ANALYTICAL APPLICATIONS OF NUCLEAR TECHNIQUES

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Printed by the IAEA in Austria
October 2004
STI/PUB/1181

ANALYTICAL APPLICATIONS OF NUCLEAR TECHNIQUES

INTERNATIONAL ATOMIC ENERGY AGENCY
VIENNA, 2004

IAEA Library Cataloguing in Publication Data

Analytical applications of nuclear techniques. — Vienna : International
Atomic Energy Agency, 2004.
p. ; 24 cm.
STI/PUB/1181
ISBN 92–0–114703–1
Includes bibliographical references.

1. Nuclear industry. 2. Nuclear medicine. 3. Nuclear chemistry.
4. Environmental monitoring. I. International Atomic Energy Agency.

IAEAL 04–00379

FOREWORD

Isotopic and nuclear techniques play an important role in many facets of our daily life and are an integral part of our socioeconomic development. Be it in medical diagnostics and treatment, in food security, in industrial process control or in luggage screening at airports, these techniques serve basic human needs, strengthen industrial competitiveness or increase our understanding of nature and its processes. However, triggered in part by accidents in the field of nuclear power, a segment of the general public perceives anything nuclear as inherently unsafe, ignoring the great number of nuclear applications beneficial for health, welfare and the environment. Most of these sentiments are caused by a lack of information and by a misconception. This situation can only be rectified by showing the many opportunities and advantages provided by nuclear applications.

The idea of compiling a book such as this emerged from the fact that, parallel to a general decline in interest in studying the natural sciences, an obvious lack of students interested in nuclear chemistry and radiochemistry was observed during the past decade, even in the most industrialized countries. The question of how to attract students goes hand in hand with that of how to make other interested groups within society aware of the beneficial applications of nuclear analytical techniques (NATs). It became obvious that attractive and easily understandable public information material was sorely lacking. The subject is well covered in expert journals and is well represented at scientific meetings, but very little printed material is available for the general public to explain the profitable application of nuclear techniques to many kinds of problems. A call to researchers involved with these techniques to submit short and illustrative contributions yielded almost fifty contributions within six months, an indication that nuclear analysis is vital and plays an important role in the armoury of current analytical techniques.

These descriptions of useful applications of NATs were selected to be of general interest, relevant for specialists from other fields or even for the stimulation of the nuclear analytical community to go beyond the regular confines of their work and extend the scope of their efforts. This book should serve to attract the attention of young people interested in the natural sciences and could be used by teachers to disseminate nuclear knowledge to the young generation. It is hoped that more compilations of this kind from other nuclear areas will follow to enhance public awareness of the many beneficial contributions of nuclear techniques.

The IAEA wishes to thank all the authors who contributed to this publication. It is hoped that it will stimulate others to create similar reports on their fascinating work. The IAEA officer responsible for this publication was M. Rossbach of the Division of Physical and Chemical Sciences.

EDITORIAL NOTE

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Introduction

A comprehensive record of all the facets of different applications of nuclear analytical techniques (NATs) is hardly possible because of the diversity of fields where NATs have been found indispensable since their advent more than 50 years ago. Owing to emerging alternative analytical techniques being more rapid, less costly and (perhaps) more user friendly, some people consider nuclear techniques as outdated, old fashioned or just too tedious. But, as will be seen from evidence given in this book, NATs are not dead; rather they enjoy a fascinating, rich span of applications, partially covering niches where other analytical techniques might not be competitive or where they simply cannot be applied at all.

The International Atomic Energy Agency, in accordance with its mandate, has put considerable effort into the preservation of nuclear knowledge and dissemination of first hand information. With the strong support of many experts, the IAEA has compiled this overview of current applications of NATs. The contributions included in this book describe a variety of nuclear techniques and applications, such as those in the fields of environment and health, industrial processes, non-destructive testing, forensic and archaeological investigations, cosmochemistry and method validation. The contributions describe the advantages of nuclear techniques in, for example, analysing trace elements in submilligram samples of a single hair or in kilogram samples of municipal waste. Halogenated organic compounds as well as major and trace inorganic constituents are analysed in a variety of solid and liquid matrices. Several techniques are applied to investigate the authenticity of art objects and the origin of extraterrestrial material. Many applications of NATs in industrial process control or in the production of high-tech materials are described, highlighting the socioeconomic benefit of these techniques in our daily lives.

The techniques covered in this compilation range from classical instrumental neutron activation analysis (INAA), its radiochemical derivative RNAA, in-beam methods such as prompt γ neutron activation analysis (PGNAA) and accelerator mass spectrometry (AMS), to X ray fluorescence (XRF) and proton induced X ray emission (PIXE) spectroscopy. Isotopic techniques to investigate element behaviour in biology and medicine, and also to validate other non-nuclear analytical techniques, are described. Destructive and non-destructive approaches are presented, along with their use to investigate very small and very large samples, archaeological samples and extraterrestrial samples. Several nuclear analytical applications in industry are described that have considerable socioeconomic impact wherever they can be implemented.

This IAEA publication is presented to the nuclear community, non-nuclear scientists, politicians, journalists, decision makers and students (our hope for the future) as a basis for them to critically assess the potential of nuclear techniques to benefit human development, to contribute to the needs of our society, and to help in solving some particular questions that might otherwise be difficult to attack. If this book could enable some readers to better differentiate between the benefits of nuclear techniques and the risks of nuclear energy, stimulate some readers to consider a particular nuclear analytical technique for application or raise further interest in the subject, it would be a great success in the promotion of these valuable tools, which are mature but not at all obsolete. Nuclear analytical and related techniques will play a significant role in the near future, and it will be challenging as well as exciting to master their potential.

