.29 ± 0.28	4.201 ± 0.071	28.4 ± 0.6
PuO_2	16.95 ± 0.13	0.592 ± 0.011	14.8 ± 0.4

TABLE VI. ANALYSES OF HOT CELL SWIPE SAMPLES

Sample designation	Withdrawal locality	Sample type	U (µg/swipe)*	^{239}Pu (µg/swipe)* $^{239+240}$Pu (Bq/swipe)	^{238}Pu (Bq/swipe)	^{241}Am µg/swipe)* (Bq/swipe)	^{244}Cm (Bq/swipe)	^{237}Np (µg/swipe)* (Bq/swipe)
SW-1	NRI	TR, bottom	0.039*	0.001*	-	0.001*	-	0.001*
				0.0082	0.0032	≤0.0007	≤0.0007	≤0.002
SW-2	NRI	PHK-9, floor	0.098*	0.001*	-	0.001*	-	0.001*
				0.0012	≤0.0004	≤0.0004	≤0.0007	≤0.002
SW-3	NRI	PHK-10, floor	54.35*	0.001*	-	0.001*	-	0.001*
				0.14	0.045	0.0012	≤0.0007	≤0.002
SW-4	NRI	PHK-10, wall	0.384*	0.001*	-	0.001*	-	0.001*
				0.012	0.0048	≤0.0004	≤0.0007	≤0.002
SW-5	NRI	PHK-11, bottom	0.512*	0.001*	-	0.001*	-	0.001*
				0.096	0.018	0.0014	≤0.0007	≤0.002
SW-71	NFI	L	30600*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-
SW-93	NFI	PR.ST.	15600*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-
SW-94	NFI	PO	3455*	0.092	0.035	≤0.0004	≤0.0007	-
SW-95	NFI	VZ	630*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-
SW-96	NFI	KONS	28.2*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-
SW-97	NFI	TRA	4.37*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-
SW-108	NFI	VAK.SV	25.0*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-
SW-119	NFI	VAK.SV	12.0*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-
SW-1210	NFI	ROZV. EL.	20.9*	≤0.0004	≤0.0004	≤0.0004	≤0.0007	-

NRI: Nuclear Research Institute Řež plc.
NFI: Nuclear Fuel Institute Zbraslav.
PHK ... semi-hot cell, TR ... transporter, L ... press, PR.ST ... work bench, PO ... floor, VZ ... air conditioning, KONS ... construction, TRA ... girder, VAK.SV ... vacuum welder, ROZVEL ... current distribution.
All the samples mentioned were taken as dry swipes.

TABLE VII. SELECTED IMPURITIES FOUND IN HEU (87 wt% ^{235}U, UO_2 TYPE) STORED AT NRI FROM 1994

Element	Sample 1			Sample 2		
	Concentration µg/g sample	SD µg/g sample	RSD (%)	Concentration µg/g sample	SD µg/g sample	RSD (%)
Ag	0.049	0.004	8.3	0.050	0.002	4.2
Al	1.35	0.12	8.9	1.52	0.03	1.8
Ba	0.51	0.04	7.8	0.309	0.004	1.3
Be	<0.004			<0.004		
Bi	0.0013	0.0006	44	0.0011	0.0005	46
Co	0.043	0.003	7.1	0.019	0.002	10
Cr	2.96	0.11	3.7	2.49	0.02	0.8
Cu	0.46	0.02	3.7	0.589	0.009	1.6
Fe	9.79	0.66	6.8	8.02	0.09	1.2
Mg	2.95	0.17	6.0	6.17	0.11	1.8
Mn	0.486	0.013	2.8	0.46	0.01	3.1
Mo	0.217	0.007	3.1	0.213	0.006	2.8
Na	2.78	0.19	7.0	3.74	0.0599	1.6
Ni	1.49	0.07	4.8	1.63	0.02	1.5
Pb	0.356	0.008	2.4	1.78	0.02	0.9
Sb	0.0169	0.0008	4.9	0.094	0.006	6.2
Se	<0.015			0.022	0.013	60
Sr	0.158	0.004	2.5	0.276	0.002	0.7
Tc	0.029	0.009	30	0.029	0.008	27
Ti	0.58	0.11	18	0.75	0.01	1.5
Tl	0.0021	0.0002	10	0.0023	0.0002	10
V	<0.002			<0.002		
Zn	2.13	0.10	4.8	0.876	0.009	1.0

TABLE VIII. SELECTED IMPURITIES FOUND IN LEU PELLETS (3.6%, UO_2 TYPE) USED IN LR – 0 RESEARCH REACTOR

Element	Concentration (μg/g sample)	SD (μg/g sample)	RSD (%)
Ag	0.008	0.001	12.6
Al	44	3	7.3
As	0.38	0.01	3.2
B	196	29	14
Be	<0.005		
Bi	0.006	0.002	30
Ca	276	15	5.4
Cd	7.48	0.28	3.6
Co	0.176	0.003	1.9
Cr	33.7	1.5	4.6
Cu	6.7	0.2	3.2
Fe	883	51	5.8
K	117	7	6.5
Li	<0.01		
Mg	10.9	0.9	8.9
Mn	18.1	1.1	6.3
Mo	0.62	0.02	2.9
Na	140.495	13.084	9.3
Ni	12.6	0.5	4.1
Pb	<0.01		
Sb	0.083	0.004	4.9
Se	0.39	0.05	11
Sr	0.27	0.01	5.0
Ti	2.18	0.34	15
Tl	0.119	0.001	0.9
V	0.16	0.02	11
Zn	2.49	0.25	10

TABLE IX. DETERMINATIONS OF Pu, Am, Np AND ^{90}Sr ROUND ROBIN TEST

Isotope	Radioactivity Bq/g of sample	Uncertainty 1 sigma	Rel. uncertainty	Methods used
^{238}Pu	75	9	12	α-spectr
$^{239+240}$Pu	35	5	13	α-spectr
^{241}Am	1.2	0.2	12	α-spectr
^{237}Np	0.002			α-spectr
^{90}Sr	0.2			LSC

TABLE X. ISOTOPIC COMPOSITION, ROUND ROBIN TEST

Isotope	Isotopic abundance in wt%	Uncertainty 1 sigma	Rel. uncertainty
^{232}U	0.0000002		
^{233}U	0.0000002		
^{234}U	0.9599	0.0012	0.13
^{235}U	89.9349	0.0580	0.06
^{236}U	0.6432	0.0025	0.39
^{238}U	8.4620	0.0055	0.06

TABLE XI. SELECTED IMPURITIES, ROUND ROBIN TEST

Element	Concentration (µg/g of sample)	Uncertainty (1 sigma)	Rel. uncertainty (%)
Ag	0.02	0.002	8
As	≤0.20		
Al	2.82	0.28	10
B	≤0.20		
Ba	0.095	0.008	8
Be	0.008	0.003	36
Bi	≤0.010		
Cd	≤0.20		
Co	≤0.05		
Cr	0.09	0.03	33
Cu	0.29	0.02	8
Fe	0.47	0.13	28
Li	0.011	0.004	35
Mg	0.59	0.08	14
Mn	0.11	0.03	28
Mo	0.05		
Na	4.0	0.6	15
Ni	≤0.02		
Pb	0.16	0.06	35
Sb	0.04	0.01	23
Se	≤0.05		
Sr	0.04	0.01	28
Ti	0.29	0.11	38
Tl	≤0.03		
V	≤0.04		
Zn	0.58	0.10	18
Th	≤0.01		

APPLICATION OF ISOTOPIC FINGERPRINTING IN NUCLEAR FORENSIC INVESTIGATIONS: A CASE STUDY

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Abstract

Naturally occurring chemical elements show only small variations in isotopic composition. Material irradiated in a nuclear reactor undergoes nuclear reactions, prominently induced fission (n, f) and neutron capture (n, g), which lead to materials of an isotopic composition determined by reactor conditions (initial fuel composition, neutron energy spectrum, irradiation time, cooling time, etc.). Treatment, such as chemical separation as done in the reprocessing of spent nuclear fuel, does not change the isotopic composition of a chemical element. Consequently, the isotopic composition serves as an identifying fingerprint. Accurate and highly sensitive methods are required to determine variations in isotope ratios. Gamma spectrometry, alpha spectrometry, thermal ionization mass spectrometry and inductively coupled plasma mass spectrometry are employed to measure isotopic compositions of plutonium and uranium. Extensive use of this methodology was made in the context of a case of theft of radioactive material from a nuclear installation being decommissioned. Two contaminated items were reportedly stolen: a sample vial containing a small amount of waste solution, and a cleaning wipe (cellulose cloth). Radioactive contamination was detected in the suspect's apartment, where he had stored the items for more than six months. Radioactivity was detected also in the apartment of a person associated with the suspect, and, to lesser extents, at other locations, indicating cross-contamination. Samples were collected at various locations (e.g. vacuum cleaner bags, clothes, packaging of stolen items, stolen items) in order to determine whether the contamination could be uniquely related to the two (reportedly) stolen items. The investigations showed that the ratio of radionuclides (e.g. ^{137}Cs/^{241}Am) in the various samples was not constant, which can be explained only in terms of differences in sample treatment (e.g. weathering, rinsing, or washing). Solubility tests using micro-amounts of the sample were carried out to investigate relative differences under experimental conditions mimicking leaching through exposure to rainwater or washing-machine conditions. Such "treatments" may not have been performed intentionally on the stolen items; thus great care was necessary in the interpretation of these results. In contrast to that, isotope ratios (e.g. ^{235}U/^{238}U, ^{240}Pu/^{239}Pu) do not change through such chemical treatments. Consistent results were found for most of the samples, indicating that the observed contaminations were related to the two stolen items. However, one sample showed a significantly different ^{238}Pu/^{239}Pu isotope abundance ratio.

1. INTRODUCTION

In the summer of 2001, the German media reported an incident at a nuclear installation under decommissioning: radioactive material illegally removed from the plant had caused serious contamination. The case and the person became known as the “plutonium thief”. An individual, working for a subcontractor in the former process area of the facility, managed to bypass the safety and security systems and remove contaminated items from the plant. These items, stored in his apartment, caused significant radioactive contamination on all surfaces, as reported by the media. Also, his girlfriend’s apartment became contaminated to similar levels, although, reportedly, the items were never taken there.

The theft came to light after a routine incorporation measurement, which is mandatory in Germany for workers in controlled areas (i.e. where nuclear or radioactive material is handled openly). “Mr. M.” underwent the yearly examination and was found to have incorporated some kBq of Am and Pu, which triggered an investigation and led to his arrest. Although his girlfriend and, to a much lesser extent, her daughter were found to have incorporated radioactive material, the pattern of nuclides and the pathway of incorporation were not identical to those of Mr. M. Under interrogation, he admitted having taken contaminated items from the facility. Two contaminated items, or “sources”, were found and analysed. Two basic questions needed to be clarified:

- Could the incorporations (in Mr. M. and his girlfriend) be explained in terms of the two sources?
- Could the contamination (of the apartments and belongings) be explained in terms of the two sources?

Scientists at the Institute for Transuranium Elements were involved in analyses of samples, comprising the two reportedly stolen items, contaminated clothes, vacuum cleaner bags, gloves, etc. Isotopic fingerprinting was applied, in order to answer the above questions, making use of the fact that isotopic composition of an element cannot be changed by chemical means, i.e. it remains constant. On the other hand, the isotopic composition of uranium and plutonium depend very much on the history of the material, e.g. on duration of irradiation in a reactor and the reactor type.

2. EXPERIMENTAL

Level of contamination of the various items ranged from a few to several million bequerels. Upon receipt of the samples, total activities were determined by gamma spectrometry. Associated variability resulted mainly from geometric effects, as the samples were voluminous (e.g. clothes) with non-homogeneous distribution of radionuclides. Therefore, total variability was sometimes as high as 50% relative to the measured activity. Subsequently, the isotopic composition of the plutonium was measured using another gamma spectrometry instrument and applying the MAG code for spectral deconvolution and calculation of the plutonium-isotope-abundance ratios.

Samples were then taken from the contaminated items for mass spectrometric analysis. The samples were first subjected to leaching in concentrated nitric acid, then chemical separation of uranium, plutonium and the other elements was performed using extraction chromatography (UTEV® resin, EIChrom Industries). An aliquot of the separated plutonium fraction was taken for alpha spectrometric determination of the ^{238}Pu/(^{239}Pu+^{240}Pu) ratio, and another aliquot was used for mass spectrometric measurement. This was achieved either by thermal ionization mass spectrometry (TIMS) using the total evaporation technique or by inductively coupled plasma mass spectrometry (ICP-MS). The uranium fraction was taken directly to the TIMS or the ICP-MS for isotope ratio measurements.

Because important decisions had to be based on the measurement results, significant effort was spent on quality control. However, for these types of samples no standards, reference materials or quality control materials were available that mimic the geometry, or the matrix and the nuclidic and isotopic composition. Therefore, it was decided to perform repeat measurements on the same items, using analytical techniques that are based on different physical principles: gamma spectrometry, TIMS and ICP-MS.

3. RESULTS AND DISCUSSION

Reportedly, two items had been taken out of the facility and, according to Mr. M., had been stored in his apartment between the time of the theft and their seizure:

(1) **A plastic vial** containing radioactive residue (Fig. 1). The vial was found to be broken when the police secured it. It was wrapped in blue plastic gloves, which were, in turn, wrapped in red household-type plastic gloves. Inside the blue gloves we collected some 300 μL of liquid.

(2) A partially disintegrated **wiping cloth**: net-like reinforcing nylon (Fig. 2) and cellulose (Fig. 3) that absorbs liquid. These were heavily contaminated. The nylon netting and the cellulose were investigated separately.

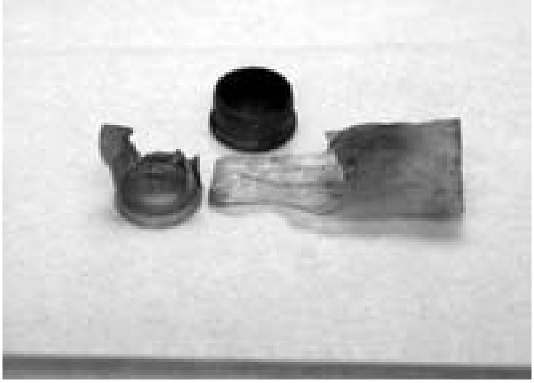

FIG. 1. *Broken plastic vial, showing brownish radioactive residue.*

The results of the isotopic analyses obtained for the three samples, using different measurement techniques, are shown in Tables I to III. The consistency of the results underlines the reliability of the determined values. Gamma

FIG. 2. *Nylon netting, originating from a reinforced wiping cloth.*

FIG. 3. Cellulose material, originating from a reinforced wiping cloth.

TABLE I. RELATIVE ISOTOPE ABUNDANCE (IN MASS%) OF THE RESIDUE ON THE PLASTIC VIAL, AS OBTAINED BY THREE MEASUREMENT TECHNIQUES. UNCERTAINTY ON THE MASS SPECTROMETRIC RESULTS IS 0.2% (REL.)

Nuclide	Gamma spectrometry (Mass%)	ICP-MS (Mass%)			TIMS (Mass%)		
		Q1.1	Q1.2	Q1.3	Q1.1	Q1.2	Q1.3
^{234}U		0.0159	0.0158	0.0158			
^{235}U		0.3480	0.3501	0.3406			
^{236}U		0.1383	0.1396	0.1361			
^{238}U		99.4978	99.4945	99.5075			
^{238}Pu	1.32 ± 0.05	1.3168	1.3156	1.3213	1.3153	1.4232	1.3428
^{239}Pu	61.47 ± 1.23	59.6647	59.6101	59.8705	59.8468	59.7217	59.7307
^{240}Pu	26.62 ± 1.04	28.1990	28.2528	28.0606	28.0721	28.0635	28.1254
^{241}Pu	5.10 ± 0.16	5.3042	5.2993	5.3225	5.3109	5.3128	5.3160
^{242}Pu	5.48 ± 0.55	5.5153	5.5222	5.4250	5.4547	5.4785	5.4849
^{241}Am	3.21 ± 0.10						

TABLE II. RELATIVE ISOTOPE ABUNDANCE (IN MASS %) OF THE NYLON GRID, AS OBTAINED BY THREE DIFFERENT MEASUREMENT TECHNIQUES

Nuclide	Gamma spectrometry (Mass%)	ICP-MS (Mass%)	TIMS (Mass%)
^{234}U		0.2003 ± 0.0100	
^{235}U		0.5830 ± 0.0117	
^{236}U		0.2782 ± 0.0083	
^{238}U		98.9385 ± 0.0989	
^{238}Pu	1.29 ± 0.03	1.3045 ± 0.026	1.307 ± 0.026
^{239}Pu	60.12 ± 0.78	59.1081 ± 0.59	60.108 ± 0.060
^{240}Pu	27.60 ± 0.52	29.1368 ± 0.4371	28.433 ± 0.028
^{241}Pu	5.09 ± 0.09	5.2547 ± 0.1051	4.9649 ± 0.0050
^{242}Pu	5.91 ± 0.60	5.1959 ± 0.1039	5.1856 ± 0.0050
^{241}Am	3.90 ± 0.07		

spectrometry was performed on the entire item, while for the mass spectrometry (combined with alpha spectrometry) three individual subsamples were taken, denoted as Q1.1, Q1.2 and Q1.3. The latter showed that the residue (dried liquid) on the plastic vial was isotopically homogeneous. Measurements on the gloves used for wrapping the vial showed that the isotopic composition did not differ significantly from the values for the vial. Clearly, the contamination on the gloves originated from the residue on the vial. Tests proved that the activity contained in the residue was, to some degree, soluble in water at room temperature.

The plutonium isotope abundances showed very little sample to sample variability (Tables I and II). According to the isotopic composition, the plutonium may have been produced in a light water reactor. The data in Table III differed slightly; however, we took into account that the wiping-cloth could have been used on a contaminated surface, or several surfaces, carrying many different types of material throughout the lifetime of the plant. The latter explains the small isotopic non-homogeneities in the primary sources, which was why we did not attempt to perform particle analysis on these items.

Dust in vacuum cleaner bags was investigated from the apartments of Mr. M. and of his girlfriend, and where the girlfriend's daughter stayed occasionally ("A", Fig. 4). In one of the apartments, a contaminated piece of cloth ("Fluse") was found below a carpet; tests showed that it was not a fragment

TABLE III. RELATIVE ISOTOPE ABUNDANCE (IN MASS %) OF THE CELLULOSE ORIGINATING FROM A WIPING CLOTH, AS OBTAINED BY THREE DIFFERENT MEASUREMENT TECHNIQUES.

Nuclide	Abundance (Mass%)
^{234}U	0.012 3 ± 0.000 6
^{235}U	0.668 2 ± 0.013 4
^{236}U	0.238 4 ± 0.007 2
^{238}U	99.081 1 ± 0.099 1
^{238}Pu	1.135 0 ± 0.022 7
^{239}Pu	62.193 3 ± 0.622 9
^{240}Pu	28.163 1 ± 0.422 4
^{241}Pu	4.666 6 ± 0.093 3
^{242}Pu	4.841 9 ± 0.096 8

of the wiping cloth. Its plutonium isotopic composition was also investigated. The multi-dimensional diagram (Fig. 4) shows the isotopic composition of the individual samples expressed relative to values obtained for the “plastic vial”. Consistent values were obtained for all the items investigated, except for the dust in vacuum-cleaner bag “A”, which had a significantly lower abundance of ^{238}Pu.

Therefore, we concluded that the contamination on all of the items could reasonably be explained in terms of the two primary sources, i.e. the vial and the wiping cloth. In order to better understand the different isotopic composition observed in vacuum cleaner bag “A”, we took into account the amount of material. The respective apartment showed no detectable surface contamination, and the uranium in the vacuum cleaner bag showed a $^{235}U/^{238}U$ ratio similar to that of natural uranium, indicating that any traces of contamination were due to cross-contamination, i.e. carried into the apartment via the clothes of individuals visiting the (strongly contaminated) apartment of Mr. M. or of his girlfriend. Furthermore, the amount of plutonium found in the vacuum-cleaner bag was extremely small, and we also took into account fallout plutonium from atmospheric nuclear weapons tests in the early 1960s. An admixture of fallout plutonium with that coming from the stolen items could explain the significantly lower ^{238}Pu abundance.

All of the contamination was reasonably explained as resulting from the two stolen items.

4. CONCLUSION

In a case of theft of radioactive material (containing milligram amounts of nuclear material), isotopic fingerprinting contributed to the clarification of the criminal case. Accurate isotopic measurements on uranium and, in particular, on plutonium clearly demonstrated that all contamination resulted from the reportedly stolen items. The investigations also showed that great care has to be taken in sampling, that factors like sample homogeneity (including isotopic homogeneity) have to be taken into account and that data interpretation requires sound knowledge and experience in this area. Isotopic fingerprinting proved to be a powerful tool for forensic and nuclear forensic investigations.

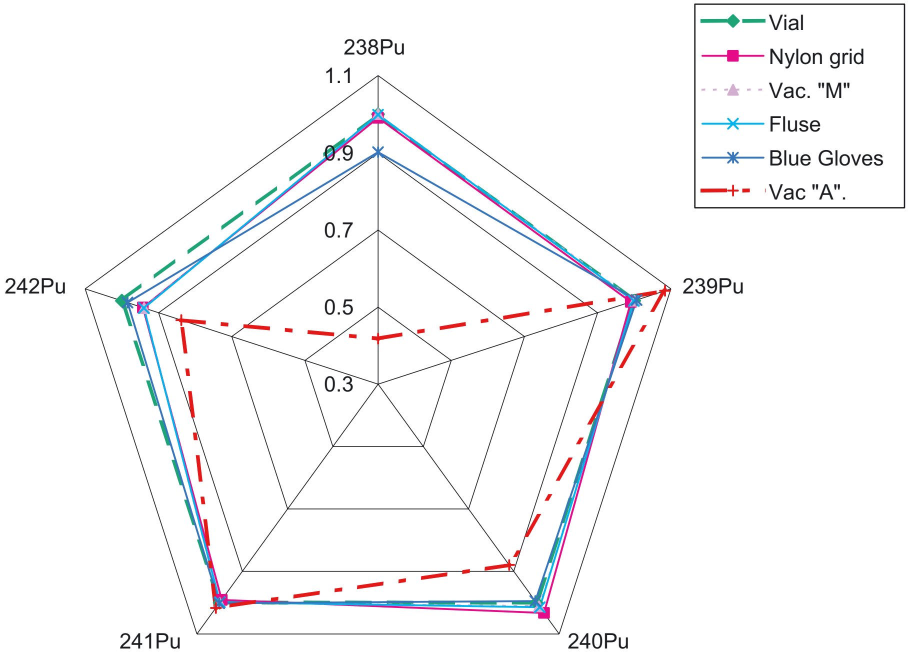

FIG. 4. Isotopic fingerprints obtained for the samples investigated. Isotopic composition of the samples and items are expressed relative to the values measured for the "plastic vial". Consistent data were obtained for all of the samples, except vacuum cleaner bag "A".

RECENT DEVELOPMENTS AND CASE STUDIES IN NUCLEAR FORENSIC SCIENCE

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Abstract

Since 1994, the Institute for Transuranium Elements has played the leading role in Europe in the development of nuclear forensic science. The Institute has been involved in the investigation of all of the major cases of illicit trafficking involving nuclear and nuclear related materials in Europe, from the first major incident at Munich airport up to the present time. Three examples illustrate different types of cases. The first is an accidental release of nuclear material: on the seabed and beaches in the vicinity of the Dounreay nuclear establishment in Scotland. The second case involves an exercise carried out in co-operation with the German Federal Police (Bundeskriminalamt) in which a “seized” sample of high enriched uranium was delivered to the laboratory for examination to determine its composition, origin and intended use. The third case addresses a removal of nuclear material with deliberate criminal intent. As part of an actual police investigation, the Institute examined stolen material along with personal items of clothing from the people involved.

1. INTRODUCTION

Since 1994, the Institute for Transuranium Elements has played the leading role in Europe in the development of nuclear forensic science. This new discipline developed by necessity following the breakup of the former Soviet Union and Eastern Bloc countries in 1989, which resulted in the emergence of a new form of smuggling — that of nuclear materials. The Institute has been involved in the investigation of all of the major cases of illicit trafficking involving nuclear and nuclear related materials in Europe since the first major incident, at Munich airport, in 1994.

The Munich airport incident gave birth to nuclear forensic science and to the concept of the nuclear fingerprint as a characteristic of nuclear materials.

Examples given here illustrate different types of cases: accidental release of nuclear material into the environment, an exercise carried out in co-operation with the German Federal Police (Bundeskriminalamt), and the removal of nuclear material from a reprocessing plant in Karlsruhe, Germany, with deliberate criminal intent. This last case is the closest approach, so far, to an act of nuclear terrorism.

2. DOUNREAY RADIOACTIVE PARTICLES

Over a period of about 10 years, highly radioactive particles — “hotspots” — about 1 mm in size were found on the seabed, and occasionally on beaches, in the vicinity of the Dounreay nuclear establishment in Scotland, following accidental discharge some years ago.

Two particles, one from the seabed and one from the foreshore, were analysed at the Institute to establish composition, origin and age. An examination was made using a Philips XL40 scanning electron microscope (SEM) that has the microscope column and pumping system separated from the control console and is mounted inside a closed glovebox for handling contaminated samples. The instrument is equipped with energy dispersive X ray (EDX) analysis facilities. Figure 1 shows a micrograph of a particle recovered from the foreshore which was about 2 mm in length. The particles were found to be encrusted with a layer that prevented dissolution in the sea water.

The particles were shown by EDX analysis to consist of UAl_3 islands in an aluminium matrix, identifying their origin as the Dounreay materials test reactor. Figure 2 is an elemental mapping of a small area of a cross-sectioned particle from the seabed, showing typical distribution of the fuel in the matrix.

Age determination using caesium isotopic ratios showed that the material had been last processed about 30 years before.

FIG. 1. An SEM micrograph of a particle recovered from the Dounreay foreshore.

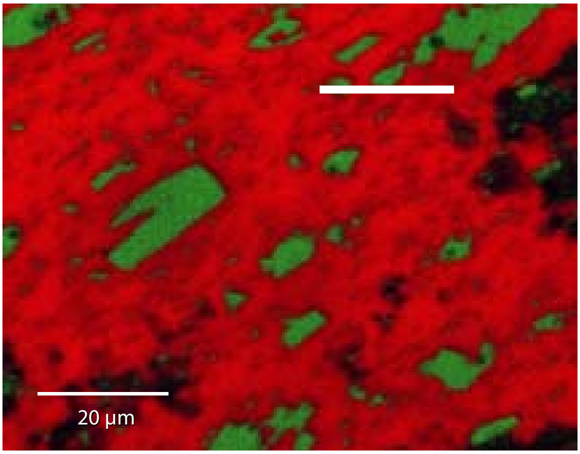

FIG. 2. An EDX elemental distribution map recorded of the cross-section of a particle recovered from the seabed showing UAl^3 *islands (green) in an aluminium matrix (red).*

3. ITWG URANIUM ROUND ROBIN TEST

The Institute was a participant in a Uranium Round Robin Test organized by the International Technical Working Group (ITWG) on nuclear smuggling. In this exercise a “seized” sample of high enriched uranium was delivered to each laboratory for examination, to determine its composition, origin and intended use.

The exercise, treated as a real case, was carried out in co-operation with specialist officers from the Bundeskriminalamt (BKA) who examined the container as delivered for a possible conventional “booby trap” explosive device. Figure 3 illustrates the X ray examination of the container in which the sample was delivered. The officers were present in the laboratories during opening and examination of the material to advise the scientists on the preservation of conventional forensic information. Much useful information on optimizing collaboration between police and nuclear scientists resulted from this exercise.

The containers and various items therein were examined for conventional forensic evidence, and a fingerprint was imaged on a contaminated brass container by cyanoacrylate vaporization under glovebox conditions.

Examination and reporting on the sample followed a scheme prescribed by ITWG: after 24 h, 1 week, and, finally, at 2 months. The sample was identified as reprocessed U_3O_8 with an enrichment of 89.89 ^{235}U (wt%), aged 22.4 ± 1.2 years.

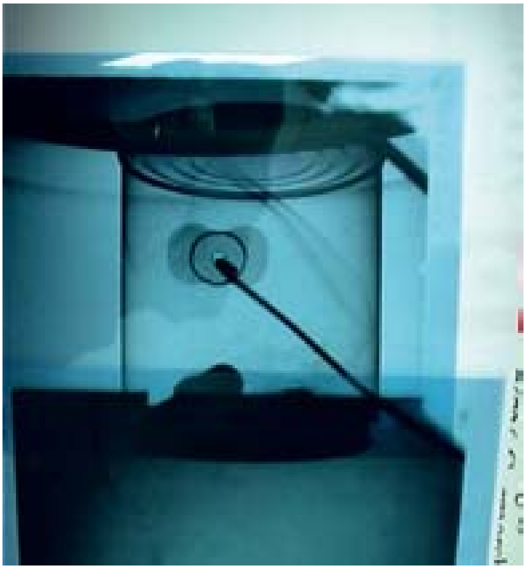

FIG. 3. X ray image of the container in which the samples were received, taken by specialists from the BKA to check for a conventional explosive device.

Three distinct morphological components were identified in the powder by SEM and by transmission electron microscopy (TEM); the isotopic compositions of all three were identical. The material was found to be very pure.

4. NUCLEAR AND RADIOACTIVE MATERIAL REMOVED FROM A NUCLEAR INSTALLATION WITH CRIMINAL INTENT

A worker, involved in dismantling a nuclear installation in Karlsruhe, removed items contaminated with nuclear materials and took them home, resulting in heavy contamination of his apartment and high body incorporation for him and his partner.

The Institute examined the stolen material that was recovered by the police, along with items of clothing from the people involved.

One of the recovered items was a broken plastic tube that had held a liquid, the dried remains of which contained ^{137}Cs, plutonium and americium. Although of plastic, the tube was shown by SEM to have undergone brittle fracture, suggesting that, at some point, it had been stored at a low temperature (Fig. 4). Analysis of a second item, a cloth used for decontamination at the plant, revealed particles containing plutonium and uranium.

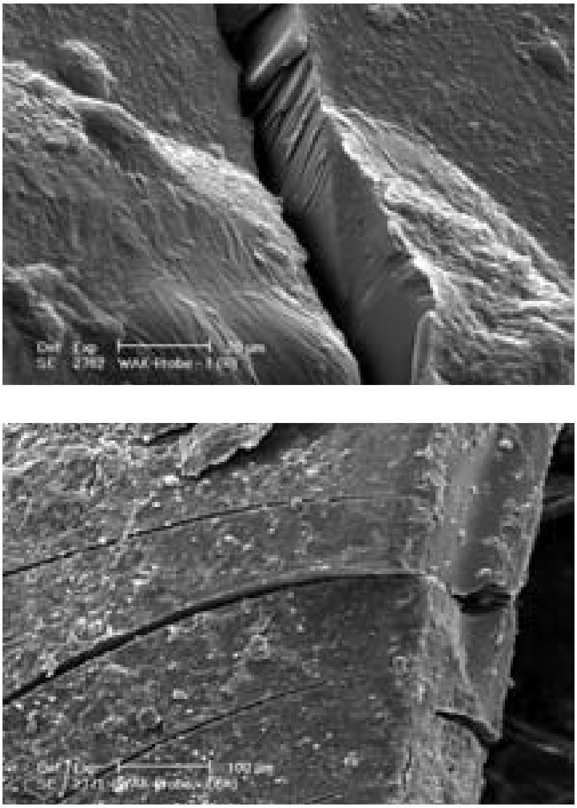

FIG. 4. Scanning electron micrographs indicating a brittle-type fracture of the plastic tube used for transport of stolen radioactive material, suggesting that the tube had been stored at a low temperature at some stage.

PROBLEMS OF ILLICIT TRAFFICKING OF NUCLEAR MATERIALS AND SAFEGUARDS STRATEGIES IN THE REPUBLIC OF TAJIKISTAN

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Abstract

Problems in illicit trafficking of nuclear materials and in devising safeguard strategies in the Republic of Tajikistan, and proposals for solution, are discussed.

An important problem for our Republic is the safe preservation of radioactive materials and radiation sources, in order to prevent incidents and unauthorized use. The international community is greatly concerned over illicit trafficking of nuclear and other radioactive materials in connection with nuclear safety and non-proliferation of nuclear weapons.

As of 1 January 2002, the IAEA and International Criminal Police Organization (INTERPOL) had registered more than 300 incidents of illicit trafficking in radioactive materials. The IAEA provided the Academy of Sciences of the Republic of Tajikistan with the complete list of illicit trafficking incidents since December 1999.

For our Republic, this problem has two aspects:

- Tight control of radioisotope sources (RISs) was lost in 1991: for example, several RISs of ^{137}Cs were lost from the Yovon Chemical Plant, and a fatal incident resulted when a RIS of ^{137}Cs was stolen from the Tajik Aluminium Plant. Current information indicates that at least seven powerful and potentially fatal RISs have been stolen from plants in Tajikistan. The Ministry of Internal Affairs is responsible for safe containment of radioactive materials.
- The routes used in illicit trafficking of radioactive materials coincide with those used in illicit trafficking of narcotics. Therefore, the situation in Tajikistan is exacerbated by its juxtaposition with Afghanistan. Thus, illicit trafficking must be considered both in terms of exportation of radioactive substances from, and importation to, the territory of Tajikistan.

To prevent further incidents and to aid the normalization of the nuclear situation, the plants of the Republic of Tajikistan made inventories of RISs with assistance from regulatory agencies, the Ministry of Internal Affairs, Ministry of

Emergency Situations, Ministry of Health Protection and Ministry of Security, with input from experts at the Academy of Sciences, the Ministry of Education, and other ministries and departments.

On the inventory list, RISs requiring burial and those for which control has been lost, with indications of reasons for that loss, have been specially marked.

The solving of the second aspect of this problem will require technical and methodological strengthening of frontier-guard and customs services for detection of radioactive materials.

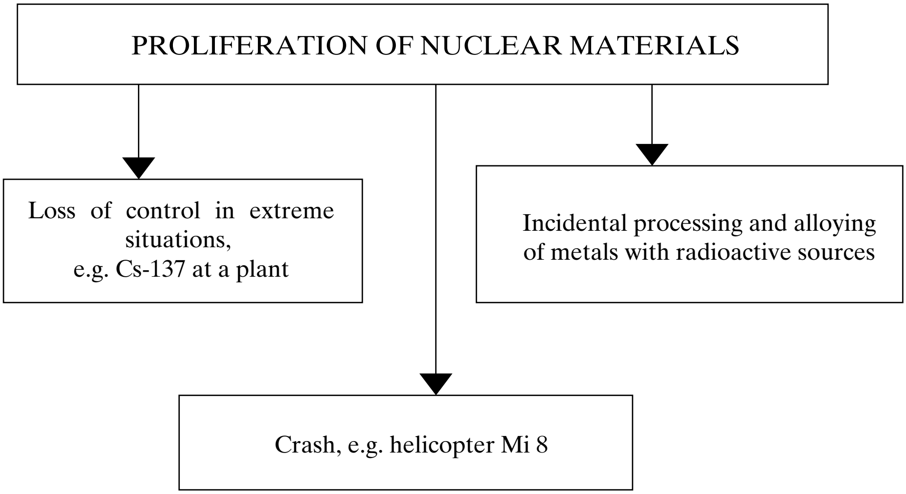
Control of illicit trafficking can be considered as consisting of three components:

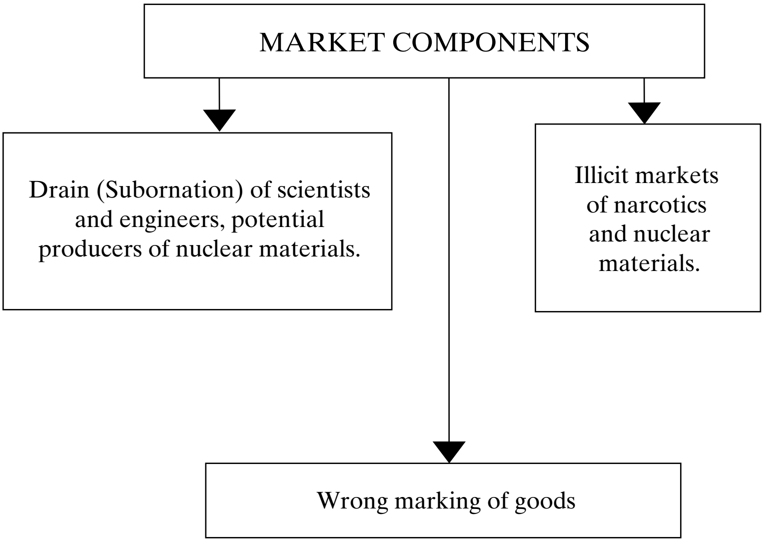
(1) Situation:
- Proliferation of nuclear materials,
- Illicit trafficking,
- Forming markets.

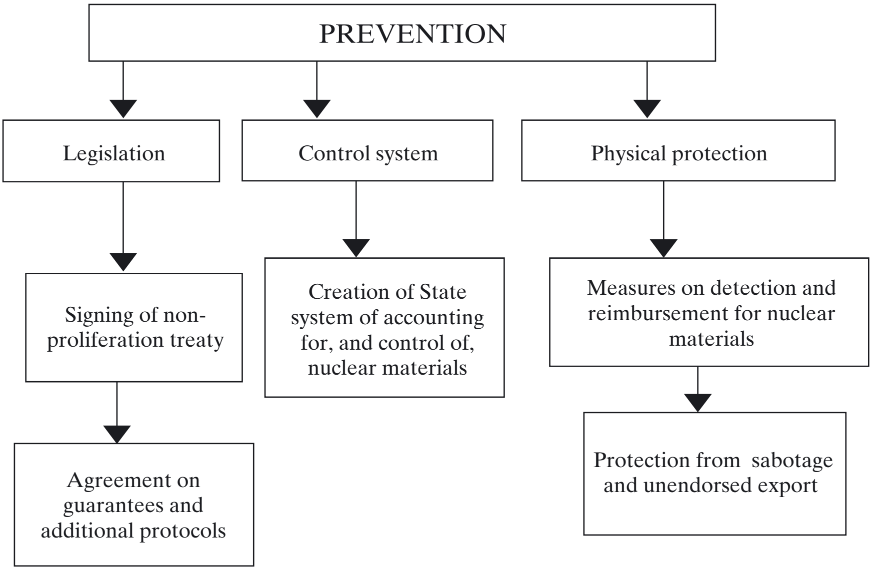
(2) Prevention:
- Legislation,
- Inspection system,
- Enterprise responsibility,
- Physical protection,
- Export and import control.

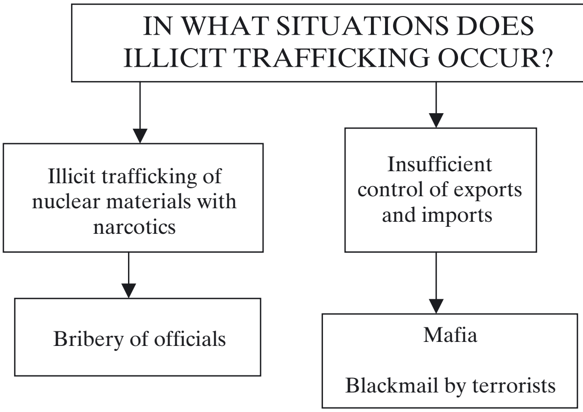
(3) Detection and inquest:
- National system,
- International system,
- Channels of information.

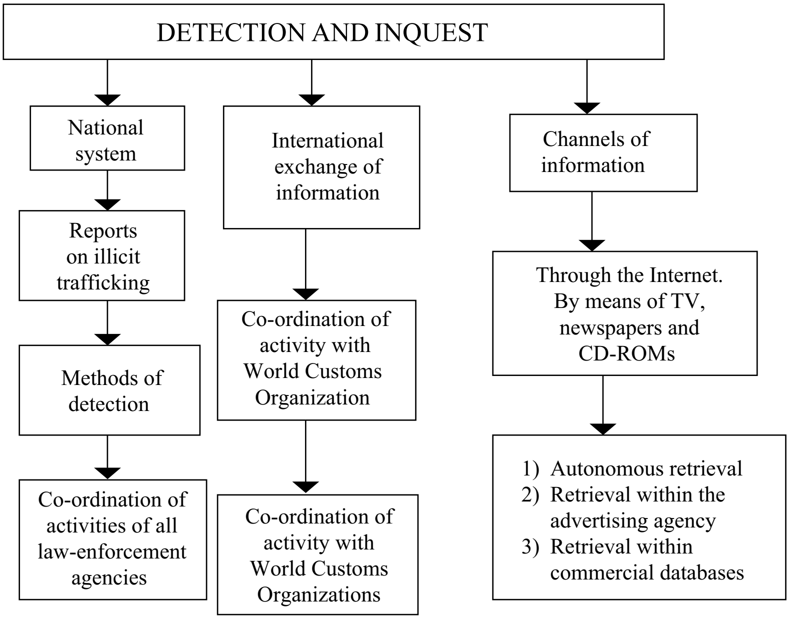
Generally, the problem of illicit trafficking control is illustrated by the following charts:

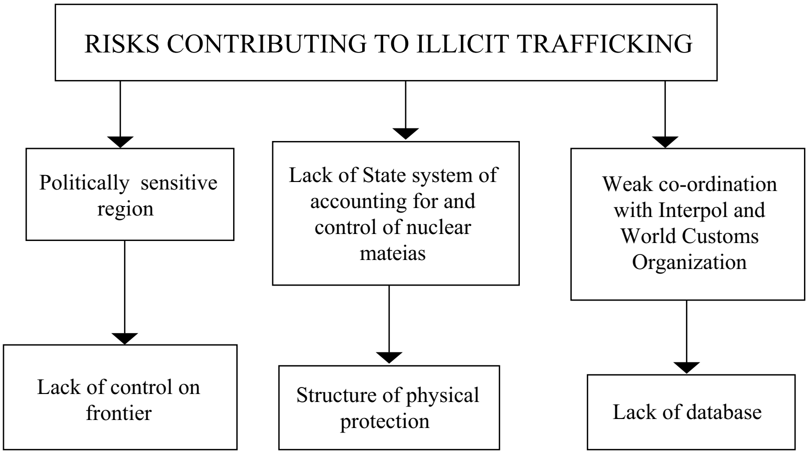

PROLIFERATION OF NUCLEAR MATERIALS
Loss of control in extreme situations, e.g. Cs-137 at a plant
Incidental processing and alloying of metals with radioactive sources
Crash, e.g. helicopter Mi 8

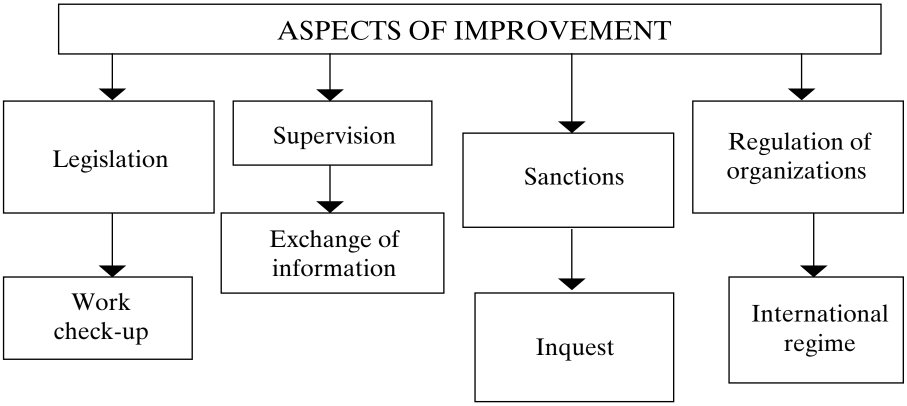

MARKET COMPONENTS
Drain (Subornation) of scientists and engineers, potential producers of nuclear materials.
Illicit markets of narcotics and nuclear materials.
Wrong marking of goods


PREVENTION
Legislation
Control system
Physical protection
Signing of non-proliferation treaty
Creation of State system of accounting for, and control of, nuclear materials
Measures on detection and reimbursement for nuclear materials
Agreement on guarantees and additional protocols
Protection from sabotage and unendorsed export


IN WHAT SITUATIONS DOES ILLICIT TRAFFICKING OCCUR?
Illicit trafficking of nuclear materials with narcotics
Insufficient control of exports and imports
Bribery of officials
Mafia
Blackmail by terrorists


DETECTION AND INQUEST
National system
Reports on illicit trafficking
Methods of detection
Co-ordination of activities of all law-enforcement agencies
International exchange of information
Co-ordination of activity with World Customs Organization
Co-ordination of activity with World Customs Organizations
Channels of information
Through the Internet. By means of TV, newspapers and CD-ROMs
1) Autonomous retrieval
2) Retrieval within the advertising agency
3) Retrieval within commercial databases


RISKS CONTRIBUTING TO ILLICIT TRAFFICKING
Politically sensitive region
Lack of control on frontier
Lack of State system of accounting for and control of nuclear mateias
Structure of physical protection
Weak co-ordination with Interpol and World Customs Organization
Lack of database


ASPECTS OF IMPROVEMENT
Legislation
Work check-up
Supervision
Exchange of information
Sanctions
Inquest
Regulation of organizations
International regime

NUCLEAR FORENSIC ANALYSIS CAPABILITIES AND EXPERIENCE AT THE OAK RIDGE Y-12 NATIONAL SECURITY COMPLEX

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Abstract

The Oak Ridge Y-12 National Security Complex has been involved in the US nuclear weapons programme since its inception in the 1940s. Known as the US “Fort Knox of uranium”, the site has a technical staff possessing unique expertise and experience related to enriched uranium and other weapons related materials. As a result of the history and mission of Y-12, the Y-12 Analytical Chemistry Organization (ACO) has broad analytical capability that can rapidly respond to nuclear forensics situations. This rapid-response capability is, in part, due to having all of the analytical instrumentation and expertise within one organization. Rapid response teams are easily formed to quickly obtain key information. The infrastructure to handle nuclear materials — chain of custody, radiological control, information management, etc. — is maintained for normal operations. As a result, the laboratory has demonstrated capability for rapid response to unusual analytical problems, such as nuclear forensic incidents. The paper discusses the Y-12’s analytical capabilities and the importance of key instruments and highly trained personnel in providing critical information.

1. INTRODUCTION

One of the original Manhattan Project sites, the Y-12 National Security Complex in Oak Ridge, Tennessee, has a long and distinguished history in the production and analysis of nuclear materials, especially high enriched uranium (HEU). The site possesses the infrastructure for safe handling and processing of HEU. Situated between the Oak Ridge National Laboratory (ORNL) and the former K-25 Uranium Enrichment Facility, Y-12 has been involved with both facilities and, as a result, possesses a unique “store-house” of data and information on HEU, from its enrichment phase to its uses in weapons and reactors.

The wide range of capabilities and experience of Y-12's Analytical Chemistry Organization (ACO) are a significant asset in its nuclear forensics role. The ACO is one of only a few "full service" laboratories in the US weapons complex with the ability to perform analyses from trace to matrix levels, within one organization. This centralization has been found to be a plus for rapid unknown identifications. The staff of the ACO Sample Receiving Department is trained and familiar with procedures for maintaining sample chain of custody that are part of normal operations. The laboratory is access limited within the protected area of the Y-12 plant. These security measures ensure the protection of samples. Radiological control protocols already exist and are also part of normal operations. The ACO can easily form teams for rapid response to unusual situations. Analytical data can be readily distributed through the existing laboratory information system (LIMS). The ACO collaborates both with State and with federal law enforcement agencies to analyse non-nuclear forensic evidence. Prior experience with these agencies facilitates understanding of their operations and enhances productivity of joint efforts.

2. DESCRIPTION OF NUCLEAR FORENSICS METHODOLOGY

When a nuclear forensic sample is obtained at ACO, a protocol has been developed to accelerate the acquisition of key data:

- Uranium isotopic composition,
- Uranium concentration,
- Chemical composition,
- Sample morphology,
- Impurity identification and concentration,
- Age since enrichment or cleanup,
- Characterization of non-nuclear materials associated with the sample.

Specific analytical techniques that provide key data are considered to be primary methods. Secondary analytical methods are employed to confirm data obtained by the primary methods or to obtain additional data to support a more detailed forensic analysis.

2.1. Nuclear forensic analysis — primary analytical methods

Scanning Electron Microscopy: A scanning electron microscope (SEM) with an energy dispersive X ray detector (EDX) is usually the first instrument used to examine a sample. The Y-12 SEM has a unique sample compartment that can accept large (25 × 25 × 5 cm) specimens. The SEM provides morphological information and qualitative data on elements above beryllium. Y-12 also has a complementary electron microprobe that can be employed to obtain quantitative information on specific elements. Elemental composition can be mapped through a material.

Davies–Gray (DG) Titration or Isotope Dilution Mass Spectrometry (IDMS): These methods are used to precisely determine the concentration of uranium. The DG titration provides slightly greater precision, but typically requires a larger sample, whereas IDMS has the added advantage that the uranium isotopic composition can be obtained as part of the overall analysis by thermal ionization mass spectrometry.

Spark-source Mass Spectrometry (SSMS): The spark source mass spectrometer is a unique instrument that can provide rapid impurity analysis covering almost every element in the periodic table down to the low parts per million level. Sample preparation is minimal; a small piece of the sample is mounted as one electrode of the system for metals or, if the sample is a powder, it is mixed with silver in a small carbon electrode. A high voltage spark is initiated between the sample and a counter electrode to ionize the sample elements.

X ray Diffraction Spectrometry (XRD): This method is utilized for identification of crystalline materials. Minimal sample preparation is required. The results can be searched in a large database of compounds. The technique is excellent for determining uranium oxides.

Alpha, Beta, Gamma Spectrometry: These techniques are used for screening and to determine radionuclides in the sample.

Age after enrichment/purification: The ^{230}Th/^{234}U system is the primary nuclide clock used for age dating at Y-12. Thorium-230 is separated from the sample and quantitatively measured by isotope dilution mass spectrometry using ^{232}Th as the spike. Eight other nuclide clocks have been identified for age dating, depending on the nature of the sample (^{232}U/^{228}Th, ^{233}U/^{229}Th, ^{234}U/^{226}Ra, ^{235}U/^{227}Ac, ^{235}U/^{231}Pa, ^{236}U/^{232}Th, ^{241}Pu/^{237}Np and ^{241}Pu/^{241}Am).

2.2. Nuclear forensic analysis — secondary analytical methods

Optical emission spectrometry: Optical emission spectrometry is used to semi-quantitatively determine impurity elements in oxides, if the elements are above the maximum concentrations for SSMS. This technique is excellent for determining elements that are hard to dissolve.

Glow-discharge mass spectrometry (GDMS): GDMS is a high resolution mass spectrometric technique used for semi-quantitative determination of impurities in metals. It can be applied to most elements in the periodic table.

Metals by inductively coupled plasma spectrometry (ICP-OES and ICP-MS): Although requiring dissolution, ICP techniques can provide quantitative information on a wide range of elements. This technique is usually used on a limited number of specific elements to determine if the unknown matches the specification of US materials.

Chromatographic methods: Various chemical separation techniques, such as gas, liquid and ion chromatography, are useful in identifying sample components. For example, ion chromatography is useful in quantitatively determining fluorine concentration.

Non-nuclear materials associated with the sample: Materials associated with nuclear samples may provide information about origin. Packing materials, wrapping, inks, fibres and particulates often provide a wealth of information. Y-12 has a number of techniques that can be used to identify these. A Fourier transform infrared spectrometer equipped with an infrared microscope can provide data on fibres, polymers, particulates, inks, coatings, etc. Surfaces and coatings can be analysed using a multiprobe. This unique instrument can perform electron spectroscopy for chemical analysis (ESCA), and Auger and secondary ion mass spectrometry (SIMS) on the surface of a sample, without removal from the instrument, thus lowering the possibility of contamination. Nuclear magnetic resonance spectrometry (NMR) can be used to determine the structure of organic compounds.

2.3. Nuclear forensics response schedule

The following schedule in Table I is used at Y-12 to provide information on unknown uranium materials:

3. NUCLEAR FORENSICS CASES

3.1. Department of Energy Exercise (1996)

In July 1996, the US Department of Energy (DOE) sponsored a nuclear forensics exercise to evaluate US capabilities in responding to a nuclear smuggling event. The exercise involved a number of DOE laboratories as well as Federal Bureau of Investigation and Department of Defence laboratories. An attempt was made to simulate materials that would be associated with a real sample. Oak Ridge received the following samples: two vials containing tan powders, one vial with a piece of paper, one vial with plastic material, and a small piece of metal. After screening for radiation, which showed the metal to be radioactive, and logging into Sample

TABLE I. SCHEDULE TO PROVIDE INFORMATION ON UNKNOWN URANIUM MATERIALS

Response time	Information	Analytical method	Sample amount
12 hours	1) U concentration (g U/g sample) 2) U isotopic composition 3) Elemental composition/ morphology	1) IDMS 2) TIMS 3) SEM	1) Use TIMS sample 2) 0.35 g 3) ~1 mg
24 hours	1) Impurities 2) Radionuclides 3) U chemical form	1) SSMS 2) Alpha, beta, HRGS 3) XRD	1) ~50 mg 2) ~100 mg 3) ~1 mg
48 hours	1) Time since sample was enriched or cleaned up 2) Surface species	1) Age after enrichment 2) SIMS	1) 0.5 g 2) 10 mg
96 hours	1) Time since separation or purification (for Pu)		1) 0.5 g

Receiving for chain of custody purposes at the Y-12 plant in Oak Ridge, the metal sample was analysed by SEM, showing that it was primarily uranium with a small amount of titanium (Fig. 1). A back scatter image of the sample is shown in Fig. 2; the light areas are uranium and the dark areas are primarily titanium. Within 2 h after receipt at the Y-12 plant laboratory, the metallic sample was tentatively identified as a US produced material (0.75% Ti oralloy). Thermal ionization mass spectrometry confirmed that the material was HEU of isotopic composition (atom%): ^{233}U = <0.0002%, ^{234}U = 1.0550%, ^{235}U = 93.232%, ^{236}U = 0.4039% and ^{238}U = 5.305%. The uranium concentration determined by isotope dilution mass spectrometry was 0.9923 g U/g. X ray diffraction showed the major phase of the sample to be α-uranium, with the possible presence of U_2Ti, UO_2 and TiO_2. SIMS analysis gave similar isotopic abundances for uranium and also showed slightly enriched ^{6}Li on the surface (possible contamination). Age dating using the ^{230}Th/^{234}U clock showed that the age since chemical purification was 8.14 years.

Determination of the impurities in the HEU sample was important for confirmation of its origin. Most weapons grade uranium (oralloy) in the US was processed at the Y-12 plant. Product certification records contain data on impurities present in oralloy. A number of analytical techniques were

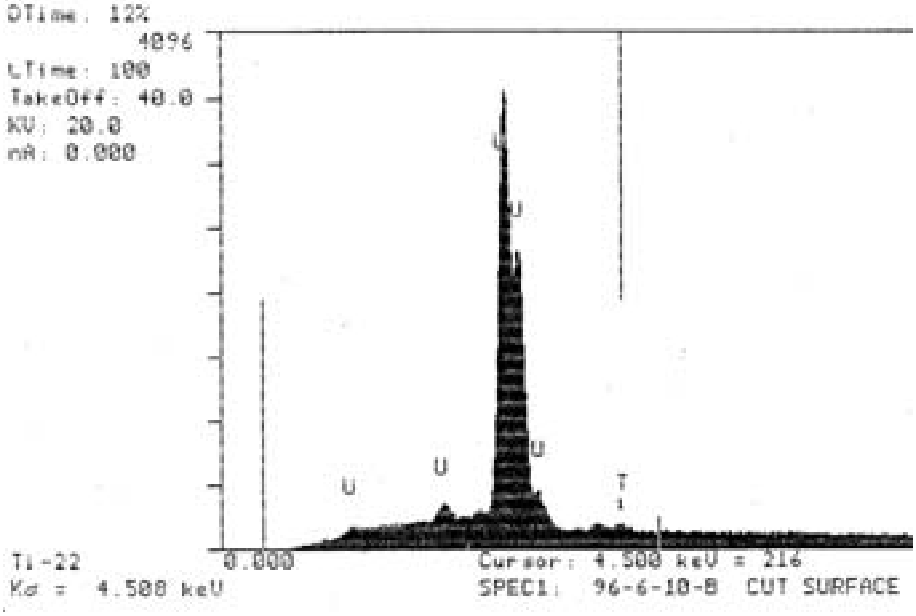

FIG. 1. SEM microprobe analysis of the nuclear smuggling exercise sample (UTi; oralloy).

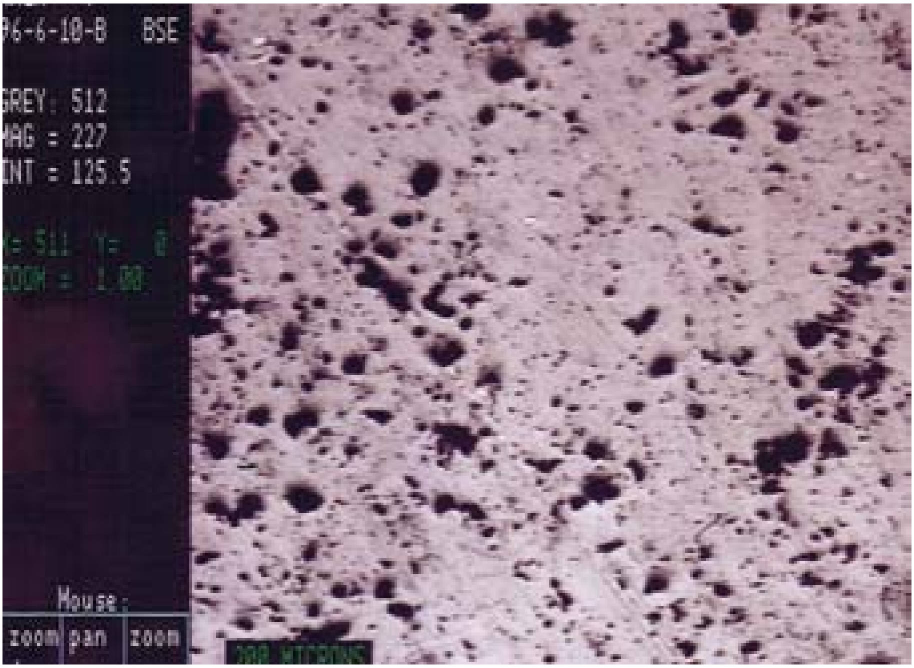

FIG. 2. SEM backscatter image of nuclear forensics sample (UTi; oralloy).

used to determine the impurities in the forensic sample, including SSMS, optical emission spectrometry, inductively coupled plasma mass spectrometry and glow discharge mass spectrometry. The impurity data were consistent with U–Ti oralloy.

The non-nuclear materials associated with the forensics sample were analysed by SEM, XRD, Raman, GC-MS and FTIR. These evaluations revealed common substances such as anatase, calcium sulphate, cellulose and polyethylene. These data were reported to assist other exercise participants in evaluating the sample; the Y-12 plant specializes in analysis and characterization of uranium, and this was the primary focus of the efforts at Oak Ridge.

3.2. Bulgarian intercept (2001)

On 29 May 1999, Bulgarian customs officers intercepted a package containing HEU at the Rousse border checkpoint. A sealed glass ampoule of the material was shipped to Lawrence Livermore National Laboratory (LLNL), California, in March 2000 for detailed forensic analysis. A 0.76g subsample was sent from LLNL to the Y-12 National Security Complex in May 2000. Except for the rapid-response schedule, the methodology described in Section 2 was applied. Even though this was a real nuclear smuggling sample, the time delay from interception to the arrival of the sample in the US for forensics analysis negated the need for a rapid response in performing the key analyses. Obtaining the highest quality data possible was deemed more important than rapid response.

Because this sample was in powder form and thought to be a uranium oxide, it was important to establish the chemical form(s) of the uranium in the sample. As shown in Fig. 3, X ray diffraction established the composition of the sample to be:

— Major component:	U_3O_8
— Intermediate component:	$UO_{2.92}$
— Minor component:	$UO_2F_{2\text{-}x}(OH)_x.2H_2O$ $(x = 0.3 \leq x \leq 1.2)$

The sample was determined to be 0.8408 ± 0.0006 g U/g by isotope dilution mass spectrometry. The isotopic composition (atom%) was ^{233}U = <0.002, $^{234}U = 1.1733 \pm 0.0040$, $^{235}U = 72.629 \pm 0.013$, $^{236}U = 12.1334 \pm 0.0026$, $^{238}U = 14.064 \pm 0.011$. From these data, and using an impurity correction of 0.2%, the overall composition of this sample was estimated to be 74% U_3O_8 and 26% $UO_{2.92}$.

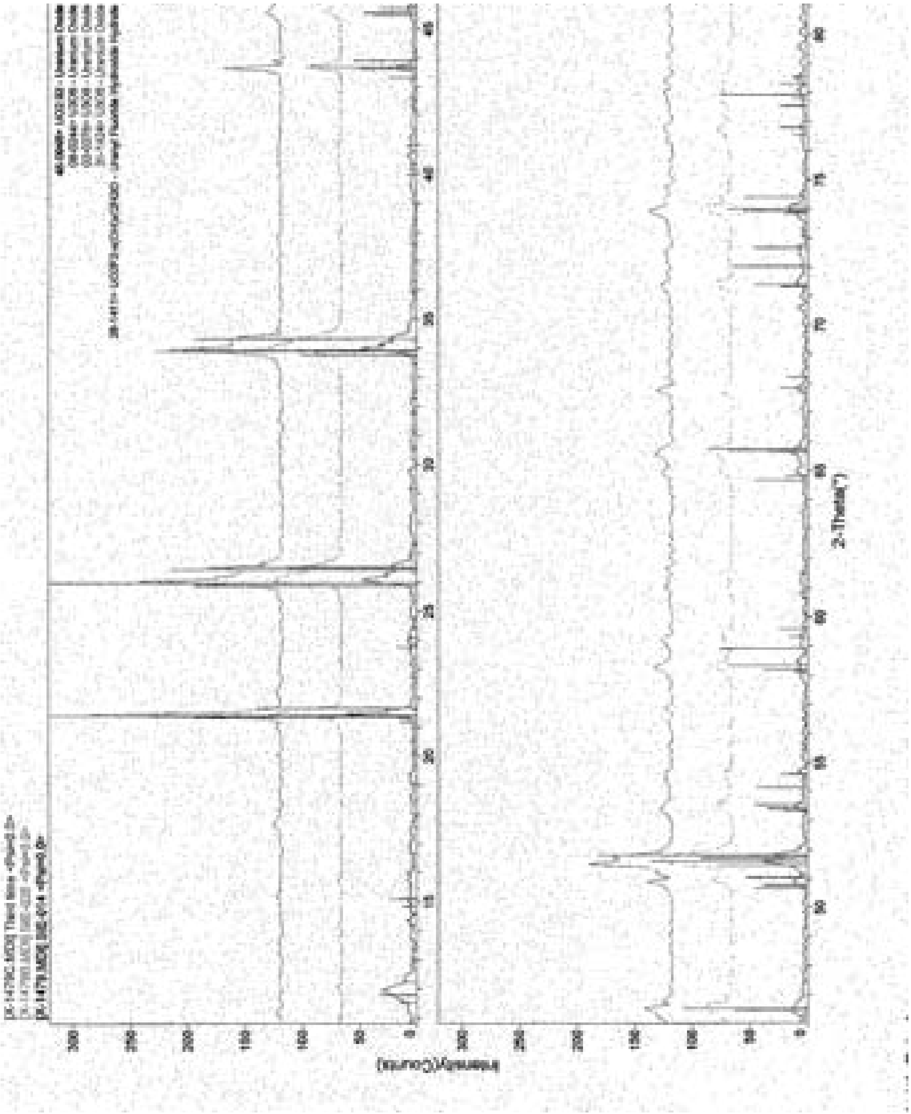

FIG. 3. X-ray diffraction of Bulgarian HEU.

During the analysis of this sample, it was found that high precision measurements of uranium and plutonium isotopic abundances are essential for rigorous evaluation of data, particularly in the area of attribution. For the Bulgarian sample, obtaining the required data proved to be difficult because of a very low level of plutonium.

4. CONCLUSIONS

Some of the key lessons learned were:

- The DOE exercise demonstrated the ability to immediately identify US origin HEU (SEM can provide immediate identification of US origin alloys).
- For the Bulgarian oxide sample, X ray diffraction was extremely important in determining chemical composition.
- Impurity analyses are important in providing a fingerprint for HEU (particularly for HEU of US origin), and for corrections in determining the uranium composition.
- Analytical instrumentation for rapidly providing key information includes older techniques such as spark source mass spectrometry and X ray diffraction.

The Y-12 National Security Complex has the broad range of capabilities required to rapidly identify nuclear forensics samples. These capabilities include not only instrumentation, but also technical expertise and materials data gained over several decades of operation. These capabilities have been demonstrated in the two cases described in this paper. Y-12 remains ready to employ these assets as needed to help reduce global nuclear proliferation.

COMBATING AND PREVENTING ILLICIT TRAFFICKING IN ROMANIA

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Abstract

In the international context of possible nuclear threats, the National Commission for Nuclear Activities Control has consolidated the existing legal framework to ensure efficient physical containment of nuclear material according to INFCIRC/225/Rev.4 (corr.) requirements. At the same time, methods for combating and preventing illicit trafficking of nuclear material and radioactive sources have been improved as a result of IAEA support and through a PECO project.

1. INTRODUCTION

The legal status and responsibilities of the National Commission for Nuclear Activities (CNCAN) are described in law No. 111/1996 and, according to Article 4, are as follows:

“(1) **The national authority competent in the nuclear field** exercising regulation, authorization and control powers provided under the present law shall be **the National Commission for Nuclear Activities Control** under government control.

(2) The National Commission for Nuclear Activities … shall draw up its own organizing and functioning regulations that shall be approved by government decision.”

Since 2001, the functions of the CNCAN have been co-ordinated by the Ministry of Waters and Environmental Protection. The Commission President, named by the Prime Minister, has the authority to approve regulations and issue an official publication. Thus, CNCAN has its own Regulations on Organization and Functioning and Regulations on Interior Discipline. The Regulations on Organization and Functioning set out the responsibilities for CNCAN, for the Commission President, and for all divisions and independent services.

The main functions and responsibilities of CNCAN are:

- To authorize nuclear activities.
- To propose laws, ordinances and government rulings regarding safety of nuclear activities.
- To set out its own regulations and regulations in common with other appropriate authorities.
- To review regulations whenever necessary for consistency with international standards and with ratified international conventions in the nuclear field, and to order measures to ensure application.
- To review, when necessary, regulations governing fees and tariffs for the authorization and control of nuclear activities with the approval of the Ministry of Finance.
- To co-ordinate at national level the design, implementation, development and maintenance of performance of physical protection systems according to national legislation and international recommendations.
- To co-ordinate national activities for combating and preventing illicit trafficking of nuclear and radioactive materials.
- To nominate, by order of the CNCAN president, persons responsible at the national level for:

  - nuclear events,
  - safeguards reports,
  - physical protection reports,
  - incidents of illicit trafficking of nuclear and radioactive materials,
  - importation and export of strategic products,
  - technical assistance co-ordination,
  - other specific activities that involve contact with international organizations.

Since February 2001, the CNCAN has taken appropriate actions designed to improve its independence, capability and resources, and also to improve efficiency as a national safety authority.

2. LEGAL FRAMEWORK

2.1. Law 111/1996 on the safe deployment of nuclear activities

Law 111 was enacted in 1996 and was modified and completed in 1998. Its specific provisions are as follows:

- A National Commission for Nuclear Activities Control is empowered according to Article 5, para. 1, “to issue regulations for specification in detail of general requirements for nuclear safety, for protection against ionizing radiation, for quality assurance, for non-proliferation of nuclear weapons, for physical protection and emergency plans for intervention in the event of a nuclear accident, authorization and control procedures inclusive, as well as any other regulations needed for authorization and control of activities in the nuclear field.”
- A condition of authorization is that the applicant, according to Article 18j, “institutes and maintains a system conforming to the specific regulations of physical protection of nuclear fuel, radioactive and nuclear materials, radioactive waste and products, as well as of nuclear facilities including storage facilities for nuclear fuel, nuclear and radioactive materials, radioactive waste.”

In 2002, the law was reviewed and amendments proposed. On 29 August 2002, the Government approved amendments that include a definition of terrorist acts (see Article 42) as follows:

- A threat to a person or a community through any means, by spreading radioactive material or by using nuclear installations, or generating devices of ionizing radiation endangering human, animal or environmental health;
- An unjustified alarm by mail, telephone or other means for a person, the public or a specialized institution to intervene in a nuclear accident involving the spread or use of radioactive material or nuclear installations to the endangerment of human or environmental health;
- Spreading and introduction to the atmosphere, water, soil or subsoil such as to endanger human or environmental health, and threats of nuclear explosion or nuclear accident if there is potential for public disorder;
- Destruction, degradation of a nuclear facility or nuclear installation that contains radioactive material, or opposition to decommissioning measures or to nuclear safety measures when the objective is to create panic and public disorder;
- Development, production, ownership, importation, export or transit of nuclear weapons detonators or other nuclear explosive devices.

2.2. The strengthening of the legal framework

New Physical Protection Regulations were enforced in 2001.

