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Use of research reactors for neutron activation analysis

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FOREWORD

Neutron activation analysis (NAA) is an analytical technique based on the measurement of characteristic radiation from radionuclides formed directly or indirectly by neutron irradiation of the material of interest. In the last three decades, neutron activation analysis has been found to be extremely useful in the determination of trace and minor elements in many disciplines. These include environmental analysis applications, nutritional and health related studies, geological as well as material sciences. The most suitable source of neutrons for NAA is a research reactor.

There are several application fields in which NAA has a superior position compared to other analytical methods, and there are good prospects in developing countries for long term growth. Therefore, the IAEA is making concerted efforts to promote neutron activation analysis and at the same time to assist developing Member States in better utilization of their research reactors. As part of this activity, the IAEA organized an Advisory Group Meeting on "Enhancement of Research Reactor Utilization for Neutron Activation Analysis" in Vienna from 22 to 26 June 1998. The purpose of the meeting was to discuss the benefits and the role of NAA in applications and research areas that may contribute towards improving utilization of research reactors.

The participants focused on five specific topics:

(1) Current trends in NAA;
(2) The role of NAA compared to other methods of chemical analysis;
(3) How to increase the number of NAA users through interaction with industries, research institutes, universities and medical institutions;
(4) How to reduce costs and to maintain quality and reliability;
(5) NAA using low power research reactors.

This TECDOC details the highlights of the discussions in the meeting along with the papers presented. The IAEA is grateful to Mr. P. Bode (Delft University of Technology, Netherlands) for compiling the publication. It is hoped that it will enhance the effectiveness of research reactor laboratories and help identify fields of application where neutron activation analysis can be of value.

The IAEA officer responsible for this publication was B. Dodd of the Division of Physical and Chemical Sciences.

EDITORIAL NOTE

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CONTENTS

1. INTRODUCTION

Over the past fifty years, research reactors have progressed through a variety of tasks. These have included materials research using neutron scattering and diffraction, materials characterization by activation analysis and radiography, isotope production, irradiation testing, as well as training, and service as centres of excellence in science and technology. There have been a number of IAEA sponsored meetings, seminars and symposia on research reactor utilization. In spite of these efforts, research reactors in some countries are still under-utilized. This is especially true in the 39 developing countries which together have 84 operational research reactors [1]. Since research reactors have a high capital cost and require a substantial operating budget, the IAEA makes efforts to assist in their effective utilization. As part of that project, the IAEA organized an Advisory Group Meeting on "Enhancement of Research Reactor Utilization for Neutron Activation Analysis" which was held in Vienna, 22–26 June 1998.

Neutron activation analysis (NAA) is a method for qualitative and quantitative determination of elements based on the measurement of characteristic radiation from radionuclides formed directly or indirectly by neutron irradiation of the material. The most suitable source of neutrons is usually a nuclear research reactor. The method's characteristics can be summarized as follows:

(1) Very low detection limits for 30–40 elements,
(2) Significant matrix independence,
(3) The possibility of non-destructive analysis (instrumental NAA or INAA),
(4) The use of radiochemical separation to overcome interference in complex gamma-ray spectra (radiochemical NAA or RNAA),
(5) An inherent capability for high levels of accuracy compared to other trace element analysis techniques.

Due to its inherent sensitivity and accuracy, neutron activation analysis has been extensively applied to environmental sciences, nutritional studies, health related studies, geological and geochemical sciences, material sciences, archaeological studies, forensic studies and nuclear data measurements. In addition to these applications, NAA has a role in the quality assurance of chemical analysis.

Since NAA requires access to a nuclear research reactor, the method is less widely applied than other analytical techniques for elemental analysis, such as atomic absorption spectroscopy (AAS), inductively coupled plasma spectroscopy (ICP) and X-ray fluorescence spectroscopy (XRF). These area all techniques for which stand-alone equipment is easily available and consequently, the call on NAA for elemental analysis is decreasing. Thus, also the utilization of the reactor is affected.

The decreased interest for NAA results partly from insufficient awareness within the applied fields regarding the opportunities of this technique. Each analytical technique has its own particular advantages and disadvantages that make it suitable (or unsuitable) for a given application. NAA is unique in several important aspects such as being largely independent of matrix effects, being suitable for analysis of materials that are difficult to dissolve (e.g. silicon, ceramics), being relatively insensitive to sample contamination and having specific means of detection. Due to these comparative advantages, sensitivity and accuracy, it has a special role as a reference technique for other analytical methods.

The purpose of the Advisory Group meeting was to discuss the benefits and the role of the NAA in many applications and research areas that may contribute towards improving utilization of research reactors.

The discussion included the following subjects:

(1) Current trends in NAA;
(2) The role and opportunities of NAA compared to other methods of chemical analysis.
(3) How to increase the number of NAA users through interaction with industries, research institutes, universities and medical institutions;
(4) How to reduce costs while maintaining the quality and reliability of NAA;
(5) NAA using low power research reactors such as the Miniature Neutron Source Reactor (MNSR) or the SLOWPOKE reactor.

These topics are relevant in that several NAA laboratories are run in a way that is far from optimum as regards the needs of the institution and the country.

This publication summarizes the discussions and conclusions resulting from the meeting. In Annex I a brief introduction is given in the methodology on NAA. In Annex II, presentations of the individual experts are given that describe in more detail typical, or illustrative, applications of NAA or such applications that can be considered typical for a particular country.

This TECDOC is expected to benefit the NAA laboratories associated with research reactors that could support a broad range of research and applied projects.

2. CURRENT TRENDS IN NEUTRON ACTIVATION ANALYSIS

2.1. Trends

It is generally accepted that NAA is a mature technique. The principles of the method are well understood and there are almost no fundamental aspects in the method that imply further development, innovation or for which technological breakthroughs are foreseen, that would change the role of NAA dramatically. Therefore, in this chapter the focus is on trends in applications of NAA.

It is hard to point out international trends in the use of NAA. It is important to realise that by definition “trends” imply a contemporary process. Moreover, the applications are often initiated by the national needs, e.g. to serve the local industry and economy, or for local environmental studies. As such, trends in the use of NAA in East Asian countries for example will differ from those in Latin American countries.

One of the trends that can be derived from the recent literature is that laboratories are increasingly using other methods of analysis complimentary to NAA to widen the information content in their studies. For instance, AAS offers the opportunity to get data on Pb, which is still considered an important element in many environmental studies. Equally so, AAS and ICP are much easier to use for water analysis; but are complimentary again, if NAA is applied for sediment studies.

A new market segment, developing fast in many countries, is metrology in chemical measurements. As mentioned previously, for a long time NAA has been used in many

countries in the characterization of candidate reference materials. Nowadays there is a trend to establish national reference laboratories for metrology in chemistry. Facilities with NAA capability can play a role in this, not only in the development of reference materials but also for the verification of reference methods and for validation of other methods of elemental analysis. Under extreme conditions with respect to the methodology, and in particular the conduct of the analysis, NAA may fulfil the requirements to serve as a "primary ratio method" for determinations of amount of substance [2].

Although often the accuracy of NAA is taken for granted, there is a trend that may have a reverse effect on analytical quality. Physicists always have been involved in the development stage of NAA as an analytical technique. In several NAA laboratories these pioneers of the 1960s and 1970s are now, at the turn of the millennium, close to retirement. It appears to be difficult to find their replacement by young physicists because NAA does not offer an outlook for many challenges. Consequently, there is a trend now that many NAA laboratories are occupied and managed by chemists. It cannot be excluded that due to insufficient background in the underlying physics sources of error may be underestimated or not recognised at all, with negative effects for the analytical quality of these laboratories.

In recent years, a decline may be seen concerning the NAA applications in geochemistry, mineral exploration, and in materials science, especially in developed countries. One of the reasons is the need for isotope specific information for certain elements. This is information that is often easier to obtain via ICP-MS. In addition, improvement of matrix correction algorithms for X-ray fluorescence spectrometry has boosted this technique as well, particularly since the sensitivity is sufficient for the determination of the major constituents. The role of NAA in biomedical studies, in quality assurance and in the preparation of reference materials appears to be firmly established, while a number of environmental and health-related applications, including nutritional studies seems to be slightly increasing. Moreover, new types of applications such as large sample analysis [3], [4] and chemical speciation studies [5] have also appeared.

Finally, there is a trend to assess the position of NAA via the number of related scientific publications. This number is declining, both in absolute terms as well as relative to the number resulting from the use of other analytical techniques. Such evaluations do not give details on the type of papers, viz. if they are related to fundamental development without opportunities for application, practical innovations, applications or troubleshooting, and therefore can be misleading. However, to some extent the declining number of NAA papers may partly reflect the closing of nuclear research reactors in several countries, and with it, the reduction in the number of NAA laboratories.

2.2. Typical applications

It is hardly possible to provide a complete survey of current NAA applications, however, some trends can be identified. At specialized institutions, NAA is widely used for analysis of samples within environmental specimen banking programmes [6]. The extensive use of NAA in environmental control and monitoring can be demonstrated by the large number of papers presented at two symposia organized by the IAEA in these fields: "Applications of Isotopes and Radiation in Conservation of the Environment" in 1992 [7] and "Harmonization of Health-Related Environmental Measurements Using Nuclear and Isotopic Techniques" in 1996 [8]. Similar trends can also be identified from the topics discussed at the regular conference on "Modern Trends in Activation Analysis (MTAA)" and at the symposia on "Nuclear Analytical Methods in the Life Sciences" [9–11]. The above mentioned proceedings

can be considered not only as sources of information on already existing applications, but also as an inspiration for future possible developments.

Additional sources of recent information on utilizing NAA in selected fields, such as air pollution and environmental analysis, food, forensic science, geological and inorganic materials as well as water analysis can be found in the bi-annual reviews in Analytical Chemistry, for instance cf. Refs [12–20]. It follows from these reviews that NAA has been applied for determining many elements, usually trace elements, in the following fields and sample types:

(1) Archaeology — amber, bone, ceramics, coins, glasses, jewellery, metal artefacts and sculptures, mortars, paintings, pigments, pottery, raw materials, soils and clays, stone artefacts and sculptures.
(2) Biomedicine, animal and human tissues activable tracers, bile, blood and blood components, bone, brain cell components and other tissues, breast tissue, cancerous tissues, colon, dialysis fluids, drugs and medicines, eye, faeces, foetus, gallstones, hair, implant corrosion, kidney and kidney stones, liver, lung, medical plants and herbs, milk, mineral availability, muscle, nails, placenta, snake venom, rat tissues (normal and diseased), teeth, dental enamel and dental fillings, thyroid, urine and urinary stones.
(3) Environmental science and related fields — aerosols, atmospheric particulates (size fractionated), dust, fossil fuels and their ashes, flue gas, animals, birds, insects, fish, aquatic and marine biota, seaweed, algae, lichens, mosses, plants, trees (leaves, needles, tree bark), household and municipal waste, rain and horizontal precipitations (fog, icing, hoarfrost), soils, sediments and their leachates, sewage sludges, tobacco and tobacco smoke, surface and ground waters, volcanic gases.
(4) Forensics — bomb debris, bullet lead, explosives detection, glass fragments, paint, hair, gun shot residue swabs, shotgun pellets.
(5) Geology and geochemistry — asbestos, bore hole samples, bulk coals and coal products, coal and oil shale components, crude oils, kerosene, petroleum, cosmo-chemical samples, cosmic dust, lunar samples, coral, diamonds, exploration and geochemistry, meteorites, ocean nodules, rocks, sediments, soils, glacial till, ores and separated minerals.
(6) Industrial products — alloys, catalysts, ceramics and refractory materials, coatings, electronic materials, fertilizers, fissile material detection and other safeguard materials, graphite, high purity and high-tech materials, integrated circuit packing materials, on-line, flow analysis, oil products and solvents, pharmaceutical products, plastics, process control applications, semiconductors, pure silicon and silicon processing, silicon dioxide, NAA irradiation vials, textile dyes, thin metal layers on various substrates.
(7) Nutrition — composite diets, foods, food colours, grains, honey, seeds, spices, vegetables, milk and milk formulae, yeast.
(8) Quality assurance of analysis and reference materials — certification of element contents and homogeneity testing of mainly biological and environmental reference materials of chemical composition, method intercomparisons (more on these topics can be found in Refs [21–25] and in Proceedings of the Int. Symposia on Biological and Environmental Reference Materials (BERM), for instance cf. Refs [26–28]).

3. THE ROLE AND OPPORTUNITIES OF NAA COMPARED TO OTHER METHODS OF CHEMICAL ANALYSIS

3.1. Developments with other methods for elemental anaysis

Over the years, the IAEA has regularly evaluated the role of NAA among methods for elemental analysis. Some years ago, a special TECDOC was published on this issue [29]. Basically, not so many things have changed over the years although increasingly the alternative methods for elemental analysis are being applied in studies in which in the past NAA was once the method of choice. The reasons for this development are many, including:

(1) Equipment for methods based on AAS, ICP and XRF is commonly available, and can be installed 'on-the-spot', i.e. in the laboratories related to the applied sciences. Thus, there is no need for contracting-out services.
(2) The industry supporting the equipment for these other techniques offers a much stronger service and back-up to the buyers than the industry related to nuclear spectroscopy. The modern AAS, ICP and XRF equipment comes with user-friendly software packages resulting in full analysis reports without the need for extensive calibrations. Moreover, there are continuously new developments, such as laser ablation for solid state ICP, solid-state AAS and total-reflection XRF. In addition, dedicated sample changers can be easily integrated with AAS, ICP and XRF, thus allowing for a large sample throughput.
(3) The microwave digestion technique has taken away the drawback of sample digestion in many applications.
(4) Many NAA laboratories are not equipped for handling requests for the analysis of a large series of samples, or for analysis of several different batches of samples simultaneously. Automation in NAA is often under-developed. Sample changers are not easily available and typically have to be developed 'in-house'. Commercially available software is not user-friendly enough to process samples and gamma-ray spectra without intervention.
(5) NAA has a reputation of being a technique with a long turnaround time, whereas with other methods of analysis results may be available within minutes after introduction of the analytical portion.
(6) Vendors of equipment for other methods of analysis emphasise the ultra low detection limits in their promotion of their products. These detection limits are typically based upon 'interference free' conditions, and do not represent the situation if dealing with real samples. Since the NAA 'family' usually does not quote the detection limits for interference free conditions, the discrepancy between these ultimate values works negatively towards the perception of the capabilities of NAA.
(7) In environmental and health-related sciences there is an on-going interest in the element Pb, for which NAA has nothing to offer.

3.2. Characteristics of INAA compared to other methods of elemental analysis

Although there are many situations in which NAA has theoretically better analytical characteristics than other methods of elemental analysis, it is important to remain realistic in evaluating the role of NAA. Therefore, the most typical analytical characteristics are revisited in view of the alternatives available (see also Annex I):

(1) Sensitivity and applicability for minor and trace elements in a wide range of matrices.
This now applies equally well to AAS, ICP(MS) and even TR-XRF.
(2) Virtual absence of an analytical blank.
This is still an advantage of NAA.

(3) Relative freedom from matrix and interference effects.
This is still an advantage of NAA.

(4) The possibility of performing non-destructive analysis using instrumental neutron activation analysis (INAA).
Nowadays laser-ablation ICP, solid-state AAS and TR-XRF offer similar opportunities with much shorter turnaround times and sometimes better detection limits.

(5) High specificity based on the individual characteristics of the induced radionuclides.
This is still an advantage of NAA.

(6) The capability of INAA for multi-element determination, often allowing 30 to 40 elements to be determined in many matrices.
Applies equally well or even better for ICP and TR-XRF.

(7) An inherent potential for accuracy compared to other analytical techniques. Since the theoretical basis of NAA is well understood, a complete uncertainty budget can be made
This is still an advantage of NAA.

(8) The totally independent nature of the method as a nuclear-based property in contrast to the electronic nature of most other analytical techniques.
This is still an advantage of NAA.

(9) The isotopic basis of the method offers a choice of analytically independent routes for element determination.
Since different nuclides of one element can be determined either simultaneously or via different protocols, NAA has a self-verifying character.

(10) In cases where the induced radionuclides of trace elements are masked by matrix activity, radiochemical separation provides interference-free detection limits close to the theoretical ones. Thus, in the radiochemical mode of NAA (RNAA), the technique has other advantageous features.
The laborious activities related to RNAA have to be compared to the simplicity of ICP for example, which often offers comparable or even better detection limits.

(11) Trace and ultra-trace (radio) chemistry can be performed under controlled conditions by using inactive carrier additions.
Alternatively, stable isotope tracer techniques can be followed if ICP(MS) is available.

(12) The chemical yield of the separation can be obtained by simply using carrier budgeting or the radiotracer method.
This is still an advantage of NAA.

3.3. Evaluation, and opportunities for INAA

It can be concluded that in principle one or more of the other analytical techniques may be preferred for elemental analysis, thus bypassing the drawbacks of NAA as discussed above. However, the evaluation of the characteristics outlined above also makes it clear where to find the niches for NAA. These include:

(1) Studies involving samples for which other methods of analysis have difficulties in the calibration step due to chemical matrix effects. This applies particularly to studies in which the matrix composition varies considerably in an unpredictable way, or for which no matrix-matching reference materials are available.

(2) Samples in which the trace element levels are so low that contamination or losses may occur easily during the sample dissolution or digestion step.

(3) Analyses requiring a high degree of accuracy, but even more reliability, to ensure full comparability of data obtained over a long period of time.

(4) Samples with a high degree of inhomogeneity, requiring the processing of a relatively large analytical portion.

(5) Samples in which the element concentration may vary over several orders of magnitude; here the linearity of NAA pays off.

It is often argued that NAA has a long turn around time. In principle this may be true. However, if analyses can be done on the basis of the measurement of short half-life radionuclides (half lives varying from seconds to a few hours), results may be reported even on the same day as the receipt of the sample. Similarly, if turn around time is important, activation analysts should consider abandoning the traditional analysis protocols involving measurements 1 week and 4 weeks after irradiation. These protocols may indeed be optimal to obtain complimentary information on as many elements as possible but they have never been designed to yield optimal information in an as short as possible turn around time. Modern day gamma-ray spectrometers are stable at high count rates allowing for measurements only 2 or 3 days after irradiation thereby allowing turnaround times of one week or less. In principle, prompt-gamma NAA (PGNAA) offers another opportunity to reduce turnaround times considerably. Some elements can be determined within a few hours whereas in normal NAA decay times of several weeks may be needed. However, detection limits in PGNAA may be different than in conventional NAA.

NAA, in particular INAA has the advantage that the method can handle any new type of sample matrix without the need for development of matrix-dedicated procedures, the search for matrix-matching reference materials and consequently full matrix-dedicated validation. It has been observed that, especially if solid materials have to be analysed, often laboratories employing alternative techniques have equal or even longer turnaround times than NAA laboratories.

This advantage of INAA, resulting in a high degree of reliability, can be used at its advantage to support regulatory agencies such as for testing of imported and locally produced goods.

It is also often argued that other methods of analysis are less expensive than NAA. In such comparisons and discussions it is important to evaluate the costs properly, including not only the sample digestion procedure, but also the costs of the validation of the digestion procedure and the costs of validation if chemical matrix interferences or non-linearity occur. Typically, NAA becomes economically more attractive than other techniques if more than 5 elements are reported and/or if a wide variety of matrices has to be analysed. This is because validation in NAA can be done almost ‘once and for all’, unlike other techniques. However, for some customers demonstrable reliability and accuracy may be often more important than rapid answers.

3.4. Additional niches

Except for the many (traditional) areas in which NAA is currently already applied (see paragraph 2.2), laboratories employing NAA and gamma-ray spectrometry may also consider taking advantage of some other niches.

The Comprehensive Test Ban Treaty Organization (CTBTO) is evaluating various destructive and non-destructive techniques to look for specific elements (fission products) that would be volatilized and could be used as evidence of an underground nuclear test. These elements include chlorine, bromine, iodine, tin, and certain transition metal chlorides. NAA has the sensitivity and multi-element capability required to support some of the CTBTO analysis requirements.

Neutron activation of machine components and test samples (known as coupons) produce radionuclides throughout the material. The rate of release or dissolution can then be monitored on-line using gamma-spectrometry. This provides the rate of corrosion or wear as a function of various environmental conditions. Conversely, NAA can be used to analyse oils for corrosion or wear products in them.

The IAEA has organized a network of Agency Laboratories for Monitoring Environmental Radioactivity [30]. NAA is one of the few methods besides AMS that can provide results for ^{129}I at environmental levels. This network should provide emergency measurements in the case of the accidental or intentional release of radioactivity. The network also should participate in proficiency tests to demonstrate the accuracy and response time of the various laboratories.

Many scientific studies can take advantage of stable, but activable isotopic tracers. The possibility of measuring very low concentrations of certain elements by INAA makes it possible to apply non-radioactive substances if there is a radiological hazard or if the decay time of the available radionuclides is too short. The disadvantage is that the system under study has to be sampled, which involves a delay that is not always accepted. Stable, activable tracers are being used in industry (metallurgy, chemical engineering) and in environmental research (e.g. via labelling with enriched lanthanides or elements such as In, Dy, Ir) [31], [32].

4. HOW TO INCREASE THE NUMBER OF NAA USERS

4.1. Introduction

The enhanced utilization of nuclear reactors for NAA and increased contact with potential users should be encouraged. These users could include universities, industry and institutions in interdisciplinary fields such as nutrition, biomedicine, material science, environmental science, geology. The NAA laboratory should also aim at national goals and to try to make an effort to connect the unique features of NAA to the country's social needs. This is, in fact, a very strong impetus to pursue and stimulate NAA activities in a strategic way. The situation in China may serve as an example. The Chinese government has set national goals for the development of science and technology for the period 2000–2010 which will include six areas: environment, human health, population, energy and resources, agriculture and materials. Thus, it is reasonable for Chinese NAA laboratories to apply the existing NAA methods towards these directions as well as developing further areas. It is also probably the sole way for many facilities to obtain government support and to get funds to run and maintain their NAA laboratories.

Naturally each country, especially a developing country, has its own problems to be solved. These might include such issues as environmental pollution, epidemic diseases, or the shortage of energy and other resources. NAA laboratories should be aware of the important role they have in informing society about how nuclear techniques (including NAA) can be very beneficial to social advancement and the welfare of the population.

However, NAA laboratories, and particularly their leaders should also be well aware of the type of role the NAA laboratory is expected to fulfil in solving such problems. For instance, is the NAA laboratory expected to carry out the entire scientific study, i.e. from problem definition to interpretation of the data in view of this definition? If so, the choice of NAA may not as much be given by its suitability but rather by its availability. If this is the mission of the laboratory, the question arises if the employees of the laboratory may have sufficient

background in the applied fields to deal with problem definition and interpretations. Moreover, the NAA laboratory may wish to be active in more than one type of study. Clearly, nutritional studies require a much different expertise than environmental studies do.

Or is there going to be a partnership where the NAA laboratory collaborates with specialists from the particular field that defines the problem? In which case the NAA laboratory may still wish to help define some things like the sampling protocol.

Finally, there is the alternative to operate NAA in a somewhat commercial way, where there is not a significant scientific involvement, and where the work is selected because of analytical and economical reasons.

4.2. Credibility

A reactor centre, whether it be in a university or other institution, is a substantial investment in the human and financial resources of a developing nation. The reactor centre must therefore be closely integrated into national programs. It has a great potential to contribute to a large number of programmes which in turn lead to socio-economic development while strengthening the science and technology base of the country. For example, remarkable contributions can be made in the areas of agriculture, water, environment, pollution studies, the coastal zone, forensic investigations, health and nutrition, resource estimation and mining. If used in collaboration with relevant governmental ministries and institutions the impact can be very large. Moreover, while providing data and information there can also be a considerable contribution to the development of interdisciplinary scientific effort.

As a prerequisite, the centre must establish a reputation for accuracy, reliability, high throughput, and a willingness to respond to end-user needs and views. This may include the need to develop methodologies, improve equipment and software, and try new projects and sample types.

In this process regular validation is vital. This may be done by the use of reference standards and by checking NAA analyses with other methods of measurement both in the centre and in collaborating institutions.

Regular publication of results and analyses in peer reviewed scientific journals is also very important to demonstrate technical competence.

4.3. Leadership

An enthusiastic and knowledgeable person has to be appointed to take the lead in promoting NAA activities. This person should, by preference, be someone who has a high position in the organisation or institute. This will contribute to his or her respect with potential end-users. This person should have, or seek to win, the confidence of the scientific community, the heads of scientific and professional government institutions, and members of policy making bodies as far as possible.

The promoter should be aware of the potential opportunities for the use of NAA in solving problems of national interest and contributing to scientific development in the nation and region. There are likely to be opportunities within the private sector which would be suitable for applications using NAA. Also, the promoter should be aware that the use of NAA introduces other aspects of the peaceful use of nuclear science and technology. These include

radiation protection and familiarity with uses of radiation and radioactive material that can have wider interest.

This vision, together with the mission statement of the laboratory and the existing scientific and technical competence should be used to decide if the laboratory can be considered sufficiently capable to carry out applied research on its own at a level that it will successfully pass a review by peers in this applied field. However, it may be envisioned that an application may imply a long lasting involvement of the NAA laboratory, or may require crucial decisions related to sampling, sampling processing and interpretation that exceed the capabilities of the current staffing. In such cases, the NAA laboratory should consider hosting a scientist from that applied field on a semi-permanent basis. Eventually, if work in this field continues, this person may become a permanent staff member. As an example, a nutritionist may be attracted if the laboratory wants to develop itself as the national reference laboratory for food additive studies. A geochemist or mineralogist may be needed if the laboratory continues to support studies of national resources.

If the laboratory envisions involvement in several applied fields without having an opportunity to contribute, in depth, to the problem definition and/or interpretation, the formation of multi-disciplinary teams is a necessity to bridge the applied scientists with the analytical scientists.

The main task of this promoter to 'break the ice', to establish new fields to target within the applied sciences and to establish contacts. If a contact results in a deeper level of interest, the contact should be delegated to persons who are directly responsible for the conduct of the analysis.

At this next level of contacts, much is asked of the NAA analyst with respect to the attitude towards the potential new end-user. It will be important to listen carefully to the end-user's needs and to assess the end-user's priorities. Is the end-user interested in NAA because of the technique's analytical characteristics or has there been some shortcomings with the techniques which are available in-house? Will, for example, multi-element determinations be important or is the turn-around time critical? A course or some training on 'commercial communications' may prove its value for such work. One of the things to learn is that it is usually unwise to immediately say that NAA is a solution to any chemical analysis problem the customer may have.

In all contacts it will be important that the representatives of the institute or NAA laboratory try to refrain from the use of jargon. End-users are typically not interested in such details as the characteristics of the germanium-detector but are more likely to be concerned about the way the laboratory organizes sample custody, project planning, costs and how reliability and quality are assured.

4.4. Markets to target

In attempting to identify potential end-users of NAA a variety of factors must be taken into account. These will include the nature of the reactor being used, the irradiation and counting facilities available, the industrial base and importance of that particular target industry to the country, as well as political considerations.

The irradiation facilities and reactor fluxes may be important in influencing which potential end-users should be approached. If the reactor has the ability of irradiating large numbers of samples on a routine basis (i.e., the schedule of the reactor consistently provides irradiations at

least several days every two or three weeks) it may be possible to operate on a service basis to industries like mineral exploration. If on the other hand, the reactor only has the capacity of irradiating a small number of samples irregularly, it would probably be a better idea to approach end-users with a demand for a small number of samples. This may be more of a research or co-operative effort although a small volume of high value analyses may be useful.

The industrial base of the country can determine who are the potential end-users. For example, if there is no advanced electronics material industry, there is unlikely to be any local interest in the analysis of pure silicon. If, however, agriculture is an important industry, then this group is a potential end-user. Political considerations are also important. If the reactor is located at a university, it is obviously in the best interest of the university to support research in university departments. If funding comes from governmental departments, it would be advantageous to support government as well. Generally it is useful to show that there are end-users in all aspects of government, higher education, and industry.

Information on potential end-users can be derived from governmental authorities, such as ministries of the environment, health, trade, industrial development, and agriculture as well as their related research institutes. Similarly, the comparable county and municipal authorities are sources of information. In addition, data can be gathered from the national geological survey, from chambers of commerce, from listings of import/export activities, from university programs, and from the activities of other analytical laboratories within the country. Another opportunity is to study the catalogues of producers of reference materials. This also provides a good clue to the fields in which NAA may be of value. Generally, reference material programs will only produce such materials where a demand is foreseen. In effect, they are doing part of the market research.

Once an application has been identified, it becomes important to collect background information, or to do some market research. One important item is to gain some basic understanding as to why the end-user needs trace element data, and what sorts of analyses would be of added value to him. Another opportunity is to collect annual reports, brochures or any other relevant report of the targeted new end-user.

Once interest is shown in the technique and applications, it is usually a good idea to obtain some material to test the application. The quality of the results obtained and the speed of analysis are important to show the potential of the technique. Generally, samples should be analysed rapidly and the results discussed with the end user.

4.5. Presentation

The first presentation of the laboratory to the potential end user may be of crucial importance. In this presentation the laboratory has to demonstrate what NAA has to offer to the end user, and how the laboratory has made adjustments to serve the new customer as much as possible. The presentation should be directed to an audience which is not knowledgeable on NAA. In all aspects of the presentation it should be remembered that the focus should be on “why the customer should be interested in NAA” rather than “what are the attractive aspects of NAA from the analyst’s viewpoint?”.

A typical time frame for such a presentation is 10-15 minutes. A good set of transparencies or slides should be prepared using a large font to ensure readability. This also provides a safeguard against putting too much information onto one sheet. Keep graphs and tables as simple as possible. Round-off data where possible and present only data which may be of

value and interest to laymen. One may consider preparing several types of introductions. For example, one could be on the principles of the technique, one a review on applications and one directly focused to the field of interest being targeted. To enhance the impact of a presentation, practice in front of a camera using videotape is recommended.

Additionally, the laboratory should have a brochure to be handed out. There are numerous variations on this theme, but most of them are usually not larger than 2–4 pages, with relatively little text, some interesting photographs and information on addresses and people to contact. The latter should be left off if there is frequent turnover of staff. If the Internet is available in the country, then a facility web site could also be of benefit.