Part I

BASIC RESEARCH, COSMOCHEMISTRY

Nuclear fission is no invention of humans: The natural reactor of Oklo two billion years ago

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Problem

On 2 December 1942 — and thus almost exactly four years after the discovery of nuclear fission — Enrico Fermi and his co-workers achieved the first self-sustaining chain reaction under the grandstand of the football stadium of the University of Chicago. However, since 1972 we have known that — as happens frequently in the history of science — nature was far ahead of modern physics. Nature created a nuclear reactor almost two billion years ago, when there were as yet no humans on the Earth. This reactor must have functioned for more than several hundred thousand years and thereby set free around 100 billion kW·h of heat — as much as a modern nuclear power plant would produce as nuclear energy in just four years. More than 10 t of uranium would thereby have fissioned, forming in the process about 4 t of plutonium and around 10 t of fission products. How can this be investigated?

On 7 July 1972, in a routine isotopic analysis of a sample of uranium ore that was sent from the west African state of Gabon (Fig. 1) to the French isotope separation plant Pierrelatte, a content of only 0.7171 atomic per cent (at.%) of ^{235}U, instead of 0.7202, was determined. However, a discrepancy of only 0.4%, because of the accuracy of the mass spectrometer of ±0.0006 at.%, was striking. The possibility that this sample could be explained as a mixture with depleted uranium from nuclear technology was excluded by the contents of ^{236}U and ^{234}U. The former would have had to be formed in a nuclear reactor and the latter would have been enriched with the ^{235}U fraction during isotope separation. The technicians who carried out these analyses were very exact, and they checked the analysis records of previous batches from the Oklo mine. They then noticed greater departures (eventually finding contents as low as 0.296 at.%!). These showed that the isotope depletions were greater for higher total uranium contents. Since geochemical isotope effects in such heavy elements are excluded, the only explanation was that nuclear fission was somehow involved. Thereupon analyses were undertaken of associated elements, e.g. neodymium, that are formed in high yield in nuclear fission. Here anomalies in the isotope composition relative to natural neodymium were explained on the basis of their known nuclear fission yields (Fig. 2). Clear proofs for nuclear fission were also shown in other elements from zinc (atomic number (Z) = 30) to dysprosium (Z = 66). The clearest is the low abundance of ^{142}Nd, since it is not formed in fission.

How has this come about?

The conditions for a self-sustaining chain reaction are: enough uranium with the right enrichment (with normal water as moderator, a minimum content of 50% uranium with at least 1 at.% of ^{235}U is necessary), enough moderator (at least 6% water is needed to moderate the fast spontaneous fission neutrons) and as little neutron poison (e.g. lithium, boron and rare earths) as possible.

The half-lives of uranium isotopes with mass numbers 235 and 238 differ substantially, and ^{235}U decays more than six times faster than ^{238}U. That means the isotope content of ^{235}U two billion years ago must have amounted to approximately 3–4 at.% (the ^{235}U content is 3.3% in today's light water reactors).

The uranium content of ores from Oklo was especially high, so we can imagine that the entrance of rainwater could have started a self-sustaining chain reaction, initiated by neutrons from the spontaneous fission of ^{238}U or by neutrons formed by secondary reactions of cosmic radiation. Also, if the neutron flux was very low, approximately 10^7–10^8 $n \cdot cm^{-2} \cdot s^{-1}$ (small research reactor fluxes are typically 10^{11}–10^{12} $n \cdot cm^{-2} \cdot s^{-1}$), this configuration must have led to temperatures becoming so hot that the water vaporized and the reactor cyclically shut itself down.

What about fission products and plutonium?

The burnup is calculated to be approximately 4 × 10^5 MW·h/t, corresponding to a not insignificant amount of fission products. These are no longer detectable today, after such a long time, since they have been transformed through radioactive decay into stable isotopes. From changes in isotope ratios, however, with modern mass spectrometry one can learn a lot about the migration of fission products. Thus it is possible to

FIG. 1. Geographic location of Oklo.

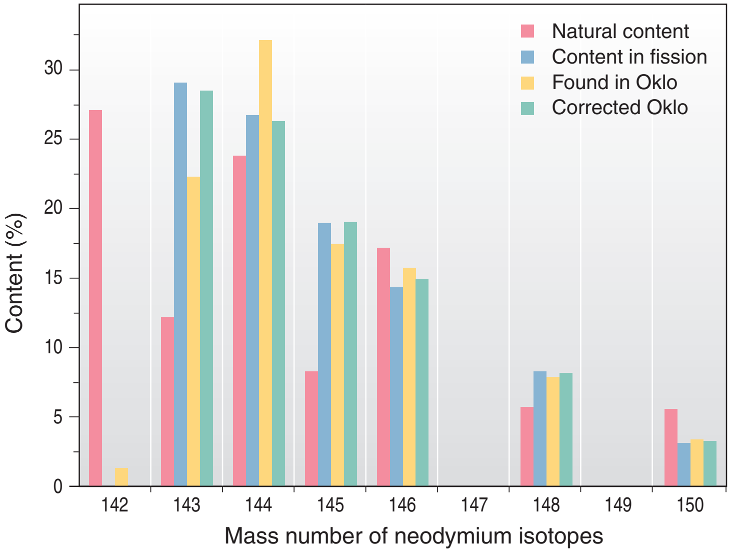

FIG. 2. Proof of nuclear fission has been obtained from isotopic changes in neodymium, an element that occurs rarely in nature.

obtain a ‘glimpse’ of a final repository after millions of years, a better picture than any computer simulation has been able to provide. And although no technical barriers and no optimized geological conditions hindered the migration of fission products and plutonium, this picture shows that uranium, neptunium, plutonium, niobium, yttrium, technetium, zirconium and the rare earth metals have remained in their original places. Elements that have migrated are alkali metals, e.g. rubidium and caesium, the alkaline earth metals barium and strontium, the noble gases, molybdenum, cadmium, lead and iodine. It must also be noted that, in this historical final repository, the heat production of approximately 50 W/m^2 (through the intermittent chain reaction) was many times higher than in the final repositories planned today for highly radioactive waste.

Since the discovery of Oklo other natural nuclear reactors have been looked for, but so far no others have been detected with certainty.