- According to Article 2, the "Physical Protection Systems design *is based on the "Design Basis Threat" document.* The Design Basis Threat is issued by the authority to each protected facility, to define the features of a possible adversary and the dimensions of a Physical Protection System to combat threats."
- According to Article 18a, the Design Basis Threat for each protected facility must be issued by the Authority to cover risk analysis and the design and evaluation of Physical Protection Systems by the operator.
- Article 20: When the Design Basis Threat is modified, the Authority must inform the authorization holder accordingly and determine if the modifications are incorporated in the physical protection plans and measures and if they are included in the operator's physical protection measures.
- Article 26: The authorization holder must upgrade the Physical Protection System in accordance with the Design Basis Threat issued by the Authority. Other factors should be considered such as: possibilities of response in emergencies and necessary actions and measures to enable the organization to maintain control over protected facilities and materials.

Regulations on qualification requirements for guards and security personnel are included in the CNCAN requirements for authorization holders, enforced in 2002. Regulations on using the Design Basis Threat were enforced also in 2002.

As stipulated in Article 3, the Design Basis Threat for protected facilities within Romania is issued by the Authority based on documents received from appropriate organizations." In Article 4 it is stipulated that "Physical Protection Systems designing for protected facilities and for storage, use and transport of protected materials is based on the Design Basis Threat." Article 6 stipulates that "The Authority has the responsibility to define and review the Design Basis Threat for physical protection of protected facilities and materials."

The Design Basis Threat document for each nuclear facility was drawn up by CNCAN in co-operation with other State institutions in 2002. CNCAN also specified Fundamental Norms for safe transport of radioactive materials and Norms for International Shipments of radioactive materials involving Romanian territory. CNCAN has proposed to the government an ordinance regarding a list of materials, devices, equipment and information relevant to nuclear weapons proliferation that are in the process of being approved.

3. STRENGTHENING PHYSICAL PROTECTION OF NUCLEAR MATERIALS AND NUCLEAR FACILITIES

The CNCAN policy on strengthening the system for physical protection of nuclear materials and nuclear facilities can be described in terms of the following actions taken by CNCAN:

Fulfilment of the INFCIRC/225/Rev. 4 requirements;

- IPPAS Missions in Romania in 1997 and 2002;
- Construction of a database at CNCAN on illicit trafficking incidents involving nuclear material and radioactive sources;
- In April 2001, CNCAN, IAEA and Sandia National Laboratories (Livermore, CA, USA) organized a Design Basis Threat National Workshop in Romania;
- In November 2002, IAEA and CNCAN organized a national workshop in Romania on physical protection of nuclear materials and nuclear facilities;
- CNCAN promotes close co-operation with other Romanian institutions to combat and prevent illicit trafficking actions taken against nuclear facilities and nuclear materials, particularly when such materials are transported across the country;
- To decrease the response time in emergency cases including illicit trafficking incidents, a Mobile Unit was created by Order No. 205 of the commission president in 2001. This Mobile Unit is able to intervene at short notice in the following situations:
  - radiological emergency,
  - illicit trafficking of nuclear material,
  - announced or unannounced directives to authorization holders,
  - other specific actions concerning activities in the nuclear field.

The Mobile Unit has 12 experts on nuclear safety, applications of ionizing radiation, radioprotection, environmental radioprotection, safeguards, physical protection, and illicit trafficking. The Mobile Unit is composed of:

- A mobile laboratory,
- Two cars,
- Fifteen gamma dose rate portable instruments,
- Twelve gamma dose rate personal instruments,
- A Canberra Inspector MCA with HPGe detector,
- Two FieldSPECs with NaI detectors received from the IAEA through a technical assistance project,

- A mini MCA 166 with a CdZnTe detector,
- Individual protection costumes (two types),
- Individual protection shoes.

4. NUCLEAR MATERIAL CONTROL

In 2001, the IAEA organized a national workshop in Romania on the "Implementation of the Additional Protocol", and, in 2002, the IAEA organized a regional workshop on the same subject in Bucharest.

In 2001, CNCAN organized a national seminar in Bucharest on the "Nuclear material control" to instruct managers of nuclear facilities on legal requirements related to the use of materials, equipment and information pertinent to nuclear weapons proliferation.

Since 2001, CNCAN has created three databases in order to keep strict account and control of nuclear material and radioactive sources:

- For all radioactive sources and for all CNCAN authorizations issued related to radioactive sources;
- Safeguards concerning all changes in nuclear material inventories;
- All plutonium sources, depleted material containers and all authorizations for internal transfer of nuclear material, import/export of material and equipment pertinent to nuclear-weapons proliferation, and all authorizations related to the nuclear fuel cycle.

5. ILLICIT TRAFFICKING INCIDENTS IN ROMANIA

Since 1994, there have been 25 illicit trafficking incidents: 14 involving radioactive sources, ten involving natural uranium and one low enriched uranium (Fig. 1). Ten occurred in Bucharest. All were reported to the IAEA.

6. INTERNATIONAL CO-OPERATION

In co-operation with CNCAN, the IAEA has organized seminars, workshops, training sessions for using NDA instruments, and has provided two FieldSPECs for safeguards and illicit trafficking cases.

CNCAN has had very good co-operation with the US Department of the Energy (DOE) and Sandia National Laboratories to improve physical protection systems for Romanian nuclear facilities.

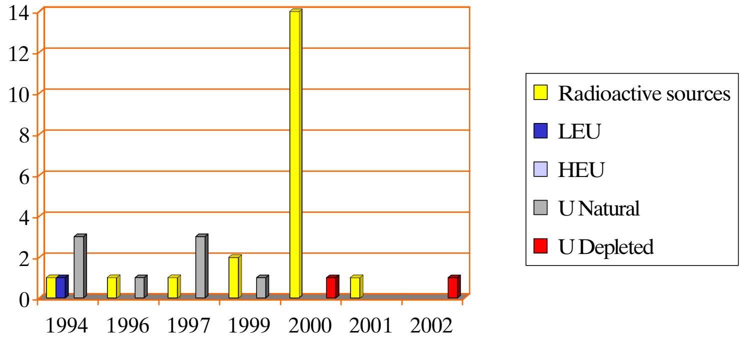

FIG. 1. Illicit trafficking incidents in Romania

Since 2001, CNCAN has been the beneficiary of a PECO grant initiated by the European Commission for combating and preventing illicit trafficking incidents involving nuclear material and radioactive sources. This project has the following objectives:

- Production of a manual in the Romanian language, for response in cases of illicit trafficking of nuclear material and radioactive sources, that describes all institutions involved;
- Organization of a national exercise on illicit trafficking;
- Training for law enforcement officers;
- Training for scientists at institutes with designated expertise;
- Participation in the database at the Institute for Transuranium Elements (ITU), Karlsruhe.

7. NATIONAL EXERCISE FOR COMBATING AND PREVENTING ILLICIT TRAFFICKING

The objective of the exercise is to evaluate initial responses of relevant Romanian organizations to reports of nuclear material incidents, including aspects of communications, timeliness of response, measuring capability, situation evaluation, and interfacing procedures. It is a field exercise with deployment of all involved organizations: CNCAN, Ministry of Waters and Environmental Protection, the laboratory for radiation control at the Ministry of Health, and the General Directorate for Combating Organized Crime and Anti-Drugs at the Ministry of Interior.

The exercise was evaluated by experts from the Office for Physical Protection and Material Security, IAEA, and from ITU. The scenario involved a private property search for jewellery by local police, during which an unusual package was discovered. Because the officers were unable to identify the material, they called police headquarters to say that they suspected that it was nuclear. The police headquarters contacted the Nuclear Unit of the General Directorate for Combating Organized Crime and Anti-Drugs.

After cordoning off the area, the police measured dose rates and verified that certain toxic gases were absent outside the perimeter. Forensics officers took fingerprints and pictures. The pictures were e-mailed to CNCAN for preliminary appraisal (Figs 2–6).

The police called in scientists from the Laboratory for Radiation Control to make dose rate determinations of the suspect material and within the isolated area.

CNCAN personnel arrived at the site and were briefed by the police and the scientists. It appeared that there were four radioactive sources and pellets of nuclear fuel. The CNCAN personnel established the following strategy:

- They made their own dose rate measurements,
- They split into two groups: one to identify the radionuclides for four radioactive sources and the other to identify the nuclear material,
- They provided their contamination measurements to the team.

The CNCAN team prepared a document for the police containing:

- the instrument types used,
- dose rates for each type of material,

FIG. 2. Deployment of the Police Nuclear Unit.

FIG. 3. Safeguards experts from CNCAN taking measurements of the seized nuclear material.

— their conclusion: four radioactive sources (^{22}Na, ^{60}Co, a beta source, an alpha source) and forty natural uranium pellets.

The CNCAN scientists prepared the items for transportation: one labelled container for the radioactive sources and one labelled container for

FIG. 4. CNCAN contamination measurements.

FIG. 5. CNCAN representatives prepare the final documents.

the nuclear material. The containers had documents prepared by CNCAN for transportation, stating, for example, that the radioactive sources would be transported to the Nuclear Research Institute.

FIG. 6. CNCAN representatives give the documents and transport containers to the police.

8. CONCLUSIONS

During the exercise the institutions involved demonstrated good co-operation and professional skills. After the exercise, the CNCAN personnel and the police held a press conference. Subsequently, the importance of good co-operation in cases of illicit trafficking of nuclear material and radioactive sources was reported in the press and on television.

FORENSIC ANALYSIS OF SMUGGLED HIGH ENRICHED URANIUM INTERDICTED IN BULGARIA

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Presented by N.G. Wimer

A sample of high enriched uranium (HEU) was seized in Rousse, Bulgaria, on 29 May 1999, at a border crossing into Romania. Search of a suspect's vehicle uncovered a lead canister in the trunk. The initial examination of the contents by Bulgarian scientists indicated that the sample was, indeed, HEU, and arrangements were made for a US team of nuclear forensic scientists from several national laboratories to conduct a thorough examination. This report provides a summary of the results.

The HEU sample was contained in a glass ampoule embedded in yellow wax that filled a cylindrical lead container. A broad set of techniques was used to examine both the nuclear and the non-nuclear materials. Our general experimental approach has been previously described at meetings of the Nuclear Smuggling International Technical Working Group (ITWG), but this case represents the application of the most diverse set of nuclear forensic measurements for an actual seized sample.

Analysis of the HEU itself included particle characterization, stoichiometry, impurity elements, residual nuclides, age dating, and uranium and plutonium isotopics. Measurements by XRD, SEM and TEM showed that the sample was mostly U_3O_8, with minor amounts of two other phases. The powder was extremely fine grained (160 nm mean) and quite uniform in size. Most grains (95%) are equidimensional, with the remainder rod or plate shaped. The uranium was 72.7% ^{235}U with a high ^{236}U abundance of 12.1%. The sample was reprocessed, reactor irradiated material. The original uranium enrichment was 90% and the irradiation burned up about 50% of the initial ^{235}U. Plutonium was present at a very low level (3 ppb); the ^{239}Pu abundance was 82% with 240/239 = 0.12. Three fission products were detected at low levels, giving unambiguous evidence of fuel recycling. The total impurity content was about 600 ppmw (mostly S, Cl, Fe and Br), which we interpreted as indicating a batch processing operation because the impurities were too high for a laboratory scale operation.

We determined the age of the chemical reprocessing by using seven nuclide systems. The multiple clocks enabled us to evaluate the validity of the assumptions in the dating schemes. Slightly higher ages for Am and Ac chronometers are consistent with a Purex process. The mean age of the remaining clocks is 30 October 1993, with an uncertainty of only 25 days. The similar age for the Pu/Am clock suggests that the plutonium was not from post-processing contamination.

The non-nuclear materials provide a number of forensic clues. The yellow waxy liner material was an uncommon type of paraffin wax that had unusual organic compounds (naphthalene derivatives). The yellow colourant was barium chromate, which is rare in Europe and the United States but common in Brazil, China, India and Eastern Europe. The ampoule was common borosilicate glass. We noted that ampoules have been used as containers for archiving nuclear samples, but a glass ampoule had not been previously reported as a container for smuggled nuclear material. Two pieces of paper were analysed. One was attached to the exterior of the lead container and the other was wrapped around the ampoule. Both contained softwood and hardwood species, and the fibres were produced by the Kraft pulping process. The species of wood were not from North America or Western Europe, but were consistent with Eastern Europe. Finally, the lead container was hardened with 5 wt% antimony. The lead isotope composition excluded US ores, but was consistent with lead from several European and Asian mines. Taken altogether, the non-nuclear evidence was most consistent with assembly of the package in Eastern Europe from local sources.

Nuclear isotopics can be used to constrain the type of reactor in which the HEU was irradiated. Detailed reactor calculations, using WIMS and GLASS codes for a pin fuel cell geometry, pointed to a light-water reactor with a very thermal spectrum. We calculated that a burn-up exposure of more than 300 000 MW·d/MT was required to match the uranium isotopics. However, we found it quite difficult to simultaneously match the uranium and plutonium isotopics using these codes and the assumed geometry. Our preferred interpretation is that it was a research reactor.

Although we are not able to pinpoint the type of reactor, we emphasize that we identified a number of distinguishing characteristics of this HEU sample that would enable its linkage to other samples from the same reactor or reprocessing environment. The very low abundances of the minor uranium isotopes, ^{232}U and ^{233}U, coupled with the high abundance of ^{236}U, are one such feature. Coupling the plutonium isotopics to the uranium composition provides an especially distinctive signature. The particle size distribution was also highly unusual for a reactor fuel. The accuracy with which we determined the time the material was last chemically processed also offers a potential pathway to attribution. If nuclear regulatory agencies maintain chronological records of activities at known reprocessing facilities, the physical and chemical characteristics discussed here may be sufficient either to identify a specific facility or, at least, to eliminate a large number of potential reprocessing facilities.

ANALYTICAL TECHNIQUES

(Session 3)

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APPLICATION OF ACCELERATOR MASS SPECTROMETRY TO NUCLEAR SAFEGUARDS

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Abstract

For radionuclides with half-lives greater than a thousand years, mass spectrometers equipped with atom counting detection systems offer greater sensitivity than is possible by radiometric techniques. However, conventional mass spectrometers are ultimately limited by interferences from isobars, molecules or neighbouring abundant isotopes. The techniques employed in accelerator mass spectrometry have the potential to eliminate or greatly reduce these interferences. Accelerator mass spectrometry can achieve isotopic abundance sensitivities of 10^{-15} and detection limits of less than 1 fg. This technique has been widely used for radiocarbon dating and related applications. In this paper, we address its application to detection of nuclear signatures at trace levels, in support of international nuclear safeguards, focusing on the utilization of the radionuclides ^{129}I and ^{236}U.

1. INTRODUCTION

Improvements in the safeguards system in the last 10 years have focused on verifying the completeness of declarations made by Member States. Environmental sampling has been introduced within and around declared facilities [1]. It is based on the assumption that operation of nuclear facilities results in routine or accidental releases of small amounts of radionuclides that may be deposited in the surrounding areas, either within buildings or in the external environment. Analysis of surface wipe samples from within buildings or of environmental samples reveals the nature of the processes used in the facility, and can, therefore, be used to verify the declared activities at that facility.

To provide assurance of the absence of undeclared facilities, the concept of wide-area environmental sampling (WAES) has been proposed and studied [2]. For WAES, an array of sampling sites would be distributed across a region. Sampled materials may include soil, vegetation, water, or aerosols captured by

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air filtering devices. Analysis of such samples could reveal the presence of an undeclared facility at some distance from the sampling station. The key signatures of a reprocessing facility include ^{85}Kr, ^{90}Sr, ^{134,137}Cs, ^{129}I, and plutonium isotopes [2]. Uranium-236 also has great potential [3], as it has higher yield in uranium irradiation than any fission product.

The practicality of WAES depends on the capability of detection techniques to distinguish a signal from background levels at significant distances from the source (10–100 km). The expected levels of the WAES signature radionuclides are very low and pose considerable challenges to sampling and detection techniques. In the cases of ^{129}I and ^{236}U, AMS offers the most sensitive detection method available. While ^{129}I has been measured for a number of years by AMS at the Australian Nuclear Science and Technology Organisation (ANSTO), we have pioneered the measurement of ^{236}U in environmental materials by this method [4].

2. ACCELERATOR MASS SPECTROMETRY

Accelerator mass spectrometry [5] differs from other kinds of mass spectrometry in accelerating ions to energies in the range 10 to 100 MeV. Isotopic ratios are measured, by counting the ions of the rare radioisotope while measuring the beam current of the corresponding stable isotope. The long-lived radionuclides most commonly analysed by AMS are ^{14}C, ^{10}Be, ^{26}Al, ^{36}Cl and ^{129}I. These have half-lives from thousands of years to a few million, and occur naturally in the environment at very low levels. This technology has also been used for the detection of many other radionuclides with long half-lives, including ^{41}Ca, ^{59}Ni, ^{99}Tc, ^{237}Np, and plutonium isotopes.

Figure 1 shows a schematic of the ANTARES (Australian National Tandem Accelerator for Applied Research) accelerator at ANSTO, which is a typical layout used for AMS. ANTARES is a 9 MV tandem accelerator that has been upgraded to ensure high voltage stability better than one part in 5000. The figure shows the high-energy beamline dedicated to the analysis of ^{236}U and other heavy radionuclides.

With the use of a tandem accelerator, the AMS technique has three key properties:

(1) Negative ions are injected, which eliminates stable isobars of elements that do not form negative ions, for example ^{14}C is free from ^{14}N interference, and ^{129}I is free from xenon interference;

(2) Interfering molecular ions are destroyed by stripping ions to high charge states in the high voltage terminal, for example $^{14}C^{3+}$ is transmitted

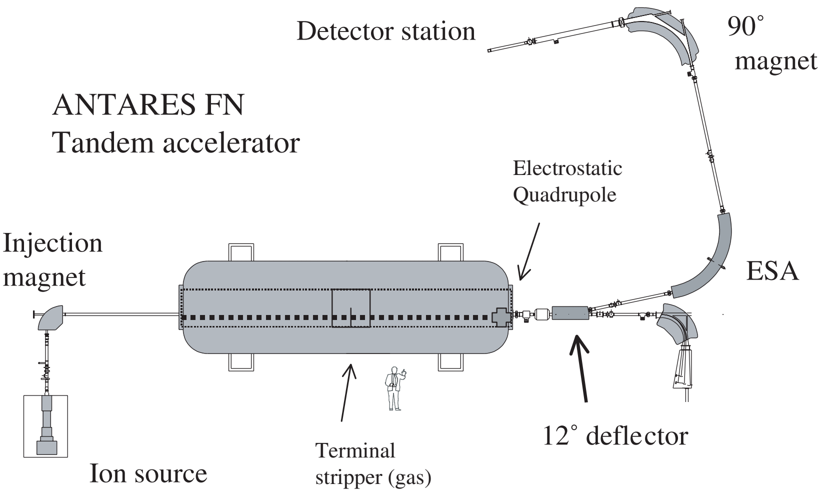

FIG. 1. The ANSTO AMS system including components used for ^{129}I and ^{235}U analysis.

through the accelerator, while the interfering mass-14 molecule ^{13}CH breaks up when electrons are stripped from the molecule, and by the same process ^{236}U is separated from ^{235}UH;

(3) At high energies, ions can be positively identified through precise measurement of their energy, rate of energy loss, and time of flight, for example ^{36}Cl can be distinguished from ^{36}S and ^{129}I can be distinguished from scattered ^{127}I ions.

As a result, AMS has a very high isotopic abundance sensitivity: in some cases, isotopic ratios can be measured with a detection limit as low as 10^{-15} (for example, radiocarbon, where the ^{14}C:^{12}C ratio is measured in samples containing about 1 mg carbon, this ratio corresponds to an age of 55 000 years). In the case of uranium, where a few grammes of a typical environmental sample yields about 1 μg of uranium, the current detection limit that we have achieved is 10^{-9} for the ^{236}U:^{238}U ratio. This corresponds to a detection limit of around 1 fg for ^{236}U. Accelerator mass spectrometry has also been shown to have this level of sensitivity for plutonium isotopes and ^{237}Np [6].

3. IODINE-129

Iodine-129 has been recognized as one of the most promising nuclear signatures for the purpose of WAES. It has a moderate fission yield (0.54%)

and a long half-life (15.7 million years). Most significantly, iodine readily takes on a volatile form, and is, therefore, relatively difficult to contain during reprocessing, resulting in a release fraction far greater than most elements. However, unlike noble gases, it is deposited in the local environment following release, creating an environmental footprint around a facility.

Prior to AMS, few measurements of ^{129}I in the environment had been performed due to the difficulty of its detection. Using AMS, very low concentrations of ^{129}I are being measured, contributing to an understanding of its global background variability and transport, and facilitating its use as a monitor of nuclear activity. It has been shown to occur naturally, with an isotopic ratio ^{129}I:^{127}I in the range 10^{-11} to 10^{-14}. However, anthropogenic sources of ^{129}I now dominate in all environments exposed to global fallout. Anthropogenic ^{129}I has been detected as originating from many sources, including reprocessing facilities, accidents at nuclear facilities and nuclear weapons tests [7]. Some of these have resulted in general global fallout of ^{129}I, while other studies have shown local and regional distributions from specific sources.

Studies conducted around reprocessing facilities have shown that the ^{129}I signal is readily detectable in the range 5 to 20 km [8], in soil, water and sediment samples. A study of moss samples at up to 60 km from the Sellafield reprocessing plant in the UK found levels one hundred times background even near the extremities of the study area [9].

4. URANIUM-236

Uranium-236 ($T_{½}$ 23.4 million years) is produced with a yield of 20% in thermal neutron capture by ^{235}U. It is also the daughter product of the alpha decay of ^{240}Pu ($T_{½}$ 6570 years), and exists naturally, at very low levels, in uranium ores due to the small neutron flux occurring in ore bodies. The ^{236}U:^{238}U ratio has been found by AMS to be in the range 10^{-10} to 10^{-11} by measuring milligram-sized samples [10]. The low natural level contrasts sharply with nuclear fuel, in which the ^{236}U:^{238}U ratio builds up to 10^{-2} to 10^{-4} during irradiation. Such high ratios relative to the naturally occurring value make its measurement a promising signature of irradiated uranium contamination in the environment.

It has been shown [3] that measurement of the 236:238 ratio is a much more sensitive indication of fuel-residue contamination than the 235:238 ratio. Very small admixtures of irradiated uranium in samples dominated by natural uranium are detectable through their ^{236}U content. In the same samples, the corresponding change to the 235:238 ratio would be too slight to be detected.

Recent results for environmental samples show that, in areas of expected contamination, ^{236}U:^{238}U ratios are elevated relative to sites remote from sources of contamination

[11]. For example, sediments from the Irish Sea close to the Sellafield reprocessing site exhibited ratios of 10^{-5} to 10^{-6}, about one thousand times higher than sediments from areas unaffected by direct sources of contamination. Similarly, soil samples from areas affected by the Chernobyl accident exhibited elevated ^{236}U; measurements of the ^{236}U:^{238}U ratio in soil profiles can be used to track the destruction and migration of fuel particles in the soil.

Uranium-236 has been detected in the vicinity of former nuclear test sites [12]. The contribution from the decay of ^{240}Pu is likely to be most significant in these areas. Uranium-236 is also present in depleted uranium (DU), as a result of the use of recycled uranium in enrichment plants, and it has been detected in soils affected by the use of DU munitions in Kosovo.

5. DISCUSSION

There is clear evidence from a variety of studies that radioisotopes ^{129}I and ^{236}U can be used as environmental signatures of nuclear activity. Both are detectable by AMS at significant distances from their sources, at levels well above environmental background. We are currently engaged in further studies of the distribution of ^{236}U, in particular its behaviour in the marine environment and in the environs of a former nuclear test site.

The value of these and other nuclear signature radioisotopes in the context of WAES can be assessed only with extensive field trials.

Aerosol sampling was highlighted in the WAES report [2] as the technique of choice. Rosenberg et al. [13] recently reported their experiences with aerosol sampling in the field. The measured signature radionuclides included ^{137}Cs and uranium and plutonium isotopes, using α and γ spectrometry and ICP-MS. Beryllium-7 was used as a monitor of the high volume aerosol-sampling equipment. They examined the variability of the detected signals. Recently, we measured ^{129}I and ^{236}U from high volume aerosol samplers. Both radioisotopes showed clear signals, far in excess of background, for samples in proximity with a nuclear facility.

ACKNOWLEDGEMENTS

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ULTRATRACE ANALYSIS OF URANIUM AND PLUTONIUM BY MASS SPECTROMETRY

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Abstract

At the Pacific Northwest National Laboratory (PNNL), we have developed highly sensitive methods to analyse uranium and plutonium in environmental samples. Our most sensitive, well developed methodologies employ thermal ionization mass spectrometry. However, recent advances in inductively coupled plasma mass spectrometry have shown considerable promise for detecting uranium and plutonium at environmental levels. An overview is presented of the mass spectrometric methods used at PNNL to measure actinide elements in environmental samples. We compare these techniques and present results from recent studies that represent the techniques used.

1. INTRODUCTION

In the past 10 years or so, considerable interest has developed in measuring actinides at trace levels in environmental samples that typically contain sub-picogramme quantities of plutonium [1–9]. Such measurements require high sensitivity and, as a consequence, sensitive mass spectrometric-based methods have been developed. Thus, the analysis of actinide elements has gone from counting decaying atoms to counting atoms, with considerable increases both in sensitivity and in precision for these isotopic measurements.

At the Pacific Northwest National Laboratory (PNNL), we have developed highly sensitive methods to analyse plutonium and uranium in environmental samples [10, 11]. The development of trace analysis capability for measuring actinide elements arose from a need to detect and characterize environmental plutonium associated with the nuclear industry. Our most sensitive methods employ thermal ionization mass spectrometry (TIMS); however, recent developments in inductively coupled plasma mass spectrometry (ICP-MS) have shown considerable promise for detecting actinides at environmental levels [11–15]. The work at PNNL has included the development of chemical separation and purification techniques, as well as the development of mass spectrometric instrumentation and techniques.

2. URANIUM AND PLUTONIUM ANALYSIS

The analysis of actinides in environmental samples poses a range of challenges. The behaviour of uranium and of plutonium is similar in the mass spectrometer regardless of instrument type, given that these elements have comparable isotopic mass ranges, chemical behaviours, ionization potentials, etc. Conversely, typical environmental levels of uranium and plutonium differ by orders of magnitude. Soils and natural waters generally contain ppm and ppb levels, respectively, of natural uranium. Plutonium, being solely of anthropogenic origin, is present at sub-ppt levels in soils and waters. Accordingly, different methods are needed to prepare environmental samples for uranium and plutonium analysis. For instance, chemical processing can introduce background uranium from sources such as chemical reagents and glassware. Typical process blank levels for bulk uranium analysis are in the picogramme to nanogramme range. Similar difficulties are not encountered with plutonium, and process blank levels are correspondingly lower. Thus, once extracted and separated, the relatively large amounts of uranium in environmental samples mean that overall sensitivity of the instrument measurement is less important than the precision and accuracy of the isotopic analysis. Even typical process blanks contain sufficient uranium for complete isotopic analysis. For plutonium, the main issue for mass spectrometry is sensitivity.

3. THERMAL IONIZATION MASS SPECTROMETRY

Typical environmental samples, such as soils, are prepared for analysis by wet ashing, followed by spiking with isotopic tracers. Analyses of uranium and plutonium require different approaches and, generally, initial sample solutions are gravimetrically split. A typical solution is split into a 90% aliquot for plutonium analysis and two 5% aliquots for uranium analysis. The plutonium aliquot is spiked with ^{244}Pu, while one of the uranium aliquots is spiked with ^{233}U for quantitation and the other is analysed unspiked for accurate isotopic analysis. All aliquots are separated and purified using a combination of precipitation and anion exchange chromatographic steps. The final purification steps utilize microlitre volumes of analyte. The last step of the chemical procedure consists of quantitatively adsorbing the analyte onto an anion exchange resin bead, which is then loaded onto high purity rhenium mass spectrometer filament. After carburization, the filament is analysed on a triple sector mass spectrometer. The resin bead technique has been combined with a thorough knowledge of the physicochemistry of thermal ion emission [16] to achieve femtogramme detection limits for the TIMS analysis of uranium and plutonium in environmental samples. Descriptions of the chemical methods, filament preparation and mass spectrometric techniques have been published [10, 17, 18].

Thermal ionization mass spectrometry has been used to measure the isotopic composition of actinide elements in a variety of environmental samples, including soils and groundwater [1–5, 17, 18]. Examples are shown in Figs 1 and 2. Typical concentrations of global fallout ^{239}Pu in soils are ~0.05 pg/g.

4. INDUCTIVELY COUPLED PLASMA-MASS SPECTROMETRY

Over the past decade, developments in ICP-MS have led to considerable improvements in sensitivity and precision [8, 11–15]. Experiments were conducted using a ThermoElemental PQ ExCel, quadrupole ICP-MS. Experiments to measure sensitivity and precision of ICP-MS have been systematically

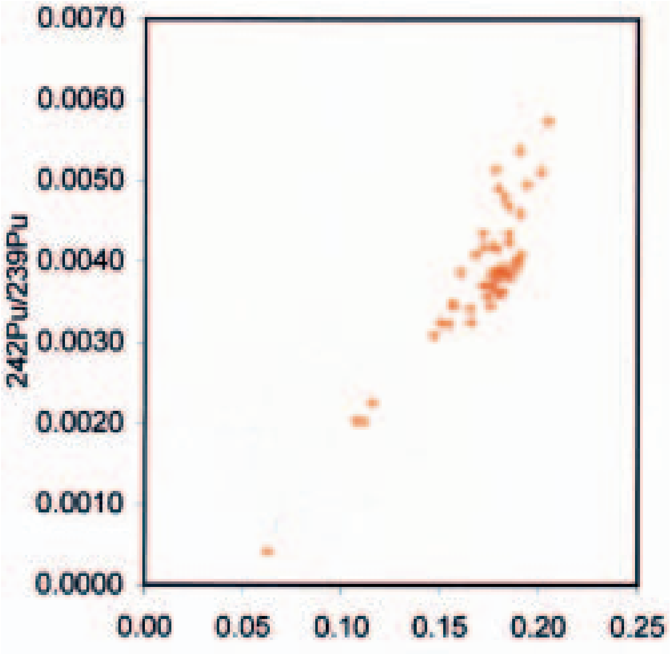

FIG. 1. The isotopic composition of global fallout plutonium (plotted as ^{242}Pu/^{239}Pu versus ^{240}Pu/^{239}Pu ratios) in soil samples collected around the world. The samples were collected by the US Department of Energy Environmental Measurements Laboratory, and analysed at PNNL [4].

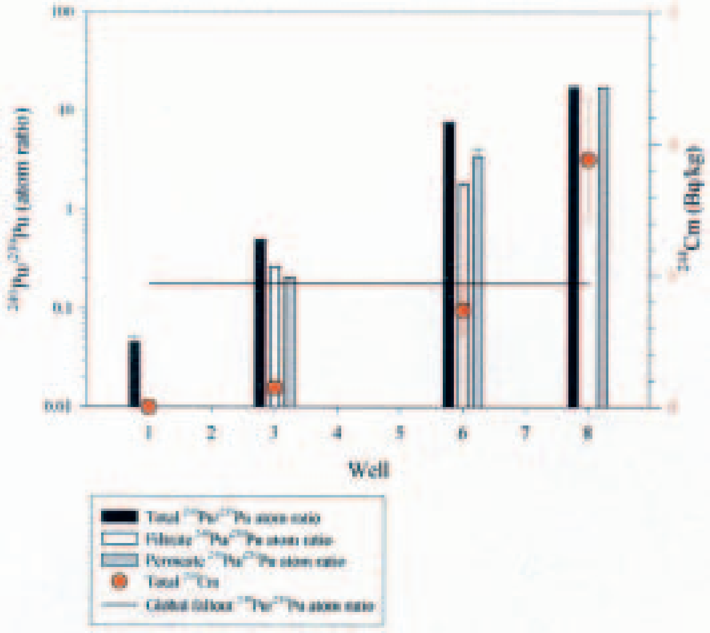

FIG. 2. Isotopic composition of plutonium in groundwater from the Savannah River site F-area. Elevated $^{240}Pu/^{239}Pu$ ratios are due to the decay of ^{244}Cm. The samples were collected and processed by the Woods Hole Oceanographic Institute and analysed at PNNL [18].

conducted using natural and synthetic uranium standards as demonstration vehicles. Recent results at PNNL have yielded several GHz/ppm sensitivity (at very low sample flow rates) for uranium and a background count rate of 0.1 counts per second. This performance is comparable to that reported by McLean et al. [15]. When coupled to low flow rates (20 μL/min), detection efficiencies of 0.1% (ion detected/atoms injected) can be achieved for the detection of actinide isotopes. This corresponds to detecting a measurable signal from a 0.01 fg/min sample flow rate. Analyses of the uncertainties associated with the measurement of isotope ratios in low level samples have shown that ICP-MS is capable of achieving precisions near the Poisson limit. For example, Table I shows precisions for uranium isotope ratio measurements for various quantities of total U.

The experiments described above were conducted with pure solutions, with no matrix interferences. For environmental samples, the performance differs due to the presence of matrix constituents and the need to chemically process to extract, purify and concentrate actinide elements. Recent results from IAEA NWAL (network of analytical labs) swipe samples, presented at a

TABLE I. ICP/MS PERFORMANCE

Isotope ratio	Precision	Efficiency	Sample size	Reference
$^{235}U/^{238}U$ (natural)	0.1%	0.15%	10 pg	[19]
$^{235}U/^{238}U$ (natural)	~1%	0.15%	10 fg	[19]
$^{234}U/^{236}U$ (SRM U-030)	3–4%	Not measured	<5 fg	PNNL Instrument Acceptance tests

recent workshop [20], have shown that the performance of ICP-MS compares favourably to TIMS. Detection limits for plutonium on swipe samples were ~10 fg and for process blanks were ~25 fg. Analyses of groundwater samples from the Hanford site [21, 22] have also demonstrated that ICP-MS is capable of providing good sensitivity and precision. Data were obtained on uranium isotopes, as well as on long-lived and stable fission products. These data showed that multiple and distinct sources contributed to a contaminant plume near tanks containing high-level reprocessing waste.

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APPLICATION OF NUCLEAR AND ALLIED TECHNIQUES FOR THE CHARACTERIZATION OF FORENSIC SAMPLES

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Abstract

Forensic science deals with the application of various techniques — physical, chemical, and biological — for crime investigation. The legal implications of such analyses put considerable restrictions on the choice of techniques. Moreover, the unknown nature of materials, the limited availability of samples, and the large number of elements to be analysed put considerable strain on the analyst to select appropriate methods. The availability of nuclear techniques has considerably enhanced the scope of forensic analysis. Multi-technique approaches, involving nuclear and non-nuclear analytical methods, have proven to be valid and versatile. In this paper we present recent results from the use of nuclear and allied analytical methods for forensic applications. Some of the forensic samples recently analysed in our laboratories will also be discussed. One of the major types of samples handled pertains to the identification of gunshot residues, and nuclear techniques have considerably simplified interpretation of results. Analysis of unknown materials like powders or metallic fragments for the possible presence of illicit nuclear material is becoming more essential. Characterization of materials is also of importance in view of the possible dumping of toxic wastes from developed countries in developing countries. Detection of gold in a smuggling case was possible using X ray fluorescence and neutron activation analysis even though the smuggler used an innovative approach and converted the gold to a colourless cyanide complex to prevent its easy detection. Analysis of commercial pharmaceutical or medicinal preparations for toxic metals is also becoming important in view of the illegal use of materials like heroin. The increasing volume of illegal and criminal activities requires judicious application of nuclear and non-nuclear techniques for the conviction of criminals and, more importantly, for acquittal of the innocent.

1. INTRODUCTION

Forensics is the application of science to solve crimes. It helps investigating authorities to reach definitive conclusions and it aids the reconstruction of the crime. Application of modern analytical techniques is a key component, providing accurate, precise and unambiguous data on forensic samples. The development of simultaneous multi-element techniques has been a boon to forensic science, since only minute quantities of samples are needed to provide information on the nature of the material and its composition, and can provide information on source, authenticity and the presence of unusual components. Recent developments in the application of nuclear radiation have broadened the scope of these methods.

Among the various nuclear techniques available, neutron activation analysis is among the most valuable. It has the unique advantage of not requiring a blank. For both the instrumental and radiochemical neutron activation analysis (INAA and RNAA) techniques, the blank determines the detection limit. Realizing the role of nuclear techniques, a unit of the Central Forensic Science Laboratory of the Government of India was set up in the Analytical Chemistry Division, Bhabha Atomic Research Centre (BARC), Mumbai. This group has been actively engaged in the application of nuclear techniques, including INAA and RNAA, for the analysis of samples received from various forensic laboratories. The analytical results are supplemented by data using other techniques for constituents with which nuclear techniques have poor sensitivity, and this combination of nuclear and allied techniques has resulted in the successful solution of many problems of forensic importance.

2. EXPERIMENTAL

Neutron activation analysis has been carried out using mainly an Apsara reactor at BARC. It provides a flux of about 10^{11} to 10^{12} n/cm^2/s and is convenient for the analysis of forensic samples. The samples are placed in small polythene bags that are then doubly sealed in another polythene bag, and, along with a suitable standard, are irradiated in the reactor for a predetermined duration. After cooling to allow short lived radioactivity to decay, the samples are assayed for their gamma activity using a high performance germanium (HPGe) detector. With samples of short lived activity, a chemical separation is carried out. This procedure simultaneously removes unwanted activities due to sodium or other radionuclides. The identification of the various elements is carried out using an 8K multichannel analyser along with suitable software.

For other analytical measurements, atomic absorption spectrometry (AAS), inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and other electrochemical techniques are employed. For non-destructive testing of some suspect materials, energy dispersive X ray fluorescence (ED-XRF) was employed.

3. RESULTS AND DISCUSSION

The NAA unit of the Central Forensic Science Laboratory (CFSL), located in the Analytical Chemistry Division, BARC, receives various types of evidentiary forensic materials. Based on the nature of the sample, various analytical techniques are employed.

3.1. Gunshot residues

Ballistic samples are of particular importance. The objective is usually to determine whether a hole or other damage to a sample was caused by passage of a bullet and, if so, to identify the nature of the bullet using suspect material, if available. It is also often necessary to give an opinion about firing distance and direction. Experience gathered over the years enables the provision of definite answers to these questions, using both nuclear and allied AAS techniques to generate analytical data.

That a hole was caused by a bullet is indicated by the presence of lead, detected using AAS, that is absent from a control sample of the same material. Furthermore, elements such as arsenic and antimony are often added to lead to make it hard and the presence of copper suggests that the bullet was copper-jacketed. Zinc and nickel have been used as additional indicators of the nature of the bullet. Efforts are being made to use tin as an additional indicator element for obtaining information on the nature of firearm material.

Approximate distance of firearm discharge can be determined from the presence of materials required for ignition, barium for example. The direction of discharge is indicated by the concentrations of major and trace constituents at the suspected entry and exit points. By careful evaluation of analytical data, it is possible to distinguish the entry and exit points. This information is valuable in differentiating between suicide and murder, and in reconstructing the events in the crime scene.

The analysis of gunshot residue samples is often vitiated by the presence of extraneous material including additives and/or preservatives. For example, the presence of sodium is a source of uncertainty in the direct INAA approach. Moreover, the use of marker pens to identify areas to be analysed may also become a source of error due to the presence of halides. The absence of a proper control can be a handicap in accurate interpretation of results. In view of this, guidelines have been drawn up for the proper dispatch of samples with precautions to be observed in using preservatives. Periodic workshops that educate investigators on protocols for despatching samples have substantially enhanced the utility of nuclear techniques for forensic applications. Typical areas in which samples have been handled in recent years are given in Tables I and II.

TABLE I. ANALYSIS OF GUNSHOT/FIREARM DISCHARGE RESIDUES

Matrix	Elements determined	Remarks
Gunshot residues		
1. Cloth, natural, synthetic or blend (Mostly from wearing apparel)	Group of characteristic elements taken either singly or in combination(s) like Ba, Cu, Hg, Sb, Pb, Ni and Sn	Quantitative determination of one or more elements taken together, at trace or lower level in and around suspected hole/dent and comparing their abundance in controls successfully provided desirable information
2. Leather	— ditto —	
3. Synthetic fibre	— ditto —	
4. Wood	— ditto —	
5. Glass	— ditto —	
6. Metallic pieces	— ditto —	
7. Wall scrapping	— ditto —	
Firearm discharge residues		
Whatman filter paper or cotton material drenched with dilute nitric acid	Principal elements of firearm discharge suitable for this category are Ba and Sb	The positive FDR on the hands/toes of deceased/ suspect at trace or lower level can help answer or support suicide/homicide discrimination and hence to identify shooter.

TABLE II. FORENSIC MATERIALS ANALYSED BY NAA

Type of exhibit	Element	Remarks
Transmission copper wire pieces	Ag, Au, Sb and Se (at trace level)	Discriminating parameters established and reported for SC/100
Transmission aluminium wire pieces	Mn, Cr, Hf, Sc and Fe (at trace level)	— ditto —
Glass pieces	Eu, U, Co, Fe, Th, Sb and Sc	Reported trace element pattern observed
Cannabis	Mn, Cu, K, Cl, Br, Fe, Sc, Hf and Zn	Observed and reported trace element profile
Animal hair	Mn, Cl, Na, K, Cu, Br, Au and Zn	General picture with respect to different varieties of animal hair samples. This can be helpful to ascertain differentiation between human and animal hairs.
Ornamental gold	Cd, Zn, Cu, As and Ag	Nature of composition can provide proper characterization particularly relevant to burglary cases.

3.2. Identification of unknown and suspect materials

Identification of unknown and suspect materials is a major task for the forensic scientist. In view of legal requirements and often limited amounts of samples, analyses have to be carried out using sensitive, but non-destructive methods. The applications of NAA and XRF have been very valuable. The XRF technique provides clues on the nature of materials that are confirmed by the use of NAA.

In connection with a criminal case, a shining piece of metal was recovered from an incoherent suspect. It was not clear whether the metal was radioactive or precious. Chemical analysis was not possible in view of the need for preservation as evidence and the absence of information on possible composition. The use of an HPGe detector confirmed the absence of radioactivity while X ray analysis indicated that the material was steel and, with more detailed analysis, it was possible to infer the nature of the alloy.

In a similar manner, we were able to identify an unknown white powder. An XRF analysis indicated the presence of gold, which was confirmed by NAA. Further study suggested that the compound might be a gold cyanide complex, which was later confirmed by chemical analysis. By this procedure, it was possible to determine that gold was being smuggled as a nondescript white powder.

Neutron activation analysis is a powerful tool for analysis of metals, even in very minute amounts. In an interesting case, the analysis of the jacket belt of a person suspected to be smuggling gold indicated the presence of traces of gold. This helped the investigating officer to decide whether the suspect was involved and whether the belt was the means of carrying the gold. But for the availability of a very sensitive technique like NAA, it would have been difficult to establish the role of the belt.

Nuclear analytical techniques are valuable for studies connected with source correspondence. One of our studies was in connection with the theft of copper transmission wires. The trace element profile provided a valuable clue as to the nature of material. In this respect, NAA is a valuable technique in view of its high sensitivity and specificity, and the absence of need for a blank, normally associated with solution techniques. Thus, NAA is useful for analysis of hair, nail, body tissues, vegetable products, medicines, etc., for source correspondence. Some of the matrices analysed for forensic purposes are summarized in Table III.

Another area in which analytical techniques, especially NAA, are becoming important is the characterization of medicinal preparations.

TABLE III. BIOLOGICAL, PHARMACEUTICAL AND RELATED PRODUCTS ANALYSED BY NAA AND ALLIED TECHNIQUES

Nature	Elements
Hair, nail, bones, body tissues, blood for detection of heavy-metal poisons	As and Hg in general
Ayurvedic drugs, synthetic medicines, tea, materials of plant origin for estimation of trace quantities of toxic elements	As, Hg, Se, Sb, Pb, Al
Acetic anhydride (used as a reagent in the preparation of heroin)	Trace element abundance for information on the source of raw materials and chemicals

Investigation of illicit trafficking in narcotics requires information on sources of raw materials and chemicals used for preparation, and identification of products from various cities or countries. For example, in the case of preparation of heroin, acetic anhydride is used as a reagent. Materials may be grown illegally or smuggled from other countries. A trace element profile may provide more insight on the nature of a material than major component analysis by indicating the nature of the raw materials, the catalyst employed during synthesis, the method of synthesis, and the trace metal ions that have leached from the container during storage and transport. In this connection, an analysis of acetic anhydride manufactured by different companies was carried out by nuclear and atomic absorption analysis method. A direct analysis by AAS was not possible in view of the high viscosity of the sample, and dilution of the sample limited the scope of analysis for the presence of metal ions at trace or ultra-trace levels. This necessitated various pre-concentration procedures such as evaporation of acid, removal of matrix material by suitable oxidation or other separation procedures. Nuclear techniques have a definite advantage in this analysis in view of the direct irradiation of the sample. The matrix induced activity is not generally significant since the common constituents of organic materials like carbon, hydrogen, oxygen and nitrogen do not contribute to matrix activity while the presence of even traces of metallic ions is indicated by their characteristic γ rays after irradiation of the sample. This procedure considerably enhances the scope of analytical techniques for characterization of organic compounds or pharmaceutical products for toxic metal ions. A radiochemical procedure enhances specificity by removal of unwanted radioactivity.

An important aspect of accurate analysis is the removal of effects due to the matrix materials. This activity calls for considerable insight into the chemistry of the process so as to use the best route for analysis. It also requires considerable expertise in sample preparation and group separation of the constituents in order to avoid interference from the commonly occurring materials like sodium, manganese, bromine, chlorine, etc. Some of the procedures developed and employed are listed in Table IV.

4. CONCLUSION

Characterization of forensic samples is a challenging task in view of the unknown nature of the materials, their limited availability and the need to preserve samples for possible subsequent investigation. These requirements make the analyses very specialized, requiring judicious use of sensitive analytical techniques, clean operating conditions, use of non-destructive and multi-element analytical techniques, and proper cross-validation of results. These

TABLE IV. SEPARATION PROCEDURES DEVELOPED FOR FORENSIC APPLICATIONS

Method	Elements/Usefulness
1. A sequential RNAA procedure in combination with complementary analytical techniques like AAS or DPASV	Ba, Cu, Sb, Pb, Ni, Zn
2. A sequential RNAA procedure for trace analysis of various bullet leads of Indian origin	Sn, Cu, As, Sb for characterization
3. Simultaneous determination of an additional indicator for GSR — a sequential RNAA procedure	Sn along with Ba, Cu and Sb
4. A method for trace analysis of lead in copper matrix employing DPASV technique — by use of ion exchanger DOWEX 1 × 4	Quantitative separation of Pb from the matrix followed by determination
5. Zinc as one of the characteristic trace elements in GSR/bullet residues apart from Ba, Cu and Sb by a sequential RNAA	Zinc included in the RNAA steps along with Ba, Cu, Sb
6. An anion-exchange separation method for As(iii) for As(v) from aqueous mixture for speciation of inorganic arsenic forms in water	Concentration of As(iii) in the effluent and that of As(v) in the eluted solutions will allow to assess toxicity level due to arsenic in matter

requirements make nuclear analytical techniques vital for the characterization of forensic samples. Modern separation and complementary analytical techniques are a very powerful aid in forensic analysis for conviction of criminals and, more importantly, for acquittal of the innocent.

ACKNOWLEDGEMENTS

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ATTRIBUTION OF NUCLEAR MATERIAL BY NON-DESTRUCTIVE RADIATION MEASUREMENT METHODS

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Abstract

The paper briefly introduces the foundational principle of non-destructive analysis for the attribution of nuclear material. Facility in processing and simplicity in analysing mean that this method will provide effective support in the prevention of trafficking and smuggling in nuclear materials.

1. INTRODUCTION

Special nuclear material is defined as enriched uranium and plutonium. In all countries, these materials are strictly accounted for and controlled, to safeguard against trafficking and smuggling, and they are categorized in order to facilitate attribution. Containment measures utilize non-destructive monitoring of radiation.

2. METHODS OF MEASUREMENT OF URANIUM AND PLUTONIUM

2.1. Characteristics of uranium and plutonium

Isotopes of uranium and plutonium exhibit radioactive decay. Uranium-235 and ^{238}U and their daughters are present in uraniferous materials; the gamma rays that are characteristic of ^{235}U have energies of 143.8, 163.36, 185.7, 194.94 and 205.31 keV. Although no gamma rays are emitted from ^{238}U, its daughter, ^{234}Pa^{m}, is a gamma emitter at 250.26, 766.36 and 1001.03 keV. Most of the plutonium isotopes, including ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu, emit gamma rays. The characteristic gamma rays of ^{239}Pu have energies of 129, 375 and 413 keV. Abundance and enrichment can be determined by measuring the gamma rays.

Fission neutrons are emitted by isotopes of plutonium. The quantity of isotopic plutonium in a material can be determined by counting spontaneous fission neutrons by passive neutron measurement. Because the probability of spontaneous fission is very low in uranium, to detect the content of ^{235}U, a neutron source (such as ^{252}Cf) has to be used to induce nuclear fission. This method is called positive neutron measurement.

2.2. Attribution of nuclear material

Attribution of nuclear material requires analyses of component isotopic uranium and plutonium. Uraniferous material is variously defined as natural uranium, low enriched uranium or high enriched uranium, depending on the ^{235}U enrichment. If ^{236}U is present, further testing is required.

Spontaneous fission neutrons are usually measured first for materials containing plutonium, to determine the quantity of ^{240}Pu, then the abundance of plutonium isotopes is estimated by gamma spectrometry; attribution is then possible. The abundance of ^{240}Pu is especially significant — in general, in spent reactor fuels it is <20%, whereas in production-type reactors it is <7%.

2.3. Abundance measurement

The non-destructive methods chiefly used to characterize nuclear material are coincident neutron counting and gamma spectrometry.

Nuclides of uranium and plutonium and their abundance or enrichment are defined by their characteristic gamma rays. A high resolution, high purity germanium (HPGe) detector system is used. The spectrum reveals the characteristic gamma rays of each nuclide present (Fig. 1). After peak area calculation, ratio correction, detector efficiency and half-life correction, the ratio of the isotopes contained in the sample is determined:

$$N_1/N_2 = [A_1/A_2][T_{1/2.1}/T_{1/2.2}][P_{r2}/P_{r1}][\varepsilon_2/\varepsilon_1] \tag{1}$$

where

N_1 and N_2 are the atomic numbers for the specific isotopes, respectively,
$A_1$and A_2 are the peak areas for gamma rays, respectively,
$T_{1/2}$ is the half-life,
P_r is the ratio,
ε is the respective efficiency.

In quantitative analysis, a standard source is used to calibrate the detector, while abundance measurements depend on the relative counting technique. The characteristic gamma rays from each isotope in the sample can

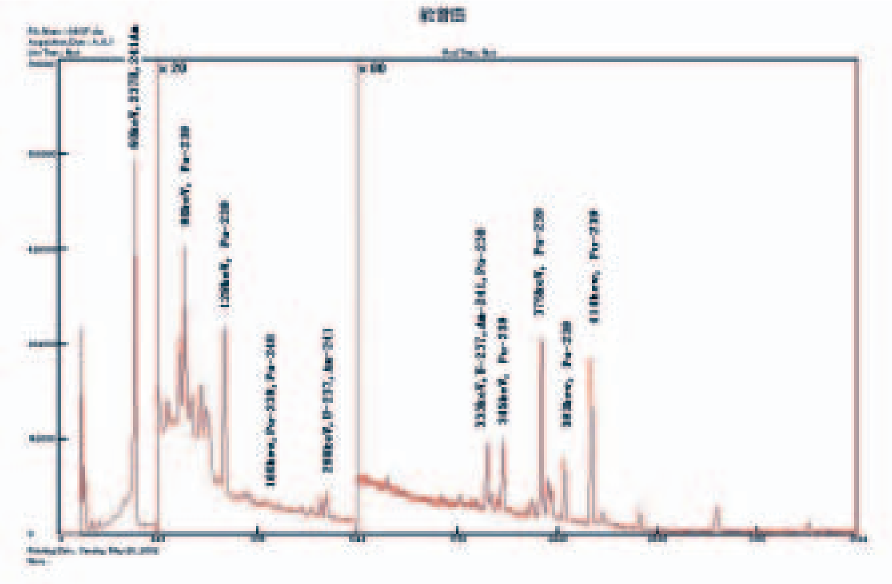

FIG. 1. A gamma spectrum of a plutonium sample.

be used as "self-calibration" — a form of relative calibration, so that difficulties due to differences in the shape, size, chemical components and wrapping material can be circumvented.

Normalizing the total number of atoms of isotopes to 100%, the abundance of each isotope can be determined. Since ^{242}Pu is not a gamma emitter, the following equation is used to calculate the ratio of atom number for ^{242}Pu and ^{239}Pu:

$$^{242}\mathrm{Pu}/^{239}\mathrm{Pu} = 0.53[^{242}\mathrm{Pu}/^{239}\mathrm{Pu}][^{241}\mathrm{Pu}/^{239}\mathrm{Pu}] \tag{2}$$

Techniques to measure abundance of uranium differ somewhat from those used for plutonium. Most characteristic gamma rays for isotopic plutonium are distributed in the low-energy area (≤420 keV and ≤120 keV); the phenomenon of overlap is a serious problem. In this area, a planar HPGe detector is used for its higher resolution, and multigroup analysis (MGA) software may be used for gamma spectrum analysis. For energies greater than 120 keV, characteristic gamma rays are relatively simple, a coaxial HPGe detector is suitable, and PC/FRAM (fixed-energy, response function analysis with multiple efficiency) software may be used in spectrometric analysis.

The characteristic gamma rays for isotopic uranium energies are greater than 120 keV; a coaxial HPGe detector, with special PC/FRAM software, is also suitable for determinations. Because gamma rays are less characteristic for isotopic uranium, error is greater as a result of efficiency calibration fitting. In addition, gamma rays of 250.26 keV (from $^{234}Pa^{m}$, the ^{238}U daughter) are important in efficiency calibration.

2.4. Quantity determination

To determine uranium and plutonium contents, quantitative analysis is needed. In general, abundance determinations are made first, then uranium or plutonium content is measured by neutron counting, which is non-destructive. Spontaneous fission can occur for all isotopes of plutonium, and its content can be determined by spontaneous fission counting with probability correction after abundance determination. The probability list of spontaneous fission for plutonium is shown in Table I. Probabilities of spontaneous fission with even mass numbers are five orders of magnitude higher than those with odd mass numbers. Plutonium-240 is highest in abundance and the spontaneous fission number of ^{240}Pu is taken as the standard in normalizing.

TABLE I. YIELD OF SPONTANEOUS FISSION NEUTRONS

Isotope	Gross half-life (a)	Spontaneous fission half-life (a)	Yield of spontaneous fission (n/s.g)	Spontaneous fission average neutron	Induction fission average neutron
^{238}Pu	87.7	4.77×10^{10}	2.59×10^{3}	2.21	2.90
^{239}Pu	2.41×10^{4}	5.48×10^{15}	2.18×10^{-2}	2.16	2.88
^{240}Pu	6.56×10^{3}	1.16×10^{11}	1.02×10^{3}	2.16	2.80
^{241}Pu	14.4	2.50×10^{15}	5.0×10^{-2}	2.25	2.80
^{242}Pu	3.76×10^{5}	6.48×10^{10}	1.72×10^{3}	2.15	2.81

INVESTIGATION OF CORRELATIONS IN CHEMICAL IMPURITIES AND ISOTOPE RATIOS FOR NUCLEAR FORENSIC PURPOSES

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Abstract

The Institute for Transuranium Elements has worked in the area of nuclear forensic science since 1992, when the first seized sample was analysed. In the beginning, analytical tools for seized materials were adapted from safeguard measurements and from materials science. Especially in view of the origin, determination the spectrum of parameters to be taken into account had to be widened. In addition to the development of a comprehensive database on nuclear materials for power reactor fuels, experimental investigations were begun to identify characteristic parameters. These systematic investigations comprised the development of methodologies for age determination of plutonium and of highly enriched uranium, surface roughness determination of UO_2 pellets, on $n(^{18}O)/n(^{16}O)$ measurements in uranium oxides, and on measurement of impurities. Particularly with respect to the latter, a more thorough understanding of the nature of characteristic chemical impurities and their propagation throughout the entire process appeared necessary, in particular for uranium materials. Therefore, a systematic study was launched in order to better understand which chemical impurities might be considered as characteristic of the origin of the base material and which are introduced incidentally or intentionally during processing. These impurities might be characteristic of the process used or of the plant. Impurity measurements were carried out on uranium ores, on intermediate products (ammonium diuranate or yellow cake) and on (natural) uranium oxides, all originating from the same mine, hence “vertically” throughout the process in individual facilities. Furthermore, we compared materials obtained from different mines in order to identify patterns that allow facilities to be distinguished. $n(^{18}O)/n(^{16}O)$ ratio measurements provided useful additional information on geographic origin of materials. Therefore, we investigated the $n(^{18}O)/n(^{16}O)$ isotope ratios in these different compounds in order to obtain further experimental evidence for a consistent set of materials reportedly originating from the same geographic location.

1. INTRODUCTION

Before uranium can be used in a nuclear reactor as fuel, it has to be processed. This comprises several steps, for which a simplified flow chart is shown in Fig. 1. The present investigation focuses on natural uranium materials. Depending on the type of deposit from which the ore is mined, slightly different methods can be used. However, in the normal procedure, the ore is crushed and leached, and the uranium is recovered from sulphuric acid solution by anion exchange or by extraction. Then the intermediate product, “yellow cake”, is precipitated as ammonium diuranate. Afterwards, it is dried and converted in a furnace to uranium oxide (U_3O_8).

Australia is the second largest uranium producer in the world (after Canada) at nearly 10 000 t/year from three mines, namely Ranger, Olympic Dam and Beverley. Each mine is formatted differently (unconformity-related deposit, Breccia complex deposit and sandstone deposit, respectively), thus their different mineral compositions were expected to be reflected in impurity patterns of the processed uranium materials.

2. INSTRUMENTATION

The methods were based on Refs [1–6].

A multicollector inductively coupled plasma-mass spectrometer (ICP-MS) from NU Instruments was used to measure the impurities. The instrument is equipped with twelve Faraday cups and an ion counter. The accompanying elements and impurities in the ores were determined using a Faraday cup (measurement time 2 s/mass), whereas impurities in the yellow cake and

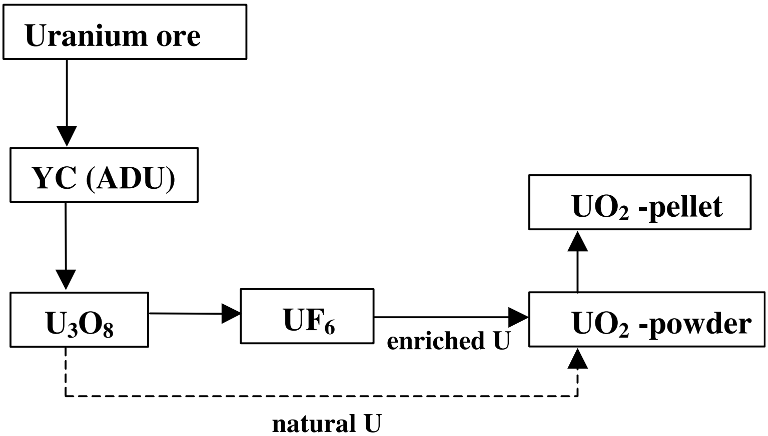

FIG. 1. Uranium products (YC = yellow cake, ADU = ammonium diuranate).

uranium oxides were determined using the ion counter (4 s/mass). Each measurement contained five cycles, and two or three independent repeat measurements were made on each sample. An external calibration curve obtained from a multi-element standard composed of six elements (Li, Co, Y, In, Ho and U) was used for the concentration calculations.

n(^{18}O)/n(^{16}O) ratio measurements in the uranium oxides were made using a Cameca 6f secondary ion mass spectrometer (SIMS). A caesium primary-ion source with a current of 1 × 10^{-10} A was used to bombard the samples. The accelerating voltage for the secondary ions was 5 kV. Resolution of 2500 was used to separate the ^{17}O^{1}H ions from the ^{18}O. Around twenty particles per sample were measured using 6 s counting time for the ^{18}O and 1 s for the ^{16}O, and, in total, five blocks of ten cycles each were acquired.

3. RESULTS

3.1. Impurities

As expected, elemental composition of the ores differed significantly between the mines (Figs 2 and 3). Generally, Olympic Dam ores were of lower uranium content, thus showing high concentrations for most of the elements measured. The samples were also very non-homogeneous, as indicated by the

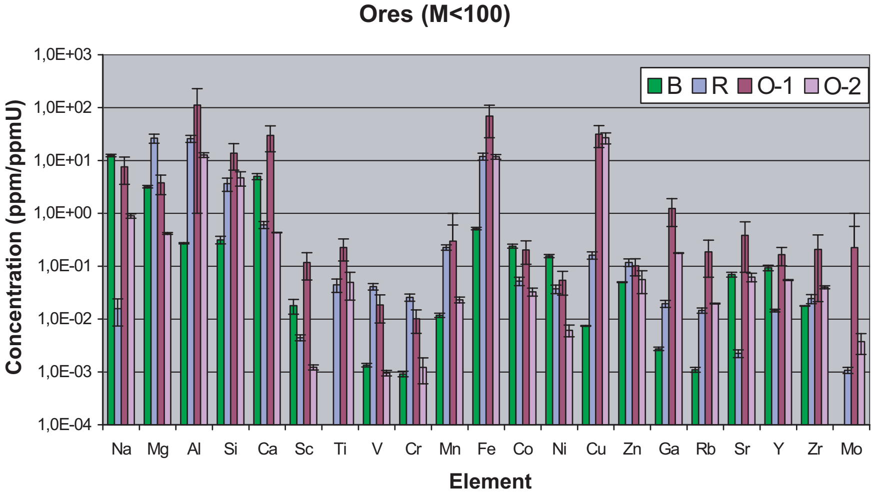

FIG. 2. Ore composition (elements of molecular weight <100).

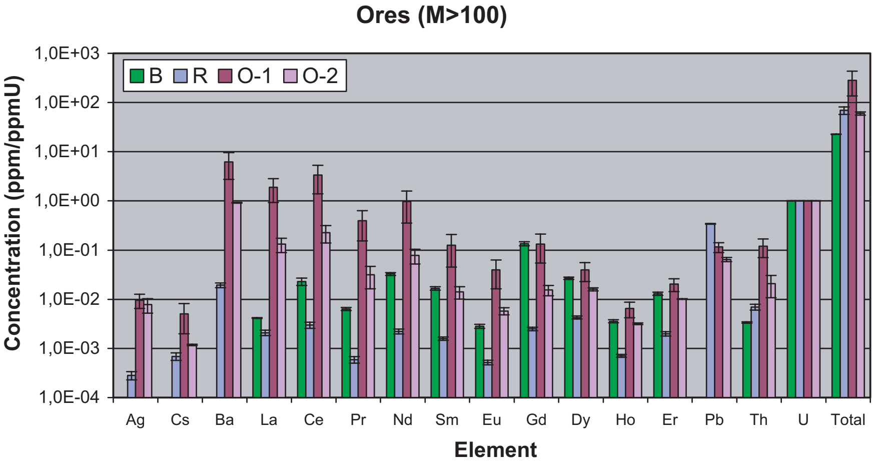

FIG. 3. Ore composition (elements of molecular weight >100).

large uncertainty bars. Two of the totally eight Olympic Dam samples were “cleaner”, thus they formed a separate group (marked as O-2). Beverley mine ores had very low concentrations for some of the elements (e.g. Ti, Mo, Ag, Cs, Ba and Pb), most probably due to the different processing method, i.e. in situ leaching. During the measurements, we noted that the isotopic compositions of the lead in the different mines were significantly different. However, this shall not be further discussed in the context of the present paper.

Next, we made a vertical comparison between different uranium products (i.e. ores, yellow cakes and uranium oxides) within each mine to determine whether impurity level changed during processing and if the impurity pattern was affected (Fig. 4). Reductions of ~10^3 in the impurity level were seen after processing. Impurity patterns were not much affected (except in the case of Pr), and still followed the same trend, especially for the rare-earth elements.

Finally we made a “horizontal” comparison within individual products (yellow cake/ADU) but between mines, to see if we could identify characteristic differences. It was noted that three groups of elements could be separated (Fig. 5). The first “group” was the zirconium alone, where Beverley had the lowest content and Olympic Dam the highest. The second group was formed by lanthanum, cerium and praseodymium, where Beverley mine had the highest content and Ranger the lowest. The last group was formed by samarium, europium, dysprosium, erbium and thorium, where Beverley still had the highest content, but Olympic Dam was lowest.

These observations can be summarized in individual figures that provide a measure for distinguishing origin: the ratio of concentrations of selected chemical elements. Going this route, the figure (ratio) became independent of

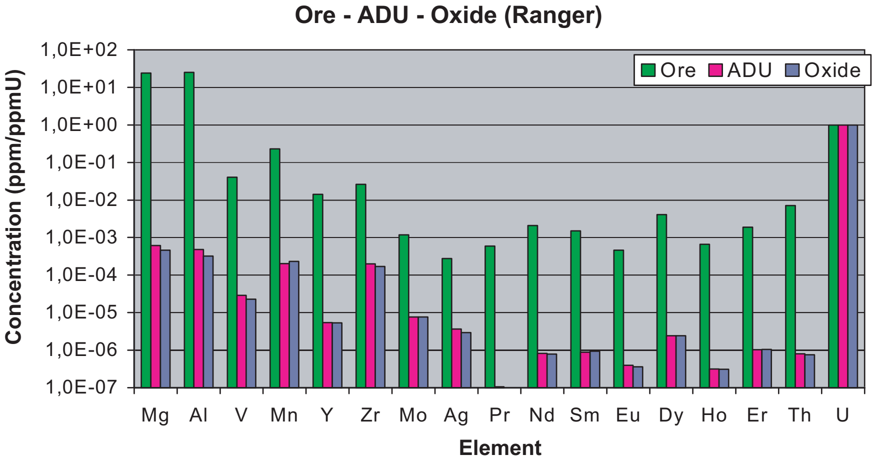

FIG. 4. Vertical comparison of impurity levels in the different uranium products.

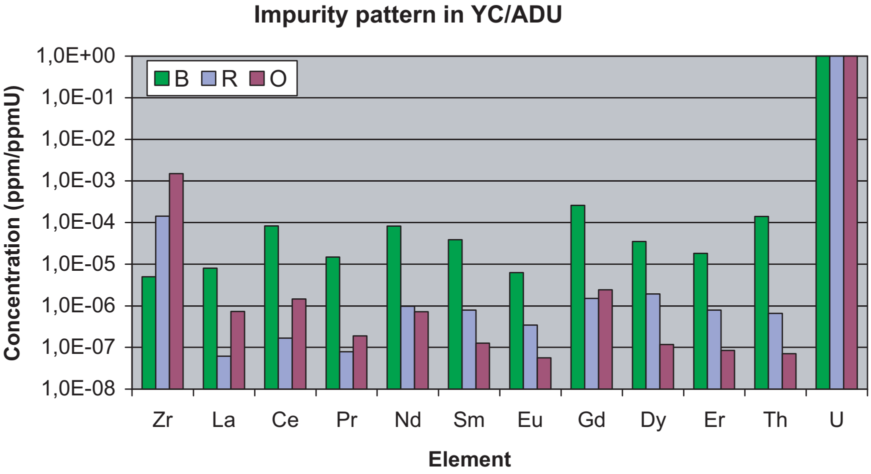

FIG. 5. Horizontal comparison of impurity levels and patterns in uranium intermediate products.

the actual level of impurity showing that elements of similar chemical behaviour maintained a relatively constant ratio throughout the process. The observed ratios, e.g. for Zr/Th — both being tetravalent elements — did not change significantly from ADU to the corresponding U_3O_8. Yet, for the two other mines, this ratio changed by orders of magnitude. This is illustrated in Table I, where we selected two elemental pairs. The Zr/Th and Ce/Dy ratios

TABLE I. ELEMENTAL RATIOS SHOWING SIGNIFICANT DIFFERENCE BETWEEN THE MINES

Mine	Elemental ratios				Additional characteristic impurities
	Zr/Th		Ce/Dy		
	YC	Oxide	YC	Oxide	
Ranger	217	11.7	0.09	0.14	Mg, Al, V, Mn, Y, Mo, Ag, Ho
Olympic	21 000	12 200	12.4	17.9	Cu, Mo, Ag
Beverley	0.036	—	2.36	—	Al, Sc, V, Sr, Y, Ho

differed by several orders of magnitude between the mines and, thus, by determining these two ratios only, the mine of origin was revealed. There are also additional signatures or elements that can be used to underscore the results. For example, Olympic Dam products contained copper, which was not detected in the other two mines, and the same situation applied with magnesium and manganese for Ranger, and with scandium and strontium for Beverley.

3.2. $^{18}O/^{16}O$ ratio

Four samples of U_3O_8 from Ranger and Olympic Dam mines were measured by SIMS. The results between the mines did not differ significantly, but clear differences emerged when comparing samples of other origin (i.e. France, Russian Federation, or USA) (Fig. 6).