Many institutions routinely prepare an annual report. Annual reports are sometimes appreciated in the latter stages of developing a new user, and may serve to enhance the credibility of the laboratory, especially if references are given to existing partners in research and customers.

4.6. Management

Because of the likely scale and the numbers of samples and individuals involved, precise planning and project management are essential. This will include normal operational flexibility, but particular attention needs to be paid to sample management, custody, and storage. Details of samples must be maintained.

From time to time there will be a turnover in staff so it is necessary to have complete documentation of procedures (including laboratory procedures), processes, and operations. All manuals must be prepared, verified, updated, and readily accessible. This information must be transmitted to all workers and their successors. Each centre should have comprehensive safety procedures and a safety manual which must be strictly followed.

Such programmes are assisted by in-house and overseas training from time to time. Visits by experts from the IAEA and collaborating laboratories and organizations can be helpful.

4.7. Networking

Enhanced interest in NAA can also be assisted by building a network of contacts within various fields of science and technology. To this end, the promoter and colleagues (e.g., the head of the NAA laboratory) should attend (inter-) national non-nuclear meetings, such as those in chemistry, biology, agriculture, archaeology, geology, and environmental science. Even civil engineering science may be considered since NAA may be of use in studies of sewage sludge treatment. Papers and posters on NAA efforts should be presented at such meetings. Reviews may be given on what has been done worldwide in that particular applied science. It all serves as a stepping stone to establish the network of contacts and to introduce the laboratory and the techniques at other institutions and universities. In fact, every opportunity should be used to elucidate and to introduce the unique merits of NAA to scientists in various disciplinary fields, to officials responsible for the allocation of research funds, and to managers in the industrial community.

Another opportunity to raise interest in NAA is to organize an open house and to invite some key persons from applied fields. Such an activity is often willingly accepted since non-nuclear scientists are usually interested in seeing a nuclear research reactor as well. In some cases, it may be worthwhile to send an ‘eye-catching’ application or a special NAA analysis result to a newspaper as well.

4.8. Publicity

It should be realised that most end users may probably not read the media which are used by the NAA society, such as the *Journal of Radioanalytical Nuclear Chemistry, Nuclear Instruments and Methods*, the *Journal of Applied Radiation Isotopes*, and *Analytical Chemistry*. Sometimes this is because of language difficulties. Nor will they necessarily be aware of the activities of the IAEA and the information supplied by this organization. This also means that end users may not be aware of the characteristics of NAA and its potential. Indeed they may not even be aware of the existence of such a method for elemental analysis.

Public awareness is important to maintain the interest in, and the growth of, the centre. One way of ensuring this is by the centre providing support and encouraging publication of articles in local journals and the news media. These articles could document and explain achievements of national importance such as environmental findings, agricultural developments, as well as archaeological and resource studies. Organization and participation in national and regional science events including seminars, conferences and national debates will maintain public interest.

Another group of end users to target is laboratory technicians. These are the persons who deal with the everyday work and the problems associated with the samples they receive. This group of people is best addressed via a simple 1–2 page article in a trade or a technical journal which can be found in almost every country. These typically have names such as 'Laboratory News', or 'Research and Development'. Newsletters from a chemical society or something similar may also serve this purpose.

In such papers (which should be written in the national language) a balance should be found between scientific content and accessibility for the non-expert. Emphasis should be on the typical characteristics of NAA (both advantages and limitations). It is worthwhile putting this in a context of the limitations of other techniques, under such topics as non-destructivity, matrix independence, linearity and dynamic range.

Support for science teachers and science education is also an important contribution to the national goals.

In the end, it is often the public that pays for the existence and programs of the reactor centre. Therefore, the centre's output must address issues of public interest and take into account the needs of the private sector. This must be reflected in the setting of goals and priorities for the centre. Goal setting must take into account the overall national needs. A useful step in this process is the preparation of a strategic plan that covers a five year period and is reviewed annually. This requires full discussion and collaboration with peers in other scientific fields and with policy makers.

5. HOW TO REDUCE COSTS AND TO MAINTAIN QUALITY AND RELIABILITY OF NAA

The total costs of an NAA procedure is composed of several factors. These include: reactor costs (consumption of neutrons), costs of equipment (depreciation), costs of consumables and chemicals (vials, reference materials and chemicals, particularly if chemical separations are applied) and labour costs. It is useful to calculate the analysis costs in order to assess the laboratory's competitive position. The total analysis cost does not necessarily have to be the price charged. A laboratory may consider charging a price lower than the total costs if it is more important to have end-users than to be fully sustainable on this income source alone. As

such, the reactor costs may be dropped (which is often done, it being argued that 'the reactor and the neutrons are there anyhow'). Alternatively, a laboratory may charge a higher price than just the break-even costs if competition allows.

Cost analysis also clarifies which components need to be improved to reduce the cost. If the reactor costs is important, short irradiations and measurements at a higher counting efficiency may be considered. Thus, a new and larger Ge detector (e.g. a well-type Ge detector) may suddenly become an economically attractive alternative, especially on the long term. Also the use of short half-life radionuclides may then contribute to reduce the overall costs.

If the depreciation costs of equipment is the dominant factor, shorter counting times, and thus higher throughput, should be considered. Automation via sample changers is another way to increase the throughput and thus the contribution of equipment in the analysis costs. Eventually, larger sample masses and higher induced activity may be considered. Shorter counting times may result in a poorer precision but often there is no need to count until peak statistics are better than 1%. Ten percent or perhaps even 25% counting statistics may already be enough to satisfy the customer. It implies a dramatic reduction of counting time and increase of throughput.

There are only a few remedies if the costs of vials, reference materials and chemicals are determining the analysis costs. Reference materials are necessary for validation of methods, and sometimes for internal quality control. In case of the latter, a laboratory may consider producing its own internal quality control material, or establishing a network with other regional laboratories for exchanging samples.

Labour costs may be a determining component in the analysis costs. Labour may be related to the sample preparation step, preparation of standards, chemical separations, sample changing and spectrum analysis and interpretation. Labour costs related to preparation of standards and spectrum analysis/interpretation may be reduced if the number of elements to be reported is reduced. It has been observed (see Annex II) that many customers are interested in a few elements only rather than needing full multi-element scans to be done. In such a case, the simple relative method for calibration has to be preferred above more sophisticated comparator or k_0 methods that require more calibrations and dedicated software. Many of the software modules for NAA, distributed by vendors of gamma-ray spectroscopy equipment, are capable of producing element concentrations if the relative method is applied.

Labour costs can also be reduced by further automation. However, only a few sample changers are commercially available, requiring a considerable investment and often extra modifications to accommodate the laboratory's specific vials. Still, simple changers based on a rotating wheel can be developed in-house at relatively low costs, and these would at least allow multiple measurements overnight and on the weekends.

Sometimes laboratories choose to reduce labour costs by having the analysis done by lower paid staff and sometimes by hiring students. On the other hand, this development has to be also seen in the light of the need to demonstrate technical competence. Sometimes components of the work such as sample weighing are given to lower grade personnel than more skilled work such as spectrum interpretation or chemical separation. In all cases, the quality of the work has to be monitored carefully. In addition schedules have to be in place for in-house training whereas there should be clear and unambiguous, quantified criteria for taking decisions at hold points in the procedures, and for actions in situations of non-conformance.

Whatever measures are taken to reduce the costs of the analysis, such as reduction of irradiation/counting/turnaround times, reduction of labour, less expensive quality control material, the laboratory should have quality assurance measures in place. These are often interpreted by customers as 'reliability'. A first step in this direction is a full assessment of all potential sources of error, not just the technical but also the organisational. Then, the laboratory should decide how to monitor these sources of error, and what the criteria should be to determine if the process can be continued or if it has to be interrupted.

Quality control and quality assurance principles are often already to some extent present in many laboratories. The IAEA offers various opportunities for further improvement in this respect. A good tool to monitor the quality of the process is by control charts. As has been demonstrated [33], control charts can not only be used to monitor the trend of, for example a concentration with time, but even the performance a certain employee with time or in comparison with other employees.

6. CASE STUDY OF AN NAA SERVICE LABORATORY

The Nuclear Analytical Methods research group supervises the facilities of the laboratory for INAA [34] at Delft[1]. The main task of this group is research and development of physical and mathematical methods of radioanalysis, with the emphasis on gamma-ray spectrometry and neutron activation analysis.

For a long time, the facilities have been made available for 'routine' use to non-radiochemists from other universities. Interactively operating software and manuals enable these guests to perform INAA on their own after a short introductory period. No special demands were set to the educational level of the users and universities were not charged for use of the facilities. However, in the case of extensive projects the partner university occasionally contributed to the costs of the analyses by payment in kind, for example via the purchase of components of gamma-ray spectrometers.

In the early 1980s, other (governmental) research institutes gained interest in the potential of INAA and co-operation started on projects with a large sample throughput. In these projects some financial support was included. Over the years, the number of requests for multi-element determinations via INAA grew steadily, not only from the universities, which were now also routinely charged for a part of the total analysis cost, but also from industry.

Difficulties arose for the Nuclear Analytical Methods group since the group had to balance its efforts between 'making money' to relieve the department's financial situation, and innovative research and development. It was decided upon an organizational separation of the INAA services from the research group. However, the research group retained responsibility for technical support and provided advice on the feasibility and optimal conduct of analyses, and on the quality assurance of the analyses. Both for quality assurance reasons as well as because of customer requests (international acceptance of results), a quality system complying with EN45001 standard (closely following ISO/IEC Guide 25) was developed, and accreditation was

[1] The Institute operates a 2 MW light water reactor with 100 h week cycle, and with normal pneumatic and fast rabbit systems and a large sample facility. The counting facilities for INAA comprise 3 well types with sample changers, 3 coaxials with sample changers, 2 stand alone coaxials, one big coaxial for the big samples, one coaxial with sample changer at one of the fast rabbit systems and a stand-alone coaxial with the other. All detectors are linked to a local area computer network with in-house developed spectrometer interfaces. In-house software was developed for gamma-ray spectrum analysis and interpretation. Quantification is done via the single comparator method. The total capacity of the spectrometers allows for 15,000 samples per year.

achieved in early 1993. This also enabled the laboratory to remain competitive with other commercial service laboratories

The analysts in the commercial INAA group have either fixed or temporary contracts with their salaries paid from the revenues of the analyses. The group was initially managed by the institute's commercial services manager with administrative support. Planning systems exist to allow for the analysts' capacity and the use of the irradiation and counting facilities. One of the analysts has a coordinating task that includes the distribution of samples and advising the manager on the remaining capacity. The manager was responsible for administration, marketing research and sales promotion. Since the manager had no background in NAA, often one of the staff members of the research group joined the meetings with customers. Finally, it was decided in 1996 to abandon this position and to return the commercial group's management to the research group leader.

The laboratory for INAA identifies 'external' and 'internal' customers. Scientists from other universities or research establishments, governmental bodies and industry form the first category. The internal customers are scientists within the home institute, mainly from the Department of Radiochemistry. Some of these internal customers are trained by the laboratory to carry out the analyses on their own. The external customers are fully charged for the analyses whereas the internal customers only pay for the consumables (capsules, internal quality control samples etc). The revenues of the services return, except for an overhead charge by the institute, to the laboratory for INAA in order to accommodate the salary costs of the extra technicians and the other costs related to the analysis such as consumables, depreciation of equipment, costs of the quality system and costs for marketing activities. It should be noted that these revenues are ear-marked for usage.

Each analyst can handle about 1000 samples for multi-element analyses per year. An analysis may comprise two irradiations and three measurements. Samples are handled in batches of 14. To each batch a control sample and a blank is added together with neutron flux monitors. Measurements are performed on gamma-ray spectrometers with automated sample changers. Three of these spectrometers are equipped with well-type detectors. An extensive quality control has been developed, which has already been partly performed by the locally written software itself. If the results of the first control by the analyst are in accordance with the criteria, the report is double-checked by one of the staff members of the research group. Only after this approval will the manager release the report to the customer.

Typically, the laboratory carries out approximately 2000–2500 analyses per year for external customers and approximately 1000 analyses per year for internal customers. In Annex II an overview is given of the types of samples analysed and the analysis protocols.

Except for the request from the market sector, the quality system was also developed because of an internal driving force, viz. to improve in a structured manner the organization of the external ('commercial') services. A different approach had to be followed for the planning, conduct of analysis, quality assurance, documentation and customer satisfaction. In such external services one cannot afford to repeat analyses because of organizational mistakes. Moreover, the quality of the results should be immediately and unambiguously established. Such an attitude to work is often not entirely present in a pure research environment. Internal and external audits, and a customer satisfaction evaluation have shown that the services are carried out in a manner that satisfies the customers and does not result in complaints.

7. USE OF NAA IN INDUSTRY

Neutron activation analysis has been widely used in industry and over the years has played a key role in the development of manufacturing process as well as monitoring of the process flow. In this context NAA has been utilized both in research and development (R & D), and in the factory as a flexible analytical tool. For instance, Dow Chemical owns and operates a research reactor for analytical measurements of samples generated in both R & D, and manufacturing area in its plant in Midland, Michigan, USA. However, most industries do not have reactors on their campus but routinely use an off site reactor. The NAA laboratory of DSM Research in The Netherlands uses the nearby (60 km) reactor in Belgium for instance. Other industries often have in-house neutron sources such as a ^{252}Cf used primarily for NAA. Such sources are also intensively applied for on-line bulk measurements.

In most industrial materials analysis laboratories NAA is part of a number of analytical techniques such as ICP-AES, ICP-MS, AA, SIMS, XRF, TXRF. Analysis of complex industrial samples may require data from each of these methods to provide a clear picture of the materials issues involved. With the improvement of classical analytical techniques, and the introduction of new techniques e.g. TXRF the role of NAA continues to be a key bench mark technique that provides accurate and reliable data. The strength of the NAA in bulk analysis is balanced by its weakness in providing surface sensitive or spatially resolved analysis as is required by many applications.

The list of typical applications in industry includes the analysis of catalysts, electronic materials (such as high purity Si, Ga and semiconductor materials), many types of polymers, ceramics, emulsions, slurries, liquid hydrocarbons, halogens, agricultural chemicals.

The principal advantages of NAA over other analytical techniques (such as ICP-MS) are considered to be (i) little sample preparation, thereby minimising the possibility for contamination; (ii) adequate sensitivity for most elements and (iii) a relatively rapid analysis with turnaround times of only a few days. The latter may be surprising, but it should be borne in mind that often new sample types are offered for analysis. Many other methods, although instrumentally much faster than NAA, may require quite some time for assessing the quality of chemical destruction steps, method calibration and/or validation.

Industries usually do not apply NAA in an universal way, as often is done by many university NAA laboratories, but select the method for its specific strengths for a given application. Examples of such cases are: the determination of trace impurities in high purity Si in order to determine contamination; the determination of impurities in plastics to avoid complicated destruction steps; the determination of halogens (F, Br) in plastics; and the assessment of volatile elements such as Hg and As in liquid hydrocarbons.

The examples demonstrate that there are many analytical problems in which NAA may very well be the only (economical) method with desired characteristics. NAA is being selected from a wide variety of methods directly accessible which are often considered as a threat to NAA. It emphasizes the opportunities for NAA laboratories at universities and research institutions to serve the need of their national industry. Of course, it should be borne in mind that in such a case industry may impose specific demands regarding turnaround time, quality control and quality assurance and reduction of analysis costs. There even may be a conflict with reactor operating schedules if analyses have to provided rapidly. However, such problems can be solved.

Many industries need on-line analysis and process control. INAA has certain advantages for this because of the high penetrating power of both the incident neutrons and the emitted gamma-rays. This also reduces the effect of inhomogeneities by particles or in slurries. Systems usually consist of a conveyor belt which passes a neutron generator or an isotopic neutron source. A INAA laboratory associated with a reactor center may contribute to the development and optimization of such systems, taking full advantage of their expertise. Such applications do not directly contribute to an enhancement of the use of the reactor but any such a collaboration may ultimately result in (off-line) analytical support by conventional INAA.

The continued use of NAA in industries critically depend on having NAA trained professionals in the industrial organizations. It has been used most widely and innovatively when a NAA professional was part of the materials analysis laboratory. Interaction of the NAA professional at the research reactor with the industrial analytical laboratories is also very important for enhanced use of the technique. However, this is not quite as effective as having someone inside the industrial analytical laboratory. Therefore training of young professionals in NAA, and other nuclear analytical methods is a key for the increasing use of the research reactors for materials analysis needs.

8. NAA USING LOW POWER REACTORS

Low power reactors are here defined as reactors with a peak thermal neutron flux of less than 1×10^{13} $cm^{-2}s^{-1}$. For practical execution of NAA, a reactor should have a peak neutron flux of at least 10^{11} $cm^{-2}s^{-1}$. The IAEA Research Reactor Database, lists 55 reactors that fit into this category out of 278 reactors operating world wide. Twenty two reactors have a peak thermal flux from $>10^{11}$ to $<=10^{12}$ $cm^{-2}s^{-1}$, and 33 reactors have a peak thermal fluxes from $>10^{12}$ to $<=10^{13}$ $cm^{-2}s^{-1}$. Typical low power reactor types are some TRIGAs, SLOWPOKEs and MNSRs.

Although the reactors have been classified on basis of their peak thermal neutron flux, the available neutron flux in the irradiation facilities is typically a factor of 2–5 lower. A neutron flux in the order of 0.5 to 5×10^{12} $cm^{-2}s^{-1}$ is still quite acceptable for many neutron activation analysis purposes, as has been demonstrated by many laboratories. Moreover, such low neutron flux reactor facilities offer additional advantages for NAA.

(1) They typically have a relatively low gamma-ray dose, allowing for relatively long irradiations with samples packed in plastic foils or capsules.
(2) They have low fuel burn-up, resulting in a much higher neutron flux and neutron spectrum stability with time. Thus, fewer re-calibrations are required. However, whereas the SLOWPOKE reactor type is well known for its high stability over time, the stability of the comparable MNSR type reactor is less, and re-calibrations and flux measurements are more frequently needed.
(3) Smaller reactors often have less demand for other types of experiments or isotope production. Thus, reactor schedules can be more reliable than with multi-purpose high flux reactors in which the reactor schedule may have to be tuned to the wishes of the different users.
(4) Often, reactors such as SLOWPOKEs and MNSRs require lower overhead costs since fewer reactor operators may be required, whilst the entire installation is less complicated.

(5) In addition, for SLOWPOKE and MNSR reactor types the reactor operator training for licensing is relatively simple, thus making the facility much more accessible and reducing the operating costs.

(6) Not only is SLOWPOKE simple to operate but it provides a relatively large and remarkably stable neutron flux over long periods of time. The variation of the flux with respect to the irradiation site and sample position in the irradiation capsule is less than 3%. The flux stability allows the use of equation (1) in which the mass m, of a particular element is calculated from the peak area, A,

$$m = A.\{ke^{-\lambda t_d}(1-e^{-\lambda t_i})(1-e^{-\lambda t_c})\}^{-1} \quad (1)$$

where: $k = z\,\theta N_A\,\sigma\,\varphi M^{-1}/\lambda$,
z = detector efficiency,
θ = abundance of the activated nuclide,
N_A= Avogadro's number = 6.023 x 10^{23},
σ = isotopic activation cross section,
φ = neutron flux,
M = atomic weight of the irradiated element,
t_I, t_d and t_c are the times of irradiation, decay and counting respectively.

The values of k are determined by the use of suitable single element standards a or combination of up to four interference-free elements.

(7) The relatively low neutron flux can easily be accommodated for by longer irradiations, cyclic and pseudo cyclic NAA procedures (see Annex I, paragraph I.3.5.) or by taking larger sample masses (see Annex I, paragraph I.3.1). Samples with masses of 1–5 gram, which are at least ten times the typical sample mass used in NAA, may be used without too many problems with respect to neutron and gamma-ray self-attenuation. Moreover, the extent of both these effects can easily be assessed experimentally.

However, because of the relatively low neutron flux, small reactor types are less suitable for studies of impurities in high purity materials, such as Si. For such analyses, a very high neutron dose rate is necessary, often accomplished by many hours' irradiation in neutron fluxes > 5×10^{13} $cm^{-2}s^{-1}$.

Annex II includes two contributions with examples of NAA using small reactors. More information is available at various Internet web-sites related to SLOWPOKE reactors.

9. CONCLUSIONS

Neutron activation analysis in its various forms is still active and there are good prospects in developing countries for long-term growth. This can be achieved by a more effective use of existing irradiation and counting facilities, a better end-user focus, and perhaps marginal improvements in equipment and techniques. Therefore, it is recommended that the Member States provide financial and other assistance to enhance the effectiveness of their laboratories and to provide assistance through the IAEA in identifying fields of application where neutron activation analysis can be of enhanced value to countries.

In view of the above, it is recommended that Member States promote the use of neutron activation analysis using their low and medium flux reactors. The focus should be on:

(1) Reduction of the total analysis time by developing neutron activation analysis based on short lived radionuclides.

(2) Development of optimised analysis protocols. Use of larger sample quantities to compensate for low neutron fluxes and to reduce counting times.
(3) Use of neutron activation analysis for validation of other methods of elemental analysis.
(4) Feasibility studies for samples related to industrial production, such as fossil fuels, mining, food, agricultural products, and waste management and recycling.
(5) Optimization of neutron beam quality for prompt gamma neutron activation analysis, which provides additional elements and/or may result in reduction of analysis time.

Close co-operation between experienced neutron activation analysis laboratories and new or inexperienced facilities associated with research reactors is highly desirable.

From the experience accumulated to date on the usage of reactors for neutron activation analysis in Canada, China, Jamaica and others it is concluded that low flux research reactors are a good choice for developing countries wishing to embark on neutron activation analysis.

REFERENCES

[1] INTERNATIONAL ATOMIC ENERGY AGENCY, Research Reactor Database, http://www.iaea.org/worldatom/rrdb/.

[2] BODE, P. DE NADAI FERNANDES, E.A.N., GREENBERG, R.R., Metrology for Chemical Measurements: Purism, Pragmatism and the Position of INAA, Accepted for publication in J. Radioanal. Nucl. Chem.

[3] OVERWATER, R.M.W., BODE, P., DE GOEIJ, J.J.M., Gamma-ray spectroscopy of voluminous sources: corrections for source geometry and self-attenuation, Nucl. Instr. Methods, A324 (1993) 209–218.

[4] BODE, P., OVERWATER, R.M.W., DE GOEIJ, J.J.M., Large sample neutron activation analysis: status and prospects, J. Radioanal. Nucl. Chem., Articles, 216 (1997) 5–11.

[5] ZEISLER, R., STONE, S.F., "Environmental specimen banking", Applications of Isotopes and Radiation in Conservation of the Environment (Proc. Int. Symp. Karlsruhe, 1992), IAEA, Vienna (1992) 331–350.

[6] ROSSBACH, M., EMONS, H., GROEMPING, A., OSTAPCZUK, P., SCHLADOT, J.D., "Quality control strategies at the environmental specimen bank of the Federal Republic of Germany", Harmonization of Health-Related Environmental Measurements Using Nuclear and Isotopic Techniques (Proc. Symp. Hyderabad, India, 1996), IAEA, Vienna (1997) 89–100.

[7] INTERNATIONAL ATOMIC ENERGY AGENCY, Applications of Isotopes and Radiation in Conservation of the Environment (Proc. Symp. Karlsruhe, Germany, 1992), IAEA, Vienna (1992).

[8] INTERNATIONAL ATOMIC ENERGY AGENCY, Harmonization of Health-Related Environmental Measurements Using Nuclear and Isotopic Techniques, (Proc. Symp. Hyderabad, India, 1996), IAEA, Vienna (1997).

[9] ZEISLER, R., GUINN, V.P., (Eds), Nuclear Analytical Methods in the Life Sciences, Biol. Trace El. Res., 26/27, (1990), Humana Press, Clifton, New Jersey (1990)

[10] KUCERA, J., OBRUSNIK, I., SABBIONI, E., (Eds), Nuclear Analytical Methods in the Life Sciences, Biol. Trace El. Res., 43/45 (1994), Humana Press, Totowa, New Jersey (1994).

[11] CHAI, Z., (Ed.), Nuclear Analytical Methods in the Life Sciences, Biol. Trace El. Res.71 (1999), Humana Press, Totowa, New Jersey (1999).

[12] EHMANN, W.D., YATES, S.W., Nuclear and radiochemical analysis, Anal. Chem. **58** (1986) 49R-65R.

[13] EHMANN, W.D., YATES, S.W., Nuclear and radiochemical analysis, Anal. Chem. **60** (1988) 42R–62R.

[14] EHMANN, W.D., ROBERTSON, J.D., YATES, S.W., Nuclear and radiochemical analysis, Anal. Chem. **62** (1990) 5OR–70R.

[15] EHMANN, W.D., ROBERTSON, J.D., YATES, S.W., Nuclear and radiochemical analysis, Anal. Chem. **64** (1992) 1R–22R.

[16] EHMANN, W.D., ROBERTSON, J.D., YATES, S.W., Nuclear and radiochemical analysis, Anal. Chem. **66** (1994) 229R–251R.

[17] APPLICATION REVIEWS, Analytical Chemistry **63**, No. 12 (1991) 1R-324R.

[18] APPLICATION REVIEWS, Analytical Chemistry **65**, No. 12 (1993) 1R-484R.

[19] APPLICATION REVIEWS, Analytical Chemistry **67**, No. 12 (1995) 1R-583R.

[20] APPLICATION REVIEWS, Analytical Chemistry **69**, No. 12 (1997) 1R-328R.

[21] BYRNE, A. R., Fresenius J. Anal. Chem. **345** (1993) 144.

[22] DYBCZYNSKI, R., J. Radioanal. Chem. **60** (1980) 45.

[23] BECKER, D. A., Fresenius J. Anal. Chem. **345** (1993) 298.
[24] DYBCZYNSKI, R., Fresenius J. Anal. Chem. **352** (1995) 120.
[25] GREENBERG, R. R., "The role of neutron activation analysis in the development and certification of NIST environmental standard reference materials", Harmonization of Health-Related Environmental Measurements Using Nuclear and Isotopic Techniques, (Proc. Symp. Hyderabad, India, 1996), IAEA, Vienna (1997) 137–144.
[26] Fresenius J. Anal. Chem. **345**, Nos 2–4 (1993) 79–350.
[27] Fresenius J. Anal. Chem. **352**, Nos 1–2 (1995) 1–270.
[28] Fresenius J. Anal. Chem. **360**, Nos. 3–4 (1998) 275–504.
[29] INTERNATIONAL ATOMIC ENERGY AGENCY, Report of the 1st ALMERA Workshop, November 17, 1997, IAEA/AL/113, IAEA, Vienna.
[30] GILATH, C., "Industrial applications of non-destructive activation analysis", Non-destructive activation analysis, (AMIEL, S., Ed.), Elsevier (1981) 303–319.
[31] ONDOV, J. M., KELLY, W. R., Tracing aerosol pollutants with rare earth isotopes, Anal. Chem. **63** (1991) 691A–697A.
[32] BODE, P., VAN DIJK, C. P., Operational management of results in INAA utilizing a versatile system of control charts, J. Radioanal. Nucl. Chem. **215** (1997) 87–94.
[33] BODE, P., Automation and Quality Assurance in the Neutron Activation Facilities in Delft, accept. for publ. in J. Radioanal. Nucl. Chem. (2000).
[34] BODE, P., Operational management of results in INAA utilizing a versatile system of control charts, J. Radioanal. Nucl. Chem. **215** (1997) 51–57.

ANNEX I
METHODOLOGY OF NEUTRON ACTIVATION ANALYSIS

In this Annex, those aspects of the methodology of NAA are presented that may be of value in finding ways to improve utilization of the method. For more details on the methodology it is recommended to consult the various textbooks [I-1 to I-3].

I.1. Neutron activation analysis procedure

An NAA procedure may involve some or all of the following steps:

(1) Sampling;
(2) Pre-irradiation sample treatment (such as cleaning, drying or ashing, pre-concentration of elements of interest or elimination of interfering elements, sub-sampling and packing);
(3) Irradiation (and prompt γ-ray counting in PGNAA);
(4) Radiochemical separation (only in RNAA);
(5) Radioactivity measurement;
(6) Elemental concentration calculation;
(7) Critical evaluation of results and preparation of the NAA report.

I.2. Concentration calibration

Calibration or standardization is the determination of the proportionality factors that relate the measured activity (peak-area in the γ-ray spectrum) to the amounts of the elements present in the sample under experimental conditions. Basically there are two standardizations used in NAA, viz. the relative and the non-relative methods.

I.2.1. The relative method

Sample and element standards are irradiated simultaneously (or sequentially in short half-life NAA with a co-irradiated neutron flux monitor) and later measured under the same counting conditions. The concentration of the element(s) of interest is calculated by comparison of the measured activity between the sample and the standard. The relative method promises the highest accuracy when the standard and sample match each other well in composition, irradiation and counting conditions. On the other hand, the relative standardization on the basis of element standards is not immediately suitable when aiming at the full multi-element power of INAA. It is virtually impossible to produce a multi-element standard containing known amounts of all detectable elements with sufficient accuracy in a volume closely matching the matrix, size and shape of the sample. Some laboratories therefore prefer to use (certified) reference materials as their standards. This has consequences for the final uncertainty of the results due to propagation of the uncertainty in the reference value. For many elements only indicative concentrations are known.

I.2.2. The non-relative method

Multi-element INAA is feasible in the non-relative method or single comparator method [I-4]. Assuming stability in time of all relevant experimental conditions, standards for all elements are co-irradiated each in turn with the chosen single comparator element. Once the calibration factors for all of the elements relative to the comparator element have been determined (the k-factor), only the comparator element has to be used in routine measurements instead of

individual standards for each element. The k-factors can be determined accurately enough so that the single comparator method offers an accuracy comparable to that in the relative method. However, the k-factors are only valid for a specific detector, a specific sample shape, a specific counting geometry and a specific irradiation facility. An example of this single comparator method using zinc as the comparator element is given in [I-5].

At the Institute for Nuclear Sciences in Ghent, Belgium, an attempt has been made to define and determine the k-factors which should be independent of neutron flux parameters as well as of spectrometer characteristics. This so called k_0-standardization method is well established [I-6], [I-7]. It calculates the concentration for element(s) of interest from co-irradiated comparators and experimentally determined neutron flux parameters and the detector efficiency. The k_0-method has been implemented at various laboratories, and the user community has established its own web-site for exchange of information (http://iriaxp.iri.tudelft.nl/~rc/fmr/k0www/k0conten.htm).