Final destination: Earth

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Problem

Cosmic ray particles induce nuclear reactions in extraterrestrial matter. The resulting nuclides, called cosmogenic nuclides, reflect the history of the irradiated body (e.g. meteorites, the Moon, Mars) [1]. So meteorites found on the Earth preserve information about their whole 'lifetime' (Fig. 1), which means the time the material was:

- Part of the parent body, e.g. an asteroid, a moon or a planet (2π exposure age);
- Part of a smaller body, a meteoroid travelling through space (4π exposure age);
- Shielded from cosmic rays by the Earth's atmosphere between its fall and recovery (terrestrial age).

The production rates of these nuclides are functions of the individual shielding conditions, namely the shielding depth of the analysed sample in the parent body and the meteoroid, but also of the preatmospheric radius of the meteoroid. Naturally, the buildup of the nuclides is time dependent. The number of atoms of any stable nuclide steadily increases at constant rates during the irradiation, whereas the number of radionuclides increases and eventually approaches the radionuclides' saturation values as a function of their half-lives. When we compare depth dependent and size dependent production rates evaluated from physical model calculations with experimental data of meteorites, we are able to reconstruct the exposure and, in the case of meteorite finds,

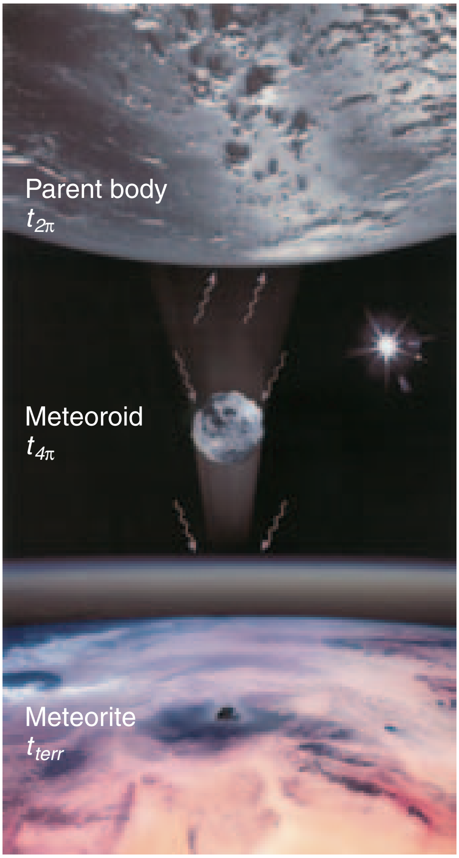

FIG. 1. A meteorite's history.

the terrestrial history of the meteorites. Moreover, the meteorites can also yield information on the constancy and spectral distribution of the cosmic radiation itself. Finally, the terrestrial ages of meteorites can help in reconstructing phenomena on Earth, for example in glaciology (Antarctica) or climate research (hot deserts).

Why nuclear analytical techniques?

Owing to the scarcity of the investigated material and the low concentrations of the cosmogenic nuclides, a highly sensitive analytical technique is needed. For long lived cosmogenic radionuclides, accelerator mass spectrometry (AMS) meets this requirement.

AMS, like conventional MS, detects the absolute number of atoms not yet decayed, unlike less sensitive counting techniques that monitor radionuclide decay. The difference between MS and AMS is mainly the energy to which the ions are accelerated. The use of higher ion energy (MeV instead of keV), which allows the extraction of negative (molecular or elemental) ions from the ion source and charge changing to multicharged positive ions by shell electron stripping, results in the elimination of interfering isotopes (injected molecular ions) and isobars. Consequently AMS has a sensitivity about five orders of magnitude higher than traditional MS. Detailed information on the technique and numerous applications can be found in Refs [2, 3].

In principle, a number of nuclear analytical techniques (NATs) are suitable for determining concentrations of long lived radionuclides in natural materials. However, AMS is more sensitive and generally faster than other NATs such as:

(a) Radiochemical neutron activation analysis (RNAA) for radionuclides such as ^{53}Mn and ^{129}I (half-lives of 3.7 million years and 15.7 million years, respectively);
(b) Radioactive decay counting techniques for ^{10}Be, ^{14}C, ^{26}Al, ^{36}Cl, $^{59/63}$Ni, ^{60}Fe (half-lives of 100 years to 1.5 million years), etc.

Less than 1 million atoms or 10^{-15} g of the analyte chemical isolated from the matrix of a sample can be quantified by AMS.

How to solve the problem?

As an example, we describe the techniques and the results for one of the most interesting and hence most extensively investigated meteorites, the lunar meteorite Dar al Gani 262 (DG262) [4]. A single piece of 513 g was found in the Libyan Sahara by a commercial expedition on 23 March 1997 (Fig. 2).

A crushed aliquot of 73 mg was made available to us through the Institut für Planetologie, Münster, for the determination of the long lived cosmogenic radionuclides ^{10}Be, ^{26}Al and ^{53}Mn via AMS. Radiochemical separation of aluminium, beryllium and manganese from the matrix was performed after addition of adequate amounts of stable carrier. ^{10}Be and ^{26}Al were measured at the PSI/ETH 6 MV tandem accelerator facility in Zurich, while the development of a gas filled

FIG. 2. Lunar meteorite DG 262 at the find site in the Libyan part of the Sahara. The red magnet is ~1 cm × 1 cm in size.

analysing magnet system (GAMS) in conjunction with a 14 MV tandem in Munich gave us the ability to analyse ^{53}Mn contents. For the transformation of measured radionuclide ratios into activities, we used the following half-lives: ^{10}Be ($t_{1/2}$ = 1.51 million years), ^{26}Al ($t_{1/2}$ = 0.705 million years) and ^{53}Mn ($t_{1/2}$ = 3.7 million years). From the same sample a liquid aliquot was taken for the measurement of the main target elements (aluminium, calcium, iron and magnesium) by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis. The results were used as an input for the model calculations performed.