4. CONCLUSIONS AND OUTLOOK

There are several impurities in natural uranium products that can be used to distinguish between samples from different mines. Furthermore, impurity patterns in the products strongly reflected the starting material, i.e. the ore. More samples will be analysed from different geographical origins. Additionally, a study on the isotopic composition of lead in uranium products will be initiated to see if it may be used as a signature.

The $^{18}O/^{16}O$ratio determination again showed utility for geolocation of uranium origin. In future, a vertical comparison of uranium products from the same mine will be made using SIMS and TIMS.

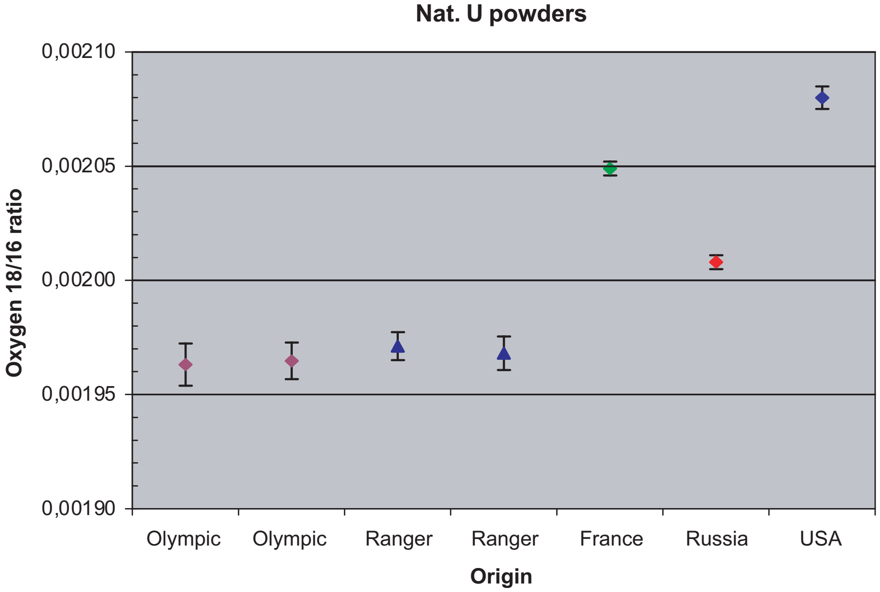

FIG. 6. Comparison of $n(^{18}O)/n(^{16}O)$ ratios of various origins.

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INFLUENCE OF SIZE AND SURFACE STRUCTURE OF MICROPARTICLES ON ACCURACY OF MEASUREMENTS OF URANIUM ISOTOPIC COMPOSITION

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Abstract

The paper examines the kinetics of dispersion of micron and submicron uranium particles during measurements of isotopic composition by secondary ion mass spectrometry. One source of possible systematic error was determined. A technique to control accuracy of measurement is suggested. The influence of the initial size of the particle as well as the inner structure of the particle on the speed of particle dispersion is assessed.

1. INTRODUCTION

The strengthening of IAEA safeguards, designed to ensure detection of undeclared nuclear activity, will require intensification of efforts to develop methods of analysis of environmental samples from the environs of nuclear fuel cycle plants [1].

One of the most essential elements of this analysis is the determination of isotopic composition of uranium and plutonium in microparticles in industrial dust, which corresponds to isotopic composition of nuclear materials processed at the plant [2]. Therefore, on the basis of results of analysis of microparticles and comparison with declared nomenclature of processed materials, conformity or discrepancy between the character of processes at the plant and declared nuclear activity may be assessed. Clearly, there is necessity for strict accuracy of measurement of isotopic composition of uranium and plutonium in microparticles.

The most widespread method of determination of isotopic composition of uranium and plutonium in microparticles, secondary ion mass spectrometry, is characterized by gradual sputtering of microparticles during analysis. Measurement of the isotopic composition of microparticles of standard nuclear materials has shown that values of the mass ratio of ^{235}U to ^{238}U can deviate. These deviations are not always within statistical error, necessitating investigations of systematic sources of variability.

One possible source of systematic error during measurement of isotopic composition is fast dispersion of microparticles: the knocked-out ions decrease during acquisition of a mass-spectrum in the direction of larger mass. Measured mass ratio ^{235}U to ^{238}U can exceed true values.

The purpose of this work was to research changes in measured values of mass ratios of ^{235}U to ^{238}U as a consequence of sputtering of particles, and to determine the influence of size and surface structure of particles.

2. EXPERIMENTAL MEASUREMENTS

Individual particles were photographed on the scanning electron microscope before and after sequential measurements of uranium isotopes. The ion beam current during sputtering of particles was about 15 nA, and the duration of each sputtering was 15 s.

Two groups of particles were investigated. The first group comprised 34 particles of various, previously not known, isotopic composition. Initial sizes were from 0.5 × 0.2 μm to 3.5 × 2 μm. They were of irregular shape (except for one spherical) and of varied surface structure. Results are shown in Table I.

Fourteen particles from this group, from 0.5 × 0.2 μm to 2.2 × 1.5 μm, were completely dispersed during the first sputtering, illustrating that this can occur even with relatively large particles, >1 μm. However it is necessary to take into account that the particles differed in form, for example particles 22 (Fig. 1) and 25 (Fig. 2), with the latter deposited on other objects. Some particles were very thin, which may explain their fast dispersion.

Two measurements were made on 12 particles of 0.7 × 0.5 μm to 2 × 1.5 μm, for six of which the second measured value was larger then the first, and four particles had smaller second values. For particles 18 and 28, with statistical errors of isotope ratio smaller than 10%, the measured values were almost identical. Thus, it is possible that a statistical error smaller than 10%, practically guaranteed that the relative error of measurement was within 1%.

Fast dispersion of comparatively large particles, particle 33 for example, apparently resulted from a spongy structure (Fig. 3).

Three sequential measurements of isotopic composition were carried out for six particles of from 0.7 × 0.5 μm to 2.5 × 2.2 μm. For four particles (20, 26, 27 and 32), the third values were the highest after two equal or very close values. Statistical errors for the two first values were less than 10% for three of these particles. It is clear that the first two values were close to actual. All four particles were larger than 1 μm. The images of these particles, after the first and second sputterings, indicated that their thickness after the first measurement remained larger than 0.3 μm and after the second was 0.1 to 0.2 μm. Thus, a size

TABLE I. SIZE OF PARTICLES IN THE FIRST GROUP AND ISOTOPIC COMPOSITION OF URANIUM

Part· no.	1st measurement			2nd measurement			3rd measurement			4th measurement		
	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%
1	0.5 × 0.2	0.018	100									
2	0.5	0.011	15									
3	0.6 × 0.3	0.0053	17									
4	0.7 × 0.3	0.0067	25									
5	0.7 × 0.4	0.0085	13									
6	0.7 × 0.5	0.0059	10									
7	0.7 × 0.5	0.0074	11	0.5 × 0.1	0.0089	25						
8	0.7 × 0.6	0.0086	14	0.4 × 0.3	0.0091	21						
9	0.7	0.0055	22									
10	0.7	0.0062	13	0.5	0.0072	13						
11	0.75	0.014	5	0.5	0.011	8	0.3	0.013	13			
12	0.8 × 0.4	0.016	6	0.5 × 0.3	0.018	26	0.1	0.014	50			
13	0.8 × 0.6	0.0038	26									
14	0.8 × 0.7	0.0041	15									
15	0.8	0.0059	9	0.5	0.0070	13						
16	0.9 × 0.7	0.0097	12	0.5	0.0079	14						
17	1 × 0.7	0.0087	9	0.5 × 0.2	0.0073	19						
18	1.1 × 0.6	0.027	5	0.7 × 0.5	0.026	9						
19	1.1 × 0.7	0.0087	14									

TABLE I. CONT.

Part. no.	1st measurement			2nd measurement			3rd measurement			4th measurement		
	Size, μm	^{235}U/^{238}U	δ,%	Size, μm	^{235}U/^{238}U	δ,%	Size, μm	^{235}U/^{238}U	δ,%	Size, μm	^{235}U/^{238}U	δ,%
20	1.2 × 0.7	0.0095	7	1.0 × 0.4	0.0096	8	0.6 × 0.2	0.011	15			
21	1.2	0.0082	4	0.9	0.0081	9	0.5	0.0075	15	0.3	0.0094	25
22	1.5 × 1	0.017	7									
23	1.5 × 1	0.018	5	0.6	0.023	21						
24	1.5	0.0060	7	0.9	0.0072	63						
25	1.7 × 0.8	0.0025	28									
26	1.7 × 1	0.015	6	1.3 × 0.7	0.016	6	0.7 × 0.4	0.020	15			
27	1.8	0.0046	4	1.5	0.0044	9	0.9	0.0052	13			
28	2 × 1	0.019	3	1.0 × 0.6	0.019	5						
29	2 × 1.5	0.0078	12	0.7	0.0063	29						
30	2 × 1.8	0.022	10									
31	2.2 × 1.5	0.0023	74									
32	2.5 × 2	0.0071	3	1.5	0.0071	7	1.0	0.0094	21			
33	2.5 × 2.2	0.0064	6	0.8	0.0052	8						
34	3.5 × 2	0.0064	3	2.2	0.0059	31	1.8	0.0071	5	0.8 × 0.2	0.0111	24

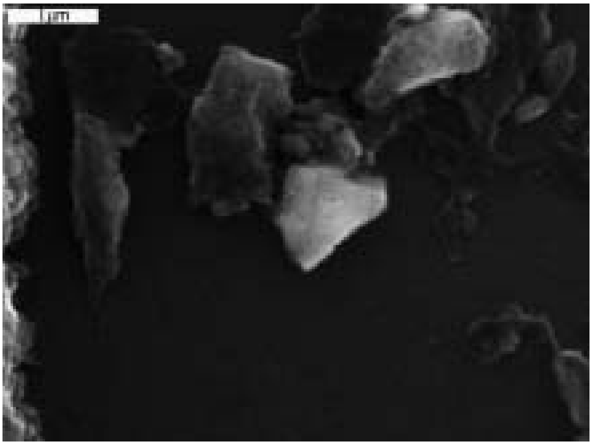

FIG. 1. Particle 22.

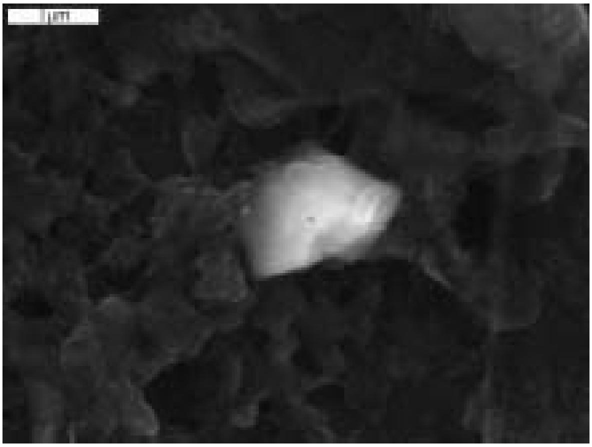

FIG. 2. Particle 25.

of about 0.5 × 0.3 μm may be sufficient for accurate measurement of isotopic composition.

Particle 12 had a second measured value larger than the first, and the third value was less than both previous values. The accuracy of the third measurement was low, because only four pulses of ^{235}U were registered. However, in the first measurement, which was characterized by a statistical error of only 6%, the measured value was very close to actual. Thus, we conclude that secondary ion mass spectrometry allows precise determination of isotopic composition of uranium in particles with sizes also of approximately

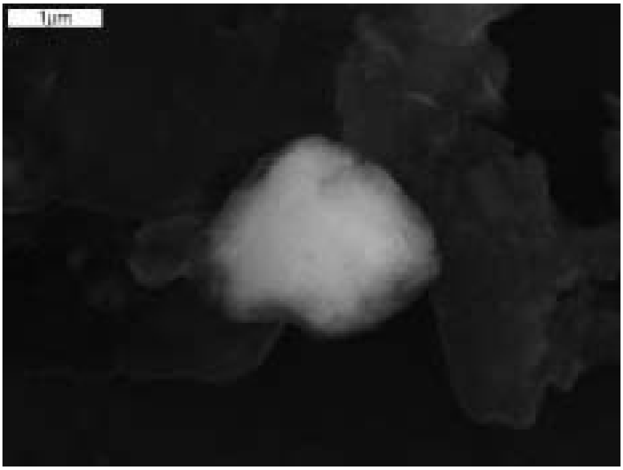

FIG. 3. Particle 33.

FIG. 4. Particle 12.

0.5 µm, if they have dense internal structure. Figure 4 shows the initial image of particle 12, and Fig. 5 shows it before the last, third, measurement.

Particle 11 had a second measured isotopic ratio less than the first, whereas the third ratio was larger than the second. This can be explained by the presence of a thin film of uranium above the particle. The film and the particle may have uranium of different isotopic compositions. Figures 6 and 7 show this object before and after the first sputtering, respectively. A bright transparent film can be seen in Fig. 6, but not in Fig. 7.

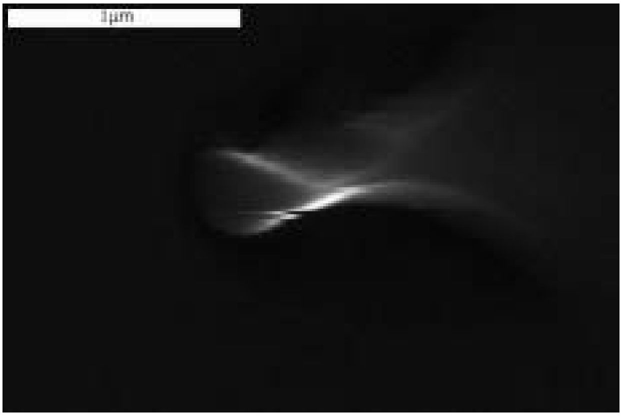

FIG. 5. Particle 12 after two measurements.

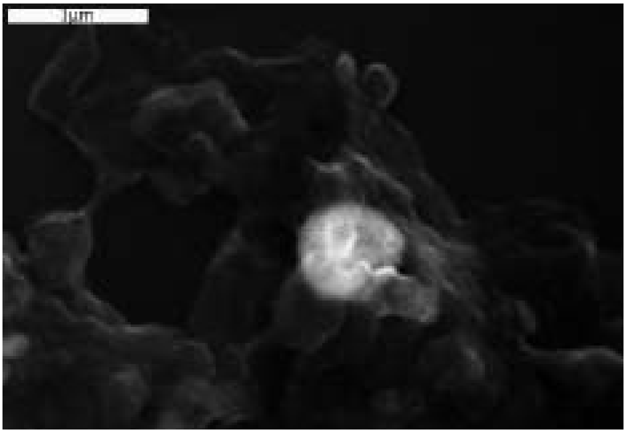

FIG. 6. Particle 11.

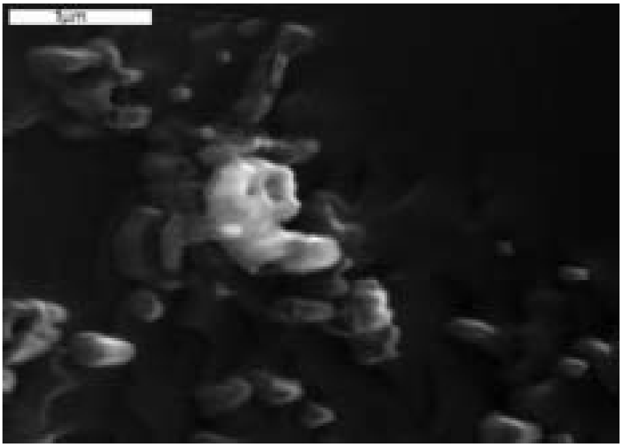

FIG. 7. Particle 11 after the first measurement.

Two particles with initial sizes of 3.5 × 2 µm and 1.2 µm were measured for isotopic composition four times. The largest values were obtained in the last measurements for both particles, and differences between the last and the three previous values were larger than fluctuations in the three previous measurements.

Figures 8 to 11 show secondary electron images of particle 21 before its sputtering by the ion beam, after the first, second and third measurements, respectively.

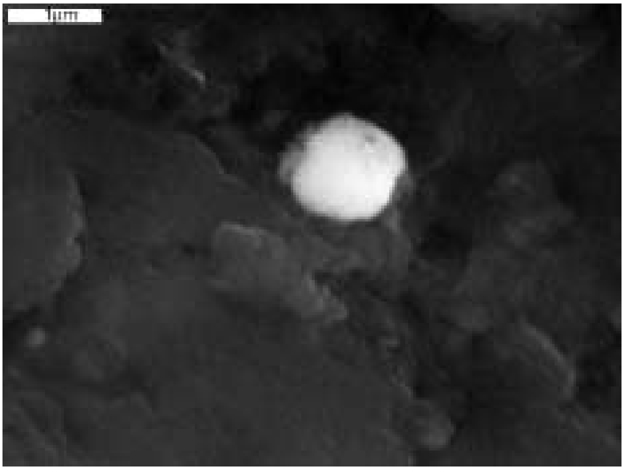

FIG. 8. Particle 21.

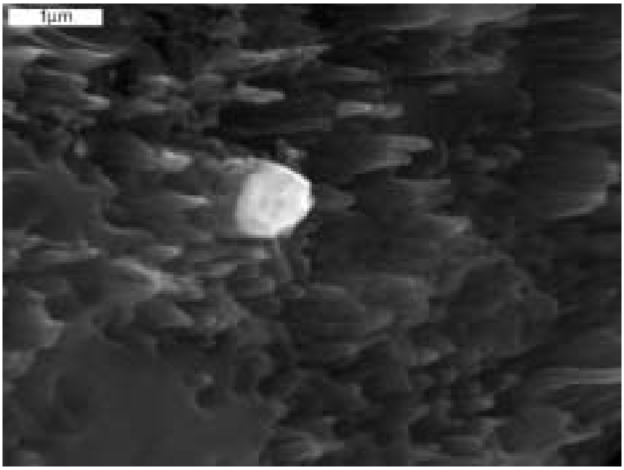

FIG. 9. Particle 21 after the first measurement.

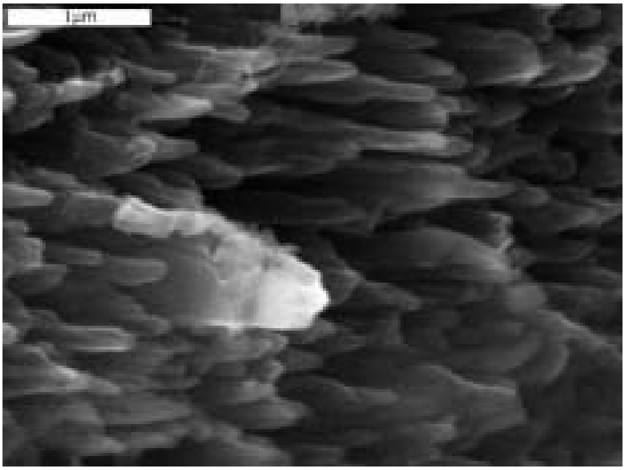

FIG. 10. Particle 21 after the second measurement.

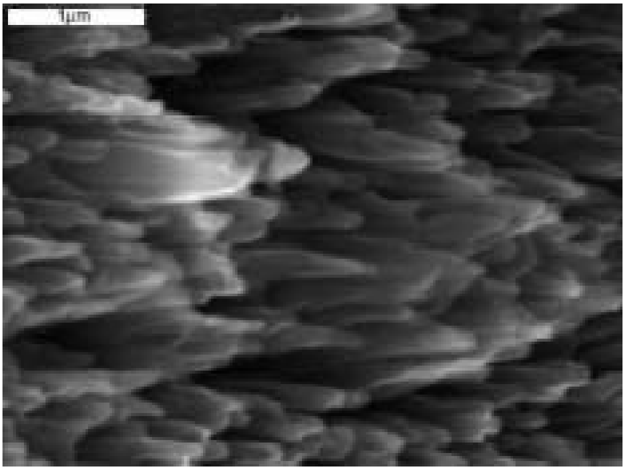

FIG. 11. Particle 21 after the third measurement.

The size of particle 21 decreased from 1.2 to 0.75 μm after the first measurement, to 0.5 μm after the second measurement, and to 0.25 μm after the third. As a result of the fourth measurement, during which the remaining fragment of the particle was dispersed, the isotopic ratio was overestimated. However, that the difference in this value from the true value was small confirmed that good results can be received with isotopic analysis of particles of initial size approximately 0.3 μm with a dense inner structure.

The second group comprised twenty-two spherical particles of UO_2 with 3.7% ^{235}U abundance [3]. Initially, the particle size ranged from 0.7 to 2.4 µm. The particles were of varied surface structure and, as discovered during the experiment, they were also of varied internal structure.

Results are given in Tables II and III. Table III does not contain data for the second or third measurements, because they coincided with those for the first and fourth measurements. Initially the particles were spherical, but, after the first measurement, became pyramidal with a rounded base; the values decreased with each sputtering. Figures 9 to 11 provide an example of a pyramid sequence. The base diameters and corresponding heights of the "pyramids" are provided in Tables II and III.

Particles 19 and 21 did not disperse fully and should be measured again (Table III). Increases in isotope ratio occurred with particles 15 from 17 particles, between the third and sixth measurements (Table III).

From the data and the photographs of the particles, it was concluded that speed of dispersion depended not only on particle size, but also on internal structure. After the second measurement, there was less dispersion from particle 21, which was dense (Fig. 12), than from particle 22, which was spongy (Fig. 13).

3. CONCLUSIONS

Fast dispersion of micron and submicron particles and decrease of flow of secondary ions from particles during analysis can be appreciable sources of systematic errors in the measurement of uranium isotopic composition by secondary ion mass spectrometry.

The speed of dispersion of particles and reliability of results of the analysis of isotopic composition depends on size and structure of the particles.

The minimum size of particle of dense internal structure, for which reliable mass spectrum data may be obtained, is approximately 0.3 µm.

Sequential sputtering of a particle with fixing between measurements is necessary for determination of data quality.

Conditions for the confirmation of Item 4 were investigated. Six sequential measurements of the same micron-sized uranium particles were made with determinations of particle state after each measurement. Such conditions could be adopted for a round robin, in which the same particles would be analysed in different laboratories and results compared.

TABLE II. SIZES OF PARTICLES IN THE SECOND GROUP (PARTICLES 1 TO 12) AND ISOTOPIC COMPOSITION OF URANIUM

Part. no.	1st measurement			2nd measurement			3rd measurement			4th measurement		
	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%
1	0.7	0.040	12	0.6 × 0.1	0.042	12	0.5 × 0.03	0.042	14	trace	0.045	25
2	0.8	0.040	21									
3	1.0	0.037	7	0.9 × 0.3	0.038	9	0.8 × 0.1	0.040	10			
4	1.0	0.038	8	0.9 × 0.1	0.039	8	0.7 × 0.1	0.043	12			
5	1.1	0.039	7	1.0 × 0.1	0.040	9	0.8 × 0.1	0.041	10	trace	0.048	17
6	1.1	0.037	7	1.0 × 0.1	0.038	7	1.0 × 0.1	0.040	10			
7	1.2	0.038	7	1.1 × 0.3	0.037	9	1.0 × 0.2	0.039	9	0.8 × 0.2	0.042	12
8	1.2	0.039	7	1.1 × 0.4	0.039	7	0.9 × 0.2	0.040	8	0.7 × 0.2	0.044	14
9	1.3	0.037	6	1.2 × 0.2	0.037	6	1.0 × 0.1	0.038	7	0.7 × 0.1	0.045	12
10	1.3	0.038	6	1.2 × 0.3	0.039	7	1.0 × 0.2	0.044	12			
11	1.4	0.037	5	1.3 × 0.3	0.038	5	1.2 × 0.1	0.038	6	1.0 × 0.4	0.042	11
12	1.4	0.038	5	1.3 × 0.4	0.038	5	1.2 × 0.2	0.039	6	1.0 × 0.7	0.041	9

TABLE III. SIZES OF PARTICLES IN THE SECOND GROUP (PARTICLES 13 TO 22) AND ISOTOPIC COMPOSITION OF URANIUM

Part. no.	1st measurement			2nd measurement			3rd measurement			4th measurement		
	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%	Size, µm	$^{235}U/^{238}U$	δ,%
13	1.0	0.036	7	0.6 × 0.2	0.037	10	0.3 × 0.1	0.043	12			
14	1.1	0.039	7	0.8 × 0.1	0.038	9	0.6 × 0.1	0.045	11			
15	1.1	0.039	6	0.5 × 0.2	0.038	7	0.4 × 0.1	0.039	9			
16	1.2	0.040	8	0.7 × 0.2	0.040	10	0.4 × 0.1	0.042	11	trace	0.047	25
17	1.5	0.038	4	1.3 × 0.2	0.038	5	1.0 × 0.1	0.039	6			
18	1.7	0.038	6	1.4 × 0.2	0.040	8	1.2 × 0.1	0.038	9			
19	2.0	0.036	6	1.5 × 0.3	0.038	6	1.3 × 0.1	0.038	7	1.0 × 0.1	0.038	7
20	2.1	0.036	4	1.6 × 0.2	0.037	6	1.4 × 0.1	0.043	8	**trace**	**0.044**	**15**
21	2.1	0.036	2	1.5 × 0.9	0.039	2	**1.4 × 0.9**	**0.039**	**7**	**1.1 × 0.8**	**0.039**	**8**
22	2.4	0.037	2	2.0 × 0.4	0.039	3	1.8 × 0.2	0.039	3			

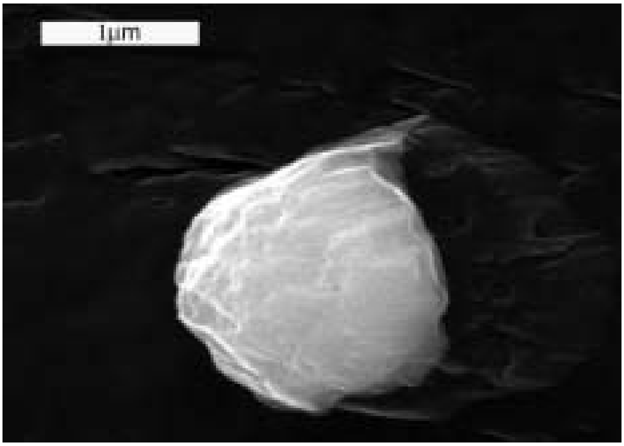

FIG. 12. Particle 21 after second measurement.

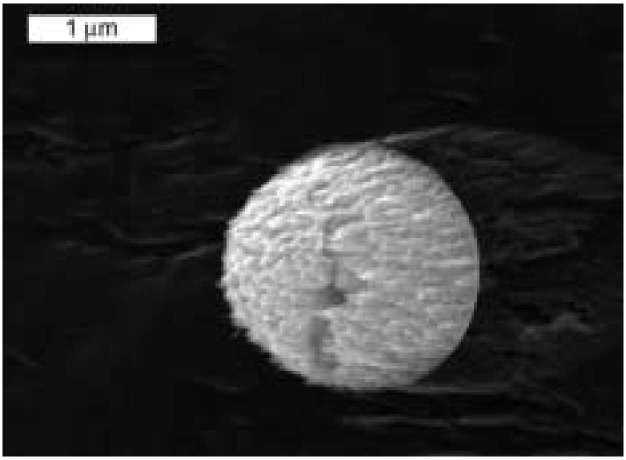

FIG. 13. Particle 22 after second measurement.

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[2] PELLAUD, B., HOOPER, R., IAEA safeguards, International Life Moscow **7** (1997).

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IMPROVED ENVIRONMENTAL AND FORENSICS MEASUREMENTS USING MULTIPLE ION COUNTERS IN ISOTOPE RATIO MASS SPECTROMETRY

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Abstract

A new detector system designed for isotope ratio mass spectrometers provides improved precision on measurements of samples with very low amounts ($<10^{-11}$ g) of analyte. An array of continuous dynode electron multipliers has been installed on a new ThermoFinnigan MAT Triton thermal ionization mass spectrometer acquired by the New Brunswick Laboratory. These ion counters are modifications of miniaturized, commercially available continuous dynode electron multipliers. They can be readily installed to replace individual Faraday cups in a multidetector mass spectrometer or bundled together and located along the detector plane with a set of Faraday cups. On the New Brunswick Laboratory mass spectrometer, nine Faraday cups, one conventional discrete dynode electron multiplier and seven miniaturized ion counters were installed. The size of the miniaturized ion counters is identical to the standard Faraday cups, and thus the ion counters can be aligned with unit mass spacing for the measurement of high mass elements such as uranium and plutonium. Six of the small ion counters were bundled together and positioned on the low mass side of the Low 4 Faraday cup. One additional ion counter was positioned on the high mass side of the Low 4 Faraday cup. This arrangement allows simultaneous measurement of either all uranium (including ^{233}U) or plutonium (including ^{244}Pu) isotopes, also a combination of the two, and allows the measurement of larger ^{238}U intensities on the Faraday cup, if needed. Compensation for small mass dispersion differences at unit mass spacing of uranium, plutonium or other actinides with slightly different masses is readily achieved by the use of a mass dispersion zoom lens. The advantage of multiple ion counting is the simultaneous collection of isotopes. It overcomes many of the problems such as transient signal variation in sample emission and ionization, which would significantly reduce the attainable precision of a single collector measurement. For a given sample, multiple ion counting generates a greater number of counts for each isotope relative to single detector ion counting and provides improved counting statistics by a factor of two or more. In addition, multiple ion counting eliminates the need for drift correction algorithms that are required in single collector measurements and thus eliminates a potential source of systematic error. Initial tests indicate that the multiple ion counters exhibit high counting efficiency, a dark noise of less than 10 counts per minute and typically less than 1 count per minute, and show linear response characteristics over four orders of magnitude using standard deadtime correction algorithms. For higher count rates in excess of about 100 000 counts per second, additional correction schemes such as the RLR algorithm can be used. The stability of the detectors at high count rates as a function of time is being investigated, and likely will require the incorporation of this parameter into a correction algorithm. The miniaturized continuous dynode electron multipliers have sufficient stability to yield a repeatability of 0.1% RSD on the $^{235}U/^{238}U$ ratio in a 10×10^{-12} g uranium samples of CRM U500. These data were obtained by measuring in the total evaporation mode. Further test results are presented.

1. INTRODUCTION

Electron multipliers used in thermal ionization and inductively coupled plasma mass spectrometry (TIMS, ICPMS) are designed for ion counting of isotopes with integrated ion currents below 10^{-13} to 10^{-14} A. The advantage of ion counting in mass spectrometry is the ability to determine isotope ratios on extremely small quantities of analyte, well below 10^{-10} g. Analysis of these quantities of analyte can provide important forensics information. Where sample quantity is limited and/or where transient signals, with often erratic signal fluctuations, have to be measured, it is advantageous to be able to measure all isotopes of interest simultaneously, as opposed to the current state of the practice in ion counting, where multiple isotopes are measured sequentially and drift correction algorithms are applied.

A new multiple ion counter (MIC) detector system has been installed on a ThermoFinnigan Triton thermal ionization mass spectrometer at the New Brumswick Laboratory, and an initial set of performance characteristics are reported. This is the first commercial MIC detector system to be installed and tested extensively using certified reference materials. The development of this new system borrows from earlier experiences with a prototype MIC system [1].

2. PRINCIPLES OF CONTINUOUS DYNODE ELECTRON MULTIPLIERS

Continuous dynode electron multipliers (CDEMs) are detectors that respond to positive and negative ions, electrons, hard and soft X rays, and ultraviolet radiation. When a potential is applied between the input and output end of the CDEM, the internal resistive surface forms a continuous dynode. An ion or photon that strikes the funnel shaped input aperture of the CDEM typically produces two or three secondary electrons. These electrons are accelerated down a channel, typically applied with a positive bias, striking the interior surface of the channel walls where they then generate further secondary electrons (Fig. 1). The resulting avalanche process produces an easily detectable output pulse of charge containing as many as 10^8 electrons with a duration (FWHM) of about 10 ns.

The charge from the electron cloud is collected at an anode, and has the form of a sine wave pulse on an oscilloscope. For an input of one primary particle, a CDEM produces a cloud of about 10^8 electrons. The output pulses can be readily detected using a discriminator, a preamplifier and a counter. The output pulse is amplified by a pulse preamplifier when the signal is greater than the pre-set discriminator level in the pulse counting system. For every output pulse of the CEM, the preamplifier transforms the negative signal into a standard rectangular or square topped pulse that is fed into a counter.

3. DESCRIPTION AND CHARACTERISTICS OF NEW ELECTRON MULTIPLIERS INSTALLED ON THE TRITON TIMS

The ThermoFinnigan CDEMs are approximately the same size as the Faraday cups used on the Triton or Neptune, and are produced to fit inside a metal frame assembly that accommodates either a Faraday or a CDEM detector. These miniaturized ion counters can be mounted in place of one or more Faraday cups, or can be bundled together as an array at isotopic unit mass spacing for relatively high mass elements such as uranium or plutonium. In the design requested by the New Brunswick Laboratory, called the “six pack plus one”, six ion counters are mounted side by side at unit mass spacing for U/Pu and positioned on the low mass side of the Low 4 Faraday cup. One additional ion counter was positioned on the high mass side of the Low 4 Faraday cup. The

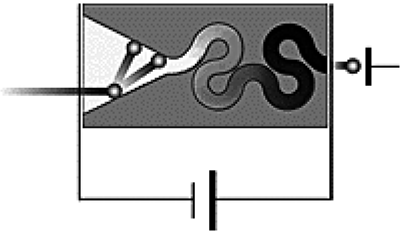

FIG. 1. Schematic of an ion striking a CDEM detector (source: Sjuts Optotechnik GmbH).

flexibility of this arrangement for various actinides and nuclear materials is shown in Table I. The MIC array can be modified by the user, allowing MICs to be moved onto other cups or into other bundled arrangements.

Continuous dynode electron multiplier ion counters are custom designed by Sjuts Optotechnik GmbH (Göttingen, Germany) according to the needs of the Triton multicollector, from a sintered ceramic material and constructed with a lead–silicate glass coating on the inner wall. Silver layering is used to establish electrical contact, for example from the funnel shaped input aperture and the output end of the CDEM. In the design chosen by ThermoFinnigan, the ceramic body of each CDEM serves as an insulator, making it possible to stack multiple arrays of single channel CDEMs together for simultaneous measurement of multiple isotopes. The internal resistance of the CDEM is approximately 250 Mohm. A schematic assembly of a ThermoFinnigan ion counter, as used on a Triton TIMS or a Neptune ICPMS, is shown in Fig. 2. The input of the CDEM is held at ground potential and the anode or signal extraction plate is held at a positive high voltage of about 2.35 kV. A high voltage (HV) capacitor is placed between the signal extraction plate and the pulse discriminator, producing a capacitative decoupling of pulses that helps to avoid electronic interference and allows the pulse counting electronics to be held at ground potential. Because CDEMs have a tendency to produce multiple pulses from one ion event, a discriminator setting of 12 mV and a dead time of 70 ns are applied to effectively eliminate multiple pulses and cross-talk.

Continuous dynode electron multipliers require a conditioning or burn-in period before the gain is stable. This period requires accumulating about

TABLE I. CONFIGURATION OF CDEM MULTIPLE ION COUNTERS (MICs) ON THE NEW BRUNSWICK TRITON TIMS[a]

MIC 1	MIC 2	MIC 3	MIC 4	MIC 5	MIC 6	FARADAY	MIC 7
Static U Multiple Ion Counting							
^{233}U	^{234}U	^{235}U	^{236}U		^{238}U		
Static U Multiple Ion Counting + Faraday + ^{239}Pu Monitor							
	^{233}U	^{234}U	^{235}U	^{236}U		^{238}U	^{239}Pu
Static Pu Multiple Ion Counting							
	^{238}Pu	^{239}Pu	^{240}Pu	^{241}Pu	^{242}Pu		^{244}Pu

[a] The six MIC-FAR-MIC configuration is termed six pack plus one. All of the configurations can be achieved readily with minor adjustment of the zoom optics that changes dispersion of the ion beam on the Triton/Neptune mass spectrometers.

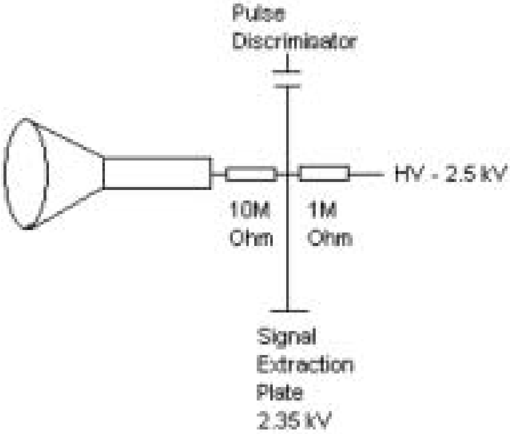

FIG. 2. Schematic of a CDEM assembly.

10^{10} counts of an appropriate ion, and has been achieved by 14 h overnight runs of strontium at 200 000 counts/s. After the burn-in procedure, the operation voltage needs to be increased by 600 to 700 V to about 2600 V. The count rate responses of CDEMs also change as a function of time due to degradation of the detector inner glass surface. A drift of 0.15 to 0.2%/h has been observed at a count rate of 100 000 counts/s. For small samples of ca. 10 pg that are consumed during an analysis in about 10 min, the drift accounts for 0.03% variation in a measured isotopic ratio. This value is smaller than the change in the ratio due to mass fractionation and smaller than the differences in MIC detector efficiencies. Note also that these detectors may be best suited to count rates below approximately 100 000 counts/s, due to the rate of degradation of the small internal surface areas, and are well suited to the total evaporation measurements of small samples that are completely evaporated from a filament in 5 to 10 min.

Linear responses of CDEMs were tested using Sr over a range of 300 to 500 000 counts/s. It was found that the CDEMs exhibited non-linearity similar to that observed with discrete dynode electron multipliers [2], and for which accurate corrections can be made. It was possible to achieve counting efficiency of 90 to 95% at a plateau voltage of about 2.7 kV. The dark noise measured on a total of ten different CDEMs was found to be typically below or about 1 count per minute (counts/min). One detector showed considerably more noise, about 10 counts/min, and was replaced. Estimated lifetime for the new CDEMs, based on a limited number of samples, is 135 to 150 h at a count rate of 100 000 counts/s. This is sufficiently long to allow ca. 800 to 900 samples to be analysed for 10 min/run. At a cost of US $1500 to $2000 per CDEM, the cost per sample analysed could be less than US $2. In practice, the count rates for many isotopes could be lower (<50 000 counts/s) for actual samples and detector lifetime proportionately greater.

4. CALCULATION COMPARING STATISTICS OF SINGLE VERSUS MULTIPLE ION COUNTING

A calculation was performed to estimate the advantage of static multi-detector ion counting compared to single collector ion counting with peak jumping, based solely on peak measurement times. The results showed a two-fold improvement in precision based on counting statistics (Table II). From a determination of actual peak measurement times in single detector ion counting, the on-peak duty time was approximately 60%. Measurements were integrated for 8 s, with a total analysis time for each cycle (bkg1, 234, 235, 236, 238, bkg2) of 45 s. Background in multiple ion counting was measured once per block. The calculation is based on the analysis of 10 pg of certified reference material (CRM) U030-A, which is expected to run for 300 s with a ^{238}U intensity of 50 000 counts/s.

In addition to enhanced performance due to improved counting statistics, the simultaneous measurement approach will also improve measurement repeatability resulting from the minimization of errors due to erratic signal fluctuations and inappropriate drift correction algorithms as used in single collector measurements.

5. MULTIPLE ION COUNTING DATA

Initial tests of the MIC system were performed using small, environmental level quantities of uranium. Ten pg of CRM U500, CRM U010 and

TABLE II. COMPARISON OF SINGLE VERSUS MULTIPLE ION COUNTING STATISTICS

	Single ion counter		Multiple ion counter	
	Count	%Std. dev.	Count	%Std. dev.
^{234}U	791	3.6	4 296	1.5
^{235}U	43 324	0.48	470 400	0.15
^{236}U	16.6	25	89.9	11
^{238}U	1 381 146	0.085	15 000 000	0.026

CRM 112A were evaporated onto specially cleaned, zone refined rhenium filaments and analysed in total evaporation mode [3]. The results from the first four samples of U500 are shown in Table III. The uncorrected $^{238}U/^{235}U$ ratios yielded a small relative standard deviation of 0.15%. Two of the four CRM runs were treated as samples (14 and 17) and two were treated as comparators (15 and 18) to correct the samples for the combined effects of mass bias/fractionation, detector efficiency and drift. This approach was taken rather than attempting to obtain empirical correction factors for efficiency and response differences between ion counters. Even though the drift characteristics of the detectors with time might be predictable or expressed as a mathematical function, a simple normalization approach using reference material comparators in a sample/standard bracketing sequence appears to be one successful solution for making the necessary corrections. Comparison of corrected isotope ratios with the certified values of CRM U500 showed excellent agreement, with deviations ranging from 0.003 to 0.46% for both major and minor isotope ratios.

TABLE III. TOTAL EVAPORATION MIC MEASUREMENTS OF 10 pg LOADS OF CRM U500

	$^{234}U/^{235}U$	$^{236}U/^{235}U$	$^{238}U/^{235}U$
Measured sample:			
U500-17[a]	*0.0131935*	*0.002147*	0.9810389
U500-18	0.010259	0.001574	0.983468
U500-14	0.0101899	0.001613	0.98097
U500-15	0.010165	0.0015831	0.983536
RSD	0.48%	1.28%	0.15%
Bias factor:			
U500-18	1.0166683	0.9675985	1.0171149
U500-15	1.0260698	0.9620365	1.0170446
Average	1.0213691	0.9648175	1.0170798
RSD	0.651%	0.408%	0.005%
Corrected sample[b]:			
U500-17[a]	*0.0134754*	*0.0020715*	0.9977949
U500-14	0.0104782	0.0015186	1.0002654
CRM value	0.01043	0.001523	1.0003

[a] Italics denote outlier values.

[b] Corrected values obtained by a set of bracketed measurements of the U500 comparator.

Table IV presents data for CRM 112A, a normal uranium material produced by the New Brunswick Laboratory. Nine samples of CRM 112A were measured along with ten samples of CRM U010 loaded on a single turret. The two different CRMs were interspersed on the turret and CRM U010 was used as a comparator. A linear regression was generated for each measured isotopic ratio of the comparator versus mean measurement time, and each sample of CRM 112A was corrected on a time basis using the calculated regression parameters. The use of a comparator and the regression approach were intended to correct for multiple bias effects due to differences in CDEM efficiencies, changes or differences in HV gain, and Rayleigh fractionation. The data acquisition was performed in total evaporation mode and took 10 to 15 min for each

TABLE IV. TOTAL EVAPORATION MIC MEASUREMENTS OF 10 pg LOADS OF CRM 112A (NORMAL U)[a]

	^{235}U/^{238}U	^{234}U/^{238}U	^{236}U/^{235}U
Corrected sample:			
CRM 112A-2	0.007284	0.000059	*0.000018*[b]
CRM 112A-4	0.007234	0.000051	0.000006
CRM 112A-6	0.007311	0.000049	0.000003
CRM 112A-8	0.007256	0.000052	0.000006
CRM 112A-10	0.007249	0.000051	0.000007
CRM 112A-12	0.007271	0.000056	*0.000014*[b]
CRM 112A-14	0.007205	0.000050	0.000005
CRM 112A-16	0.007199	0.000051	0.000006
CRM 112A-18	0.007187	0.000051	0.000009
Average	0.0007244	0.0000522	0.0000060
Uc	0.000020	0.0000013	0.0000006
SD	0.000042	0.0000032	1.70E-06
RSD	0.58%	6.08%	28.29%
RSE	0.19%	2.03%	9.43%
RSE — Poisson statistics	0.27%	3.04%	7.16%
Comb. Rel. Uc (incl. comparator)	0.28%	2.54%	9.64%
Comb. Rel. Uc (Poisson statistics)	0.33%	3.83%	7.48%
Accepted value (Triton, NBL M-TE/SEM)	0.0072502	0.00005284	<5.2E-09
Deviation from accepted	–0.09%	–1.30%	

[a] Corrected relative to a linear regression of multiple measurements of CRM U010, which were measured as bracketing standards between samples of CRM 112A. The CRM U010 comparator was used to correct for the combined influences of mass bias, detector efficiencies, gains, etc.

[b] Italics denote outliers.

sample and comparator. The total numbers of counts acquired for each run were about 3×10^6 for ^{238}U, 3×10^4 for ^{235}U, 150 for ^{234}U and 20 to 200 for ^{236}U (for CRM 112A and CRM U010). The results for the ^{235}U/^{238}U ratio showed a combined relative uncertainty of 0.28%, which includes the uncertainty of the comparator. This uncertainty is similar to the value of 0.33% calculated on the basis of Poisson counting statistics, and indicates that, in the range of total counts for these samples, the counting statistics control the precision and the uncertainty budget. This condition has been noted for elements other than uranium at low count rates [1].

The measured ^{236}U/^{238}U ratio of 6×10^{-6} (Table IV) is dominated by a dark-noise contribution from the MIC used for the detection of ^{236}U (about 20 counts within a 15 min analysis time, which is typical for secondary electron multipliers). For analyses at count rates of 5000 counts/s for the ^{238}U major isotope, the usable dynamic range for the ^{234}U/^{238}U and ^{236}U/^{238}U minor ratios will always be limited, in this case to about six orders of magnitude. But, as also shown in this example, for a ^{234}U/^{238}U isotope ratio as low as about 5×10^{-5}, the MIC data are shown to be quite accurate.

Measured results for the ^{235}U/^{238}U isotope ratio of CRM 112A also agreed well with the accepted values, and showed a relative deviation of –0.09% and a combined relative uncertainty of 0.28%. This demonstrates the validity of the measurement procedure and the approach used to correct for differences in gain effects, time dependent drift in CDEM efficiencies, and mass fractionation.

This first set of data indicates that the MIC technique is a potentially valuable analytical tool for nuclear safeguards and forensic analyses. Picogramme quantities of samples of natural uranium can be distinguished from slightly enriched (or potentially contaminated) samples by measuring the ^{235}U/^{238}U isotope ratio with a precision of about 0.3%.

Work is in progress to establish a modified total evaporation technique [4] for MICs. This modification will allow for multidynamic measurements that can effectively cancel differences in detector efficiencies. The method can also be used to normalize minor isotope ratios to an internal or known ratio.

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AUTHENTICITY CHECK OF A CERTIFICATE SIGNED BY MADAME CURIE

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Abstract

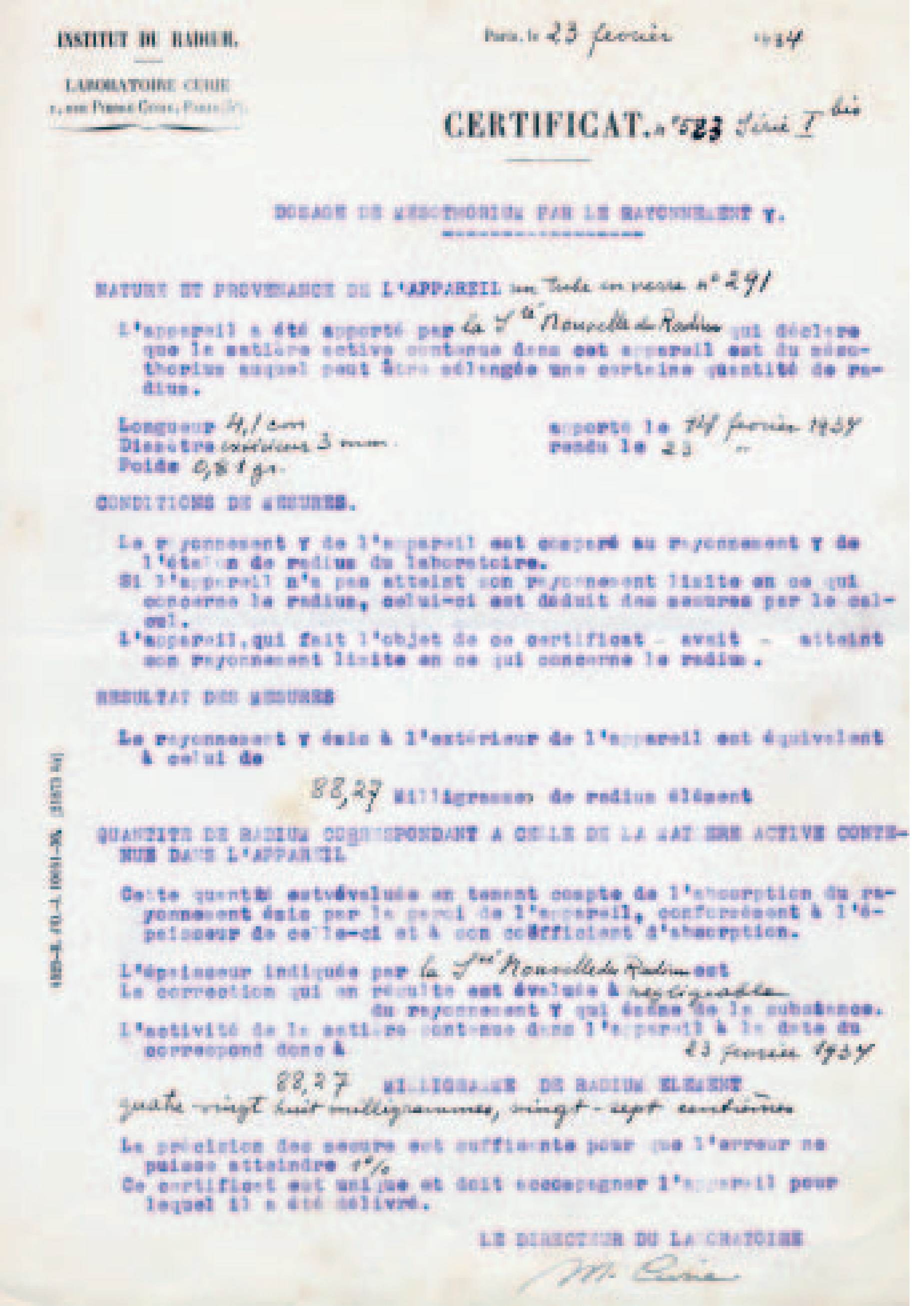
Some years ago, the German/Swiss Association for Radiation Protection purchased a certificate bearing the signature ‘M. Curie’. In a time when counterfeiting is possible simply with a colour copy machine, the question arose: is the document genuine? Audioradiography and measurement of radium contamination suggest that it was, in fact, signed by Marie Curie.

1. INTRODUCTION

In 1996, the Museum of Radiological Protection of the German/Swiss Association for Radiological Protection was offered, at a higher price, what was purportedly an original document, dated 23 February 1934, in which Marie Curie certified that an instrument that had been given to her institute emitted gamma radiation corresponding to 88.3 mg of radium (Fig. 1). The importance of the document lies in the fact that it apparently bears the personal signature of Madame Curie, then director of the laboratory and twice winner of the Nobel Prize.

2. DESCRIPTION OF SCENARIO

The Museum of Radiological Protection decided to purchase the certificate. Soon the question of authenticity was raised. It was suggested that, if genuine, it would continue to show traces of radioactivity. Therefore, autoradiography was carried out at the Federal Office for Radiation Protection. A photo plate that had been placed between strengthening foils in an X ray cassette was placed on the certificate and exposed for two months. Specks from exposure to radioactivity could be seen clearly on the developed plate (Fig. 2). Localization of the contamination is shown in Fig. 3.



INSTITUT DU RADIUM.
LABORATOIRE CURIE
1, rue Pierre Curie, Paris (5e)

Paris, le 23 février 1934

CERTIFICAT. n° 523 Série I bis

DOSAGE DE MESOTHORIUM PAR LE RAYONNEMENT γ.

NATURE ET PROVENANCE DE L'APPAREIL un Tube en verre n° 291

L'appareil a été apporté par la Sté Nouvelle du Radium qui déclare que la matière active contenue dans cet appareil est du mésothorium auquel peut être mélangée une certaine quantité de radium.

Longueur 4,1 cm
Diamètre extérieur 3 mm.
Poids 0,81 gr.

apporté le 14 février 1934
rendu le 23 "

CONDITIONS DE MESURES.

Le rayonnement γ de l'appareil est comparé au rayonnement γ de l'étalon de radium du laboratoire.
Si l'appareil n'a pas atteint son rayonnement limite en ce qui concerne le radium, celui-ci est déduit des mesures par le calcul.
L'appareil, qui fait l'objet de ce certificat - avait - atteint son rayonnement limite en ce qui concerne le radium.

RESULTAT DES MESURES

Le rayonnement γ émis à l'extérieur de l'appareil est équivalent à celui de

88,27 milligrammes de radium élément

QUANTITE DE RADIUM CORRESPONDANT A CELLE DE LA MATIERE ACTIVE CONTENUE DANS L'APPAREIL

Cette quantité est évaluée en tenant compte de l'absorption du rayonnement émis par la paroi de l'appareil, conformément à l'épaisseur de celle-ci et à son coefficient d'absorption.

L'épaisseur indiquée par la Sté Nouvelle du Radium est
La correction qui en résulte est évaluée à négligeable
du rayonnement γ qui émane de la substance.
L'activité de la matière contenue dans l'appareil à la date du
23 février 1934
correspond donc à

88,27 MILLIGRAMMES DE RADIUM ELEMENT
quatre-vingt huit milligrammes, vingt-sept centièmes

La précision des mesures est suffisante pour que l'erreur ne puisse atteindre 1%
Ce certificat est unique et doit accompagner l'appareil pour lequel il a été délivré.

LE DIRECTEUR DU LABORATOIRE

M. Curie

FIG. 1. Certificate signed "M. Curie".

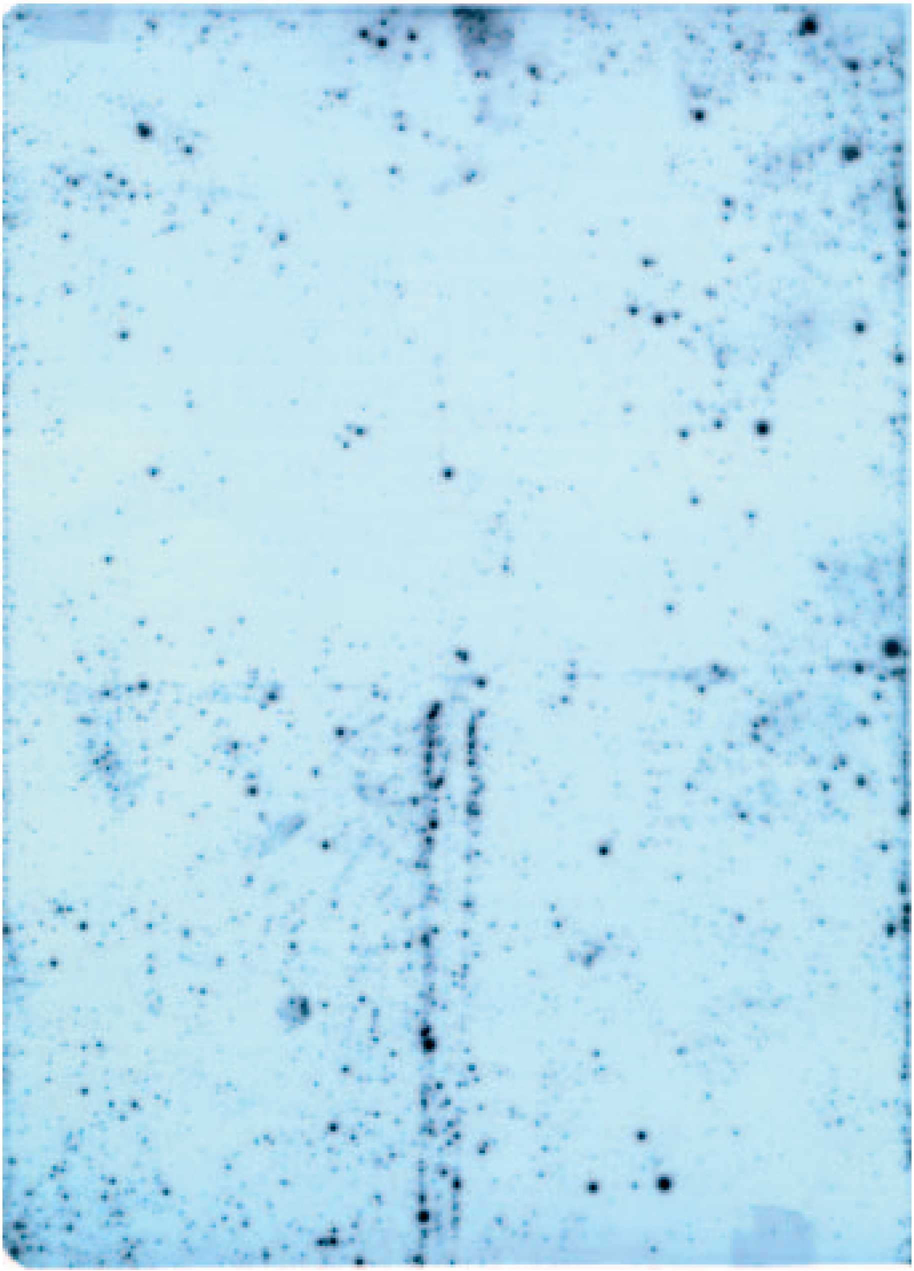
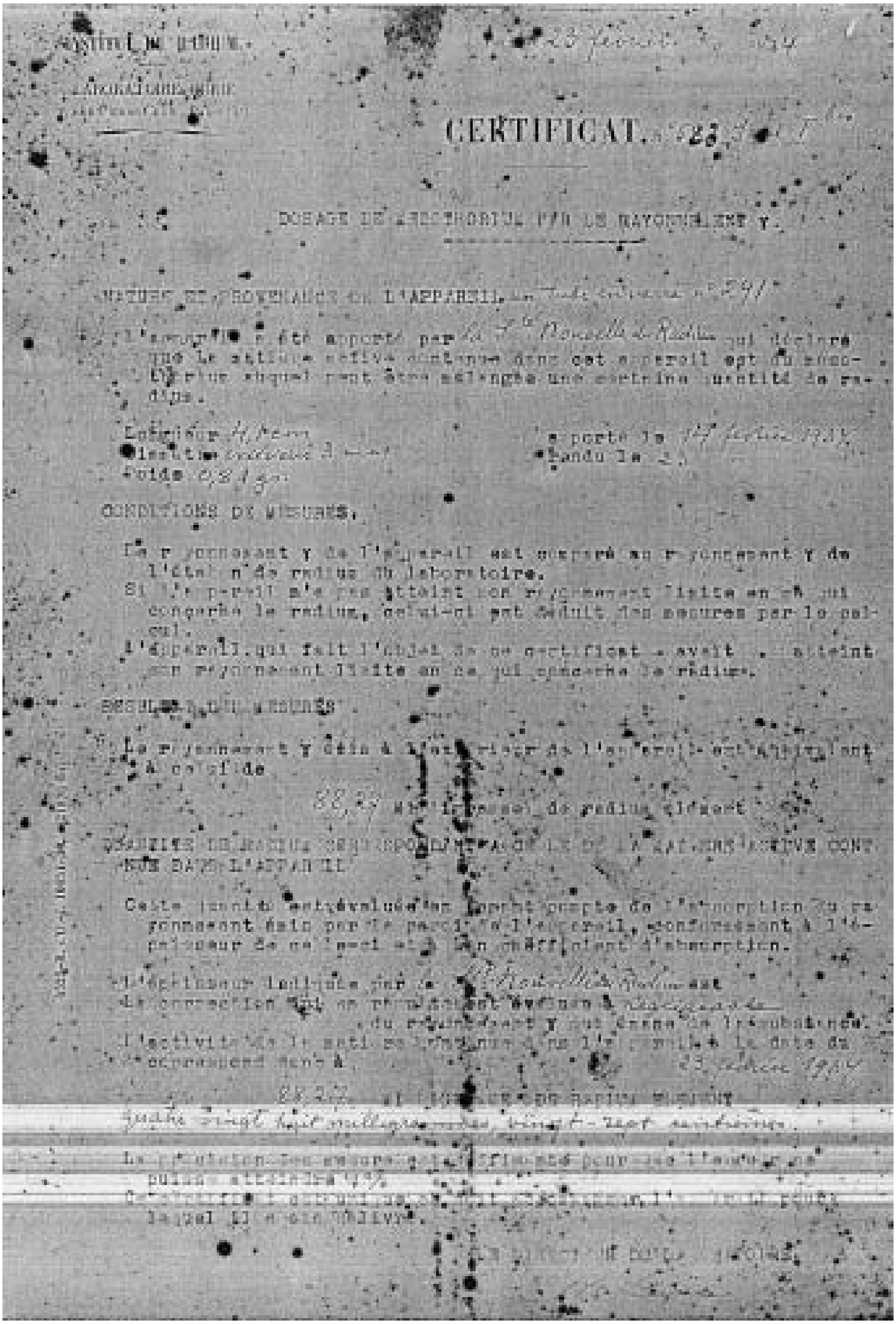


FIG. 2. Black specks on the photo plate caused by radioactive contamination.



CERTIFICAT.

DOSAGE DE [illegible] PAR LE RAYONNEMENT γ.

NATURE ET PROVENANCE DE L'APPAREIL. [illegible]

L'appareil a été apporté par [illegible] qui déclare que la matière active contenue dans cet appareil est du méso-thorium auquel peut être mélangée une certaine quantité de radium.

Longueur [illegible]
[illegible]
Poids 0,81 gr.

Apporté le 14 [illegible] 1934
Rendu le [illegible]

CONDITIONS DE MESURES.

Le rayonnement γ de l'appareil est comparé au rayonnement γ de l'étalon de radium du laboratoire.

Si l'appareil n'a pas atteint son rayonnement limite en ce qui concerne le radium, celui-ci est déduit des mesures par le calcul.

L'appareil qui fait l'objet de ce certificat [illegible] atteint son rayonnement limite en ce qui concerne le radium.

RÉSULTATS DES MESURES.

Le rayonnement γ dû à l'extérieur de l'appareil est équivalent à celui de

88,27 milligrammes de radium élément

QUANTITÉ DE RADIUM [illegible] DE LA MATIÈRE ACTIVE CONTENUE DANS L'APPAREIL

Cette quantité est évaluée en tenant compte de l'absorption du rayonnement émis par la paroi de l'appareil, conformément à l'épaisseur de celle-ci et à son coefficient d'absorption.

L'épaisseur indiquée par [illegible] est [illegible]

La correction qui en résulte [illegible] du rayonnement γ qui émane de la substance.

L'activité de la matière [illegible] à la date du 23 [illegible] 1934 correspond donc à

88,27 [illegible] DE RADIUM ÉLÉMENT

quatre-vingt-huit milligrammes, vingt-sept centièmes.

La précision des mesures [illegible] pour que l'erreur ne puisse atteindre 1%.

[illegible] lequel il a été délivré.

[illegible]

FIG. 3. Traces of exposure following autoradiography.

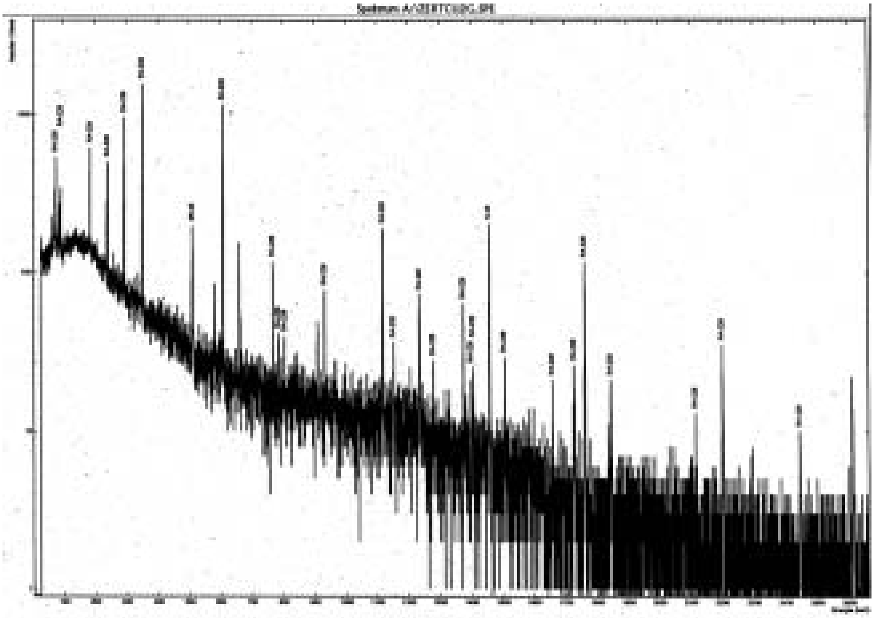


FIG. 4. Gamma analysis of the specks on the document.

This begged the question of whether the nuclides marking the photo plate could be identified. The certificate was examined in a body counter, also at the Federal Office for Radiation Protection. The result indicated that the dark specks resulted from contamination with ^{226}Ra and its decay products ^{214}Pb and ^{214}Bi (Fig. 4).

3. CONCLUSION

Analyses proved that the certificate is genuine and the Association could be pleased that they had not been defrauded by a swindler.

FROM THE SEM (IAEA) TO THE SIMS (ITU): RELOCATION EXPERIMENT OF MICROMETRE SIZED PARTICLES — INITIAL RESULTS

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Abstract

Multiple analyses, elemental and isotopic, of individual radioactive particles in the µm range are key tools in environmental research and in nuclear forensics. They require the ability to precisely locate particles of interest (POIs) in the secondary ion mass spectrometer (SIMS), or other instrument, after they have been identified in scanning electron microscopy (SEM). A triangulation location method, based on microscopic reference marks imprinted on the sample holder, has been developed and successfully implemented in the IAEA (Seibersdorf) Clean Laboratory at Seibersdorf. We describe a feasibility round-robin-type test, performed jointly by the IAEA and the Institute for Transuranium Elements (ITU). A sample loaded with uranium oxide particles was prepared at the ITU and sent to the IAEA, where 25 POIs were selected after being identified in an automated particle search. Then, the sample was returned to the ITU, where the same particles were located and analysed, both in the SEM and in the SIMS. The location precision was better than 10 µm in the SEM and 20 µm in the SIMS over the whole sample area, 2 cm in diameter. The experiment proved that the method facilitates repeated analyses of individual µm sized particles in different instruments.

1. INTRODUCTION

Nuclear forensic analysis of individual radioactive particles in the µm sized range can be performed in two steps: in the first, an automated scanning electron microscopy (SEM) screening of the loaded sample holder, particles of interest (POIs) are identified and classified according to their elemental composition and size. In the second, the sample is transferred to a mass spectrometer, usually a secondary ion mass spectrometer (SIMS), and individual POIs are located and further analysed for their isotopic composition. Alternatively, selected POIs can be extracted after SEM screening or fission track analysis, and then analysed in a thermal ionization mass spectrometer (TIMS) or inductively coupled plasma mass spectrometer (ICPMS). In the SIMS, which has imaging capability, the whole sample is manipulated to bring specific POIs to the ion beam point of impingement. In all of these cases, including revisiting POIs in the SEM, a precise location method is essential.

The location of POIs in the SIMS, after they have been identified as such in the SEM, is based on a triangulation method [1]. A set of μm sized reference marks is "printed" by vacuum deposition of metallic thin film patterns on the sample holder, a flat polished graphite planchet. The marks, each easily recognizable and precisely measurable by both instruments, serve as a co-ordinate system embedded in each sample. The stage co-ordinates of any POI, co-planar with the reference marks, can be expressed as a linear combination of the vectors pointing at three non-linear reference marks, with coefficients that are independent of the choice of the co-ordinate system. In other words, regardless of instrument or the specimen stage used, a POI will have the same coefficients with respect to the reference marks. This is the basis of the triangulation method [1], which allows predicting the location co-ordinates for POIs in one instrument based on those measured in another.

The initial particle search, as well as the subsequent location process, can be done either in an automated (A) or a manual (M) mode. The feasibility of the location method, as reported in this paper, was tested in three types of SEM-to-SEM experiments (A/A, A/M, M/M), and in an SEM-to-SIMS experiment. The latter was invariably of the M/M type, in view of the destructive nature of SIMS analysis, which requires a thorough SEM characterization (and hence manual location) of the selected POIs *before* the sample is transferred to the SIMS.

The SEM screening provides a list of POIs, each with a data profile comprising stage co-ordinates, composition and size. The measurements of the stage co-ordinates of at least three linearly independent reference marks in the SEM and in the SIMS allows predicting the SIMS stage co-ordinates where the POIs can be found. The calculation is based on a three point algorithm, the so-called triangulation method [1].

It has been demonstrated in SEM to SEM transfer experiments [1] that a 1 μm particle can be located within an accuracy better than 10 μm, and, in most cases, better than 5 μm, over the entire sample area, 2 cm in diameter. In a well calibrated SEM, even higher accuracy can be achieved. A thorough error analysis [1] showed good agreement between these values and the calculated expanded uncertainty.

Preliminary SEM to SIMS transfer experiments, performed at the Agency's Laboratories at Seibersdorf, indicated that location within 20 µm is readily achievable [1]. The accuracy can be improved by increasing the number of reference points from three to six, and averaging the results. A POI can thus be brought close to the centre of the SIMS field of view, visually located, and analysed.

In this paper we describe a joint IAEA–ITU experiment aimed at testing the feasibility of the location method in two independent laboratories.

We intend to broaden this experiment to a "round-robin" involving other laboratories.