As opposed to the relative method, any form of the non-relative method requires good knowledge about reactor neutron flux as well as the detector's peak and total efficiency. A reliable NAA software package is necessary to deal with burn-up, cascade coincidence effects, pile-up and dead-time corrections, peak efficiency evaluation for the actual sample and comparator counting condition, and, eventually, to calculate the needed neutron flux parameters and element concentration.

I.3. Various forms of activation analyses

I.3.1. Instrumental neutron activation analysis

INAA is often referred to as non-destructive NAA or as NAA without post-irradiation radiochemical separation. It is a multi-elemental method whereby γ-ray spectroscopy is applied to radioactivity measurements. INAA promises reliable analytical results, because the possible error due to contamination and element loss can be easily avoided.

INAA is capable of analysing relatively large samples varying from a several grams to several kilograms [I-8], [I-9].

I.3.2. Radiochemical neutron activation analysis

RNAA involves a post-irradiation radiochemical separation procedure to isolate one or a group of elements, or to eliminate interfering nuclides. Application of a carrier and hold-back carrier makes chemical separations much more convenient. The chemical yield can be calculated from re-determination of the added carrier when it is a stable isotope. When the carrier is a radioactive one, chemical yield can be obtained directly from the sample γ-ray measurement.

I.3.3. Epithermal neutron activation analysis

In ENAA, a sample is irradiated in an epithermal neutron flux by covering it with cadmium foil or putting it in a borated capsule. Some reactors provide epithermal irradiation facilities by having the irradiation position suitably surrounded by such materials. Q_0 is defined as the resonance-to-thermal cross-section ratio. ENAA is mainly used to determine a high Q_0 nuclide(s) when a low Q_0 nuclide(s) is the interference. When irradiated in an epithermal neutron flux, a high Q_0 nuclide like ^{114}Cd (n, γ)^{115}Cd ($Q_0 = 39.6$) will be more activated than

a low Q_0 nuclide like ^{23}Na (n, γ) ^{24}Na ($Q_0 = 0.59$) if compared to the activation in 'normal' NAA. Consequently, a lower detection limit for Cd determination can be expected.

I.3.4. Prompt gamma-ray neutron activation analysis

In PGNAA, the prompt γ-rays emitted during the nuclear reaction are measured. It is a non-destructive and multi-elemental method [I-10], [I-11]. PGNAA may provide elemental contents and depth profiling for elements H, B, C, N, P, S, Cd, Pb and some rare earth elements, especially Sm and Gd. Most of these elements either cannot, or cannot easily, be determined with normal NAA, so PGNAA is a complementary method. To carry out PGNAA, a neutron beam guide and a γ-ray detector assembly are needed.

I.3.5. Cyclic neutron activation analysis

This is most frequently used in short half-life NAA. In this method, a sample is repeatedly activated, and the γ-ray spectra after each irradiation are summed [I-12]. The repetition can continue till the accumulated activity from long lived nuclides is too high. Cyclic NAA is used to improve the counting statistics of the peak-area of short-lived nuclides. To avoid the accumulation of the longer-lived nuclide activity, this cyclic activation can be performed using a series of fresh samples: pseudo-cyclic NAA [I-13].

I.4. Detection limits

The detection limit represents the ability of a given NAA procedure to determine the minimum amounts of an element reliably. The detection limit depends on the irradiation, the decay and the counting conditions. It also depends on the interference situation including such things as the ambient background, the Compton continuum from higher energy γ-rays, as well as any γ-ray spectrum interferences from such factors as the blank from pre-irradiation treatment and from packing materials. The detection limit is often calculated using Currie's formula [I-14]:

$$D_L = 2.71 + 4.65\ \sqrt{B}$$

where D_L is the detection limit and B is the background under a γ-ray peak. It is valid only when the γ-ray background (counting statistical error) is the major interference.

However, practically, the INAA detection limits depend on:

(1) *The amount of material to be irradiated and to be counted.* This is often set by availability, sample encapsulation aspects and safety limits both related to irradiation (irradiation containers) and counting (e.g. with Ge well-type detectors), and possibly because of neutron self-shielding and gamma-ray self-absorption effects. For these reasons practically the sample mass is often limited to approximately 250 mg.

(2) *The neutron fluxes.* These are clearly set by the available irradiation facilities.

(3) *The duration of the irradiation time.* This is set by practical aspects, such as the limitations in total irradiation dose of the plastic containers because of radiation damage. The maximum irradiation time for polyethylene capsules is usually limited to several hours, for instance 5 hours at $5 \times 10^{17}\ m^{-2}s^{-1}$.

(4) *The total induced radioactivity that can be measured* is set by the state-of-the-art of counting and signal processing equipment, with additional radiation dose and shielding considerations. As an example, the maximum activity at the moment of counting may have to be limited to approximately 250 kBq.

(5) *The duration of the counting time.* A very long counting time may set limits to the number of samples processed simultaneously in case the radioactivity decays considerably during this counting time. Moreover, it reduces sample throughput.

(6) *The total turn-around time.* Although sometimes better detection limits may be obtained at long decay times, the demands regarding the turn-around time often imply that a compromise has to be found between the longest permissible decay time and customer satisfaction.

(7) *The detector size, counting geometry and background shielding.* The detector's characteristics may be set in advance by availability but several options exist.

Table I. Detection limits in $mg.kg^{-1}$ as observed in plant material and soil material

	Plant	Soil		Plant	Soil
Na	2	10	K	200	1500
Ca	700	4000	Sc	0.001	0.02
Cr	1	1	Fe	8	100
Co	0.02	0.3	Ni	2	30
Zn	0.4	6	Ga	2	10
As	0.2	0.8	Se	0.1	1
Br	0.3	0.8	Rb	0.4	6
Sr	5	60	Zr	5	80
Mo	4	10	Ag	0.2	2
Cd	3	8	Sn	10	20
Sb	0.02	0.2	Te	0.3	3
Cs	0.02	0.3	Ba	10	40
La	0.1	0.3	Ce	0.2	1
Nd	0.7	8	Sm	0.01	0.03
Eu	0.006	0.05	Tb	0.008	0.1
Yb	0.03	0.2	Lu	0.004	0.02
Hf	0.01	0.1	Ta	0.01	0.2
W	0.3	1	Re	0.08	0.2
Os	0.1	0.6	Ir	0.0006	0.004
Au	0.003	0.01	Hg	0.05	0.4
Th	0.01	0.1	U	0.2	2

Experimental conditions: plant: t_{ir} = 4 h @ 5 * 10^{16} $m^{-2}s^{-1}$, t_d = 5 days, t_m = 0.5 h at coaxial detector, followed at t_d = 3 weeks and t_m = 2 h at well-type detector; sample size = 200 mg; soil: t_{ir} = 1.5 h @ 5 * 10^{16} $m^{-2}s^{-1}$, t_d = 5 days, t_m = 1 h at coaxial detector followed at t_d = 3 weeks and t_m = 1 h at well-type detector; sample size = 200 mg.

It all emphasizes that a limit of detection for a given element by INAA may be different for each individual type of material, and analysis conditions. In Table I [I-15] are given, as an indication, typical detection limits as derived from the analysis of a plant and a soil material.

I.5. Quality control and quality assurance

The physical nature of NAA, and the identifiable potential sources of error allow for much preventive quality control and quality assurance as well as corrective actions if needed. For any NAA laboratory it is of the utmost importance to draft a list of these potential sources of error. These can include analytical (e.g., quality of chemicals), technical (e.g., geometry effects) and organizational (e.g., transposing errors and other human errors) factors. Quality assurance activities should be embedded in a managerial quality system. To this effort, suggested readings are References [I-16], [I-17].

I.6. Analytical quality

The IAEA provides NAA laboratories several means to assess the analytical quality of their data. These include certified reference materials and opportunities to participate in intercomparison studies. It should be noted however, that certified reference materials are a precious commodity. In principle, they should only be used for verification of the analytical quality and eventually to serve as a tool for traceability. The materials should not be used for technique calibration (or standardization) because of the subsequential high consumption rate and the consequences for the propagation of uncertainty. For day-to-day quality control a laboratory may easily develop its own in-house control standards. Material, resulting from intercomparison rounds may be used for this.

REFERENCES

[I-1] DE SOETE, D., GIJBELS, R., HOSTE, J., Neutron Activation Analysis, Wiley Interscience, London (1972) 836 pp.

[I-2] EHMANN, W.D.,VANCE, D.E., Radiochemistry and Nuclear Methods of Analysis, John Wiley, New York (1991) 531 pp.

[I-3] PARRY, S. J., Activation Spectrometry in Chemical Analysis, J. Wiley, New York (1991) 243 pp.

[I-4] GIRARDI, F., GUZZI, G., PAULY, J., reactor neutron activation analysis by the single comparator method, Anal. Chem. **37** (1965) 1085–1092.

[I-5] DE BRUIN, M., KORTHOVEN, P.J.M., Computer oriented system for non-destructive neutron activation analysis', Anal. Chem. **44** (1972) 2382–2385.

[I-6] SIMONITS, A., DE CORTE, F., HOSTE, J., Single comparator methods in reactor neutron activation analysis, J. Radioanal. Nucl. Chem. **24** (1975) 31–46.

[I-7] DE CORTE, F., SIMONITS, A., HOSTE, J., DE WISPERAERE, A., Accurcau and applicability of the k_0 standardization method, J. Radioanal. Nucl. Chem. **113** (1987) 145–167.

[I-8] BODE, P., LAKMAKER, O., VAN ALLER, P., BLAAUW, M., Feasibility studies of neutron activation analysis with kilogram-size samples, Fresenius J. Anal. Chem. **360** (1998) 10–17.

[I-9] GWOZDZ, R., GRASS, F., Activation analysis of large samples, to be publ. in J. Radioanal. Nucl. Chem.

[I-10] LINDSTROM, R.M., ZEISLER, R.,VINCENT, D.H.,GREENBERG, R.R., STONE, C.A., MACKEY, E.A., ANDERSON, D.L., CLARK, D.D., Neutron capture prompt gamma-ray activation analysis at the NST cold neutron research facility, J. Radioanal. Nucl. Chem. **167** (1993) 121–126.

[I-11] MOLNAR, G., BELGYA, T., DABOLCZI, L., FAZEKAS, B., REVAY, Z., VERES, A., BIKIT, I., KISS, Z., OSTOR, J., The new prompt gamma activation analysis facility at Budapest, J. Radioanal. Nucl. Chem. **215** (1997) 111–115.

[I-12] SPYROU, N.M., Cyclic activation analysis-a review, J. Radioanal. Chem. **61** (1981) 211–242

[I-13] DE SILVA, K.N., CHATT A., A method to improve precision and detection limits for measuring trace elements through short-lived nuclides, J. Biol. Trace Microprobe Techn. **1** (1983) 307–337.

[I-14] CURRIE, L.A., Limits for qualitative detection and quantitative determination — Application to radiochemistry, Anal. Chem. 40 (1968) 586–593.

[I-15] BODE, P., Instrumental and organizational aspects of a neutron activation analysis laboratory, Ph.D. dissertation, Delft University of Technology, Delft (1996).

[I-16] INTERNATIONAL ATOMIC ENERGY AGENCY, Quality Assurance in Biomedical Neutron Activation Analysis, IAEA-TECDOC-323, Vienna (1984).

[I-17] BODE, P., “Total quality management to prevent incorrect results and a waste of resources", Harmonization of the Health Related and Environmental Measurements Using Nuclear and Isotopic Techniques (Proc. Symp. Hyderabad, India), IAEA, Vienna (1997) 49–62.

ANNEX II

PAPERS PRESENTED AT THE ADVISORY GROUP MEETING

IS ACTIVATION ANALYSIS STILL ACTIVE?

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Abstract. This paper reviews some aspects of neutron activation analysis (NAA), covering instrumental neutron activation analysis (INAA), k_0 method, prompt gamma-ray neutron activation analysis (PGNAA), radiochemical neutron activation analysis (RNAA) and molecular activation analysis (MAA). The comparison of neutron activation analysis with other analytical techniques are also made.

1. INTRODUCTION

Over sixty years have passed since Hevesy and Levi first utilized a neutron source to analyze dysprosium in Y_2O_3 by NAA in 1936. No doubt, the NAA has played a very important role in science and technology, especially at its early development stage as a unique analytical arsenal characteristic of nuclear properties. Its extremely high sensitivity for most elements in the periodical table, good accuracy and precision, non-destructiveness, less matrix effect and multi-elemental analysis ability, etc. are so fascinating that the NAA has become an authorized method in the trace elemental analysis, even the sole selection in some cases, e.g. activable stable isotope tracing, in vivo analysis, fine solid particle (cosmic dust and atmospheric aerosol) analysis, etc. However, with the development of other non-nuclear analysis methods in recent years, e.g. Inductively-Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES), Inductively-Coupled Plasma-Mass Spectroscopy (ICP-MS), Laser Photoionization Spectroscopy (LAPIS), the NAA seems to lose the past eminence. Naturally, a question arises: *Is Activation Analysis Still Active?*

2. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS (INAA)

With the advent of high purity Ge detector, the INAA has become a main member in the nuclear analysis field. Due to its simplicity and good accuracy it has been accepted as a recommended method in certifying the reference materials and applied in multidisciplinary studies, from extraterrestrial matter to deep-sea sediment, from large archaeological relics to very fine atmospheric particles, etc. However, some major obstacles which hinder its development as follows:

— sophisticated hardware. Most reactors used for INAA in the world are so huge and expensive that it is very difficult to access for non-nuclear scientists;
— radiation damage and radioactive waste;
— time-consuming and relatively expensive.

To overcome the first obstruction, a compact reactor, like the Canadian SLOWPOKE or Chinese Miniature Neutron Source Reactor (MNSR), should be exploited. In fact, they can be more or less regarded as a neutron source, instead of a true reactor, which are so safe that they are permitted to be installed at hospitals, universities, even in the downtown area.

To solve the second and third problems, the INAA based on short-lived radioactive nuclides should be thoroughly studied. As an alternative, it can be combined with simple preconcentration procedure to improve its sensitivity and selectivity. Consequently, the INAA is still a unique analytical tool in the fields of major, minor, trace and ultratrace elements.

3. K_0 METHOD

In the past twenty years a number of NAA groups, mostly in Europe, are involved in establishing this method, which is regarded to hold the following merits:

— the troublesome preparation of chemical standards can be avoided;
— the radioactivity counting time for standards can be saved;
— quantitative results for elements, but absent in chemical standards, can be obtained;
— some nuclear parameters, e.g. the cross section of neutron capture reaction and the branching ratio of the gamma-ray emitted by the radioactive nuclide, can be re-evaluated.

In fact the main purpose of this method is to simplify the routine NAA, which benefits the extension of utilization of NAA in non-nuclear fields.

4. PROMPT GAMMA NEUTRON ACTIVATION ANALYSIS (PGNAA)

Although its poor sensitivity for most elements, high radioactive background and complicated gamma spectrum, the PGNAA is developing rapidly due to the improvement of the facility, use of cold neutron and alleviation of background level, which has made it as a unique supplement to the conventional NAA, especially for analysis of H, B, Cd, Sm and some others.

It is worthwhile to mention the related work performed in Japan, USA, Germany, Canada and other countries. The very fascinating feature of PGNAA is to be able to non-destructively analyze large samples, and this method will find a broad application in archaeology. Another potential application field of PGNAA will be in radiotherapy via a boron-containing complex selectively absorbed by cancer tissue.

5. RADIOCHEMICAL NEUTRON ACTIVATION ANALYSIS (RNAA)

The use of RNAA is unlikely to expand significantly in near future, but will remain in specialized areas, e.g. determination of platinum group elements (PGEs) and biologically essential trace elements at low level. Up to now the RNAA is still the only way to be able to analyze all 6 PGEs in various matrices, although the ICP-MS and NTIMS (Negatively Thermolized Ionization Mass Spectroscopy are constituting a true threat to RNAA.

The role of RNAA in the analysis of REEs is fading, but it is still superior to other techniques for small sample analysis. The determinations of some essential trace elements, e.g. Cr, I, V, Mn, Co, etc. highly rely on RNAA, especially at ultratrace level, e.g. serum and sub-cell fractions.

6. MOLECULAR ACTIVATION ANALYSIS (MAA)

The term of MAA refers to an activation method that is able to give information about the chemical species of trace elements in systems of interest, though its definition has remained to be assigned. Its development is strongly stimulated by the urgent need to know the chemical species of elements. Total concentrations are often without any meaning when assessing health or environmental risks or in the explanation of geochemical processes. Recently the study of chemical species is implicitly increasing.

The critical point in the MAA is that it is not permitted to change the original chemical species of elements in systems, or the change has to be under control; in the meantime not allowed to form the "new artefact" originally not present in systems.

Some latest practical examples of the MAA are in the studies of the essential elements (Cr, Fe, Co, Se, I), toxic elements (Hg, As) and unknown elements (REEs, PGEs) in life science.

The important biological effects of chemical species of essential and toxic elements in environmental and biological systems have given a strong impetus to develop the MAA and will further enhance its necessity, and for the foreseeable future it is difficult to imagine how such studies can be pursued without a heavy reliance on the MAA.

Although there are some similarities between the MAA and preconcentrating NAA, the ultimate purpose is quite different. The MAA is aimed at chemical speciation of trace elements in samples of interest, whereas the latter is only to overcome matrix interference or to enhance the analytical sensitivity.

7. COMPARISON OF NAA WITH OTHER ANALYTICAL TECHNIQUES

Comparing analytical methods for trace elements is always very difficult. In fact, each coin has two sides and every method has its own merits and drawbacks. One has to take account of the following factors while doing this comparison:

- sample matrix;
- sensitivity and accuracy;
- contamination danger and blank correction;
- available sample amount;
- speed and cost;
- multi-elemental analysis ability;
- possibility of chemical species study, etc.

Another important factor in the selection of analytical methods is the personnel expertise. Some practical examples for this comparison will be given in this paper, especially in the analysis of platinum group elements, rare earth elements and other interesting elements.

Anyhow, the NAA is a valuable technique due to its nuclear-oriented character, unlike other techniques based on the atomic behaviors. Thus, as an independent arsenal, it will continue to occupy a reasonable position in the analytical kingdom. As a conclusion, what we can say is that activation analysis will still be active , even though it is not like before.

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MOLECULAR ACTIVATION ANALYSIS FOR CHEMICAL SPECIES STUDIES

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Abstract. The Molecular Activation Analysis (MAA) mainly refers to an activation analysis method that is able to provide information about the chemical species of elements in systems of interest, though its exact definition has remained to be assigned. Its development is strongly stimulated by the urgent need to know the chemical species of elements, because the bulk contents or concentrations are often insignificant for judging biological, environmental or geochemical effects of elements. In this paper, the features, methodology and limitation of MAA were outlined. Further, the up-to-date MAA progress made in our laboratory was introduced as well.

1. INTRODUCTION

The study of trace elements in biology, environment and geology has roughly experienced two stages: (1) on existence and bulk composition of trace elements in sample of interest; and (2) on correlation between total contents or concentrations of one element and another, and corresponding synergetic or antagonic effect. During these two development stages the Neutron Activation Analysis (NAA) and other nuclear analysis methods, e.g. PIXE, have made a major contribution. However, with development of trace element research, more and more emphasis is being oriented to their chemical species, rather than the bulk analysis, which is meaningless in many cases when assessing biological, environmental or geochemical effects of elements [1]. A literature survey clearly demonstrated an implicitly increasing tendency for speciation study of elements [2], from a few papers in this field in early seventies to hundreds nowadays annually. In literature one can quite often find two terms: species and speciation. Both are arbitrarily used without any difference. Strictly speaking, the "species" means a chemical form, state or valence of an element in a medium, e.g. Cr^{3+},CrO_4^{2-}, $Cr_2O_7^{2-}$ or low molecular weight chromium compound, etc. refer to the possible species of chromium element, whereas the "speciation" means an action resulting in transformation, alteration or variation from one species to another. Of course, more discussion on their definitions is desirable.

In order to meet this challenge in species analysis of trace elements, a number of nuclear and non-nuclear techniques were established, in which the so-called MAA can play a unique role in the species analysis (e.g. [3–10]). The term of MAA refers to an activation analysis method that is able to provide information about the chemical species of elements in system of interest, though its definition remains to be assigned. Since the MAA was first proposed in 1986, it has become one of the main techniques for species analysis. In this paper its features, methodology and limitation will be outlined. In the meantime, some practical MAA examples recently performed in our laboratory will be presented as well.

2. FEATURES OF MAA

In general, the MAA inherits the merits of conventional NAA, e.g. high sensitivity, good accuracy and precision, small sampling amount and multi-elemental analysis ability, etc. During analytical process, it is easier for MAA to keep the original chemical species of elements unchanged than for other non-nuclear methods. In some cases the MAA is even a sole choice to do speciation analysis.

However, the critical point of the MAA is that it is not permitted to alter the original chemical species of elements existing in system of interest, or the alteration must be under strict control and is able to be traced; in the meantime not allowed to form the "new artefact" originally not present in system.

3. METHODOLOGY OF MAA

The methodology of MAA, in fact, is a combination of conventional nuclear analysis methods with physical, chemical or biological separation procedures. For example, in order to study the chemical species of trace elements in biological samples, e.g. distribution patterns of trace elements in cell and subcellular fractions, and their combination with biological macromolecules (protein, enzyme or nuclear acid, etc.), the first step is to selectively separate various species fractions, followed by identification and determination. For this purpose the physical or chemical characteristics of biological macromolecules, e.g. size, charge, solubility, mobility or specificity of biological functions are often utilized. The chemical stepwise dissolution, phase separation, ion exchange chromatography, coprecipitation, ultracentrifugation, gel chromatography, PAGE gel electrophoresis, etc. are of common practice combined with NAA. Besides, the PIXE is also a valuable nuclear analysis technique for chemical species research, which possesses the unique scanning characteristics providing a two-dimensional distribution information of element species [11, 12].

Another important factor which has to be taken account is the quality assurance for chemical species analysis. Unfortunately, only a few reference materials for species analysis are available [13, 14]. The preparation and certification of more species reference materials are desirable.

4. PRACTICAL APPLICATION OF MAA

Since 1986 the MAA has been widely used in environmental and biological fields to study the chemical species of trace elements in various samples, e.g. tissue, hair, urine, blood, sediment and water [2–10] and rarely in geology [15]. The recent progress made in our laboratory in this field is briefly introduced as follows:

4.1. MAA for iridium in Cretaceous and Tertiary boundary clay

Iridium, one of 6 platinum group elements, is often used as an extraterrestrial indicator in geochemistry and cosmochemistry [16]. Further, the chemical species of Ir is associated with its origin. According to the known chemical behaviors of Ir 5 possible iridium species in nature are available, i.e. (1) soluble complex ion; (2) sulfide; (3) metallic phase; (4) noble nugget; (5) organic complex. Thus, we attempted to reveal the origin of anomalous Ir at the Cretaceous and Tertiary (K-T) boundary samples via its chemical species analysis by a newly-developed MAA procedure based on a chemical stepwise dissolution and radiochemical and instrumental NAA [15]. Figure 1 shows the distribution patterns of Ir at 4 K-T boundary samples. It is clear from Fig. 1 that the residue phase is the main host phase of Ir for all K-T boundaries, no matter what they are marine or continent sediment. Our MAA results provide more evidence to favor the extraterrestrial origin of anomalous Ir at K-T, although the volcanic activity and geochemical processes also play more or less role in the Ir enrichment.

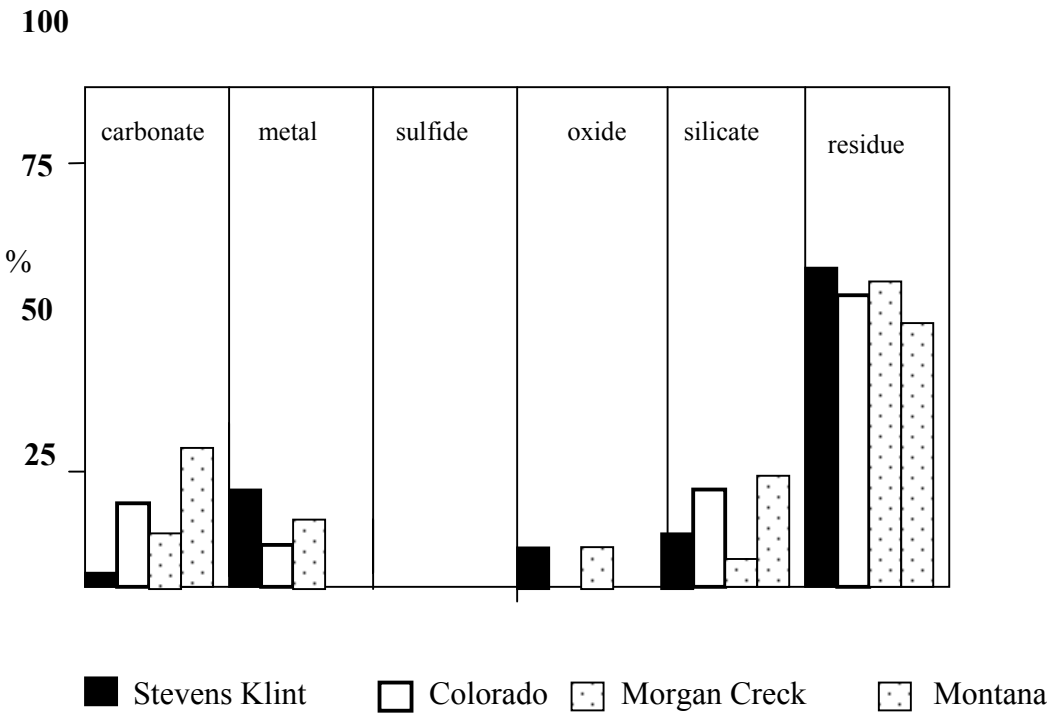

FIG.1. Distribution patterns of Ir in K-T boundary samples.

4.2. MAA for I in algae and human liver

Up to now, the study on chemical species of iodine in marine algae is scarce and some available data are controversial [17, 18]. Taking into account of the fact that algae are becoming a well-received green food and a main source of dietary iodine for Chinese people, of whom 40% live in the I-deficient area, we studied the chemical species of I in 7 marine algae *Codium fragile, Ulva pertuse, Monostroma nitidum, Gracilaria confervoides, Sargassum kjellmanianum, Dictyopteris divaricata and Laminaria japonica* by a newly-established MAA procedure based on leaching, precipitation and NAA. The experimental results for the I species in 7 algae indicate that the contents of total iodine and various species of iodine are different in different alga specimen. 99% of total iodine are soluble in *Laminaria japonica*, whereas in other algae, the soluble iodine contents range from 16 to 41%. In leachates of marine algae, 61 to 93% of soluble iodine exist as I^- with less than 5% IO_3^- and 5 to 37% organic iodine [19, 20].

Besides the thyroid, the human liver is also an important target organ for iodine accumulation. At the moment we are studying the chemical species of iodine in human liver. The preliminary results are listed in Table 1.

4.3. MAA for Hg in human hair

It is known that the methylmercury (Me-Hg) has a strongly toxic effect on human embryo, which is evidently different both qualitatively and quantitatively from that on adult. This hazard can be seen during the prenatal and postnatal stages. In order to study the transfer mechanism of mercury, mainly Me-Hg, from pregnant women to their new-born infants, we developed two simple MAA procedures to determine the longitudinal variation of total, inorganic and organic mercury contents in their hair sample [21, 22]. One is based on the

Table 1. Distribution of iodine in the subcellular fraction of human liver (A = percentage of iodine content of pre- over post-permeation; B = percentage of iodine content of subcellular fraction in whole liver)

Subcellular fraction	iodine μg/g (d.w.)				A ?%?	B ?%?
	pre-permeation		post-permeation			
	whole sample	protein	whole sample	protein		
liver	0.321	4.472	0.531	2.917	78.3	
nuclei	0.932	6.413	1.194	5.346	12.4	48.0
mitochondria	0.825	7.015	0.891	5.412	22.1	15.7
lysosome	0.681	9.238	0.900	8.746	80.7	10.6
microsome	0.171	1.471				1.0
cytrose	0.135	1.120				17.7

selective extraction of methylmercury from hair by hydrochloric acid (see Fig. 2) and other is to take advantage of the volatility of methylmercury cyanide. The hair sample is mixed with potassium hexacyanoferrate and sulfuric acid. Then the resulting methylmercury cyanide is absorbed by cysteine paper, which is irradiated in reactor and directly counted. The interlaboratory comparison demonstrates that their accuracy, precision and reproducibility are satisfactory.

4.4. MAA for rare earth elements (REEs) in fern

The fact that REEs are being widely used in China and other countries to modern industry and agriculture, is resulting in the higher level of REEs in environment. However, until now little work on their chemical species in natural plant has been reported. The information about whether there is REE-bound macromolecules in natural plant specimen is not available. Thus, we established a new MAA procedure based on pH variation , out salting, ultracentrifugation, gel filtration chromatography and electrophoresis, etc. and INAA, to study the REE-bound proteins in a natural plant fern, *Dicranopteris dichotoma*. Our results (Fig. 3) identified two new REE-bound proteins (RBP-1 and RBP-2) in this species of fern. The molecular weights (MW) of RBP-a and RBP-2 on Sephadex G-200 are about 8×10^5 and less than 1.24×10^4, respectively. Their SDS-PAGE graphs show that both contain two protein subunits with MW 14100 and 38700, that seem to be conjugated proteins, glycoproteins with different glyco-units [23, 24].

4.5. MAA for Se in human liver

Because of essentiality of selenium to human-being, its biological effect and chemical species have been substantially studied. However, the report on its distribution and behavior in human liver is still scarce. For this reason we recently used MAA to study the subcellular location of Se and cytosolic distribution of Se contained in human liver. Our results indicated that almost half of Se existed in the nuclei fraction, followed by cytosol and mitochondria. A very few percentages of Se were present in lyzosome and microsome. Further Sephadex G200 gel chromatographic experiment found 4 Se-containing components with MW 335±20, 70±5, 45±1.5 and 14±3 kD in the soluble fractions of human liver (see Fig. 4). The most abundant Se-containing component, peak II, accounted for 70% of the total cytosolic Se. The peak II was subjected to be further purified via DEAE Sepharose fast flow ion exchange chromatography with a linear gradient of 10 to 500 mmol/L $(NH_4)_2CO_3$ buffer. It is clear that the peak II consists of 4 Se-containing proteins. The identification of these Se-containing proteins in human liver is in progress [25].