Under the a priori, but very likely, assumptions that the last relevant irradiation time on the Moon (2π geometry) was long, and the terrestrial age of DG262 was short (as generally expected for meteorite finds from hot deserts) compared with the half-lives of the investigated radionuclides, we can uncover the secrets of DG262's history. Comparing all three radionuclide concentrations of DG262 with experimental data of lunar depth profile samples, which are similar to the meteorite with respect to the main target elements, the only consistent explanation is a deep lying, shielded origin (depth: 55–85 g/cm^2) of DG262 on the Moon. Furthermore, we can estimate, by comparison with model calculations for a 4π geometry, a maximum value of less than 150 000 years for the Moon–Earth transit time for DG262 as a small meteoroid (radius about 10 cm).

For meteorites originating from the Moon, the identification of paired meteorites is of special interest. This means not only determining whether two pieces found on Earth belonged to the same meteoroid (terrestrial pairing), as is the question for every meteorite find, but also determining if two pieces started their travel from the Moon through space at the same time (ejection pairing). Unfortunately, samples brought back from the Moon showed that different petrological and chemical features do not exclude a neighbouring origin. The main evidence against an ejection pairing is a large difference in cosmogenic nuclide concentrations. The mean values of ^{10}Be and ^{26}Al activities of another lunar meteorite found in Antarctica in 1993, Queen Alexandra Range 93069 (QUE93069), for example, agree perfectly with those of DG262. Their ejection times and terrestrial ages are also nearly the same. Furthermore, there are some other hints of a common origin for these meteorites, for example a nearly identical Ca/Ti ratio (an indicator of highland or mare origin) and high iridium and nickel abundances, which can be interpreted as meteoritic contamination (during the time on the Moon). At present, a joint launch of the paired meteorites QUE93069/QUE94269 and DG262 cannot be ruled out. For more detailed information on lunar meteorites, see Ref. [4] and references therein.

Acknowledgements

We are grateful to S. Neumann and R. Michel, University of Hannover, for performing the model calculations. This work was partially funded by the German Research Foundation (DFG) and the Swiss National Science Foundation.

References

[1] HEIDE, F., WLOTZKA, F., Meteorites. Messengers from Space, Springer-Verlag, Berlin (1995).

[2] GOVE, H.E., From Hiroshima to the Iceman: The Development and Applications of Accelerator Mass Spectrometry, Institute of Physics Publishing, Bristol (1998).

[3] TUNIZ, C., TUNIZ, J.R., FINK, D., HERZOG, G.F., Accelerator Mass Spectrometry: Ultrasensitive Analysis for Global Science, CRC Press, Boca Raton, FL (1998).

[4] BISCHOFF, A., et al., Petrology, chemistry, and isotopic compositions of the lunar highland regolith breccia Dar al Gani 262, Meteorit. Planet. Sci. **33** (1998) 1243–1257.

Chemical characterization of extraterrestrial materials returned from space by mission programmes

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In this century, our activities in science and technology will be greatly expanding. Following the Apollo missions of the USA, not a few space mission programmes aiming to collect and return extraterrestrial matter from space have been planned and will continue to be planned, not only in the USA but also in Japan and other countries. Once a sample is returned to the Earth, very serious limitations exist on its analysis for element composition, especially if the sample amount is small. Our task is to determine the exact chemical composition of such a small amount of sample non-destructively.

Why nuclear analytical techniques?

There are several requirements for analytical techniques to be applied to a limited amount of sample recovered from space. First of all, non-destructive analysis is desirable; the same specimen used for chemical analysis can be reused for other purposes, including detailed chemical analysis by destructive methods. Secondly, the method of chemical analysis used must have high analytical sensitivity for as many elements as possible. Thirdly, the analytical data thus obtained need to be highly accurate. In consideration of these requirements, it can undoubtedly be concluded that activation analysis is the most suitable method. Here activation analysis covers neutron induced prompt γ ray analysis, instrumental neutron activation analysis and instrumental photon activation analysis. These three are all methods of non-destructive analysis. In order to satisfy the second and third requirements, these methods are successively performed, as explained below in detail.

How to solve the problem?

It is well known that activation analysis has high sensitivity in determining the chemical composition of solid samples. Recently, inductively coupled plasma mass spectrometry (ICP-MS) has been increasingly used for determining chemical composition, mainly because it has high analytical sensitivity for many elements and does not involve chemical procedures for assaying. Thus ICP-MS can compete with activation analysis and is even believed by some to be superior to it in analytical sensitivity, and especially in cost performance, which must be generally admitted. One of the advantages of activation analysis over ICP-MS is that activation analysis can analyse solid samples without destruction. This means that the same specimen can be used for duplicate analyses using the same or different analytical methods and even for other observations such as physical and petrological analyses. This advantage becomes very significant when the sample size usable for analysis is very limited, as is the case of samples returned from space.

We used two types of activation analysis — neutron activation analysis (NAA) and photon activation analysis (PAA). In NAA, instrumental NAA (INAA) is commonly used. In addition to INAA, we also used neutron induced prompt γ ray analysis (PGA). PGA is a relatively new methodology in NAA and has several merits as a non-destructive analytical tool: PGA can be applied to large samples such as pottery and meteorites [1], most major elements constituting geological and cosmochemical samples can be non-destructively determined [2], residual radioactivities are as low as natural background levels [3], and so on. The last named feature enables us to reuse the same sample used in PGA for INAA and instrumental photon activation analysis (IPAA). IPAA, which can be performed by using a linear electron accelerator, is as effective as INAA in analysing solid samples and can work somewhat as a complementary analytical tool to INAA [4]. As both INAA and IPAA are non-destructive methods, the same specimen can be used for both methods if a sufficient time interval for the decay of induced radioactivities is allowed between INAA and IPAA.

The analytical procedure we designed was applied to real meteorite samples weighing 100 mg as follows. Samples were first analysed by PGA. For this analysis, we used a cold neutron beam to enhance the analytical sensitivity, because the sample amount usable for PGA was about 50 mg for each sample. We could determine a total of 16 elements by using a comparison method in which several reference standards were adopted. The remaining samples were divided into two portions, which were subsequently subjected to INAA and IPAA. In INAA, samples were successively irradiated three times with different irradiation times (10 s, 1 min and 20 min) using two different reactors at the Japan Atomic Energy Research Institute. As a result, a total of 26 elements were determined. For determining element abundances, we used a comparison method, which will be replaced with a k_0 method in the near future. In IPAA, samples were activated with photons of 30 MeV end point energy. In determining element concentrations, we adopted a comparison method using chemical reagents and geological and cosmochemical reference samples. The samples were irradiated twice successively for 30 min and 6 h.