2. METHODOLOGY

The objective of this feasibility study was to identify a group of particles by an automated as well as by a manual SEM search in one laboratory, as would be the case in real events, then determine if the same particles could be located for further analyses in other instruments (SEM, SIMS) in other laboratories.

The manual stage co-ordinates (MSCs) of a particle were defined as the specimen stage co-ordinates measured when the particle was at the centre point of the field of view of the SEM, or at the impingement point of the ion beam of the SIMS. The automated stage co-ordinates (ASCs) were defined as the stage co-ordinates of a POI as identified and measured in the automated search. It should be borne in mind that the ASCs are determined by the software as a sum of a real stage vector representing the search field, usually its centre, and an image vector pointing at the particle in the pixel map, the image plane. Consequently, the measurement uncertainty associated with any possible image distortion will be reflected in the precision of the ASC [1].

Three instruments were used in the location/relocation experiments: the SEM at IAEA (FEI XL-30 with EDAX Particle Analysis ver. 3.2 software), where the initial measurements — automated and manual — were made, the SEM at ITU (R.J. Lee, GSR dedicated) and the SIMS at ITU (CAMECA IMS-4FE6 with ver. 4.1 software). It is noteworthy that the specimen stages in the instruments used were of the standard motor driven type, not equipped with optical position indicators for readout or feedback. This bears on the achievable accuracy of stage positioning.

The sample used was a flat polished graphite planchet, loaded with a small number (a few hundreds) of synthetic 1 µm sized particles of uranium oxide, a standard reference material produced at ITU. The sample was prepared using the NIST (National Institute of Science and Technology, Gaithersburg, MD, USA) method (C.J. Zeissler, unpublished) in the ITU clean laboratory, and then sent to the IAEA Clean Laboratory. There, the reference mark pattern was "printed" on the planchet by vacuum deposition of a thin layer of copper through "finder grid" masks [1] (Fig. 1), leaving the particles intact. The sample was then screened in the XL-30 SEM, using the automated particle analysis software, and about a hundred uranium containing POIs were identified and their locations defined in several repeated runs.

Prior to each run, the sample was removed from the XL-30 stage and re-inserted in an arbitrary new position, where the MSCs of several reference marks were measured. Care was taken to select the same group of marks in all runs and from all six grids printed on the planchet, allowing some redundancy. Useful marks, easily identifiable and measurable in both the SEM and the SIMS, are the dots within the W, V, 9, 8, etc., in Figs 2 and 3.

FIG. 1. The sample used in the IAEA–ITU experiment: pyrolitic carbon planchet with U_3O_8 particles at centre, vacuum deposited 6 'finder' grid Cu thin film patterns, and orientation signs. The image is a photomontage of SEM-BSE images. The particles at the centre are hardly visible at this low magnification.

From the particles identified in the first run, Autorun3, twenty-one uranium-containing particles and four others (e.g. Al, SiO_2) were selected. Each particle from this group was revisited by "dialling in" the ASCs of AutoRun3, then manually correcting for the deviation, namely the additional displacement required to bring the particle to the exact centre of the screen. There, the MSCs as well as the deviation were measured. In cases of ambiguity in identification — when two close uranium particles rather than a single one could match a single source POI — both were included in the list.

Low-magnification images of the search areas, aimed at serving as particle maps (e.g. Fig. 6), have proven to be invaluable navigation and orientation aids, particularly in cases of densely loaded sample areas. The maps play a role in avoiding ambiguity in visual identification of individual particles according to their distribution patterns.

AutoRun3 was the preparatory stage that provided the baseline data for the whole experiment.

Two additional independent runs (manual and automated) were conducted on the XL-30, and their results cross-correlated with the baseline data. In other words, the MSC from the baseline data was used to predict the

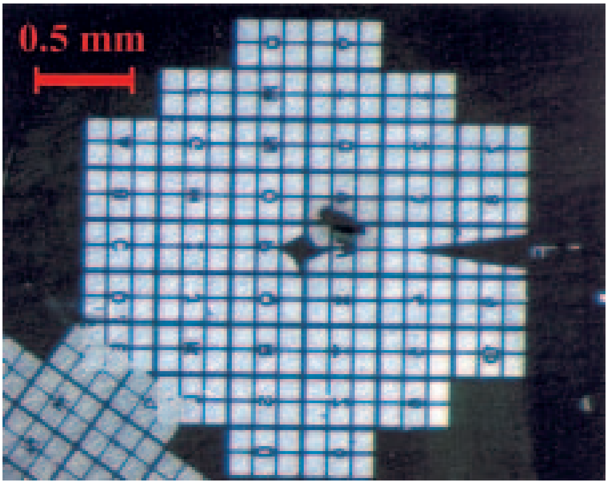

FIG. 2. A close-up look on 'finder' grids (in this case, aluminium) printed on the graphite planchet.

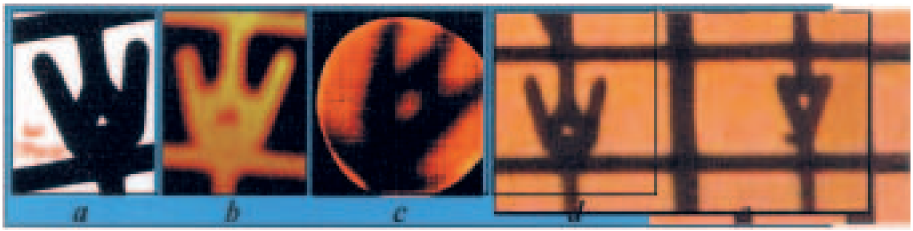

FIG. 3. Close-up images of the 'W', the point inside which serves as a reference mark. (a) SEM-BSE image; (b) SIMS carbon image, scan mode; (c) SIMS carbon image, RAE mode; (d) SIMS CCD image before analysis; (e) SIMS CCD image after the analysis, showing the damage caused by ion beam sputtering.

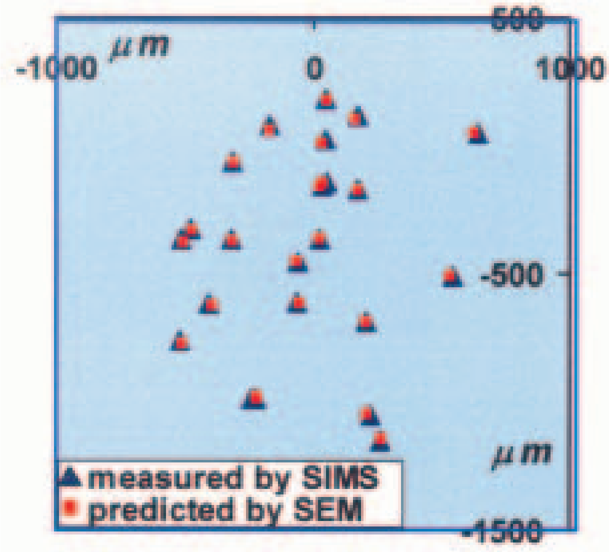

FIG. 4. POI distribution map as measured in the SIMS-ITU specimen stage co-ordinates, and their locations as predicted from the SEM-IAEA screening.

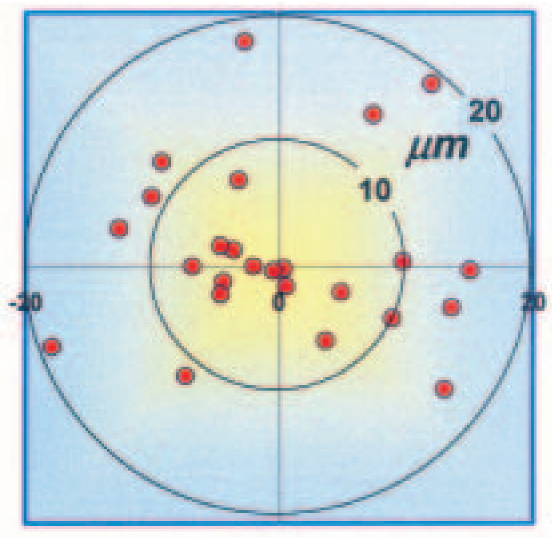

FIG. 5. Deviation of the POIs' actual locations in the SIMS-ITU from their locations predicted on the basis of the SEM-IAEA measurements.

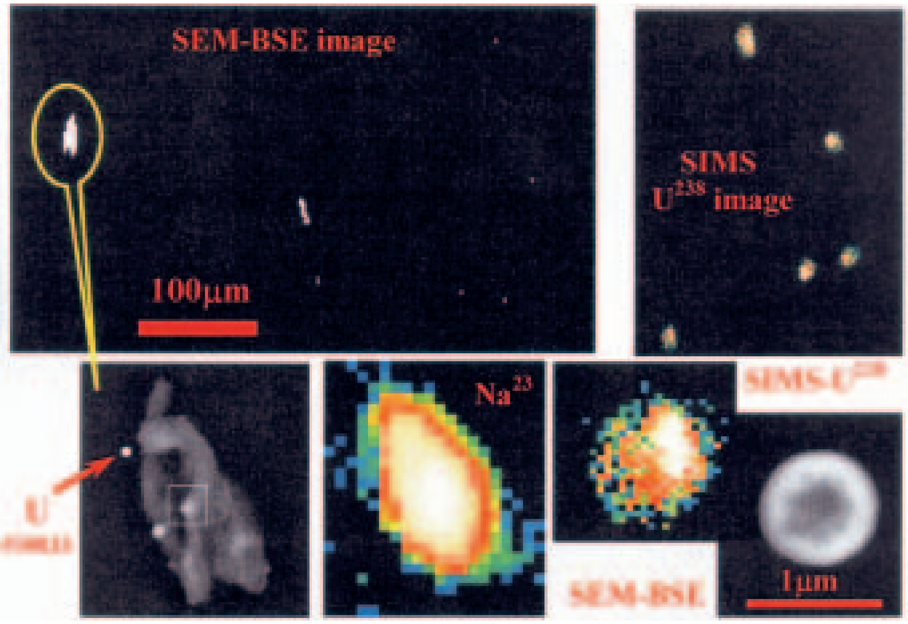

FIG. 6. From the SEM-IAEA to the SIMS-ITU: the same particles identified and analysed in the two laboratories, proving the feasibility of the triangulation method for particle relocation.

location where a certain POI would be expected to be found in the next run, the calculation based on the triangulation method; then, this POI was searched for at that "address", allowing some circle of uncertainty around it. After the identification was established, aided by the particle maps, the deviation of the actual from the predicted location was determined.

Having concluded the described analysis, the sample was shipped to ITU, together with a list of MSCs of the reference marks and the 25 POIs, and the SEM image maps. The SEM and SIMS operators at ITU were asked to select from the list and use those reference marks most suitable in their judgement, and measure and feed their co-ordinates to the algorithm and repeat the experiment described above, with the aid of the particle maps for ID verification. The SIMS operator also performed mass spectrometric analysis and imaging, in the scanning, RAE and TV modes, thus obtaining conclusive, unequivocal identification of the POIs.

3. RESULTS AND DISCUSSION

In A/A relocations, particles from two partially overlapping groups with different internal order (resulting from two automated runs) need to be matched. A circle of uncertainty is associated with each particle, which adds to the complexity of the problem. The A/A case is beyond the scope of this paper, therefore, we will limit our discussion to manual-to-manual (M/M) relocations.

Figures 1 and 2 show the sample used in the experiment, with the particles (barely visible) at the centre, the six "finder grids", and several orientation signs near the rim. Figure 3 provides close-ups of one of the reference marks, the dot within the W, in four imaging modes of the SEM and the SIMS. It also shows the damage caused by the ion beam to the sample, as it sputtered away at the impingement point of the beam. The dot within the W, as with the other reference marks used, was clearly recognizable and unequivocally identifiable in both instruments, being practically invariant under the image mirroring that takes place in the SIMS.

Figure 4 is a distribution map of the POIs as measured in the SIMS-ITU. Superposed are their predicted locations, based on the SEM-IAEA screening.

Figure 5 is a plot of the deviations between the actual positions of the POIs as measured in the SIMS-ITU, and their locations predicted on the basis of the SEM-IAEA measurements.

It is noteworthy that the relocation experiments, SEM-IAEA to itself and SEM-IAEA to SEM-ITU, yielded very similar distribution maps and deviation plots.

Figure 6 shows a gallery of SEM and SIMS pictures, at lower and higher magnifications, of the same particles. While the SEM-BSE images reflect the Z number contrast and show all particles in the field of view, each SIMS image (left–right mirrored here, to facilitate comparison with the SEM images) is confined to one isotope alone. Consequently, the uranium particle (#30033) was not discernible in the ^{23}Na image, and vice versa.

It should be pointed out that SEM-to-SEM experiments, namely subsequent runs on the XL-30 and on the R.J. Lee-ITU SEM, yielded very similar charts, showing that most particles were found within 10 µm or less of their predicted locations.

A problem that requires care is that of particle identification. As mentioned above, the A/A case is beyond the scope of this paper and will be discussed elsewhere. However, the problem exists even in the M/M case, where the stage co-ordinates of each particle were measured after each had been manually brought to the centre of the SEM field-of-view. Although the image distortion component is eliminated in this case from the location uncertainty, other stage problems prevail [1], leading to the formation of an "uncertainty circle" around each predicted location. The operator, who dials in and sends the specimen stage to the predicted address, has to decide which particle is the real one, occasionally out of several that are close to the screen centre. The particle maps play an important role, which should not be overlooked, particularly in cases of densely loaded samples. Of the twenty-five measured particles, we had two cases of ambiguous ID that could have been avoided had we given more weight to the particle maps in the baseline run.

One particle (#30064) was probably detached from its position during the experiment. The next closest particle, about 220 µm away, was too far to be considered, therefore it was ignored and 30064 declared a "total loss". Particle migration on the planchet may occur, but we have no way of verifying it. Therefore, care should be taken in handling the samples. By the same token, particles 30095A and 30095B, a pair of close particles, were both wrongly linked to particle 30095, which may also have been lost.

Eighteen of the twenty-one uranium POIs and all four non-uranium POIs could be identified unequivocally, as verified by picture maps and by SIMS imaging (Fig. 6). The relocation precision was better than 10 µm in the SEM and 20 µm in the SIMS over the whole sample area, 2 cm in diameter (Fig. 5). Bearing in mind that the size of the SIMS field of view was 150 µm, this level of attainable precision allows bringing any POI reasonably close to the centre of the SIMS field of view, and then visually identifying and analysing it.

The experiment has proven that the method facilitates repeated analyses of individual µm sized particles in different instruments and laboratories.

4. CONCLUSION

The experiment demonstrated that the triangulation method is a powerful, fast, low cost, easy to apply tool for routine, precise location of individual μm-sized particles, a problem of practical importance in environmental particles research and in nuclear forensics. Particles identified by automated or manual SEM screening can be located for further analyses in the SEM, with accuracy better than 10 μm, and, in the SIMS, better than 20 μm. The uncertainty associated with the measurements is in good agreement with error propagation calculations [1], based on the analysis of error sources in the SEM and in the SIMS, and the mathematical algorithm used.

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CHALLENGES AND ALTERNATIVE APPROACHES

(Session 4)

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LEGAL AND SCIENTIFIC SCRUTINY OF FORENSIC ‘SCIENCES’ AND ‘EXPERTS’

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Abstract

Traditional areas of forensic science, such as handwriting and fingerprint examinations, and the newer sciences, such as molecular biology, are increasingly being scrutinized and challenged by the legal and scientific communities. These older forensic disciplines are targets for critics and sceptics as they are not founded on the traditional sciences, but have rather an empirical basis and are supported by what may be considered quasi-validated data. The paper discusses, in broad terms, the basis of these legal and scientific attitudes and various solutions to overcoming negative perceptions.

“An expert is someone who knows some of the worst mistakes that can be made in his subject and who manages to avoid them.”: Werner Heisenberg (1901–1976; German physicist).

1. INTRODUCTION

Forensic science in Australia and internationally has, over the last two decades, undergone significant changes. Many of these changes have been made as a result of external scrutiny of practices and procedures that were in place in the 1980s, and, in Australia, as a consequence of infamous criminal cases such as Splatt [1] and Chamberlain [2], both of which resulted in Royal Commissions. The Royal Commissions reviewed the conflicting forensic evidence, lack of documented procedures, and questionable scientific practices, and results that led to severe and, in some instances, warranted criticisms. Similar circumstances to those in Australia had eventuated in the United Kingdom with the highly publicized “Birmingham Six” and “Guilford Four” cases.

The external stimulus for change was clearly evident, and it was reasonably assumed that in order to re-establish credibility and confidence in forensic science amongst the judiciary, legal community, and public, changes were necessary. New technologies such as those involving DNA were emerging and it was foreseen that, in order to maintain the integrity of these new tools, strict guidelines would need to be adhered to. This recognition was initially identified in the United States of America, where a working group was established to develop guidelines for forensic laboratories in which the new technologies were being utilized.

In the early 1980s, again in the United States of America, a body of senior forensic scientists, the American Society of Crime Laboratory Directors, developed and implemented a Laboratory Accreditation Board (ASCLD/LAB) [3]. The principal objectives of the board were to improve the quality of forensic-laboratory services provided to the criminal justice system and to create a mechanism to independently assess a laboratory's operational performance against given criteria and standards.

The concept of accreditation was quickly adopted by the Australian equivalent of ASCLD, the Senior Managers of Australian and New Zealand Forensic Laboratories (SMANZFL). In 1992, the board of the newly formed National Institute of Forensic Science (NIFS) supported SMANZFL in its views. The NIFS board comprised representatives from law-enforcement agencies throughout Australia, the judiciary, forensic science, and academia.

In the early 1990s the National Association of Testing Authorities (NATA) superseded the ASCLD/LAB as the accreditation authority in Australia for forensic laboratories. The NATA criteria were based on, and adhered to, international standards, ISO Guides 9002, 25 and 43.2 [4].

Even as ASCLD and SMANZFL both identified the need for change brought about by an external stimulus and strategically introduced accreditation as a mechanism for achieving change, the need for further changes and development has not lessened.

In the early 1990s, a body similar to ASCLD and SMANZFL was being formed in Europe. This body, the European Network of Forensic Science Institutes (ENSFI), held its founding meeting in 1995. Its aims and ideals were consistent with those of ASCLD and SMANZFL.

The 1990s saw increasing scrutiny of the forensic sciences and expert testimony by the general scientific community and the judiciary. Traditional forensic disciplines, such as fingerprints, handwriting and toolmark examinations, were challenged on a regular basis in courts of law in the USA. The bases for these challenges were a consequence of several landmark cases including *Daubert v. Merrell Dow Pharmaceuticals* [5] and *Kumho Tire Co. Ltd. v. Carmichael* [6]. In Australia, the focus has been on problems associated with the perceived bias of expert evidence as detailed in reports by Freckleton et al. [7], in papers such as that by The Hon. Justice Sperling [8] and the Western Australia Review of the Civil and Criminal Justice System Consultation Paper [9].

As the *Chamberlain* and *Splatt* Royal Commissions acted as a catalyst for the forensic community to introduce accreditation, legal challenges and criticisms of forensic sciences — in particular the disciplines of fingerprint, handwriting and toolmark identification — should initiate further development of these fields in line with accepted practices in the scientific community. The issue of partisanship on the part of expert witnesses is an observation that all forensic disciplines need to address. The legal system, particularly in Australia, is seeking to remedy this issue by developing various models and expert-witness guidelines that would effectively modify the adversarial system.

In this paper, I discuss the obligations of forensic practitioners to initiate solutions to the shortcomings revealed by scientific and legal scrutiny of their particular disciplines and of expert testimony in general. I will also discuss various research projects in the field of forensic handwriting identification being conducted to address these issues.

2. LEGAL AND SCIENTIFIC PERSPECTIVE — SCIENCE

The case of *Frye v. United States* [10] involved the determination of admissibility of opinion relating to polygraph evidence. The nature of the scientific evidence was to be admissible providing it met the criterion of “general acceptance” in the relevant field of science to which it belongs. This became generally known as the *Frye* test for determining the admissibility of expert opinion evidence. In 1975, the United States Federal Rules of Evidence [11] superseded the general-acceptance criterion, and provided a standard for admitting expert testimony. Rule 702 relates to scientific, technical or other specialized knowledge that will assist the trier of fact to understand the evidence or to determine a fact in issue, provided that:

- The testimony is based upon a sufficiency of facts and data,
- The testimony is a product of reliable principles and methods,
- The witness has applied the principle and methods reliably to the facts of the case.

The admissibility of expert evidence in Australia is premised by the expert witness possessing specialized qualifications or experience, and the expertise must form part of a body of knowledge or experience that is sufficiently organized or recognized to be accepted as a reliable body of knowledge. Not surprisingly, science is often defined in a dictionary as “any domain of knowledge accumulated by systematic study and organized by general principles.”

Wigmore on Evidence [12], when referring to the criminal appeal in *R v. Gilmore* [13], discussed that the appellate court had jurisdiction to review both the question as to whether or not a particular witness qualifies as an expert, and whether the respective field on which the expert evidence is based is recognized and therefore permissible for expert knowledge and consequently testimony.

In the United States Supreme Court case of *Daubert v. Merrel Dow Pharmaceuticals* [5] the court stated that evidence based on novel scientific principles should be admitted only if the evidence is reliable and scientifically valid. *Daubert*, unlike the *Frye* test of general acceptance, discussed four factors required for the acceptance of "novel sciences". These are now commonly referred to as the *Daubert* factors:

(1) Testing (theory or technique),
(2) Peer review (theory or technique),
(3) Error rates (known or potential), and
(4) Widespread acceptability in the relevant scientific discipline and scientific community.

In *Kumho Tire Co. Ltd v. Carmichael* [6], the United States Supreme Court extended the scope of *Daubert* factors to include the testimony of "technical or specialized knowledge" and subsequent expert testimony, the difference being that the *Daubert* factors set forth the criteria for determining whether the expert testimony met the requirement for "scientific knowledge."

Bruce [14] described the United States Federal Rules of Evidence with particular reference to Rule 702, and stated that it "was not to restrict expert testimony to a narrow set of "scientific" disciplines, but to … make certain that an expert, whether basing testimony upon professional studies or personal experience, employs in the courtroom the same level of intellectual rigor that characterizes the practice of an expert in the relevant field."

In the case *US v. Starzecpyzel* [15] the Southern District of New York found that the forensic document-examination expertise constituted technical or specialized knowledge outside the scope of *Daubert*. In *US v. Velasquez* [16], the Second Circuit held that when the district court determined handwriting to be a field of expertise, it should have permitted the defendant to challenge the field of expertise. The Appellate Court found that handwriting evidence satisfied the liberal requirements of *Daubert*, and in *US v. Jones* [17] the Court applied *Daubert* to the case of handwriting experts and determined that the handwriting expert qualified as a scientific expert.

From the above cases in the USA, it is evident that interpretation of the *Daubert* factors is quite liberal and broad. Due partially to the multi-jurisdictional nature of the US legal system, there is a lack of uniformity in the judiciary's interpretation of what constitutes a technical versus a scientific field of expertise.

The past several years have seen an increase in the number of court challenges regarding handwriting, fingerprint and toolmark identification in the USA — the *Daubert* factors being the principal tool of challenge. Though forensic handwriting evidence and fingerprint evidence have been routinely given in courts of law for numerous decades, they have not been exempt from challenge, despite the *Daubert* factors, primary focus on "new" or "novel" sciences. The US case of *People v. Leahy* [18] held that the determination of whether a technique was new is not based on its history of use in the scientific community, but rather whether it was "settled in law". The Court further held that if the technique was "repeatedly challenged in court" and had "a recent history of legal challenges to (its) admissibility ... it seems appropriate that we deem the technique new or novel for the purposes of *Kelly/Frye*" [19].

Australian courts have seen few challenges to forensic disciplines in comparison with the USA. On the contrary some members of the judiciary in Australia, such as The Hon Justice H.D. Sperling [8], recommended that the *Daubert* gatekeeper approach not be implemented. This view was supported by a study conducted by Freckelton et al. [7] reported in The Australian Law Reform Commission, Adversarial Background Paper on Experts [20], where it was stated that "In its consultations, the Commission has not heard that there are significant problems caused by the admissions of expert evidence from novel scientific or technical fields or disputes over admissibility. The Australian Institute of Judicial Administration (AIJA) empirical study did not reveal majority support for new exclusionary criteria based on reliability of expert evidence."

Despite the lack of challenges in court throughout Australia and the general acceptance of handwriting evidence, the criticisms of this type of evidence in the USA should not be ignored. On the contrary, criticisms, as detailed by such authors as Saks, Risinger and Denbeaux, clearly identify a need to review the premises on which these forensic identification sciences are based. In his paper, Saks [21] discussed the issue of the identification sciences not having been developed from the more traditional sciences, but instead were invented by police investigators to meet the needs of the criminal justice system. Saks stated that the forensic identification sciences lack the undergirding of basic science. Saks and Risinger [22] were critical of attempts to validate the fields by proficiency-testing techniques, and stated that validation studies have essentially failed to meet the required scientific rigour due to poor design and testing procedures; they claimed that results of proficiency testing and trials to date demonstrated unacceptable error rates. Although I consider that at least some of the criticisms by Saks et al., of attempts by the forensic identification sciences to satisfy scientific scrutiny, to be unwarranted, there exists an element of truth that cannot be ignored.

Accreditation of forensic facilities and the requirements to undertake routine proficiency tests go some way to introducing quality control and quality-assurance measures in line with the general scientific community. Validation work in the field of handwriting identification conducted by researchers such as Kam et al. [23] and Found et al. [24–28] have contributed substantially to the development of the field. The extensive validation trials conducted by Found have tested aspects both of the validity of the methods used and of the practitioner.

In the case *US v. Plaza* [29] a fingerprint expert stated that errors could be attributed to either the method or the practitioner. In order to satisfy the *Daubert* factors the "rate of error" for a particular field of science would need to be established. Bruce Budowle, an FBI agent giving expert testimony at the same hearing, stated that the error rate determination in the science of fingerprinting is not relevant and that practitioner error could be corrected by quality-control procedures of peer review. Furthermore, Budowle discussed methodology-error rate in identification sciences as being difficult to determine and that it is not a cumulative event to calculate.

Found's research and validation studies have focused on forensic handwriting identification and have established the error rate of practitioners' opinions. Found's research encompasses both peer- and non-peer-reviewed opinions. Since the inception of those validation studies in the mid-1990s, it has been observed that participants' error rates have decreased. It is not known if this can be attributed to modifications in the methodology or to practitioner awareness of the limitations of the practitioner to proffer opinions regarding some aspects of identification or non-identification. The research conducted to date has caused a re-evaluation or re-assessment of some of the underlying premises previously considered sound and reported in numerous texts on the subject. Irrespective of the cause in reduction of error rates, the research conducted by Found, both in Australia and overseas, is a significant contribution to the development of the field.

Forensic identification scientists in general need to validate the criteria upon which their work is based. This validation should and must be subjected to the rigour expected by the general scientific community irrespective of whether the field is classified as technical or scientific. The author concurs that the United States Federal Rules of Evidence 702 have summarized what should be considered the minimal expectation for forensic identification practitioners, namely that, whether basing testimony upon professional studies or personal experience, the same level of intellectual rigour should be expected. Accreditation of forensic facilities and disciplines has achieved this end to some degree; however, the expectations by the scientific and judicial communities are not without merit and should be considered an incentive to improve rather than a barrier to overcome.

3. LEGAL AND SCIENTIFIC PERSPECTIVE — EXPERT EVIDENCE

In the USA, the focus of expert testimony has been on the science rather than on the presentation of the testimony, whereas in Australia, over the past several years, the focus has been on:

- The independence of the expert witness,
- Methods of improving utilization of experts in the adversarial system.

Probably the most extensive research hitherto undertaken regarding the bias and partisanship of expert witnesses was conducted in Australia by Freckelton et al. [7], who made a survey of Australian judges related to expert evidence. The results of the survey indicated that a significant number of judges had encountered either bias or partisanship in expert witnesses appearing in their courts.

The Hon. Justice Sperling discussed the findings of the survey in his paper [8], and stated that “this is what one would expect. In the adversarial system, experts who will support an opinion at one extreme or the other are selected.” The survey results as discussed in his paper did not differentiate between civil and criminal proceedings or whether the perceptions were equally shared amongst the judiciary that routinely hear cases in both courts.

In a review conducted by the Law Reform Commission of Western Australia pertaining to Expert Evidence in Civil Proceedings [9] and the subsequent review on expert evidence, there was agreement that “a significant problem in the process of civil litigation within the adversarial system is that it produces expert testimony that is not impartial.”

The problems of bias amongst expert witnesses are not a recently identified phenomenon. In an 1873 case, *Lord Arbinger v. Ashton* [30], the judge stated, “Undoubtedly there is a natural bias to do something serviceable for those who employ you and adequately remunerate you. It is very natural, and it is so effectual, that we constantly see persons, instead of considering themselves witnesses, rather consider themselves as the paid agents of the person who employs them.”

Ongoing issues of bias and partisanship have resulted in the development of rules, models and guidelines for the presentation of expert testimony. Though, at this point in time, no clear distinction is made between expert advisers and expert witnesses, proposals have been put forth that a practice and procedure be implemented to maintain a clear distinction between these two roles of experts.

In 1993, Creswell [31] developed a code involving the duties and responsibilities of expert witnesses known as the *Ikarian Reefer.* In 1999, the *Ikarian Reefer* was in some form or another adopted in the United Kingdom as the core set of rules, replacing those previously used in the Supreme Court and County Court.

The Federal Court of Australia has developed its own guidelines [32] for expert witnesses in proceedings in Federal Court. These guidelines, like the *Ikarian Reefer,* detail expert witnesses' duties to the court, namely:

- An expert witness has an overriding responsibility to assist the Court on matters relevant to the expert's area of expertise.
- An expert witness is not an advocate for a party.
- An expert witness's paramount duty is to the Court and not to the person retaining the expert.

As with the various rules and guidelines being implemented, a number of changes have been proposed to reduce the time and cost of expert witnesses appearing in contested matters before the court. These proposals are mainly directed towards the use of expert witnesses in civil litigation matters, and include the following:

- The practice of the Court should encourage single experts. This proposal recommends that opposing parties be encouraged to use single experts who receive instructions from both parties in the form of letters and the instructions to be detailed in the expert's report.
- Court appointed experts to adjudicate conflicting expert reports and to assist the judiciary where necessary.

Numerous other recommendations have been proposed to minimize the difficulties raised by the perceived bias or partisanship of expert witnesses. The problems encountered in criminal matters, particularly those of notoriety, will need to be addressed in the future.

The Australian and New Zealand Forensic Science Society has attempted to reduce the problem of pseudo-experts by developing a formalized method of registering peer-recognized experts, the Registered Forensic Practitioner (RFP) scheme. In order to be registered, the practitioner is required to provide three referees and demonstrate that they are practicing forensic experts. The forensic community is slowly adopting this system of registration but, until such time as the legal community embraces such a process, the concept of registration remains moot and of little value.

Again, the forensic community should actively participate in the development of models and codes of conduct that the courts would consider of value in assessing the bona fide of the expert presenting evidence in court. There has been an increasing education process in ensuring that expert witnesses understand their legal responsibilities and duties to the court, nevertheless this process needs to be formalized as part of expert training. Where appropriate, this training should be conducted or monitored by the courts and by the judiciary to ensure that individuals who routinely provide expert evidence clearly understand those responsibilities and duties. Such a course could form part of a requirement to be registered with the courts as an expert.

4. CONCLUSION

This paper has focused predominantly on the more traditional forensic identification sciences; however, the discussions and issues can be equally applied to the developing sciences, where the complexities and relevance of the sciences will be determined by the courts of law. The factors being determined by the judiciary, legal fraternity and members of the public, whether in an adversarial or inquisitorial legal system, will be judged on the merits of the science and the expert alike. These two factors, the science and the expert witness, cannot be easily distinguished as they are intrinsically entwined from the legal perspective. It is, therefore, the responsibility of forensic science practitioners and the forensic community to ensure that the mechanisms, such as the scientific quality standards, meet the challenges of both scientific and legal scrutiny. Equally, for those who provide expert testimony, it is their responsibility to ensure that they fully comprehend their responsibility to the courts.

Forensic practitioners should embrace the challenges and scrutiny from the scientific and legal communities and consider these as mechanisms for continued improvement.

As Heisenberg stated, “An expert is someone who knows some of the worst mistakes that can be made in his subject and who manages to avoid them.” It should not require others to determine where the errors or inadequacies exist in the “subject”. Where inadequacies have been identified, they should give impetus for correction and advancement.

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ROLE OF PROPER RESPONSE SCHEMES, LEGISLATION AND REGIONAL CO-OPERATION IN COMBATING ILLICIT TRAFFICKING OF NUCLEAR MATERIALS IN DEVELOPING COUNTRIES

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Abstract

Bulgaria's geographical location — between Europe, the former Soviet Union, and the Middle East — exposes it to much illegal trafficking: of people, arms, drugs, etc. The trafficking of nuclear and radioactive materials in Bulgaria can be divided in two main parts — internal and transit. Internal trafficking consists of stolen radioactive sources such as counters and densitometers, irradiation devices, tools for removing static electricity, and smoke detectors, which mainly contain the isotopes ^{137}Cs, ^{60}Co, ^{192}Ir, ^{226}Ra and ^{241}Am. The external trafficking of illicit nuclear materials is connected with transfer of raw materials and expensive metals from the former Soviet Union to countries in Western Europe and the Middle East, including aluminium, osmium, caesium, scandium, rare earth elements, red mercury, plutonium and enriched uranium. Detecting internal and external trafficking poses serious problems for the Bulgarian authorities, in terms of equipment and qualified personnel at the borders and inside the country. Developing countries need protocols for detecting and responding to illicit trafficking of nuclear materials, which is a new threat that requires rapid implementation of comprehensive measures and efforts, novel approaches, co-ordination of services and institutions, and even new legislation. The paper describes a three step model for better and more rapid responses for combating illicit nuclear trafficking in Bulgaria. The steps involve developing first response protocols, using non-destructive analytical means to categorize materials on-site, followed by in-depth analysis. It is also important to initiate contacts with neighbouring countries to foster regional collaboration among lawenforcement agencies, customs authorities, analytical laboratories, etc., to improve efficiency in combating illicit trafficking of nuclear materials.

1. INTRODUCTION

Its geographical location — at the "crossroads" between Europe, the former Soviet Union, and the Middle East — exposes Bulgaria to much illegal trafficking: of people, arms, drugs, etc. In recent years, a new criminal phenomenon has surfaced: transport of stolen radioactive sources. In most of these cases, criminal possession of radioactive substances is by people of low culture and education, attempting to make money on something that is hard to sell.

Illicit trafficking of nuclear and radioactive materials is a serious violation of non-proliferation laws, as well as a risk to public and environmental health. Stolen fissile materials may be used in the construction of nuclear weapons, may be applied to conventional explosives, or may pose a threat to residential areas, water supplies, etc.

Therefore, the European Commission is fostering international co-operation to combat illicit trafficking in nuclear materials by formalizing mutually supportive efforts of law-enforcement agencies, and customs and other authorities in countries that are at particular risk.

Trafficking of nuclear and radioactive materials in Bulgaria has two main components: internal and transit.

2. INTERNAL TRAFFICKING

Internal trafficking consists of stolen radioactive sources, mainly from the former Soviet Union, and equipment from companies or plants that were privatized or stopped functioning due to the economic changes in that country. There have been attempts to divert materials from the uranium-mining industry, including stored quantities of “yellow cake”.

There have also been cases involving radioactive sources and isotopes that were used in industry, again imported mainly with Soviet equipment. These items of equipment consisted of:

- Counters,
- Densitometers,
- Devices for removing static electricity,
- Weighing instruments,
- Parts of irradiation devices,
- Smoke detectors, etc.

There have been a few cases of theft of materials and devices containing natural or depleted uranium containers or shielding, applied to gamma defectoscopy.

Internal trafficking has included cases involving highly radioactive devices containing ^{137}Cs, ^{60}Co, ^{192}Ir, ^{226}Ra, ^{241}Am, etc.

Although the handling and transport of these substances needs special equipment and licensing prescribed by Bulgarian legislation, trafficking often involves incompetent individuals who endanger their own health and subject others to harmful radiation.

3. EXTERNAL TRAFFICKING

External trafficking of illicit nuclear materials is connected with the movement of raw materials and expensive metals from the former Soviet Union to Western Europe and the Middle East. This trafficking involves aluminium, osmium, caesium, scandium, rare earth elements, red mercury, plutonium and enriched uranium.

Trafficking of the last three items is of greatest concern, and should be ascribed the highest priority.

3.1. Responses to illicit trafficking of nuclear materials

Detection of internal and external trafficking generates serious problems for the Bulgarian authorities in terms of lack of equipment and qualified personnel at the borders and inside the country. The creation and institution of protocols for developing countries is important for initiating procedures for combating and eventually preventing illicit trafficking of nuclear materials. Particular efforts need to be directed against trafficking of fissile materials produced in the former Soviet Union. Reported thefts of nuclear materials raise the possibility of nuclear terrorism.

There is a need to reinforce strategies for controlling existing stockpiles of fissile material and to lower future production and use of such materials.

Illicit trafficking of nuclear materials is a new threat that requires rapid implementation of comprehensive, broadly acceptable measures and efforts, novel approaches, co-ordination of services and institutions, and even new legislation.

The Institute for Nuclear Research and Nuclear Energy (INRNE) is the largest of its kind in Bulgaria in the field of nuclear science. Its main activities are in research, nuclear energy, radiation safety and radio active waste management. It has equipment and qualified personnel for analysis of nuclear materials, and for performing alpha, beta and gamma ray spectroscopy of solid and liquid samples from the nuclear industry and from the environment. Radiochemical procedures, for analysis of radionuclides and trace metals, are performed in a dedicated laboratory with hot cells and glove-boxes for handling highly radioactive gamma sources, except plutonium.

The equipment available at INRNE includes:

- — alpha spectroscopy chambers,
- — low level gamma spectrometers,
- — X ray fluorimeters,
- — electron microscopes.

Scientists at INRNE collaborate with the Bulgarian law-enforcement and customs authorities by analysing interdicted non-fissile nuclear materials.

In 1998, a PHARE project, titled "Assistance to the Institute for Nuclear Research and Nuclear Energy of the Bulgarian Academy of Sciences in upgrading non-destructive analysis capacities for nuclear materials of unknown origin **(**FONSAFE**)**", was initiated and co-ordinated by the Institute for Transuranium Elements (ITU), Karlsruhe, Germany.

The project objectives were:

- — To improve capacity for analyses of nuclear samples of unknown origin in Bulgaria, in particular for on-site U/Pu categorization;
- — To exchange technical experience related to the treatment and analysis of illicit materials;
- — To extend the analytical database at ITU, including information on nuclear material seized in Bulgaria;
- — To co-operate in analysing interdicted radioactive samples, interfacing complementary analytical procedures at ITU as needed.

Also, a Specialized Laboratory for Analysis of Illicit Nuclear Materials was created to meet urgent needs for rapid responses to new cases in Bulgaria.

Under the PHARE project, sophisticated portable equipment was supplied to the Specialized Laboratory:

- — A DART™ portable gamma spectrometer with a 1000 mm^2 HPGe planar detector,
- — A MiniMCA portable gamma spectrometer with a 500 mm^3 CdZnTe detector.

4. ACTION SCHEME FOR ILLICIT RADIOACTIVE OR NUCLEAR MATERIAL

It was felt that a new action scheme was needed to improve response times of the Bulgarian authorities with regard to illicit nuclear trafficking.

4.1. First step

- — Health physics analysis (gamma and neutron doses),
- — Preservation of evidence (using protocols adopted by law enforcement).

4.2. Second step

- — Non-destructive analyses (NDAs) for on-site categorization of radioactive material:
    - Radioactive, non-fissile material;
    - Nuclear fuel (^{235}U content <20%);
    - Plutonium and/or enriched uranium (^{235}U content >20%);
- — Ge(Li) highresolution gamma spectroscopy;
- — Passive neutron interrogation for plutonium.

4.3. Third step

- — In-depth analysis at the Specialized Laboratory:
    - Analysis of the matrix and of packaging material;
    - Element composition of the nuclear material;
    - Impurities, traces, etc.

5. SETTING UP A LEGAL AND ADMINISTRATIVE FRAMEWORK

The creation and enforcement of a model scheme is important for initiating the process of combating and preventing illicit trafficking of nuclear materials in developing countries.

Such a model will also foster improvements and rapid upgrading of capabilities, as needs demand. It is also important to initiate contacts with neighbouring countries for regional collaboration of law enforcement agencies, customs authorities, analytical laboratories, etc., to improve efficiency in combating illicit trafficking of nuclear materials.

5.1. First and second steps

Co-ordination of services involved:

- — What law enforcement agency is in charge?
- — Who calls the nuclear experts: health physics expert, NDA expert, other authority?

- Expert team for NDAs.
- Packing the seized material for transport: who arranges and authorizes transport to intermediate storage or directly to a specialized laboratory?
- Reports for prosecution purposes: in what time-frame should evidence be provided to the courts?

5.2. Third step

- Is it necessary to involve a specialized laboratory for further analysis?
- Is authorization and packing of the material needed for shipment of the seized material to another country?
- Are arrangements for joint analyses necessary (in another laboratory inside the country or in conjunction with a specialized laboratory outside the country)?
- What kinds of expert reports will be required?

5.3. Actions on-site:

- Examination for occupational and publich health hazards:
  - Gamma/neutron radiation dose,
  - Alpha–beta surface contamination.
- Law enforcement action:
  - First check for booby traps,
  - Preserve evidence, ensure chain of custody.
- On-site categorization of seized material using mobile NDA instrumentation:
  - Natural sources (e.g., fertilizers, plants),
  - Scrap material,
  - Contaminated material from nuclear activities,
  - Waste (e.g. spent fuel, resins),
  - Radioactive sources,
  - Nuclear material:
    - fuel,
    - weapons utilizable,
    - weapons grade.
- Store material safely until transportation,
- Preparation for and transport to a specialized laboratory (for eventual re-packing),
- Transport the material to the investigating laboratory,
- In case the specialized laboratory cannot perform certain analyses, a sample of the material could be shipped to an external specialized laboratory,

- Compare results with an appropriate database; appraise need for further investigations.
- Issue an analytical "expert-opinion" report on the analysed material for provision to law-enforcement authorities.

In general, the prevention of illicit trafficking is complex. It is recognized that threats posed by organized crime are a challenge to the global community and should be addressed appropriately through all available means.

It should be pointed out that there is urgent need for international and regional co-operation in combating illicit trafficking of radioactive and, especially, nuclear materials. Nuclear non-proliferation rests on three pillars: safeguards, physical protection and export control. The same should be applied in combating illicit trafficking. It is clear that more reliable results can be obtained through regional co-operation of all responsible institutions: law enforcement agencies, customs authorities, etc. The training of personnel should encompass regional considerations and action plans to fight organized crime groups that already function internationally.

The enactment of joint projects, exercises and other measures should also be a high priority in the European Community, especially in newly associated States that are building their economies and are subjected to many kinds of illegal trafficking.

ROLE OF THE NATIONAL NUCLEAR CENTRE OF THE REPUBLIC OF KAZAKHSTAN IN COMBATING NUCLEAR TERRORISM

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Abstract

After the collapse of the Soviet Union, most of the nuclear sites in Kazakhstan territory — strategic defence bases, weapons test sites, and research institutions developing nuclear technologies for defence and space purposes — were liquidated or reoriented to peaceful endeavours. The Soviet system of control over handling of nuclear and radioactive materials was dismantled, and new measures are of limited efficacy. National defence potential and lawenforcement efficiency have been eroded. Laws addressing nuclear terrorism also require upgrading. There have been cases of illicit trafficking of nuclear and radioactive materials. This situation is open to exploitation by radical terrorist groups. Due to its geographical location, the Republic of Kazakhstan is a transit route for nuclear and radioactive materials from other former-Soviet countries, therefore, an efficient system to combat nuclear terrorism is of the utmost priority. Major nuclear research institutions and substations were consolidated into the Republican State Enterprise National Nuclear Centre of the Republic of Kazakhstan. Many of the Centre's activities are focused on preventing nuclear terrorism, including: projects to dismantle the infrastructure of former nuclear sites; withdrawal of nuclear materials from circulation by placement in long term storage; and seismological monitoring of nuclear weapons test site activity. Close co-operation between scientists at the Centre with regulatory authorities such as the Kazakhstan Atomic Energy Committee, the Sanitary-Epidemiological Service and law enforcement agencies should foster the creation both of an efficient system for detection of nuclear materials and for combating and preventing nuclear terrorism in Kazakhstan.

1. INTRODUCTION

The Republic of Kazakhstan inherited a complex nuclear legacy from the Soviet Union. Enterprises in Kazakhstan were actively engaged in a closed nuclear fuel cycle as part of the Soviet Union. In addition, Kazakhstan territory housed strategic nuclear military bases, nuclear weapons test sites, and research institutions engaged in development of nuclear technologies, including those for defence and space purposes. After gaining independence, the Republic of

Kazakhstan made efforts to eradicate many components of this system: military bases were closed; nuclear weapons were removed; nuclear test sites were closed; many fuel cycle enterprises lost orders for their products and had to reduce output or close down; scientific and other research institutions were reoriented to peaceful uses for nuclear and radiation technologies. Not only were these activities appreciated by the international community at a political level, promoting the integration of the newly independent State into the global economy, but they also were necessary prerequisites for qualitative improvements in Kazakhstan's ecology.

2. THE EXISTING SITUATION IN KAZAKHSTAN

There have also been negative consequences of the collapse of the old political system, including significant loss of control over nuclear and radioactive materials within Kazakhstan. The former Soviet system of control over location, transfer and use of these materials was compromised, and a new system is still evolving. Laws governing the procedures for handling nuclear and radioactive materials that were inherited from the Soviet period subsequently had little effect. No international agreements were in effect on export, import and pass-through of these materials. Reductions in volume of work and forced closure of some factories led to a situation in which materials — including those categorized as nuclear — were no longer under the control of appropriate authorities and became available to persons and organizations with little or no experience in proper methods of storage and transportation. Theft of nuclear and radioactive materials and their uncontrolled transfer became a significant danger. Sale of nuclear and radioactive materials — fuel elements, ampoule neutron sources, etc. — is occurring in Kazakhstan. Repeated attempts are on record to illicitly remove radioactive and nuclear materials and radioactive wastes from Kazakhstan.

Since the beginning of the millennium, numerous radical terrorist groups have increased their activities. The situation in Kazakhstan is open to exploitation by such organizations bent on acquiring nuclear and radioactive materials for terrorist purposes. It is likely that some groups acquire these materials to sell to third parties, including foreign terrorist organizations, rather than for criminal activity within Kazakhstan. Due to structural reorganization of lawenforcement agencies and erosion of their power and capabilities, the general threat of terrorist acts for companies using nuclear and radiation technologies has increased. In addition, due to its geographical location, the Republic of Kazakhstan is a transit route between Europe and Asia. Hence, numerous cases of transit shipments and attempts to sell nuclear materials from other countries, including former Soviet republics, have been recorded (e.g., fuel elements from the Chernobyl nuclear power plant). These factors reveal an unprecedented necessity to institute measures for combating nuclear terrorism in the Republic of Kazakhstan. The current system of control of nuclear and radioactive materials does not meet these pressing requirements; efficiency and general capabilities urgently need to be upgraded to avoid considerable economic losses and potential political difficulties in international relations.

3. NATIONAL NUCLEAR CENTRE AND ITS ACTIVITIES IN THE FIELD OF THE NUCLEAR TERRORISM COUNTERACTION

Major nuclear research institutions and substations within independent Kazakhstan have been consolidated into a single organization: the National Nuclear Centre of the Republic of Kazakhstan. Four institutions now function under the aegis of the Centre: the Institute of Atomic Energy, the Institute of Geophysical Research, the Institute of Radiation Safety and Ecology (all in Kurchatov), and the Institute of Nuclear Physics (in Alatau, near Almaty). The branch institutions operate three research reactors and one “moth-balled” reactor, a charged particle accelerator, a subcritical test-bench, test benches modelling nuclear reactor core melting processes, and IRAS, NM, and RW storage facilities. Research laboratories are in operation at the institutes, well equipped for work in nuclear and radiation physics, radiochemistry, etc.

At this time, many of the Centre’s activities are focused on combating and preventing nuclear terrorism, of which the most important are national and international programmes, as follows:

- Projects to eliminate infrastructure necessary for the creation of weapons of mass destruction, in particular, closure and permanent sealing of tunnels for nuclear weapons testing.
- A project on irreversible shutdown and decommissioning, with subsequent long-term preservation, of a BN-350 fast power reactor in Aktau, Kazakhstan, designed for electrical power generation, water desalination and ^{239}Pu breeding.
- A project on transportation of high plutonium content BN-350 spent fuel to the Baikal-1 test bench, which is one of the Institute of Atomic Energy facilities for testing individual elements and prototypes of nuclear rocket engines. Nuclear material will be moved from the Caspian region, which borders on geologically unstable zones, to the northern-east region of Kazakhstan, the former weapons test site territory of Semipalatinsk.

— Design and construction of a BN-350 spent fuel storage facility at the Baikal-1 testbench. This work is at the behest of the Kazakhstan Government.

— Design and construction of a storage facility for ampoule neutron sources. This will allow withdrawal from circulation of a large quantity of potentially dangerous nuclear material, plutonium-beryllium sources, fabricated from ^{239}Pu. Currently, sources with more than 3 kg of total ^{239}Pu content are temporarily stored at the Centre. According to available data, approximately 100 000 different ionizing radiation sources pass through Kazakhstan. The precise number of neutron sources is undefined, due to lack of reliable data. However, the amount of plutonium in these sources is estimated at dozens of kilograms. There have been numerous cases of interdiction of plutonium-beryllium. Unfortunately, this work is performed under a national programme only; insufficient funding precludes an international component.

— Radiological survey to identify sites and areas of radionuclide contamination.

— Seismological studies within Kazakhstan. Seismological arrays generated at the Institute of Geophysical Research are incorporated into the international seismic network, not only recording seismological phenomena but also monitoring nuclear weapons test site activity, particularly those located in Asia.

— Recently, cases of unlawful transport of nuclear materials through and from Kazakhstan have become more frequent. Scientists at the Centre play an active role in the investigation of such episodes. Branches of the Centre identify interdicted materials and secure them in long term storage after conclusion of legal proceedings.

Thus, the National Nuclear Centre is the key and principal operating element in new efforts to control and regulate the use and transfer of nuclear and radioactive materials within the Republic of Kazakhstan, employing various non-destructive, established, as well as newly developed, inspection methods. It is expected that close co-operation of the Centre with regulatory authorities such as the Kazakhstan Atomic Energy Committee, Sanitary-Epidemiological Service and law enforcement agencies will lead to the creation both of an efficient system for detection of nuclear materials and of methods for combating and preventing nuclear terrorism within Kazakhstan.

QUALITY ASSURANCE AND REFERENCE MATERIAL REQUIREMENTS AND CONSIDERATIONS FOR ENVIRONMENTAL SAMPLE ANALYSIS IN NUCLEAR FORENSICS*

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Abstract

High-sensitivity nuclear environmental sampling and analysis techniques have been proven in their ability to verify declared nuclear activities, as well as to assist in the detection of undeclared nuclear activities and facilities. Following the Gulf War, the capability and revealing power of environmental sampling and analysis techniques to support international safeguards was demonstrated and subsequently adopted by the International Atomic Energy Agency as routine measures in safeguards inspections and verifications. In addition to having been proven useful in international safeguards, environmental sampling and analysis techniques have demonstrated their utility in identifying the origins of 'orphaned' nuclear material, as well as the origin of intercepted smuggled nuclear material. Today, environmental sampling and analysis techniques are being applied in six broad areas to support non-proliferation, disarmament treaty verification, national and international nuclear security, and environmental stewardship of weapons production activities. Consequently, an increasing number of laboratories around the world are establishing or expanding capabilities to meet these growing applications, and, as such, requirements for quality assurance and control are increasing.

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The six areas are: nuclear safeguards; nuclear forensics/illicit trafficking; ongoing monitoring and verification; Comprehensive Test Ban Treaty; weapons dismantlement/materials disposition; and research and development/environmental stewardship/safety. Application of environmental sampling and analysis techniques and resources to illicit nuclear material trafficking, while embodying the same basic techniques and resources, has unique requirements for sample management, handling, protocols, chain-of-custody, archiving and data interpretation. These requirements are derived from needs of how data from nuclear forensics analyses are to be used in legal proceedings, and also in investigative research. From the legal perspective, one must assume that any results obtained would be used as evidence in a court of law for prosecution of criminal acts. Consequently, quality-assurance requirements are very demanding and unforgiving. For example, forensics analysis results that cannot be independently verified against certified reference materials of known composition and isotopics may not be accepted in a court of law as reliable evidence. Thus, the ability to provide certified and traceable reference materials used in the analyses is extremely important in nuclear forensics. In addition to nuclear signatures, other signatures such as any organics or plant and animal residue that are also on the intercepted materials become important in identifying origin, and will require traceable, known standards. In this paper we describe the quality-assurance requirements and considerations that must be adopted and developed for application and use in nuclear forensics. Recommendations and minimum requirements for standardization of a nuclear forensics quality-assurance programme that could be internationally accepted will also be presented.

1. INTRODUCTION

Modern analytical approaches, using both destructive and non-destructive methodologies, provide forensics investigators with a vast array of tools for detecting undeclared nuclear activities, and for verifying the identity of smuggled or discovered nuclear material. Governments and international organizations rely on these analytical tools to find, characterize and attribute radioactive materials and weapons of mass destruction, and to thwart clandestine and terrorist activities. In this paper, we focus on defining the infrastructure needed to generate technically sound and legally defensible measurement data that may be critical to a forensics investigation. We believe that many needs exist to expand and improve the forensics infrastructure, particularly in the following areas:

- Nuclear safeguards,
- Nuclear forensics/illicit trafficking,
- Ongoing monitoring and verification,
- Comprehensive Test Ban Treaty,

— Weapons dismantlement/materials disposition,
— Research and development/environmental stewardship/safety.

Many analytical tools for detecting nuclear material find uses in all of these areas, although sensitivity and accuracy requirements may be quite different depending, to a large extent, on whether the tools are being used on-site, in the field, or in the laboratory. It should be recognized that an inaccurate analysis could trigger a series of costly and unwarranted administrative actions, or, worse, they could underestimate a potential danger. Similarly, if inadequate care is given to quality assurance and chain-of-custody of a sample from the time of its acquisition through analysis, its utility in any legal proceedings could be compromised.

For all of these areas of interest, one must assume that the information gained will eventually be used in legal proceedings, which places unique quality-assurance requirements on the application of these analytical tools. The results must ultimately be traceable to certified reference materials. To achieve this traceability, each step in the analytical chain must be performed using protocols that guarantee sample integrity, high quality of analysis and adequacy of uncertainty statements.

In this paper, we do not address the problem of sample acquisition, which can be the result of a lengthy intelligence effort, a planned monitoring of specific activities, or a single lucky break or intercept. Regardless of origin, many steps must be correctly performed and documented before the information contained in the sample can be converted into a useful picture of the activities that produced the sample. It is these steps that this discussion seeks to identify and describe.

2. ORGANIZATIONAL CONSIDERATIONS

To adequately develop a forensics analysis system capable of converting information contained in a raw sample into a useful report for interested parties, the organizational infrastructure must provide significant oversight and control. These organizational entities must be in place before any attempts to process the raw sample are taken. At a minimum, the following organizational entities must be operational:

— Sampling organization;
— Quality assurance oversight authority for on-site measurements and network laboratories;
— Information management authority;
— Reference materials support system.

While this infrastructure may eventually be organized on an international level, it seems more likely that the organization will be first driven by national interests and answer to a national authority. A detailed discussion of each of these organizational entities is beyond the scope of this paper. However, a brief review of the responsibilities of each will serve to show the magnitude of the task ahead.

2.1. Sampling organization

The sampling organization would have the following responsibilities:

- Creation of a project plan that establishes methods and a rationale for defining the sample to be measured and the preferred measurement technique (i.e. performing a non-destructive assay on the total item in the field versus acquiring a subsample and sending it to a laboratory for analysis). The plan should identify the sampling approach, the statistical basis for sampling, and should define those agencies responsible for collection and the chain-of-command.
- Establish protocols for in-field analysis that defines the criteria used to decide whether an analysis is sufficient or if more analyses are warranted that may require more subsampling, shipment and off-site analysis.
- Preparation and distribution of a verifiably, uncontaminated sample collection and containment materials for sampling.
- Collection and packaging of subsamples and associated blank materials as required.
- Documentation of appropriate sampling protocols.
- Preparation of chain-of-custody documents.
- Documentation of all known circumstances associated with sample acquisition.
- Transport of collected samples to the sample management authority.

2.2. Quality assurance oversight authority for on-site measurements and network laboratories

- A QA oversight authority that administers a programme to verify measurement capability for all samples analysed, as part of a forensics analysis system, would have the following responsibilities:
- Draw up a protocol to establish quality assurance/quality control procedures for verifying that on-site equipment and techniques meet required standards.

- Serve as the data-gathering authority to maintain records for on-site protocol compliance and QA/QC measurement data.
- Establish a QA/QC programme for off-site analyses and maintain a network of laboratories qualified to perform the specified analyses.
- Act as an independent administrator of a QA/QC programme to ensure that network laboratories can perform sample analyses with the accuracies required. This can be accomplished by creating an inter-laboratory sample exchange measurement programme and by the use of technical audits.
- Ensure that measurement techniques with associated measuring equipment are qualified, i.e., in a state of compliance with requirements for their intended use. This confirmation requires a set of calibrations or measurements to verify the measurement process.
- Identify and qualify additional on-site equipment and network laboratories as new analytical requirements are developed.
- Operate a facility for splitting, repackaging, distributing and tracking samples.
- Establish liaisons with other entities that have similar analytical needs for other programmatic missions.
- Establish measurement traceability to the International System of Units (SI) by means of an unbroken chain of calibrations or comparisons linking them to relevant primary reference materials or standards. This is accomplished by linking measurements to national measurement reference materials [i.e., New Brunswick Laboratory (NBL) certified reference materials (CRMs), National Institute of Standards and Testing (NIST) standard reference materials (SRMs), etc.] and working reference materials produced for forensics needs.
- Develop and document analytical procedures and methods for data reduction, transfer and storage.
- Implement a documented training programme that ensures that personnel remain capable of meeting their analytical missions.
- Ensure that analytical facilities are maintained with appropriate cleanliness and calibration standards.
- Demonstrate the adequacy of analytical performance by participating in ongoing performance-assessment programmes with other national or international organizations.
- Establish a defendable basis for the uncertainty statements that accompany reported analytical results (reference Guide to the Expression of Uncertainty in Measurement for combining uncertainty components and presenting results). Ensure that each laboratory provides an estimate of uncertainty for each reported value.

2.3. Information management authority

The information management authority will have the following responsibilities:

- Establish a series of origin specific databases that, at a minimum, include:
  - Isotopic content of nuclear materials of known origin.
  - Elemental content of nuclear materials of known origin.
  - Biomass database of pollens, seeds, grasses, etc., from areas of specific interest.
  - Soil composition database for areas of specific interest.
- Review and interpretation of analytical results reported by the sample management authority.
- Request additional analytical data where they may help identify the activity that produced the sample or the origin of the sample.
- Prepare and classify final interpretation reports.
- Distribute reports to the appropriate national entities.

2.4. Reference material support system

The use of certified reference materials provides critical statistical control and traceability on measurements for nuclear materials accountability, forensics analysis and a host of other issues. National metrology laboratories can provide forensic nuclear standards certified to national/international standards reference bases as an important step in expanding forensics monitoring and analysis capabilities.

At a minimum, the reference-materials support system should include the capabilities of, for example, the NBL for nuclear based reference materials and the NIST for radioactive, biomass and soil reference materials. It is important to understand that, while working standards prepared by the network laboratories are quite useful for developing analytical methods, the values assigned to these working standards must be traceable to reference materials that have been certified by an appropriate metrology laboratory if they are to be acceptable in a court of law. In the USA, the appropriate metrology laboratories are NIST and NBL. Reference materials that have been jointly certified by the appropriate metrology laboratories of several countries will be given even greater credibility in disputes between sovereign nations.

Reference materials may be utilized for calibration of measurement instrumentation, development of defendable uncertainty statements, intercomparison of analyses performed by different laboratories and third party evaluations of laboratory performance. Quality assurance reference materials should be used in a measurement evaluation (QA/QC) programme as blind standards the certified or traceable values of which are unknown to the user. Measurements of these materials are used primarily to provide independent and objective measurement status, and to test and assess the qualification of a laboratory. They are used to test the accuracy and precision of analyses and procedures, test for elemental sensitivity, test effects of matrix composition, and test the total procedural blank generated during the course of sample-processing and analysis.

In the field of nuclear forensics, reference materials are required to support isotopic and elemental concentrate measurements of several nuclear elements. These elements include, but are not limited to, uranium, plutonium, americium, neptunium, cobalt, strontium, technetium, caesium, iodine, xenon and krypton. In addition to pure compounds of these elements, it will also be desirable to have reference materials of specific physical characteristics, such as sealed sources of small particle size, specialized matrix characteristics or morphological characteristics.

3. SPECIAL CONSIDERATIONS

Because nuclear forensics has the goal of both identifying the type of undeclared activities and determining the geographic origin of captured materials, other artefacts, such as pollen, seed, and dust composition, will be of interest in some cases. This places an additional burden upon sample management.

The area of nuclear forensics/illicit trafficking presents additional unique problems for a system for managing these studies. For nuclear safeguards, ongoing monitoring and verification, comprehensive test ban activities, weapons-dismantlement activities and environmental stewardship, there are usually well defined protocols for sampling in support of such activities.

For nuclear forensics/illicit trafficking, the acquisition of samples is likely to involve intelligence operations, political defections, mistakes by poorly trained couriers, customs interceptions, and deliberate attacks against specific targets of interest. These incidents may occur at any time or place. The discovery of the incident may be made by personnel who are ill equipped to properly control and document sample acquisition. For this reason, it will be necessary to establish protocols and training for law-enforcement agencies that may be first involved in the sample acquisition, organizations preparing analytical requests, the information management organization interpreting results, and the reference material support organizations to provide a very broad spectrum of reference materials.

4. SUMMARY

Modern analytical approaches provide investigators with a vast array of tools to detect undeclared nuclear activities. To properly take advantage of these capabilities, it will be necessary to organize these resources in a manner that ensures the application of well documented quality assurance protocols at every step of the analytical chain. This will include sample acquisition, choice of useful artefacts to be measured, analysis on-site or in well equipped laboratories, and competent interpretation of the analytical results. The use of CRMs to support the qualification of the chosen methods will be a critical part of this system. A very broad spectrum of analytical capabilities and reference-material support will be required for successful completion of this mission. Six areas where application of these resources can be effective have been identified. Each of these areas will require a similar operational structure. The same analytical resources can support the missions of each of these areas of application. In every case, the same quality assurance resources will be needed. It seems reasonable to set up only one quality assurance system to serve all of the six missions. The operating entity for this system will require the authority to restrict the handling of acquired samples to properly trained and equipped personnel. Communicating this requirement to all of the agencies that may acquire samples may be the most difficult task of all.

IAEA CO-ORDINATED RESEARCH PROJECT ON IMPROVEMENT OF TECHNICAL MEASURES TO DETECT AND RESPOND TO ILLICIT TRAFFICKING OF NUCLEAR AND OTHER RADIOACTIVE MATERIALS*

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Combating illicit trafficking of nuclear and other radioactive materials includes screening vehicles, cargo and individuals at borders to: (1) search for smuggled materials; (2) locate, measure and characterize sources of radiation; and (3) fully characterize confiscated material. Currently available instruments used for field measurements are not optimized for this purpose, and may fail to detect shielded plutonium or highly enriched uranium. Confiscated radioactive materials need to be characterized with macro- and micro-analysis techniques to fully understand the significance of the material and to provide credible evidence in the event of prosecution of traffickers. Although most Member States have national laboratories capable of determining the basic characteristics of such material, only a few have the sophisticated analytical capability necessary to perform proper forensics analysis. A Co-ordinated Research Project on 'Improvement of Technical Measures to Detect and Respond to Illicit Trafficking of Nuclear and other Radioactive Materials' was established to:

- Improve detection capability and performance of hand-held and portable isotope-measurement devices, including upgrading technical and functional specifications;
- Standardize procedures to examine suspicious packages and to assess the hazard of confiscated material;
- Develop recommendations and guidelines for establishing a system to provide nuclear forensics support to Member States for the characterization of seized material.

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* Only an abstract is given here as the full paper was not available.

Related to nuclear forensics support, it should be noted that, with the inception of its nuclear security programme in 1995, the IAEA has offered the services of its laboratories in Seibersdorf and associated laboratories to assist States in analysing confiscated nuclear materials. Since 1993, the IAEA has received reports of over 300 cases of smuggling of nuclear and other radioactive materials, in about thirty of which enriched uranium and/or plutonium of varied quality, form and quantity were seized. Although requests for assistance in characterizing such materials have been infrequent, it is anticipated that, in the current climate of concern over nuclear terrorism, the need will increase. Therefore, it is prudent to develop a coherent plan for providing this assistance in an effective and timely manner within the framework of the established Co-ordinated Research Project.

ROLE OF A NATIONAL REGULATORY AUTHORITY IN MONITORING RADIOACTIVITY AND AFTER SEIZURE OF RADIOACTIVE OR NUCLEAR MATERIAL

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Abstract

The system for monitoring radioactivity available in the Radiation Protection Centre of Lithuania is described. It is intended to be used also in cases of radiation accidents, and has already been used to identify seized radioactive and nuclear materials. Combined with a national register of sources of ionizing radiation, which is kept at the Radiation Protection Centre, and the possibility of using more complex analytical capabilities at other centres, the system represents an optimum solution for countries of similar size and resources to Lithuania.

1. INTRODUCTION

According to the International Basic Safety Standards [1], national radiation protection authorities shall ensure that appropriate arrangements are made for detecting any build-up of radioactive substances in the general environment. This and other responsibilities, imposed by different standards and recommendations, dictate that a system of monitoring radioactivity in different matrixes shall be available in each country. Under normal conditions, this system is used for assessment of dosages from different sources to members of the public, radiation workers and patients undergoing medical radiological procedures. However, the system can be used where accidents have occurred. Seizure of illegally stored or transported radioactive or nuclear material can be considered as a radiation accident, because it is an unintended event, the potential consequences of which are not negligible from the point of view of radiation protection, as defined in Ref. [1].

Since radioactivity measurements are costly, it is expedient to consider using the system of monitoring radioactivity for identification of basic characteristics of seized radioactive or nuclear material, particularly so in countries with rather limited resources and of small size, as is Lithuania.

2. LITHUANIAN NATIONAL REGULATORY AUTHORITY

According to the Lithuanian Radiation Protection Law, the Radiation Protection Centre co-ordinates the activities of public institutions and municipalities involved in radiation protection, and exercises State supervision and control of radiation protection, and monitoring human exposure [2]. The Radiation Protection Centre is the key regulatory authority in radiation protection in Lithuania.

Among other responsibilities, the Radiation Protection Centre investigates the effects of ionizing radiation on human health, makes proposals for optimizing radiation protection, creates and implements principles and criteria for radiation protection, oversees registration and security of sources of ionizing radiation, supervises and controls requirements of the Radiation Protection Law and related laws and licences, organizes and performs investigations of radiation accidents, predicts their consequences and gives proposals on their prevention and mitigation, organizes and performs monitoring of dosages to members of the public and radiation workers under normal conditions and in cases of radiation accidents, keeps the National Register of Sources of Ionizing Radiation and Occupational Exposure, organizes and performs dosimetric, radiometric and spectrometric investigations of exposure of members of the public and workers, in home, working and social environments, organizes and performs monitoring of radioactive contamination of air, foodstuffs, drinking water, construction materials and other items, which may cause exposure to humans, and it issues documents, certifying contamination with radioactive substances, with permission to or prohibition from use.

The activities of the Radiation Protection Centre may be divided into two main parts: regulatory and analytical. Each of these parts is autonomous, although results generated by the analytical service are used in regulatory activities and vice versa. This assists in making available resources operate more effectively.

3. MONITORING OF RADIOACTIVITY

Measurements of concentrations of gamma emitters, ^{90}Sr, ^{137}Cs, ^{14}C, and plutonium isotopes in foods, gamma emitters in construction materials, gross beta and alpha activities, tritium, radon, and radium in water, various radionuclides in biological samples, radon within buildings are performed. Dose-rate and surface-contamination measurements are also carried out. Personal dosimetric service is the measurement of personal dosages to radiation workers.

Some of these measurements are performed on a routine basis, e.g., concentrations of ^{137}Cs and ^{90}Sr in foodstuffs, gross alpha and beta activity in drinking water, natural radionuclides in construction materials, indoor radon concentrations, and personal dosimetry measurements. The objective of this monitoring is to evaluate trends in exposure of the Lithuanian population, to identify the most important sources of exposure, and to prepare recommendations for optimizing protection.

In order to ensure high quality data, standardized measurement procedures have been created and used, a quality-assurance system implemented, and inter comparison and proficiency tests performed. The laboratory is preparing for accreditation according to ISO 17025 standard, which will be a part of the Phare programme, "Creation of Radiation Protection Infrastructure and Supporting Services".