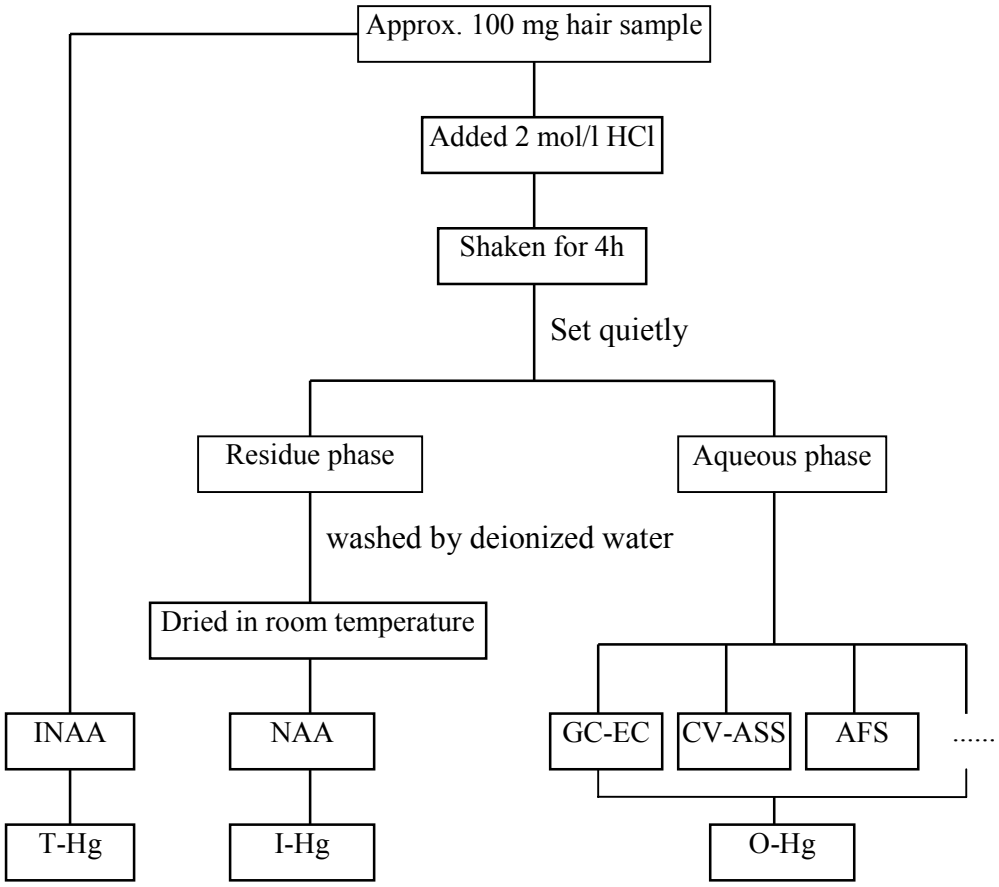

FIG.2. Flow chart of isolation of inorganic and organic Hg from the hair sample by HCl (T-Hg, I-Hg and O-Hg mean total, inorganic and organic mercury, respectively).

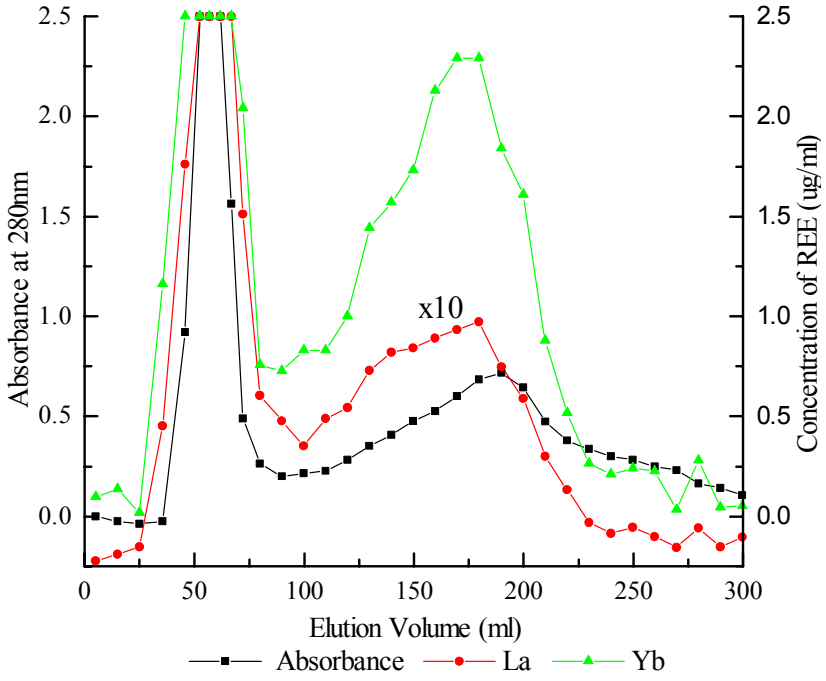

FIG. 3. Two new REE-bound proteins found in a species of fern by a combination of NAA and UV absorption spectrometry.

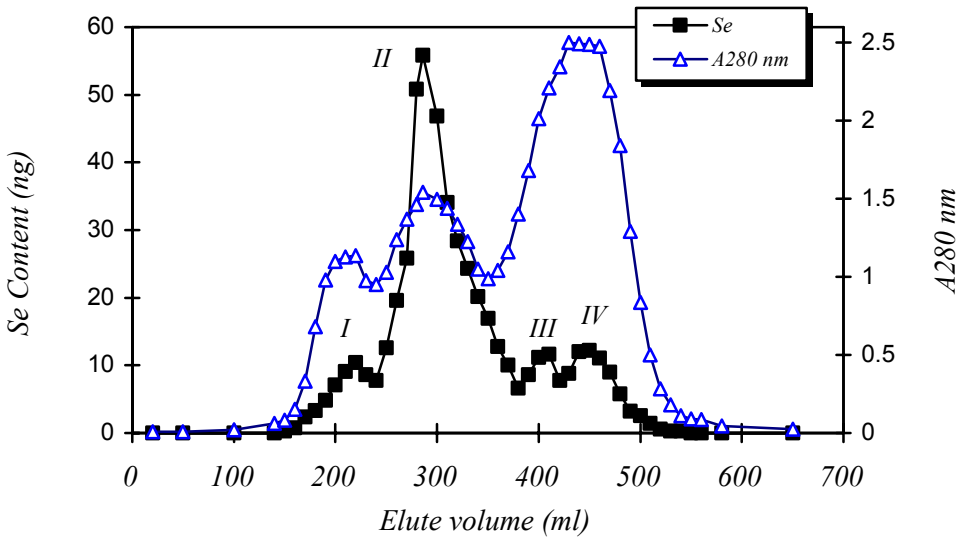

FIG. 4 Profiles of selenium content and protein of human liver cytosol on Sephadex G-200 gel chromatography

The above-mentioned examples have clearly demonstrated that the important biological effects of chemical species of essential and toxic elements in environmental and biological systems and geochemical explanation of indicative elements have given a strong impetus to develop the MAA and will further stimulate its necessity, and for the foreseeable future it is hard to imagine how such studies can be pursued without a heave reliance on the molecular activation analysis. The new application topics will need to improve the available methodology of MAA and more new MAA procedures will come out under this impact.

ACKNOWLEDGEMENTS

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REFERENCES

[1] QUEVAUVILLER, Ph., MAIER, E.A., GRIEPINK, B., Fresenius J. Anal. Chem. **345** (1993) 282.
[2] DAS, H.A., Speciation of trace elements with special reference to the use of radioanalytical methods, ECN, Petten (1993).
[3] LAURA RANES, O.B., Molecular neutron activation analysis, Ph.D. Dissertation, The University of Nebraska, Lincoln (1985) 213.
[4] BLOTCKY, A.J., HANSEN, G.T., Anal. Chem. **59** (1987) 2063.
[5] STONE, S.F., HANCOCK, D., ZEISLER, R., J. Radioanal. Nucl. Chem. **112** (1987) 95.
[6] STONE, S.F., BERNASCONI, G., HASELBERGER, N., MAKAREWICZ, M., OGLIS, R., WOBRAUSCHECK, P., ZEISLER, R., Biol. Trace Elem. Res. **43–45** (1994) 299.
[7] JAYAWICKREME, K., CHATT, A., J. Radioanal. Nucl. Chem. **110** (1987) 583.
[8] JAYAWICKREME, K., CHATT, A., Biol. Trace Elem. Res. **30** (1990) 503.
[9] BEHNE, D., WEISS-NOWAK, C., KALCKLOESCH, M., WESTPHAL, C., Biol. Trace Elem. Res. **43–45** (1994) 287.

[10] BEHNE, D., SCHEID, S., HILMERT, H., GESSNER, H., GAWLIK, D., KYRIAKOPOULOS, A., Biol. Trace Elem. Res. **26–27** (1990) 439.
[11] SZOEKEFALVI-NAGI, Z., Biol. Trace Elem. Res. **43–45** (1994) 73.
[12] SZOEKEFALVI-NAGI, Z., BAGYINKA, C., DEMETER, I., KOVACS, K.E., QUYNH, L.H., Biol. Trace Elem. Res. **26–27** (1990) 93.
[13] INTERNATIONAL ATOMIC ENERGY AGENCY, Survey of Reference materials, Vol. 1, Dec. 1995 IAEA-TECDOC-854 and Vol. 2, May 1996, IAEA-TECDOC-880, IAEA, Vienna (1995 and 1996).
[14] NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, Standard Reference Materials Catalog 1995–1996, Special Publication 260, 1995.
[15] CHAI, C.F., KONG, P., MAO, X.Y., MA, S.L., J. Radioanal. Nucl. Chem. Articles, 192 (1995) 101.
[16] CHAI, C.F., Isotopenpraxis **24** (1988) 257.
[17] ISHIKAWA, M., KITAO, K., IMASCK, H., ISHIJ, T., UCHIDA, S., J. Radioanal. Nucl. Chem. Articles **82** (1984) 189.
[18] SCOTT, R., Nature **173** (1954) 1098.
[19] HOU, X.L., CHAI, C.F., QIAN, Q.F., YAN, X.J., FAN, X., Sci. Total Environ. **204** (1997) 215.
[20] HOU, X.L., CHAI, C.F., QIAN, Q.F., FAN, X., YAN, X.J., Study on chemical species of iodine in some seaweeds (II) Iodine-bound biological macromolecules, Marine Biology (to be published).
[21] FENG, W.Y., CHAI, C.F., QIAN, Q.F., J. Radioanal. Nucl. Chem. Letters **212** (1996) 61.
[22] CHAI, C.F., FENG, W.Y., QIAN, Q.F., Biol. Trace Elem. Res. **43–45** (1994) 423.
[23] GUO, F.Q., WANG, Y.Q., SUN, J.X., CHEN, H.M., J. Radioanal. Nucl. Chem. Articles **209** (1996) 91.
[24] WANG, Y.Q., XU, L., SUN, J.X., GUO, F.Q., CHEN, H.M., CHAO, G.Y., Scientia Sinica, Series B **27** (1997) 64.
[25] CHEN, C.Y., HOU, X.L., ZHANG, P.Q., CHAI, Z.F., Subcellular location of selenium and cytosolic distribution of Se-containing protein in human liver, submitted to Biol. Trace Elem. Res.

SELECTED ENVIRONMENTAL APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS

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Abstract. NAA is very useful for the determination of trace and minor elements in many environmental applications. While instrumental NAA (INAA) has a number of valid applications in this field, radiochemical NAA (RNAA) prior to, or post irradiation provides some significant advantages. One of the major focus points for environmental applications of NAA is to assess the magnitude of various pollutants. This paper discusses doing this via two methods, namely air monitoring and biological monitoring.

1. INTRODUCTION

In the last three decades, neutron activation analysis (NAA), namely its non-destructive mode (instrumental neutron activation analysis – INAA), has been found to be extremely useful in the determination of trace and minor elements in many environmental applications. The advantageous features of the method have been summarized in Chapter 1 of this publication.

Although it is mostly possible to determine a great number of elements in a variety of environmental matrices by INAA, some essential or toxic elements can only be determined on condition that the bulk of matrix activity is eliminated or the respective radionuclides are isolated by chemical separation. The most convenient way is to perform totally post-irradiation separation (radiochemical NAA – RNAA), because this mode retains one the most important advantages of NAA — the virtual absence of the analytical blank. Another possible way to eliminating matrix or interference activities which is quite powerful for certain elements consists in selective activation and measurement procedures as discussed in Chapter 3 of this publication.

However, the increasing availability of clean laboratories (Class 10 or 100) and quality of chemicals, which are the prerequisites for preventing sample contamination prior to irradiation, makes removal of matrix and/or interfering activity by pre-irradiation separation a good alternative for determination of selected elements, especially for those forming short-lived radionuclides. Moreover, this way of separation is becoming increasingly important for chemical speciation analysis. Methods of NAA aimed at providing information on chemical species of elements in a system of interest are sometimes termed molecular NAA-MAA.

The importance of employing NAA in environmental applications will be demonstrated using examples of air pollution monitoring and biological monitoring of environmental pollution.

2. AIR POLLUTION STUDIES

Large amounts of pollutants are yearly discharged into various compartments of the environment worldwide, although many countries have already establishing measures towards decreasing pollution of the environment. Many pollutants enter primarily the atmosphere in the form of inorganic or organic gases and inorganic or organic particulates. The major sources of atmospheric pollution are generally recognized to be industry, power generation and home-heating, transport, and waste incineration. The material discharged into the atmosphere is dispersed in aerosols, tiny liquid or solid particles. The processes involved in the formation of the atmospheric aerosol are schematically depicted in Fig. 1 [1]. The solid

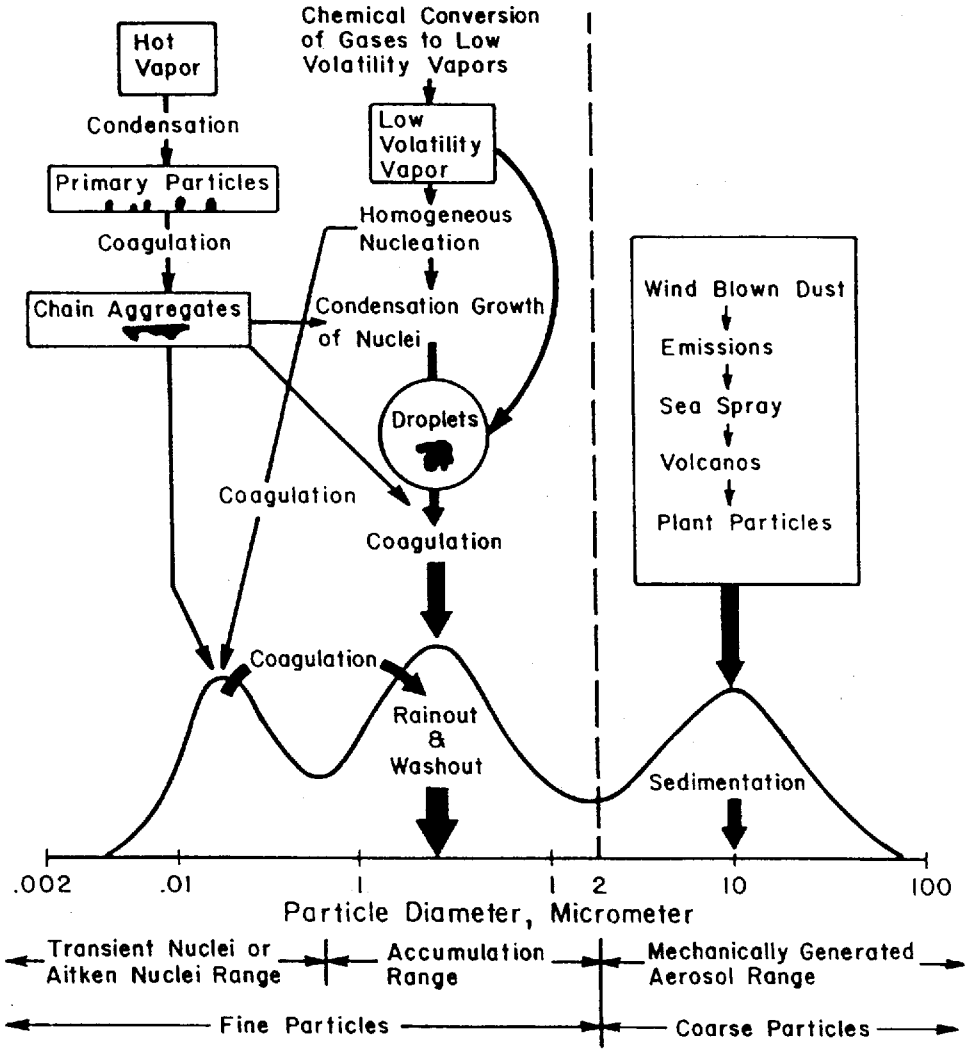


FIG.1. Processes involved in the atmospheric aerosol formation and resulting particle size distribution [1].

component of this aerosol, which has diameters in the range from about 1 nm to "giant" particles of several hundred μm, is frequently referred to as airborne particles or air particulate matter (APM). However, most of their mass is in the size range from about 0.1 μm to 10 μm. Depending on the particle size and the atmospheric conditions, APM resides in the air for various periods of time, typically from a few days to a few weeks, and can be transported by the winds over distances of thousands of kilometres. Eventually, APM is removed by precipitation in rainfall or by gravitational fallout. Therefore, there is a continual transfer of contaminants from the atmosphere into the hydrosphere or into the soil, so that the air provides a route for the contamination of the rest of the biosphere.

Because of the variability in production and the relatively short lifetime, the concentrations, size distributions and chemical composition of APM vary widely in time and space. Although aerosols form only a small part of the total mass of the atmosphere (about 1 part in 10^9), they play an important role in atmospheric chemistry, have effects on human and animal health and welfare, and they influence climate [2]. The climatic effect of aerosols is in the direction of cooling (under most circumstances) and is of a magnitude comparable to that of the

greenhouse gas warming [3]. However, there is still a large uncertainty associated with the aerosol forcing estimate which reflects the unsatisfactory knowledge regarding the sources, distributions, and properties of atmospheric aerosols.

APM larger than 1 μm show a high sedimentation velocity and can move independently of the wind, while APM smaller than 1 μm show a low sedimentation velocity and move with the wind. It is probable, therefore, that APM smaller than 1 μm exert a strong influence on human health and the environment [4]. The potential negative effects of aerosols on human health have been recognized many years ago. Recently, renewed interest in the health risks of aerosols has been generated by the finding of a correlation between the increased mortality and the concentration of airborne particles in metropolitan areas in the United States [5]. The US studies, together with similar research in the European Union, Brazil and elsewhere, consistently link higher levels of APM to increased risks of respiratory-, cardiovascular-, and cancer-related mortality, as well as pneumonia, lung functions loss, hospital admissions, asthma, and other respiratory problems. In most studies, the correlations examined were those between mortality and PM 10 particles (smaller than 10 μm equivalent aerodynamic diameter - EAD), but other studies indicated that the association with increased mortality was even higher when PM 2.5 particles were examined instead of those with PM 10. This is probably due to the relationship between the diameter of the APM and its precipitation in the human lungs. The respiratory air passages begin at the nasal cavity, pass through the trachea, bronchi and bronchioles, and end at the alveoli. The diameter of these passages and the velocity of air flow through them also decrease in this order. Larger APM are therefore unable to penetrate into the narrow branches of passages, but smaller particulates can easily reach the alveoli (Cf. Fig. 2). Clearly, therefore, it is important to investigate the size distribution of APM in addition to simple quantitative observations on their total mass. For these purposes, various sampling techniques of APM exist which has already been reviewed [4, 6]. Details of INAA methodology and a survey of reference materials available for quality assurance of air pollution studies have also been described [6].

2.1. Data reporting and treatment

Results for the element concentrations in APM are usually expressed in a mass of an element per cubic meter of air, i.e. in ng m^{-3}, μg m^{-3}, etc. Therefore, it should be emphasised that at least the same attention should be given to the appropriateness and quality assurance of sampling of APM, i.e. calibration and control of the air flow through a collection device, checking of tightness of the device to avoid possible leakages, etc., as to its analysis, because otherwise larger uncertainties of results may be expected due to the sampling process than those of analysis. In addition, the concentration of an element in APM can be calculated as a mass fraction. However, in this case the exact mass of the material collected must be known. This means that proper weighing procedures must be followed [6].

A first exploratory step in the interpretation of the element concentrations determined is to compare the level of pollution in the impact (polluted) and clean (background) regions, and to evaluate time trends, especially if sampling was performed in regular intervals for a sufficient period of time. More broadly, this type of the data treatment concerns evaluation of spatial and seasonal variability of elemental composition of APM.

A useful way of the data evaluation is the use of enrichment factor (EF) calculations. An EF is defined as the double ratio of the concentration of the element of interest, c_x, in APM to that of a reference element, c_r, in APM divided by the ratio of the same elements in a reference material (e.g. the earth crust, soil, sea water, etc.) according to the relation:

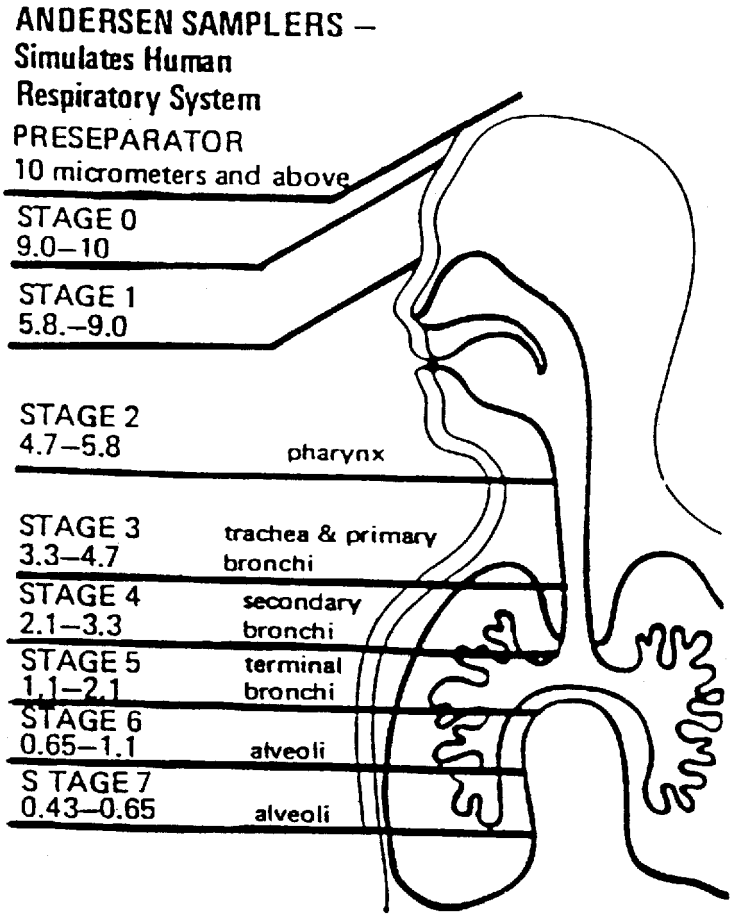


FIG. 2. The human respiratory system and its various cutoff points.

$$EF = \frac{\left(\frac{c_x}{c_r}\right)_{APM}}{\left(\frac{c_x}{c_r}\right)_{ref}} \tag{1}$$

In general, for EF calculations in APM, aluminium or scandium is taken is taken as the reference element both in APM and the reference material for which the earth crust is most frequently employed. Evaluating of EF presumes that the atmosphere is always loaded with APM originating both from the natural (soil erosion, sea aerosol) and anthropogenic (man-made) sources. An EF value close to one is indicative that the main source is of the crustal and/or marine origin, while values of EF exceeding ten (sometimes these values can reach several thousands) are indicative of significant anthropogenic contribution.

In order to develop rational and effective strategies for improving air quality, it is necessary to have an understanding of the relationship between the pollutant sources and their impact at receptor sites. Qualitative information of this kind can be inferred from the increased occurrence of specific elements which serve as markers for particular source emissions. Examples of marker elements are given in Table 1 [6].

Table 1. Characterization of emission sources according to marker elements [6]

Source	Elements
Coal-fired plants	As, Se, S
Oil-fired plants	V, Ni, rare earths
Motor vehicles	Br, Pb
Refuse incineration	Ag, Zn, Sb, Cd, Sn, Pb
Limestone/concrete	Ca, Mg
Soil	Al, Fe, Mn, Sc, Si, Ti
Wood burning	C (elemental and volatile), K
Refineries	Rare earths
Sulphide smelters	In, Cd, As, Se, S

More sophisticated approaches involve source or dispersion models which predict the concentration of pollutants at a receptor site using diffusion models with emission inventories and meteorological data. The predicted element concentrations can then be compared with the measured ones.

There is a number of mutlivariate statistical techniques which can be used for these purposes. *Receptor modelling* infer source contributions at receptor sites using statistical models with the data measured at the receptor site. *Principal component analysis* (PCA) is frequently employed for identifying pollutant sources. PCA attempts to explain the variance of a large set of intercorrelated variables (measured element concentrations in APM) with a smaller set of independent variables (the principal components). PCA is one of method of qualitative and quantitative techniques for data analysis which are collectively termed *factor analysis*. An introduction to data analysis of airborne particle composition has recently been published within the framework of one the IAEA Research Co-ordinated Programmes in this field [7] and there are numerous literature sources on this topic, as well, for instance [8,9]. Moreover new techniques are being developed, such as APCA, ”Source profiles by unique ratios technique” (SPUR), ”Positive matrix factorization” (PFA) [10, 11]. *Chemical mass balance* (CMB) methods are designed to apportion the APM mass of each sample quantitatively amongst a number of contributing sources. This is possible if each source is characterized by a specific chemical pattern (source profile) and as many variables are available as sources.

3. BIOLOGICAL MONITORING OF ENVIRONMENTAL POLLUTION

Biomonitoring, i.e. the use of biological indicators to detect changes in the physical and chemical properties of the abiotic environment, represents an interesting alternative to direct measurements of the physical and chemical properties of the environment. Biological indicators are those tissues, organisms or populations of which their occurrence, vitality and responses change under the impact of environmental conditions [12]. Biomonitoring takes one of two approaches: i) direct monitoring which is based on measuring the quantity of pollutants in suitable organisms rather than in samples from the environment; ii) indirect monitoring which is based on interpreting of biological signals due to changes of the environment such as the study of morphological, physiological and cytological responses of organisms, changes of abundances of certain species, etc. Only the former approach will be treated in this work.

Although data provided by physical and chemical monitoring are indispensable for evaluating the changes of the environment, application of an (ideal) biomonitor can show several advantages compared to the use of direct monitoring techniques:

— the concentration of pollutants in the monitor tissue or organism are often higher than in the system to be monitored. This may facilitate accurate sampling and analysis, which are very difficult at the low levels occurring in many compartments of the environment;
— sampling of the tissue or organism used as a biological monitor is in general easier than most direct sampling procedures and no long term use of expensive sampling equipment is required;
— the intricated equilibria existing in many parts of the environment can easily be distorted by sampling itself, which may lead to erroneous results. When using biological monitors, this distortion is minimized;
— most tissues and organisms reflect external conditions averaged over a certain time, depending on e.g. the biological half-life of a specific substance in that organism. This is important when monitoring levels may change rapidly in time;
— concentrations of pollutants in organisms may give insight into the bio-availability of that pollutant. This information may be as relevant as the absolute concentration in a certain part of the environment;
— biological monitors are already present in the environment and monitoring continuously.

In direct biomonitoring of atmospheric element pollution, the relevant information is deduced from concentrations of elements in the monitor tissues. They have to meet specific requirements which are as follows:

— abundant occurrence in the area of interest, independent of local conditions;
— available for sampling in all seasons;
— tolerant to pollutants at relevant levels;
— response to quantity to be monitored known and understood;
— element uptake independent of local conditions other than the levels of elements to be monitored;
— element uptake not influenced by regulating biological mechanism or synergistic effects;
— averaging over suitable time period;
— absence of appreciable element uptake from sources other than atmospheric;
— low background concentrations;
— easy sampling and sampling preparation;
— element accumulation to concentration levels accessible by routine analytical techniques.

Many human, animal and plant species can be used for air pollution monitoring, because they can meet most of the above requirements. Human and animal species and/or tissues usually reflect complex changes of the environment, i.e. air, water, soil pollution, and element intake from their diet, so that their use for studying only air pollution may be rather difficult to interpret. Nevertheless, some of them proved to be very useful, such as analysis of human and/or animal hair and other ectoderm derivatives, for instance nails. Certain plant species appear to be especially suitable to indicate elemental air pollution and therefore advantages and pitfalls of their possible use as biomonitors for air pollution studies will also be briefly discussed.

3.1. Hair

The feasibility of human hair as a material easily accessible for non-invasive sampling in individuals or population groups, to demonstrate criminal, occupational or environmental

exposure to toxic elements has received a great deal of attention in the literature. Besides many papers scattered in various journals, two monographs and two review articles have been published [13–17]. Hair analysis is also facilitated by the availability of the generally recognized washing procedure which has been suggested in one of the IAEA Research Co-ordinated Programmes in the mid- seventies [18]. It this is very important to use a standardized hair cleaning, because there is no single washing procedure which would completely remove the external contamination without influencing the endogenous element contents. While a generally accepted washing procedure exists for hair (for monitoring of environmental pollution) and thus comparable data on elemental hair composition are available from many countries, no such standardized washing is widely used for nail cleaning which can also be used for biological monitoring as another ectoderm derivative.

Numerous examples of application of hair analysis for studying environmental pollution can be found in the above (and other) literature sources. Therefore, the usefulness of hair analysis for these purposes will only be shown in one example which demonstrates a correlation between arsenic content in hair of children living in various distances from a pollution source and the expected degree of arsenic contamination of the air (Cf. Fig. 3 [19]). Noteworthy, a similar correlation was obtained when urinary arsenic levels of children were determined (Cf. Fig. 4 [19]). This demonstrates that urine is also a very suitable indicator to assess environmental exposure, however, the arsenic (and many other elements) determination in urine is much difficult compared to hair, because RNAA is required for this purpose to eliminate high matrix activity.