On the basis of the data obtained by three non-destructive nuclear analytical methods, we could characterize the samples cosmochemically. For characterizing extraterrestrial material in terms of chemical composition, several groups of elements play important roles. Volatile elements are highly sensitive to the thermal activity the sample experienced. By PGA, H and S can be non-destructively analysed. Refractory lithophile elements also are an important group of elements. For instance, Ca/Si and Mg/Si ratios are characteristic of individual groups of meteorite samples. Refractory siderophile elements are another group of elements that are recognized to be as informative as refractory lithophiles.

After the initial analysis using non-destructive activation methods, we plan to analyse the same sample using destructive analytical methods such as radiochemical activation analysis and ICP-MS for detailed studies. Needless to say, the applicability of nuclear analytical methods described here can be extended to small sized solid samples other than geological and cosmochemical samples, for example soil and sediment samples.

References

[1] NAKAHARA, H., et al., Some basic studies on non-destructive elemental analysis of bulky samples by PGA, J. Radioanal. Nucl. Chem. **244** (2000) 405–411.

[2] LATIF, S.K., et al., Prompt gamma-ray analysis (PGA) of meteorite samples, with emphasis on the determination of Si, J. Radioanal. Nucl. Chem. **239** (1999) 577–580.

[3] EBIHARA, M., OURA, Y., Applicability of prompt gamma-ray analysis to the initial analysis of the extraterrestrial materials for chemical composition, Earth Planet. Sci. **53** (2001) 1039–1045.

[4] EBIHARA, M., et al., How effectively is the photon activation analysis applied to meteorite samples, J. Radioanal. Nucl. Chem. **244** (2000) 491–496.

Confirmation of the common origin of two meteorites that fell in widely separated locations on the Earth

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Problem

On the sunny afternoon of 25 August 1994 the Baszkówka meteorite (Fig. 1) fell on a farmer's freshly ploughed field in the vicinity of Warsaw. It was spotted by a woman working in a nearby garden and soon recovered, while still warm. It was secured, and a few months later it was acquired by the National Geological Institute in Warsaw.

Meteorites, which are sometimes poetically called 'messengers from space' [1], are extraterrestrial objects the analysis of which can provide unique information on the composition of the Earth's interior, i.e. the region that is not and probably never will be accessible to our direct observation. It is generally assumed that the Earth as a whole has a composition the same as that of the oldest meteorites, called chondrites, which represent the oldest matter in the Solar System.

FIG. 1. The Baszkówka meteorite.

Meteorites are rare findings. Although it is estimated that over 4000 meteorites fall to the Earth each year, only a small percentage of them are recovered. The world collection by 1969 amounted roughly to 3000. A further 10 000 have been found since then in the hot and cold deserts of the Antarctic, Australia and Africa.

The full list of Polish meteorites does not exceed 20, and the second most recent one (Łowicz) fell in 1935. Baszkówka is unique, because it is a single, oriented stone (i.e. it was recovered as an unbroken stone that had maintained a constant position during its passage through the atmosphere) weighing 15.5 kg and covered with a beautiful glassy crust of solidified melted rock (regmaglypt), which suggests that the meteorite did not somersault when passing through the Earth's atmosphere.

Thanks to the fact that the fall was observed and the meteorite was collected soon afterwards, it was preserved almost intact and is a very beautiful and precious object. Such well preserved meteorites are extremely rare and represent only a fraction of a per cent of all collected meteorites. An initial investigation carried out in Polish and foreign laboratories showed that although it is an ordinary chondrite, classified as belonging to chemical class L and petrographic group 5, it shows some peculiar features which indicate that it is in many respects a unique specimen.

Soon afterwards it was noted that this object was very similar to another meteorite that had fallen three years earlier, on 21 August 1991, in Niger, and which was later renamed the Mount Tazerzait meteorite. The news about this meteorite reached the scientific community through the Swiss Meteorite Laboratory about five years after it fell to Earth. The fall was observed by local Tuaregs, who broke the original stone, which weighed about 110 kg, into numerous fragments. Fortunately the fall occurred on the birthday of the son of one of the Tuaregs, so the date of the event could be easily established.

The similar abundances of noble gases and their isotope composition, the very long exposure ages (60–70 million years) of both meteorites, and the similarities of their exteriors, petrological properties and dates of fall (25 and 21 August, respectively) suggested that both meteorites might have been members of a meteoroid stream and were ejected from the same source region of their parent body. On the other hand, although both meteorites were given a preliminary classification as L chondrites, some peculiar features in their structure might indicate an origin and cosmic history different from those of the other known and described chondrites of this group.

Why nuclear analytical techniques?

Confirmation or rejection of such hypotheses would be made possible only by accurate measurement of the chemical composition of the meteorites. When our laboratory was entrusted with this task, the choice of neutron activation analysis (NAA) as a principal analytical method seemed to be a logical one. NAA is known as a reliable method capable of determining many trace elements from the same small sample with favourable detection limits. One should remember that each meteorite is a rare, unique and precious object, hence the masses that can be destined for analysis are as a rule small. Moreover, NAA has the unique feature, in comparison with other methods of inorganic trace analysis, of being essentially free from blank. Several elements can be determined by purely instrumental NAA without sample dissolution. For these reasons it is especially well suited for the analysis of such unique samples as meteorites. No wonder that it has very often been the method of choice for the analysis of precious meteorite samples, also in the past.

How to solve the problem?