The results of permanent monitoring of radioactivity indicate that no large temporal or spatial deviations of artificial radioactivity exist in foodstuffs originating in Lithuania. Only natural radionuclides (with small exceptions for wood) have been detected in construction materials. Some areas with increased indoor radon concentrations have been identified and investigated in more detail [3]. Concentrations of radon in drinking water do not exceed the recommended limit of 100 Bq/L [4].

Measurements of radioactivity result in data on concentrations of radionuclides and on dosages. They assist the creation of an analytical system to be employed in cases of radiological accidents, including seizure of illegal radioactive or nuclear materials. Procedures for assessment of dosages in cases of radiological accidents have been elucidated and will be soon adopted; they include methods of sampling, sample preservation, radiation protection during sampling, in situ and laboratory measurements, and data presentation. Some of these procedures are expressed simply as possible for use by rescue personnel after appropriate training.

4. MEASURES TO BE TAKEN WHEN RADIOACTIVE OR NUCLEAR MATERIAL IS SEIZED

According to the approved procedures, in cases of seized radioactive or nuclear material, the Radiation Protection Centre will identify the necessary means of protection for members of the public and emergency workers, perform in situ measurements of dose rate and radioactive contamination, and, if necessary, evaluate dosages received from the interdicted material.

New possibilities for in situ identification of radionuclide content of seized material have been developed with technical help from the IAEA.

FieldSpec, with appropriate software, is now available at the Radiation Protection Centre. Initial trials of this equipment showed sufficient sensitivity and precision. For example, ^{99}Tc was detected in the body of a patient some time after a diagnostic procedure using nuclear medicine. Since there frequently is need for rapid in-situ identification of radionuclides, this be instrument will very useful. Lithuania is a small country (the maximum distance within Lithuania from the Radiation Protection Centre is 350 km), therefore a single instrument is sufficient for primary evaluation of situations and decisions on what radiation protection measures should be taken and what further steps are necessary for analysis of seized material.

Since the Radiation Protection Centre has departments in the largest cities of Lithuania, dosage rates and radioactive contamination measurements can be made quickly and advice on radiation protection measures given expeditiously. Practical experience shows that appropriate measures can be taken within 2 or 3 h.

The Radiation Protection Centre has its own means of laboratory identification of radionuclides in seized materials: HPGe spectrometers (Oxford and Canberra), equipment for radiochemical separation of uranium, plutonium and actinides, an alpha spectrometer, a liquid scintillation spectrometer and a neutron REM counter are available.

There have been cases when seized material had to be analysed. Contaminated scrap metal, orphan sources and uranium pellets have been found in various places of Lithuania, and it was necessary to define their activity and isotopic content. Another type of case is connected with hospital patients who enter Lithuania after nuclear medicine procedures.

The following scheme is used when radioactive or nuclear material is seized: measurements of dose rate and radioactive contamination are made in the vicinity of the seized material, evaluation of what radiation protection measures need to be taken, transportation of the material to the laboratory, its analysis starting with more detailed measurements of dose rate and radioactive contamination.

When an increased radiation level is detected in a person's body and there is no reason to assume that the source is outside the body, the conclusion is made that the person was exposed to nuclear medical procedures. The individual is interviewed, and appropriate radiation protection advice given. According to Lithuanian radiation protection legislation and written recommendations, if necessary a certificate shall be given to such a patient by the physician [5]. It facilitates border crossing, and precludes detailed investigations of the nature of increased radiation level.

Laboratory analyses are combined with data at the National Register of Sources of Ionizing Radiation and Occupational Exposure. Part of this register concerns sources of ionizing radiation. Characteristics of sources, such as the type of radionuclide, its activity, means of identification, and place of installation or storage are included in the register. If the seized source bears any markings, steps to identify its owner are taken. Furthermore, the register and regular inspections are preventive measures against loss of sources.

There is co-operation with other Lithuanian institutions, such as the Ministry of Environment, Institute of Physics, in the identification of seized materials.

5. CONCLUSIONS

The described system is rather simple. It helps in the analysis of seized material within a short period of time. Its main disadvantage is the fact that more complex analysis is often needed for nuclear forensics.

However, the data on sources of ionizing radiation available in the Radiation Protection Centre and its analytical capabilities, combined with analytical capabilities at other laboratories in Lithuania, often provide answers to questions of what radiation protection measures are to be taken, what is the origin and possible route into Lithuania of the seized material, and what further steps should be taken for identification.

Despite the restricted possibilities in nuclear forensics, such a system may be close to optimum for Lithuania and other countries of limited resources and expertise. The system, which is used for monitoring radioactivity, allows determination of the most urgent means of obtaining radiation protection and the basic characteristics of seized material.

Close relations among research centres in other countries, with capabilities of performing the complex analyses, are very important. Lithuanian experts may take part as observers in the analysis of seized material in these research centres. However, the most urgent analyses should be done in Lithuania. For this reason, the following needs may be identified: training in analysis of radioactive and nuclear materials and evaluation of dosages due to them, assistance in creating a quality-assurance system for analytical laboratories, and expert advice on measurement procedures.

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RESULTS OF PROTECTIVE MEASURES AGAINST IONIZING RADIATION AT BORDER CROSSINGS IN THE FEDERAL REPUBLIC OF YUGOSLAVIA*

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Abstract

The Institute of Security has, in accordance with a directive from the Federal Government, designed and placed stationary monitors of gamma-radiation at border crossings at Kelebija, Horgos, Vatin, Gradina, Presevo, Djeneral Jankovic, Batrovci, and at the Djerdap-I shiplock. Some of the results of these protective measures are described in the paper. Radiological checks at border crossings are vital for every country, in view of current concerns over smuggling of strategic radioactive material, problems related to nuclear-waste disposal, etc. In the Federal Republic of Yugoslavia, several authorities are involved — including the Federal Secretariat for Labour, Health and Social Security, institutions responsible for protection against ionizing radiation, and institutes authorized in the field of operative dosimetric spot-checks — to ensure compliance with protocols for radiological controls at border crossings.

1. INTRODUCTION

The Institute of Security, in the Ministry of Internal Affairs of the Republic of Serbia (MIA R Serbia) has, in accordance with ruling no. 39/01 published in the Official Gazette of the Federal Republic of Yugoslavia (FRY), been appointed as responsible for the following operations in the field of protection against radiation: dosimetry and control of industrial environments; measurement of exposure of professional persons (personal dosimetric

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* Name changed to Serbia and Montenegro as of 4 February 2003.

** Present address: Institut Bezbednosti, Belgrade, Serbia and Montenegro.

control); examination of levels of external radiation; gamma-spectrometric examination of nucleotide content of samples from the environment; examination of strontium content in samples from the environment; examination of radon content in air; and appraisal of suspected criminal events and resultant action. The Institute has been authorized by the Federal Committee for Ionizing Radiation of FRY to be responsible for some of these endeavours since 1986.

Measurements of levels of radioactive contamination of samples are made in accordance with the needs of the MIA R Serbia, Federal MIA, and Federal Secretariat for Labour, Health and Social Security-Federal Sanitary, Veterinary and Phytosanitary Inspectorate and Economy. The responsibilities of the operative group for spot dosimetry determination include monitoring of levels of radioactive contamination of goods arriving at border crossings, commissioning and maintenance of stationary detection systems at border crossings, as well as training of personnel in methods of protection against ionizing radiation.

In this paper we describe several examples of discovery of smuggling of radioactive materials and attempts to import contaminated goods.

2. RADIATION PROTECTION PROCEDURES

2.1. Discovery of a radiation source at the Presevo border crossing

In May 1996, a radioactive source was discovered on a bus on the Skopje–Belgrade highway at the Presevo border crossing, by means of a stationary MZ-100 detector. The source was packed in a red metal box bearing Chinese script. Such boxes, commonly sold in markets, contain analgesic (“Tiger”) ointment. They have a diameter of about 2.5 cm with a depth of 0.8 cm. The source was grey and cylindrical in shape; its diameter was 4 mm, height 7.5 mm, and mass 0.84 g.

We took a smear, and performed gamma spectrometry in our laboratory, using an ADCAM MCA-350 (ORTEC®) that has a high resolution HPGe detector (1.85 keV for energies of 1.33 MeV and detection efficiency of 28%). Based on characteristic energy peaks of 1.17 MeV and 1.33 MeV in the spectrum, it was immediately clear that the radiation originated from ^{60}Co. Intensity of the dosage measured with the MZ-100 at the border checkpoint, during passage of the vehicle, was around 21 pCi/kg/s at a distance of approximately 4 m. Dosage as a function of distance was examined at the Institute of Security, with a PD-4 ionizing chamber at distances of 0.5 to 10 m; the functional dependence is shown in Fig. 1. The distances for which intensities of

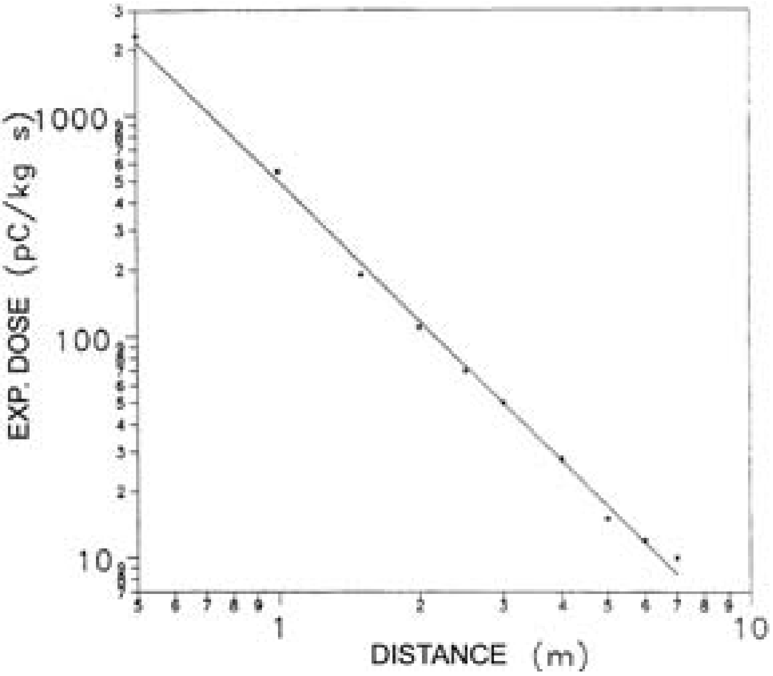

FIG. 1. Dependence of exposure rate on the distance.

exposure were measured were much larger than the dimensions of the radiation source, so it may be regarded as a point source. The calculated radioactivity of the source was 220 MBq, while mass radioactivity was 260 GBq/kg. Based on these data, it may be assumed that all persons within 10 m were exposed, with the dosage depending on length of time within the radiation field and distance from the source.

Based on the above estimates and topography of the radiation field, the person who packed the source in aluminium foil and paper and then placed it in the box, as well as the person who carried the box, received dosages that could cause headache, exhaustion, nausea, vomiting, anaemia and other symptoms of radiation sickness. These persons were surely not aware of the consequences of manipulating this material.

It is stated in the literature, as well as known in practice, that sources of such dimensions and activity are used in medicine for therapeutic purposes (e.g. the “cobalt bomb”), in the metal industry for examining defects in materials (known as defect-scopes), for standardization and calibration of dosimetric devices, as well as for irradiation of various types of materials in studies of physical and chemical changes caused by radiation, etc. It is assumed that the source in question was stolen from one of these devices.

Considering its high level of radioactivity, the source could have been used for criminal purposes, for infliction of radiation injury, etc.

The results of the measurements made at the Institute of Security were submitted to the MIA R Serbia, Federal MIA, and the Federal Ministry responsible for ionizing radiation, and to the Federal Customs Administration [1].

2.2. Radioactive reinforcing steel bars at Port Veliko Gradiste

Consistent with procedures for control of goods imported across the State borders, the federal sanitary inspector of the Belgrade border area, upon request from authorized representatives, ordered a check for radioactive contamination on a shipment of reinforcing steel bars from Ukraine, on the vessel *Kremencug*, at the Veliko Gradiste border crossing, on 12 April 2001 [2].

Upon request of the importer and on an order from the federal sanitary inspector, a representative of the Institute of Security, MIA R Serbia, as the authorized institution, examined the shipment on the *Kremencug* on 13 April 2001.

Spot measurements revealed that the absorbed dose on the surface of the goods was significantly above background radiation. Using gamma-radiation spectrometry, the presence of a gamma-emitter of artificial origin was identified, ^{60}Co, in contravention of Article 20 of the Book of Regulations regarding limits of radioactive contamination of the environment and methods for decontamination (Official Gazette of FRY, No. 9/99). Figure 2 shows a gamma radiation spectrum for the steel bars.

The report from the Institute of Security stated that the radioactivity of the interdicted shipment was 1680 ± 125 Bq/kg. It was stated also that, in materials obtained from iron ore and used within FRY, activities of ^{60}Co have not been discovered above the limit of system detection (<<1 Bq/kg), although more than a hundred gamma-spectrometry measurements of similar types of goods had been performed in the previous 5-year period [3].

According to Article 20 of the Book of Regulations on limits of radioactive contamination of the environment and methods of decontamination (Official Gazette of FRY, No. 9/99), the radioactivity of imported goods must not be above levels for similar goods produced internally. Therefore, importation of these bars was disallowed and the vessel was turned away.

Also, on several occasions, trucks with imported goods have activated stationary alarm monitors at the Horgos, Kelebija and Vatin border crossings.

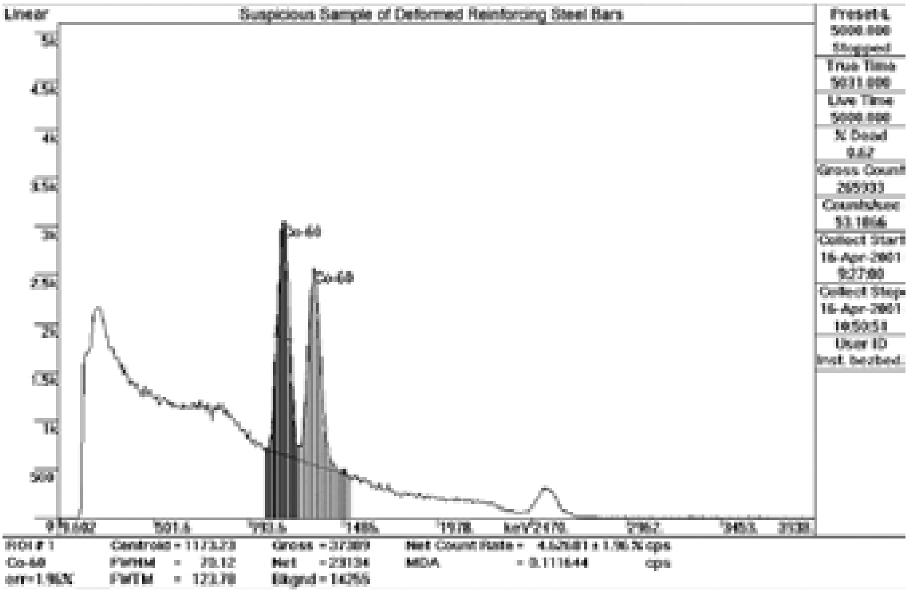

FIG. 2. Spectrum of gamma radiation from shipment of reinforcing steel bars.

Thorough laboratory checks verified increased levels of radiation from natural beta-gamma emitters (KCl, artificial fertilizers, ceramic materials, granite, etc.), importation of some of which is prohibited.

In 1991, after gamma-spectrometric and alpha-spectrometric measurements, importation of slag from a West European country was prevented because concentration of uranium was about 100-fold higher than the legal limit.

2.3. Review of protocols for radiological control and related problems

Measurement of radioactive contamination of imported goods is performed according to defined protocols for radiological control at FRY border crossings, based on the Book of Rules on limits of radioactive contamination of the environment and methods for decontamination (Article 20, Official Gazette of FRY, No. 9/99), directives of the Federal Customs Administration, 1-0 No. D-4098/2-94 and 01/3 No. D-14515/1-00, regarding implementation of regulations for border controls, and for protection from ionizing radiation (Official Gazette of FRY No. 39/01).

Stationary alarm radiation monitors at border crossings have given satisfactory results. Problems relate to maintenance and insufficient experience on the part of personnel in charge.

There have been numerous problems in controlling goods arriving on river vessels. Placing of probes at Djerdap-I locks has not proven justifiable although it is clearly the best location for screening vessels. The probes are a significant distance from the freight, which greatly reduces sensitivity of the detection system. Of greatest concern are barges that are closed with metal hatches of up to 10 cm in thickness. Goods in covered barges are mostly sealed, and only employees of the customs authorities at border river ports have removal authorization.

Based on many years of experience in measuring ionizing radiation under laboratory and field conditions, in our opinion, installing detectors of ionizing radiation at river crossings cannot achieve the necessary levels of preliminary radiological control, or operative dosimetric control, in accordance with the above-stated directives of the Federal Customs Administration.

We should also mention that definitive laboratory analysis is achieved with highly sensitive gamma-radiation spectrometers with pure germanium as the detection material. For example, a concentration of uranium of 1 ng/g may be detected without difficulty, which is equivalent to identifying a thief among nine million people. Discussion of the number of samples of food that did not meet regulations for several years after the Chernobyl accident, and had to be returned, is outside the scope of this paper. But we can state that radionuclides have not been detected in samples of imported food above the limits set by the law.

Table I provides a review of numbers of performed radiological analyses from 1996 to 2001. Presumably many more analyses were done immediately after the Chernobyl accident.

TABLE I. NUMBER OF PERFORMED RADIOLOGICAL CONTROLS, 1996 – 2001

1996	791
1997	870
1998	958
1999	378
2000	1012
2001	2408

3. SUMMARY

Radiological control at border crossings is important for every country, especially in view of present day problems: smuggling of strategic radioactive materials, disposal of nuclear waste, possibilities of use of radiation sources for subversive and other criminal purposes, etc. As far as our country is concerned, broad administrative co-operation — from the Federal Secretariat for Labour, Health and Social Security, as the competent institution for ionizing radiation, to institutes dealing with operative dosimetric field control — is helping to ensure adherence to regulations and protocols for radiological control at border crossings into FRY.

Significant work lies ahead, since our methods of radiological control at our border crossings need to be harmonized with those implemented in the European Union. Further training of our expert teams is planned, as well as the procurement of high sensitivity equipment for use at FRY border crossings.

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POSTER SESSION

(Session 5)

XRF ANALYSIS OF LEAD IN SUSPENDED AIR PARTICULATE MATTER COLLECTED USING GLASS FIBRE FILTERS*

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Abstract

A new method for X ray fluorescence (XRF) spectrometry determination of lead in suspended particulate matter collected from air in glass fibre filters is described. Since 1997, total suspended particulate matter has been collected in Córdoba City, Argentina, in compliance with a United States Environmental Protection Agency standard, in order to monitor ambient air quality. This standard is the most frequently referred to in terms of environmental regulation in Córdoba. In accordance with Title 40 of the Code of Federal Regulations, samples have been taken using high volume equipment with glass fibre filters. The method was developed in order to minimize matrix and grain size effects, in comparison with data obtained by direct irradiation of the filter surface. The detection limit obtained is 0.3 ng/m^3 for lead in air. The procedure can be applied to the determination of various high and low atomic number elements in such samples. Data determined by XRF spectrometry were compared with those obtained by analytical electrochemistry. All information shows that lead is not a serious pollutant of air in Córdoba City.

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1. INTRODUCTION

One of the most important aspects in formulating ambient air quality standards is specifying the measurement methods for determining and attaining compliance. Samples taken for compliance are often pushed beyond their original purpose to identify sources, to evaluate the effectiveness of controls, and to determine relationships between pollution levels and public health. In Argentina, it is usual to set local environmental regulations in accordance with guidelines of the United States Environmental Protection Agency (USEPA). For example, the National Ambient Air Quality Standards (NAAQS) are frequently cited. These standards were prescribed by the 1970 Clean Air Act to protect health in the USA, and they are currently established for carbon monoxide, nitrogen dioxide, sulphur dioxide, ozone, particulate lead, and suspended particulate mass. Each of the standards relates to a specific chemical element or compound except those for suspended particles. Particulate lead measurements are made from samples collected in glass fibre filters. The particles are removed from the air with a high volume sampler for total suspended particles (HVS-TSP). Samples are acquired once per week and the NAAQS do not permit concentrations to exceed 1.5 $\mu g/m^3$ for a three month average [1, 2].

X ray fluorescence spectrometry (XRF) is considered one of the methods useful for routine non-destructive determination of elemental composition of particulate matter loaded filters. Direct irradiation of collected samples avoids chemical treatment, with the advantage both of rapidity and of unaltered preservation of the sample for possible further assays [3]. But there are two problems. One is imprecise correction of matrix effects. Due to significant penetration of the particles into the filter medium, considerable attenuation can occur, both of incident and of fluorescent X rays, especially for light elements. This attenuation has complex theoretical modelling because the profile of particulate matter in the filter is usually unknown [4–6]. The other problem is the particle size effect due to non-homogeneous distribution of grain size in the analytical volume. In this case, X ray absorption by larger particles may be significant [5, 7]. Furthermore, if the samples are collected in cities of only moderate industrial activity, as Córdoba, it is imperative to obtain the lowest possible limit of detection.

We present a method to determine lead in particulate matter, collected in glass fibre filters, that achieves a lowest limit of detection (LLD) one order of magnitude less than direct irradiation methods. In this new procedure, an exposed filter is divided into twin parts. One half is ground and the resultant powder is pressed into a pellet, which is analysed by XRF to determine the lead concentration. Also, the remaining filter material may be analysed by chemical techniques, and the pressed disk can be preserved for further investigations.

2. EXPERIMENTAL

The city of Córdoba is located at 31º41' S, 64º11' W. It was founded in a natural depression traversed by the Suquía River, and has a population of approximately 1 300 000. Automobile fabrication factories, at the periphery of the city, represent the most important industrial activity. Commercial and administrative activities are concentrated in a small area downtown, the microcentre. Traffic on the main thoroughfares in the microcentre reaches 30 000 vehicles per day. Some 360 000 vehicles are registered.

The city's Environmental Observatory has an automatic monitoring system composed of two mobile stations that determine in real time the concentrations of carbon monoxide, nitrogen dioxide, sulphur dioxide, and ozone, and suspended particles of aerodynamic equivalent diameter less than 10 μm (PM_{10}). The stations also record meteorological information. Air quality diagnostics indicate that both particulate suspended matter and carbon monoxide are the most important pollutants for Córdoba. The most complicated area is the micro centre. Annual averages for PM_{10} are 50% over the standard established by the USEPA, reaching 75 μg/m^3. In addition, 24-h averages have been greater than 150 μg/m^3 on six occasions over three consecutive years.

For the reasons described above, the Environmental Observatory incorporates a manual monitoring system to collect samples of air suspended material in order to determine compliance with the standard for lead and to typify suspended particulate matter. This monitoring system operates with three high volume samplers (HVS-Graseby/GMW). Two of these HVS collect total suspended particles (TSP-HVS) and the other collects only in the PM_{10} range (PM_{10}-HVS). The measuring sites were chosen taking the predominant wind direction into consideration: northeast to southwest. In 1998, a TSP-HVS was positioned in the microcentre and a PM_{10}-HVS was placed 7 km from downtown, in the southwest of the microcentre. In 1999, the second position was eliminated because it duplicated the critical conditions of the microcentre, and was moved near the first position where it continues in operation. The second TSP-HVS sampler is being used to explore the best sites for a new stationary manual station. The samples are taken once per week and the sampling period is 24 h.

2.1. Particulate sampling

Aerosol samples are most often acquired by drawing ambient air through a filter material, using a pump, with subsequent quantification of particle mass and its chemical components by off-site laboratory analysis. Reference methods (Code of Federal Regulations, USA) require equilibration and weighing of the filter in the laboratory before exposure. After that, chemical analysis of filter deposits gives values for the various constituents. Environmental samples analysed in this work were collected by one of the Graseby/GMW HVSs, described above, with volumetric airflow control. The filter for particle sampling consists of a tightly woven fibrous mat or a plastic membrane penetrated by microscopic pores. The HVS-TSP and PM_{10} methods require glass fibre and quartz fibre filters, respectively. The filters used in this work were G810 Graseby/GMW, 20.3 cm long, 25.4 cm wide and approximately 2.7 g in weight. The particulate mass collected averages 200 mg.

2.2. Analytical methods

Appendix G of CFR 40 Part 50 gives the reference methods for the determination of lead in suspended particulate matter collected from ambient air. The title Principles and Applicability describes procedures to be applied by atomic absorption spectrometry (AAS). In 1998 and 1999, the Environmental Observatory of Córdoba used an electrochemical analytical system rather than AAS. The Eco Chemie Autolab PGSTAT20 system has a mercury drop electrode controlled by a PC computer. Lead in the particulate matter is solubilized by extraction with an oxidant solution of $HNO_3/HClO_4/H_2O_2$ in the proportion 2:1:1 facilitated by heat. Table I shows an example of collected samples electrochemically analysed in 1998. For various reasons, the electrochemical method is complex and slow.

TABLE I. LEAD CONCENTRATION IN AMBIENT AIR SAMPLES MEASURED IN 1998, DETERMINED BY ELECTROCHEMISTRY OF SQUARE WAVE CYCLIC VOLTAMPEROMETRY

Sample identification	Pb concentration (ng/m^3)
12-TSP98	< 5
15-TSP98	< 1
24-TSP98	< 3
26-TSP98	14 ± 5
31-TSP98	11 ± 1

In order to introduce a more rapid and efficient method for lead analysis, a new procedure was devised, using two well known spectrometric techniques: XRF and AAS. The procedure consists of weekly routine determinations of lead by XRF analysis, contrasted periodically (every 3 months) with AAS on a duplicate set of samples. The XRF component is presented in full here. The equipment used was a Bruker SRS 3400 sequential wavelength X-ray spectrometer, with a 4 kW power excitation source, with a rhodium end-window X-ray tube associated with a beryllium window of 75 μm thickness. This set up is optimized for sensitivity to light elements. The spectrometer has six analyser crystals: OVOB, OVOC, OVO55, PET, LIF 200 and LIF 220, which allow determination of elements from boron to uranium.

2.3. Preparation of samples for XRF analysis

Uniformly loaded thin filters may be considered as nearly ideal targets for XRF, for exposure to a straight line of X-ray photons. This procedure avoids any preliminary treatment of the sample, but introduces strong matrix effects as described before. Nevertheless, a set of lead Kα intensities was measured by direct irradiation to determine the limit of detection for lead. Discs of 4 cm diameter were cut from the remaining filters that had not been completely digested with acid in the electrochemical procedure. These discs were loaded into the spectrometer supported by a thin mylar film (6 μm) in order to obtain low background. The irradiated surface was 3.4 cm in diameter. A correlation between lead Kα intensities and lead electroanalytical concentrations for all the samples permitted calculation of the LLD. An LLD of 40 ppm (approximately 4 ng/m^3 in air) was calculated for TSP loaded glass fibre samples. It was concluded that the LLD for lead is insufficient for use in the direct irradiation method for suspended particulate matter in Córdoba.

An alternative sample preparation procedure was developed to improve detection limits. In this new procedure, the filter is divided into twin parts. One half is subdivided into several small pieces (roughly 25 mm^2) and ground in a SPEX 5400 mixer/mill for 16 min in an acrylic container with three methacrylate balls of 1 cm diameter. The resultant powder is a homogeneous mixture of glass fibre from the filter substrate and particulate matter. That powder, approximately 1.6 g, is mixed with addition of microwax to 20% of the total mass for 8 min. Finally, a pellet disk of 40 mm diameter is prepared by pressing the powder on a 4-g cellulose substrate with a force of 10 t (cellulose is not included in the analytical matrix). Disc depth is approximately 4 mm, with powder from the filter mixed with microwax reaching 1 mm. These pellets are analysed for diverse chemical elements and can be preserved for further essays. This procedure needs only one half of the filter, and the other half is preserved.

2.4. Calibration curve

Secondary standards were prepared from clean glass fibre filters by adding aliquots of a lead solution. All materials used to prepare solutions were of analytical reagent quality. The liquid was added after imbibing the small pieces of filter. The material was dried and then ground in the mixer/mill applying the procedure described above.

3. RESULTS AND DISCUSSION

Measurements of Compton scattering in standards is almost equal to measurements in ambient air loaded filters, when both are prepared with the new procedure. This means that matrix effects at Compton energy (19.41 keV) are the same in standards as in loaded filters [8]. The difference in the two kinds of samples is the presence of particulate matter in the latter. Therefore, the effects of particulate matter in the matrix at 19.41 keV are rather small with the new procedure. This is because particulate matter represents an average of only 5% of the total mass of the loaded filter, it is homogeneously distributed, and it is essentially composed of light elements.

The above argument can be extended to lower energies, especially for incident and L shell XRF in lead. Thus, it is possible to conclude that particulate matter has low influence on matrix effects in loaded filter samples prepared with the procedure here described. This marks a strong contrast with the direct irradiation method, with which particulate matter has a substantial effect that is difficult to correct for. This is one advantage of the proposed analytical procedure over direct irradiation of exposed filters. As a corollary, the total mass of particulate matter in loaded filters has little influence on elemental quantification of lead and its variability introduces insignificant inaccuracy.

Figure 1 shows the close correlation between concentrations of lead determined in twin parts of a filter. This set of twin pellets was prepared as described above using half of an environmental sample for pellet A and the other half for pellet B. The procedure has excellent reproducibility, with error less than 5%.

Figure 2 shows a calibration curve obtained with standard samples prepared as described above. Aliquots of increasing amounts of lead were added to a clean filter. Following the described pressed pellet procedure, it was possible to get calibration samples containing 59, 85, and 108 ppm of lead. As declared by the manufacturer, 10 ppm of lead in the clean filter were taken into account. The calibration curve had an average relative error of less than 4%.

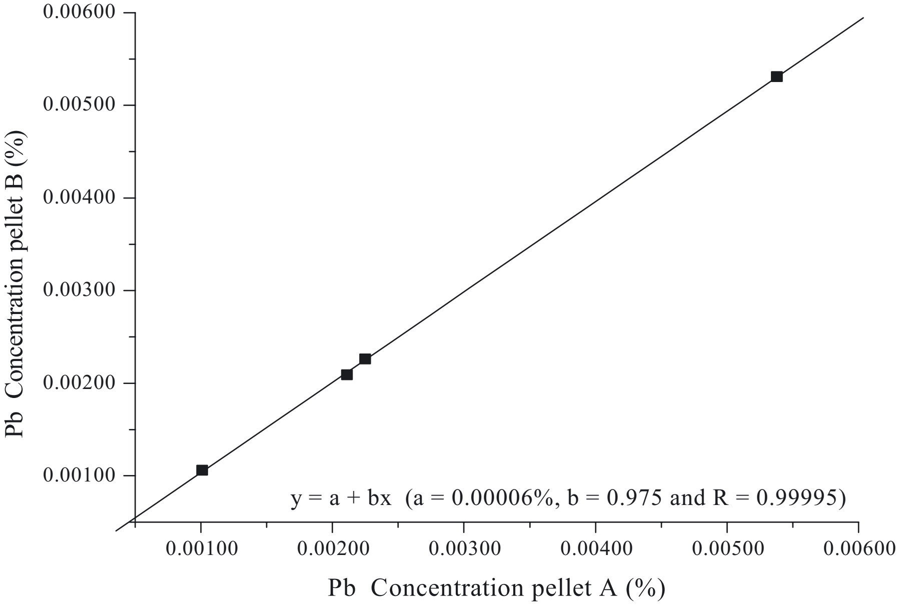

FIG. 1. Correlation between values of lead concentration analysed in twin pellets. These sets of twin pellets were prepared following the new procedure using one half part of an environmental sample for pellet A and the another half part for pellet B.

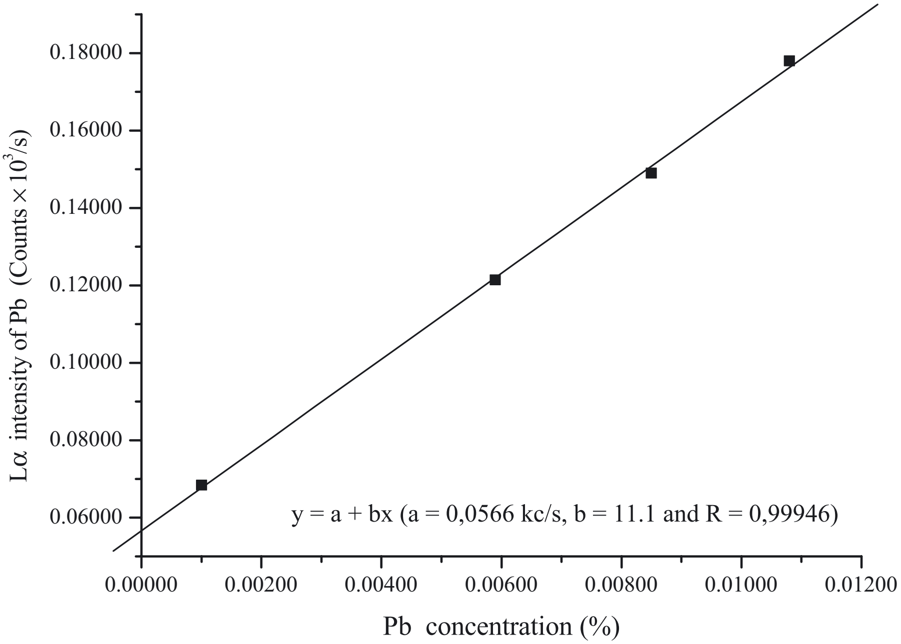

FIG. 2. Calibration curve obtained from the measurement of standard samples.

The well known fundamental parameters method, incorporated in the XRF spectrometer software [9] used in this work, was employed to calculate the lower limit of detection for pressed pellets. To do this, the fluorescent intensities for all of the elements present in a clean G810 filter pressed disc were measured. By correlating into the software the intensities for the filter elemental composition (matrix effects), the LLD for lead was calculated at 2.2 ppm, closely equivalent to 0.3 ng/m^3 in air. This value for LLD is one order of magnitude lower than that obtained by the direct irradiation method, and is sufficiently low to quantify lead in total suspended particulate matter collected in Córdoba.

Table II shows results for lead in samples, obtained by XRF spectrometry following the proposed method, collected since 1998. The accuracy estimated for lead concentration – by propagation of all errors involved, including those in particulate sampling – was less than 10%. By recourse to a simple statistical calculus performed over more than 100 loaded filters (some of which are shown in Table II) the average lead concentration was estimated at 3.5 ± 1.5 ng/m^3. This value is much lower than 1500 ng/m^3, which is the highest acceptable lead concentration in air, according to local legislation in concurrence with USEPA. These lead concentrations were in the same order of magnitude as previous results obtained by the electrochemical technique.

TABLE II. XRF LEAD CONCENTRATION IN THE AIR OF CÓRDOBA BY THE METHOD EXPLAINED IN THIS WORK

Sample identification	Lead concentration (ng/m^3)
36-TSP98	2.0
42-TSP98	1.1
03-TSP99	3.2
04-TSP99	15.0
08-TSP99	1.5
44-TSP99	< LLD
76-TSP00	4.6
82-TSP00	7.2
90-TSP00	3.0

4. CONCLUSION

From an environmental point of view, we conclude that lead is not a significant pollutant of air in Córdoba, because concentrations were far below 1500 ng/m^3 in all cases. However, it is important to continue quantifying lead to provide information about sources of emissions.

The method proposed has the advantages of controlling matrix and particle size effects for elemental quantification in loaded glass fibre filters, especially for lead. In addition, this method has an LLD one order of magnitude lower than that obtained by direct irradiation XRF analysis. Although the preparation of pressed pellets from filter material is rather more elaborate, it is inexpensive, rapid, and allows long term preservation of part of the sample. It has good reproducibility, with an average error of less than 5%.

The ranges of lead values determined by both the electro-analytical and XRF methods proposed in this work were similar. The comparison of XRF spectrometry with the other independent technique revealed that the former is satisfactory. Currently, we are working on a more extensive comparison with AAS, and preliminary results are promising. It is possible to expand the application of this novel analytical method to quantify other elements in air, including light elements, such as chlorine and sulphur. It can be applied to elemental analysis of PM_{10} because the same sample preparation can be practised in quartz fibre filters, which are recommended for PM_{10} high volume sampling.

ACKNOWLEDGEMENTS

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RADIATION PROTECTION IN THE REPUBLIC OF AZERBAIJAN

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Azerbaijan is not a nuclear State. It does not have a nuclear power plant or a nuclear fuel manufacturing industry. Radioactivity results from natural factors, and some peculiarities have come to light. Sandy localities of the coastal zone of the Apsheron Peninsula have lower background levels than areas of clay soil. Also, mountainous areas that are wooded register less radioactivity than areas without tree cover.

Over the past three decades there has been a deterioration in the quality of the water in the tributaries of the rivers Kur and Araz that flow through Georgia, Armenia and the Islamic Republic of Iran. Pollution with nuclear and other toxic wastes has occurred, including from the Metsamor Nuclear Power Plant in Armenia.

Factors that have contributed to the worsening of the radiation situation in Azerbaijan include:

- Armenian Nuclear Power Plant;
- Rostov Nuclear Power Plant, Russian Federation;
- Nuclear fuel upgrading plant (Aktau, Kazakhstan);
- Chernobyl Nuclear Power Plant;
- Nuclear related activities in the Islamic Republic of Iran and Iraq;
- Nuclear tests in central and eastern Asia.

Furthermore, quantities of used sources of radioactivity are present in Azerbaijan in research institutions and business enterprises, and on military bases. Because of loss of nominal characteristics, these materials are no longer of practical use, but still constitute a threat to human and environmental health. Many radioactive sources exist on military bases that were abandoned by the Soviet Army.

Mining of oil is an important source of radioactive contamination in our republic. Deep layer waters containing radium, thorium, uranium, iodine and other radionuclides, released onto the soil surface, accumulate on land or flow into the Caspian Sea. A further source of radioactive waste results from importation of instruments, equipment and other technology that contain radioactive sources.

The above considerations dictate the need for control of sources of radioactivity for human and environmental protection in Azerbaijan, which comes under the authority of the Radioecology Centre of the Nuclear Monitoring Service (NMS) of the Ministry for Ecology and Natural Resources (MENR), and a special isotopes plant for burial of radioactive wastes under the authority of the Civil Defence. Academic organizations and the NMS must control, monitor and record the use of radioactive sources. The Civil Defence and the NMS are authorized to store, transport, deactivate and bury radioactive sources and wastes that are received from many institutions. The function of the special isotopes plant for burial of radioactive waste must be reorganized; a new burial facility is needed, taking account of modern technical requirements to accommodate industrial needs and all kinds of radioactive wastes.

Monitoring of all aspects of nuclear materials throughout the Republic will be under the authority of NMS-MENR. For the solution of problems, the NMS will require new technology (radiometric, dosimetric, spectrometric, etc.), and a monitoring network throughout the Republic is needed. Co-operation with the IAEA will lead to improvements in the system for radiation protection in Azerbaijan in the short term.

RADIOLOGICAL ASSESSMENT AND MANAGEMENT OF A RADIOACTIVE SPILL AT A LIQUID WASTE TREATMENT FACILITY: A CASE STUDY

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Abstract

The radiological assessment and management of a radioactive spill from a liquid waste treatment facility is presented. An area around the facility was contaminated with various radionuclides that were dispersed into the soil. A method based on the European Basic Safety Standards was used to contain the risks associated with the contamination. This method is based on several stages: removal of doubt, pre-diagnosis, initial diagnosis, a simplified risk study, a detailed risk study, and assistance in the selection of the remedial strategy. The adopted guideline criteria enable the assessment sequence to be interrupted and appropriate decisions to be taken. The introduced case study proceeded to the simplified risk study stage, since the site was small and it was relatively easy to remove and store the contaminated soil. An area contamination monitor was used to locate hot spots while preliminary investigations of the samples were made using a high resolution gamma spectrometer with a hyper pure germanium detector and a low level alpha–beta counter. According to the obtained results, the removal of the surface 30 cm would be considered as appropriate remedial action to resume background levels.

1. INTRODUCTION

One of the most important basic concepts of radiation protection in nuclear facilities is continuity of monitoring radiological releases to the environment. As a consequence of the atmospheric tests of nuclear weapons in the 1960s, human-made radionuclides were dispersed globally. Only very small amounts of radioactivity are discharged from nuclear facilities in effluents and air exhausted to the environment. Recent screening [1] of natural and artificial radionuclides in soil samples from the investigated area revealed normal background concentrations with no anomalies. The accidental release of radioactive liquid waste from a small scale waste treatment facility led to finite contamination with some radionuclides, which spread over the surrounding area. *Thus it was necessary to provide not only site management principles, but also precise descriptions of each stage of assessment*. Since the adopted guidelines are intended to deal with various situations that might be encountered in practice, the approach involves several stages [2]. It might not be necessary to implement all of these stages. In some cases, it should be possible to interrupt the process when it is relatively easy to prove that the site has not been contaminated. In other cases, the site might be contaminated, but on a small scale with the contamination profile relatively easy to grasp. In such cases, a simplified risk study can be carried out and a satisfactory remedial strategy advocated.

2. RISK ASSESSMENT AND MANAGEMENT

The method used for assessment and management of radiation risks from the contaminated site is based on several stages: removal of doubt, pre-diagnosis, initial diagnosis, a simplified risk study, a detailed risk study, and assistance in the selection of the remedial strategy [2, 3]. The guideline criteria enable the assessment sequence to be interrupted and appropriate decisions to be taken. This study proceeded to the simplified risk study stage, since the site was small and it was relatively easy to remove and store the contaminated soil:

- *Removal of doubt:* This process is based on a rapid investigation in which radioactivity measurements are made in the areas and buildings that are believed to be contaminated. Determination of gamma radiation and associated dose rates and the use of specific alpha–beta monitors are suggested. Contamination of the soil surface is examined using a contamination monitor to determine hot spots. Unescorted access to the contaminated area is limited to personnel directly concerned with the operation.
- *Pre-diagnosis*: The objective is to identify and assess real or potential risks of radiation exposure of persons at the site or in its vicinity, so that necessary action for short term protection may be taken. To this end, a preliminary survey of the site should be made.
- *Initial diagnosis*: The objective is to establish a site status report in terms of past activities (historical analysis) and vulnerability of the environment (soil, groundwater, surface water, air), and to make a radiological characterization (mapping of the surface and initial studies at depth, and radioactivity measurements of environmental samples). These data are essential in order to carry out the simplified risk study.
- *Simplified risk study*: This involves calculation of the potential dosimetric impact associated with various scenarios for later use of the site

based on the results of the radioactivity measurements of the surrounding soil and buildings. The assessment of the individual effective dose ($mSv\cdot a^{-1}$) associated with the specific contamination unit of the soil ($Bq\cdot g^{-1}$) is carried out, taking into account the highest specific activities measured in the studied zone or the most pessimistic contamination hypothesis.

— *Assistance in the selection of the remedial strategy*: It should be noted that the remedial strategy depends on the future use of the site. A change in use often facilitates the cleanup or it may obviate the need for it. In the majority of cases, however, cleanup techniques should be investigated. Available techniques should, therefore, be examined (removal of soil, in situ confinement, installation of shielding, etc.). These techniques should be combined with available interim storage or disposal of the generated waste in order to determine available remedial strategies. These should be characterized in terms of radiological impact and in terms of economic costs, duration of remedial efficiency, and the potential need for long term monitoring of the site.

2.1. Sampling for the simplified risk study

A grid-like sampling plan was designed to facilitate the radiological survey. The contaminated area was divided into 1 m^2 squares and soil samples were collected to a depth of 25 cm. Four of the squares were considered as hot spots. Soil from the hot spots was sealed in plastic bags, moved to the laboratory, weighed, and dried overnight in a muffle furnace at 110°C prior to analysis to identify the released radionuclides.

3. EXPERIMENTAL

3.1. Gamma spectrometry

Aliquots of about 50 g of each sample were transferred into aluminium containers and sealed in the same shape and geometry as the calibration source. A high resolution gamma spectrometer based on a hyper-pure germanium detector (HPGe) from EG&G ORTEC® was used for the gamma analysis. The HPGe crystal had a diameter of 64.5 mm and a length of 69.9 mm, a relative efficiency of 50%, a peak to Compton ratio of 62, FWHM of 1.9 keV at the 1.33 MeV ^{60}Co transition and 753 eV at the 122 keV ^{57}Co transition. The efficiency calibration for the system was explained in a recent publication [4]. In addition, a mixed gamma source solution of the same type and configuration was used to determine the absolute efficiency curve.

3.2. Low level alpha–beta counter

A rapid method was used for the determination of ^{90}Sr/^{89}Sr in soil samples [5, 6]. Strontium, caesium and barium carriers were added to 1–2 g samples that were leached in 100 mL HNO_3 for approximately 1 h, then centrifuged, and this step was repeated for the residue. Both solutions were combined, and alkaline earth elements (Ca, Sr and Ba) were precipitated as nitrate using fumic nitric acid. The precipitate was dissolved in 1:1 fumic HNO_3/H_2O to eliminate calcium. Barium was separated as chromate using 25% sodium chromate solution. Strontium was precipitated from the solution as carbonate using ammonium carbonate, which was, thereafter, converted to strontium nitrate using fumic nitric acid. Yttrium carrier (10 mg) was added and yttrium hydroxide was precipitated using ammonia. The aqueous phase was collected, the step was repeated, and a carbonate precipitate was prepared on a Teflon® disc for ^{90}Sr/^{89}Sr measurements. For ^{90}Sr measurement through ^{90}Y, a growth period of 14 before yttrium oxalate precipitate was prepared has been considered. The source was counted on a Berthold LB 770 ten channel, low level alpha–beta counter. The detector is a gas flow proportional counter for measuring alpha and beta activities. The sample detector, which features an ultra-thin entrance window with P-10 counting gas (a mixture of argon and methane) within the detector chamber, offers minimum attenuation of particles of interest that pass through the window. The detector is biased with a high voltage to collect the charge generated by the interaction of the radioactivity with the counting gas. The detector is lead shielded from the naturally occurring background radioactivity and a second gas flow proportional detector against high energy cosmic radiation also guards the system.

The decision regarding remedial action is based on the preliminary results obtained from the gamma measurements.

4. RESULTS AND DISCUSSION

The activity in the investigated hot spots showed about 80% on the surface soil layer, about 25% within the next 10 cm and less than 1% between 10 and 25 cm. Figure 1 shows variation factors and the count rates of fractions at different depths, and Fig. 2 illustrates the average specific activity distribution of ^{137}Cs,

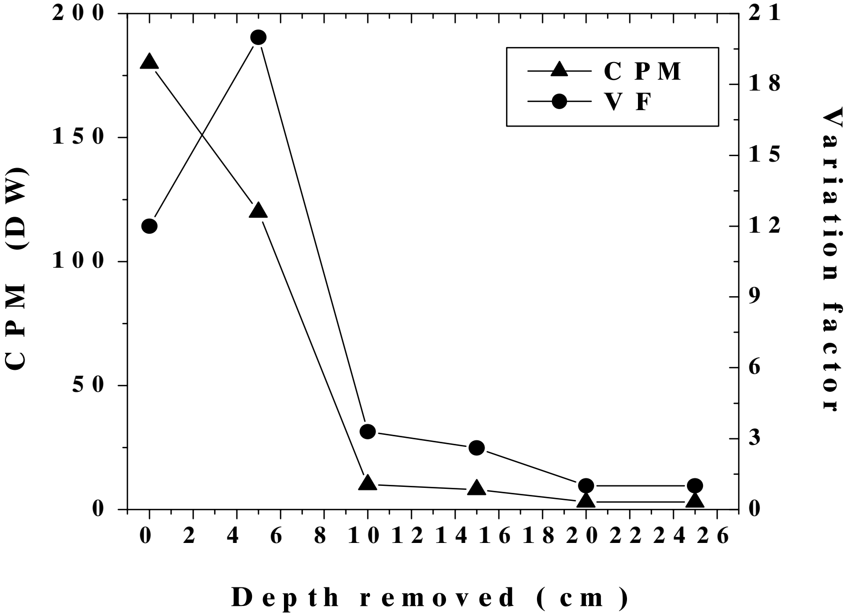

FIG. 1. The variation factor and the count rate of fraction loading at various depths.

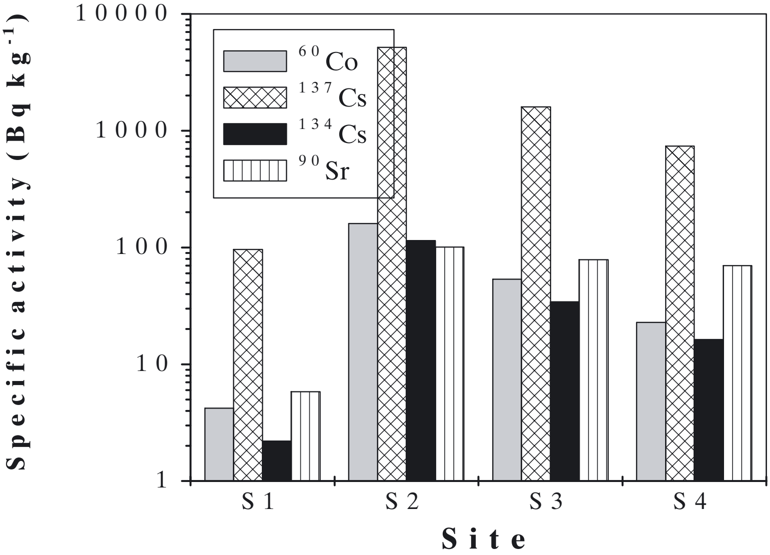

FIG. 2. Total activity distribution and the measure of deviation tendency for ^{137}Cs, ^{134}Cs, ^{60}Co and ^{90}Sr (Bq·kg^{-1} DW) in the investigated samples.

^{134}Cs, ^{60}Co and ^{90}Sr (Bq·kg^{-1} DW) within the investigated hot spots. The ranges (and means ±SD) for the concentration ratios of ^{137}Cs, ^{134}Cs, ^{60}Co and ^{90}Sr, with respect to the total activity, were 33 to 88% (62% ± 22), 0.7 to 1.5% (1.1% ± 0.3), 1.1 to 2.2% (1.7% ± 0.54) and 89 to 98% (94% ± 4), respectively. Soil profiles showed greater activity concentrations in the surface layer, which could be attributed to the fact that the discharge was relatively new. However, considerable concentrations of various radionuclides were found also in the deeper layers. According to these findings, the removal of the upper 30 cm of the surface soil would reduce activity concentrations practically to normal background levels.

5. RECOMMENDATIONS

Although the remedial action was quite successful, further investigations are needed to verify that the objectives were achieved. The possibility of contaminant transport through weathering and migration should be examined. Dose assessment and source term calculations should be planned.

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DETERMINATION OF ^{238}Pu AND $^{239+240}$Pu BY DESTRUCTIVE ASSAYS

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Abstract

Analysis of plutonium in environmental samples is one of the measures recently included in international safeguards. Plutonium and some other actinides, and fission and activation products in environmental samples, are currently used as indications of undeclared nuclear activities. Two destructive assays are presented for determination of ^{238}Pu and $^{239+240}$Pu in environmental samples. Alpha spectrometers were utilized to identify the isotopic composition of plutonium. The results show coincidence of the determined plutonium concentrations with certified values. The U test was used as a quality control indicator of the presented procedures and results. The levels of ^{238}Pu and $^{239+240}$Pu in the samples ranged from 1.6×10^7 to 4.2×10^8 atoms, and from 2.2×10^{10} to 2.6×10^{11} atoms, respectively. Both methods could be applied for accurate, low level analysis to indicate plutonium origin.

1. INTRODUCTION

In the framework of modern approaches in the international community to strengthen non-proliferation measures, analyses of environmental samples by destructive assay (DA) and non-destructive assay (NDA) will be used for discovery of undeclared nuclear activities [1, 2].

The problem of accurately detecting extremely low levels of plutonium is gaining increased importance in the application of nuclear counter-proliferation, verification, and environmental and waste management. In the environment, plutonium isotopes originate from atmospheric nuclear weapons testing, re-entry burnup of a ^{238}Pu auxiliary powered navigational satellite (SNAP-9A), nuclear fuel reprocessing plants, nuclear accidents and discharges from nuclear reactors. Discrimination between sources of anthropogenic plutonium requires both precise and accurate isotope ratio determination at environmental levels [3].

The Earth's crust contains negligible quantities of natural plutonium [4]. In the environment, the mean specific activity of human-made ^{239}Pu is close to 10^{-13} g/g (0.23 mBq/g) for surface soil. In some places — nuclear weapons testing sites, sites of nuclear reactors producing plutonium, and close to factories where plutonium is chemically extracted from nuclear fuel elements — specific activity can exceed the normal level by a factor greater than 10^2 [5].

Observation of significant change in the isotope ratio of plutonium, ^{238}Pu/$^{239+240}$Pu, indicates the presence of material from sources other than global fallout. Whereas the activity ratio due to weapons test fallout and satellite burnup is 0.081, ratios of discharges from nuclear installations are up to 2.4 [6]. The ^{241}Pu/$^{239+240}$Pu activity ratio varies greatly, depending on origin of the isotopes. For fresh fallout from nuclear weapons tests, this activity ratio is approximately 12 to 16, whereas for spent nuclear fuel from power reactors it is about 130 [5].

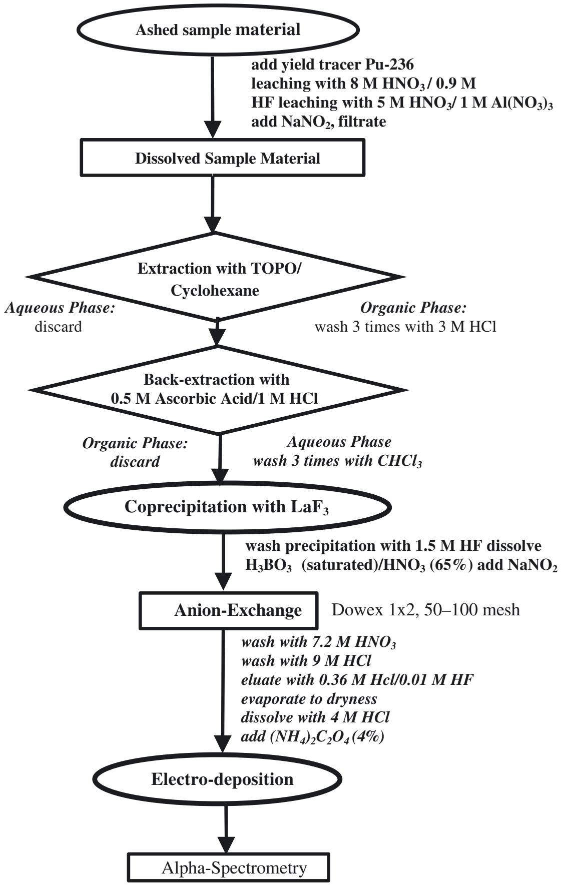

FIG. 1. Flow chart illustrating the basic elements of the LLE radiochemical procedure for plutonium analysis.

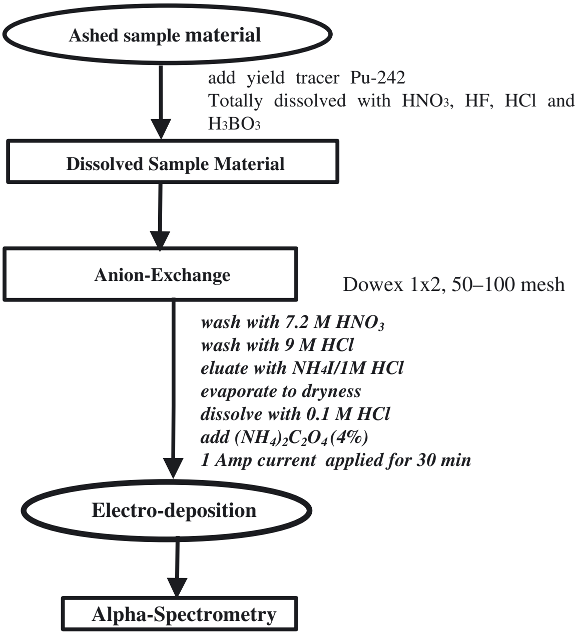

FIG. 2. Flow chart illustrating the basic elements of the IEC radiochemical procedure for plutonium analysis.

The objective of this work was to examine the relative convenience of two destructive procedures for the determination of plutonium isotope composition of various sample types.

2. DESCRIPTION OF THE PROCEDURES

Two radiochemical procedures for analysis of plutonium isotopes (^{238}Pu and $^{239+240}$Pu) were investigated for their relative convenience. Flow charts of the procedures are given in Figs 1 and 2. Determination of plutonium in environmental samples by alpha spectrometry involves tedious radiochemical procedures to separate the radionuclides from the matrix. The first step in plutonium isotope separation from the matrix is the conversion of the plutonium into an acid soluble form. For plutonium activity concentration and chemical yield determination, ^{236}Pu or ^{242}Pu was used as internal tracer. In the first procedure (LLE), plutonium isotopes were quantitatively converted into acid soluble forms by leaching from 100 g ashed samples in two steps with HNO_3/HF and HNO_3/$Al(NO_3)_3$ solutions. In the second procedure (IEC), 10 g ashed samples were totally dissolved with HNO_3, HF and HCl acids. In the LLE procedure, plutonium was separated from most of the matrix elements by extraction with trioctylphosphine oxide (TOPO)/cyclohexane and back–extraction with hydrochloric/ascorbic acid. Then, the plutonium fraction was purified radiochemically by co-precipitation with LaF_3 and anion exchange chromatography. In the IEC procedure, plutonium was separated from most of the matrix element and purified using ion exchange chromatography. The concentrations of the alpha ^{238}Pu and $^{239+240}$Pu were measured using alpha spectrometers after electroplating in oxalate/HCl medium [7, 8].

For determination of plutonium isotope activity concentration and their ratio, the electroplated disks were measured using alpha spectrometers based on passivated implanted planar silicon (PIPS) detectors with a 450 mm^2 surface area, approximately 25% efficiency, and about 20 keV resolution at 4.41 MeV of ^{241}Am. The detector was calibrated by using a mixed standard source containing ^{239}Pu, ^{241}Am and ^{244}Cm. The samples were measured for 60 000 to 80 000 s.

Both methods were tested against standard reference materials and certified samples to estimate the accuracy and reliability of the results. Accuracy was evaluated using the U test [9].

3. RESULTS AND DISCUSSION

The ^{238}Pu and $^{239+240}$Pu data obtained by the LLE and IEC procedures are given in Tables I and II, respectively. The concentration levels of ^{238}Pu and $^{239+240}$Pu in the analysed samples ranged from 1.56×10^7 to 4.24×10^8 atoms (from 3.92 to 106 mBq/g), and from 2.2×10^{10} to 2.6×10^{11} atoms (from 20.3 to 236.0 mBq/g), respectively.

The results were evaluated using the U test score as given in the following equation [9]; the physical meaning of the U score value is given in Table III.

$$U_{test} = \frac{\left| Value_{IAEA} - Value_{Analyst} \right|}{\sqrt{Unc_{IAEA}^2 + Unc_{Analyst}^2}}$$

Regarding sample preparation (double leaching with HNO_3/HF and $HNO_3/Al(NO_3)_3$, and total sample dissolution), both showed results that passed the U test, which means that both succeeded in bringing the refractory compounds of plutonium in the reference samples into an acid soluble form [10].

Regarding time needed for analysis, for batches of four samples the LLE procedure was shorter. However, for larger batches (up to 18 samples) the IEC

TABLE I. QUALITY CONTROL DATA FOR REFERENCE AND CERTIFIED SAMPLES ANALYSED USING THE LLE PROCEDURE AND ALPHA SPECTROMETRY FOR PLUTONIUM ISOTOPES

Sample code	^{238}Pu			$^{239+240}$Pu			Comments
	Certified (mBq·g^{-1})	Measured (mBq·g^{-1}	U test	Certified (mBq·g^{-1})	Measured (mBq·g^{-1})	U test	
IAEA-384 Sediment	39.0 ± 1.1	35.4 ± 2.3 (1.41 × 10^{8} atoms)	2.5	108 ± 2.5	100.5 ± 6.3 (1.1 × 10^{14} atoms)	1.11	Accepted
Soil-131[a]	35.9 ± 0.7	34.0 ± 3.0 (1.36 × 10^{8} atoms)	0.61	77.0 ± 1.6	68.0 ± 5.0 (7.4 × 10^{10} atoms)	1.66	Accepted
Standard Sol. 134	14.0 ± 2.3	106.0 ± 9.0 (4.24 × 10^{8} atoms)	0.86	244.0 + 4.9	236.0 + 18.0 (2.6 × 10^{11} atoms)	0.41	Accepted
Standard Sol. 635	—	—	—-	191.0 + 3.8	190.0 + 4.3 (2.1 × 10^{11}atoms)	0.02	Accepted

[a] mBq/sample: 1 Bq ^{239}Pu = 1.09 × 10^{12} atoms, 1 Bq ^{238}Pu = 3.99 × 10^{9} atoms.

TABLE II. QUALITY CONTROL DATA FOR CERTIFIED SOIL SAMPLES ANALYSED USING THE IEC PROCEDURE AND ALPHA SPECTROMETRY FOR PLUTONIUM ISOTOPES

Sample code	^{238}Pu			$^{239+240}$Pu			Comments
	Certified (mBq·g^{-1})	Measured (mBq·g^{-1})	U-test	Certified (mBq·g^{-1})	Measured (mBq·g^{-1})	U test	
00.38894	3.81 ± 0.15	3.92 ± 0.31 (1.56 × 10^{7} atoms)	0.3	25.90 ± 0.74	25.70 ± 1.33 (2.8 × 10^{10} atoms)	0.1	Accepted
00.38890	11.47 ± 0.37	12.16 ± 0.56 (4.85 × 10^{7} atoms)	1.0	22.20 ± 0.74	23.03 ± 0.96 (2.5 × 10^{10} atoms)	0.5	Accepted
00.32154	20.72 ± 0.70	18.5 ± 0.78 (7.38 × 10^{7} atoms)	2.1	20.35 ± 0.63	20.32 ± 0.84 (2.2 × 10^{10} atoms)	0.03	Accepted

TABLE III. PHYSICAL MEANING OF THE U TEST SCORE VALUES

Condition	Probability	Status
$u < 1.64$	Greater than 0.1	The reported result does not differ significantly from the expected value
$1.95 > u > 1.64$	Between 0.1 and 0.05	The reported result probably does not differs significantly from the expected value
$2.58 > u > 1.95$	Between 0.05 and 0.01	It is not clear whether the reported result differ significantly from the expected value
$3.29 > u > 2.58$	Between 0.01 and 0.001	The reported result is probably significantly different from the expected value
$u > 3.29$	Less than 0.001	The reported result significantly differs from the expected value

procedure showed better performance. The LLE procedure results in a mixed organic radioactive waste, whereas the IEC procedure produces only aqueous radioactive waste, which is easier to dispose of. The lower limits of detection obtained by the LLE and IEC procedures were 1.0 and 0.74 mBq/sample (3.99×10^6 and 2.9×10^6 atoms for ^{238}Pu, and 1.09×10^9 and 8.1×10^8 atoms for ^{239}Pu), respectively. Limits of detection as low as 2.9×10^3 atoms for ^{238}Pu could be reached, depending on the procedure parameters such as sample size and counting time.

4. CONCLUSIONS

Analyses of plutonium isotope composition in environmental samples, by the destructive assays presented, were very promising and fulfilled requirements of recent international safeguards. Data as low as 3.99×10^4 and 2.9×10^5 atoms of ^{238}Pu and 1.09×10^7 and 8.1×10^7 of ^{239}Pu were obtained by the LLE and IEC procedures, respectively. The procedures could be used also for swipe sample analysis. Efforts to develop procedures to reach lower detection limits for plutonium are ongoing.

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RADIOCHEMICAL ASSESSMENT OF CORE WATER AS AN INDICATOR OF FUEL RELIABILITY BEHAVIOUR: A CASE STUDY

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Abstract

Evaluation of coolant activity during nuclear reactor operation is the first step in assessing fuel reliability. Monitoring the activity of selected fission product isotopes in the off-gas system or in the primary coolant provides useful information on fuel status. Non-destructive and destructive methods were used to determine fission products as well as activation products in liquid samples taken from the ET-RR-1 research reactor core water, and examined for indications of fuel leakage during operation. The ET-RR1 is a 2 MW light water reactor at Inshass, Egypt, operated with aluminium cladded 10% enriched uranium oxide. Gamma spectrometry, based on a hyperpure germanium detector, was used to evaluate specific activities of present radionuclides. The release rate of ^{137}Cs was used to characterize the fuel assemblies while investigating the presence of corrosion pits along the external fuel clad. Radiochemical analysis of core water before and 1 h after full power operation indicated high activity of ^{137}Cs. About 70% of the ^{137}Cs was already present in the core water before operation. Caesium-137 to ^{60}Co ratios, before and after operation, were similar at 274 and 210, respectively. As ^{239}Np was detected in core water after operation (58 ± 1.4 kBq·L^{-1}), the total uranium content in the water before operation was determined using laser fluorimetry to evaluate U traceability, if any. The total uranium content of the core water before and after operation was 0.9 and 1.6 ppm, while water samples from the new and old spent fuel pools showed 1.2 and 2.1 ppm, respectively. Neptunium-239 can be effectively employed as an indicator of degraded fuel conditions and of significant fuel loss. Among others, ^{131}I, ^{133}I, ^{135}Xe, ^{134}Cs, ^{137}Cs, ^{91}Sr, ^{90}Sr, ^{140}La and ^{140}Ba were determined. The specific activities of ^{137}Cs and ^{90}Sr measured in the reactor core water before and after operation were about 18 and 12.7 kBq·L^{-1}, and 26 and 15.3 kBq·L^{-1}, respectively. The specific activities of ^{134}Cs, ^{137}Cs, and ^{90}Sr in water samples from the new spent-fuel pool were 753, 43, and 41 kBq L^{-1}, respectively, in comparison with 3.4, 128 and 113 kBq·L^{-1}in water samples from the old spent fuel pool. These findings raise questions about possible fuel failure and the efficiency of the purification system for water treatment.

1. INTRODUCTION

In 1991, a new criterion to indicate nuclear fuel leakage during operation was introduced, based on the amount of solid fission products in liquid samples taken during a sipping test [1]. Continuous fuel failure evaluation during operation has two major goals: to detect and remove leaking fuel assemblies that could lead to high activity release or significant fuel loss in operation, and to find the root causes of failures in order to provide feedback and take corrective actions if necessary. Qualitative and quantitative characterization of the state of defected fuel is usually based on three families of nuclides that do not produce significant deposits on the circuit walls and for which correlation between defected rod leakage and activity are easily established [2]. The radionuclides from these families that are easy to measure by gamma spectrometry and can be used in the diagnosis are:

Noble gases:	^{133}Xe, ^{133}Xe^{m}, ^{135}Xe, ^{138}Xe, ^{85}Kr^{m}, ^{87}Kr, ^{88}Kr
Iodine:	^{131}I, ^{132}I, ^{133}I, ^{134}I, ^{135}I
Caesium:	^{134}Cs, ^{137}Cs

As a result of their chemical passivity, the escape of fission noble gases is governed only by physical factors such as diffusion and defect size. In contrast, the escape of the other fission products is influenced both by chemical and physical behaviour: solubility, volatility, chemical affinity, etc. Iodine, in particular, can be easily trapped in the gap between fuel and cladding, and will be released into the primary coolant only if water or steam enters the gap. Other fission products, in large quantities in the fuel — such as those belonging to the alkaline earth group (barium, strontium) or to the lanthanide group (lanthanum, cerium) — are not volatile and have a very low diffusion in uranium dioxide. Therefore, they are not released in appreciable quantities into the primary coolant during normal operating conditions. Nevertheless, into the case of large clad defects, it may happen that water comes into direct contact with oxide fuel pellets, leading to *fuel erosion*. The fissile material is then transferred to the primary coolant together with the contained fission products. Perrotta et al. [3] described the fuel qualification under irradiation by performing only non-destructive tests at the reactor pool. Visual inspection, gamma scanning and sipping were the only tests performed on the fuel assemblies. Galvanic corrosion between a spent fuel plate and a stainless steel storage rack led to corrosion pits along external fuel plates in spite of excellent pool water characteristics [4]. Matsson and Grapengiesser [5] discussed methods for the determination of fission gas release, axial caesium redistribution, and burnup and loss of uranium from failed fuel rods using gamma scanning of irradiated nuclear fuel.

In the work described here, the activity of selected fission products in the primary coolant was determined to provide information on fuel status during operation. Non-destructive (gamma spectrometry) and destructive methods (laser flourimetry, LSC) were used to determine fission products as well as activation products in samples taken from the ET-RR-1 research reactor core water, which were interpreted to indicate possible fuel leakage during operation. Determination of loss of uranium from failed fuel rods is highlighted.

2. EXPERIMENTAL

2.1. Non-destructive methods

Core water samples collected before and after 1 h of full power operation were analysed using a hyperpure germanium (HPGe) detector. One hundred mL of core samples were diluted to 1 L, put in a Marinelli beaker and counted after various decay times (24 h, 2 days, 7 days, 17 days and 1 month). Results were corrected for dead time and decay. The used HPGe crystal had a diameter of 64.5 mm and a length of 69.9 mm, relative efficiency of 40%, peak to Compton ratio 62, and FWHM of 1.9 keV at the 1.33 MeV ^{60}Co transition. Efficiency calibration for the system was performed using a mixed gamma source solution of the same type and configuration to determine the absolute efficiency curve.