Similarly to human hair, the hair of some rodents, such as the Common Hare (*Lepus europaeus*) and the Common Vole (*Microtus arvalis*) proved to be a very useful indicator of environmental pollution. This can be supported by the finding that similar heamatological changes were found in hares as in children living in regions burdened with industrial emissions [20].

3.2. Other biomonitors

Recently, a review has been published by the present author [21] on using herbaceous plants, trees, bryophytes, and lichens for biomonitoring of air pollution. Of the various herbaceous plants, a positive correlation has been found between the chemical composition of the leaves of *Taraxanum officiale* and the local impact of air pollution for a number of elements. Other plants have been recognized especially suitable to indicate loading with selected elements.

There are two broad-leaved trees which seem to have found the widest application as indicators of air pollution, mostly because of their resistance to pollutants and wide distribution in Europe and almost throughout the world: *Populus nigra* ssp. *italica* (Italian poplar) and *Robinia pseudoacacia* (the black locust tree). Coniferous trees are more sensitive indicators of air pollution than the deciduous trees, because they are exposed to air pollution over a longer period of time than leaves due to a longer life span of needles (3-4 years). Thus, most of the coniferous trees can respond to low pollutant concentrations. *Taxus baccata, Picea abies, Pinus silvestris* and *Pseudotsuga menziesii* are most frequently used indicators of elemental air pollution. Similarly as with leaves, the chemical composition of needles of coniferous trees is influenced by two factors: i) by their nutritional status, i.e. by uptake of nutrients and/or pollutants by roots from soil; ii) by retention of air pollutants on the needle surface. In the case of spruce needles, aerosol retention is facilitated by the very rugged structure of epicuticular wax. Tree bark is also exposed to long-term air pollution and it accumulates certain elements and sulphur dioxide.

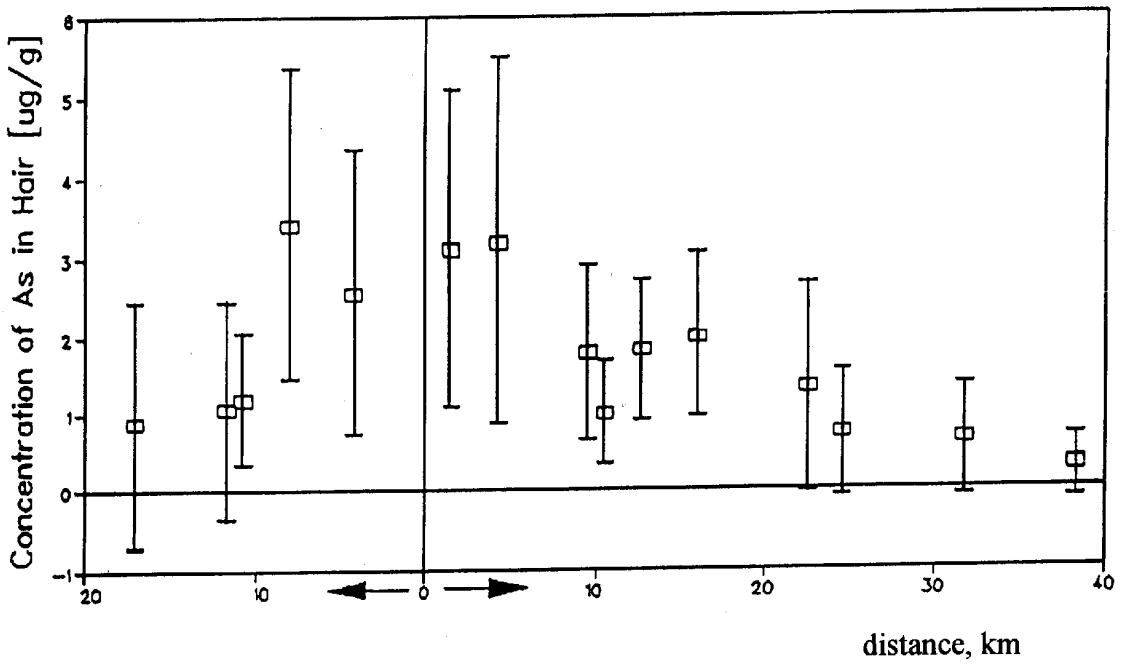


FIG. 3. Arsenic concentrations (mg/kg, mean ± s.d.) in the hair of 10-year boys residing adifferent distances from a coal fired power plant (0–emission source, ➢–distance in the direction of prevailing winds, ➢– distance against the direction of prevailing winds) [19].

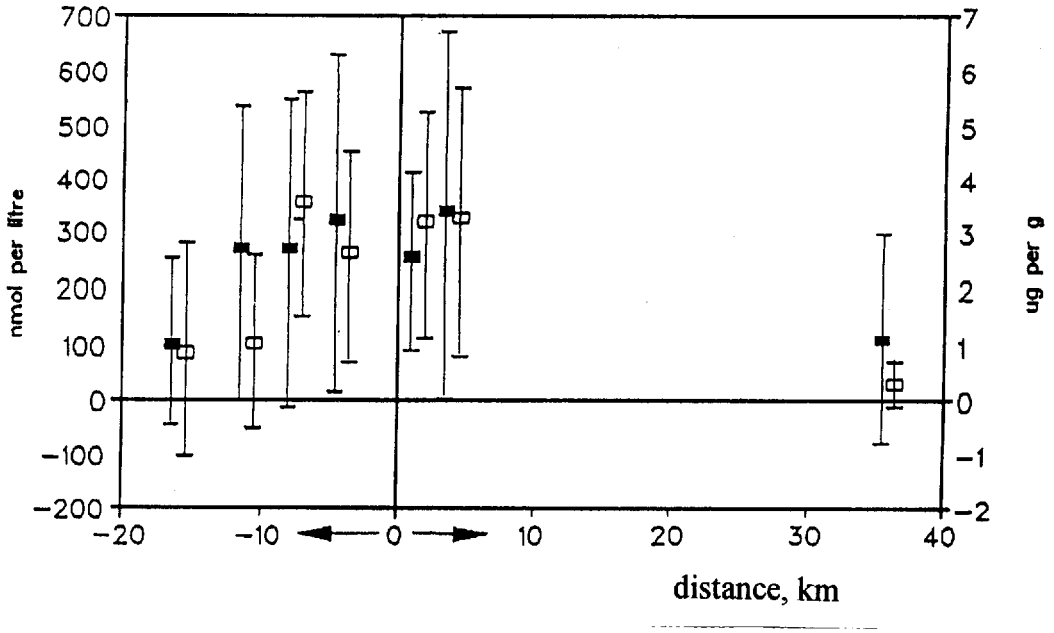


FIG. 4. Arsenic concentrations in the urine (■ – mean ± s.d.) and hair (□ – mean ± s.d.) of 10– year boys residing in different distances from an emission source (symbols as in Fig. 3) [19].

Bryophytes are especially suitable for biological monitoring of air pollution due to several specific features. They are evergreen and (with a few exceptions) perennial plants, so that they can be utilized throughout the year. Most bryophytes species do not posses a cuticle and, therefore, can take up water over the entire plant surface. As a consequence, they obtain their nutrients directly from atmospheric deposition, i.e. dustfall and precipitation. Especially useful are some moss species that have a layered habit and produce distinct annual segments. The most frequently used moss species are *Hylocomium splendens* and *Pleurozium schreberi* which have the ability to accumulate many metals in extremely high concentrations. The usefulness of the use of the feather moss *Hylocomium splendens* to study the geographical deposition and time-trend pattern was demonstrated by Steinnes (Cf. Fig. 5) [22].

Lichens are specialized organisms in which a fungus and an alga form a nutritional and physiological unit. The autotrophic alga supplies nutrients for both itself and the heterotrophic fungus. Lichens react to the pollutant emissions. Their high sensitivity to various air pollutants:

— in comparison with higher plants — can be ascribed to both morphological and physiological differences which namely include:
— in the absence of a cuticle, pollutants find an easier way into the thallus;
— corticolous lichens absorb both water and nutrients directly from the air;
— lichens accumulate various materials without selection;
— the material once absorbed will accumulate since there is no excretion.

About seventy lichen species have been reported as suitable indicators of elemental pollution. Of these, *Hypogymnia physodes* (L.) Nyl. and *Parmelia sulcata* are the most frequently used species for biomonitoring in Europe. The former species is widespread in Northern Europe and in mountain regions. It has many advantages which are important for application as a biomonitoring organism, compared to other lichen species [21]. A certain problem of utilizing lichens (and also tree bark) for monitoring air pollution may be due to stem flow which may bring to these indicators additional nutrients and/or pollutants not necessarily associated with air pollution.

The use of biological indicators for air pollution monitoring was introduced about 30 years ago. Since then, a variety of organisms has been proposed for biomonitoring purposes. Importance of particular biomonitors can be inferred from frequency of their use in various national and international programmes. For instance, the following biomonitors of air pollution are being collected for the German Environmental Specimen Bank: grass, poplar and beech leaves, spruce and pine shoots [23]. Grasses and other herbaceous plants may be useful indicators, especially if they are grown on standard soil in exposure containers (pots) [24]. Mosses have been very popular in both local and long-term, large-scale studies in Nordic countries since seventies [22, 26] and using these bioindicators have also been included in the LRTAP programme [27]. In the Netherlands, national trace-element air pollution monitoring survey using epiphytic lichens has been started in 1982 [28–30] and continues on international scale until now. The element gradients obtained from the lichen data set (1982–1983) agreed with the calculated atmospheric element gradients (1983) as is illustrated for arsenic in Fig. 6 [31]. Lichen analysis followed by a specific multivariate statistical procedure known as "Target Transformation Factor Analysis" has successfully been employed in the Dutch studies for apportionment of emission sources inside and outside the country [28–30]. To obtain the relevant information of this kind, multi-element analysis is required. For this purpose, nuclear analytical methods, namely instrumental neutron activation analysis, proved to be very effective tools.

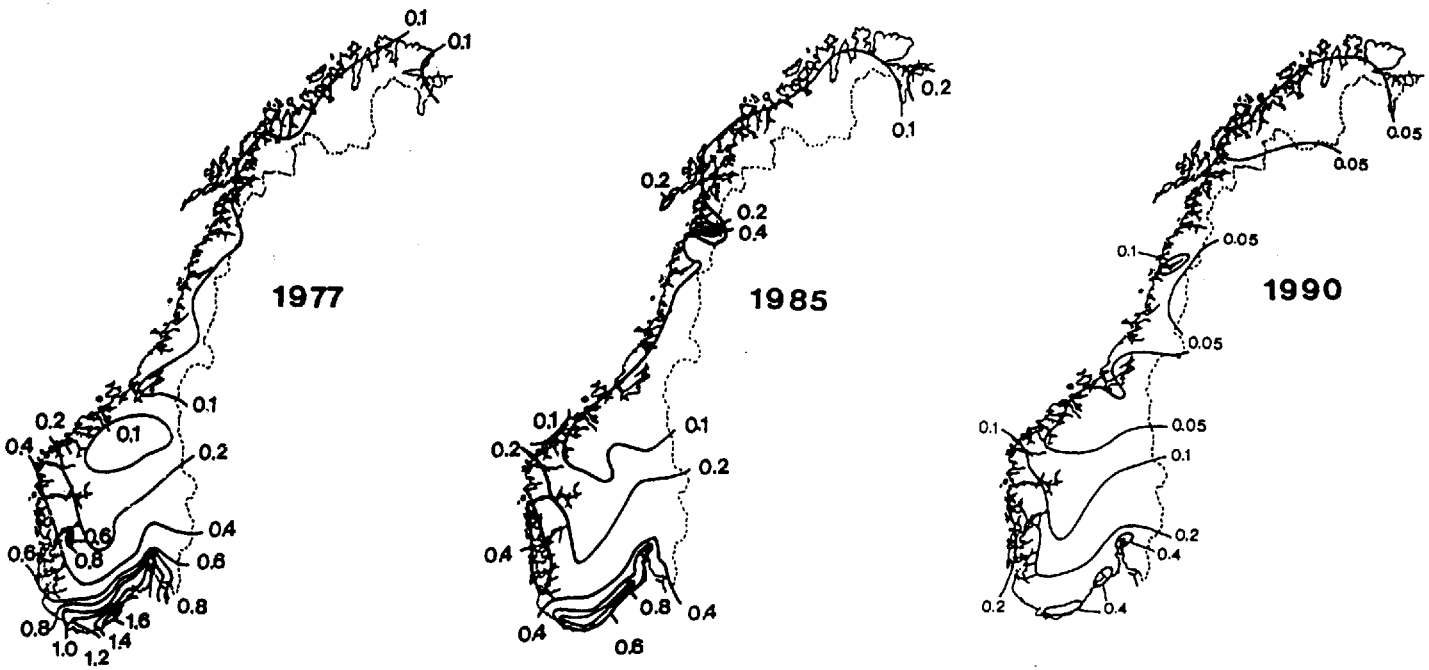
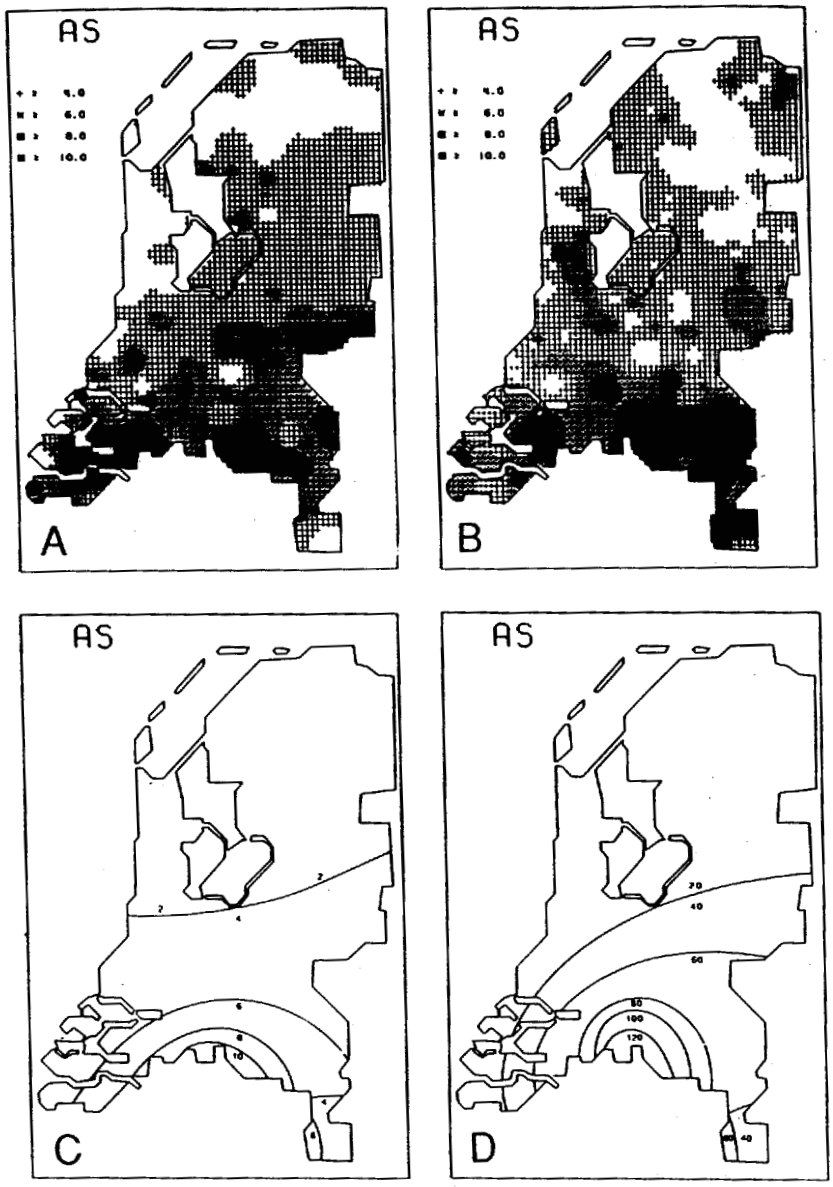


FIG. 5. Atmospheric deposition of antimony in Norway at three different times as indicated by INAA of moss samples.



FIGs 6. A, B. Arsenic concentrations in Parmelia sulcata (mg/kg) (A=1982–1983; B=1986–1987). The geographical concentration patterns contain five element concentration classes. Elemental concentration Class 1 (unshaded) ranges from the minimum concentrations determined to Class 2 (shaded with plus signs). Consequently, Class 5 (darkest shading) ranges up to the maximum concentrations determined. Classes 1-5 for 1982-1983 (values for 1986–1987 in brackets): 1.7 (0.5), 4.0, 6.0, 8.0, 16.6 (17.0).

FIGs 6. C, D. Calculated 1983 atmospheric concentrations (ng/m^3) for arsenic (C) and calculated 1983 total (wet and dry) deposition of arsenic (nmol/ha/y) (D) [31].

Table 2. Detection limits of 45 elements in selected environmental matrices by INAA*

Element	Coal mg/kg	Coal fly ash mg/kg	Atmospheric particulate matter, ng m^{-3}	Soil, sediment mg/kg	Spruce needles mg/kg
Ag	0.5	1.5	0.04	0.7	0.05
Al	20	35	5	30	15
As	0.05	0.25	0.015	0.45	0.05
Au	0.001	0.01	0.005	0.01	0.001
Ba	20	100	3	50	3
Br	0.05	0.3	0.1	0.4	0.04
Ca	100	500	30	500	300
Cd	0.5	4	0.1	5	0.3
Ce	0.15	1.5	0.15	1	0.2
Cl	50	300	15	400	50
Co	0.015	0.1	0.03	0.05	0.01
Cr	0.5	3.5	1	1.5	0.2
Cs	0.05	0.1	0.03	0.1	0.015
Cu	1	5	1	15	0.4
Dy	0.05	0.05	0.01	0.05	0.03
Eu	0.015	0.04	0.005	0.03	0.005
Fe	30	150	10	75	10
Ga	0.5	3	0.2	10	0.08
Hf	0.05	0.15	0.01	0.1	0.015
Hg	0.05	1	0.02	1	0.05
I	2	15	0.4	20	1
In	0.02	0.05	0.03	0.05	0.02
K	20	100	10	300	20
La	0.03	0.07	0.05	0.15	0.01
Lu	1	2.5	0.25	1	0.05
Mn	2	5	0.5	8	1
Mo	0.1	2.5	0.35	2.5	0.3
Na	2	4	10	10	0.3
Ni	10	40	2.5	60	10
Nd	2	4	0.2	5	1
Rb	5	10	0.5	7.5	0.5
Sb	0.03	0.1	0.015	0.075	0.01
Sc	0.005	0.010	0.003	0.005	0.001
Se	1	4	0.1	3	0.15
Sm	0.01	0.02	0.005	0.03	0.005
Sr	30	100	2	50	5
Ta	0.05	0.2	0.01	0.07	0.01
Tb	0.05	0.3	0.02	0.1	0.05
Ti	300	500	6	400	150
Th	0.03	0.1	0.015	0.05	0.015
U	0.1	0.5	0.03	0.5	0.01
Yb	0.1	0.3	0.05	0.3	0.03
V	0.3	1	0.05	1.5	0.05
W	0.2	0.5	0.03	1	0.05
Zn	2	10	1	5	0.5

*Experimental conditions: Short- and long-time irradiation of 100-200 mg samples (except for APM which mass amounts to 0.5- 1 mg) in a neutron fluence rate of 5.10^{13} cm^{-2} s^{-1} for 1 min. and 10 h, respectively, followed by gamma-ray spectrometric measurements using a HPGe detector (rel. efficiency. 21%). For decay and counting times, and counting geometry see [34].

On the other hand, for all biomonitors employed, the mechanism of pollutants uptake and retention is usually not sufficiently known due to intricated element and water fluxes in an ecosystem. Consequently, the quantitative relationships between the pollutant's concentration

in the monitor's tissue and its concentration in a relevant compartment of the atmosphere are mostly not predictable. Therefore, without extensive calibration under all relevant conditions, the use of even of one of the most suitable biomonitor will frequently yield only qualitative information on atmospheric levels as a function of time or place [32].

There are many more biomonitors and other matrices suitable for the assessment of the environmental pollution. For instance, from nation-wide surveys of natural surface soils in Norway it has become evident that the long range atmospheric transport of heavy metals apparent in the moss survey is also reflected in the chemical composition of surface soil [22]. A similar relationship as for the level of pollution of the atmosphere and that of surface soil is usually found between surface waters and sediments and/or water suspended matter. Stratigraphic distribution of elements and other biomarkers in undisturbed lake sediments may even be used to trace the history of atmospheric and water pollution several hundred years back [33]. While for water analysis other analytical techniques are predominantly used, such as AAS, electrochemical methods, ICP-MS (because water is almost an ideal matrix for these techniques), for soil and sediment analysis INAA offers many advantages as it follows from detection limits for 45 elements in selected environmental matrices shown in Table 2.

REFERENCES

[1] Environmental Particles, Vol. 1. (BUFFLE, J.O., VAN LEEUWEN, H.P., Eds), Lewis Publishers Inc., Boca Raton, Chelsea, Michigan, USA.

[2] Aerosol Forcing of Climate (CHARLSON, R.J., HEINTZENBERG, J., Eds.), John Wiley & Sons, Chichester (1994).

[3] J. T. HOUGHTON et al. (Eds.), Climate Change 1994: Radiative Forcing of Climate and an Evaluation of the 1992 Emission Scenario, Intergovernmental Panel on Climate Changes (IPCC), Cambridge University Press, Cambridge, UK.

[4] OIKAWA, K., Trace Analysis of Atmospheric Samples, Halsted Press Book, Kodansha Ltd., Tokyo, John Wiley & Sons, New York, London, Sydney, Toronto (1977).

[5] REICHHARDT, T., Environ. Sci. Technol. **29** (1995) 360A.

[6] Sampling and Analytical Methodologies for Instrumental Neutron Activation Analysis of Airborne Particulate Matter, Training Course Series No. 4, IAEA, Vienna (1992).

[7] HOPKE, P.K., Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques, NAHRES-19, IAEA, Vienna (1994) 215.

[8] HOPKE, P.K., Receptor Modelling in Environmental Chemistry, J. Wiley & Sons Inc., New York (1985).

[9] MARTENS H., NAES, T., Multivariate Calibration, John Wiley & Sons, Chichester, UK (1989).

[10] PAATERO, P., TAPPER, U., Chemom. Intell. Lab. Syst. **18** (1993) 183.

[11] PAATERO, P., TAPPER, U., Environmetrics **5** (1994) 111.

[12] Biological Indicators in Environmental Protection (KOVACS, M., Ed.), Akadémiai Kiadó, Budapest 1992.

[13] VALKOVIČ, V., Trace Elements in Human Hair, Garland Publ. Inc., New York (1977).

[14] KATZ, S.A., CHATT, A., Hair Analysis, Application in the Biomedical and Environmental Sciences, VCH Publishers, Inc., New York, Weinheim (1988).

[15] SUZUKI, T., Hair and Nails: Advantages and pitfalls when used in biological Monitoring, , Biological Monitoring of Toxic Metals (CLARKSON, T.W., FRIBERG, L., NORDBERG, G.F., SATER, P.R. (Eds) Plenum Press, New York and London (1988) 623–640.

[16] BENCZE, K., Fresenius J. Anal. Chem. **337** (1990) 867.

[17] BENCZE, K., Fresenius J. Anal. Chem. **338** (1990) 58.

[18] RJABUCHIN, YU.S., Report IAEA/RL/50, IAEA, Vienna (1978).

[19] BENCKO, V., Toxicology **101** (1995) 29.
[20] KUČERA, J., Chemosphere **34** (1997) 1975.
[21] KUČERA, J., Applied Research on Air Pollution Using Nuclear-Related Analytical Techniques, NAHRES-19, IAEA, Vienna (1994) 265.
[22] STEINNES, E., Proc. Int. Symp. Appl. of Isotopes and Radiation in Conservation of the Environment, Karslsruhe, 9–13 March 1992, IAEA, Vienna (1992) 387.
[23] SCHLADOT, J.D., STOEPPLER, M., KLOSTER, G., SCHWUGER, M.J., Analysis Magazine **20** (1992) M 45.
[24] CERCASOV, V., SCHREIBER, H., J. Radioanal. Nucl. Chem. **114** (1987) 21–27.
[26] MÄKINEN, H., In: K.Pócs et al. (Eds), Proc. IAB Conference of Bryoecology, Symp. Biol. Hung. **35** (1987) 777–794, Akadémiai Kiadó, Budapest.
[27] Convention on Longe-Range Transboundary Air Pollution (LRTAP), Field and LRTAP laboratory manual, National Board of Water and Environment, Environmental Data Centre, Helsinki, 1989.
[28] DE BRUIN, M., VAN WIJK, P.M., Trace-element patterns obtained by INAA as a basis for source identification, J. Radioanal. Nucl. Chem. **123** (1988) 227.
[29] SLOOF,J.E., WOLTERBEECK, H.TH., Patterns in trace elements in lichens, Water, Air, and Soil Pollution **57–58** (1991) 785.
[30] SLOOF, J.E., WOLTERBEECK, H.TH, National trace-element air pollution monitoring survey using epiphytic lichens, Lichenologist 23 (1991) 139.
[31] SLOOF, J.E., Environmental lichenology: Biomonitoring trace-element pollution, Ph.D. Thesis, Technical University Delft, The Netherlands (1993)
[32] DE BRUIN, M.,Applying biological monitors and neutron activation analysis in studies of heavy-metal pollution, IAEA Bulletin 4/1990, 22.
[33] VESELÝ, J., et al., J. Paleolimnol. **8** (1993) 211.
[34] KUČERA, J., SOUKAL, L., J. Radioanal. Nucl. Chem. Articles **121** (1988) 245.

ENHANCEMENT OF RESEARCH REACTOR UTILIZATION FOR NEUTRON ACTIVATION ANALYSIS

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Abstract. Analytical Chemistry Division has been utilising NAA for the past 4 decades for trace analysis of a number of materials. Some of the procedures developed recently for the trace element determination of high purity hi-tech and nuclear pure materials, geological, environmental and forensic samples by radiochemical neutron activation analysis (RNAA) are discussed here. Nearly complete characterization of high purity (>4N) As & Ga is possible by the procedures developed which are simple, rapid and elegant and can be used easily for the process samples. It is to be emphasised that though the INAA is simple and being widely followed, the RNAA alone can address the problems of analysis for elements present at ultra trace levels in many matrices.

1. INTRODUCTION

India is happy to participate in this IAEA Advisory Group meeting. Analytical Chemistry Division has been pursuing neutron activation analysis for nearly four decades and applying this technique for major, minor and trace elements in a wide variety of matrices. This division is being associated with IAEA and has organised workshops/ seminars apart from training many IAEA fellows.

I thank IAEA for extending the invitation to attend this meeting. The Nuclear Methods Section (NMS), of Analytical Chemistry Division (ACD), Bhabha Atomic Research Centre (BARC) is actively pursuing NAA and in the continuous process of developing methods, particularly radiochemical neutron activation analysis (RNAA) for solving many problems with respect to trace and ultra trace analysis in various fields viz. materials science (High purity Hi-tech, Nuclear pure materials) [1–4], geological [5–8], environmental [9–12], biological [13], forensic [14–16] sciences. NMS is catering to the needs of inter and intra departments, academic institutions (IIT, University), Industry etc. with respect to Analyses, particularly trace and ultra trace analysis for solving many of their problems. “Apsara” a swimming pool type reactor (~10^{12} n. cm^{-2}. sec^{-1}) is mostly being used because of its versatility. The centre of the core (D_4 position) has the highest neutron flux (Thermal and fast) and is being used in special cases. NAA is extensively applied routinely to geological and forensic samples at ACD. This report highlights some of the recently developed methods for various materials.

2. MATERIALS SCIENCE

2.1. High purity Hi-tech materials like Ga & As

Trace and ultra trace quantities of various elements in high purity Ga and As [1] have been determined after the quantitative separation of the matrix from the analytes using ion exchange separation (Dowex 1, Chelax 100), thus avoiding the matrix interferences in many of the determinations. Because of this matrix separation, larger amounts of samples can be taken for analysis, thus achieving pre concentration of analytes, thereby enabling to determine lower amounts of impurity elements present in them. Thus alkali, alkaline, earths, rare earths, Al , Fe, Co, Ni, Mn, V, Cu, Zn, Mo, Sn, Cd, Ag, Au, PGM, Bi, Pb, etc. in high purity As and Ga have been determined and thus enabling a complete characterisation of the materials [1]. Tables 1 & 3 give the results, while Table 2 lists the relevant nuclear data.