In our work we have irradiated 100–250 mg samples of pulverized meteorites together with several elemental standards and certified reference materials (CRMs) for 3 min in the nuclear reactor MARIA at a thermal neutron flux density of 1.6×10^{13} n · cm^{-2} · s^{-1} (ϕ_{fast}/ϕ_{th} = 0.005) and cooled the samples for at least 4–6 h. Several γ ray spectrometric measurements were then performed after decay times ranging from 7 h to 2 months. The following elements could be determined in this way: As, Au, Co, Cr, Cu, Eu, Fe, Ga, Ir, K, La, Mn, Na, Ni, Os, Sc, Se, Sm, Yb and Zn.

In addition, Au, Pd and Pt were determined by radiochemical NAA after preirradiation preconcentration on a chelating resin, Chelex 100. Details of the analytical procedure have been published [2–4].

NAA is not the most appropriate technique for the determination of macroconstituents. Therefore some elements were determined by classical methods (Al and P spectrophotometrically, Si gravimetrically, and Ca, Mg and Fe by complexometric titration). In addition, Hg was determined with an automatic Hg analyser employing two step Au amalgamation, heating decomposition and cold vapour atomic absorption.

The comparison of concentrations of individual elements in the Baszkówka and Mount Tazerzait meteorites is shown in Fig. 2. It can easily be seen that when the data obtained for Mount Tazerzait (y) are plotted against analogous data for Baszkówka (x) on a log–log scale, a straight line is obtained, which can be described by an equation: $y = 1.01256x - 0.0629$ (the coefficient of correlation amounts to $R = 0.9982$).

If the data for Pd are excluded (which would probably be justified, because Pd has the tendency to be concentrated in the metallic phase of the chondrite and hence it may be inhomogeneously distributed), the equation has the form $y = 1.006989x - 0.02972$, i.e. it represents almost a perfect fit ($y = x$) with the coefficient of correlation $R = 0.9997$.

Thus we could conclude that the Baszkówka and Mount Tazerzait meteorites have practically identical chemical compositions and it is almost certain that they have a common parent body.

On the other hand, while both meteorites are more similar to L chondrites than to any other group of meteorites, there are some features which indicate their difference from the population of L chondrites known until now. Wherever deviations from the mean composition of L chondrites were observed, the data for Baszkówka and Mount Tazerzait showed a similar trend, confirming once again the similarity of bulk composition of the two meteorites. It cannot be excluded that their common parent body may be different from those typical for most of the other L chondrites.

Reaching these conclusions would not be possible if NAA — the most powerful of the nuclear analytical techniques — were not available in our laboratory.

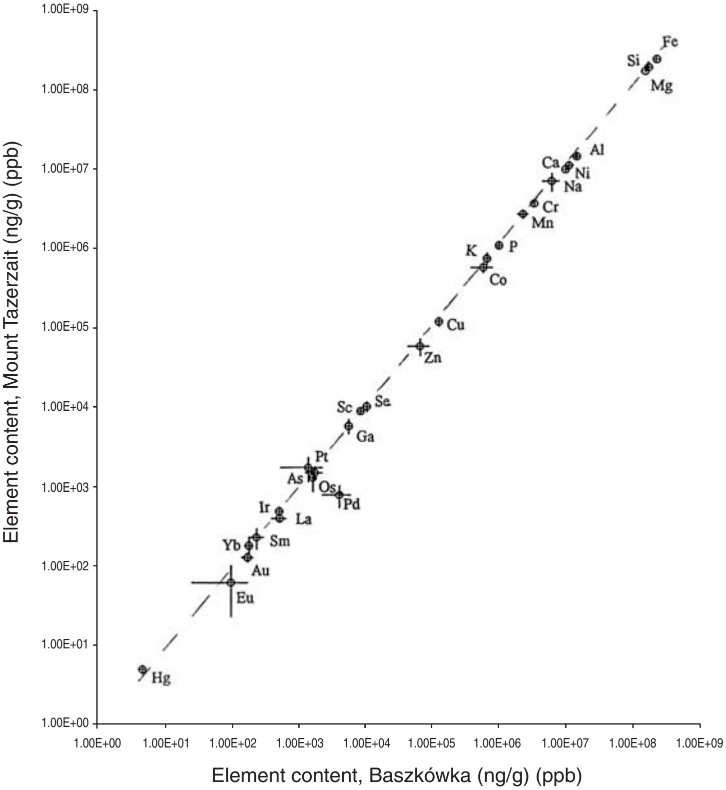

FIG. 2. Element concentrations of the Mount Tazerzait and Baszkówka meteorites.

References

[1] HEIDE, F., WLOTZKA, F., Meteorites, Messengers from Space, Springer-Verlag, Berlin (1995).

[2] DYBCZYŃSKI, et al., First chemical characterization of the new Polish meteorite "Baszkówka" by neutron activation analysis, Chem. Anal. (Warsaw) **44** (1999) 471–484.

[3] DYBCZYŃSKI, et al., The investigation of genetic relationship between the Baszkówka and Mt. Tazerzait chondrites by NAA and other methods, Chem. Anal. (Warsaw) **46** (2001) 477–488.

[4] DYBCZYŃSKI, et al., A study on chemical composition of Baszkówka and Mt. Tazerzait chondrites, Geol. Q. **45** (2001) 289–301.

Study of the migration behaviour of uranium in reactive barriers

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Problem

A radioindicator technique was used to investigate the migration behaviour of uranyl ions in layers containing adsorptive agents mixed with sand. A solution of uranyl nitrate prepared from natural uranium was doped with uranium ions activated by photonuclear reaction and was allowed to pass through columns containing different sorbents mixed with coarse grain sand. The path of the uranium through the column was traced by cyclic scanning measurements of the γ and X ray emission of the radioisotope from outside the column. An initial condition for the representativeness of the values obtained is equal migration behaviour of the natural uranium and the radiotracer. The aim of this work was to investigate the retention potential of the sorbents under study against uranium ions.

Why nuclear analytical techniques?