2.2. Destructive methods

2.2.1. Laser fluorimetry for uranium analysis

Uranium was determined by laser fluorimetry (Scintrix UA-3), based on the fluorescence of a uranyl complex formed by the addition of a buffered inorganic complexing reagent, FLURAN, to the sample during analysis. Unlike conventional fluorimetry, the excitation source is UV light provided by a nitrogen laser tube, which emits a 337.1 nm pulse. The limit of detection of uranium in water is 0.05 $ng \cdot g^{-1}$ and the precision is about 15% at the $ng \cdot g^{-1}$ level [6]. Samples were fumed with nitric acid and taken up in a $Ca(NO_3)_2$ solution. Uranium was extracted with methyl-isobutyl ketone (MIBK). After stripping uranium from the MIBK solution into 0.001 M nitric acid, it was measured with the laser fluorimeter [7]. Quenching effects caused by interfering elements such as iron, manganese, copper and nickel were eliminated either by dilution or by using an internal standard spike. Uranium concentration ($ng \cdot mL^{-1}$) was calculated using the following formula:

$$U = \frac{D_1}{D_2 - D_1} \frac{V_1}{V_2} C \qquad (1)$$

where

D_1 is the reflection due to sample,
D_2 is the reflection due to sample and standard,
V_1 is the volume of standard addition (mL),
V_2 is the total volume in the cell (mL),
C is the concentration of the standard.

2.2.2. Liquid scintillation counting for strontium analysis

A rapid method was used for the determination of ^{90}Sr through radiochemical separation and energy discrimination of ^{90}Y ($E_{\beta max}$ = 2.28 MeV), applying Cerenkov counting [8]. Y^{3+}, Sr^{2+}, Ba^{2+}, Cs^{+} and La^{3+} (1 mg·mL^{-1}) carriers were added to (1 mL) samples, and yttrium was extracted with tributylphosphate and precipitated with iron — using ethanol and ammonia — as iron oxide and yttrium hydroxide. Yttrium was finally precipitated as yttrium oxalate using 6M HNO_3 and 2% NH_4 oxalate, and given to the LSC for determination of ^{90}Y activity. Strontium-90 decays to ^{90}Y (half-life 64 h) by emission of beta particles with maximum energy of 2.283 MeV, and, for most practical purposes, they are always in equilibrium, which is a significant and useful feature for measurement of ^{90}Sr through Cerenkov counting. This allows discrimination from other beta emitters. A liquid scintillation counter was used (Packard, Tri-Carb 3170 TR/SL).

3. RESULTS AND DISCUSSION

Table I shows average specific activities of radionuclides in core water determined by gamma spectrometry before and after 1 h of full power operation, and previously measured specific activities. Several fission as well as activation products were determined. Long lived fission products (^{137}Cs, ^{90}Sr, ^{60}Co and ^{134}Cs), gaseous and soluble fission products provide essential information in assessing the in-reactor fuel performance. The release of the longest lived isotopes (^{135}Xe (9.14 h), ^{133}I (20.8 h), ^{132}I (2.28 h) and ^{131}I (8.04 days)) is due mainly to fuel failure, and uranium contamination effects can be ignored for these isotopes if no large open failures are present in the core [1]. Short lived fission products, such as ^{97}Zr, ^{133}I and ^{135}Xe, determined after operation, showed elevated concentrations when compared to values before operation and those obtained 10 years ago. The previously determined radionuclides produced in the primary cooling water due to reactor operation reported much lower specific activities of most of the fission products as well as activation products, as shown in Table I. Only 7% of the ^{137}Cs measured in this study was detected, which could be attributed to accumulation over years. This was not the case with ^{134}Cs — an activation product with a shorter half-life — the activities of which were similar before and after operation. The slight decrease in the activity after operation is a matter of spectrum evaluation, since the complicated spectrum and elevated Compton edge affected the statistical evaluation. The differences in ^{24}Na activities were probably due to water quality and the purification system. Seventy percent of the radioactive contaminants were reported to be retained by purification through reactor filter resin [10]. Effective control of water chemistry in the primary system is crucial for maintaining good fuel performance. The primary water chemistry concern for fuel performance is the potential for corrosion related cladding failures and associated excessive hydrogen pickup with resultant embrittlement of the cladding. However, the limits of water chemistry, cladding materials, operating temperature and heat flux have not been fully defined except for specific local applications [1].

The chemical characteristics of the water of the primary cooling system of the ET-RR-1 are given in Table II. The reactor body and the primary conduit pipes are made of aluminium alloy, while the feedwater supply tanks are made of stainless steel 1 × 18H9T sheets that have anti-corrosion properties [10]. Some ions could cause pitting corrosion in stainless steel, such as Cl^- (Fe^{+3}, Cu^{2+}), especially at stagnation condition. Figure 1 shows the specific activities of selected isotopes in reactor core water before and after operation.

It shows that the obtained specific activities of ^{137}Cs, ^{90}Sr, ^{60}Co and ^{134}Cs before and after operation were — to great extent — similar, whereas other radionuclides showed scattered values. About 70% and 84% of the specific activities of ^{137}Cs and ^{90}Sr were registered in core water after operation. The presence of ^{90}Sr in appreciable quantities in the primary coolant might be attributed to large defects in cladding where water could have been in direct contact with the fuel pellets, leading to *fuel erosion*. This might explain the presence of an element belonging to the alkaline earth group, which is not volatile and has a very low diffusion in uranium dioxide. To confirm the obtained results, two water samples from the old and new spent fuel pools were investigated. Figure 2 shows the measured specific activities of ^{137}Cs and ^{90}Sr in the reactor core water and spent-fuel pool water. They showed good agreement between the specific activities of both radionuclides, with an exponential growth trend from core water to spent fuel pool water. Where fuel rods are cracked, ^{90}Sr and ^{137}Cs would be present in water samples from the spent fuel pool. Nevertheless, their presence in reactor coolant water in such quan-

TABLE I. ANALYSIS OF ET-RR-1 REACTOR CORE WATER COLLECTED AFTER 1 h OF OPERATION AT A POWER OF 2 MW

Isotope	Half-life ($T_{1/2}$)	Specific activity before operation (Bq·L^{-1})[a]	Specific activity after operation (Bq·L^{-1})[a]	Specific activity (Bq·L^{-1})[b]	Production modes
Cs-137	30.17 a	18 063 ± 4	26 053 ± 390	1262	Fission
Sr-90	28.15 a	12 703 ± 241	15 210 ± 241	N.D.	Fission
Sr-91	9.5 a	N.D.	125 706 ± 1188	N.D.	Fission
Cs-134	2.06 a	365 ± 3	293 ± 18	1299	Cs-133 (n,γ)
Co-60	5.27 a	66 ± 3	124 ± 15	19425	Co-59 (n,γ)
Mo-99	66.02 h	N.D.	16 343 ± 269	N.D.	Mo-98 (n,γ); Fission
Zr-97	16.74 h	N.D.	375 798 ± 171	N.D.	Zr-96 (n,γ); Fission
Zr-95	64.09 d	1251 ± 2	20 226 ± 202		Zr-94 (n,γ); Fission
I-131	8.04 d	314 ± 1	28 597 ± 247	20 276	Fission Precursor: Te-131 ($T_{1/2}$ 24.99m)
I-133	20 h	N.D.	2 142 238 ± 1484	3 922	Fission
Na-24	14.96 h		559 845 ± 557	13 4310	Na-23 (n,γ); Mg-24 (n, p); Al-27(n,α)
La-140	40 h	475 ± 1			La-139 (n,γ); Fission,
	(24 h after collection)		36 084 ± 299	13 786	Precursor: Ba-140 ($T_{1/2}$ 12.75d)
	(3 d after collection)		199 023 ± 448		Buildup
Ba-140	12.75 d	492 ± 3	53 771 ± 870	12965	Fission
Xe-135	9.14 h		241 110 ± 215		Xe-134 (n,γ); Fission
Ce-144	284.9 d	8468 ± 6	8543 ± 233	N.D.	Fission
Nb-95	34.9 d		10 632 ± 104	N.D.	Zr-94 (n,γ); Fission Precursor: Zr-95
Np-239	2.36 d		207 632 ± 63 308	123 025	U-238 (n,γ) Precursor: U-239 ($T_{1/2}$ 23.47m)
Zn-65	243.9 d	153 ± 1			Zn-64 (n,γ)
Sb-125	2.73 a	2087			Sn-124 (n,γ); Sb-123(2n,γ); Fission, Precursor: Sn-125 ($T_{1/2}$ 9.64 d)
U total		11.1 ± 0.1	20		Natural

[a] Results of water samples corrected for radioactive decay to collection date, n = 4.

[b] Radionuclides in ET-RR-1 primary cooling water [8].

TABLE II. SPECIFICATIONS OF WATER SUPPLY TO THE PRIMARY COOLING SYSTEM [10]

Electrical conductivity	<2 346[a] <2[b]	$\mu S \cdot cm^{-1}$
pH	5.5–6.5 7.1[a] 4.5–7.5[b]	
Al^{3+}	<0.05 5.8[a]	ppm
Cu^{2+}	<0.02 0.1[a]	ppm
C^-	<0.05 17[a]	ppm
Fe^{2+}	<0.05 0.4[a]	ppm

[a] The tap water of Inshass site feedwater.

[b] The IAEA limiting condition for 2 MW pool reactor.

tities should not be considered normal. The ratios of $^{90}Sr/^{137}Cs$ among the investigated samples were 70, 58, 96 and 88% for core water before operation, core water after operation, new spent fuel pool and old spent fuel pool, respectively. The roughly estimated release rate of ^{137}Cs in the ET-RR-1 core water would lead to about 8.14 $mBq \cdot mL^{-1} \cdot h^{-1}$. Perrotta et al. [3] recorded a maximum release rate of 11.8 $mBq \cdot mL^{-1} \cdot h^{-1}$ of ^{137} Cs in sipping tests of the IEA-R1 spent fuel. The allowable coolant or off-gas activity during normal operation can be different from plant to plant and from one country to another: 37 $kBq \cdot cm^{-3}$ (dose equivalent ^{131}I) is a typical coolant activity limit in the USA, but half this value is sometimes used in Europe. The limitations on the specific activity of the reactor coolant or off-gas minimize personnel exposure and ensure that the resulting dose at the site boundary will not exceed an appropriately small fraction of dose guideline values following a reactor incident [1].

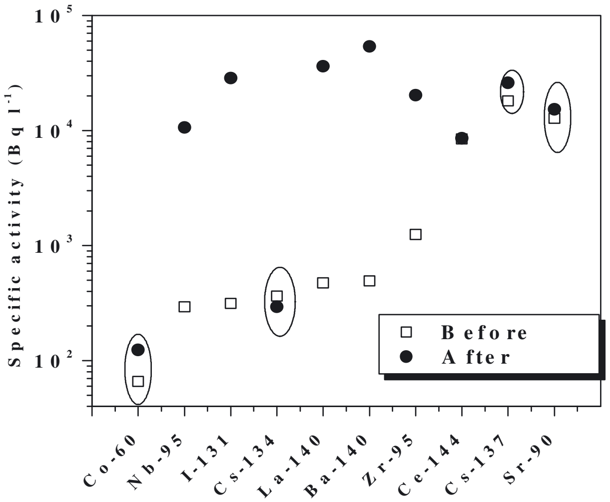

FIG. 1. *Specific activities of selected radionuclides in reactor core water before and after operation.*

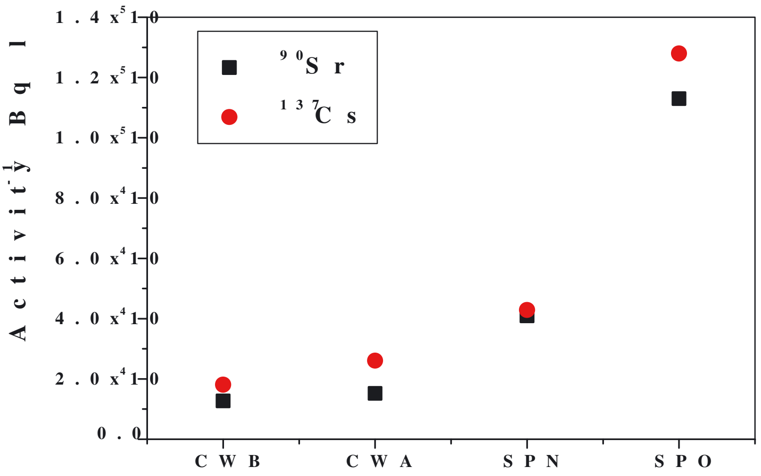

FIG. 2. *Specific activities of ^{137}Cs and ^{90}Sr in the reactor core water and spent fuel pool water, CWB is core water before operation, CWA is core water after operation, SPN is new spent fuel pool and SPO is old spent fuel pool.*

4. CONCLUSIONS

Releases of some fission products, such as ^{137}Cs and ^{131}I, into coolant water can indicate the presence of corrosion pits along the external fuel clad. In spite of its chemical passivity, ^{135}Xe — as a one of the fission noble gases — has been detected in coolant water. Its release is governed by physical factors such as diffusion and defect size. The escape of ^{239}Np is a good indicator of degraded fuel conditions and fuel loss. The presence of ^{90}Sr in both reactor coolant and spent fuel pool water may be related to fuel erosion. The fissile material is then dispersed in the primary coolant together with the contained fission products. The presence of about 70% of the ^{137}Cs in reactor coolant before operation would indicate buildup and, consequently, a relatively long term release. The reliability of the purification system and the water chemistry in the primary system is critically important for maintaining good fuel performance. This could be a potential cause for corrosion related cladding failures and associated excessive hydrogen pickup with resultant embrittlement of the cladding.

5. RECOMMENDATIONS

A detailed study, based on operating runs with various working conditions of the ET-RR-1, was essential to reach a definite conclusion. Possible fuel leakage in operation, based on the amount of solid fission products in the liquid samples taken during a sipping test, could be determined in addition to fuel element scanning to visualize the defect. This would allow fuel failure evaluation, possible identification of the leaking fuel assemblies which could be the reason for the released high activity or significant fuel loss in operation, and finding the root causes of failures in order to provide feedback and take any necessary corrective actions. Intensive analysis of the ionic filter used in the primary system, as well as water samples before and after the filter, are highly recommended.

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DETERMINATION OF THE PLUTONIUM CONTENT OF PLUTONIUM–BERYLLIUM NEUTRON SOURCES: A FEASIBILITY STUDY

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Abstract

A non-destructive method of analysing sealed plutonium–beryllium sources is under development, using a combination of γ spectrometric determination of the plutonium isotope composition and neutron counting. A passive neutron collar was designed with nine ^{3}He counters embedded in a polyethylene moderator surrounding the sources to be measured. The measurement cavity is lined with cadmium to shield the source against slow neutrons diffusing backwards from the moderator. The electronics consist of a home-made, nine channel chain of pulse amplifiers and discriminators as well as a commercial shift register. The determination of plutonium content seems to be possible by establishing the neutron yield of the sources on the basis of total neutron counting, by adopting specific (γ,n) reaction yields of individual plutonium (and americium) isotopes from the literature. The coincidence counts are due to self-multiplication, i.e. neutron induced fission of the odd plutonium isotopes.

1. INTRODUCTION

Plutonium–beryllium sources are causing concern both for safeguard reasons and as a result of illicit trafficking. Many sealed plutonium–beryllium neutron sources were exported from the former Soviet Union to Hungary between 1960 and 1985. These sources are now mostly out of use, and have been acquired for temporary storage at our institute. Their plutonium content is to be accounted for and regularly reported to, and inspected by, the IAEA. However, the plutonium contents of the Soviet-made sources are not known; only the original neutron yields are given. The bookkeeping is still based on a calculation starting from the neutron yield, using a specific yield value of 6.17×10^{4} n/s per g plutonium informally given by the manufacturer. Since the conversion factor for ^{239}Pu is 6.17×10^{-2} Ci/g, this corresponds to the lower limit of the (γ,n) specific yield given as 1 to 2×10^{6} n/s per Ci for ^{239}Pu–beryllium sources in the literature, implying at the same time that assumed pure ^{239}Pu contents were considered. However, since the γ activities of the various plutonium isotopes differ substantially, the neutron yield depends very much on the actual isotopic composition. Therefore, our aim was to study the possibility of developing a non-destructive assay for determining the plutonium content of plutonium–beryllium sources. To our knowledge, such a method is not described in the literature.

After the determination of the isotopic composition by high resolution γ ray spectrometry, we tried to establish plutonium content by combining the results with neutron measurements. It was also necessary to adopt specific (γ,n) reaction yields for the other plutonium isotopes. For ^{238}Pu and ^{240}Pu, the lowest values found in the literature, 3.36×10^7 and 3.5×10^5 n/s per g, respectively, were taken. The ^{241}Pu and ^{242}Pu yields were not considered; they were of the order of 10^3 and negligible at the usual isotopic ratios. Similarly, the neutron yields from spontaneous fission of the even isotopes were neglected.

2. DETERMINATION OF ISOTOPIC COMPOSITION

Large-area planar (50 mm diameter, 20 mm thick) and coaxial (47 cm^3) germanium detectors were used, shielded with cadmium foil to prevent them from neutron induced damage. In addition, the cadmium shield improved the quality of the evaluation by decreasing the high intensity 60 keV peak of ^{241}Am. Spectra were taken for 10–15 min counting time at 50 to 60 cm source to detector distances, while the sources were out of their containers. Sources of up to 66 g (real) plutonium content were examined, and three with nominal plutonium contents of 37, 85 and 178 g; the measured isotopic compositions are indicated in Table I. The isotopic compositions were evaluated by the commercial MGA^{++} program. The data were extrapolated back to the dates of production, because the decays of ^{238}Pu (half-life 87.7 a) and ^{241}Pu (half-life 14.3 a) during the elapsed times could not be neglected. The actual neutron yields were calculated taking into account the decay of ^{238}Pu and the production of ^{241}Am, adopting a yield value of 6.65×10^6 n/s per g for the latter. The calculated and measured ^{241}Am contents were in good agreement with the assumption that most of the freshly produced sources did not contain americium.

The original neutron yields originally had a 10% uncertainty. These and the actual data, both measured and calculated, as well as the actual plutonium contents determined on the basis of the measured isotopic composition, are indicated in Table II. The uncertainties were less, since they did not include the unknown uncertainties of the specific neutron yields of the individual isotopes.

The nominal plutonium contents still being recorded in the files were much higher than the real (or at least more realistic) data.

TABLE I. ORIGINAL AND ACTUAL ISOTOPIC COMPOSITIONS OF NEUTRON SOURCES

	Isotopic composition					
Source	Nominal “37”g		Nominal “85”g		Nominal “178”g	
Isotope	actual	original	actual	original	actual	original
^{238}Pu	0.99 ± 9%	1.212 ± 10%	0.00757 ± 74%	0.0102 ± 80%	1.315 ± 3.3%	1.566 ± 4%
^{239}Pu	77.98 ± 3%	75.91 ± 3%	94.91 ± 0.2%	94.817 ± 0.2%	75.7 ± 1.2%	73.4 ± 1.2%
^{240}Pu	18.9 ± 11%	18.4 ± 11%	5.012 ± 4.55%	5.002 ± 4.5%	20.24 ± 3.8%	19.62 ± 3.8%
^{241}Pu	0.652 ± 12%	3.04 ± 20%	0.04 ± 6.44%	0.2271 ± 9%	0.828 ± 5.9%	3.57 ± 10%
^{242}Pu	1.48 ± 10%	1.44 ± 10%	0.01673 ± 10%	0.01670 ± 10%	1.92 ± 10%	1.86 ± 10%
^{241}Am	2.48 ± 8.7%	—	0.2179 ± 2.4%	0.03 ± 2.4%	2.96 ± 3.3%	—
^{235}U	—	—	—	—	10.76 ± 28%	10.76 ± 28%

TABLE II. ORIGINAL AND ACTUAL NEUTRON YIELDS OF THE SOURCES AND THEIR TOTAL PLUTONIUM CONTENTS

Source (nominal)	Original neutron yield (n/s)	Plutonium content (g)	Actual calculated neutron yield (n/s)	Actual measured neutron yield (n/s)
“37” g	$(2.6 \pm 0.26) \times 10^6$	4.36 ± 0.56	$(2.6 \pm 0.4) \times 10^6$	$(2.58 \pm 0.26) \times 10^6$
“85” g	$(5.27 \pm 0.53) \times 10^6$	66.45 ± 7	$(5.5 \pm 0.7) \times 10^6$	$(6.49 \pm 0.65) \times 10^6$
“178” g	$(1.1 \pm 0.11) \times 10^7$	17.2 ± 1.8	$(1.25 \pm 0.14) \times 10^7$	$(1.38 \pm 0.14) \times 10^7$

3. NEUTRON MEASUREMENTS

A passive neutron collar was designed with nine ^{3}He counters embedded in a moderator surrounding the sources to be measured. A double-walled cylinder of 25 cm diameter by 42 cm height and 1.5 cm thickness was made of moderating polyamide (TerraMid, density 1.2), provided with a lid and a bottom plate. The inner cylinder, 8.8 cm diameter, accommodated the sources to be measured. The cavity was lined with cadmium to shield the source against slow neutrons diffusing backwards from the moderator. Empty spaces within the tubes were filled with granular polyethylene (density 0.6).

A nine-channel signal processing unit, consisting of preamplifier–amplifier–discriminator chains, was built and connected to the detectors. The independent channels have the advantage of diminishing signal processing dead time. A commercial shift register was used for coincidence counting.

The thickness of the moderator arrangement was chosen so that detection efficiency would be limited to between 2 and 4%, and so that the coincidence dead time would not to be too high, taking into account expected counting rates from sources with yields of 10^5 to 10^7 n/s. On the other hand, the moderator thickness should not be such that detection efficiency is too low, or coincidence rates would likewise be too low. As a compromise, the present arrangement resulted in a neutron die-away time of 70 μs, measured by a ^{252}Cf source. The gate length of the shift register was accordingly set to 64 μs. The total and coincidence dead times were established as 0.37 and 2.1 μs, respectively, with the aid of two ^{252}Cf sources of strengths differing by an order of magnitude. A counting efficiency of 2.6% was determined using plutonium–beryllium sources. The stability of the system and the reproducibility of the results were studied by taking out the sources and re-inserting them in the measurement position, and good agreements were obtained. Also, the results of the simultaneous measurements of several sources agreed well with the summed-up counts of single measurements.

The actual neutron yields of the sources were determined on the basis of the total counts. Agreements with calculated values were reasonable (Table II). Deviations between the measured and calculated yields increased with plutonium content, possibly due to a moderating effect of beryllium.

The coincidence counts were also recorded, but their interpretation is difficult. The contribution of spontaneous fission neutrons from the even plutonium isotopes to the number of coincidences was estimated to be of the order of 10^{-3} relative intensity, i.e. fully negligible. Hence, determination of the ^{240}Pu$_{eff}$ content is impossible. For all practical purposes, neutron induced fission of the odd plutonium isotopes, i.e. self-multiplication, was responsible for the coincidences. Further experiments and studies are under way in order to solve this problem and to find an independent method, utilizing the recorded coincidences for the determination of the odd plutonium isotope content. It is expected that the method could be used for safeguards verification and for determining the plutonium content of smuggled and seized or accidentally found samples, or of those of lost documentation.

IAEA-CN-98/9P

LABORATORY METHODS APPLIED TO QUALITATIVE AND QUANTITATIVE ANALYSES OF SEIZED NUCLEAR MATERIALS AND RADIOACTIVE SOURCES

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Abstract

The National Radiation Hygiene Preparedness Service, operated by the National Research Institute for Radiobiology and Radiohygiene and the alpha and gamma spectrometric laboratories of the Institute, plays a central role in the detection and identification of illicit nuclear substances and radioactive sources found in Hungary. The first measurements of seized nuclear material were made in 1990–1991. Since then, a few dozen cases have been investigated. The calibration of the gamma spectrometer and results from characteristic cases are detailed. Investigated uranium samples can be divided into three main groups, according to the ratios of uranium isotopes of mass numbers 235 and 238: CANDU type pellets, boiling water reactor or pressurized water reactor type pellets, and samples of depleted uranium.

1. LEGISLATION AND ORGANIZATIONAL BACKGROUND

Smuggled nuclear or radioactive material can be interdicted in the following ways:

- On-site investigation by the National Radiation Hygiene Preparedness Service (NRHPS) following a warning signal from a monitoring system at a border station;
- Notification from law enforcement agencies or national security services.

The process of monitoring for illicit trafficking of nuclear materials or lost radioactive sources can be divided as follows:

- On-site detection of nuclear or radioactive substances with hand-held or otherwise portable measuring devices, installed monitors, etc.;
- Identification of the type, activity and quantity of the material by in situ or laboratory analysis.

The NRHPS is operated by the National Research Institute for Radiobiology and Radiohygiene (NRIRR) on a 24 h basis. The main task of the NRHPS is the determination of duties and supervision of cleanup as a consequence of incidents or accidents involving radioactive substances or equipment emitting ionizing radiation, with the exception of incidents, including emergencies, in nuclear facilities.

Hungarian regulations dictate that initial investigation of seized or found radioactive material is performed at the NRIRR; subsequently, the material is transported to the Institute of Isotopes of the Hungarian Academy of Sciences for further analysis and storage. The main goal of the initial investigation is identification of the main nuclear and other characteristics of the seized substance to decide whether it falls within the scope of the Atomic Energy Act.

2. METHODS OF ANALYSIS

On-site and initial laboratory investigations of seized or found radioactive material must be reliable and rapid — there is insufficient time for sophisticated radioanalytical methods, such as alpha spectrometry.

The main investigational tool for identification of seized radioactive material at our laboratory is gamma spectrometry. Instead of the usual gamma spectrometric measuring equipment for environmental or other small samples, a totally shielded whole body counter is available to ensure a flexible geometry and for sources of large size or very high activity [1]. The whole body counter requires special calibration methods and care is needed to avoid contamination of the equipment.

The types of seized nuclear or radioactive substances investigated at our laboratory have been mainly non-irradiated uranium fuel element pellets of various ^{235}U enrichment, and closed ^{226}Ra radioactive sources.

Gamma spectrometric analysis of uranium pellets required different features in comparison with measurement of environmental samples containing natural uranium, such as:

- Different attenuation as a function of gamma energy due to much higher self-absorption from high physical density and atomic number;
- The absence of most of the easily measurable gamma emitting daughters;
- Ratios of ^{235}U to ^{238}U different from natural values.

A consequence of the above is the inadequacy of special nuclide libraries and photoenergy efficiency calibration curves derived for natural radionuclides in environmental samples.

The quantitative analysis of uranium pellets needs an approach different from the rapid, simple method developed for measurement of ^{235}U enrichment in arbitrary samples [2]. Our efficiency calibration for laboratory investigation of uranium pellets was performed with a thin layer sample prepared by precipitation and based on radiochemical preparation and alpha spectrometric measurement of the sample, using the nuclear decay characteristics of the radionuclides [3]. Knowing the chemical yield, and consequently the activity of this thin sample, the total activity of the original sample is calculated. The decay properties of gamma rays used for calibration and for quantitative analysis of sized uranium samples are listed in Table I.

The efficiency calibration curves used for the analysis of environmental samples and of uranium pellets are shown in Fig. 1. Gamma ray efficiency for the uranium pellets steadily increased as a function of energy, whereas the efficiency curve for thin or environmental samples generally peaked in the 60 to 80 keV region.

3. RESULTS

The main radionuclides in samples investigated at the NRIRR were: ^{235}U, ^{238}U, ^{234}Th and ^{234m}Pa (uranium pellets), and ^{226}Ra (found radioactive sources).

Data generated with seized nuclear substances are summarized in Table II. It is noteworthy that smuggling of uranium pellets in Hungary was most common in the early 1990s.

TABLE I. MAIN NUCLEAR CHARACTERISTICS OF GAMMA RAYS USED FOR EFFICIENCY CALIBRATION AND GAMMA SPECTROMETRIC ANALYSIS OF NUCLEAR MATERIALS [3]

Radionuclide	Half-life	Gamma energy (keV)	Abundance
U-235	2.57×10^{11} d	143.8	0.105
		163.3	0.047
		185.7	0.54
		205.3	0.047
Th-234 (U-238)	2.41×10^{1} d	63.3	0.0381
Pa-234m (U-238)	8.13×10^{-4} d	766.6	0.00207
		1001	0.00589

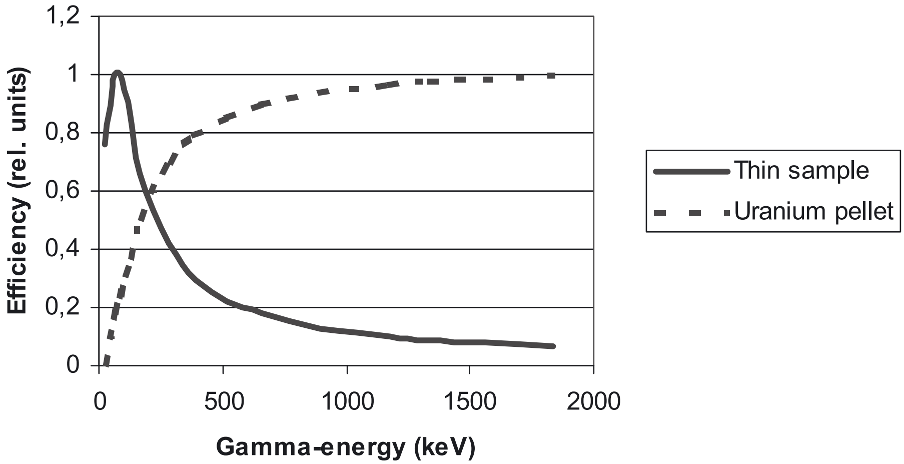

FIG. 1. Gamma ray efficiency curves for a thin environmental sample and for uranium pellets in relative units.

The uranium samples investigated can be divided into three main groups according to N_{235}/N_{238} ratio (Table II):

TABLE II. MAIN PHYSICAL AND NUCLEAR CHARACTERISTICS OF THE INVESTIGATED NUCLEAR SUBSTANCES

Case No.	Dimensions (D × L) (mm)	Density ($g{\cdot}cm^{-3}$)	Specific activity (kBq/g)		N_{235}/N_{238} (%)
			U-235	U-238	
1	12.2 × 13.2	10.5	0.59 ± 0.02	12.2 ± 0.6	0.76 ± 0.07
2	11.1 × [a]	2.3	0.083 ± 0.004	1.80 ± 0.20	0.72 ± 0.10
3	[b]	10.4	2.8 ± 0.17	12.2 ± 1.3	3.6 ± 0.7
4	11.5 × 14.2	10.2	1.0 ± 0.1	9.0 ± 1.3	1.7 ± 0.4
5	11.4 × 14.3	10.4	1.1 ± 0.1	10.0 ± 1.0	1.7 ± 0.3
6	7.4 × 10.2	10.3	2.9 ± 0.2	12.0 ± 2.2	3.8 ± 0.8
7	175 × 115[c]	—	—	—	0.2–0.3
8	11.4 × 14.3	10.4	1.4 ± 0.1	11.0 ± 1.2	2.0 ± 0.3
9	5.7 × 10.4	2.7	0.16 ± 0.01	11.6 ± 1.5	0.22 ± 0.04
10	11.5 × 14.2	10.2	1.2 ± 0.15	10.7 ± 1.0	1.8 ± 0.3

[a] The pellets had different lengths.

[b] Two pellets with different diameters and lengths.

[c] The nuclear material was built into a lead and steel container.

The pellets from the first group (1 and 2) were presumably of the CANDU type as they contained natural uranium.

The samples of the second group (3–8 and 10), containing slightly enriched uranium (1.7–3.8%), were probably fuel element pellets for conventional PWRs and BWRs.

The pellets of sample 9, containing depleted uranium, originated probably from by-products of fuel element fabrication. Sample 7 was a container filled with depleted uranium for radiation shield purposes.

Investigation of seized or found radioactive sources in two cases indicated the presence of ^{226}Ra with average activities of 15 and 580 kBq. Because of irregular source geometry, quasi-point-source geometry was used for calibration and for identification. We were able to give only approximate activities in these cases; however, it was possible to qualify the radioactive sources, whether or not they fell within the scope of Hungary's Atomic Energy Act.

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PROMPT GAMMA NEUTRON ACTIVATION ANALYSIS AS AN ACTIVE INTERROGATION TECHNIQUE FOR NUCLEAR MATERIALS

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Abstract

Prompt gamma neutron activation analysis (PGAA) is proposed as an instant, non-destructive method for the analysis of fissile materials and fission products. Measurements by PGAA were made on technetium and uranium compounds, the latter with various enrichments. Measurements were carried out in thermal and cold neutron beams at the Budapest Research Reactor. A beam chopper was used to collect the delayed decay gamma radiation from short lived nuclides separately. Accurate partial gamma ray production cross-sections were determined with internal standardization for a set of prompt and decay gamma rays following neutron capture in ^{235}U, ^{238}U and ^{99}Tc and compared to those from the literature. In the case of ^{235}U fission, prompt gamma lines were also applied. These cross-sections can be used for non-destructive analyses of uranium and technetium and also for the determination of the enrichment of uranium by prompt gamma activation analysis and neutron activation analysis.

1. INTRODUCTION

Uranium is the most frequently used fissile material for nuclear energy production. Therefore, its assay is of great importance. The analyses must provide the amount of uranium in the sample and the mass ratio of the uranium isotopes. Nuclear analytical methods counting the radiation (typically gamma photons) may answer both questions.

Passive interrogation techniques, based on the analysis of natural radioactive decay gamma rays from the major isotopes of uranium, have long been used in nuclear safeguards [1]. Due to the small decay constants of ^{235}U and ^{238}U, the specific activities are low; therefore, the acquisition of the gamma spectrum is a lengthy procedure. Moreover, gamma rays emitted during natural decay are of relatively low energy, therefore their attenuation within the sample can be significant, which makes evaluation uncertain in some cases.

Many active interrogation techniques are based on activation with neutrons. Uranium-238 has a medium capture cross-section (2.68 b) [2, 3], so the prompt gamma radiation induced by the neutrons enables an accurate determination of this isotope, if it is a major component. The decay gamma rays from the daughter nuclides of ^{239}U can also be used for the purpose of analysis. Uranium-235 has a high capture cross-section (99 b). However, the fission cross-section is even higher (583 b) [2], which makes possible the assay of low enrichment uranium (LEU) as well. The decay gamma rays from fission products are also useful for analysis.

A technique based on counting decay gamma rays induced by neutron absorption has already been developed [4]. In the neutron activation analysis of uranium, the decay gamma rays of ^{239}Np produced after neutron capture by ^{238}U, and of ^{140}Ba, produced in the fission of ^{235}U, are counted. Because of interferences caused by short lived nuclides, the counting of the activated samples must be performed after 1 day, and again after 1 and 2 weeks, which makes the analysis rather time consuming.

The artificial radionuclide ^{99}Tc is important from many viewpoints. Its 6 h isomer, ^{99}Tc^{m}, is the most frequently used radioisotope in diagnostic nuclear medicine. Both forms are produced in nuclear fission, partly independently but mostly via the beta decay of ^{99}Mo. Along with ^{129}I, ^{99}Tc constitutes 95% of the long lived (>500 years) nuclear waste from pressurized water moderated reactors. Its ability to migrate and the efficient uptake by living organisms make ^{99}Tc a hazardous radiotoxic material. Furthermore, the extremely long half-life (2.1×10^5 years), the low beta decay endpoint energy (294 keV), and the single weak (6.5×10^{-4}%) low energy (89.5 keV) gamma ray [5], superimposed on a high bremsstrahlung background, make difficult the non-destructive assay of ^{99}Tc using passive nuclear methods.

Fortunately, ^{99}Tc can be transformed by neutron capture into ^{100}Tc, which decays with a 15 s half-life to stable ^{100}Ru. This is the basis of transmutation of technetium contained in nuclear waste [5]. The γ radiations produced can, in principle, be used for assaying technetium. The neutron activation analysis (NAA) technique has been applied in the TARC (Transmutation by Adiabatic Resonance Crossing) experiment at CERN [6] for controlling the transmutation process.

Another non-destructive technique, PGAA, is proposed in this paper for the assay of nuclear materials. It is also an active method; the sample is irradiated in a neutron beam. Prompt gamma rays, from neutron capture or fission, and the decay gamma radiations from the radionuclides are detected. Using a beam chopper, the decay gamma rays can be acquired separately, so the spectral interferences with prompt gamma rays can be identified. Both the element content and the isotope ratio can be determined using high energy gamma rays, which are not perturbed by self-absorption. As in most cases in which PGAA is used, no sample preparation is needed. Moreover, the analysis can be performed even on samples held in containers made of material of low cross-section. In the present work, accurate partial cross-sections have been determined for the major gamma rays from ^{235,238}U(n,γ) capture and ^{235}U(n,f) fission reactions as well as the ^{99}Tc(n,γ) capture reaction, and the subsequent beta decays for PGAA and NAA, respectively.

2. EXPERIMENTAL

The samples were irradiated in the PGAA facility at the Budapest Research Reactor using both thermal and cold neutron beams. The former [7] had a thermal equivalent neutron flux of 2×10^6 cm$^{-2}\cdot$s^{-1}. The gamma rays were detected with a Compton suppressed HPGe detector placed at 23.5 cm from the target [7]. The new cold beam had a thermal equivalent neutron flux of 5×10^7 cm$^{-2}\cdot$s^{-1}. The detector system remained unchanged.

A beam chopper [8] was used in some of the measurements. The activation or in-beam phase was set to 50% of the full period. Two types of spectra were collected simultaneously. The two 40% long counting periods were set in the middle of the activation and the decay phases, respectively. In the activation phase, the detector collected the prompt radiation and the decay radiation at the same time, while in the decay phase only the decay gamma rays were detected. Due to the 5% delay in counting after the beam was shut off, the recording of prompt radiation induced by even the slowest neutrons was avoided. In the activation phase, the count rate was significantly higher than in the decay phase. The frequency of the chopper was set to 25 Hz. This resulted in a 20 ms activation phase and 16 ms counting phases for both types of spectrum.

In all cases, the spectra were evaluated using the Hypermet PC program [9]. To obtain emission rates, peak areas were corrected for counting efficiency [10] and also for saturation of activity [11]. Spectra acquired in the chopped beam also needed correction for various dead, activation, and counting times.

2.1. Measurement of uranium

Figure 1 shows spectra acquired during the activation and decay phases of a chopped beam PGAA measurement of a U_3O_8 sample with an enrichment of 95%. Since the half-lives of the most important fission products are typically longer than a second, the activity of the sample remained practically constant during the decay phase. The count rate of the decay spectrum is an order of

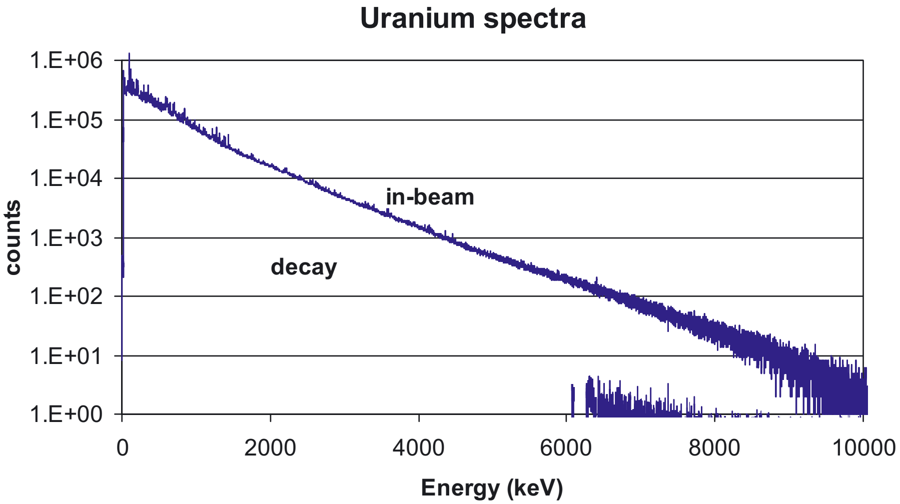

FIG. 1. Uranium spectra acquired in prompt gamma measurement in a chopped neutron beam. Upper spectrum: activation phase, lower spectrum: decay phase.

magnitude lower, which makes the evaluation of the spectrum easier. Chopped beam PGAA investigations of enriched uranium samples are in progress.

Uranium compounds with different enrichments were irradiated in both beams, as shown in Table I. Compounds of known stoichiometry were used for the determination of partial gamma ray production cross-sections of the major gamma lines via internal standardization. Hydrogen, emitting a single 2223 keV gamma ray, is an ideal comparator, as its total capture cross-section is also accurately known [2, 3]. The procedure and its validation are described elsewhere [12–14]. Uranium oxide samples of various enrichments were irradiated to obtain an enrichment calibration curve, derived from the peak count ratios of the gamma lines of both isotopes.

After irradiation, all samples were counted to measure the decay radiation from long lived isotopes. Several such decay measurements were performed: the first immediately after irradiation, and three others after 1 day, 1 week and 2 weeks cooling, as prescribed in the procedure for NAA of uranium [4]. Quantities of the two isotopes were also determined from the natural radioactivity [1].

2.2. Measurement of technetium

In the case of technetium, ammonium pertechnetate (NH_4TcO_4) was chosen as the standardizing compound due to its chemical stability. Partial

TABLE I. URANIUM SAMPLES IRRADIATED AT THE THERMAL AND COLD NEUTRON PGAA FACILITIES IN BUDAPEST

Chemical form	Enrichment	Neutron beam	Purpose
U_3O_8	Natural	Thermal	Enrichment calibration
U_3O_8	19.1%	Thermal	Enrichment calibration
U_3O_8	36%	Thermal	Enrichment calibration
$UO_2\,(NO_3)_2 \cdot 6H_2O$	Natural	Thermal	Standardization
$UO_2\,(CH_3COO)_2 \cdot 6H_2O$	Natural	Thermal	Standardization
$UO_2\,(CH_3COO)_2 \cdot 6H_2O$	Natural	Cold Cold chopped	Standardization
U_3O_8	~95%	Cold Cold chopped	Fission product identification

cross-sections for the strong 172, 223 and 263 keV capture gamma rays [15, 16] as well as for the 539 and 591 keV gamma rays from ^{100}Tc decay [17] were determined from the same in-beam spectrum. The spectrum shown in Fig. 2 was collected in the cold beam for about 18.5 h to attain the best possible statistics. Self-absorption in the target amounted to a few percent at the lowest energies, and was accounted for by calculation using the PC code XMuDat [18].

In order to reveal possible interferences, the prompt (capture) and decay gamma rays were studied in greater detail by using a target of metallic ^{99}Tc (supplied by Oak Ridge National Laboratory, USA). An 0.5 g aliquot was pressed into a disc of 13 mm diameter and encapsulated in an aluminium container with a wall thickness of 0.2 mm. Applying a beam chopper, the in-beam spectrum (containing prompt and decay gamma lines together) and the off-beam decay spectrum could be collected simultaneously. A background spectrum was also measured under similar conditions. No contaminants were found to disturb the gamma rays of interest, nor did the major prompt and decay lines interfere.

Finally, the spontaneous decay of ^{99}Tc was also measured, using an unshielded, smaller (15% efficiency) HPGe detector with a thin carbon fibre

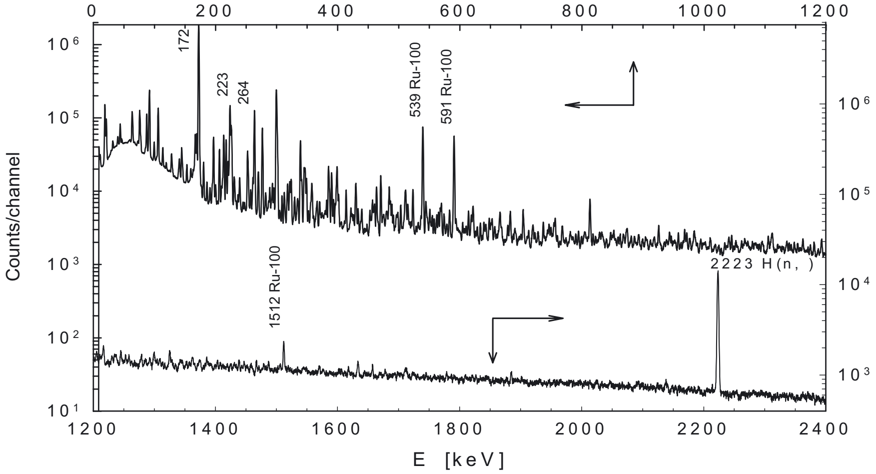

FIG. 2. Gamma ray spectrum from the ^{99}Tc(n,g) reaction using an ammonium pertechnetate target. The ^{100}Tc decay lines are labelled by the excited product nucleus ^{100}Ru.

window at a similar target to detector distance. The count rate for the 89.5 keV gamma ray, adjusted for the standard spectrometer, served as the basis of comparison of analytical sensitivities.

3. RESULTS AND DISCUSSION

The partial gamma ray production cross-sections for the major gamma lines from the irradiated uranium and technetium were determined relative to the 2223 keV gamma line of hydrogen. The ratio of partial gamma ray production cross-sections equals the ratio of emission rates multiplied by the molar ratio [9]. The following data were used: neutron capture cross-section of hydrogen, 0.3326(7) b [2, 3]; H/U molar ratio in uranyl acetate, 10; H/Tc ratio in ammonium pertechnetate, 4; mass of the samples, 424 mg and 112 mg, respectively.

3.1. Uranium

A set of prompt gamma lines from neutron capture and fission and of decay gamma lines from daughter nuclides of ^{239}U and fission products of ^{235}U was selected. The gamma lines were identified using an Evaluated Nuclear Structure Data File (ENSDF) [19]. The spectral interferences were resolved by comparing the spectra acquired in the activation and decay phases of the chopped beam measurements. In some cases, the interfering lines were also used, provided that the contributing components were identifiable. Emission rates and partial gamma ray production cross-sections were calculated from the peak areas. Whenever accurate literature data were available, the same quantities were also determined using the fission and capture cross-sections [2, 3], the fission yields [20] and the gamma yields [19]. The partial gamma ray production cross-sections calculated from the present measurements and from the literature data are listed for comparison in Table II. The lines observed in the spectra acquired during the in-beam activation were more intense; their count rates were at least an order of magnitude higher than those attained with NAA and passive counting.

The proposed PGAA method was validated in two ways. First, the decay lines from natural radioactivity were counted. Their rates are also shown in Table II. After correction for self-absorption [18], the mass ratio of the uranium isotopes was determined from the count rates of the 186 keV and 92 keV peaks. The calculated value of 0.71 ± 0.02% agrees well with the natural isotopic ratio. Masses calculated from the neutron flux and the partial cross-sections, and also from the emission rates of the natural decay lines, agreed well with those calculated from the chemical composition and the total mass of the sample.

A series of PGAA measurements were also performed in the thermal beam on U_3O_8 samples of various enrichments: natural, 19.1% and 36%. A calibration curve was constructed for $^{235}U/^{238}U$ mass ratio versus the count rate ratios of the highest energy capture prompt gamma lines. The 4060 keV peak was used in the case of ^{238}U, and the 6395 keV peak for ^{235}U. The advantage of using these high energy gamma rays is that their absorption in the sample is

TABLE II. COUNT RATES AND PARTIAL GAMMA RAY PRODUCTION CROSS-SECTIONS (σ_γ) FOR DIFFERENT GAMMA RAYS DETECTED DURING THE IN-BEAM ACTIVATION OF NATURAL URANYL ACETATE COMPARED TO LITERATURE DATA

Orig. nuclide	Parent nuclide	Type of meas.[a]	Cooling time	Meas. time	Energy (keV)	Half-life	Peak count rate (cps)	Meas. σ_γ (b)	Calc. σ_γ (b)
^{238}U	^{239}U	P		24 h	4060	0	0.994(4)	0.191(2)	
	^{239}Np	D	23 h	64 h	278	2.36 d	0.0740(10)	0.382(6)	0.383(6)
	^{234}Th	N		69 h	92	4.468×10^9 a	0.0450(11)		
^{235}U	^{236}U	P		24 h	6395	0	0.0112(5)	0.0038(2)	
	^{134}Te	CP–CD		4.1 h	297	0	1.60(16)	0.22(2)	0.22(2)
	^{134}Te	CP		4.1 h	1279	0	0.49(2)	0.20(1)	0.22(2)
	^{140}Ba	D	211 h	69 h	537	12.75 d	0.0122(5)	0.066(3)	0.064(1)
	^{235}U	N		69 h	186	7.037×10^8 a	0.073(1)		

[a] P: PGAA measurement; D: decay measurement; CP: chopped beam PGAA (activation phase); CD: chopped beam PGAA (decay phase); N: natural radioactivity.

weak; thus the measurement is insensitive to sample size, geometry, and even the packing material. The 4060 keV prompt gamma line overlaps with a decay line of the short lived ^{90}Rb nuclide. The interference was corrected using the 4135 keV peak of the same nuclide, and the intensity ratios were taken from ENSDF [19]. The following equation was formulated:

$$I_{net}(4060) = I_{tot}(4060) - I(4135) \times 0.035 \tag{1}$$

Its accuracy is within 7.5%. The 4135 keV line can also be used as a marker for ^{235}U, therefore, it also can be used for determination of enrichment. The calibration lines are shown in Fig. 3: ratios of count rates are plotted against the isotopic mass ratios. The lines are linear in the mass ratio range of 0 to 0.5.

3.2. Technetium

The thermal partial gamma ray production cross-sections for the strongest gamma rays of ^{100}Tc were determined from the yields measured in cold neutron capture and subsequent beta decay, respectively, as described above. A 1/v relationship was assumed to hold also for ^{99}Tc and the hydrogen comparator. The new cross-sections are listed in Table III. The uncertainty is about 0.9%, which essentially comes from the relative efficiency calibration. This should be contrasted with the 9% uncertainty of the emission probability for the 539 keV decay gamma ray [17], which was used in Table III for renormalizing the measured gamma ray yields. The reported uncertainty for absolute intensity of the ^{99}Tc decay gamma ray was even higher, about 23% [5].

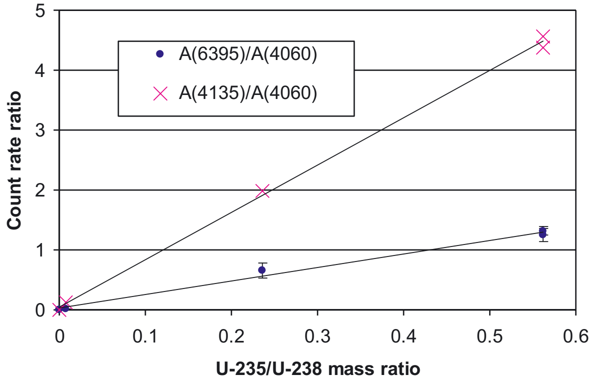

FIG. 3. Count rate ratios for different gamma lines taken from PGAA spectra of uranium with different isotopic mass ratios.

TABLE III. PARTIAL GAMMA RAY PRODUCTION CROSS-SECTIONS OF CAPTURE AND DECAY LINES FOR A ^{99}Tc TARGET

E_γ (keV)	Origin	P_γ (γ/100 captures or decays)	σ_γ (b)	Sensitivity (cps/mg)
172.1	^{99}Tc(n,γ)^{100}Tc	67 ± 6	16.61 ± 0.15	3.0
223.4	^{99}Tc(n,γ)^{100}Tc	6.1 ± 0.6	1.472 ± 0.013	0.24
263.5	^{99}Tc(n,γ)^{100}Tc	5.9 ± 0.5	1.425 ± 0.012	0.21
539.5	^{100}Tc (β^-)^{100}Ru	6.6 ± 0.6[a]	1.604 ± 0.014	0.14
590.7	^{100}Tc (β^-)^{100}Ru	5.5 ± 0.4	1.296 ± 0.011	0.10
89.5	^{99}Tc (β^-)^{100}Ru	$(6.5 \pm 1.5) \times 10^{-4}$ [b]		4.3×10^{-3}

[a] Value from Ref. [17], used for normalization here.

[b] From Ref. [5].

Table III clearly demonstrates the order of magnitude differences in partial cross-sections and gamma ray intensities. For the ^{99}Tc assay, the highest sensitivity was offered by PGAA, based on the detection of the 172 keV line; NAA provided the next highest sensitivity, while the least favourable method was passive gamma ray counting. For orientation, analytical sensitivities characteristic of our measuring system have also been included in Table III, in units of counts per second (counts/s) per milligram of material. It is striking that the sensitivity for the 1720 keV capture line was a thousand times higher than for the 89.5 keV line from spontaneous decay of ^{99}Tc. On the other hand, the corresponding total rate was only doubled, i.e. 18 and 9.6 counts/s, respectively, for the energy range of 7 keV to 4 MeV.

4. CONCLUSION

Prompt gamma neutron activation analysis is suggested as an instant result method for the assay of uranium and also for the determination of ^{235}U enrichment. Several gamma lines are proposed for analysis both of ^{235}U and ^{238}U. Partial gamma ray production cross-sections were determined using internal standardization. The measured values agreed well with those calculated from literature data. The method proved to be more sensitive than passive gamma ray counting. A linear calibration curve was derived for high energy gamma rays emitted by the two isotopes, which can be used at least up to a mass ratio of 0.5 for the determination of enrichment.

The new partial gamma ray production cross-sections for neutron capture and decay gamma rays allow non-destructive assay of the ^{99}Tc long lived fission product and on-line monitoring of its transmutation rate into stable ^{100}Ru, by using either NAA or PGAA. In addition to much higher accuracy, analytical sensitivities are about a thousand times higher for PGAA in comparison to passive gamma ray counting. The technetium results were published in more detail in Ref. [21].

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APPLICATION OF ADVANCED NUCLEAR AND INSTRUMENTAL ANALYTICAL TECHNIQUES FOR CHARACTERIZATION OF ENVIRONMENTAL MATERIALS

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Increasing realization of the toxic effects of metal ions in the environment has given an impetus to research on analytical techniques for their characterization. Large numbers of analytes are present at very low levels, necessitating the use of sensitive, selective and element specific techniques. Concern over precision and accuracy of such analyses, which have socioeconomic implications, has emphasized the need for certified reference materials and the use of multi-technique approaches to ensure unambiguous characterization of analytes. Recent work on these aspects at the Analytical Chemistry Division, Bhabha Atomic Research Centre, is described in this paper.

Increasing use of fossil fuels has led to the generation of large quantities of fly ash, which poses problems of safe disposal. The application of these materials to landfills is a convenient option, but trace amounts of toxic metals — mercury, arsenic, lead, etc. — may adversely affect the environment. In view of the non-homogeneous nature of the material, efficient sample processing is important, in addition to validation of results by the use of appropriate standards. Analysis was carried out on fly-ash samples received as reference materials, and also as samples from commercial sources, using a combination of nuclear techniques, including INAA and RNAA, as well as other techniques like AAS, ICPAES, cold vapour AAS for mercury, and hydride generation techniques for arsenic. Similar analyses using nuclear techniques were employed for the characterization of air particulates.

Biological materials often serve as sensitive indicators of pollution. They are also employed for studies on the uptake of toxic metals, like uranium, thorium, cadmium, lead and mercury. The presence of large amounts of organic materials necessitates an appropriate sample dissolution procedure. In view of the possibility of loss of certain analytes, like cadmium, mercury and arsenic, by high temperature dry ashing, the use of a wet ashing procedure is also important for proper sample dissolution. Both Bethge digestion and microwave assisted dissolution are attractive options, but have inherent limitations. The roles of nuclear and allied spectroanalytical techniques were assessed for the analysis of biological samples for various critical impurities of environmental significance. Standard reference materials, like apple leaves and peach leaves, were also employed. The selection of the sample dissolution and analysis procedures was evaluated from the values obtained for the certified reference materials. The results demonstrated that nuclear and spectrochemical techniques are appropriate analytical tools, along with the use of primary or secondary standard reference materials, for the validation of analytical procedures.

INSPECTION AND CONTROL OF RECYCLED METALS IN THE ISLAMIC REPUBLIC OF IRAN

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Abstract

Recently, the metal recycling industry has become aware of radioactive materials in metal scrap. There have been some cases where radiation sources were unintentionally smelted in the course of recycling scrap. Industry representatives and regulatory authorities have jointly undertaken initiatives to increase awareness of the problem. Radiation detection systems have been installed by customs services and at mills to lessen risks to public health from radiation contamination and to avoid financial losses. The paper discusses the means by which the National Radiation Protection Department has reduced the importation of contaminated materials.

1. INTRODUCTION

The metals industry is international in scope, encompassing trade in scrap and in semi-finished and finished metal products. There is growing awareness in the industry of the importance that their materials are free of radioactive contamination. However, with increases in numbers of suppliers of metals, the potential for contamination has grown. Radioactive contamination may enter the metal supply in various ways, including:

- Sealed sources removed from instrumentation (“orphan” sources),
- Scrap containing undetected contamination,
- Scrap contaminated with naturally occurring radioactive materials (NORM).

The presence of radioactivity in scrap is mainly due to orphan sources in imported materials. Therefore, the National Radiation Protection Department (NRPD) is focusing most of its effort on interception of contaminated imported scrap and on recovery of orphan sources.

The NRPD has also developed standards to control the problem nationally.

2. TYPES OF SOURCES

Today, many types of radioactive sources are in use in industry and medicine:

- Radiography sources have activities that can cause severe injury.
- Gauges containing radioactive material used in control devices in manufacturing processes are safe in the original fabricated form. However, they tend to be forgotten with time and become 'orphans', after which there is the possibility of their being dismantled and becoming hazardous.
- Radionuclide teletherapy sources are intended for radiation treatment, with sources located at a certain distance from the patient's body. It is estimated that several thousand teletherapy sources exist worldwide.
- Brachytherapy involves radioactive therapy applied close to or inside a tumour. Prior to 1950, radium was the only radioactive source in common use. However, as other radionuclides have become available, ^{226}Ra has been gradually replaced, and these sources now constitute a special problem. They have been donated and exchanged, even internationally, and accountability and traceability are now uncertain.

3. DISCOVERY OF RADIOACTIVE MATERIALS

Scrap metal recycling is an international industry. Iran imports millions of tons of scrap and semi-finished and finished metal products each year, therefore, it is important to ensure that they are not contaminated with radioactive materials. In co-ordination with the customs services, scrap yards, and steel mills, NRPD has established a nation wide monitoring system that provides rapid and effective identification, removal, and deposition of radioactive sources. If such sources go undetected it can present serious health hazards and cost millions of dollars in lost production and decontamination expenses.

This system has been successful in identifying over thirty radioactive sources or devices since 1999 (Table I). Fig. 1 shows the main locations for control of metal scrap in the Islamic Republic of Iran.

With the assistance of NRPD staff, the radiation surveillance system has been installed at major customs facilities and metal mills to detect radioactive sources in scrap metal shipments. These systems are sophisticated in design, sensitive in operation, and expensive to install.

Figs 2+3 show two types of gate monitoring gamma scanners in the Islamic Republic of Iran.

FIG. 1. Main control locations for scrap metal in the Islamic Republic of Iran.

Tables II and III show seizures of radioactive sources between 1999 and 2001 by element and origin.

4. MEASURES TO SOLVE THE PROBLEM

In the Islamic Republic of Iran, the Government and the metal industry have undertaken a number of measures with the objective of lessening the potential of radioactive contamination.

— It is required that radiation sources be kept secure, and, if any is lost, stolen, or decontrolled, it must be reported immediately to the regulatory authorities. Possession of radioactive materials requires authorization and their use requires registration and licensing. The security of radioactive material is of particular importance. Accountability includes periodic checks of inventories.

FIG 2. A gamma scanning gate monitor at a border crossing at Astara (Exploranium system).

FIG. 3. A gamma scanning gate monitor at a border crossing at Jolfa (Rados system).

- Radiation monitoring systems have been operational at steel plants and customs check points for several years.
- Responses to emergencies resulting from loss or theft of radioactive material or discovery of radiation sources are different from emergencies at nuclear reactors. Exercises are carried out to improve quality of response in actual emergencies.

TABLE I. SEIZURES OF RADIOACTIVE SOURCES (1999–2000)

No.	Year	Metal	Origin	Contaminant	Monitoring results
1.	1999	Al	Armenia	Sr-90	3,500 Ci/s
2.	1999	Al	Armenia	Ra-226	50,000 Ci/s
3.	2000	Al	Armenia	Ra-226	20,000 Ci/s
4.	2000	Al	Armenia	Ra-226	4,520 Bq/sample
5.	2000	Al	Armenia	Ra-226	135 Bq/sample
6.	2000	Al	Armenia	Sr-90	3,500 Ci/s
7.	2000	Al	Armenia	Unknown	Unknown
8.	2000	Al	Nakhjavan	Sr-90	75 μSv/h
9.	2000	Al	Georgia	Unknown	15,000 Ci/s
10.	2000	Al	Armenia	Unknown	Unknown
11.	2000	Al	Armenia	Ir-192	15,000 Ci/s
12.	2000	Fe	Azerbaijan	Sr-90	2 mSv/h
13.	2000	Al	Armenia	Unknown	15,000 Ci/s
14.	2000	Al	Azerbaijan	Unknown	5,000 Ci/s
15.	2000	Al	Georgia	Ra-226	20 μSv/h
16.	2001	Al	Armenia	Unknown	5,000 Ci/s
17.	2001	Al	Armenia	Ra-226	5,000 Ci/s
18.	2001	Al	Armenia	Ra-226	7,500 Ci/s
19.	2001	Al	Armenia	Sr-90	15,000 Ci/s
20.	2001	Al	Turkmenistan	Unknown	0.22 mSv/h
21.	2001	Al	Iraq	U-238	0.3 μSv/h
22.	2001	Fe	Unknown	Ra-226	1.67 μSv/h
23.	2001	Al	Armenia	Unknown	1,500 Ci/s
24.	2001	Al	Turkmenistan	Ir-192	142 μSv/h
25.	2001	Al	Georgia	Unknown	12,000 Ci/s
26.	2001	Al	Georgia	Unknown	13,000 Ci/s
27.	2001	Al	Georgia	Th-232	12,000 Ci/s
28.	2001	Al	Georgia	Unknown	12,000 Ci/s
29.	2001	Fe	Turkmenistan	Ra-226	6,500 Bq/kg
30.	2001	Fe	Turkmenistan	Th-232	3,700 Bq/kg
31.	2001	Fe	Turkmenistan	Ra-226	850 Bq/kg
32.	2002	Al	Turkmenistan	Ra-226	7.8 μSv/h
33.	2002	Fe	Unknown	Unknown	25 mSv/h
34.	2002	Fe	Kazakhstan	Ra-226	2,550 Bq/sample

TABLE II. SEIZURES OF RADIOACTIVE SOURCES BY ELEMENT

Radioactive element	Number of cases	% cases
Radium	12	36
Strontium	5	15
Iridium	2	6
Uranium	1	3
Thorium	1	3
Unknown	12	36

TABLE III. SEIZURE OF RADIOACTIVE SOURCES BY ORIGIN

Country	Number of cases	% cases
Armenia	15	44
Georgia	6	18
Turkmenistan	6	18
Azerbaijan	2	6
Kazakhstan	1	3
Nakhjavan	1	3
Iraq	1	3
Unknown	2	6

It is clear that a comprehensive international approach is needed to cope with the problem of radioactive sources. The IAEA, the main international centre for scientific and technical co-operation in the nuclear field, has developed an integrated management approach with the aim of achieving adequate national radiation and waste safety infrastructure in the majority of Member States.

5. CONCLUSION

The appearance of radioactivity in metal scrap is a problem that clearly demonstrates a need for improvements in controlling radioactive sources. Implementation of IAEA radiological guidelines will provide the first barrier against the importation of radioactively contaminated metal shipments. Screening incoming materials at border crossings and the use of detection systems at scrap metal recycling factories will provide additional protection (Figs 4, 5).

FIG 4. Scrap iron at the Jolfa border crossing.

FIG. 5. Aluminium scrap, at Shoshmi on the border with Iraq.

IMPROVEMENT IN URANIUM BULK ANALYSIS AT THE CLEAR FACILITY FOR SAFEGUARDING ENVIRONMENTAL SAMPLES*

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In order to contribute to the IAEA's strengthened safeguards system, a project was initiated at the Japan Atomic Energy Research Institute (JAERI) in 1998. A clean room facility — the Clean Laboratory for Environmental Analysis and Research (CLEAR) — was constructed in June 2001 at JAERI, and analytical techniques are being developed for detecting ultra-trace nuclear materials in environmental samples.

As for bulk analyses, performance of inductively coupled plasma mass spectrometry (ICP-MS) was mainly examined because sample preparation for ICP-MS is simpler than that for thermal ionization mass spectrometry (TIMS). Interference from polyatomic ions (such as $PtAr^+$) and coexisting elements (such as sodium) on the uranium ions, as well as mass bias caused by ICP-MS operating conditions, have been investigated for precise measurement of uranium isotope ratio [1]. The authors have also studied uranium blanks using the sample treatment process. Blanks were found to have uranium values below 10 pg, which originated from elution of Teflon covered vessels after acid treatment and drying of samples by heating [2]. Work is in progress to minimize blank values.

Compared with the process blank and the minimum amount of uranium detectable for isotope ratio measurements by ICP-MS (c. 10 pg for natural uranium), the swipe cotton (Texwipe-304) that is currently recommended for IAEA environmental sampling contains much higher amounts: several ng of natural uranium [3]. If the amount of uranium collected on a Texwipe-304 is small, reliable measurement of isotope ratio would be impossible by bulk analysis. The authors are seeking alternative swipe materials that contain less uranium.

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Recently, one of the authors devised an effective technique for recovery of uranium containing particles from a Texwipe-304 [4]. The vacuum suction method uses a combination of polycarbonate membrane filters and a macro-pipette tip that is connected to a vacuum pump with flexible tubing (Fig. 1). By scanning the surface of the Texwipe-304 with the top of the tip, particles are collected on the filter. Figure 2 shows micrographs of the Texwipe-304 surface: (a) unused, (b) particle swiped, and (c) particles recovered by the vacuum suction method. Most of the particles were removed from the Texwipe-304 by suction. Preliminary examination suggests that the particle recovery yield is at acceptable levels and that the process blank is low. The method will provide a useful means of improving the reliability of bulk analysis of ultra-trace amounts of uranium, even in cases where the Texwipe-304 must be used.

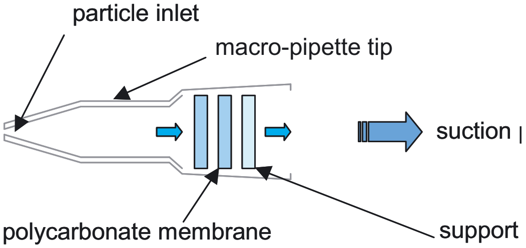

FIG. 1. Schematic drawing of the vacuum suction method.

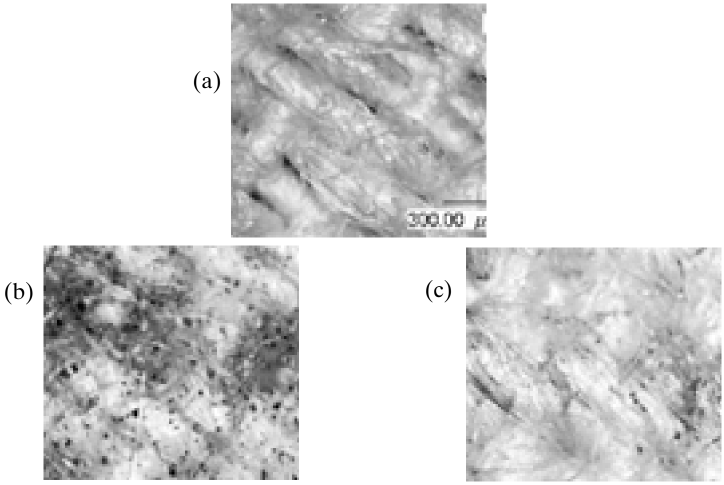

FIG. 2. Recovery of the particles from Texwipe-304 by means of the vacuum suction method. (a) Unused; (b) before particle recovery; (c) after particle recovery.

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SEQUENTIAL ANALYSIS FOR DETERMINATION OF ARTIFICIAL RADIONUCLIDES IN ATMOSPHERIC SAMPLES FROM DAEJEON, REPUBLIC OF KOREA

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Artificial radionuclides in atmospheric samples can be used as indicators of nuclear weapons tests in nearby countries and of accidents at nuclear facilities like Chernobyl. Because of low activity of some of the nuclides and difficulty of collecting atmospheric samples, precise data can be difficult to obtain.

Here we describe a new method for the sequential analysis of ^{90}Sr, ^{137}Cs and plutonium isotopes in atmospheric samples. After adding caesium and strontium carriers, and plutonium tracer to the atmospheric samples, the artificial radionuclides in the samples were extracted with nitric acid, and then co-precipitated with ferric hydroxide. The supernatant solution was acidified with nitric acid and then passed through a column containing ammonium 12-molybdophosphate (AMP) for the analysis of ^{137}Cs. Strontium-90 in the eluent was purified by the fuming nitric acid method. Precipitation was used for the determination of Pu isotopes. Plutonium isotopes in the precipitate were purified by an on-line sequential injection method, and then measured by sector field inductively coupled plasma mass spectrometry (SF-ICPMS) [1].