Table 1. Analysis of Ga, As_2O_3, and As (ng/g)
The separated analytes in 10–25 ml final volume

Element	*4 N Ga (0.5–2 g.) n = 4*	*5 N Ga (0.5–2 g.) n = 3*	*AR grade As_2O_3 (0.5–2 g.) n = 4*	*Specpure As_2O_3 (0.5–2 g.) n = 4*	*5 N Arsenic (0.5–2 g.) n = 3*	*5 N Ga + 5 N As (0.5 g. each) n = 3*
Li	ND	270 ± 20	ND	ND	ND	155 ± 20
Na	ND	ND	ND	ND	ND	ND
K	ND	ND	ND	ND	ND	ND
Ba	1150 ± 50	340 ± 25	ND	ND	ND	220 ± 25
Ca	510 ± 25	ND	ND	ND	ND	ND
Sr	ND	ND	ND	ND	ND	ND
Al	800 ± 40	380 ± 25	ND	ND	ND	250 ± 25
Mg	900 ± 45	600 ± 30	ND	ND	250 ± 10	410 ± 15
Mn	ND	ND	ND	ND	ND	ND
Fe	4500 ± 140	2640 ± 115	ND	ND	134 ± 5	1450 ± 30
Co	350 ± 10	260 ± 8	ND	ND	225 ± 5	295 ± 10
Ni	1400 ± 55	30 ± 3	4400 ± 90	1440 ± 45	2980 ± 80	1550 ± 60
Cu	110 ± 33	845 ± 22	ND	ND	ND	410 ± 20
Cd	ND	ND	ND	ND	99 ± 10	55 ± 5
Bi	225 ± 10	ND	ND	ND	ND	ND
Ag	340 ± 5	ND	ND	ND	ND	ND
Pd	ND	ND	ND	ND	ND	ND
Pt	ND	ND	ND	ND	ND	ND
Sb	870 ± 15	506 ± 16	ND	ND	ND	275 ± 25
Sn	6450 ± 145	3455 ± 100	1100 ± 55	850 ± 30	1490 ± 50	2470 ± 100
Mo	140 ± 8	100 ± 5	ND	ND	ND	60 ± 10
Zn	ND	ND	ND	ND	158 ± 6	75 ± 10
Pb	60 ± 3	6 ± 0.5	ND	ND	348 ± 15	175 ± 5
Cr	ND	ND	600 ± 25	ND	149 ± 12	74 ± 10
V	ND	ND	ND	ND	ND	ND
Hg	650 ± 35	225 ± 30	ND	ND	ND	–
REE	ND	ND	ND	ND	ND	ND

Table 2. Conditions for activity measurements

Isotope	Half-life $t_{1/2}$	Cooling T_o	Energy keV
^{28}Al	2.32 min.	5–10 min.	1779
^{52}V	3.75 min.	5–10 min.	1434
^{27}Mg	9,46 min.	10 min.	1014
^{165}Dy	2.32 h	30 min.	96
^{56}Mn	2.58 h	30 min.	847
^{152m}Eu	9.3 h	2–4 h	122
^{42}K	12.4 h	2–4 h	1524
^{153}Sm	53 h	24 h	103
^{140}La	40.2 h	24 h	816
^{122}Sb	2.71 d	1–2 d	564
^{51}Cr	27.8 d	2–4 d	320
^{181}Hf	27.8 d	2–4 d	482
^{86}Rb	18 d	10 d	1076
^{134}Cs	2.05 y	10–20 d	604

Table 3. Results of 5 N Ga & As metal
(ng/g; * = conc in μg/g) A = 5N Ga, B = 5N As

Element	GFAA		INAA		RNAA		ICP-AES*		ICP-MS	
	A	B	A	B	A	B	A	B	A	B
Al	380	ND	–	ND	–	–	< 1		200	740
Co	260	225	300	295	–	–	< 1		18	380
Zn	ND	158	ND	ND	ND	220	< 1		<25	–
Mo	100	ND	ND	ND	< 100	ND	< 1		< 6	–
W	ND	ND	ND	ND	–	–	–		–	–
Sb	506	ND	532	ND	550	ND	< 1		25	800
Cu	845	ND	920	ND	885	ND	< 1		400	500
Ag	ND	ND	ND	ND	ND	ND	< 1		84	–
Re	ND	ND	ND	ND	ND	ND	–		–	–
Pt	ND	ND	ND	ND	ND	ND	–		< 5	–
V	ND	ND	ND	ND	–	–	–		< 200	–
Mg	600	250	<1000	<1000	–	–	< 1		< 200	2000
REE	ND	ND	ND	ND	ND	ND	< 1		–	–
Se	–	–	ND	ND	ND	ND	–		–	–
Te	–	–	–	–	ND	ND	–		–	–
Hg	–	–	–	–	225	ND	–		–	–
Rb	–	–	ND	ND	–	–	–		–	–
Cs	–	–	ND	ND	–	–	–		–	–
Cr	–	149	ND	ND	–	—	–		<150	–
Hf	–	–	ND	ND	–	–	–	–	–	–

Table 4. Analysis of U and thorium dioxide for REE by NAA (in μg/g)
Sample weight: 10g for U metal and 5 g for ThO_2 Process blank (30 g/800 ml acid+water) La = 39 ng, Eu = 4 ng, Sm= 4.5 ng, Dy = 3.3 ng

Element	REE in U			REE in ThO_2		
	Unspiked	spiked added	Matrix Recovered	Unspiked	spiked added	Matrix recovered
La	0.26	0.52	0.83	0.04	–	–
Ce	0.2	5.0	5.2	<0.15	4.0	4.1
Pr	<0.2	5.1	5.9	<0.01	4.1	4.4
Nd	<0.2	5.1	4.7	<0.1	4.0	3.8
Sm	0.02	1.25	1.26	0.014	1.0	1.1
Eu	0.01	0.25	0.26	0.017	0.2	0.22
Gd	<0.2	5.1	5.1	<0.01	4.1	4.2
Tb	<0.2	1.98	2.07	<0.01	1.6	1.6
Dy	0.01	0.5	0.52	0.01	0.4	0.4
Ho	<0.2	2.59	2.54	–	2.1	2.1
Er	<0.2	5.24	5.02	<0.004	4.2	4.2
Tm	0.2	2.53	2.45	0.03	–	–
Yb	<0.2	2.65	2.64	<0.01	2.1	2.1
Lu	<0.2	1.27	1.29	<0.001	1.0	0.98

Table 5. Results for ThO_2 and U analysis (μg g^{-1})
Sample description: A = 5.056 g of ThO_2; B = 9.9535 of ThO_2; A* = average of replicate analyses of A and B, Sx(n = 4); C = 3.2001 g of NBS SRM 960 U metal; D = 6.3869 g of NBS SRM 960 U metal; C* = average of replicate analysis of C and D S_x(n = 4; E = average of analyses of 0.5, 1.0, 1.5, and 2 g of U metal from UMP, BARC, S_x(n = 4)

Element	ThO_2			U			
	A	B	A*	C	D	C*	E
Mg	3	3	3 ±0.08	4.5	4.53	4.51±0.006	13 ±0.23
Ca	ND	ND	–	3	3.1	3.05±0.055	ND
Cu	18	17	17.78±0.53	4.2	4.45	4.33±0.069	13±0.49
Zn	4	4.3	4.13±0.15	4.0	4.27	4.18±0.058	12±0.53
Cd	0.01	0.01	0.011±0.001	0.017	0.018	0.017±0.004	0.05±0.002
Mn	0.3	0.03	0.305±0.02	3.4	3.41	3.4±0.003	2.5±0.09
Al	36	35	35.9±0.33	19	19	19.05±0.08	96±1.06
Fe	30	32	31.1±1	43	43	42.95±0.06	213±2.15
Co	0.14	0.14	0.14±0.002	1.5	1.55	1.54±0.02	2.4±0.08
Ni	0.04	0.04	0.04±0.001	13	12.8	13.05±0.11	2.5±0.13
Ag	0.005	0.005	0.005±0.0003	ND	ND	–	0.134±0.008
Pb	0.358	0.365	0.362±0.019	0.225	0.22	0.222±0.001	0.339±0.004
Bi	ND	ND	–	0.02	0.02	0.02±0.003	ND

2.2. Nuclear pure U and ThO_2

Another crucial area, viz. nuclear pure U & ThO_2, where trace elements particularly REE in them is needed, have also been taken up for developing methods for the same. Here again the matrices, which will interfere in the analysis of impurities have to be separated. Ion exchange separations, using Chelax 100 have been developed for the quantitative removal of -the matrices from the analytes [17–18]. Tables 4 and 5 list the results of the analysis. It is worth mentioning here that the NBS (NIST) SRM 960 Uranium had only Fe and V as certified value, whereas more elements (Mg, Ca, Cu, Zn, Cd, Mn, Al, Co, Ni, Ag, Pb, Bi) have been reported from this laboratory [3]. See Table 6.

2.3. Cladding material Zr-2.5 wt% Nb

Zr-2.5 wt% Nb has replaced Zircaloy as a cladding material in Candu -PHW reactor and it has a stringent specification of < 0.1 ppm with respect to chlorine. RNAA has been developed for the determination of Chlorine in this [4]. The chlorine content ranges from 0.1 to 2 ppm, with electron beam melted material giving the lowest content of chlorine (0.1 ppm).

3. EARTH SCIENCES

Nuclear Methods Section, ACD is helping the geologists of this country for the trace elements investigation of their specimens for petrogenesis and other geological processes [5–8]. NAA has been applied to important mineral specimens and for their characterisation [19,20]. Zircon is a ubiquitous radioactive accessory mineral which has been widely studied in diverse field of earth sciences. A number of zircon separates from diverse geological setting in India have been analysed for Zr, Hf, Sc, U, Th, Ta and REE by NAA reported first by the author [19]. The positive anomaly observed in some of the Zircon REE pattern, first reported for a magmatic environment, is being followed by other geologists now [21]. Sc in these zircons appears to be a sensitive indicator for mineral paragenesis — an observation made first time.

The above developed procedures have been utilised for the determination of U, Th, Pb, REE, Sc, Ta in the detrital zircons from the basal quartz pebble conglomerate (QPC) of the Dhanjori group, Singhbhum Craton, Eastern India [8, 22]. The chemical ages and REE patterns of these zircon have helped to find the source rocks (provenance) for these zircons.

INAA can be generally used for the geochemical studies of the rocks, sediments, minerals, etc. In the cases of low abundances of elements particularly platinum group metals (PGM), only RNAA can give the desired results. Recently geologists show lots of interests in the PGM analysis of geological specimens, for understanding the various geological processes and for prospecting of the PGM, which have economic importance. A RNAA procedure has been developed for the determination of Pt, Pd, Ir and Au in geological samples [23] and has recently applied for the determination of Au, Pd, Pt and Ir in ultramafics, gabbroic and chromitites rock samples (Table 7).

4. FORENSIC APPLICATIONS

NAA unit of Central Forensic Science Laboratory (CFSL), Hyderabad, Bureau of Police Research and Development of Ministry of Home Affairs, located at ACD, BARC under the guidance of NMS, ACD is utilising the research reactors at Trombay for the forensic investigations. This Unit has handled 289 forensic cases containing 2127 exhibits involving 10473 determination from 1974 to 1997. NAA Unit, apart from routinely utilising the NAA for the various forensic case samples, also develops innovative procedures for the complex materials. Periodically, the procedures developed applied to complicated and interesting

forensic cases have been presented/published in journals/symposia [14–16]. RNAA of Cu, Sb, As and Sn in bullet lead have been utilised for the forensic comparison of bullet lead. Ba, Cu, Sb and Pb are the indicator elements for Gunshot residues (GSR). In case of synthetic fibres, Sb being present in these up to% level, Sb cannot give a clue to GSR.

It is seen that bullet lead of IOF and some foreign ammunition contained Sn from 130–3300 ppm [24]. RNAA of Ba, Cu, As, Sb and Sn in GSR based on the above earlier procedures has been developed and the results of Sn contents range from 21–183 ppm in GSR which are much above the control samples [16]. Thus it is seen that Sn can be another useful indicator element.

5. ENVIRONMENT

5.1. Recoveries of various rare metals from process/ industrial wastes

5.1.1. Recoveries of heavy rare earths including Y & Sc from zirconium raffinate

Zircon is the starting material for the production of zirconium metal, used in the nuclear industry. Zircon contains significant amounts of heavy rare earths [19]. In the production of Zr from zircon using solvent extraction separation, the heavy rare earths (HREE) do not get extracted and goes with the raffinate which is thrown as wastes. NAA of these raffinate cakes obtained from ZOP plant, NFC, Hyderabad showed high levels of HREE (200–6000 ppm) [25]. A solvent extraction procedure has been worked out for the separation of Sc from the HREE [26]. Sc which is very costly finds very many application in many Hi tech fields. Thus by recovering these rare metals as by products from the wastes, the environmental pollution also can be reduced. Thus these costly metals which go to waste in the raffinate cake can be recovered.

5.1.2. Recovery of rare metals from various stages of copper mill

It is known that many rare and precious metals are present at trace and ultra trace levels in copper ores. A RNAA procedure has been developed to find various trace elements present at the various stages of the copper mill [27]. Tables 8 and 9 show the results of the various samples. From the results it can be seen that various elements are concentrated at different parts. Hindustan copper company has set up a stream for economic recovery of Se. This study show that a waste which will pollute can be a useful resources for recovering rare metals, thus bringing a point that pollution can turn into useful value added by product.

5.1.3. Recovery of PGM from various processes of Jaduguda ore

The copper ores of Singhbhum Shear Zone (SSZ), Bihar, contain significant trace quantities of valuable metals like Au, Ag, Te, Se, Bi, Co & Ni is known and some of them are recovered from anode slimes during electrolytic refining of Cu in the smelter of HCL, at Ghatnila, Bihar. The contents of PGE, Au & Ag in the different U ore deposits of SSZ have been reported recently [28–30]. It is worthwhile to recover the PGE, Ore dressing section of BARC has taken up for concentration of these fraction. Table concentrate of bulk sulphide float have been analysed for Pt, Pd & Au by RNAA (Table 10). It is worthwhile to look at the Analytical data to work out the possible recoveries of the PGM.

Thus a close look at the industrial/ process wastes by analysing for various elements can give astonishing effect besides the reduction in pollution of the environments. These studies are limited but if undertaken on a broader perspective wherever possible will be very much fruitful and give a boost to analyst, for helping to solve the pollution to certain extent.

Table 6. Results of analysis of NBS SRM-960 U by GFAAS and DC - arc OES (μg/g)

Element	**GFAAS[a]**	**Certified[b]**	**DC arc OES**	
			A[c]	**B[c]**
Mg	4.52 ±0.006	–	6	< 6
Ca	3.05±0.055	–	<5	–
Cu	4.33±0.069	–	<2	–
Zn	4.18±0.058	–	<5	–
Cd	0.017±0.004	–	<0.1	<0.1
Mn	3.4±0.003	–	7	8
Al	19.5±0.075	–	<10	–
Fe	42.95±0.056	42	29	–
Co	1.54±0.02	–	<5	<1
Ni	13.05±0.11	–	<5	<12
Ag	ND	–	<0.1	–
Pb	0.222±0.0001	–	<5	–
Bi	0.02±0.003	–	–	–

[a]Mean ± standard deviation S_x (n = 4); [b]Only Fe and V values are given as certified values for NBS SRM 960;
[c]A and B are results obtained by two independent analysts.

Table 7. Results of analysis of geological samples

Sample		Content (μg/g)			
		Pd	Pt	Ir	Au
1. Iron meteorite	INAA RNAA	– 0.8±.09	– 26±1.2	44 39±0.4	0.55 0.47±0.05
2. PCC-1 [#]	RNAA “ Lit. value	– – –	18 16 3.5–13.5	2.0 4.5 2.9–6.9	1.5 3.0 0.67–3.4
3. Mixed rock (chromite + sulphide)	RNAA				
3.1 B / 0 / 4	“	12.0	–	0.05	0.2
3.2 NF / 12	“	6.1	–	–	0.61
3.3 FCS / 7	“	17.9	–	0.07	1.22
3.4 0 / 1	“	–	–	0.11	0.1
3.5 0 / 2	“	–	–	0.04	0.02

[#] ng/g.

Table 8. Results of the analysis of typical samples from different stages of a copper mill by RNAA (concentration in μg/g). Values in parentheses show SD with n = 3

	Sample description							
	Cupro-nickel slag from brass foundry	Boiler flue dust flash smelter	Converter flue dust flash smelter (Fl. Sm.)	ESP dust (Fl. Sm.)	Mosabiai conc.	Liberator sludge	Mist	LOD*
Re	< 0.1	2.4	< 0.1	7	< 0.1 –	0.2 0.01	180 (10)	0.05
As	1.3	620	670	2850	85 (6)	4500 (300	3100 (200)	0.02
Se	40	250	150	540	350 (35)	9800 1000	27300 (2700)	2
Sb	10	4	25	16	10 (8)	1000 85	65(5)	0.01
Pt	< 0.1	< 0.1	< 0.1	< 0.1	<0.1 –	< 0.1 –	< 0.1 –	0.1
As	0.2	1.7	3	0.8	11.2 (1)	220 (15)	0.8 (0.1)	0.01
Ag	7	35	75	90	50 (35)	2100 (180)	40 (2.5)	0.1
La						4.5 (0.2)	23 (1.5)	0.05
Ce						8.5 (1)	45 (5)	0.1
Sm						0.1 0.05	2.3 (0.1)	0.01
Eu						0.2 0.01	0.3 (0.08)	0.001
Dy						0.2 0.02	2.2 (0.02)	0.001
Er						0.3 0.02	0.8 (0.1)	0.005
Yb						0.2 0.02	1.5 (0.02)	0.005
La						0.2 0.01	0.3 (0.03)	0.002

* Limit of detection by RNAA.

Table 9. INAA results for samples from different stages of a copper mill (concentration in μg/g)
Values in parentheses show SD with n = 3.

No.	Sample description	Co	As	Se	Sb	Te	Re	Au
1.	Rakka Tails	56	.2.5	16	0.7	50	ND	0.06
2.	Sludge from H_2SO_4 plant	260	4600	1130	ND	150	4.5	3.4
3.	Composite boiler dust	1400	390	230	6	500	35	0.2
4.	Composite ESP dust	100	560	250	9	700	6.1	0.2
5.	Composite converter dust	550	160	400	6	360	1.4	4.4
6.	Composite SCF dust	1150	90	30	3	640	0.6	2.4
7.	Composite SCF dust	2650	35	340	6	130	2.3	3.7
8.	Composite SCF slag	1850 (200)	11 (1.5)	40 (5)	4 (0.5)	120 (10)	43 (4)	0.01 (0.001)
9.	Composite anode sample	11 (1.5)	ND –	540 (50)	3 (0.02)	350 (30)	0.6 (0.05)	10 (0.05)
10.	Mist	48 (5)	2200 (200)	25000 (2800)	46 (5)	1100 (120)	150 (20)	0.5 (0.025)
	LOD*	0.1	0.1	5	0.1	1	0.1	0.005

*Limit of detection.

6. INTERCOMPARISON EXERCISES – IAEA

Participated in many IAEA Inter comparison exercises/co-ordinated research projects, etc. Recently participated in the Inter comparison Run on determination of toxic and other main and trace elements in IAEA-390 a set of three algae materials (IAEA-391 algae (low level) IAEA-392 algae (environmental level) IAEA-393 algae (elevated level). In these samples, it was observed that elements like Cu & Zn seem to be inhomogeneous which was mentioned while reporting (Oct. 1, 1996). We are awaiting for the final compiled results from IAEA.

To conclude, the high potential of NAA technique has to be tapped fully by more innovative ideas/ research to solve problems in very many areas. Thus NAA may surpass most of the technique in its usefulness as a very versatile technique for trace and ultra trace analysis, of course the limitation being the availability of a research reactor.

Table 10. Precious metal contents Jaduguda uranium ore

Sample	Content (ng/g)		
	Pt	**Pd**	**Au**
1. Narwapahar	ND	169	ND
2. Surda Cu concentrate plant tailing	ND	ND	2.4
3. Surda U plant table concentrate	ND	8.7	10.0
4. Rakha Cu plant tailing	ND	7.5	1.0
5. RURP table concentrate	ND	ND	4.1
6. Mosabani Cu conc. Plant tailing	ND	18.7	4.2
7. MURP table conc.	ND	ND	58.5
8. Coarse fraction of Jaduguda mill tailings	0.89 #	34.0	29.2
9. Fine fraction of Jaduguda mill tailings	ND	24.0	3.9
10. Bulk sulphide float from BRP, Jaduguda	24 .0#	166.0	191.0
11. BRP Cu conc.	2.76 #	19.1	69.0
12. Magnetic conc. from Jaduguda tailing	ND	ND	8.2

μg/g.

7. SUGGESTION FOR CONSIDERATION

We would like to suggest that a feed back is very much necessary in case of intercomparison exercises and the final compiled analytical data from IAEA, at their earliest is necessary and may enable us to evaluate our analytical data. We have responded to the analytical quality control services (AQCS) – performance survey form and in the guiding questionnaire sent by Mr. Dale W. Jacobs (Consultant of IAEA). We have suggested that there should be more intercomparison runs for biological, geological and if possible forensic samples. Now analytical methods for Au, Ag and PGM are needed for the geological community, because of their economic importance/ significance, we suggest that IAEA can think of preparing reference materials for the above purpose and also for high purity/hitech materials. These may have a demand from the researchers who are working in these fields for use as a International standard samples for evaluation of their analytical process. We also support the idea to generate a comprehensive general purpose. Quality assured nuclear data library specialised for NAA application. This is discussed in the Appendix to the paper.

REFERENCES

[1] KAYASTH, S.R., RAJE, N., ASARI, T.P.S., PARTHASARATHY, R., Anal. Chim. Acta **370** (1998) 91–103.

[2] KAYASTH, S.R., RAJE, N., ASARI, T.P.S,Anal. Chim. Acta, 318 (1996) 211–219.

[3] KAYASTH, S.R., RAJE, N., ASARI, T.P.S, GANGADHARAN,S., Anal. Chim. Acta **290** (1994) 371–377.

[4] VERMA, R., PARTHASARATHY, R., J. Radioanal. Nucl. Chem. Lett. **214** (5) (1996) 391–397.

[5] NATRAJAN, M., BHASKAR RAO, B., PARTHASARATHY, R., KUMAR, A., GOPALAN, K., Precamb. Res. **65** (1994) 167–181.

[6] BISWAL, T.K., GYANI, K.C., PARTHASARATHY, R., PANT, D.R., Precamb. Res.,**87** (1998) 75–85

[7] PAWASKAR, P.B., SANKAR DAS, M., VILADKAR, S.G., Gondwana geol. Mag., Spl. Vol. **2** (1996) 171 –184

[8] SUNILKUMAR, T.S., KRISHNA RAO, N., PALRECHA, M.M., PARTHASARATHY R., SHAH, V.L., SINHA, K.K., J. Geol. Soc. Ind. **51** (1998) 761.

[9] VERMA, R., KUMAR, S., PARTHASARATHY, R., J. Radioanal. Nucl. Chem. **218** (1997) 189–191.

[10] GUHAMAJUMDAR, CHAKRABORTY, A.K., GHOSE, A., GUPTA, J.D., CHAKRABORTY, D.P., DEY, S.B., CHATTOPADHYAY, N., Bulletin of the World Health Organization **66** (1988) 499–506.

[11] CHATTOPADHYAY, N., BASU, A.K., TRIPATHI, A.B.R., BHADKAMBEKAR, C.A., RAO, M.S., PARTHASARATHY, R., KRISHNAMOORTHY, T.S., Proceedings of XI th ISAS national symposium (PETPHAR CHEM - 95) 2–4 Nov. 1995, p 32.

[12] SADAGOPAN, G., NAMBI, K.S.W., VENKATARAMAN, G., SHUKLA, V.S., KAYASTH, S., Radiation Protection Dosimetry **71** (1997) 51.

[13] CHATTOPADHYAY, N., Presented at International Conference on Arsenic in ground water, cause, effect and remedy, 6–8 Feb, 1995, Calcutta, p 66.

[14] BASU, A.K., CHATTOPADHYAY, N., RAO, M.S., PARTHASARATHY, R., J. Ind. Acad. For. Sci. **33** (1994) 57.

[15] PARTHASARATHY, R., KAYASTH, S., KRISHNAMOORTHY, K.R., VERMA, R., PAWASKAR, P.B., PANT, D.R., KRISHNAMOORTHY, T.S., CHATTOPADHYAY, N., RAO, M.S., "Neutron activation analysis and its applications", International seminar on developments on enhancement of research reactor utilisation, Trombay, Mumbai, India 11–15, March 1996. IAEA-SR-198/62.

[16] CHATTOPADHYAY, N., BASU, A.K., TRIPATHI, A.B.R., RAO, M.S., ANIL S., KUMAR, PARTHASARATHY, R., MATHUR, P.K., "A radiochemical NAA method for the determination of Tin, Barium, Copper and Antominy: Role of Tin as an indicator for gum shot residues", International conference on applications of radioisotopes and radiation in industrial development (ICARID-98) (SOOD, D.D., REDDY, A.V.R., IYER, S.R.K., GANGADHARAN, S., SINGG, GURUSHARAN, Eds) (1998) p 64.

[17] KAYASTH, S.R., DESAI, H.B., SANKAR DAS, M., Anal. Chim. Acta **187 (**1986) 271–277.

[18] KAYASTH, S.R., DESAI, H.B., SUNDARESAN, M., Anal. Chim. Acta **219** (1989) 313–315.

[19] MURALI, A.V., PARTHASARATHY, R., MAHADEVAN, T.M., SANKAR DAS, M., Geochimica et Cosmochimica Acta, 47(1983), 2047–2052.

[20] PARTHASARATHY, R, DESAI, H.B., KAYASTH, S.R., J. Radioanal. Nucl. Chem. Lett. **105** (1986) 277–290.

[21] HINTON, R.W., UPTON, B.G., Geochim. Cosmo Chim. Acta **55** (1991) 3287.

[22] SUNILKUMAR, T.S., PARTHASARATHY, R., PALRECHA, M.M., SHAH, V.L., SINHA, K.K, KRISHNA RAO, N., Current Science **71** (1996) 482–486.
[23] KUMAR, S., VERMA, R., GANGADHRAN, S., Analyst **118** (1993) 1085–1087.
[24] DESAI, H.B., PARTHASARATHY, R., J.Radioanal. Chem. **77** (1983) 235–240.
[25] PARTHASARATHY, R., SUDERSANAN, M., IYER, R.K., "Concentrations of Rare Earths, Y and Sc in the raffinate of Zr/Hf extraction from zircon for possible recoveries", Advances in Rare Earth Research (PAI, B.C. PILLAI, DAMODARAN, M.A.D., Eds), Regional Research Laboratory, Trivandrum (1993), p 72.
[26] SUDERSANAN, M., PARTHASARATHY, R., IYER, R.K., The separation of Sc and Rare Earths from the raffinate of Hf extraction by solvent extraction, ibid., p 67.
[27] KAYASTH ,S.R., GANGADHARAN, S., J. Radioanal. Nucl. Chem. Art. **181** (1994) 425–431.
[28] SANKARAN, R.N., KRISHNA RAO, N., RAO, K., BALARAM, V., DWIVEDY, K., Current Science **72** (1997) 673.
[29] PANT, D.R., KAYASTH, S.R., PARTHASARATHY, R., "Recovery of rare earth elements from copper concentrate tailings and other by-products of UCIL, Jaduguda: a preliminary study", Proceedings of Nuclear and Radiochemistry Symposium, SINP Calcutta, Jan 21–24, 1997 (NUCAR. 97) (RAMAKUMAR, K.L., PUJARI, P.K., SWARUP, R., SOOD, D.D., Eds.) LIISD, BARC, Mumbai (1997) p 358.
[30] KAYASTH, S.R., PANT, D.R., Search for recoverable elements from different stages of process plants of uranium: an overview, ibid., p 360.

ANNEX

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At the IAEA Advisory Group Meeting on "Computer Software for Neutron Activation Analysis" held during 25–30, at Seoul, Republic of Korea, the experts identified that there is a need for a specialized nuclear data library for NAA. It was also suggested that this could be done by appropriate coding of gamma ray lines in a more general nuclear data library.

The nuclear data that we should have information on are the characteristic energies and intensities of gamma rays emitted by radionuclides which are commonly used as fingerprints for nuclide or isotope identification. The various techniques such as Neutron Activation Analysis (NAA), Prompt Gamma-Ray Activation Analysis (PGAA), and Neutron Depth Profiling (NDP) which are often used for research in the environment, biomedicine, geology, archaeology, industry etc all make use of basic nuclear data. Over the years significant technological improvements have taken place in gamma-ray detectors, and the construction of more intense neutron sources leading to a variety of applications of neutron activation analysis, and very precise nuclear analytical techniques. All these techniques are based on "isotope or nuclide fingerprint" identification. These techniques, however, require the availability of suitable and up-to-date nuclear data libraries.

Typical computer programs for analyzing gamma-ray spectra in activation analysis use data from libraries of gamma-ray energies, intensities, thermal neutron cross sections, isotopic abundance, half-life of radionuclides, etc. Although most of these libraries are subsets of the Evaluated Nuclear Structure Data File (ENSDF), their cut-off dates may not be uniform and thus contain data from different vintages.

Many users in developing countries use old handbooks. The use of 10–15 year old data libraries in activation analysis, especially in developing countries is not uncommon. The numerical values are generally reliable for well known cases (e.g. Cs-137, 662 keV line) but not necessarily so for complex cases.

This situation may be attributed to technical difficulties for accessing on-line services via the Internet available from the classical nuclear data service centres such as the IAEA-NDS. The ENSDF using Telnet and the World Wide Web can be accessed for specific data Thus in principle, the scientists working on NAA can make retrieval and processing of updated nuclear data for analytical work using the IAEA-NDS on-line systems to access data and perform appropriate analyses.

The creation of a new nuclear data library on prompt neutron-capture gamma rays for activation analysis can make use of the general activation library FENDL/A-2 created recently at the IAEA Nuclear Data Section for studying neutron activation rates. FENDLA/ (contains the library FENDL/A, version 2.0 of March 1996, of pointwise neutron activation cross section data as assembled by the Culham/ECN team at UKAEA Culham in March 1996. The basic pointwise data include non-zero cross sections below 20 MeV for 13006 neutron reactions on 739 target nuclides (including metastable states).

The appropriate coding of the gamma ray lines should be added to the FENDL/A-2 library so that the specialists working on NAA will be able to have easy access to a Quality Assured Nuclear Data library. This can be distributed on a CD-ROM. This task is suitable for a Co-ordinated Research Programme.

UTILIZATION OF THE SLOWPOKE-2 RESEARCH REACTOR

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Abstract. SLOWPOKEs are typically low power research reactors that have a limited number of applications. However, a significant range of NAA can be performed with such reactors. This paper describes a SLOWPOKE-based NAA program that is performing a valuable series of studies in Jamaica, including geological mapping and pollution assessment.

1. THE CENTRE FOR NUCLEAR SCIENCES (JAMAICA)

The SLOWPOKE reactor in Jamaica is presently the only reactor in the Caribbean. It first achieved criticality in March 13, 1984 and is used mainly for neutron activation analysis in programmes which aim to:

(1) Introduce Caribbean scientists and technologists to peaceful applications of nuclear sciences;
(2) Carry out inter-disciplinary research of national and regional importance that is likely to contribute to the development of the region;
(3) Be a resource to other institutions, as appropriate;
(4) Provide suitable training.

2. INFRASTRUCTURE AND RESOURCES

2.1. Premises

The Centre is located on the Mona Campus of the University of the West Indies and is near to most of the main science and technology activities in the island. It occupies a modern air-conditioned building of 946 m^2 in area, which houses laboratories, a nuclear reactor room, sample preparation and clean rooms, computer rooms, a liquid nitrogen production plant, offices, conference/seminar rooms, and a public area for external users.