The conventional non-active approach to this problem requires continuous sampling of the solution at different levels inside the column and subsequent determination of uranium by, for example, spectrophotometry. This procedure has significant drawbacks. First, during sampling the normal flow of the solution is interfered with, which probably leads to non-representative results. Second, the sampling positions have to be predetermined at practical distances, thus the spatial resolution of measurement is limited. Third, the analyte concentration near the migration front might be beneath the limit of detection of the particular analytical method employed, so the actual front might not be clearly detectable. Finally, the influence of the natural uranium background, i.e. the matrix-inherent uranium, might render the tracer concentration insignificant, particularly near the migration front.

In contrast, using a radioindicator has the following advantages. First, no sampling is necessary since the measurement is carried out non-invasively. Second, since the measurement can be performed on a continuous scale at any level of the column (Fig. 1), the resolution of the concentration function can be selected as desired. Third, the sensitivity of measurement can be enhanced as required, without using excessive analyte concentrations, by providing a correspondingly large specific activity of the radioindicator. Moreover, the matrix background does not interfere, since it is not activated.

How to solve the problem?

Mixtures of coarse grain sand and either iron granulate or hydroxy apatite were prepared and transferred into polyethylene columns of 10 cm inner diameter and a height of 20 cm (Fig. 1). Thereafter an aqueous solution of uranyl nitrate (total uranium concentration 2.8 µg/mL) doped with ^{237}U as a radioindicator was pumped at a constant flow rate through the

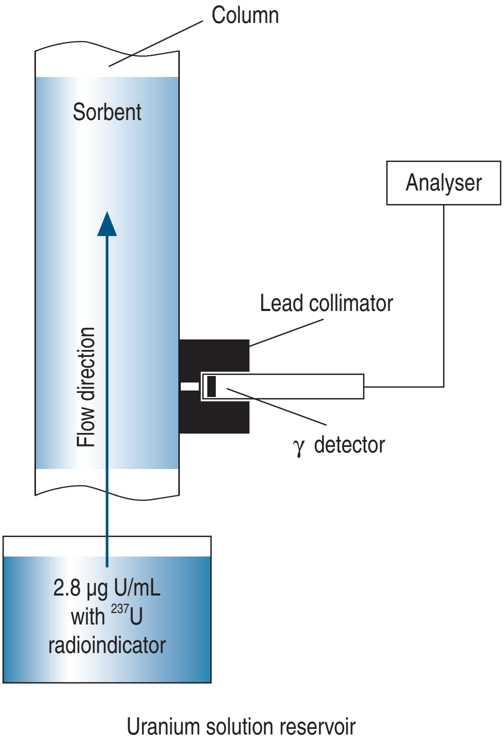

FIG. 1. Scanning radiation spectrometry.

column from the bottom upward. The radioindicator had been produced through a photonuclear reaction by irradiating U_3O_8 containing natural uranium with the bremsstrahlung of an electron linear accelerator. Over a total experimental period of about 800 h the uranium migration front was monitored by regularly scheduled scanning measurement of the photon emission of the radioindicator along the length of the column. This experiment was repeated using different concentrations of sorbents. The results allowed the time of breakthrough of the uranium at the end of the sorbent layer to be predicted with high precision. Furthermore, with the help of X ray radiography and computer aided tomography, the actual spatial distribution of the uranium in the column could be obtained.

Following the described experimental strategy, the migration behaviour of nearly any species (e.g. environmental pollutants) in any medium can be studied with comparatively little effort.

Bibliography

GARDNER, R.P., GUO, P., AO, Q., DOBBS, C.L., Appl. Radiat. Isot. **48** (1997) 1273–1280.

LANGMUIR, D., Geochim. Cosmochim. Acta **42** (1978) 547–569.

SIMON, F.G., MEGGYES, T., Removal of organic and inorganic pollutants from groundwater with permeable reactive barriers, Part 1. Treatment processes for pollutants, Land Contam. Reclam. **8** 2 (2000).

Measurement of nanoscale vacancies in materials

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Problem

Many characteristics of engineering materials, particularly hardness, electrical conductivity, gas permeability and so on, are determined not only by the constituent molecules but also by the vacancies that are created as a result of molecular packing. A macroscopic probe cannot be used to investigate these characteristics since these vacancies are of an atomic scale. A conventional atomic size probe, for example, consists of nitrogen gas which is made to adsorb in the vacancies to be measured. However, nitrogen molecules are not small enough for very small vacancies of around 0.1 nm. It is also impossible to measure 'hidden' vacancies totally inaccessible from the outer surface.

Why nuclear analytical techniques?

The positron is the antiparticle of the electron. It can be implanted in substances like metals or semiconductors and, since it has positive charge, it is captured in a vacancy where positive ions are lacking. In insulating materials, the positron can combine with an electron to form a neutral atom called positronium ($e^+ + e^-$: Ps). It is the smallest and the lightest of all atoms, and properly sits in a small vacancy. Both the positron and positronium can be implanted at some depth within a substance; even 'hidden' vacancies are accessible.

Once they are captured in a vacancy, the positron and positronium are annihilated with a lifetime which is determined by the vacancy size such that the larger the vacancy size the longer the lifetime (Figs 1 and 2). The relationship of the positron or positronium lifetime to the vacancy size is now well known both theoretically and experimentally.

How to solve the problem?

The lifetimes of the positron and positronium are very short, from 0.1 to several nanoseconds, but the technique is very simple (Fig. 3). Positrons are emitted from the radioisotope ^{22}Na implanted into the sample material. A 1.28 MeV γ ray that is emitted simultaneously with the positron is used to define the time of 'birth' (start) of the positron, and one of the

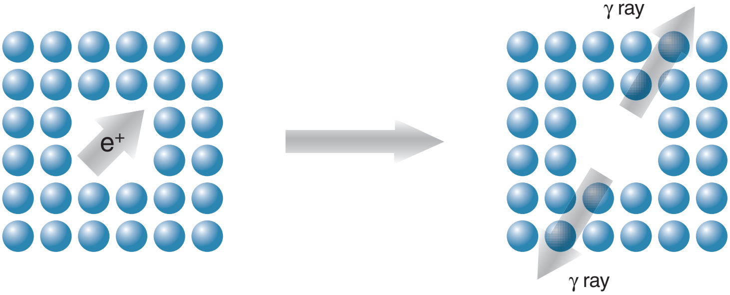

FIG. 1. Illustration of positron annihilation in a vacancy. The larger the cavity the longer the lifetime of the positronium before annihilation.