Caesium-137 was adsorbed onto the AMP column together with natural rubidium. The column was rinsed with 150 mL of 2M ammonium nitrate solution to remove rubidium, and then the AMP in the column was dissolved with 20% sodium hydroxide solution. After removing ammonia and molybdate, 1 mL of 10% hexachloroplatinic acid was added to the AMP solution to make caesium chloroplatinate precipitate. The purified ^{137}Cs was measured with a low background gas proportional α/β counter. Figure 1 shows the analytical flow schema. The reliability of this method was confirmed by comparison with certified reference fallout materials [2]. The sensitivity to ^{137}Cs of this method was better than that of γ spectrometry. The chemical yield of caesium was above 80% and the detection limit of ^{137}Cs was a few μBq/m^3 for airborne dust and mBq/m^2/month for total deposition (fallout and rainwater).

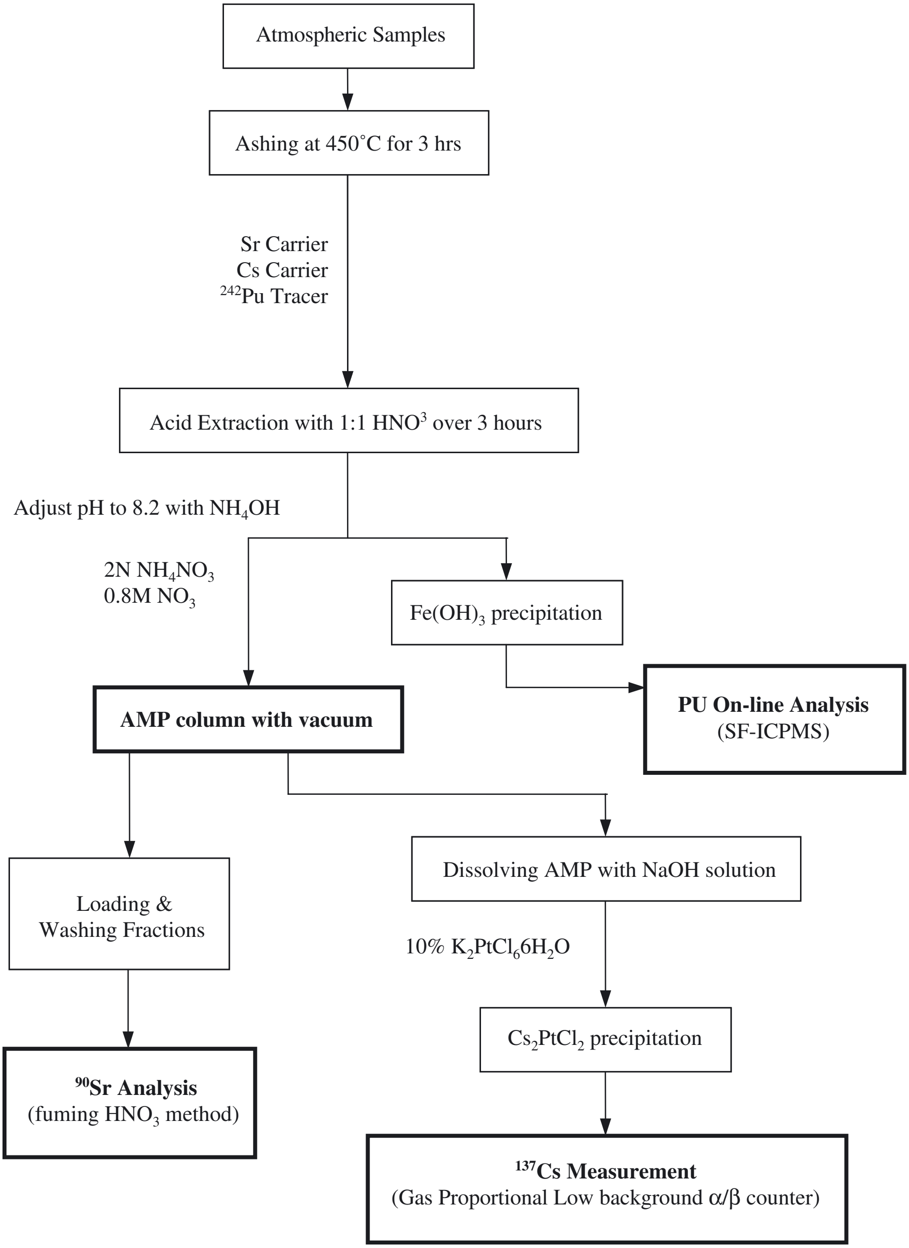

FIG. 1. Flow chart for sequential analysis of atmospheric samples.

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IDENTIFICATION OF NUCLEAR AND RADIOACTIVE MATERIALS IN LATVIA

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Unauthorized transfer of nuclear and radioactive materials has become a worldwide problem in recent years. Various international organizations are addressing illicit trafficking of nuclear materials. In order to establish collaboration between governmental institutions in Latvia, for detection of unauthorized transfer of nuclear materials, the Handbook of Response was published. In it, the duties and responsibility of each institution (customs services, border guards, police, Radiation Safety Centre, scientific experts, etc.) are described, to detect and prevent the smuggling of nuclear materials. Characterization of nuclear materials is the most important part of the handbook.

A goal of this work was to elucidate the current situation and possibilities of identification and characterization of nuclear and radioactive materials in Latvia.

Illicit radioactive materials are detected with stationary and portable equipment. Nineteen stationary systems are installed at 14 border crossings and seaports in Latvia, consisting of 13 gamma and 6 neutron detectors. The border crossings are also supplied with 61 portable radiometers and 20 radiation pagers. In cases where the presence of the nuclear materials is suspected, experts from the Radiation Protection Centre are called in. The experts have a mobile laboratory with special equipment consisting of a GR 320 gamma spectrometer and a GPS instrument. Exploranium 130 and FieldSpec portable spectrometers and the PM1402M neutron dosimeter are also in use.

Two institutions in Latvia are involved in the international project “Combating Illicit Trafficking of Nuclear Materials” for the identification and characterization of radioactive materials:

- Radiation Protection Centre,
- RAPA Ltd.

The following equipment is used for preliminary identification of nuclear and radioactive materials in mobile laboratories from the Radiation Protection Centre:

- PM 1402M neutron dosimeter,
- Portable FieldSpec gamma spectrometer for the identification of ^{233}U, ^{235}U and ^{238}U.

The radioactive material testing laboratory of RAPA Ltd is organized on the basis of the staff and equipment of the former Nuclear Research Centre. The laboratory is licensed by the Latvian National Accreditation Bureau for radioactive and environmental material testing, accordingly, to ISO/IEC 17025 standards. The laboratory has high resolution germanium gamma spectrometers.

Currently, examination of environmental samples and reactor materials includes determination of:

- Long lived fission products (^{137}Cs, ^{154}Eu, etc.) in various matrices;
- Long lived radionuclides from neutron activation processes (^{60}Co, ^{65}Zn, ^{54}Mn, ^{152}Eu, etc.).

Preliminary results have been obtained by analysing uranium samples of various masses and physical (liquid, crystals, powders, discs, pellets) and chemical forms (uranyl nitrate, oxide, metal) with ^{235}U enrichment from natural (0.017%) to 90%.

IMPROVED ENVIRONMENTAL MONITORING AT THE IGNALINA NUCLEAR POWER PLANT SITE

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Abstract

Under the aegis of the IAEA technical co-operation project "Radioecology in the vicinity of the Ignalina NPP" (LIT/9/003), a high efficiency HPGe well type detector was obtained in 1998 for investigations of environmental radioactivity in Lithuania. After re-measuring aerosol filter samples, some were found to contain activation products ^{54}Mn and ^{60}Co that were not detectable when a coaxial Ge(Li) detector was used. The air samplers used for radioecological monitoring around the Ignalina nuclear power plant are oriented in directions other than from the source, at distances of 1.6 to 38 km. The new measuring technique allowed detection of artificial radionuclides at every monitoring station.

1. INTRODUCTION

Two RBMK-1500 type nuclear reactors are in operation at the Ignalina nuclear power plant (NPP) in the northeast of Lithuania (Fig. 1), on the shore of Lake Druksiai. The first reactor went into service in 1983, and the second in 1987; their design lifetime is projected for 2010 to 2015 [1].

An environmental monitoring programme was initiated at the site some years before the start of operations. Activity concentrations of globally distributed ^{137}Cs in the atmosphere were determined at 8.5 μBq/m^3 and 38 μBq/m^3, as mean annual and maximum values, respectively, from September 1979 to September 1980 [2].

Currently, the operator carries out an extensive environmental monitoring programme at the site. For continuous investigations of airborne gamma ray emitting radionuclides, seven monitoring stations are run by the operator

FIG. 1. Map showing the Ignalina NPP in the northeastern part of Lithuania.

(Fig. 2). They are oriented in directions other than towards the source, at distances of 1.6 to about 38 km (Table I). All samplers provide an airflow rate of 600 m^3/h.

In this work, attention was paid chiefly to the most sensitive techniques for monitoring radionuclide activity concentrations in ground level air as the most informative means of monitoring artificial radionuclide transport in the environment, with the possibility of drawing conclusions about the source of the activity [3]. An efficient HPGe well type detector in a standard cryostat was used; it was obtained in 1998 as part of the IAEA technical co-operation project “Radioecology in the vicinity of the Ignalina NPP” (LIT/9/003). Efficiency calibration for this detector was done in the energy range 122 to 1461 keV by using a reference standard solution with single photon emitting radionuclides. At the same time, the coincidence summing correction factor was experimentally determined for ^{60}Co [4].

FIG. 2. Map of the Ignalina NPP site showing locations of air samplers. For details see Table I.

The quality of the calibration was validated during the “Proficiency Test for Determination of Anthropogenic γ Emitting Radionuclides in a Mineral Matrix” organized by the IAEA between December 2001 and March 2002. Uncertainties in activity determination of both ^{137}Cs and ^{60}Co were better than 3%.

TABLE I. AIR SAMPLER DISTANCES AND DIRECTIONS FROM THE IGNALINA NPP

Name of location	Assigned number (Fig. 2)	Distance (km)	Azimuthal angle, (deg)
Building No.438	3	6.2	258
Tilze	1	6.7	14
Turmantas	2	11.2	330
Visaginas	4	7.9	269
Cepukai	6	7.7	187
Skladskoje	5	1.6	106
Ignalina	not shown	38.4	220

2. METHODS

Routinely, the filters are changed every 10 days at the six monitoring stations shown in Fig. 2, whereas monthly samples are gathered at the town of Ignalina, 38 km from the NPP. Thus, up to 250 samples are collected per year, corresponding to approximately 140 000 m^3 of air at each of the six “closer” stations, and more than 400 000 m^3 at Ignalina.

Normally, the aerosol filters are pressed into tablets of 10 mm depth and 75 mm diameter, and are counted on the end cap of the Ge(Li) detector. The minimum detectable activity (MDA) is relatively high for this kind of detector, and only natural ^{7}Be and globally distributed ^{137}Cs are routinely measured. Activation products ^{60}Co and ^{54}Mn have been detected in ground level air, but only rarely.

Nevertheless, investigations carried out on moss samples in 1996 showed that the site specific radionuclide ^{60}Co was distributed on the ground, mainly within a radius of 5 to 7 km of the source; the maximum activity concentration at the soil surface was 22 Bq/m^2 [5]. Therefore, it was expected that the use of 4π geometry, attainable inside the well, would considerably improve detection capability for ^{60}Co and other artificial radionuclides of NPP origin in air samples.

In order to prepare the aerosol filter samples for counting in the new geometry, they were ashed at 450°C. The final volume of the ash samples, approximately 2 cm^3, easily fitted into the well, which can accommodate samples of up to 4 cm^3. For this geometry, the MDA values for ^{60}Co and ^{137}Cs were determined as 20 mBq and 12 mBq, respectively, when counting time was set to 100 000 s [4].

At the same time, meteorological data — wind direction and velocity, air humidity, precipitation, atmospheric pressure and temperature at 2 m and 40 m from the soil surface — were collected continuously at 6 km from the NPP, and stored for further analysis.

Figures 3 and 4 show wind roses for 2000 and 2001, respectively. The prevailing winds at the NPP site were westerly and southerly.

3. RESULTS

With re-measurement with high efficiency geometry, activation products ^{54}Mn and ^{60}Co were detected in aerosol filter samples in which they had not been detected when a Ge(Li) detector was used.

The typical gamma ray spectrum obtained with the HPGe well type detector is shown in Fig. 5.

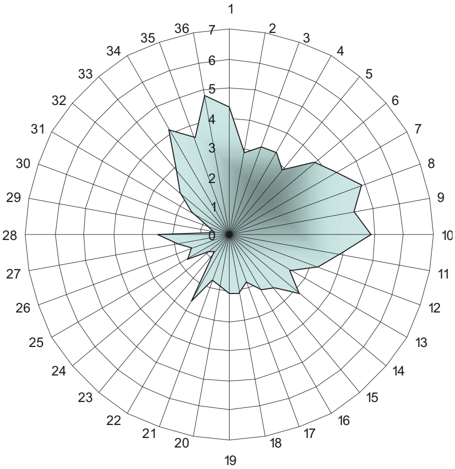

FIG. 3. Wind rose for the year 2000.

The activity of ^{60}Co was 114 ± 5 mBq, which corresponds to an activity concentration in air of 0.8 μBq/m^3. The respective values for ^{54}Mn were 14 ± 3 mBq and 0.1 μBq/m^3, which were close to the detection limit.

For comparison, we also provide the background spectrum (Fig. 6). There was no trace of artificial radionuclides in the spectrum, and only natural contaminants declared by the manufacturer were present in the system with a standard cryostat [6].

Figure 7 shows the relatively short term course of ^{137}Cs activity concentration in air determined simultaneously at two stations located in near opposite directions from the NPP. The courses were similar at both locations, with mean values of 0.63 μBq/m^3 and 0.50 μBq/m^3 at stations 2 and 5, respectively. Analysis of ^{137}Cs activity concentration in air at the “farther” station, in the town of Ignalina, provided an annual mean value of 0.49 μBq/m^3. Similarly, the annual mean for station 2 was 0.64 μBq/m^3 (Fig. 8). With respect to ^{137}Cs, there was no obvious effect on the environment through smokestack release from the NPP, and, probably, its behaviour depended mostly on resuspension.

Figure 9 shows the course for ^{60}Co determined at station 5, located closest to the source. Most of the samples from this station revealed ^{60}Co. The activity concentrations of this nuclide were usually some hundreds of nBq/m^3, and, therefore, far below detection limits achievable by common coaxial detectors. Figure 10 demonstrates the usefulness of high sensitivity

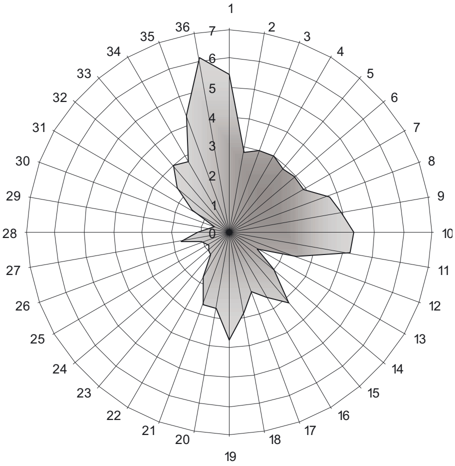

FIG. 4. Wind rose for the year 2001.

techniques. Here, the gamma spectrum indicated the presence of activation products in an aerosol sample taken 38 km from the NPP.

4. CONCLUSIONS

New measuring techniques allowed detection of various artificial radionuclides at all of seven monitoring stations around the Ignalina NPP. Activity concentrations of ^{137}Cs were one order of magnitude lower than two decades ago, before commissioning of the first NPP reactor. A correlation was noted between activity concentrations of ^{54}Mn and ^{60}Co and the prevailing wind direction during air sampling.

This improved environmental monitoring system is capable of detecting radionuclides discharged not only from the smokestacks of NPPs, but also transferred from distant unknown sources [7–9]. Hence, it can be used for any source identification.

ACKNOWLEDGEMENTS

The contributions to the investigations of environmental radioactivity in Lithuania made by the IAEA through technical co-operation projects LIT/9/003, LIT/9/004, as well as ongoing project LIT/9/005 are gratefully acknowledged.

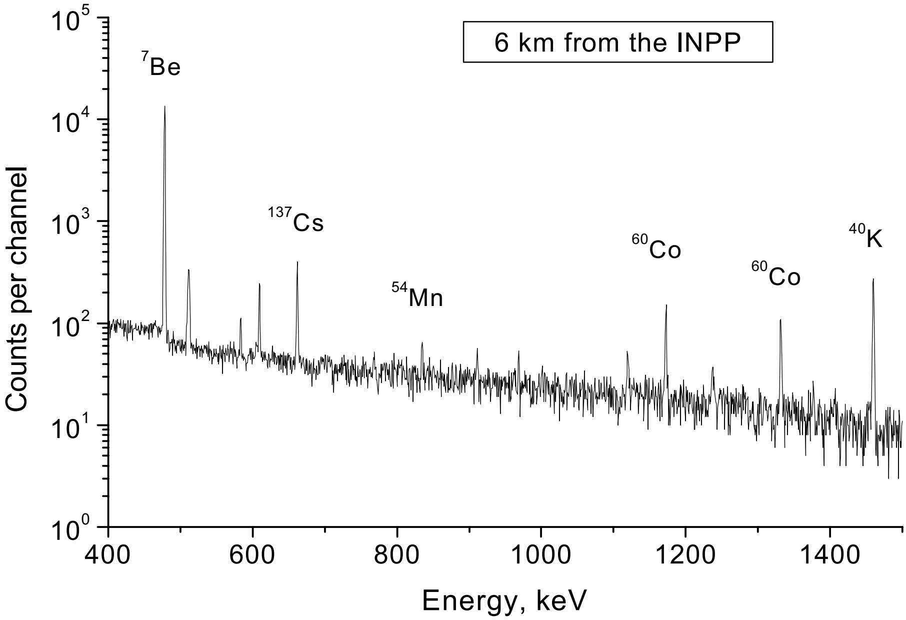

FIG. 5. Gamma ray spectrum of an aerosol ash sample taken 6 km from the NPP (station 3), measured with an HPGe well type detector. Counting time 50 000 s, sampling was performed on 2002-01 01-07.

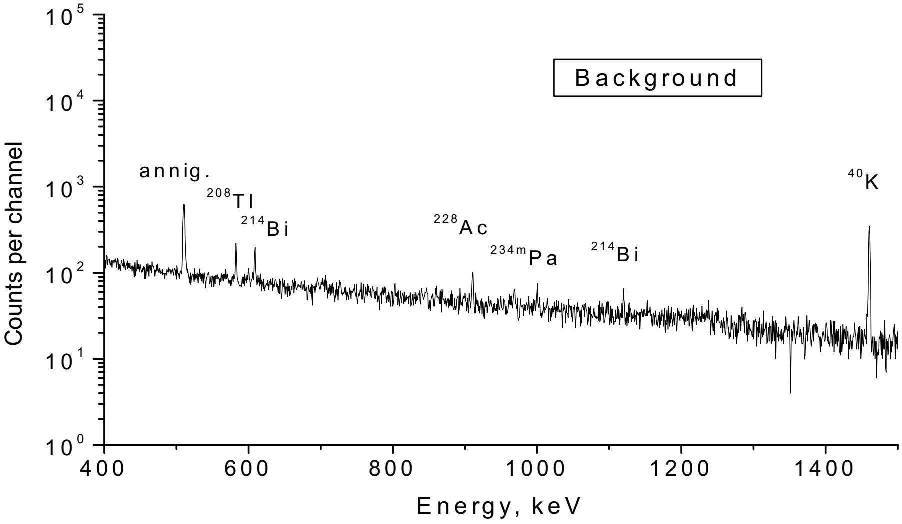

FIG. 6. Background gamma ray spectrum measured with an HPGe well type detector in a standard cryostat. Acquisition started 2 March 2002, counting time 100 000 s.

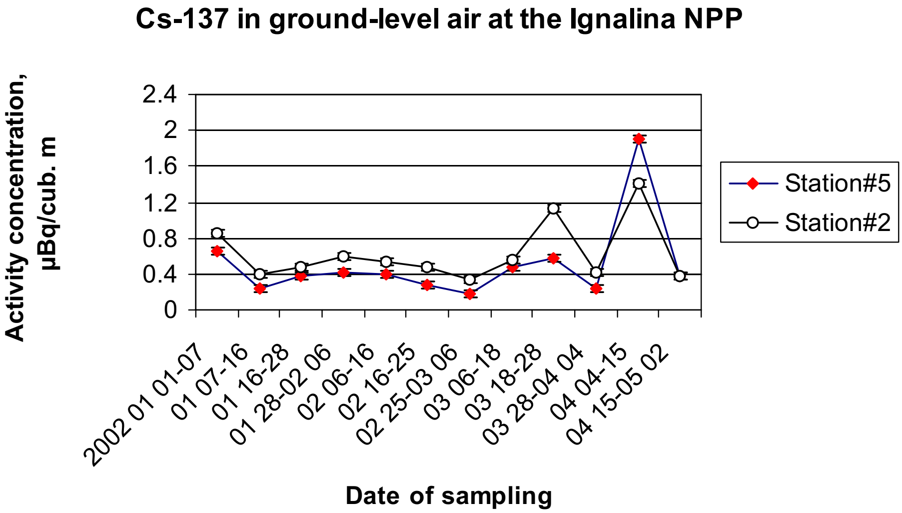

FIG. 7. The course of ^{137}*Cs activity concentration determined simultaneously at two monitoring stations located in near opposite directions from the NPP.*

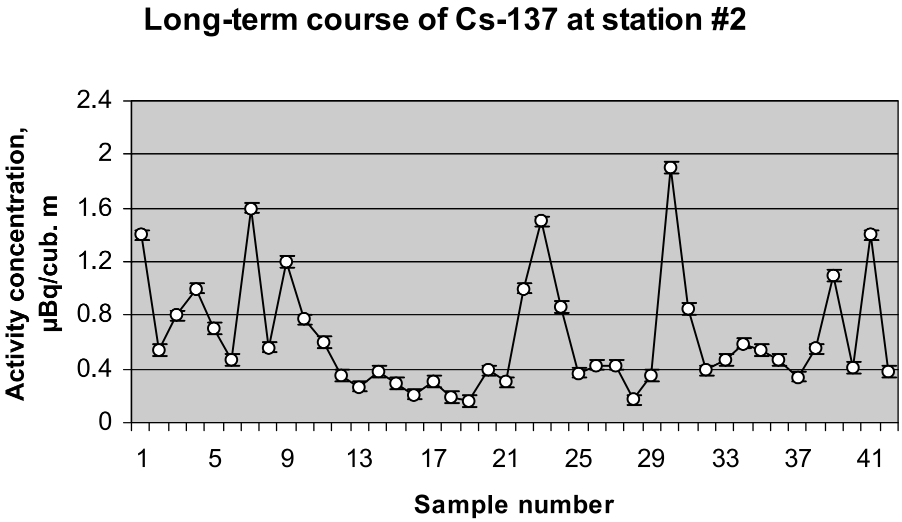

FIG. 8. The course of ^{137}*Cs activity concentration in the town of Turmantas with an annual mean of 0.64 µBq/m*^{3}*. Sampling period 2001-01-31 to 2002-05-02.*

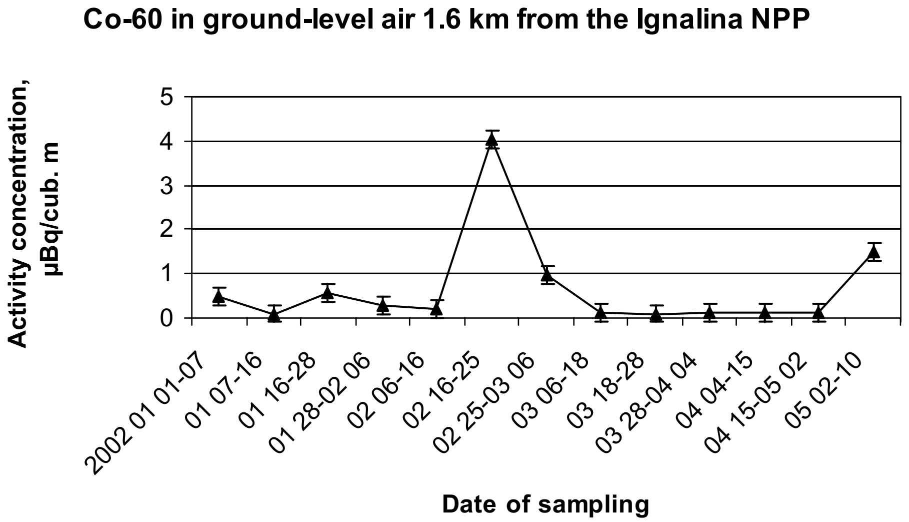

FIG. 9. The course of ^{60}Co activity concentration close to the NPP in the first half of 2002.

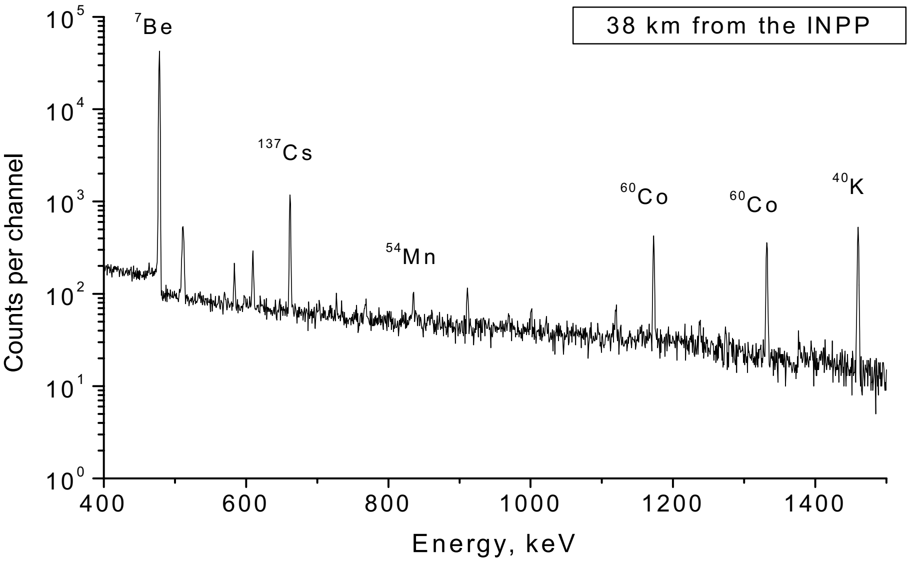

FIG. 10. Gamma ray spectrum of an aerosol ash sample taken 38 km from the NPP (monitoring station in Ignalina) measured with an HPGe well type detector. Activity concentration of ^{60}Co was 0.68 µBq/m^3. Counting time 75 000 s, sampling performed 2002-02-22 to 2002-03-21.

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DETERMINATION OF URANIUM CONTENT OF SAMPLES IN VARIOUS GEOMETRIES BY GAMMA RAY SPECTROMETRY

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Abstract

There are certain limitations to the usage of standard source methods for efficiency calibration of gamma ray spectrometers measuring in extended geometry. These limitations arise from the diversity of forms and dimensions of the objects that are to be measured during uranium fuel fabrication activities. One of the steps in the fuel fabrication cycle is radioactive waste conditioning. The Institute for Nuclear Research (ICN) operates a radioactive waste management facility both for its own purposes and for external services. Conditioning of liquid and solid wastes for interim storage is also done at the waste management facility. Located on the same site as the Institute is a radioactive fuel factory that produces natural uranium based fuel for the Cernavoda nuclear power plant. Some of the radioactive wastes processed at ICN's treatment facility originate from fuel factory activities and contain natural uranium. A large part of this uranium is recovered and, therefore, returned to the fuel factory, but there is a certain amount of uranium that has to be eliminated as radioactive waste. During waste conditioning operations there are certain stages when radioactive measurement of storage drums is required. We have developed gamma ray spectrometry equipment, using a portable MCA Canberra Inspector, an HPGe detector and an ICN manufactured collimator, which we are using as a semi-empirical means of calibrating the gamma ray spectrometer for such measurements.

1. INTRODUCTION

In order to be able to determine the radioactive content of storage drums during various procedures at our waste treatment facility, we designed and manufactured mobile equipment for "in situ" spectrometry. A portable high purity germanium (HPGe) detector was used together with a compact workstation incorporating a multichannel analyser, a spectroscopic amplifier and a high voltage power supply. Spectral data are processed on-line with a SubNote IBM 486 compatible PC using GeniePC, OS/2 based spectroscopy software from Canberra.

2. DESCRIPTION OF THE INSTALLATION

Compact, modular lead housing for the detector was designed and manufactured at ICN, using uncontaminated lead and an inner layer of copper. In front of the detector, a lead collimator with a cylindrical slit was used to reduce the range of variation in incidence angles (Figs 1, 2).

Hence, several collimators were manufactured with 10, 20, 40 and 60 mm diameter slits to ensure proper counting rates for a large range of specific activities in the drums, by simply changing the collimator.

3. CALIBRATION

Determination of the photo peak total efficiency is based on the separation of intrinsic efficiency of the detector from the geometric efficiency and the self-absorption factor. Therefore, it was assumed that the intrinsic efficiency is independent of counting and sample geometry, and this fact was made more realistic by the usage of narrow incidence angles at the detector surface through a small aperture collimator. Hence, for total efficiency, we considered the following equation:

$$\varepsilon_t = \varepsilon_d \cdot \frac{\bar{\Omega}}{4\pi} \tag{1}$$

where

$\bar{\Omega}$ is the effective solid angle presented by the source to the detector,
e_d is the intrinsic efficiency.

$$\Omega = \iint_S \frac{\overrightarrow{TP} \cdot \overrightarrow{n_u}}{\left|\overrightarrow{TP}\right|^3} d\sigma \tag{2}$$

$$\bar{\Omega} = \iint_S \frac{\overrightarrow{TP} \cdot \overrightarrow{n_u}}{\left|\overrightarrow{TP}\right|^3} F_{att} d\sigma \tag{3}$$

where

$\overrightarrow{TP}$ is the oriented segment bounding the emission point and the incidence point for a given gamma photon,
$\overrightarrow{n_u}$ is the versor normal to the detector surface,
F_{att} is the attenuation factor.

FIG. 1. The spectroscopy installation.

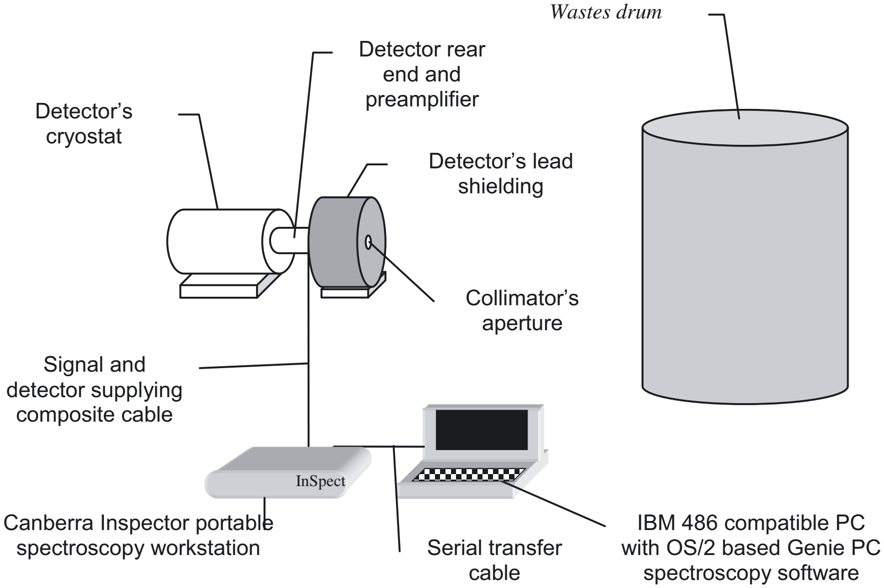

FIG. 2. Schema of the spectroscopy installation.

For simplicity, we considered that F_{att} was independent of the integration variables; thus, for an effective solid angle, we were able to write: $\bar{\Omega} = F_{att} \cdot \Omega$

To determine the value of F_{att} for a given configuration, a computer program was written based on a Monte Carlo (MC) algorithm. This program was designed to calculate the average attenuation factor for various possible trajectories of incident photons. Therefore, a special routine of the program was assigned to the selection of the emitting point and the generation of the travelling direction of the emitted photon. Another routine of the code was allotted to the calculation of photon paths within the various layers of the source, assuming that no scattering processes occur. Therefore, a path dependent attenuation factor is calculated using:

$$f_{att}^{j} = e^{-\sum_{i=1}^{m} \mu_i \cdot \delta_i^j} \tag{4}$$

where

m_I is the linear attenuation coefficient for the *i*th layer of the source,
d_i^j is the length of the path through the *i*th layer for a photon that is travelling along a given trajectory distinguished by the upper index.

The average attenuation factor is calculated using the following formula:

$$F_{att} = \frac{1}{N} \sum_{j=1}^{N} f_{att}^{j} \tag{5}$$

For geometric solid angle determination, another computer program was designed using the same MC method based algorithm, but this time to calculate certain geometric issues concerning the trajectory of unscattered photons.

4. THE ALGORITHM

The computer program was especially made to exploit the two symmetries of the measuring system, namely the axial symmetry of the cylindrical source (waste drum) and axial symmetry of the detection system (coaxial detector with cylindrical collimator). Thus, three systems of co-ordinates were considered to facilitate the mathematical modelling process. The first was the source's intrinsic cylindrical system, which served to select an emission point within the source and to define the direction of the emitted gamma. A change in the spherical associated system had to be made afterwards, to change the symmetry from that of the source to that of the detector. Finally, the detector's intrinsic cylindrical system served to select the gammas, which contribute to the photopeak. Because of the simplifying hypothesis, which was considered, concerning the possibility of decoupling the intrinsic efficiency from the total efficiency of the system, the physical properties of the modelled radiation quanta are used only to determine the self-absorption coefficient, which characterizes the path from the source. Therefore, the only property of the quanta needed for the modelling is the direction of travel.

Considering the approach described above, the algorithm used consists of the following steps:

(1) The emission point co-ordinates are generated by considering the appropriate geometry from those available (bulk cylindrical or cylindrical layer).
(2) The direction cosines of the gamma photon are generated. To speed up the computer code, the "associated probabilities" method is used by generating only the directions towards the detector and considering an associated probability for each photon to accommodate the fact that the generated direction was favoured.
(3) The mean pathway within the source and afterwards, and the attenuation factor for the travelling direction of the emitted gamma, are computed.
(4) One determines if the path of the photon passes through the aperture of the collimator. If yes, the event is counted.
(5) The above sequence is repeated from Step 2 for a predefined number of times.
(6) The effective solid angle stressed by the collimator from the selected point within the source is determined by computing the ratio between the total sum of the associated probabilities of generated photons and the number of these photons.
(7) The above sequence is repeated a predefined number of times (by selecting new points within the source and memorizing the effective solid angles).
(8) The average value is then computed for the individual effective solid angles calculated for each selected points and this is considered as being the effective solid angle of the source.

5. RESULTS AND CONCLUSIONS

The program was written in Visual Basic language and includes a graphics interface for parameter input and data output. The input parameters are stored in text files, which can be loaded, modified, or saved on disk as desired.

The program was tested to establish the stability of MC simulation and the sensitivity to the input parameters.

During the programming process, it was possible to verify some code sequences, and the results obtained showed that the model was appropriate. Figure 3 contains such a result, obtained during the solid angle assessment routine verification stage. It shows the values of the solid angle for a point source standing in various off-axis positions in front of the detector at a given distance. The emission point height is the distance to the axis of the detector.

To find out the optimal number of MC histories, which have to be modelled to obtain results of sufficient accuracy, the program was repeatedly run by changing only the number of histories. The relative deviation to the mean of the effective solid angle was calculated and is shown in Fig. 4.

The density of the source material as well as its composition can be changed by input, and in Fig. 5 are drawn for comparison of the efficiency calibration curves for source materials having the same elemental composition, but various densities ranging from 10 to 1000 kg/m^3.

The same calibration curves as the above are plotted in Fig. 6, but this time weighted to the maximum value.

Table I shows the activities of the identified radionuclides within some waste drums containing bituminized spent exchange resins

The results were in good agreement with the initial waste activity measurement; the calculated errors ranking was maximally 20%.

TABLE I. RESULTS OF SOME ACTIVITY DETERMINATIONS

	Activity per drum (MBq)								
Radionuclide	#1466	#1467	#1468	#1469	#1470	#1471	#1472	#1473	#1474
Mn-54	20.56	28.25	-	11.27	24.16	17.50	11.63	37.07	-
Co-58	86.14	69.33	10.08	29.45	85.70	60.22	51.15	99.23	33.42
Co-60	821.62	640.26	98.76	265.81	791.12	527.41	421.32	966.50	346.73
Cs-137	-	-	-	-	-	-	-	-	37.76
U-235	-	123.74	-	80.30	-	74.05	-	-	38.76

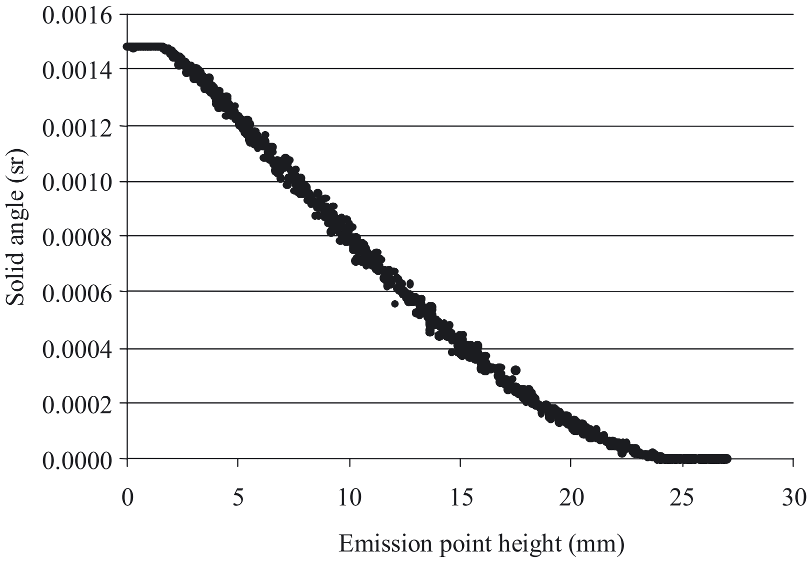

FIG. 3. Solid angle as a function of emission point position.

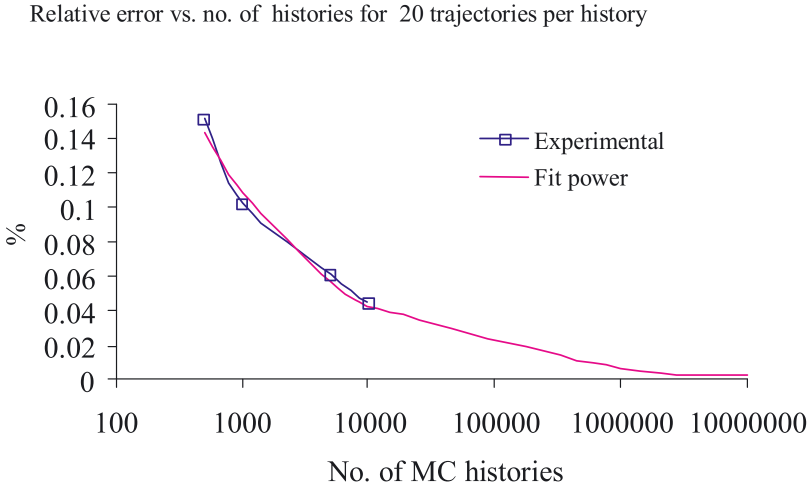

FIG. 4. Relative error versus number of histories.

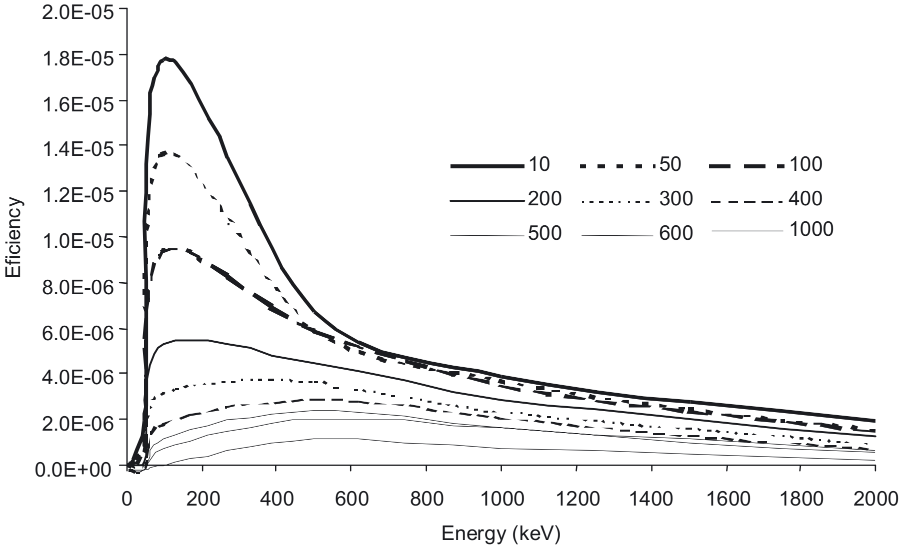

FIG. 5. Calibration curves considering different densities for drum content. A concrete shielding layer was modelled.

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DETERMINATION OF ^{90}Sr AND ACTINIDES (^{241}Am, ^{239,240}Pu, ^{238}Pu) IN NUCLEAR WASTE SAMPLES

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1. INTRODUCTION

Over recent decades, determination of ^{90}Sr and actinides in samples of waste from nuclear power plants has become a challenge for many radiochemical laboratories. In this paper we describe pretreatment of nuclear power plant samples, radiochemical separation and counting.

The studied radionuclides (^{14}C, ^{41}Ca, ^{59}Ni, ^{60}Co, ^{63}Ni, ^{79}Se, ^{90}Sr, ^{93}Mo, ^{93}Zr, ^{94}Nb, ^{99}Tc, ^{107}Pd, ^{126}Sn, ^{129}I, ^{135}Cs, ^{137}Cs, ^{151}Sm, ^{238}Pu, ^{239}Pu, and ^{241}Am) are controlled by the Nuclear Regulatory Authority of the Slovak Republic [1], and can be determined in our accredited laboratory (EN ISO/IEC 17 025 by SNAS). Activity levels of these radionuclides have to be determined in NPP waste samples, and in aerosols and water effluents from NPPs.

Accurate readings on low activity samples enable release to the environment of increased quantities of waste that meet regulated activity level requirements. Conversely, less waste has to be treated (concentration, vitrification, bitumenation, cementation, incineration or compacting) and stored.

Separation of strontium, plutonium and americium was carried out on a wide variety of sample matrices including aerosol filters (aerosol outlets from nuclear power plants), wastewater (water effluent from nuclear power plants), sludge (from reactor vessels), sediments (from industrial wastewater channels), evaporator concentrates, and ion exchange resins (from decontamination procedures).

2. SAMPLE PRETREATMENT

Sampling and pretreatment are important quality determining steps in the analysis [2].

The actinides and strontium on aerosol filter samples were transferred into solution by leaching in hydrochloric acid; solid samples were dried, ashed and leached in nitric acid. After evaporation, the samples were dissolved in nitric acid. Actinides and strontium in liquid samples were concentrated by co-precipitation or by evaporation.

In each of the pretreatment methods, carriers (Y^{3+}) and tracers (^{243}Am, ^{242}Pu or ^{236}Pu) were added to the samples.

3. RADIOCHEMICAL SEPARATION AND RADIOACTIVITY DETERMINATION

Conventional separation techniques, including precipitation and liquid extraction by tributylphosphate (TBP), were used to isolate ^{90}Y. After separation, the ^{90}Y component was used to quantify the ^{90}Sr activity by low level beta counting using DecCorr 1.3 software (WERT, Ltd).

The ^{241}Am, ^{239,240}Pu and ^{238}Pu separation method used extraction chromatography by the TRU resin cartridge (Eichrom Technologies, Inc.) [3]. After separation, the fluorides were precipitated, filtered, and counted by alpha spectrometry and the activity was determined by AlphRad software 2.13 (WERT, Ltd).

The most common problems resulted from sample origin, especially pollutants from nuclear power plants:

- Complicated matrices (high salinity, basic pH solution, mixture of organic and inorganic components, presence of complex compounds after decontamination processes, etc.).
- High activity of determined radionuclides compared to low tracer activity.
- Change of plutonium oxidation state ($Pu^{3+} \leftrightarrow Pu^{4+}$) during the separation process, etc.

4. CONCLUSION

The developed methods allow sequential determination of very low levels of strontium, plutonium and americium in a wide variety of samples. In such analyses, any reduction in time increases the capability for analysing larger numbers of samples. The objective is to develop improved separation methods to reduce staffing levels, to minimize the quantity of nuclear waste that has to be treated and to minimize disposal costs.

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USE OF RADIOCHEMICAL METHODS FOR IDENTIFICATION OF SEIZED NUCLEAR MATERIAL: A CONTAINER

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Abstract

A seized container was analysed for nuclear material at the LARCHA laboratory, which is accredited by the Slovak National Accreditation Service. The container was professionally dismantled in the hot cell at HUMA-LAB APEKO. Fragments of the compact core of the container, which had a mass of 36 kg, were analysed. The results of alpha spectrometry proved that the core of the container was composed of depleted uranium.

1. INTRODUCTION

After a long investigation in 1995, several people were arrested on suspicion of involvement in smuggling various materials from the Russian Federation. A suspicious container was seized; it was believed to have been used for transportation of radioactive and nuclear materials. In accordance with Slovak law, the container was transported to a civil defence post and police experts initiated analysis. On the basis of previous results, it was assumed that the core of the container was made of a nuclear material. The container was cut and separated into parts inside a hot cell at the HUMA-LAB, Košice, and prepared for analyses. From the shape and type of the container, it was thought that its core was composed of depleted uranium, and pieces were sent to the accredited LARCHA laboratory, Bratislava, for isotope analysis.

2. METHODS

2.1. Characterization of the container

- Container mass: 52 kg;
- Total height: 18.3 cm;
- Height of the lid: 3 cm;
- Diameter of the container: 17.5 cm;
- Lid of the container was of soft steel plate;
- Space for radioactive materials had a diameter of 4.0 cm and a depth of 9.5 cm;
- Mass of the container core: 36 kg;
- Cover was filled with lead.

The seized container is shown in Fig. 1.

2.2. Gamma spectrometric analyses

2.2.1. Wipe test

Wipes were taken from inside the container where radioactive materials may have been stored. Several locations were chosen for such samples, in accordance with chapter 4 of the Radiation Safety Guide: Monitoring Procedures with Alcohol.

Samples from different parts of the container were analysed by using HPGe-ORTEC gamma spectrometry with Gamma Vision software, version 4.10. Gamma spectrometry revealed the presence of ^{60}Co, ^{137}Cs and ^{235}U with values of 11.8, 5.6, and 3.8 Bq, respectively.

2.2.2. Core fragments

Fragments of the core were taken from the wall of the container after sawing (Sample 1 and Sample 2). During sawing of the core of the container, pyrophoric material was observed.

Gamma spectrometry confirmed the presence of ^{60}Co, ^{137}Cs and ^{235}U, with values of 3.9, 1.0 and 19.3 Bq, respectively.

2.3. Alpha spectrometric analyses

Samples from different parts of the container were analysed radiochemically using a modified Eichrom ACS 07 method, and prepared samples were

Fig. 1. The container.

measured by ORTEC SOLOIST 919alpha spectrometry with Alpha Vision software, version 1.2.

On the basis of the results, mass content (%) of uranium isotopes was determined for each sample. The results are summarized in Table I and are compared with natural and depleted uranium.

According to the Nuclear Regulatory Commission (NRC), which defines “depleted” uranium as that in which the weight percentage of the ^{235}U weight is less than 0.711%, the data unambiguously show that the core of the seized container was made from depleted uranium.

TABLE I. COMPARISON OF THE RESULTS WITH NATURAL AND DEPLETED URANIUM [1]

Isotope (%)	Natural uranium (%)	Depleted uranium (%)	Sample 1 (%)	Sample 2 (%)
^{238}U	99.2739	99.7495	99.5745	99.4512
^{235}U	0.7204	0.2500	0.4238	0.5470
^{234}U	0.0057	0.0005	0.0017	0.0018

3. CONCLUSIONS

- The container was composed of different parts, made from steel, lead and uranium;
- The wipe tests proved the presence of radionuclides ^{137}Cs and ^{60}Co;
- The core of the container was composed of depleted uranium;
- The chosen methods were suitable for analysis and identification of nuclear materials.

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SEPARATION OF PLUTONIUM FROM SOIL PRIOR TO DETERMINATION BY ICP-MS

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In the determination of plutonium in environmental materials by ICP-MS, chemical separation is often needed to remove, e.g. heavy sample matrices and interference from UH+ on m/z 239. This separation can be, and often is, performed in the same way as for alpha spectrometric analysis. There are, however, somewhat different demands on separation for ICP-MS compared to alpha spectrometry, but little has been published on the optimization of separation procedures for plutonium determination by ICP-MS. In this paper, we describe the development of a separation procedure especially suited for the determination of plutonium by ICP-MS. Focus is on parameters such as chemical yield of plutonium and decontamination from uranium, as well as time requirements and ease of performance.

The separation of plutonium was performed using various resins, such as anion exchange resin and extraction chromatographic materials. The procedures were carried out on water spiked with ^{238}U and ^{240}Pu to concentrations of approximately 300 ppb and 50 ppt, respectively. The basic separation procedure was:

- Adjustment of oxidation state for plutonium;
- Loading on column;
- Rinsing using 4 × 5 free column volumes (FCVs) of load solution, if needed in combination with 1 × 5 FCVs of another rinsing agent;
- Elution of plutonium, followed by evaporation and dissolution in a solution suitable for ICP-MS determination;
- Determination by high resolution ICP-MS.

The elution of plutonium was performed using various media, based on either reduction of Pu(IV) to Pu(III) or complex formation. The chemical yield of plutonium and the decontamination from uranium for various resin/elution combinations can be seen in Figs 1 and 2. It was found that the most efficient separation procedure in terms of yield and uranium decontamination was the combination of two extraction chromatographic materials, UTEVA followed by TRU, and elution of plutonium by 0.1 % 1-hydroxyethane-1,1-diphosphonic acid (HEDPA). In this procedure, uranium is retained on UTEVA while Pu(III) is not retained until reaching the TRU resin, which results in an efficient separation of uranium from plutonium. HEDPA forms strong complexes with the actinides, which enables complete elution of plutonium into a small volume of a relatively weak solution. The eluted plutonium can then be determined directly by ICP-MS without further treatment of the sample, which results in decreased risk of contamination and easier sample preparation.

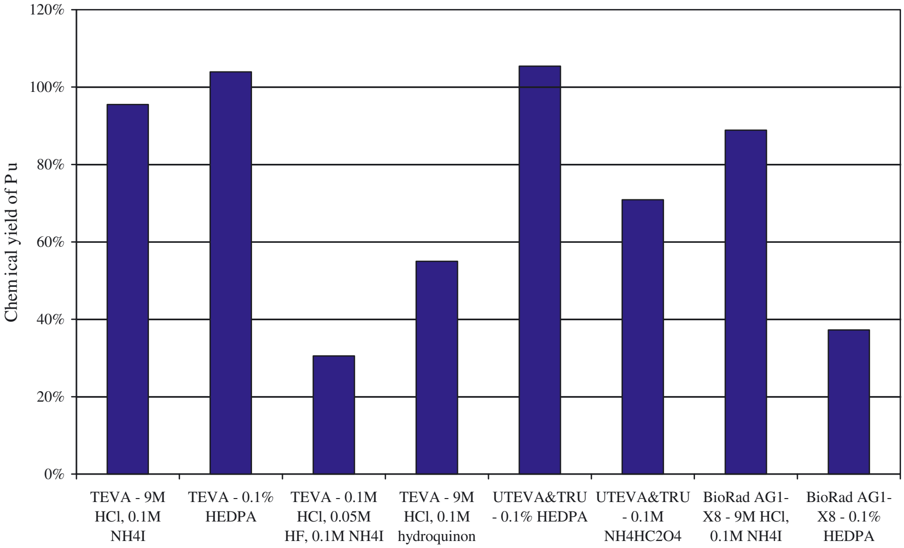

FIG. 1. Chemical yield of plutonium after separation by various resins and elution media.

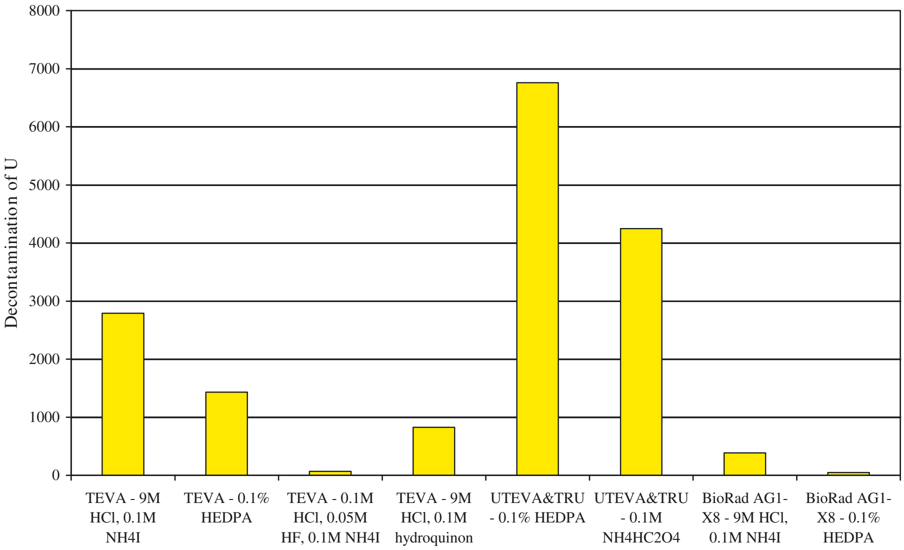

FIG. 2. Decontamination from uranium after plutonium separation by various resins and elution media.

DEVELOPMENT OF LABORATORIES FOR RADIOLOGICAL ANALYSES IN THE REPUBLIC OF TAJIKISTAN

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Abstract

The paper shows the necessity of establishing regional radiological laboratories in the Republic of Tajikistan. Considering that Tajikistan shares borders with such States as Afghanistan and China, the possibility exists for illicit trafficking of nuclear material. In this connection, in frontier districts, it is necessary to establish radiological laboratories for the purpose of combating and preventing such smuggling. To establish these laboratories, the Republic of Tajikistan will need financial aid and physical assistance.

After the break-up of the Soviet Union, the independent Central Asian States became of interest to the global community because of the richness of their natural resources. Furthermore, the scientific world was aware that Soviet nuclear weapons were made with Tajik uranium.

Much has been written about possible future development of Tajikistan's uranium mining industry. Illicit trafficking of radioactive materials (even enriched uranium) in Tajikistan has attracted media attention. We wish to inform the global community that Tajikistan's uranium factories and enrichment plants have been working at less than full capacity for a long period of time (even during the Soviet era) because of lack of raw materials. After Tajikistan became an independent republic, civil war broke out, causing many scientists, specialists, and experts in nuclear technology to emigrate. As a result, operations in factories in such cities as Chkalovsk, Taboshar Adrasmon (Northern Tajikistan) have practically halted.

During the Soviet period, only a small fraction (5–10%) of what was mined was used by industry, and the major part, which was waste, was accumulated. These wastes contain a number of elements and compounds inimical to human, animal and environmental health: uranium, radium, polonium, thorium, antimony and mercury. Tajik mining industry repositories are in a critical state. Unfortunately, considerable capital will be required for their rehabilitation. Tajik industry does not have such capital and the economy of the republic is not yet able to address this problem. However, with recent improvements in the economy, re-establishment of federal and industrial laboratories is occurring, for characterization of nuclear materials, particularly radioactive wastes, tailing dumps, etc., with a view to developing means of safe long term storage.

At present, there is a laboratory at the Chkalovsk plant in which qualified personnel carry out various radiological, dosimetry, nuclear spectroscopy, etc., analyses. Similar laboratories, albeit less well equipped, are in operation at the Ministry of Extreme Situations, the Republican Sanitary Station, the Tajik National State University, Physico-Technical Institute of the Academy of Sciences of the Republic of Tajikistan. However, there is pressing need for modern equipment in all of these laboratories.

Although relatively small in area, the Republic of Tajikistan is uniquely located geopolitically, sharing borders with China, Afghanistan and other Central Asian States, and is relatively close to India and Pakistan, which, like China, possess thermonuclear weapons. Tajikistan shares a 1382 km border with China and 511 km with Afghanistan. Some parts of the border are hard to protect. During the long running civil war in Afghanistan, the Government of Tajikistan faced not only the problems of safety but drug trafficking across the borders to other countries, and illicit shipping of nuclear materials.

These problems continue and are exacerbated by lack of modern monitoring equipment. Even checkpoints at the majority of the border crossings lack dosimeters for detection of radioactive materials. To the extent possible, the Regulating Authority of the Republic renders help to agencies that use, store, and control radioactive and nuclear materials, but the service is less than optimal. The establishment of regional laboratories is urgently needed, supplied with the necessary sensitive equipment (dosimeters, spectrometers, etc.). To that end we would welcome the help of colleagues and international funding organizations.

DISSOLUTION OF UO_2 PELLETS BY ELECTROGRAPHY FOR ISOTOPE RATIO ANALYSIS

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Abstract

A method for dissolving UO_2 pellets, using electrography, was investigated. Electrography was used widely in the 1950s for rapid identification and qualitative analysis of certain materials. However, due to certain limitations, it is rarely used today. The principle involves anodic dissolution of metallic samples and transfer of the ions to a carrier medium, usually a filter paper. Colour development is used for identification. Dissolution of sintered UO_2 pellets is difficult and time consuming. In cases of illicit trafficking, the amount of material may be limited and analytical data are usually needed urgently, therefore, dissolving whole pellets is not an option. In this study, rapid dissolution of UO_2 pellets was achieved with the electrograph. A sheet of qualitative filter paper was soaked in a suitable electrolyte, dried and placed on the cathode of the instrument. The pellet was placed between the anode and the cathode, and a DC current applied. The dissolved ions were transferred to the filter paper, which was washed and diluted to volume for analysis. Experimental variables examined were electrolyte, dissolving time and DC current. The method is rapid and uses very little sample for analysis.

1. INTRODUCTION

Electrography, a method commonly used in the 1950s for rapid identification and qualitative analysis of certain materials, depends on colour formation for identification of elements. It is based on anodic dissolution of a metal by the following reaction:

$$M^0 = M^{n+} + n\ e^-$$

The sample is placed between an anode and a cathode, and a filter paper soaked in an electrolyte is placed on the cathode. When direct current is applied, ions from the surface of the sample move to the filter paper. Colour is formed directly on the filter paper. Although the method is convenient for qualitative work, quantitative analyses are more difficult, and interferences may be observed in multicomponent systems. Today, it is used to test porosity of gold coatings on metal substrates [1, 2] and in combination with other techniques for quantitative determinations, e.g. ion chromatography and flow injection analysis for inductively coupled plasma mass spectroscopy. Electrography is used for dissolution of the sample and is often referred to as on-line electrolytic, or anodic, dissolution [3–6]. It is used for conductive samples.

Sintered UO_2 pellets are difficult to dissolve and the procedure is time consuming. In cases of illicit trafficking, there is usually an urgent deadline for analytical data, and the amount of material used in destructive analysis is also important. Dissolution of uranium oxide and gadolinium oxide pellets by electrography, investigated in a previous study, was found to be a rapid method for dissolving sintered pellets [7]. Therefore, in this study electrolytic dissolution of UO_2 pellets was investigated.

2. EXPERIMENTAL

All chemicals used were of reagent grade, and deionized or distilled water was used throughout. The electrographic equipment consisted of a variable DC power supply (0–25 V), a digital ammeter (0–500 mA), a switch, a timer, and a custom made sample holder with two graphite electrodes. The experimental set-up is represented in Fig. 1.

The experiments were carried out as follows: a dry filter paper cut to the size of the electrodes was placed on the cathode and covered with another piece of filter paper soaked (for 0.5 h) in the electrolyte (0.5M nitric acid). The UO_2 pellet was clamped into place between the two electrodes and the timer was set to a certain period when 5 to 7 V was applied. The time duration selected for this experiment was 20 s, long enough for a sufficient amount of material to be transferred to the filter paper for isotope ratio analysis by ICP-MS. The wet filter paper was removed and placed in a funnel for washing with 10 mL of 0.5M HNO_3, then made up to 50 mL with water. The isotope ratios were then measured with ICP-MS (an Agilent 7500 quadrupole instrument).

Other electrolytes, e.g. 0.5M $NaNO_3$ with 1.5M Na_2CO_3 and 3M HCl, also yielded good results. Nitric acid was preferred because of lower total dissolved solids in the final solution. Qualitative filter paper gave the best results as the carrier of the transfer medium. Synthetic sintered pellet standards were prepared from depleted uranium dioxide, natural uranium dioxide and 5% enriched uranyl nitrate hexahydrate. Standard pellet manufacturing procedures, i.e. dissolving, ammonium diuranate precipitation, calcination, reduction to UO_2, pressing and sintering, were carried out with synthetic standards.

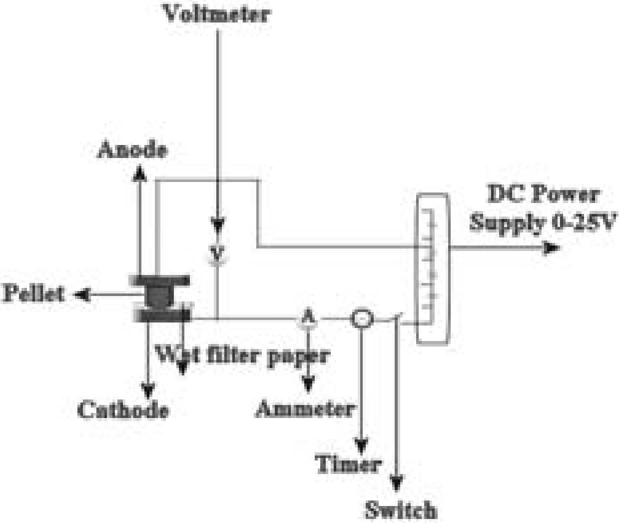

FIG. 1. Sketch of the experimental set-up.

3. RESULTS AND DISCUSSION

The isotope ratio results for WWER type pellets are given in Table I. The isotope ratio data agreed with previous results (4.51–4.66%) by gamma spectrometry. Dissolved concentrations were also determined to be within the range of 1.5–20 mg/L. The effect of concentration was investigated; a minimum amount of material was necessary to obtain reliable data. Results from 50-fold dilutions, with concentrations lower than 1 mg/L, gave lower enrichment values, whereas 10-fold dilutions had no effect. One of the most important parameters in electrography is that the surface of the sample is in contact with the electrolyte. Sample pellets with a central hole had less surface contact than did PWR pellets, therefore, measured current values were lower.

The advantages of this method are that sample preparation time is short, the amount of material used is small, and the apparatus is simple and inexpensive. Although the method is classified as destructive, in cases of confiscated material from illicit trafficking, very little of the sample is used and the rest can be preserved as evidence.

The method has limitations. It is applicable only to flat surfaces. Low results are obtained if contacting surfaces are not flat. And it cannot be used with powders or with metallic samples that have no flat surfaces.

TABLE I. ISOTOPE RATIO RESULTS FOR WWER TYPE PELLETS

U235/U238 %		U235/U238 %		U235/U238 %		U235/U238 %	
i1	4,53	i6	4,11	i11	4,44	i16	4,57
i2	3,86	i7	4,14	i12	4,53	i17	4,52
i3	4,50	i8	4,52	i13	4,57	i18	4,38
i4	4,57	i9	4,46	i14	4,58	i19	4,57
i5	4,70	i10	4,52	i15	4,59	i20	4,43

4. CONCLUSION

The method is suitable for metals, alloys and other conductive samples, as described in the literature, and was easily applied to sintered pellets. It is especially advantageous in analysis of illicitly trafficked samples because only small amounts of material are needed and it proved to be time saving when compared to conventional sample preparation.

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ENHANCED IONIZATION EFFICIENCY USING THE HIGH EFFICIENCY CAVITY SOURCE IMPLEMENTED ON A MAGNETIC SECTOR TIMS

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Abstract

Traditional thermal ionization mass spectrometry (TIMS) is the most common method for determination of isotope ratios and concentration (via isotope dilution) of uranium and plutonium. Despite its exemplary performance, the thermal ionization mechanism is inefficient. Total efficiencies (the ratio of ions detected/atoms of sample loaded) are typically of the order of 0.001 to 0.1% for uranium and 0.1 to 1% for plutonium; most of the available material is lost during analysis. With the goal of improving total efficiency for analysing uranium and plutonium by TIMS, a new cavity type ion source was developed and installed on a commercial magnetic sector mass spectrometer. The dimensions and geometry of this high efficiency cavity source (HECS) combine to provide a dramatic increase in ionization efficiency and, therefore, in sample utilization. Average ionization efficiencies for the new source were 5% for uranium and 7% for plutonium. Implementation of the HECS could significantly improve detection of uranium and plutonium in safeguards and environmental sampling programmes, in addition to having applications in other arenas where high sample utilization efficiency is critical.

1. INTRODUCTION

Traditional thermal ionization mass spectrometry (TIMS) is the method of choice for high precision, high accuracy isotope abundance ratio measurements, even though surface ionization has a very low ionization efficiency for several important elements, including uranium, plutonium and thorium. With many nuclear materials, the sample is available in abundance and there are no problems performing a traditional TIMS analysis. However, environmental sampling and nuclear non-proliferation efforts yield samples with exceedingly low concentrations of analyte. Likewise, nuclear forensics programmes depend on accurate and precise measurement of the abundances of minor isotopes in samples. In all such cases, the ion counts above background that are generated by the sample ion source are critical.

Many have suggested inductively coupled plasma mass spectrometry (ICP-MS) as a replacement for TIMS. The ICP plasma ionizes nearly 100% of the sample. However, transmission of the ions is very low. Only 0.2 to 0.3% of uranium ions were transmitted to the detector when using a sector instrument, even when special efforts, including use of a high efficiency nebulizer and a guarded electrode, were employed [1]. In addition, ICP measurements are not as accurate as TIMS measurements.

We have developed a high efficiency thermal ionization source based on a cavity design. In the traditional TIMS source, the sample is loaded onto one to three filaments that are then heated to evaporating and ionizing temperatures. In the high efficiency cavity source (HECS), the sample is placed into a narrow cavity in one end of a refractory metal rod, which is heated by electron bombardment. The high temperature (2400–2800°C) and confined geometry of the HECS produce a higher ionization efficiency than filament based TIMS.

2. METHODOLOGY AND INSTRUMENTATION

2.1. The high efficiency cavity ion source

The HECS consists of three parts, a cavity, a heating filament and an electron shield [2, 3]. The cavity temperature is regulated by bombardment of electrons formed by a heated filament. The electron shield is a metal plate that is held at the same potential as the heating filament. The voltage applied to the electron shield ensures that electrons do not escape the source area and bombard the ion lenses. Figure 1 shows the geometry and relative position of the elements of the HEC ion source.

2.2. Instrumentation

Routine analyses of uranium and plutonium at the Safeguards Analytical Laboratory (SAL) in Seibersdorf, Austria, are performed on a Finnigan MAT 262 sector mass spectrometer. A multi-sample turret, normally used to mount TIMS filaments, was modified to hold up to 13 cavities. The HECS source is completely interchangeable with the typical TIMS filament source and switching between the two ion sources takes about 8 min.

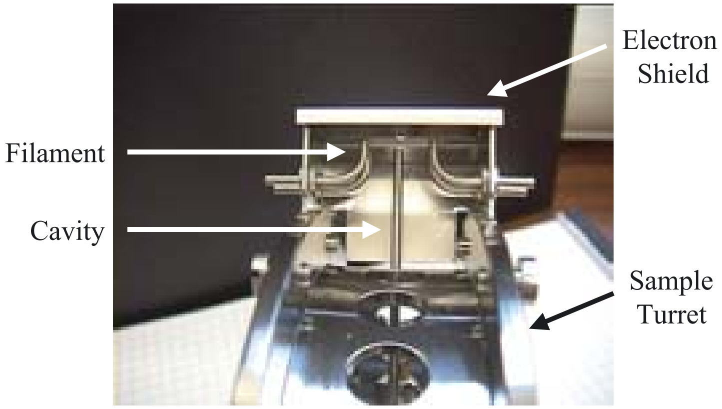

FIG. 1. High efficiency cavity ion source

2.2.1. Sample preparation

The efficiency, accuracy and precision of the cavity method were determined by analysing two certified standard reference materials. The National Bureau of Standards (NBS) U950 reference material was used to determine the ionization efficiency for uranium, and IRMM-082 was used to determine plutonium analysis efficiency. Resin beads containing 500 pg and 100 pg of uranium standard and 165 pg and 20 pg of plutonium were made. Isotope dilution analysis using TIMS verified the concentration on each batch of beads.