2.2. Equipment

The main item of equipment is the SLOWPOKE 2 nuclear research reactor. It is used mainly for neutron activation analysis of rocks, soils, sediments, air particulates, and biological samples. Other major items are:

(1) X-ray fluorescence spectrometers;
(2) A Perkin Elmer Atomic Absorption Spectrometer Model 5100;
(3) A Lachat QUICK-CHEM 8000 Automated Ion Analyser;
(4) A DIONEX 4500 Ion Chromatograph;
(5) SUN work stations, PC servers and workstations, and full access to a Convex 3440 supercomputer.

3. SPECIALISED SERVICES

A number of services are offered by the Centre. These are outlined in the following sections.

3.1. Personnel dosimetry

The Centre is the official radiation protection facility for Jamaica. It provides thermoluminescence dosimetry services for more that 600 local users and an equal number

regionally. The Centre also offers: (a) inspection and monitoring of radioactive sources as well as radioisotope contamination monitoring (b) advice on radiation sources and the handling, storage and transport of radioactive material.

3.2. Measurement of radioactivity

Since the Chernobyl incident, the Centre has been monitoring certain food imports and certifying some imports.

3.3. Analytical services

The Centre provides neutron activation analysis and other analytical services to the public and private sectors.

3.4. Main research programme

The main programme has been a set of geochemical investigations applicable to a number of environmental and resource components such as air, water, soils, rocks, and sediments. The resulting data are stored in an on-line SQL multi-purpose database which can be coupled to a geographic information system. Together they are applicable to such fields as agriculture, environmental assessment and protection, land use, natural resource identification and management, as well as animal and human nutrition and health.

4. MAJOR STUDIES COMPLETED BY THE CENTRE FOR NUCLEAR SCIENCES

4.1. Geochemical mapping of Jamaica on the regional scale

The construction of a high-precision, regional geochemical database of Jamaica is underway. An orientation study established that soil samples of particle size <150 μm provide the optimum sampling medium for a regional geochemical survey of Jamaica. Concentration and distribution data for thirty-one elements, mainly by NAA, are now available for soils at a sample density of 1 in 8 km^2. This work is the basis of most of the present and projected studies.

4.2. The gamma radiation profile of Jamaica

The total gamma activity across Jamaica has been measured using vehicle-borne equipment. In general, the enhanced gamma activity is highly correlated with the presence of bauxite and is due to enrichment in uranium and thorium but not potassium. There has been significant transport and concentration of radioactive isotopes over time in the areas below the bauxite deposits. Studies are continuing.

4.3. Air particulates

Air particulates have been surveyed at twenty-three sites across Jamaica for total suspended particulates (TSP) and the elemental contents have been measured by neutron activation analysis and x-ray fluorescence. The average values of TSP are well within the standard levels recommended by the World Health Organization (WHO). However, there are areas of heavy vehicular densities in which the values exceed the WHO limits. The results indicate that vehicle emissions are the major source of lead in particulate matter.

4.4. Assessment of arsenic risks in the parish of St. Elizabeth

A soil arsenic anomaly was discovered and defined with respect to size and arsenic levels. The area in which the arsenic concentrations exceed the 95^{th} percentile (>65 mg kg^{-1}) of the concentrations found island wide is approximately 10 km^2. The anomaly appears to be due to an ancient hot spring environment, which caused the introduction and deposition of Fe-AS-S as pyrite and arsenopyrite in the limestone. These were subsequently oxidized and weathered to yield arsenic rich soils also enhanced in elements such as Sb, Fe, and Co. Despite the high soil arsenic content, there appears to be no immediate health risk.

4.5. Mitigation of lead hazards in the Hope Mine area

The site of a school for 4-6 year olds near to the abandoned Hope Mine is highly contaminated. The blood lead levels of the school children led to interventions, including the isolation of lead waste and outcrops by covering them with a layer of marl and then cement. Subsequent blood tests showed reductions in blood lead levels, by as much as factors of three. The average has been reduced significantly and there are now values at or below the recommended U. S. Environmental Protection Agency norms.

5. FUTURE

The Centre for Nuclear Sciences (CNS) is being transformed into a node of a network of centres of excellence being established in the countries of the South. The new name, the International Centre of Environmental and Nuclear Sciences (ICENS), reflects its major interests and the continuing application of nuclear techniques to environmental problems.

This new Centre is based on and incorporates the existing CNS, the work of which will be expanded and intensified. The ICENS will increasingly become a host for a wider range of co-funded and co-sponsored projects and collaborative research, especially on problems requiring an interdisciplinary approach.

FROM SCIENTIFIC RESEARCH TOWARDS SCIENTIFIC SERVICE BY INAA: EXPERIENCES AND CONSEQUENCES

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Abstract. An evaluation has been made at the laboratory for INAA in Delft of the type of analytical protocols requested for by scientific and commercial customers. Examples are given of the differences in requests from industrial research and university research and the consequences for the analysis protocol to be selected. On basis of experience with the users and clients and customer satisfaction evaluation results, a SWOT (Strengths, Weaknesses, Opportunities and Threats) analysis has been made. This analysis makes clear that many of the frequently mentioned 'advantages' of INAA do not excite the clients. One of the typical weaknesses of the technique results from lack of automation, indispensable for effective and economic operations. This may hamper small INAA groups to become interesting for large-scale and/or parallel requests, to become competitive and self-sustainable. Suggestions are given how the weaknesses and threats may be circumvented and how the strong points and opportunities may be successfully exploited.

1. INTRODUCTION

There are several reasons why neutron activation analysis groups are nowadays requested to identify beneficiaries (customers) for their technique and to start 'commercial' activities. Many institutions deal with budget cuts; in other organizations the existence of (industrial) customers is considered important for public justification of the existence and continuation of the reactor. The NAA laboratory has to face the reality that it may have to shift part of its attention from (self-directed) scientific research to (customer directed) scientific services. Most probably, this implies a change in culture, policy and in the technical and organisational management at the laboratory.

There are various analytical problems in the applied sciences for which INAA may be the preferred technique to obtain information on elements and their concentrations. To this end, the NAA group has to understand its position in the market, and it should know that it has to offer. The questions to be answered are: " Who is interested in INAA anyhow, and why would INAA be selected? What is the added value of our activities?" There are numerous publications explaining the advantages and shortcomings of NAA, and many comparisons have been made with other methods for elemental analysis. However, nearly all of these evaluations themselves 'by radiochemists for radiochemists'. It can be of considerable more value to the NAA laboratory to understand the customers' view in this.

Several NAA laboratories from the academic community have proven to be successful in acquiring contracts for analyses. A few industries have established their own NAA laboratories to support their companies' requests[1,2]. Companies exist offering a wide range of analytical techniques for element analysis, including NAA. Each of them will have its own experience with customers, will have a different variety of samples analysed and will have a different way of dealing with customers' requests.

In this paper the experiences of the laboratory for INAA at Delft are given as a case study. The laboratory for INAA of the Interfaculty Reactor Institute at Delft has some 20 years experience with external users of the INAA facilities, and in the last 10 years a fully commercial business unit has been integrated with the research group.

2. TECHNICAL AND ORGANISATIONAL ASPECTS

The Nuclear Analytical Methods research group supervises the facilities of the laboratory for INAA[3] at Delft. The main task of this group is the development of physical and mathematical methods of radioanalysis, with the emphasis on gamma-ray spectrometry and neutron activation analysis. 'Routine' INAA is carried out by a commercial business unit, in liaison with the research group that has the final responsibility for the analytical quality. All activities related to the use of the facilities and the conduct of INAA are covered by the laboratory's quality system [4] which has been accredited for compliance with EN45001 (closely following ISO Guide 25).

The laboratory for INAA identifies 'external' and 'internal' customers. Scientists from other universities or research establishments, governmental bodies and industry form the first category. The internal customers are scientists within the mother Institute, mainly from the department of Radiochemistry. Some of these internal customers are trained by the laboratory to carry out the analyses on their own.

The external customers are fully charged for the analyses whereas the internal customers only pay for the consumables (capsules, internal quality control samples, etc).

2.1. Sample types

The sample types, which are being analysed for external customers, are given in Table 1. Plastics is currently the largest segment: a perfect niche for INAA since it can be done non-destructive. These analyses are mainly for law enforcement purposes and reliability of the analyses is very important since the results may have large economical consequences. Analysis of human toenail clippings is another major component. These are analyses for epidemiologists, and here again advantage is taken of the non-destructive nature of INAA. The samples are precious collections, analysed already several years ago for Se, thereafter archived and now processed again for other elements. There is a trend for more requests for analysis of new materials, composites, silicon carbide, carbon fiber, alumina, etc.

The samples from internal users are mostly resulting from biomonitoring projects (lichens, mosses, tree bark, soil, air particulate matter).

2.2. Analysis protocols

The traditional protocol for multi-element analysis was (and still is): 2 irradiations, 3 measurements (the shorts, one after 1 week and one measurement after about 1 month); 50–60 elements reporting. The various requests and particularly the needs of the external customers made necessary to develop different analysis protocols.

Most external customers appear not to be interested in full multi-element analysis, even not when the data is given for 'free' together with the data requested in the first place. Customers are usually oriented to one or a few given element(s) (see Table 2) whereas their main demand lies with turnaround time.

The majority of the work for external customers deals with one measurement 2–4 days after irradiation and a single element determination, or a group of some 12 elements which can be determined in this manner. The turnaround time of these measurements is about 1 week–10 days (see Table 3). This is usually acceptable for customers who compromise between number of elements and turnaround time. The perception of a short turnaround time is enhanced when taking advantage of the weekend for decay, e.g. by receiving the samples and irradiation on Thursday, counting on Sunday night and reporting on Monday afternoon or

Table 1. Sample types with percentage of the total throughput, as analysed by the Laboratory for INAA in Delft

Plastics	40%
Plants and Biomonitors	30%
Toe-nail clippings	12%
Metals	6%
High-tech materials (composites, carbides)	5%
Blood, serum	3%
Various industrial products (textile, packaging material, paint, resins, solvents, acids)	3%
Air filters	1%

Table 2. Requests (in percentage of total throughput) for number of elements to be reported for external en internal customers of the Laboratory for INAA in Delft

	External customers	Internal customers
1 element	40%	8%
2 elements	20%	4%
3 elements	8%	4%
Group of elements	20%	14%
> 3 elements	12%	70%

Table 3. Analysis protocols (in percentages of total) applied for external and internal customers of the Laboratory for INAA in Delft. S: NAA applied to short half-life radionuclides, M: NAA on basis of intermediate half-life radionuclides (e.g. measurement 1 week after irradiation), L: NAA on basis of long-lived radionuclides (e.g. measurement 1 month after irradiation)

	External customers	Internal customers
Shorts (S)	20%	13%
Medium (M)	60%	13%
Long (L)	2%	2%
S + M	1%	
S + L	1%	
M + L	2%	
S + M + L	10%	70%
Special optimised	5%	2%

Tuesday morning. In limited cases analyses are carried out with 2 days turnaround time. In addition a variable number of analyses is done with the fast rabbit systems. As mentioned before, only a few external customers are interested in total multi-element determinations.

For the academic market segment the situation is different. Here mainly full multi-element analyses are requested because a large number of more elements are needed for the factor analysis in the interpretation of the biomonitoring projects. However, it cannot be excluded that the request for multi-element data also might be influenced by the fact that these analyses are done at almost no charge. Experience with services to groups at other universities learned that requests for multi-element data changed rapidly in request for a limited number of elements when the groups were charged for the analyses. After all, an analysis consisting of one irradiation and one measurement is less expensive than an analysis consisting of two irradiations and three measurements.

2.3. Number of samples

Most of the external customers offer their samples in small batch sizes, and certainly not in hundreds at a time or so). The maximum number of samples processed simultaneously (which can be packed into one rabbit) is 14. The number of batches for external customers is about 250 per year, and for internal customers about 150. Total number of samples processed is about 4000 –4500. To this, the number of control samples, blanks and flux monitors should be added which makes the total number of capsules processed in the order of 15,000 per annum. Since some samples are measured more than once, the number of spectra analysed is estimated to be approximately 40,000 per year.

2.4. Customer satisfaction

The laboratory evaluates every 3 years its customers' opinions on the services provided. An independent bureau carries out this evaluation to avoid any conflict of interest between the customers, the laboratory and the interpretation of the evaluation. Some typical conclusions of the most recent evaluation are:

— Customers complained about the attainability of the laboratory's employees. The direct access to the various extensions was not sufficient due to the high mobility of the employees between offices, laboratory and counting room. Such a small group cannot afford a permanent telephone operator. This shortcoming now has been accounted for via the introduction of cellular phones.
— The layout of the reports is too scientific. Quite a few customers appear to be not familiar with the scientific E-format in reports, the concept of detection limits or uncertainties, and even not with the chemical symbols for the elements. It is not always trivial that, e.g., "Sb" means "Antimony". A new layout is now being developed.
— Turnaround times of one week or even longer is often still quite acceptable, differently from what is often be proclaimed as one of the drawbacks of NAA. Customers are satisfied as long as the reporting is done within the time frame, guaranteed by the laboratory in advance.
— Many customers turn to NAA after their in-house analytical techniques failed for the analysis needed. It is therefore important to invest on building awareness on the opportunities of NAA for the potential market segments.

3. STRENGTHS, WEAKNESSES, OPPORTUNITIES AND THREATS

The (potential) customers often have an entirely different perception of what NAA has to offer as an analytical technique. They often apply for the use of NAA when all other techniques have failed, as has been mentioned before. Moreover, the contracting-out is sometimes a psychological barrier to take, since it is more-or-less synonymous with 'loosing control'. The strong and weak points of NAA are balanced against the 'in-house' techniques and the disadvantage of contracting out. It can be expected that weak points of (the laboratory for) NAA get more emphasis, whereas some of the advantages as proclaimed by radiochemists, are taken as granted.

The view of outsiders helps the NAA laboratory to understand the potentials of the technique to provide (scientific) services. Such a view can be summarised in management terms as a 'SWOT' analysis; 'SWOT' being the acronym for "strengths, weaknesses, opportunities and threats".

3.1. The strong points of INAA

— The method is useful for materials which are hard to dissolve.
— The results are reliable. It can be made clear that NAA is matrix independent, and calibrant independent; that the feasibility and detection limits are predictable. Customers ask for ‘quality’ but not always in terms of accuracy and precision. Moreover, they are seldomly interested in results of reference material analysis or proficiency testing. Customers simply expect that a laboratory — especially a university laboratory — must have a good performance in this all. Their view on quality is like one of its definitions: to get what has been asked for, especially within the time frame agreed upon. It is expected that the analysis can be reproduced and eventually that the laboratory can stand-up in court to defend its results. It stresses the importance of quality management.
— The analysis can be repeated on the same material for additional information, in case of doubt and also other methods can be used to analyse the same material. Eventually, the analysed material can be returned to the customer.

3.2. The weak points of INAA

— The turnaround times may still sometimes be prohibitively long, not just because of physical problems but also because of organisational problems. And because of a too academic approach of the analytical request. Any NAA laboratory has to learn that it has to optimise its service to satisfy the customer rather than to satisfy the NAA specialist. In many cases there is no need to reach a better than 5% counting statistics precision, and even 20–30% may suit equally good. The traditional approach in INAA is to get as many as possible elemental data with as good as possible precision. It was demonstrated in the above that customers may be interested in 1–3 elements only, and even more often, they want an answer like: “is the concentration yes or not above a certain level”.
— Another way to satisfy customers is to increase capacity by shorter counting times, shorter irradiation times or to optimise in decay time. Traditionally, one of the measurements in INAA is done 3–5 weeks after irradiation. However, often already reasonably good results can be obtained some 10–12 days after irradiation when the ^{24}Na background has reduced substantially. Similarly, satisfactory results can be obtained after 3 days decay rather than to wait a full week after irradiation. Modern days’ counting equipment can easily handle moderate or high counting rates. In principle, there should be no significant difference in results obtained via a measurement with 5% dead time and with 60% dead time — if using the pulser method at constant decay rate, or ‘loss-free counting'. It all can contribute to a higher throughput and more customer satisfaction.
— There is no culture present in research laboratories to have facilities ‘stand-by’ to suit requests for analysis. Many NAA laboratories are often not equipped to handle parallel requests for analyses. Moreover, NAA is not a method of elemental analysis in which the capacity can easily be extended or with which routine analysis can be done at a high and quick throughput. This is a weak point when considered to be an alternative for laboratories employing other methods with equipment, especially developed for routine services and an organization tuned to this as well. In many cases the limited technical and organisational capacity may result in frustration with the customers and a confirmation of the existing image that research institutions are unreliable partners in scientific services. Eventually it also may adversely affect the justification of the reactor as such.

— Sensitivities are sometimes not good enough anymore to suit present day's levels of interest (environmental and industrial research); Pb cannot be determined and Cu is troublesome as well.
— Generally, NAA is poorly advertised with potential customer, like in the communities of applied sciences. Usually radiochemists speak about their technique to radiochemists only, at radiochemical conferences. At more general spectroscopic conferences hardly any contribution is found on the status and opportunities of NAA. It is an illusion to expect that the many publications on NAA and its applications have their impact. Customers, and this count in particular for the non-university market segment, do not read J.Radioanal.Nucl.Chem., Nucl. Instr. Meth. or Anal.Chem.; they are not interested in the resolution of Ge detectors, the k_0- phenomena nor in the results of reference material analysis. NAA is not an analytical technique that belongs to the package of methods taught and trained at technical schools and universities. Taking into account the overwhelming presence of techniques like AAS, ICP and XRF, it should be feared that within other analytical laboratories there is rather limited awareness even on the existence and accessibility to NAA.
— The customer has to send his samples to the NAA laboratory rather than that the analyses can be done 'in-house'. The customers may perceive this as 'loosing control', not as much on the conduct of the analyses but more on the certainty that the results will be available at a given time.

3.3. The opportunities for INAA

— The need for reliable results. Reliability is sometimes more important than level of accuracy, though the combination of reliability and accuracy is of importance when analyses have to be done for e.g. product control or law enforcement.
— Analysis of materials for which no matrix-matching reference materials are available. The common approach in other methods of elemental analysis is the use of matrix matching reference materials for calibration. The variety of materials to be analysed and trace elements sought develops itself much faster than the availability of suitable reference materials and certified concentrations. This applies especially to the material sciences and for ultra low concentrations. In many laboratories awareness exists that the reliability of the analyses is questionable if such matrix-matching reference materials are not available.
— Unique materials which should not get lost. This applies e.g. to materials of which the sampling has been tedious (e.g. cosmic dust); materials which cannot be collected again (e.g. human bioindicators such as hair, nails, tissue, blood, urine; but also materials related to environmental pollution like atmospheric dust); materials of which the same test portion may have to be analysed again, by NAA or any other technique (see for instance the example given in the above of the toe nail clippings) depending on the first results; materials related to forensic work, in which there should be no loss of evidence.

Validation of other methods for element determinations. Increasing laboratories (research, industrial and service) laboratories have to fulfil the validation criterion as laid down in ISO Guide-25 or equivalent standards. Sometimes this validation can only be done by comparison with another technique. Here there are opportunities for NAA laboratories for continuing support to external customers. Perhaps it may not result in a large supply of samples but it certainly will contribute to respect and an expressed need for the existence of the NAA laboratory.

3.4. The threats to INAA

— Too little awareness on the existence of NAA. There is a strong need for renewed awareness building on the modern' days opportunities of NAA. As has discussed in the above, it is a big mistake of the NAA community if this remains limited to the radiochemical and scientific journals only. Customers are found by contacting them in their own media, and in a language they comprehend and which is directed to their needs. Technical journals are a better choice than scientific journals. Mailings of brochures may only be of value after potential customers have asked for more information; otherwise, it ends at the pile of daily junk mail. The customer satisfaction evaluation again demonstrated how important it is to prevent the use of jargon and to be aware of the fact that the first contact might be with non-scientists.

— The attitude of researchers is too introverting. In many NAA laboratories, the technique is still applied as it has been developed 30 years ago, optimised to find as many elements as possible, at the best possible precision. It is of paramount importance to find out what is important for a customer: accuracy, precision, single or multi-element, turnaround time, sensitivity, price…. The analysis should then be optimised to the customers' request and often a protocol has to be selected different as one would do from the NAA point-of-view.

— The academic environment is almost synonymous for unreliability in planning. Deadlines are seldomly met; this applies to contributions to scientific conferences but also for reporting results. Laboratories have to introduce a style of working with commitment to planning of all aspects of the analysis, like availability of consumables, equipment checks, use of equipment etc. There should also be a rigid procedure for checking the results before reporting them, including quantifiable criteria. It might be disastrous for a laboratory if still mistakes are found after reporting. Quality management principles will also turn to be of importance to reduce the amount of repetition of work — which may result in small disasters when capacity is limited — and to carry-out timely the required performance checks, maintenance, stock control and so.

— Unreliable reactor schedules. In institutes with reactors with extensive neutron beam physics programs sometimes the reactor operation is tuned to the experimental conditions for this beam physics work. This also may apply to full power operating schedules which may be delayed due to modifications needed of the beam experiments. As thus, it may hamper the scheduled irradiations for NAA (and e.g., also for isotope production).

— Unreliable operation of NAA equipment since there is no return of revenues for replacements and investments. This is a most serious threat, since it quickly moves the laboratory in a downward spiral. Sometimes this may be by-passed by payment 'in natura', e.g. via procurement of equipment by the customer. However, there are no general guidelines to overcome this threat since it is typically a political problem within the mother organisation.

— Lower detection limits are required than can presently be attained. Large volume Ge detectors and especially well-type Ge-detectors should be considered the present days' work-horses for NAA laboratories. The better detection limits, increased throughput and good economics justify their procurement and replacement of conventional Ge–detectors [5, 6]. Moreover, high-count rate electronics is now standard available, which allows for measurements e.g. after shorter decay times of interfering radioactivity [7]. These instrumental improvements will not effect that NAA detection limits may be equally good as proclaimed by the — interference free !! — detection limits of e.g. AAS or ICP. But they are opportunities to fulfil customer's requirements at relatively low investment.

— Automation is difficult to be realised. Many laboratories are lacking the opportunities to develop their own automation. As such, throughput is limited and turnaround times may remain prohibitively long. Commercially available sample changers are scarce and

containers are not standardised; automation of software is in principle feasible but should be done by the laboratory itself, which in the practice turns out to be not always possible. The poor situation on easily available automation in NAA is in big contradiction to developments with other techniques where automation is almost a standard option.

4. CONCLUSIONS

In many countries NAA laboratories have to face the reality that the daily efforts may have to be shifted from (self-directed) scientific research to (customer oriented) scientific services. This implies a change in culture, policy and technical and organisational management at the laboratory. External customers have different requirements to the scientific services than internal customers for their scientific research. It should be noted that the examples given in this paper apply a specific case study. However, it demonstrates the differences, and NAA laboratories should be aware of the fact that external customers have their own perception of the advantages and weaknesses of NAA. The advantages of NAA, as found in numerous review articles and books, have been compiled from the inside out, rather than from the customers point-of-view. Their view on the strong points and weaknesses of the method may be different from case to case. NAA laboratories should be alert on this, and develop a flexibility to respond on it.

A weakness that can easily become a serious threat to NAA — and the opportunities for scientific services — is that the method is hardly demonstrated outside the typical radiochemical society. The number of papers on NAA in e.g. Analytical Chemistry is already declining for many years, and the method gets hardly any attention at large spectroscopic meetings. There are fewer and fewer technical schools and universities with introductions and practical training on NAA. There is little awareness on the new developments and opportunities of the method for modern days' research and requests.

A remaining problem is that automation in NAA — indispensable for effective and economic operations — is hardly commercially available, and often has to be developed in-house. This may hamper many small NAA laboratories to become interesting for large-scale and/or parallel requests, to become competitive to other methods of analysis and to obtain the funds to compensate for budget cuts.

REFERENCES

[1] ROMICK, J.D., RIGOT, W.L., QUINN, T.J., Neutron activation analysis in an industrial setting: NAA at the Dow Chemical Company, Transact. Am. Nucl. Soc. **77** (1997) 22–23.

[2] KLOK, G., BOSSUS, D., VAN SLUIJS, R., "10 Years of k_0-NAA in an Industrial Laboratory", Proceed. 2nd k_0-Users Workshop (Ljubljana, Slovenia, 1996), ISBN 86-80023-27, p. 133.

[3] BODE, P., Automation and Quality Assurance in the Neutron Activation Facilities in Delft, Accepted for publ. in J. Radioanal. Nucl. Chem.

[4] BODE, P., From misconception to a must: the measured merits of TQM and accreditation in INAA, J. Radioanal. Nucl. Chem. **215 (**1) (1997) 51–57.

[5] BODE, P., Detectors and detection limits in INAA. I. General theoretical relationships between detector specifications and detection limits, Radioanal. Nucl. Chem. **222** (1997) 117–125.

[6] BODE, P., Detectors and detection limits in INAA. II. Calculated and observed improvements in detection limits with large Ge-detectors, well-type Ge-detectors and Anti-Compton spectrometers, J. Radioanal. Nucl. Chem. **222** (1997) 127–132.

[7] ZEISLER, R., A high-capacity gamma-ray spectrometer facility in the NIST irradiation laboratory, Transact. Am. Nucl. Soc. **79** (1998) 8.

A STRATEGY FOR THE SURVIVAL AND ENRICHMENT OF NAA IN A WIDER CONTEXT

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Abstract. A review of the current trends in NAA, its applications and the use of research reactors for NAA is given. A case is made for a more versatile, interdisciplinary approach towards NAA, operating in the context of a larger national or regional nuclear analytical center where other nuclear and non-nuclear analyses can be combined.

1. INTRODUCTION: GENERAL THESIS

It should be stated at the outset that the theme of the Meeting is very timely; many experienced users and practitioners of NAA have been concerned for some years about trends in usage (or non-usage) of NAA. Indeed, in my opinion, the situation is approaching a crisis point and the topic of this meeting could without great exaggeration be retitled "How to ensure the survival of NAA and research reactors". In this revised title two worrying trends are identified: the survival and maintenance of NAA itself and the availability of research reactors: obviously the first is almost totally dependent on the second. But it is also true that the continued existence of research reactors is in turn dependent on a coherent, intelligent, useful and viable scientific programme for their utilization in which NAA should have a major role. Therefore these two strands are interconnected. However, there are other important factors and a wider socio-political context to be considered.

This paper is written from the standpoint of the developed countries, particularly in Europe. The situation in developing countries is rather different, and the priorities and problems of a different character. In Europe, the two trends mentioned above are related to some inescapable facts of life, and it is sensible to consider them, even though we may not be able to alter them greatly. The first is the anti-nuclear climate in which scientists and society as a whole are operating. In this environment it is very difficult to persuade Ministries and other bodies financing scientific investment and formulating policies to maintain (let alone enhance) a viable programme in nuclear science, with the necessary infrastructure. We all know that research reactors in the developed world are approaching the ends of their working lives – many are over 30 years old. The building of new research reactors is highly problematic (e.g. Oak Ridge, Munich), and the renovation of existing ones to extend their lifetime almost as difficult. Numerous examples illustrating these statements can be brought forward. The trend to closure of research reactors continues inexorably; for example in the UK there is now only one research reactor left (University of London). The reactor at Seibersdorf, on the doorstep of the IAEA, is now to be closed[1], and so on.

Another important factor is development and change in scientific research and changes in staffing, training and education. While NAA and other nuclear analytical methods (NAMs) have unique advantages, there have been great advances in competing techniques, which often now surpass NAA in terms of sensitivity and speed. NAA itself is a mature technique, where dramatic improvements are not to be expected. The study and practice of radiochemistry is less popular; fewer universities and institutions now offer education and training in this discipline, while the age structure of its practitioners is unfavourable, many experienced radiochemists now approaching retirement age.

[1] The Austria reactor at Seibersdorf has been shut down in 1999 (note Ed.).

In the context of the above facts I therefore feel it would be unrealistic to close our eyes to the politico-social climate and merely evaluate promising trends in NAA, identify areas of growth and development, and suggest some scientific guidelines to try to enhance the utilization of research reactors for NAA, though some suggestions in this respect will be given below.

This paper therefore puts forward the proposal that a more versatile, interdisciplinary approach is required, operating in the context of larger national or regional nuclear analytical centres. Such centres should be more cost-effective, have a greater utilization of facilities, be more goal-oriented, run educational and training courses, pool knowledge from and operate in collaboration with other relevant complementary non-nuclear methods, and be concerned with both pure and applied research and development. Such centres are much more likely to attract funding from both national and international bodies. We will return to this theme in the last section.

2. PROMISING TRENDS IN NAA

2.1. Instrumental NAA (INAA)

INAA continues to grow in importance and in the range of its capabilities and accuracy. This has been facilitated by improvements in both hardware and software. In terms of hardware we can enumerate bigger, higher efficiency detectors, increased usage of well-type detectors (with more attention given to the problems of geometry calibration, and coincidence corrections [1]), the advantages of anti-coincidence arrangements for gamma-spectrometry and improvements in the data-handling capacity of the electronics, e.g. "loss-free" systems. Software is becoming more powerful and in view of the dangers of using it simply as a "black-box", there has also been a growing awareness of the need to validate results and inter-compare different software [2] programs, evaluating their strengths and weaknesses.

The use of k_o-INAA continues to spread and extensive experience with this technique has revealed few problems and good accuracy. The present status of the technique and typical applications are summarised in the Proceedings of the 2nd Workshop on k_o-INAA, held in Ljubljana [3]. Heydorn and Damsgaard [4] also showed how k_o-factors can be used to validate and check relative standards in NAA. Recently, Bossus and Van Sluijs reviewed the range of applications for k_o-INAA in a Dutch chemicals and materials group [5]. The major applications are for panoramic analyses of solids and organic liquids, analysis of catalysts (solids and slurries), the analysis of industrial slurries, the determination of halogens, analysis of samples for which no other in-house technique has yet been calibrated, and finally as a check or referee method for a second opinion.

2.2. Quality assurance/Quality control

The role of NAA as a reference method (or referee method) is one of its more important uses and also cost-effective (inaccurate analyses are the most expensive). NAA continues to be a or even the major technique in certification of reference materials (RMs), and is important as a totally independently based method in certification and intercomparison studies. Its non-destructive and multi-element nature is particularly valuable in the assessment of possible inhomogeneity in candidate RMs [6].

One of the features of NAA which is unique and under-utilized in the above field of QA/QC is its ability to validate or cross-check the data it produces by performing independent analysis by an alternative route, either using different isotopic nuclear reactions and/or the use of INAA and RNAA. This ability to check its own data we have termed the self-validation

principle [6, 7]. Recently we developed this approach further with examples, and published a table giving alternative isotopic reactions of analytical use for over 30 elements [8].

Another aspect of QC in NAA is the growing awareness of the need to evaluate and check potential errors, the importance of performing an uncertainty budget and determining whether experimental variations fall within the limits set by the uncertainty budget. In this way the presence of unaccounted or unknown errors can be detected, and the analytical procedure be brought into a state of statistical control [9, 10]. Recommendations for improvement of the accuracy of NAA in the analysis of biological samples produced by an earlier IAEA AGM in 1984 are still relevant and worth studying [11].

2.3. Radiochemical NAA

The general trend is towards less use of RNAA, which is used generally for ultratrace analysis (e.g. As, Cr, Mn, Ni, Se, V) and for some important elements where limits of detection by INAA are often inadequate, especially in biological materials (e.g. Cu, Cd, I). In separations the tendency is to more simplicity and determination of individual chemical yields for each separation (if one is taking the trouble to perform RNAA the accuracy should be ensured by recovery measurements). Radioisotopic tracers are usually the easiest method of measuring such chemical yields; the desirable properties of such tracers and examples of their use have been considered [12, 7]. From an extensive literature we can select some examples of ultratrace analysis by RNAA for vanadium [13], thallium [14] and nickel [15]. The use of RNAA for determination of some important radionuclides is mentioned in section 3.1.

In the case of multi-element RNAA, k_o-factors can be combined with chemical yields to perform k_o-RNAA independently of the relative standard method.

2.4. Speciation analysis

The use of NAA after preseparation of particular chemical forms before irradiation, sometimes termed “chemical NAA” or “molecular NAA” is growing, and promotes the utilization of NAA in the increasingly important field of speciation. Since facilities, techniques, apparatus and reagents have all been greatly improved with respect to contamination, preseparations can often be carried out without prejudicing the results. Some of the papers presented at this meeting describe such applications of NAA in speciation analysis (Chatt [16], Chai [17]). In our group we began with speciation analysis of Cr(III) and Cr(VI) in waters [18], separation of metallothionein proteins from rat brain with RNAA for mercury metabolism [19], and speciation of arsenic in biological samples using ion exchange followed by INAA of individual fractions [20].

However, it seems evident that NAA can only be properly applicable in speciation work when the detection of the element is particularly favourable (or particularly difficult by other methods). NAA, compared to other chromatographic techniques which can be coupled on-line to an element-specific detector (e.g. ICP-MS), is slow and expensive, and crucially, basically off-line. This means the course of separation cannot be followed while it is in progress. Hence applications of NAA in speciation will be limited.

3. INCREASED UTILIZATION OF HUMAN POTENTIAL AND SKILLS — INTERDISCIPLINARY STUDIES

3.1. General

In order to enhance research reactor utilization particularly for NAA, it seems to me that increasingly interdisciplinary studies and applied and goal-oriented projects need to be undertaken on a larger scale. Activation analysts, especially those with a chemical background, have an excellent basis for co-operating in and leading such studies. In many centres such is already the case, particularly smaller groups were over-specialisation cannot be afforded and staff are of necessity versatile. At our reactor in Ljubljana, since the group is small and our institute the only one in this field in the country, we have of necessity become engaged in a very wide range of projects, co-operating with groups from many other institutions. (The nature of our funding on the basis of competition for projects also ensures that we have to seek funds over a wider sphere of interest). Such a situation is becoming common everywhere, except perhaps in larger state-financed organisations. Though many of the possible fields to which activation analysts can usefully contribute are known, it is worth listing some of these from our experience and that of others.

3.2. Radioecology

Since Chernobyl almost all groups with the ability to measure radioactivity, at least by gamma spectrometry, have become involved in radioecological studies: Activation analysts are in an advantageous position as far as radiometry is concerned with respect to traditional radioecologists, usually having a greater familiarity with the basis of radioactive measurements, and a better appreciation of problems of accuracy and precision, calibration and validation. In addition to facility in handling radioactivity, the preparation and use of tracers, and appreciation of some pitfalls in their use makes their contribution to field experiments in radioecology valuable.

With relatively little effort, activation analysts can acquire a good working knowledge of other measurement techniques such as beta counting, including liquid scintillation, and of alpha spectrometry. Radiochemically trained activation analysts or radiochemists will already be at home in these areas and can contribute to better or more rapid methods of measuring radioactivity (radiometric methods).

Some very useful combinations of NAA and radioecology are possible. For example, we showed recently [21] that traditional alpha spectrometry of the radioisotopes of uranium and thorium (used in many fields involving dating, disequilibrium studies, geological and marine tracing, radiology, etc.) can be advantageously combined with INAA of U and Th (as ^{238}U and ^{232}Th) so as to allow those two nuclides to function as internal standards. This then means that in alpha spectrometry the chemical yields and counting efficiency are not required, nor is there any need to add external isotopic tracers such as ^{232}U and ^{229}Th. Alternatively, if INAA is combined with traditional tracer-added alpha-spectrometry, an independent data set can be obtained for quality control purposes.

Other applications include using INAA to determine stable elements of interest in radioecology, e.g. Cs (the specific activity of $^{134, 137}$Cs is often important). Other similar elements e.g. Na, K, Rb are also often useful. INAA can be used with advantage to determine Sc, Al and Ti which are considered to be biologically inert elements and their presence indicative of passive physicochemical uptake, i.e. contamination of plants by soil and dust (in

determination of transfer factors), or adsorption of colloids and particulates in the case of Sc found in algae [22].

Another underused application of NAA is in the determination of a number of radionuclides. The most important of these are ^{235}U, ^{238}U, ^{232}Th, ^{230}Th, ^{237}Np, ^{231}Pa, ^{129}I and ^{99}Tc; this topic was recently reviewed and illustrated by us elsewhere [23].

For some of these nuclides NAA is an excellent method; for others it represents a useful alternative where it is necessary to have data by an independent method for certification or intercomparison studies.

3.3. Pollution studies (air, water, soil and biomonitoring)

This topic is so wide and so much has been published in the last decade that we can scarcely attempt a review here. Most activation analysts are already engaged in such studies so that they need little emphasis.

Such studies are, it should be emphasised, best performed in the context of wider interdisciplinary projects in which various types of data are combined, such as meteorological data, data on toxicity/essentiality, medical and epidemiological data, combined with data handling and statistical tools.

3.4. Other studies

The IAEA itself has for a number of years intensively promoted the use of nuclear methods, particularly NAA, in the fields listed above in 3.2 and in many other studies such as occupational health and exposure, studies of nutrition and pollutants/contaminants, medical applications, tracer-aided studies in the environment, biology, etc.

Listing in detail the role of NAA in these studies is not the purpose of this contribution; in my view it is the framework and strategy within which NAA operates and the interdisciplinary context that needs to be altered, as described elsewhere in this paper.

4. COLLABORATION WITH OTHER NUCLEAR-BASED TECHNIQUES

Nuclear analytical methods (NAMs) have a number of common features and common problems. This topic was recently reviewed by De Goeij [24]. As well as accelerator-based techniques such as PIXE, Rutherford back-scattering (RBS) and other ion beam analytical (IBA) techniques, elastic recoil detection analysis (ERDA), and nuclear-reaction analysis (NRA), important are other microanalytical methods such as scanning transmission ion microscopy (STIM) and secondary electron microscopy (SEM). The range of applications is similar to those of NAA, except that emphasis is largely on microanalysis not bulk analysis. This, together with the elements which can be determined (generally light elements) makes these NAMs highly complementary with NAA.

As well as the above mentioned NAMs, there are those techniques based on neutrons (suited to the fluxes and beams available in research reactors), many of which are related to NAA. These include neutron radiography, neutron induced autoradiography using solid-state track detectors (SS-NTDs), neutron dosimetry and depth profiling. Developments in new detectors, imaging techniques and applications are rapid. For many of these techniques and applications relatively small equipment and running costs are characteristic. These topics were reviewed at an IAEA Technical Committee Meeting in Vienna in 1993 [25], another similar meeting in

Lisbon in 1997 [26], and at the European Conferences on Non-Destructive testing (most recently in Copenhagen 26–29 May, 1998).

The group for reactor physics at our reactor centre in Ljubljana is active in all of these fields. A review of activities in this area, written in 1993, was given by Rant et al [27]. To mention a few more recent examples, improved selective radiography with NTDs using a fully automatic image analysis system allows selective imaging of ^{10}B distribution in tissue samples [28] (of great value in improving boron neutron capture therapy), or depth profiling of ^{10}B in silicon [29]. In neutron radiography, direct near-real time neutron imaging detectors such as imaging plate neutron detectors (IP-ND) or charge-coupled device cameras, in combination with Gd-based scintillating screens, enable recording of time frozen images of concentration profiles of moisture (or other hydrogenous liquids) in porous materials. This allows e.g. the efficiency of hydrophobic treatments in the building industry to be tested.

However, once again it should be emphasised that it is the co-operation of NAMs (including NAA) that is important for the survival of reactors (and other installations). Unfortunately, little real collaboration between NAA and other NAMs in goal-oriented research of an applied character seems to take place in practice. The meetings and journals of publication are also not the same, so that in spite of our common interests, we need to work at bringing NAA practitioners and others NAM users together.

Another area where little co-operation exists, in spite of many common interests, is that between radioanalysts and those who use radionuclides for diagnosis or therapy in medicine.

5. COLLABORATION WITH OTHER NON-NUCLEAR ANALYTICAL TECHNIQUES

Evidently, in all collaborative, interdisciplinary research studies and more applied projects a range of analytical techniques should be available to complement and enrich NAMs. This should include atomic absorption, fluorescence and emission spectroscopy, HPLC and GC systems with appropriate detectors, mass spectrometers for stable isotope analysis and ICP-MS. More specialised techniques such as those for protein separations, amino acid analysis, enzymatic procedures, etc. may be required in more biochemically oriented projects.

Particularly valuable are isotopically based techniques involving mass spectrometry. Extremely powerful and sensitive methods combining accelerators and mass analysers have developed in the last decade. Accelerator mass spectrometry (AMS) allows determination of 10^4–10^6 atoms in favourable cases. Determination of plutonium [30], application of ^{26}Al to tracer studies in humans [31, 32, 33], studies of ^{10}Be, ^{26}Al and ^{34}Cl in the environment and hydrology [34], as well as the better known high sensitivity ^{14}C analysis are all rapidly developing fields, which often have affinities or a close relationship to radioisotopic and radiometric techniques, and other NAMs.

6. SYNTHESIS AND STRATEGY

Although in sections 2 and 3 we identified some trends in NAA and areas where reserves exist which could be better exploited by NAA techniques, and by practitioners of NAA, as suggested by the thesis of the introductory section, in our view this will not basically influence the utilization of research reactors for NAA; a more radical integrated approach is required. One way to ensure the survival of research reactors where NAA is practised is the creation of regional nuclear analytical centres, where a range of NAMs, supplemented by non-nuclear analytical methods (especially isotopically based ones) could be practised, coupled to training and teaching in these disciplines to ensure a future supply of qualified and motivated

scientists. Evidently, the IAEA should play a leading role in the establishment and policies of such centres.

It seems to me that the establishment of such centres is a sure way to maintain the existence of NAMs and do useful research. It should also be remembered that the more isolated and fragmented are the various sectors of analytical science, the weaker their importance and bargaining power; the more interdisciplinary and united we are, the greater our chance of funding and of influencing policy!

How (and how many) such centres should be established, their staffing, particularly their organisation and structure, and their ability to perform interdisciplinary research effectively seem to be the issues which should be addressed at this meeting in the discussion sessions, and brought forward in the recommendations. One other possibility is to establish networks of co-operating specialists, linked in projects (as is the case presently for some large EU funded collaborations e.g. COST), but not necessarily structurally or organisationally united.

REFERENCES

[1] BLAAUW, M., Nucl. Instr. Methods. Phys. Res. A., 1998, in press.
[2] INTERNATIONAL ATOMIC ENERGY, Intercomparison of Gamma-ray Analysis Software Packages, IAEA-TECDOC-1011, IAEA, Vienna (1998).
[3] Proceedings 2nd Int. Workshop on k_o-INAA, Ljubljana, Sept. 30–Oct. 3, 1996, J. Stefan Institute, Ljubljana, 1997.
[4] HEYDORN, K.,, DAMSGAARD, E.,J. Radioanal. Nucl. Chem. **179** (1991) 87–91.
[5] BOSSUS, D.A.W., VAN SLUIJS, R., Czech J. Phys. **49** (1999) 255–262.
[6] BYRNE, A.R., Fresenius J. Anal. Chem. **345 (**1993) 144–151.
[7] BYRNE, A.R., Biol. Trace Element Res. **43–45** (1994) 529–537.
[8] BYRNE, A.R., KUČERA, J., "Role of the self-validation principle of NAA in the quality assurance of bioenvironmental studies and in the certification of reference materials", Proc. Int. Symp. Harmonisation of Health-related Environ. Measurements using Nucl. and Isotopic techniques (Hyderabad, 4–7 Nov. 1996), IAEA Vienna (1997) 223–238.
[9] HEYDORN, K., J. Radioanal. Nucl. Chem. **151** (1991) 139–148.
[10] HEYDORN, K., Validation of NAA Techniques, in Quality Assurance for Environmental Analyses (QUEVAUVILLER, Ph., MAIER E.A., GRIEPINK, B. Eds), Elsevier (1995) 89–110.
[11] BOWEN H.J.M., et al., "IAEA Advisory group on Quality assurance in biomedical NAA", Anal. Chem. Acta **165** (1984) 1–29.
[12] SCHELHORN, H., GEISLER, M., J. Radioanal. Nucl. Chem. **83** (1984) 5.
[13] KUČERA, J., BYRNE, A.R., in Ref. 7, 349–359.
[14] KUČERA, J., VOBECKY, M., SOUKAL, L., ZAKONCKY, D, VENOS, D., J. Radioanal. Nucl. Chem. **217** (1997) 131–137.
[15] KUČERA, J., BYRNE, A.R., J. Radioanal. Nucl. Chem. **168** (1993) 201–213.
[16] CHATT, A., This TECDOC.
[17] CHAI, Z., This TECDOC.
[18] FAJGELJ, A., KOSTA, L., Vestn. Slov. Kem. Društvo **34** (1987) 175–183.
[19] FALNOGA, I., KREGAR, I., ŠKREBLIN, M., TUŠEK-ŽNIDARIČ, M., STEGNAR, P., Biol. Trace Element Res. **37** (1993) 71–83.
[20] ŠLEJKOVEC, Z., BYRNE, A.R., DERMELJ, M., J. Radioanal. Nucl. Chem. **173** (1993) 357–364.
[21] BYRNE, A.R., BENEDIK, L., Anal. Chem. **69** (1997) 996–999.

[22] SANSONE, U., BELLI, M., RICCARDI, M., ALONZI, A., JERAN, Z., JAĆIMOVIĆ, R., SMODIŠ, B., MONTARARI, M., CAVOLO, F., Sci. Total Environ. **219** (1998), 21–28.
[23] BYRNE, A.R., 13th Radiochemical Conference, Marianske Lazne, Czech Republic, April 20–24, 1998; Czech J. Phys. **49** (1999) 263–270.
[24] DE GOEIJ, J.J.M., J. Anal. Chem. **51** (1996) 1148–1152.
[25] INTERNATIONAL ATOMIC ENERGY AGENCY, Report of a Technical Committee Meeting, Vienna, 4–7 May, 1993, Use of Neutron Beams for Low and Medium Flux Research Reactors: Radiography and Materials Characterization, IAEA-TECDOC-837, Vienna (1995).
[26] INTERNATIONAL ATOMIC ENERGY AGENCY, Proceedings of IAEA Technical Committee Meeting on Neutron Beam Research, Lisbon, Sept. 10–12, 1997, Nuclear and Technological Institute (ITN), Sacavem, Portugal (1998).
[27] RANT, J., PREGL, G., GLUMAC, B., RAVNIK, M., in Ref. 25, 55–65.
[28] SKVARČ, J., ILIĆ, R., YANAGIE, H., RANT, J., OGURA, K., KOBAYASHI, H., Nucl. Instr. Meth. B, **152** (1999) 115–121.
[29] IZERROUKEN, M., SKVARČ, J., R. Ilić, Radiat. Meas. **31**, 1–6 (1999) 141–144.
[30] FIFIELD, L.K., GRESSWELL, R.G., DI TADA, M.L., OPHEL, T.R., DAY, J.P., CLACKER, A.P., KING, S.J., PRIEST, N.D., Nucl. Instr. Meth. Phys. Res. B **117** (1996) 295–303.
[31] BARKER, J., DAY, J.P., AITKEN, T.W., CHARLESWORTH, T.R., CUNNINGHAM, R.C., DRUMON, P.V., LILLEY, J.S., NEWTON, G.W.A., SMITHSON, M.J., Nucl. Instr. Methods Phys. Res. B. **52** (1990) 540.
[32] FIFIELD, L.K., ALLAN, G.L., STONE, J.O.H., OPHEL, T.R., Nucl. Instr. Methods Phys. Res. B. **92** (1994) 85.
[33] KING, S.J., OLDHAN, C., POPPLEWELL, J.F., CARLING, R.S., DAY, J.P., FIFIELD, L.K., GESSWELL, R.G., KAXIN LUI, DI TADA, M.L., Analyst **122** (1997) 1049–1055.
[34] REEDY, R.C., TUNIZ, C., FINK, D., Nucl. Instr. Methods B, **92** (1994) 335.

ANNEX

The J. Stefan Institute (IJS), Ljubljana

The Laboratory for Radiochemistry of the Department of Environmental Sciences, IJS, has available a TRIGA MK II 250 kW reactor (upgradeable) with pulsing capability. The reactor was completely renewed in 1993. Also recently opened at the Reactor centre is the Microanalytical Centre, equipped with a new tandem accelerator, dedicated to PIXE, RBS, IBA, STIM, etc.

The Laboratory for Radiochemistry (which was completely renovated and re-equipped in 1997) has since its earliest days been oriented to applications of INAA and RNAA in environmental studies, the life sciences and nutrition, biomonitoring, studies of reference materials, as well as radioecology and applications of tracer methods.

Because of the small size of the country (2 million) and the fact that IJS is the only institution engaged in radioanalytical methods, the projects and research interests of the group are wide-ranging and interdisciplinary; collaboration with other institutions and research groups is encouraged. Since the Laboratory now operates within the framework of the Department of Environmental Sciences, multitechnique, goal-oriented interdisciplinary projects are facilitated.

An important part of the activities of the Laboratory is education and research training at B.Sc., M.Sc., Ph.D. and post-doctoral levels, in co-operation with the University of Ljubljana.

INDUSTRIAL APPLICATIONS OF NEUTRON ACTIVATION ANALYSIS

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Abstract. Neutron activation analysis has been widely used in the industry and over the years played a key role in the development of manufacturing process as well as monitoring of the process flow. In this context NAA has been utilized both in R &D, and in the factory as a flexible analytical tool. It has been used successfully in numerous industries including broad categories such as Chemical, Pharmaceutical, Mining, Photographic, Oil and Gas, Automobile, Defense, Semiconductor and Electronic industries. Dow Chemical owns and operates a research reactor for analytical measurements of samples generated in both R & D, and manufacturing area in its plant in Midland, Michigan. Although most industries do not have reactors on their campus but use an off site reactor regularly, and often have in-house neutron sources such as a ^{252}Cf used primarily for NAA. In most industrial materials analysis laboratory NAA is part of a number of analytical techniques such as ICP-MS, AA, SIMS, FTIR, XRF, TXRF etc. Analysis of complex industrial samples may require data from each of these methods to provide a clear picture of the materials issues involved. With the improvement of classical analytical techniques, and the introduction of new techniques e.g. TXRF the role of NAA continues to be a key bench mark technique that provides accurate and reliable data. The strength of the NAA in bulk analysis is balanced by its weakness in providing surface sensitive or spatially resolved analysis as is required by many applications.

1. INTRODUCTION

In the following pages first hand experiences of using NAA as a part of a larger analytical laboratory consisting of many other methods are described. The applications given below were in the Photographic, Chemical, and Semiconductor manufacturing industries. In each case NAA was a critical complementary technique needed for successful resolution of manufacturing problems.

2. APPLICATIONS IN PHOTOGRAPHIC INDUSTRY

2.1. Precise doping of silver halide crystals

A very important consideration in the manufacturing of the photographic films is the precise doping of the silver halide crystals with ultra low level impurities such as Ir, Rh, and Au. Typical levels are in the low ppb range, however the performance of the films such as speed or sharpness depend on maintaining a precise doping level in the high volume manufacturing. Analysis of these dopants was found to be best performed by NAA with a pre-irradiation separation chemistry. In a comparison of many techniques such as AA, ICP-MS, XRF, and others, NAA provided the most repeatable and reliable data over a long period of time (> 2 years). The high thermal neutron cross sections of these dopants made NAA a very sensitive technique, and analysis at ppb level could be performed with great precision. The method was susceptible to very few extraneous factors, and immune from a number of background related abnormalities. Although a pre-irradiation separation was necessary to avoid activating long lived Ag or intense halide radioactivities the final result of measuring Ir count rates proved to be highly sensitive, and precise. A shift in the manufacturing process due to dopant variation could be monitored, and reliable non-varying photographic films can be produced over a product life cycle. In this case NAA turned out to be a vital technique for the successful manufacturing of a high volume product sold through out the world.

A related monitoring application, although did not require the use of the reactor is worth mentioning. Chemically most photographic films are mixed halides e.g. AgBrCl, AgBrI etc. The mole ratio of the halides determines the sensitivity of the color films. Using an in-house ^{252}Cf neutron source the halide ratio in these mixed halides can be readily, and reliably measured. Conventional techniques requiring dissolution of these halides resulted in very

poor quality data not suitable for controlling a manufacturing process. Yet NAA provides such an easy and elegant analysis of this key industrial process proving to be an excellent application of the technique in the industry.

2.2. Impurities in Gelatin

Gelatin used as the emulsion in which Ag halides are dispersed is required to be high purity. Presence of trace impurities such as Hg, Se can be highly inhibitive to the photoactive processes and latent image formation. A reactor based NAA of the gelatin was found to provide superior quality trace analytical data when compared with other techniques such as hydride generation, and cold vapor atomic absorption.

3. APPLICATIONS IN THE CHEMICAL INDUSTRY

3.1. Iodine in polymers

Bulk chemical manufacturing often require final product to have low level impurities. For example a bulk hydrocarbon polymer may not contain any halogen impurities. In one such application where the final polymer used in the automobile industry needed to be essentially free of iodine. Iodine being volatile was difficult to analyze by conventional dissolution methods at low level. The short half life and the good thermal neutron cross section made the detection of iodine by NAA in polymers a sensitive, and reliable analysis. The level of iodine in this high volume polymer production was monitored by NAA over a long period time. Samples from the production line were collected, and periodically sent to off site reactor for accurate analysis of iodine. Using this logistic a control chart was made for the process, and maintained for the manufacturing of the polymer.

3.2. Metallic catalysts remainders in high volume polymers

A second example in this industry also involves production of high volume polymers e.g. polyester. Often time metallic catalysts are used in the manufacturing process, and are not desirable to be present as impurities in the final product. A Mn or Sb contamination can be easily picked up in the polyester or PET (polyethylene terephthalate) manufacturing. These impurities can be readily detected by NAA at a low ppm level, Methods such as XRF can be used for the metallic impurities analysis for thin polymer films. However XRF sensitivity often is not good enough to use in the low level monitoring applications. Catalytic impurities such as Sb being a toxic metal need to be controlled, particularly when the product (e.g. PET) is used in food related applications such as the beverage containers. NAA is ideal for monitoring the Sb levels resulting from the use of the Sb oxide catalyst in the manufacture of PET polymers.

3.3. Benchmarking of other methods

Use of NAA as a bench mark technique for calibration of other methods is widely practiced. In many suitable applications NAA data is highly quantitative. Since it is free from cross contamination from reagents or is not easily affected by absorption (both neutrons, and gamma rays are penetrating radiation) the analysis is robust and reliable. This makes NAA very suitable for bench marking conventional methods such as XRF, AA, ICP, etc. The role of bench marking is not limited to chemical industry alone. NAA bench marking has been used in other industries as well.

4. SEMICONDUCTOR INDUSTRY APPLICATIONS

4.1. Trace impurities in high purity Si

In the production of high purity Si needed for VLSI manufacturing NAA was very effective for the whole semiconductor industry. Trace impurities in starting Si is required to be below sub ppb level. Monitoring of bulk impurities in Si introduced during the crystal growth process is best done by using NAA. The matrix is very favorable since the half life of the radioactive Si is short (i.e. ^{31}Si, $t_{1/2}$ 2.6 hours), and the elements of interest (transition metals) have long half lives a very high sensitivity analysis can be obtained. Detection limits for some elements such as Au (highly undesirable in semiconductor Si) can be in the range of few parts per trillion. Bulk analysis by NAA has established the quality of Si used in the semiconductor manufacturing today.

A relatively new technique, Total reflection X-ray Fluorescence (TRXRF) has been widely used for trace level monitoring of surface impurities in the Si wafers. TRXRF cannot measure bulk impurities since it is designed as a surface technique. However the detection levels are in the range of $-2 \cdot 10^9$ atoms.cm^{-2}. Advantages of the TRXRF technique is the rapid turnaround time, and that the instrument can be placed inside the fabrication floor for automated analysis by semiskilled technician.

4.2. Contamination control in VLSI manufacturing

Cross contamination which is a very big issue in VLSI manufacturing can be monitored effectively by NAA. The key for this type of analysis is to have the low detection limit since semiconductor devices are susceptible to small contamination. Often times samples are clean room quality rags or wipes with irregular shape so that only a bulk analysis done non-destructively is reliable. Most other techniques suffer from sample preparation for this low level analysis. The elements of interest in this case are Co (cobalt silicide process), Cu (copper metallization), etc. NAA for these analysis can provide higher quality data compared to ICP-MS. However the turnaround time for ICP-MS is much better, and prove to be more important.

4.3. Bulk analysis of quartz

Bulk analysis of the quartz used in the furnace for Si wafer processing is another example where NAA is highly suitable, and is routinely done either by the chip manufacturers or their quartz supplier. High sensitivity and low detection limits are obtained in this matrix with little sample preparation. The competing techniques of ICP-MS and TRXRF are not as convenient, particularly TRXRF yields only surface concentrations. Use of high purity quartz is essential in the high volume chip manufacturing where low level transition metal contamination can be a disaster and lead to non functional dies. Other materials that need bulk analysis in semiconductor industry include SiC (used in vertical furnaces), various plastic packaging materials for U, and Th (precursors of alpha particle emitters), aluminium metal (used as interconnect), and thin films of silicon dioxides, Ti, TiN, W etc. However for thin film cases alternate methods such as the TRXRF provide rapid and reliable analysis, and is often the method of choice.

4.4. Use of other nuclear analytical methods

It is important to note a few important analysis for the semiconductor industry that are done using a reactor neutron source but are not neutron activation analysis by definition. These are neutron depth profiling (NDP), and prompt gamma activation analysis (PGNAA). Both of

these methods are closely related to NAA, and have similar materials analysis considerations. NDP has been uniquely used for depth profiling boron in thin CVD (Chemical Vapor Deposition) silicon oxide films (- μm) such as BSG (borosilicate glass), BPSG (borophosphosilicate glass), and BPTEOS (borophospho tetraethyl ortho silicate) films. Analysis require a neutron beam, and data is collected while the samples are under neutron irradiation. NDP can depth profile a few micrometer thick films, and is particularly suitable for the semiconductor industry since devices are manufactured as thin films on Si wafers. The boron depth profiling is also widely done using SIMS (secondary ion mass spectrometry). However NDP can provide highly quantitative data, and accurate profile free of interfacial yield problems that plague the SIMS methodology. Anytime a depth profile across an interface such as the SiO_2/Si is needed NDP has an advantage since there is no direct effect of the interface in the neutron irradiation of the boron. SIMS on the other hand has different sputtering yield across the interface and results in a profile that need to be carefully interpreted. The limitations of NDP is also its strength, i.e. only a few elements can be analyzed by this technique e.g. B, N, O (labeled with ^{17}O isotope).

The second related method, PGNAA is also very important in the semiconductor industry for measuring bulk hydrogen content of thin films produced in CVD process. Many CVD process use organo metallic gases such as TEOS or silane for silicon oxide films, TDNMT (tetrakis dimethyl amine Titanate) for CVD TiN films etc. The final thin films contain hydrogen often at a level of up to 40–50 atomic%. Hydrogen contents of these films can have significant effect on the device performance (e.g. hot carrier injection) and therefore need to be taken into account in a manufacturing process. PGNAA can measure the bulk hydrogen in CVD films quantitatively, and provide a bench mark for many of these processes. Other techniques such as FTIR and nuclear reaction analysis have been used to obtain chemical nature of hydrogen, and the distribution of hydrogen respectively. These measurements when used in conjunction with PGNAA provide the complete analysis of hydrogen for comprehensive understanding of the CVD thin films.

5. SUMMARY AND CONCLUSIONS

NAA plays a complementary role in materials analysis in an industrial analytical laboratory. There are applications where it is highly desirable, and may play the dominant role as the method of choice e.g. bulk analysis of Si. The advantages of NAA are still the minimum sample preparation, and ultra high sensitivity while turnaround time, and lack of spatial resolution is a significant limitations.

The continued use of NAA in industries critically depend on having NAA trained professionals in the industrial organizations. It has been used most widely and innovatively when a NAA professional was part of the materials analysis laboratory. Interaction of the NAA professional at the research reactor with the industrial analytical laboratories is also very important for enhanced use of the technique. This is not quite as effective as having someone inside the industrial analytical laboratory however. Therefore training of young professionals in NAA, and other nuclear analytical methods is a key for the increasing use of the research reactors for materials analysis needs.

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