The cavities were baked at between 2 000 and 2 800°C for 30 to 60 min, and allowed to cool before sample loading. A bead was placed in the cavity using a pair of fine manipulators and gently pushed to the bottom of the cavity using a clean probe. A 0.5 μL aliquot of aquadag, a graphite suspension in water, was used to hold the bead in place. A 1 μL aliquot of rhenium powder in pure ethanol was then injected into the cavity and allowed to dry before total evaporation analysis of the bead.

3. RESULTS

3.1. Efficiency measurements

Efficiency measurements were made by heating the cavity to a temperature between 2 400 and 2 800°C and collecting the signal from each of the Faraday cup detectors. The signal was totalled and then converted into ion counts. No correction was made for the detection efficiency of the detectors. The ion counts were then compared to the numbers of atoms on the analyzed beads to calculate ion yield. Table I summarizes the results of the initial testing of the HECS.

Total evaporation analysis of the uranium beads resulted in efficiencies of between 1.0 and 14.6%. Plutonium bead analysis yielded efficiencies between 0.9 and 17.4%. While analysis of samples loaded on beads was necessary in order to guarantee the amount loaded for the purposes of making efficiency measurements, it would be convenient for practical analysis if the cavity could achieve the same high ionization on drop loaded solutions. To determine the viability of drop load analysis via the cavity, three aliquots of 0.5 μL of a solution containing 100 pg Pu/μL were analysed. The experiment yielded ionization efficiencies of 8.2, 10.9 and 15.1%, respectively.

3.2. Precision and accuracy

Seven beads of uranium and eight of plutonium were selected to determine the accuracy and precision of bead analysis for the new cavity type ion source (Tables II and III). The accuracies, as indicated by the per cent error when compared to known isotope ratios of the standard materials, were 0.66% and 0.02% for uranium and plutonium, respectively. The relative standard deviations of the uranium and plutonium measurements were 1.3% and 0.13%, respectively.

4. IMPLICATIONS

The highest reported ionization efficiencies for normal TIMS measurements, using ultra pure samples and rigorous sample preparation and handling techniques, are 0.5 to 1.3% for uranium [4, 5] and 1.5 to 3% for plutonium [5, 6]. The MAT 262 spectrometer at SAL, used in our experiments, typically delivers ionization efficiencies of 0.01 to 0.1% for uranium and 0.1 to 1% for plutonium, within the expected ranges for TIMS instruments. Due to the low ionization efficiency, typical loadings of uranium on the MAT 262 ranged between 50 and500 ng. Forty ng of plutonium were necessary to run an analysis on the

TABLE I. SUMMARY HECS EFFICIENCY MEASUREMENTS

Element	Loading (pg)	Runs	Efficiency (%)	Average (%)
Uranium	500	8	1.08–12.12	5.6
	100	9	0.96–14.64	6.2
Plutonium	165	16	2.78–17.36	7.9
	20	3	0.85–3.75	2.5

Faraday cups, and 200 pg were typically run using a peak hopping mode on the electron multiplier.

The cavity ion source, despite being in the early stages of development, demonstrated much higher ionization efficiencies. The cavity source routinely delivered ion yields that were one to two orders of magnitude greater than filament measurements on the same instrument. Likewise, the signal intensity from the same amount of sample was roughly forty times greater. This indicates that significantly smaller samples can be analysed. One example of this ability is the fact that all three of the 18 pg plutonium beads were performed on the Faraday cups, a feat impossible with such a small sample loading on a filament.

Traditional thermal ionization mass spectrometry with a multicollector detector (MC-TIMS) has occupied a favoured position as the method of choice for high precision isotope abundance ratio measurements. Due to the low ionization efficiency of TIMS, MC-ICP-MS has been the focus of increased attention. However, although ionization efficiencies are much higher for ICP-MS, the low ion transmission results in effective efficiencies (ions detected/atoms loaded) for uranium and plutonium that are similar to those obtained using traditional filament based TIMS.

The HECS offers an alternative to these two ion sources. The ionization efficiency of the HECS is much higher than that of TIMS. Likewise, the ion transmission of the HECS is much higher than an ICP source. The result is an analytical ion source that operates with the simplicity of a TIMS source, but which has a higher effective ion yield than an ICP. This should result in higher precision and accuracy for very small sample loadings. Table IV compares the performance of TIMS, ICP and HEC ion sources.

TABLE II. ISOTOPIC MEASUREMENT OF U950

Sample Load (pg)	Efficiency (%)	$^{235}U/^{238}U$ Observed	$^{235}U/^{238}U$ Certified
500	12.12	0.004782	0.007249
500	4.5	0.007234	
500	1.08	0.007370	
500	10.5	0.007245	
100	2.61	0.007195	
100	1.00	0.007277	
100	13.64	0.007273	
Mean		0.007297	0.007249
Std.dev.		0.000098	

TABLE III. ISOTOPIC MEASUREMENT OF Pu IRMM-082

Sample Load (pg)	Efficiency (%)	$^{240}\mathrm{U}/^{239}\mathrm{U}$ Observed	$^{240}\mathrm{U}/^{239}\mathrm{U}$ Certified
18	3.75	0.047031	0.047096
18	3.02	0.047114	
165	12.19	0.047139	
165	6.68	0.047132	
165	11.65	0.047107	
165	4.41	0.047111	
330*	17.36	0.047100	
330*	7.31	0.047069	
Mean		0.047100	0.047096
Std.dev.		0.000035	

**Two beads containing 165 pg of Pu each were loaded.*

Table IV indicates that the accuracy of the HECS was higher than that of ICP, but not quite as accurate as conventional filament based TIMS. The relative external standard deviation (%RESD) shown in Table IV was a little high, but still acceptable considering the sample loadings were at least an order of magnitude lower than with the other techniques. As the source is refined and continuing experiments increase understanding of its operation, the precision and accuracy of the HECS is expected to improve. Although still in the initial stages of develop-

TABLE IV. COMPARISON OF TIMS, ICP-MS AND HECS

Technique	Sample	Loading (ng)	%Error	%rsd	Ion yield (%)
TIMS-MC[7,8]	NBS U500	500	0.22	0.035	0.001–0.1
TIMS-TEVAP[7,9]	NBS U500	100–200	0.007	0.007	-
MC-ICP[7,10]	NBS U500	500–1000	1.80	0.012	0.2–0.3[1]
ICP-QMS[7,11]	NBS U500	100	5.02	0.21	<<0.2
ICP-QMS[7] cross flow neb.	NBS U500	18	0.80	0.088	-
ICB-QMS[7] gross flow neb.	NBS U500	200	2.10	0.028	-
ICP-QMS[7] micro-conc. neb.	NBS U500	6.7	1.97	0.055	-
MC-HECS	NBS U950	0.1–0.5	0.70	1.3	5–6
MC-HECS	Pu IRMM-082	0.018–0.165	0.023	0.07	7–9

ment, the HEC ion source has shown excellent potential for dramatically increasing the effectiveness of environmental sample analysis.

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NUCLIDES.NET: AN INTEGRATED ENVIRONMENT FOR COMPUTATIONS ON RADIONUCLIDES AND THEIR RADIATION[*]

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Abstract

Nuclides.net is an ‘integrated environment’ for computations on radionuclides and their radiation. The integrated environment is a suite of computer programs ranging from a powerful interface, which allows the user to navigate the nuclide chart and explore the properties of nuclides, to various computational modules for decay, dosimetry, shielding calculations, etc. The product is aimed both at students and at professionals for reference data on radionuclides and computations based on these data using the latest Internet technology. It is particularly suitable for environmental monitoring and nuclear forensics.

1. DESCRIPTION OF NUCLIDES.NET

The Nuclides.net computational package (Fig. 1) [1] is relevant to the fields of environment monitoring and nuclear forensics. The ‘integrated environment’ is a suite of computer programs ranging from a powerful interface, which allows the user to navigate the nuclide chart and explore the properties of nuclides, to various computational modules for decay, dosimetry, shielding calculations, etc. The main emphasis in Nuclides.net is on nuclear science applications, such as health physics, radioprotection and radiochemistry, rather than nuclear data for which excellent sources already exist.

In contrast to its CD-based Nuclides 2000 predecessor [2, 3], Nuclides.net applications run over the Internet on a web server. The user interface to these applications is via a web browser. Information submitted by the user is sent to the appropriate applications resident on the web server. The results of the calculations are returned to the user, again via the browser. The product is aimed both at students and at professionals for reference data on radionuclides

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[*] The Nuclides.net book, together with a CD and a registration form for on-line access, is published by Springer Verlag, Heidelberg.

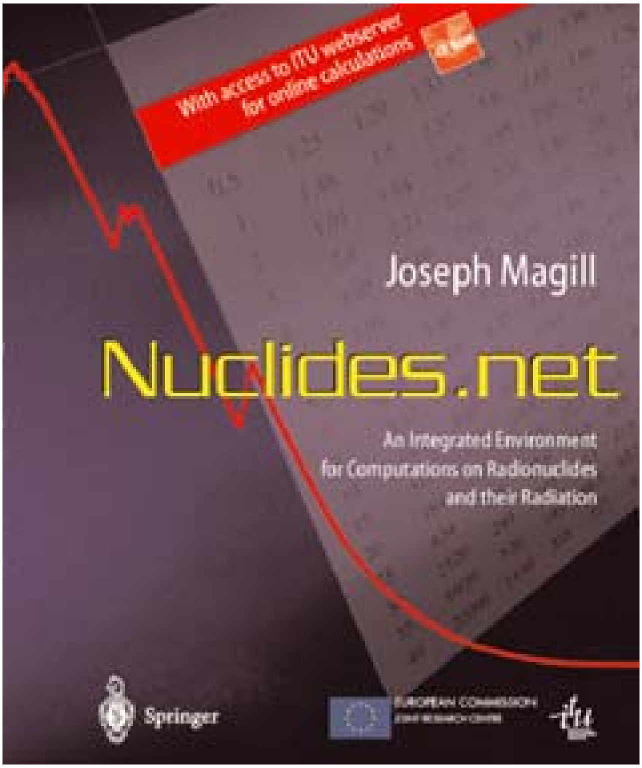


FIG. 1. The Nuclides.net package

and computations based on these data using the latest Internet technology. It is particularly suitable for educational purposes for those in the nuclear industry, and those in health physics and radiation protection, nuclear and radiochemistry, nuclear physics, astrophysics, etc.

The Nuclides.net software suite contains the following modules/features:

- A new user interface to view nuclide charts (with zoom features). Additional nuclide charts are based on spin, parity, binding energy, etc.
- There are five main applications (Fig. 2):
  - A “Decay Engine” for decay calculations of numbers, masses, activities, dose rates, etc., of parent and daughters.
  - The “Dosimetry and Shielding” module allows the calculation of dose rates both from unshielded and from shielded point sources. A choice of ten shield materials is available. Calculations of the

FIG. 2. Some application windows in the Nuclides.net environment.

required shielding thickness for a given source and a desired resulting dose rate can also be performed.

- The “Virtual Nuclides” assist the user with decay, dosimetry and shielding calculations on mixtures of nuclides (example in Fig. 3).
- The “Fission Yield” module gives the user access to fission products and yields for 36 fissioning nuclides (data for spontaneous fission and neutron induced fission with thermal, fast and 14 MeV neutrons) from the main international data files.
- The “Universal Nuclide Chart” runs locally on the user computer and displays the most important basic data. It can also be used to simulate decay processes and nuclear reaction paths.

— There are data on 3650 ground states and isomers (increased from 2656 in Nuclides 2000), from internationally recognized sources.

— “FactSheets” give important properties derived from the basic data. In addition to heat, neutron and gamma emission rates, information on radiotoxicity and nuclide transportation are provided.

— “Cross Sections” give averaged neutron cross-sections from the main international data files. Data include the cross sections for room temperature, Maxwell averaged, resonance integral, fission averaged, and 14 MeV neutrons.

— The “News” and “Forum” provide the latest information on Nuclides.net and allow information exchange.

2. CASE STUDY: DETERMINATION OF THE ‘AGE’ OF PLUTONIUM PARTICLES

At the Institute for Transuranium Elements (ITU), a range of analytical techniques is being developed for verification and detection purposes, to check State compliance with their non-proliferation commitments [4]. As part of these activities, a technique is being developed to determine the ‘age’ of plutonium particles [5]. The ‘age’ of a particle is defined as the time elapsed since the last chemical separation of daughter nuclides from the parent. The particles to be analysed can be obtained from the environment or from ‘swipes’ taken at nuclear installations where clandestine activities are suspected. In view of the pending international agreement to stop the production of weapons materials, the age of such ‘suspected’ particles is, of course, of great interest for verification purposes. For bulk samples, gamma spectroscopy can be used; however, for very small particles, because of the low activity, this technique is of no utility.

In general, fresh plutonium particles contain ^{238}Pu, ^{239}Pu, ^{240}Pu, ^{241}Pu and ^{242}Pu in various amounts, depending on the production route. With time, these nuclides decay to ^{234}U, ^{235}U, ^{236}U, ^{241}Am, and ^{238}U respectively. By determining the ratios of the parent to daughter (^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U, ^{241}Pu/^{241}Am, ^{242}Pu/^{238}U) one can deduce elapsed time and, therefore, the age of the particle. Because these ratios are measured by secondary ion mass spectrometry (SIMS), one cannot obtain the ratio ^{241}Pu/^{241}Am. In addition, if the particle has some uranium contamination, one cannot use the ratio ^{242}Pu/^{238}U. This leaves the three ratios, ^{238}Pu/^{234}U, ^{239}Pu/^{235}U, ^{240}Pu/^{236}U, as suitable for age determination.

In 1994, officials at Munich Airport seized a suspicious piece of luggage. The suitcase, delivered to ITU, was found to contain a sealed package in which several hundred grams of a radioactive powder had been concealed. Initial chemical analysis showed that the powder consisted of a mixture of oxides of plutonium and uranium. Scanning electron microscopy showed that the powder was a mixture of three components characterized by morphology and chemical composition. They were identified as plutonium oxide (PuO_2) in the form of small flat platelets forming the largest fraction of the mixture (Fig. 3-1), rod shaped plutonium oxide (PuO_2) (Fig. 3-2), and uranium oxide (U_3O_8) particles (Fig. 3-3).

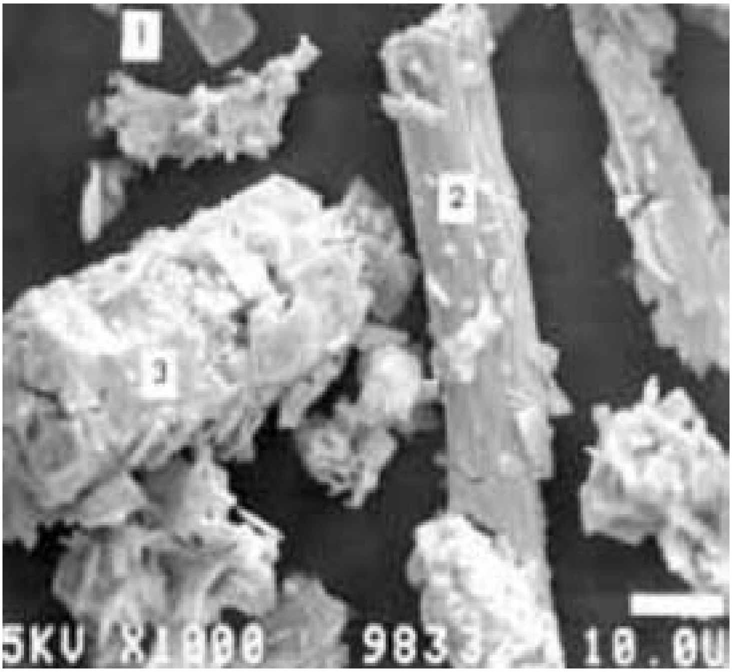


FIG. 3. Sample F19A.

The correlation between atom ratio and age was calculated using Nuclides.net. We present here, as an example, a step by step calculation of the correlation between the atom ratios of $^{240}Pu/^{236}U$. The first step is to select the nuclides of interest (in our case ^{240}Pu) in the main interface of the Nuclide Explorer, which offers eight zoom levels to locate the nuclide of interest. The nuclide can also be chosen directly using the drop down list. The position in the nuclide chart is then shown in the main window (Fig. 4).

Once the nuclide is selected, one has then to choose the decay calculation feature from the taskbar. Selecting this feature connects the Internet explorer browser to the Nuclides.net server over the web and displays the decay calculation windows.

In the decay windows, one chooses a calculation over 100 years with ten calculation steps, which thus provides ten values for building our decay curve. The results window (Fig. 5) shows the parent and daughters of ^{240}Pu in the first column. The following columns give the number of atoms, mass, activity, and gamma emission rate and gamma dose rate of the parent and daughters. The total values in each case are also given. The choice of which

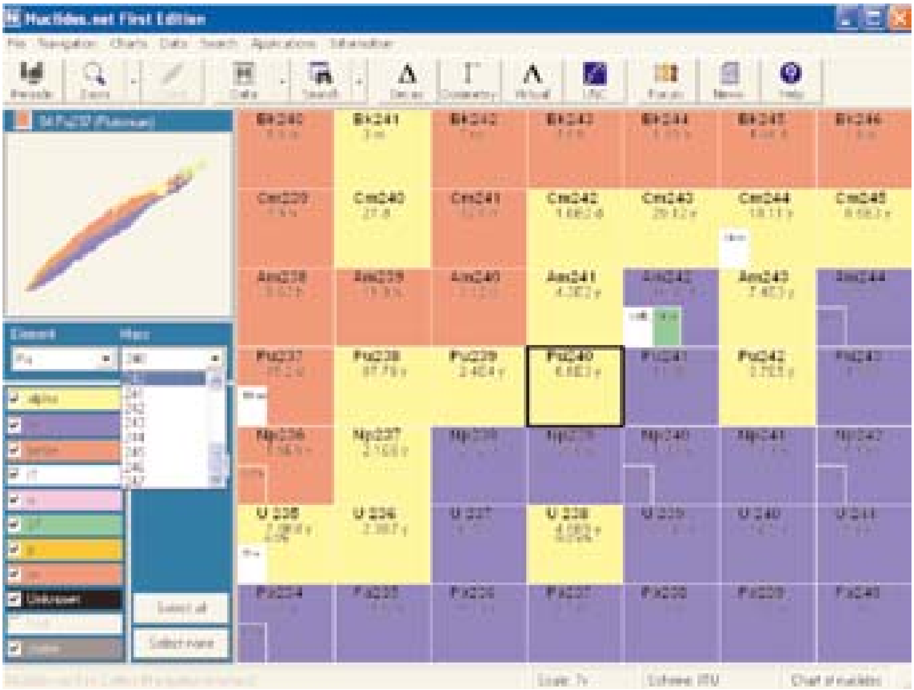


FIG. 4. The Nuclide Explorer interface. Selection of the ^{240}Pu nuclide in the advanced chart display.

properties to show in this evaluation can also be set by the user. Internally, all the linear decay chains have been evaluated, the number of chains is given in the top right hand corner. More information on the decay chain evaluations can be seen by pressing the *Details* button.

Finally, a graph of the results can be obtained with *Graph*. The decay graph is obtained from the intermediate values between times 0 and t, specified by the number of steps of input data discussed above. On pressing the *Graph* button, a graph options window (Fig. 6(a)) appears where the user can select the type of graph to be plotted. In the “Type of graph” list box, the user can choose which quantity should be shown, i.e. numbers, masses, activities, gamma emission rate and gamma dose rate. Both logarithmic and linear plots are available. In addition the region of interest can be specified for both the x and y axes. The nuclides to be plotted, however, can be specified by the user.

In our case study, we choose to plot ^{240}Pu and ^{236}U.

Pressing the “Download File” button, one can download the calculated values in the form of an Excel sheet from which the correlation between the atom ratios and age can be deduced, as shown in Fig. 7. These ratios, calcu-

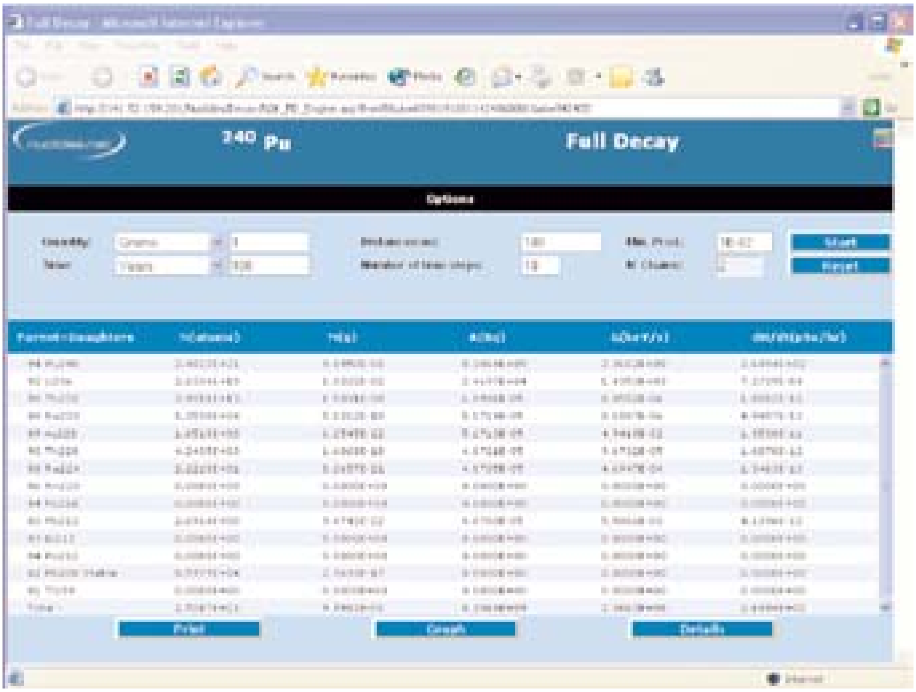


FIG. 5. Results window for the ^{240}Pu decay calculation, showing the number of atoms, mass, activity and gamma emission rates for each daughter of the decay chain of ^{240}Pu.

lated with Nuclides.net, are shown in Fig. 8. The time scale of interest was in the range 1 to 50 years.

From the calculated correlation, the 'age' of the sample can be deduced (Table I). Since the uranium contamination was significant in sample F19A, the ages determined from the ratios were at odds. The most accurate value

TABLE I. EXPERIMENTAL ISOTOPE RATIOS AND THE DEDUCED PARTICLE 'AGE' FROM THE NUCLIDES 2000 CORRELATION

Sample F19A	Expt. ratio	Age (a)
^{238}Pu/^{234}U	109.4	1.18
^{239}Pu/^{235}U	670.9	51.9
^{240}Pu/^{236}U	476.3	27.8

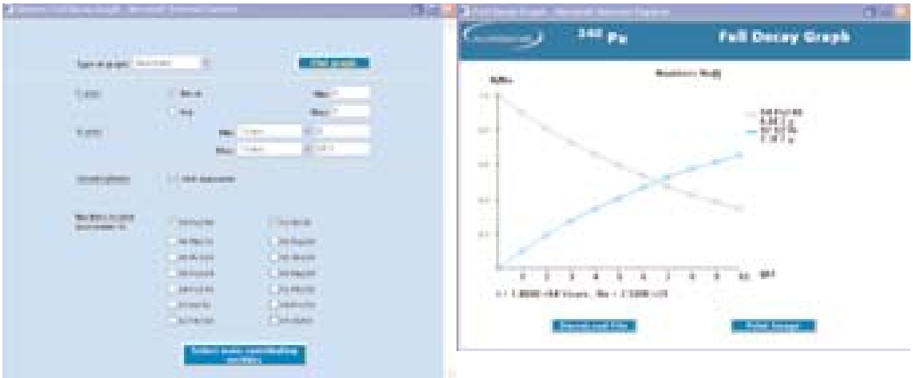


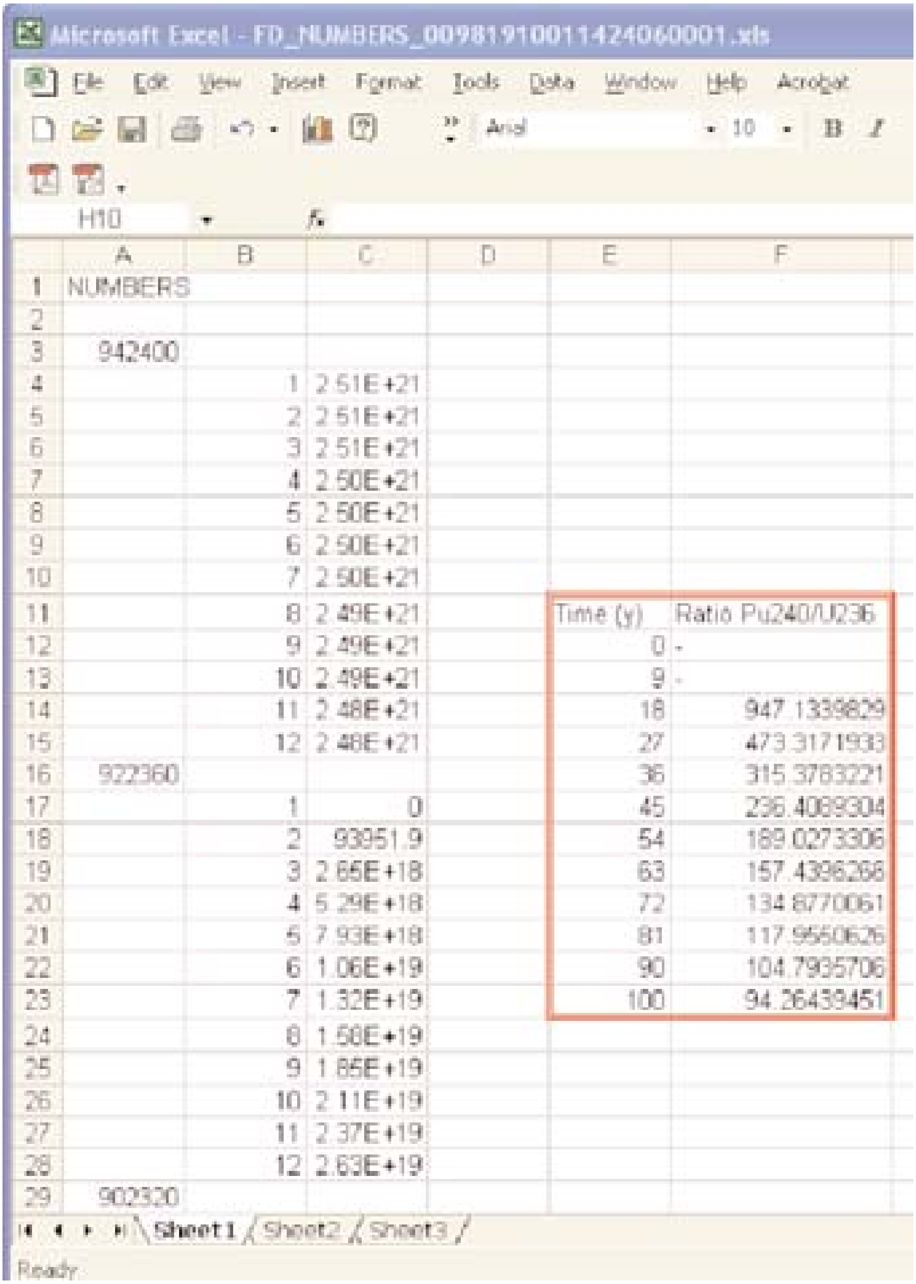
FIG. 6. (a) The options windows for the graph; and (b) the resulting graph. The decay curves of the ^{236}U and ^{240}Pu nuclides are plotted.

of 27.8 a was expected from the ^{240}Pu/^{236}U ratio since there was no ^{236}U present in natural uranium (Fig. 9).

3. CONCLUSION

Nuclides.net is an “integrated environment” for computations on radionuclides and their radiation. The integrated environment is a suite of computer programs ranging from a powerful interface, which allows the user to navigate the nuclide chart and explore the properties of nuclides, to various computational modules for decay calculations, dosimetry and shielding calculations.

Study of the determination of the “age” of a plutonium sample showed the large application field of the Nuclides.net software applied to nuclear forensics.



	A	B	C	D	E	F
1	NUMBERS					
2						
3	942400					
4		1	2.51E+21			
5		2	2.51E+21			
6		3	2.51E+21			
7		4	2.50E+21			
8		5	2.50E+21			
9		6	2.50E+21			
10		7	2.50E+21			
11		8	2.49E+21		Time (y)	Ratio Pu240/U236
12		9	2.49E+21		0	-
13		10	2.49E+21		9	-
14		11	2.48E+21		18	947.1339829
15		12	2.48E+21		27	473.3171933
16	922360				36	315.3783221
17		1	0		45	236.4089304
18		2	93951.9		54	189.0273306
19		3	2.65E+18		63	157.4396268
20		4	5.29E+18		72	134.8770061
21		5	7.93E+18		81	117.9560626
22		6	1.06E+19		90	104.7935706
23		7	1.32E+19		100	94.26439451
24		8	1.58E+19			
25		9	1.85E+19			
26		10	2.11E+19			
27		11	2.37E+19			
28		12	2.63E+19			
29	902320					

FIG. 7. Decay calculation results downloaded as an Excel file (columns A, B, C). From these results and using the Excel calculation feature, the atom ratio of ^{240}Pu/^{236}U over the ten time steps, ranging from 0 to 100 years, is shown in the red box.

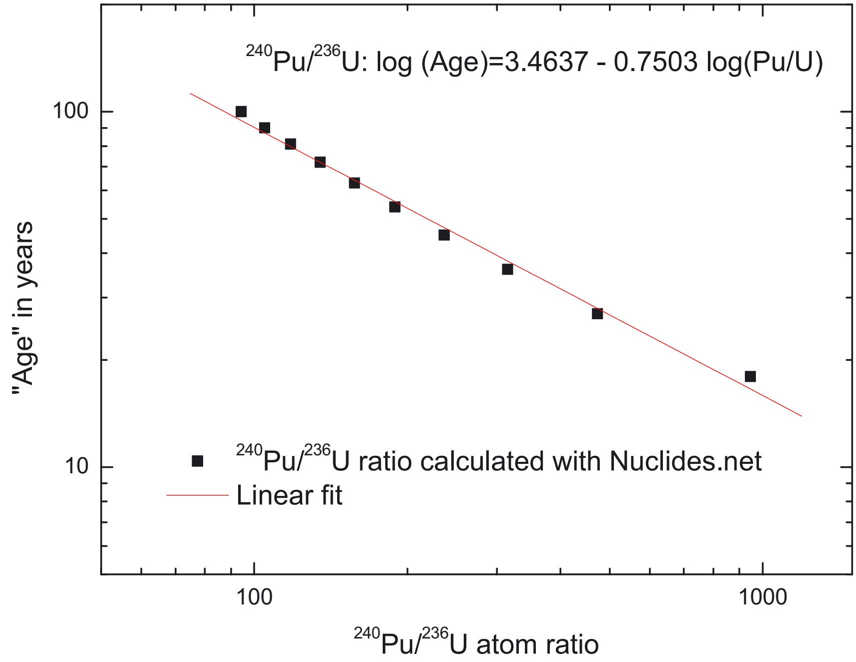


FIG. 8. Linear fit of the calculated ^{240}Pu/^{236}U atom ratio calculated by Nuclides.net.

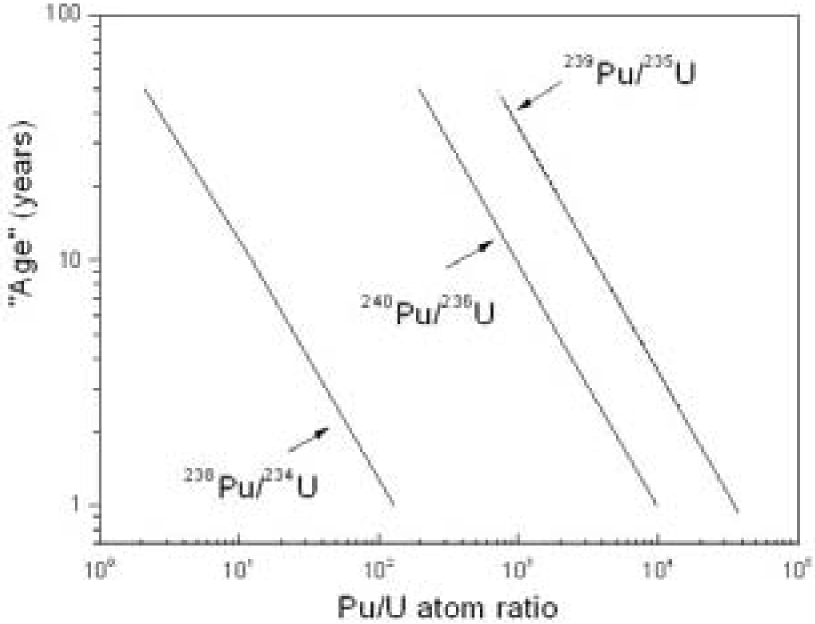


FIG. 9. Application of Nuclides.net. atom ratios to 'age' determination of plutonium particles.

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URANIUM AGE DETERMINATION: SEPARATION AND ANALYSIS OF ^{230}Th AND ^{231}Pa

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In recent years, several incidents involving illicit trafficking and smuggling of nuclear material, radioactive sources and radioactively contaminated materials have increased public concern over criminal acts involving nuclear materials. Consequently, research efforts in nuclear forensic science have been intensified in order to develop and improve methods for the identification of the nature and origin of seized materials. Information obtained from the analysis of unknown nuclear materials is of key importance to authorities charged with developing rapid and appropriate responses. For the identification of nuclear materials, various sample characteristics are of relevance, including isotopic composition, the content of chemical impurities, material properties and date of production.

Information on the production date — the ‘age’ of a nuclear material — is also of key importance in other fields of nuclear science, i.e. for verification of a Fissile Materials Cut-off Treaty (FMCT) in order to distinguish freshly produced materials from ‘old’ excess weapons. The age of nuclear materials may also be of relevance under a strengthened safeguards regime to reveal clandestine production of weapons usable materials, i.e. the separation of plutonium or production of high enriched uranium (HEU).

The age dating of plutonium samples has been described in detail for bulk samples as well as for particles [1, 2]. In this work, we focus on age determination of materials of various uranium enrichments. The radioactive decay of the isotopes provides a chronometer that is inherent to the material; in particular, the mother/daughter pairs ^{234}U/^{230}Th and ^{235}U/^{231}Pa can be used. Due to the relatively long half-lives of ^{234}U (2.46×10^5 years) and ^{235}U (7.04×10^8 years), only minute amounts of daughter nuclides are present, therefore, separation of Th and Pa from uranium must be of high chemical recovery and must afford large decontamination factors. In general, the age obtained from parent/daughter ratios refers to the last separation of the parent nuclide from its daughters, i.e. the last purification of the material. The accuracy of the obtained age, therefore, depends on the quality of the purification process and assumes that the material subsequently has not been contaminated. Obviously, the availability of two analytical methods relying on both, independent, parent/daughter pairs will, therefore, significantly increase the confidence in the experimental results.

In this work we demonstrate analytical methods for age determination of uranium samples using the ^{234}U/^{230}Th and ^{235}U/^{231}Pa parent/daughter relations. Thorium is separated from bulk uranium using extraction chromatography and subsequently quantified using α spectrometry, thermal ionization mass spectrometry (TIMS) and inductively coupled mass spectrometry (ICP-MS). Protactinium is separated by its selective sorption to silica gel followed by α-spectrometric quantification. The methods were tested and validated using reference materials of various uranium enrichments and age.

The experimental results obtained with both methods were found to agree with the assumed ages of the reference materials within the combined uncertainties of the measurements (Table I). The analysis exploiting the parent/daughter pair ^{235}U/^{231}Pa exhibited a slightly larger combined uncertainty and bias than the thorium method, but was found to be valuable in validating the experimental results by means of a second, independent analysis.

TABLE I. AGE DETERMINATION OF URANIUM BY ID-AS FROM THE ^{235}U/^{231}Pa AND ^{234}U/^{230}Th RATIOS, RESPECTIVELY

(ID-AS: isotope dilution alpha spectrometry; ID-TIMS: isotope dilution thermal ionization mass spectrometry; ICP-MS: inductively coupled mass spectrometry)

Sample	Assumed age (a)	Determined age (a)	Bias (%)	Method	Parent/daughter pair
U-500	39.3	38.7 ± 1.8	–1.7	ID-AS	^{235}U/^{231}Pa
	38.8	38.1 ± 1.4	–1.8	ID-AS	^{234}U/^{230}Th
	38.5	38.1 ± 0.4	–1.0	ID-TIMS	“
	39.1	39.8 ± 0.4	+1.6	ICP-MS	“
U-800	43.5	41.6 ± 2.0	–4.4	ID-AS	^{235}U/^{231}Pa
	43.0	42.3 ± 1.5	–1.6	ID-AS	^{234}U/^{230}Th
	42.7	41.9 ± 1.3	–1.9	ID-TIMS	“
	43.3	43.4 ± 0.9	+0.3	ICP-MS	“
U-850	44.2	43.0 ± 2.1	–2.7	ID-AS	^{235}U/^{231}Pa
	43.8	43.3 ± 1.4	–1.1	ID-AS	^{234}U/^{230}Th
	43.4	42.4 ± 0.8	–2.3	ID-TIMS	“
	44.0	45.3 ± 1.2	+2.9	ICP-MS	“

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THE CONCEPT OF A 'MICROSTRUCTURAL FINGERPRINT' FOR THE CHARACTERIZATION OF SAMPLES IN NUCLEAR FORENSIC SCIENCE

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1. INTRODUCTION

In the examination of unknown specimens of nuclear materials, the primary parameter of importance is the 'isotopic fingerprint' of the sample, mainly the ratios of the isotopes of uranium and plutonium that are present. In some cases, however, where no clear isotopic signature is found or where a mixture of materials is present, the isotopic fingerprint alone is not sufficient for a unique identification.

In this paper, the concept of a 'microstructural fingerprint' of a sample is proposed and developed. It is complementary to the isotopic fingerprint for characterization of materials under investigation in the field of nuclear forensic science. The proposal combines scanning electron microscopy (SEM), transmission electron microscopy (TEM) and energy dispersive X ray analysis (EDX) to define the microstructure of a suspect sample — a combination of techniques that has not been used heretofore in nuclear forensic science.

Microstructural information is particularly important in cases of powder samples, for the following reasons:

- An essential prerequisite to isotopic analysis, for example by thermal ionization mass spectrometry (TIMS), is knowing whether a powder sample consists of a single component or is a mixture of several. In the latter case, individual components must be analysed separately.
- Powder samples mainly represent precursor stages in the nuclear fuel cycle, and microstructural analysis gives information on the production process and conditions (for example, the grain size in PuO_2 platelets produced by calcination of oxalate precipitate, and the size and thickness distributions of those platelets).
- Powder samples can be mixed with other compounds with the deliberate intention of confusing the chemical or isotopic analysis of suspect materials. However, the microstructural fingerprint of a component cannot be altered unless the material is reprocessed as a whole.

In the case of bulk samples, for example in the form of UO_2 pellets intended for use in reactors for commercial generation of electricity, a microstructural examination is not an essential element in the investigation, since pellets can usually be rapidly and uniquely identified from their dimensions and geometrical form. Most illicit samples seized so far fall into this category of bulk material.

However, a microstructural characterization by SEM/TEM/EDX of such pellet samples would provide useful archival material, in the form of grain size distribution, pore size distribution, homogeneity, precipitation and dislocation densities. This information is then available should the material subsequently turn up in powder form or mixture of materials.

2. THE MICROSTRUCTURAL FINGERPRINT

The microstructural fingerprint of a material consists of a specific set of data resulting from a microscopic (optical, SEM, TEM, EDX) investigation that is characteristic of its physical and mechanical state and its mechanical and thermal history. This fingerprint, once established, can be used for comparing an unknown illicit sample with a known reference, or for eliminating materials of known origin as possible sources.

Even where no reference samples are available for comparison, much information about the material can be deduced from the microstructure using established principles of materials science. For example, the dislocation density and character gives information on whether the material has been deformed during manufacture and to what extent, and the grain size distribution provides clues about process temperatures and reaction rates.

3. COMPONENTS OF THE MICROSTRUCTURAL FINGERPRINT

A description is given here of parameters that are relevant to the set of data comprising the microstructural fingerprint. The data obtainable by SEM/EDX and by TEM/EDX are as follows.

3.1. Scanning electron microscopy

- Is the sample single or multi-component? If multi-component, what are the proportions of each component, and are the individual components morphologically or chemically distinct?

- Particle morphology. Characteristic shapes (platelets, spheres, rods, geometrical forms).
- Particle size distribution. Size range (30 nm upwards), average size and breadth of distribution.
- Porosity. Density and percentage of porosity, pore size distribution, crystallographic faceting, spatial distribution (for example, predominantly inter or intragranular).
- Chemical composition and chemical homogeneity by SEM/EDX. To a sensitivity and detection limit of about 1.0 at%, with a spatial resolution of about 3 nm.

3.2. Transmission electron microscopy

- Are individual particles homogeneous or multi-phasic? Electron diffraction and EDX analysis down to a spatial resolution of about 10 nm.
- Grain size distribution of the specimen. Individual grain size measurements from 1.0 nm to 5 μm, grain size distributions of up to 500 μm.
- Dislocation density in the matrix, type and distribution of dislocations. Dislocation densities in the range from about 10^6 up to 10^{11} cm cm^{-3} can be measured, in the latter case using high resolution dark field imaging techniques.
- Porosity of the matrix. Density and size distribution of small pores within the grains and on the grain boundaries in the size range 2.0 nm up to 500 nm.
- Precipitation within the matrix. Size distribution, density and composition of small precipitates within the matrix and on the grain boundaries from 2.0 nm up to 500 nm. Identification by EDX and electron diffraction.
- Crystallography of the material. Analysis of phases down to an area of 50 nm by normal electron diffraction, and 10 nm by microdiffraction.

DETERMINATION OF THE SOURCE OF RADIOACTIVE PARTICLES IN A MARINE ENVIRONMENT USING SIMS AND ICP-MS

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Abstract

The characterization, by secondary ion mass spectrometry (SIMS) and inductively coupled plasma mass spectrometry, of uranium and plutonium isotopic compositions in highly enriched particles found on the Scottish coast, allowed the determination of their origin. The particles were identified as an aluminium uranium matrix fuel irradiated in an MTR reactor to a burnup of 25 to 30%. The SIMS analysis also established the Al/U ratio in the alloy and characterized the impurities, showing that the other major elements present in the particles are not directly located with the uranium spots.

1. INTRODUCTION

The size and composition of radioactive particles determine the transport mechanisms of radionuclides in the environment as well as their bioavailability. Therefore, their characterization, as for elemental and isotopic composition, is of great importance. Considerable advances in secondary ion mass spectrometry (SIMS) have been made over the last decade in the development of precise and accurate methods for the determination of isotopic composition of individual radioactive particles [1–5]. These parameters are fundamental for the characterization of such particles in safeguards as well as in environmental and forensic applications. Particularly in nuclear forensics, the uranium and plutonium isotope ratios give important information with which to trace the origin of nuclear fuel material.

Following an accidental discharge, highly radioactive particles of a few millimetres in size were found, over a period of more than 10 years, on the seabed and occasionally on beaches in the vicinity of a nuclear establishment in Scotland. The particles were identified as an Al/U matrix fuel from a material test reactor.

2. METHODS

A double focusing SIMS, CAMECA IMS 6f (Paris, France), was used. It has been described elsewhere [3]. To search for uranium particles in the sample, the SIMS instrument was set to mass ^{238}U and, alternatively, to mass ^{235}U to obtain a mapped distribution of the uranium particles. The sample was scanned across a 500 × 500 μm area of the surface. The primary beam was then focused on a single uranium particle and the isotope ratios were calculated from the measured ion beam intensities at the mass positions of the different uranium isotopes.

A few μg of the sample were dissolved and measured by inductively coupled plasma mass spectrometry (ICP-MS). The measurements were made with a double focusing multicollector ICPMS from NU Instruments. The instrument is equipped with 12 Faraday cups and an ion counter. A desolvating nebulizer (CETAC Aridus), with an aspiration rate of 50 μL/min, was used as the sample introduction system. Three blocks of ten scans each (integration time 10 s) were performed in order to reduce the random uncertainty arising from counting statistics.

3. RESULTS

Typical imaging distribution analyses of aluminium and uranium in a sample, by SIMS, are shown in Figs 1(a) and (b). To check whether the uranium spots in the particle coincided with other elements, a series of images was recorded during the same analysis by scanning the analysed area consecutively for masses ^{23}Na, ^{24}Mg, ^{27}Al, ^{31}P, ^{40}Ca, ^{56}Fe and ^{235}U. The SIMS analyses showed the matrix to be aluminium (confirmed by the SEM analysis) and that the other major elements in the sample were not directly located with the uranium spots (Fig. 2). In fact, no contributions of uranium were evident in the areas occupied by iron particles, for instance (Figs 1(c)–(e)).

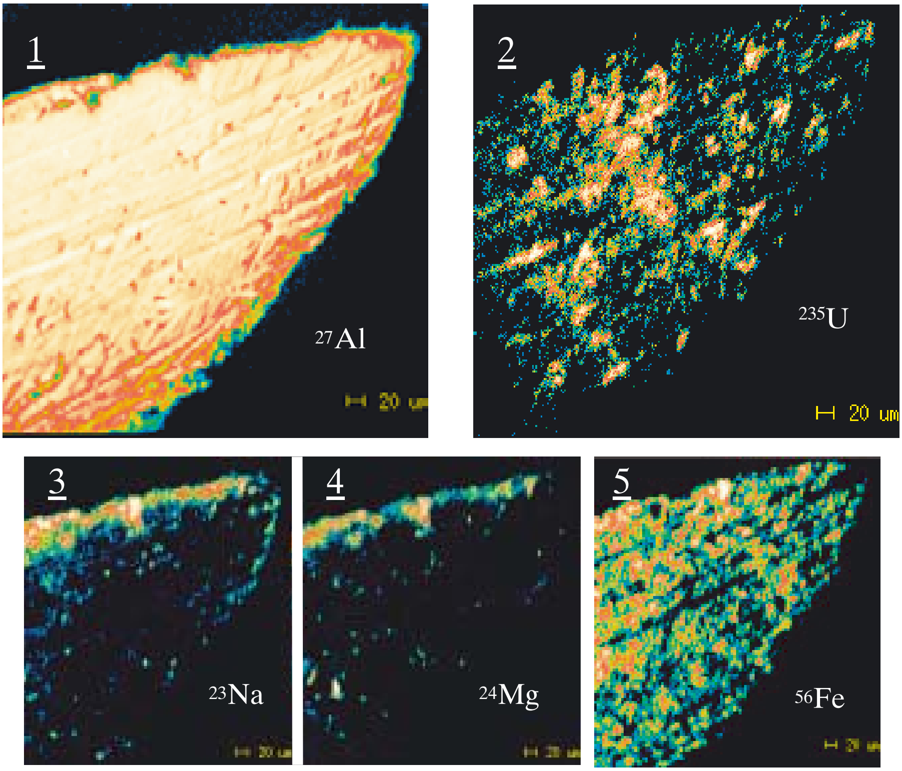

FIG. 1. Map distributions of the particles on the ^{27}Al *and* ^{235}U *masses.*

For each of the uranium particles analysed, a homogeneous distribution of the isotopes was found. The abundance of the minor isotopes was much higher than in irradiated low enriched uranium fuels. Therefore, no molecular interference at mass position 236 arose from $^{235}UH^+$. To confirm the SIMS results, a few µg of the sample were dissolved and measured by ICP-MS. The ICP-MS results were consistent with the values obtained by SIMS (Table I).

For the plutonium measurements, the primary beam was focused on a single spot, and isotope ratios ($^{239}Pu/^{240}Pu$, $^{239}Pu/^{238}U$) were calculated from the measured ion currents of the different isotopes of plutonium and uranium.

Plutonium generally has a considerably higher ionization efficiency than does uranium. Therefore, the measured Pu/U ratios have to be corrected with a “relative sensitivity” factor (RSF), which takes account of differences in the ionization efficiencies of the elements in the fixed conditions (e.g. constant primary ion beam energy and current) for the measurements. An RSF of 2.41, previously determined [6], was applied in this work for correction of the

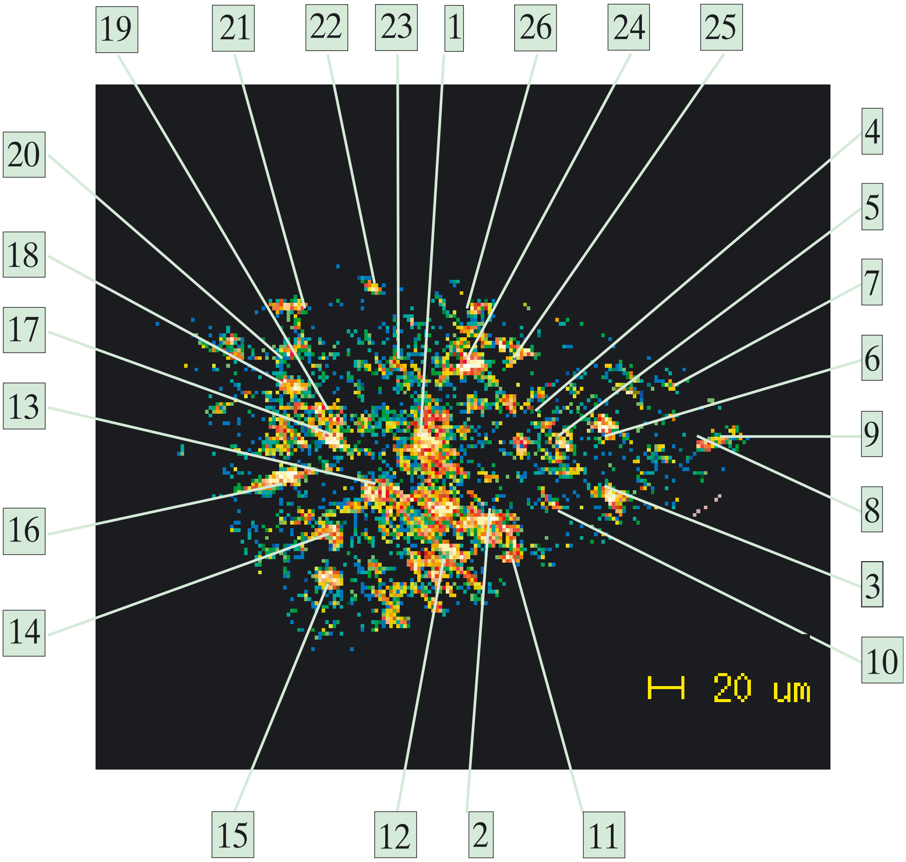

FIG. 2. Uranium spots analysed by SIMS.

TABLE I. MEAN VALUES AND RELATIVE STANDARD UNCERTAINTIES (k = 1) FOR THE URANIUM MEASUREMENTS

Isotopes	SIMS	ICP MS	Calculated (SCALE)
^{234}U at%	1.486 ± 1.5%	1.491 ±1 %	1.4
^{235}U at%	82.926 ± 1.1%	82.745 ± 1%	83.5
^{236}U at%	7.629 ± 2.6%	7.561 ± 1%	7.6
^{238}U at%	7.958 ± 2.6%	8.202 ± 1%	7.5

$^{239}Pu/^{238}U$ ratio. In Table II, the value of the $^{239}Pu/^{238}U$ ratio has been corrected with the RSF.

In the same table, the ICP-MS results of one scan measurements are given for comparison. Due to the negligible amount of ^{238}Pu, no U/Pu separation was performed. The results of the two techniques agreed quite well, demonstrating good reliability of the data. The uranium and plutonium isotope ratio results were used for identification of the sample. The results of SCALE programme calculations of highly enriched uranium (HEU) fuels were in good agreement with the SIMS and ICP-MS measured values. Further information supplied from the analysis of this sample was the Al/U ratio in the alloy. Taking into account that aluminium has a considerably higher ionization efficiency than does uranium by SIMS, an RSF of 50.36, obtained from the literature [7], was applied for correction of the Al/U ratio. A value of 6.9 was obtained by SIMS, which was confirmed by ICP-MS (Al/U = 7).

4. CONCLUSIONS

A method for the identification of the reactor and fuel type from uranium and Pu/U isotopic data, obtained by SIMS and ICP-MS, is described. The measured isotopic composition was consistent with the calculated composition of a HEU fuel (enrichment >90%) irradiated in an MTR reactor to a burnup of 25–30%. The calculated parameters confirmed values within experimental error. This method, developed at the ITU, represents a powerful technique to be applied for the analysis and characterization of particles found in environmental samples or swipes.

TABLE II. MEAN VALUES AND RELATIVE STANDARD UNCERTAINTIES (k = 1) FOR PLUTONIUM AND Pu/U RATIOS

Ratio	SIMS	ICP MS
$^{239}Pu/^{238}Pu$	6.04E+00 ± 5.22%	5.89E+00 ± 5%
$^{239}Pu/^{238}U$	1.51E-02 ± 2.45%	1.43E-02 ± 5%

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NUSIMEP-3: AN EXTERNAL QC PROGRAMME FOR THE MEASUREMENT OF URANIUM ISOTOPIC RATIOS IN SALINE SOLUTIONS

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Abstract

The external quality control programme NUSIMEP-3 has been completed. Changes from the previous programme, NUSIMEP-2, are elucidated and an overview of the results is presented. Samples of uranium of certified isotopic abundances were supplied in saline matrices, and laboratories were requested to measure the isotopic ratios of ^{234}U, ^{235}U and ^{236}U relative to ^{238}U. Participating scientists were requested to complete a questionnaire from which it was expected that conclusions could be drawn on experimental conditions necessary for the generation of reliable data from such samples.

1. INTRODUCTION

The Nuclear Signatures Inter-Laboratory Measurement Evaluation Programme (NUSIMEP) was started at the Institute for Reference Materials and Measurements (IRMM) following the successful examples of the Regular European Inter-Laboratory Measurement Evaluation Programme (REIMEP) and other IMEP QC programmes. It was specifically aimed at measuring small concentrations of nuclear materials in environmental samples and arose from recognition that analytical methods normally applied to conventional samples in the nuclear fuel cycle can be applied to typical environmental samples only with difficulty. A QC programme specific to this measurement area would, therefore, be of great advantage in allowing scientists in the field to test their measurement capabilities objectively, and also to give international organizations, such as the IAEA, an overview of measurement capabilities in general.

The IRMM conducted the REIMEPs, with typical fuel cycle samples, for 20 years, and many of the developed concepts were incorporated into NUSIMEP. In particular, the laboratories were kept anonymous; certified values were sent immediately to each laboratory on receipt of the generated data; and a final report was issued with a summing up of the laboratories' performances, usually in graphic form.

The previous programme, NUSIMEP-2 [1, 2] consisted of four 100 ng dried samples of uranium nitrate, of low enriched or depleted uranium. The laboratories were requested to measure the isotopic ratios n(^{234}U)/n(^{238}U), n(^{235}U)/n(^{238}U), n(^{236}U)/n(^{238}U). The matrix was, therefore, very simple for NUSIMEP-2; in principle, the sample was simply dissolved and the isotopic ratios measured. Nevertheless, many of the participating scientists apparently had considerable difficulty with the measurements. The techniques employed were thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP/MS), with either a quadrupole or a sector field instrument. Radiometric methods were also applied at a considerable number of laboratories, but their sensitivity and accuracy were not comparable with the mass spectrometric methods, except in certain cases.

An important factor in the measurement of uranium in environmental samples is the possibility of contamination from natural sources. The chemical handling necessary for samples in NUSIMEP-2 was simple and did not test ability to work cleanly. It was decided, therefore, to ask the scientists to measure uranium isotopic ratios again in NUSIMEP-3, but this time with a matrix that would require chemical separation before measuring.

2. DETAILS OF NUSIMEP-3

Relatively small quantities of saline solutions were available, prepared for an earlier exercise, and it was decided that they would make excellent matrices for a uranium isotopes QC programme. Approximately 20 mL aliquots of three saline solutions were available per sample and laboratory, and we decided to add uranium at a concentration of 5 ng·g^{-1} so that the total amount would be approximately 100 ng. These solutions varied in salt strength and composition, from brackish waters to sea water. A fourth solution was made up from a commercial seawater concentrate. For this matrix, a concentration of 2 ng g^{-1} was selected so that a 50 mL sample would also contain 100 ng of uranium. This material had a measurable amount of natural uranium, which was removed before use. Measurements of uranium content in this and the other matrix solutions showed levels too low to interfere with the certified uranium isotopic values. The uranium for each sample was made by mixing certified uranium as UF$_6$ in the gas phase [3]. This method produces an isotopic composition that may be precisely determined. The n(^{235}U)/n(^{238}U) ratio was certified by measurement of UF$_6$ with an electron impact gas mass spectrometer. The minor isotopic ratios, n(^{234}U)/n(^{238}U) and n(^{236}U)/n(^{238}U), were measured by TIMS and confirmed knowing the mixing ratio and the certified values of the UF_6 batches mixed.

The uranium isotopic ratios were, therefore, certified using large samples. Aliquots of the samples were then dissolved by treatment with nitric acid and successively diluted to reach concentrations where they could be added to the matrix solutions. Care was exercised and close checks were made on the dilution process: samples of the acids and wash solutions of the laboratory ware were collected and natural uranium contents measured. The solutions were stored in cleaned PTFE bottles for possible future checks. The dilutions were carried out in class 100 conditions and the laboratory ware was cleaned and the acids and water prepared in the IRMM ultra-clean chemical laboratory under class 10 conditions. Atmospheric fallout samples were also collected adjacent to where the dilutions were carried out, and measured for uranium. The cumulative effects of all these contributions were added into the dilution calculation using highly conservative assumptions, and it could be shown that the uncertainties of the ratios, as certified on the large samples, were not altered by the dilution.

The samples were packed into cleaned polythene screw capped bottles. Although interest had been shown at thirty laboratories, only twenty were registered (thirty laboratories were registered for NUSIMEP-2). Each laboratory was sent a set of the four bottles and requested to measure the three uranium isotopic ratios in each sample. A questionnaire was included, for completion and return.

3. MEASUREMENT RESULTS

The measurement results have been published in detail in the Participants' Report [4]. Values for all three ratios were not returned from all laboratories, depending on the measurement technique employed. Radiometric techniques, in particular alpha and gamma spectrometry, were the most popular techniques. The mass spectrometric technique applied in the greatest number of laboratories was high resolution ICP-MS, followed by quadrupole ICP-MS, multicollector ICP-MS, and TIMS. In one laboratory, accelerator mass spectrometry was used to measure n(^{236}U)/n(^{238}U).

Overall, the data showed more variation than did those for NUSIMEP-2, presumably a result of the chemical manipulations needed. Again, the radiometric methods yielded results that were considerably poorer than did mass spectrometry, which shows again that the former should not be used for measurements of uranium isotopic ratios in small samples.

Some of the multicollector and high resolution ICP-MS results agreed very closely with the IRMM certified values. Others varied unexpectedly and, in particular, the uncertainties reported were very variable, differing within technique and sample. We believe this is a consequence of some scientists not having their measurements under control and possibly also not including all experimental parameters in the uncertainty calculation.

In some laboratories, unexpected bias occurred to some or all of the ratios. In most cases these effects were apparent for all the samples but, in at least one case, they varied between samples. These appear, at present, to be measurement effects and not from contamination, although this will be clear only when the measurements can be analysed and discussed in detail.

One sample, low in $n(^{236}U)/n(^{238}U)$ (ca. 10^{-7}), was not measured correctly in any of the laboratories (in the sense that the certified value lay within the range of the measured value plus expanded uncertainty). Scientists in some laboratories reported only "less than" values for this sample. This inability to measure low ^{236}U abundances is noteworthy because of the present importance of depleted uranium in the environment (^{236}U is an excellent marker isotope for uranium from the nuclear fuel cycle).

It was surprising that no correlation was found between the closeness of reported results to the certified values and the presence of clean facilities reported in the questionnaire. Clean facilities did not guarantee good data, whereas good data were obtained in some conventional facilities. The isotopic abundances of the four uranium samples had been chosen carefully to bring out subtle points in the measurement capabilities of the scientists, and the matrix solutions were also chosen to highlight the contribution of clean chemical handling facilities in the laboratories. Despite the fact that a range of chemical separation schemes was used, varying in separation type and complexity, no correlation was seen between the chemistry employed and the results achieved.

4. CONCLUSIONS

The science of measuring uranium isotopic ratios in environmental samples is not yet routine, judging from the results of this programme. Measurement methods, facilities and chemical methods varied widely from laboratory to laboratory. The selection of matrices and isotopic abundances could have been simplified for this programme. However, it was encouraging to see that more scientists reported uncertainties following the GUM and nearly all laboratories were accredited or had some form of certification at the national or international level.

From the feedback received, participating scientists judged the programme to be very useful, even (or perhaps especially) when the measured results differed from the certified values. We will arrange discussions with participants and other interested parties to structure future NUSIMEP campaigns, using simplified matrices and possibly including traces of plutonium and gamma emitters.

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CLOSING SESSION

(Session 6)

Chairperson	**A. Nilsson** (IAEA)
Panel Members:	**L. Koch** (Institute for Transuranium Elements, European Commission) **D.W. Swindle, Jr.** (USA) **H. Metz** (Australia) **A.S. Strezov** (Bulgaria)

SUMMARY OF SESSION 1

THE ROLE OF NUCLEAR FORENSICS IN COMBATING ILLICIT TRAFFICKING AND NUCLEAR TERRORISM

In the opening session, the need for strengthened international co-operation was underlined in order to combat illicit trafficking and to prevent nuclear terrorism. A. Nilsson (IAEA) emphasized that co-ordinated efforts are required at all levels, comprising training, exchange of information and upgrading of equipment and ranging from physical protection, accountancy and control, safeguards, border controls, environmental monitoring and forensic analysis. For the latter, intensified co-operation between classical forensics and nuclear scientists is required to ensure that all types of evidence are preserved and can be usefully exploited. R. Schenkel (EC) stressed the fact that early detection of illegal trafficking of nuclear material is of key importance, as there is no nuclear terrorism without illegal trafficking. The methodology for nuclear fingerprinting should be enhanced and the nuclear materials database should be expanded in order to contribute to criminalistic solutions of cases and also to identify the origin of material. In order to optimize preparedness for eventual scenarios of nuclear terrorism, such scenarios should be simulated and evaluated. L. Koch (ITU) presented the efforts of the International Technical Working Group (ITWG). A "Model Action Plan" for reaction to cases of seizures of nuclear material has been worked out and is used as recommendation to Member States. In two round robins organized by the ITWG, a picture of the "state of the art" in nuclear forensic analysis was obtained on an interlaboratory basis.

Representatives of the FBI, Europol and the anti-terrorist branch of the British Metropolitan Police (New Scotland Yard) highlighted needs for preparedness for scenarios such as 'dirty bombs' and quiet dispersion of radioactive material. Furthermore, emphasis was given to the absolute need for preservation of forensic evidence at the site of an event. Proper documentation and maintenance of the chain of custody are of primary importance. Exchanges of information at the international level and close co-operation between various disciplines (nuclear science, classical forensics and criminal investigation) were called upon. An example of a comprehensive compilation and systematization of information on nuclear materials was presented by Y. Dolgov (Russian Federation) from the A.A. Bochvar All-Russia Research Institute for Inorganic Materials (VNIINM). This database plays a key role in the identification of nuclear material of unknown origin and for analytical guidance. The discussion made very clear that the more complete such a database is, the higher the likelihood of identifying origin and thus enabling the prevention of future diversion or theft of nuclear material.

SUMMARY OF SESSION 2

CURRENT CAPABILITIES AND PAST EXPERIENCES

This session focused on current capabilities and past experience in nuclear forensics. Results of two intercomparisons were presented, showing the analytical capabilities of the participating laboratories. Significant experience was gained from the first round, particularly with respect to preservation and evaluation of conventional forensic evidence. A number of nuclear analytical laboratories around the world have upgraded their capabilities or made existing instrumentation available for nuclear forensic investigations. In particular, isotopic, trace analytical and microscopic techniques are considered to be most useful and, therefore, are emphasized. Several recent cases of forensic analysis of nuclear material were reported. Theft of radioactive material from a nuclear installation under decommissioning and the interception of an illegally trafficked sample of high enriched uranium were the most recent and prominent cases. In both cases, the above mentioned techniques were applied and the respective results were presented in detail.

Measures to combat illicit trafficking and to secure nuclear material in Tajikistan were presented. Comprehensive efforts undertaken in Romania in the same areas were also presented, highlighting once more the need for coordinated efforts among the various authorities involved.

SUMMARY OF SESSION 3

ANALYTICAL TECHNIQUES

This was an interesting and wide ranging session, with topics from the nuclear and conventional forensic science fields, as well as trace and particle analysis methods. M. Hotchkis (Australia) explored the concept of wide area environmental sampling from ANSTO. The operation of undeclared nuclear activities inevitably results in the release of traces of radionuclides, but the levels are very low and thus pose challenges for detection. The relevance of the detection of ^{236}U was emphasized since it has a higher yield in uranium irradiation than any fission product. Accelerator mass spectrometry is the most sensitive detection method available. In the case of uranium, where environmental samples deliver about 1 μg of the metal, the detection limit is 10^{-9} for the ratio ^{236}U/^{238}U, corresponding to a detection limit of about 1 fg for ^{236}U.

J.F. Wacker (USA) discussed ultratrace analyses of uranium and plutonium by TIMS and ICP-MS using a resin bead preparation technique for the actinides. He achieved fg detection limits for the TIMS analysis in environmental samples. A comprehensive study of global fallout has been made, as well as environmental investigations in the vicinity of US nuclear production facilities.

M. Sudersanan (India) addressed conventional forensic science including the analysis of gunshot residues, the detection and analysis of drug samples and commercial pharmaceutical preparations. He also discussed the identification of unknown metallic samples using neutron activation analysis and X ray fluorescence. Although these did not include nuclear materials, they were relevant to the dumping of toxic waste from industrial states in developing countries.

Lin Gan (China) described the use of non-destructive analysis (simple, quick, effective) for the control of nuclear materials and physical protection. M. Wallenius (ITU) discussed the importance of correlating the impurities in uranium dioxide pellets with oxygen isotope ratios, and showed examples from four uranium mines in Australia. Important in the characterization of nuclear materials is an understanding of the propagation of impurities from the ore to the final product.

V. Stebelkov (Russian Federation) presented a study on the relevance of particle size and surface structure in the results of SIMS measurements. S. Goldberg (USA) discussed a multiple ion counter detector system designed for isotope ratio mass spectrometers to provide improved precision on measurements of samples with less than 10^{-11} g of analyte.

D. Becker (Germany) made a fascinating presentation on his investigation of the authenticity of a certificate signed by Marie Curie, using residual traces of radioactivity to prove authenticity. Lastly, U. Admon (Israel) presented his work on transferring and relocating micron sized particles from a SEM to a SIMS instrument, which allows particles of interest to be identified and analysed on multiple analytical instruments.

SUMMARY OF SESSION 4

CHALLENGES AND ALTERNATIVE APPROACHES

This session addressed issues with two main themes: challenges and alternative approaches. The challenges were seen from the point of view of so-called ‘transit countries’, i.e. those that are directly concerned by illicit trafficking because of geographic location and regional economic difficulties. Secondly, alternative approaches in forensic matters were presented, suggesting special consideration for quality assurance and legal aspects.

Four speakers discussed problems encountered in their countries, namely Bulgaria, Kazakhstan, Lithuania and the Federal Republic of Yugoslavia (now Serbia and Montenegro). Issues relating to internal trafficking (illegal handling of radioactive sources, lack of appropriate legislation) as well as to external trafficking were described, and response schemes were presented. In general, the speakers insisted on the need for comprehensive legislation, appropriate equipment for detection, training for officials to avoid wrong or bad handling of finds, and effective regional co-operation. References were made to existing international co-operation programmes and the subsequent achievements.

Two presentations highlighted the problems related to quality assurance and legal aspects of forensic sciences and experts. H.O.E. Metz (Australia) presented very interesting views and identified areas of concern, especially in terms of providing technical or scientific expertise in a court of law. Examples of cases involving non-nuclear forensic techniques that have been scrutinized and challenged by legal and scientific experts underlined the need for international quality assurance measures and guidelines in nuclear forensics. Subsequently, the IAEA made a presentation on their projects aimed at better co-ordination and also at improvements in technical measures to handle and analyse seized samples. Enhanced co-operation with law enforcement authorities definitely needs to be encouraged and pursued.

At the end of the session, N.G. Wimer (USA) made a very interesting presentation on forensic analysis of an HEU sample interdicted in Bulgaria in 1999. This presentation, which was originally scheduled for Session 2, showed impressive results and demonstrated how international co-operation between scientists and other agencies can offer added value to the work of the law enforcement community.

CHAIRPERSONS OF SESSIONS

Session 1	Chairperson	A. NILSSON	IAEA
	Co-Chairperson	R. SCHENKEL	European Commission
Session 2	Chairperson	A.S. STREZOV	Bulgaria
	Co-Chairperson	K. MAYER	Institute for Transuranium Elements
Session 3	Chairperson	I.L.F. RAY	Institute for Transuranium Elements
	Co-Chairperson	R.C. HANLEN	United States of America
Session 4	Chairperson	J.N. COOLEY	IAEA
	Co-Chairperson	G.M.J. HERBILLON	European Commission
Session 5 (Poster Session)			
Session 6	Chairperson	A. NILSSON	IAEA

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