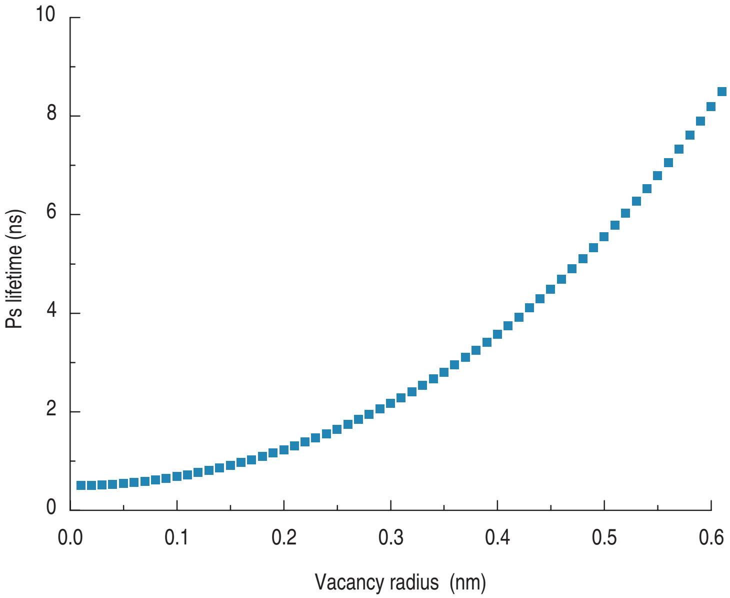

FIG. 2. Theoretical relationship between positronium lifetime and vacancy size. Using this relationship it is possible to evaluate the vacancy size from the measured positronium lifetime.

two 0.51 MeV γ rays that are emitted on positron annihilation is used to define the time of 'death' (stop). The time interval between these two γ rays is measured using fast electronic circuits.

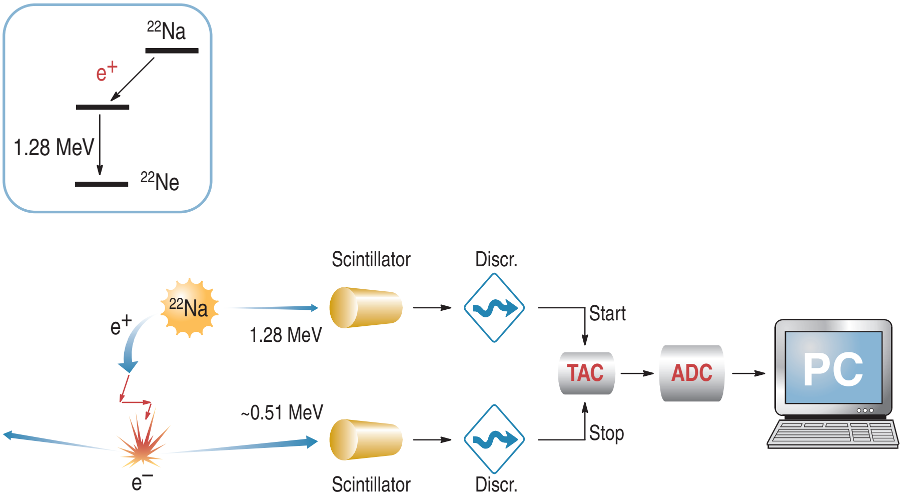

FIG. 3. Diagram of positron lifetime measurement method. Discr.: discriminator; TAC: time to amplitude converter; ADC: analogue to digital converter; PC: personal computer.

Part II

METHODS AND METHOD VALIDATION

Laser mass spectrometry

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Problem

Sensitive determination of extremely small amounts of long lived radioactive isotopes and their isotope composition, e.g. $^{239/240}$Pu, $^{89/90}$Sr and ^{41}Ca, in environmental, technical and biomedical samples by atom counting using selective laser based resonance ionization in combination with conventional mass spectrometry.

Why nuclear analytical techniques?

In the field of ultra-trace analysis of radioisotopes, the radiometrical determination of low concentrations of α and β emitters can have severe limitations: interferences from other radionuclides may exist, and the level of detection is dependent on the lifetime. For isotopes with long half-lives, measuring times of the order of up to a few days are often required, which might not be acceptable, for example in the event of an emergency. Here selective atom counting of the individual species of interest using laser mass spectrometric techniques has a number of advantages.

How to solve the problem?

Laser mass spectrometry applying resonant excitation and ionization by laser light and subsequent mass analysis (RIMS) provides a number of striking features: almost complete isobaric suppression, high to ultra-high isotopic selectivity and good overall efficiency. This allows the realization of extremely low detection limits, which presently lie in the range of about 10^6 atoms per sample, corresponding to less than 1 fg for most radioisotopes studied so far. Additionally, RIMS has the advantage of being a rapid technique, with measuring times in the range of a few hours, which makes it attractive for fast surveillance and for the case of an emergency. In comparison with most competitive techniques, only minor chemical treatments are needed for RIMS sample preparation.

At Mainz University different versions of RIMS for highly selective ultra-trace analysis have been developed that combine multistep resonance ionization in an atomic beam or vapour with well adapted mass spectrometry. By taking advantage of isotope shifts and hyperfine structures in the different atomic transitions involved, and by using narrowband continuous lasers, an extremely high isotopic selectivity can be obtained. The widespread analytical potential and applicability of the laser mass spectrometric method are utilized for the determination of long lived radioactive ultra-trace isotopes, in particular $^{239/240}$Pu, ^{99}Tc, $^{89/90}$Sr and ^{41}Ca. Apart from the determination of specific radioactive exposure in environmental and technical samples, a variety of other research problems can be tackled using this technique. These include problems in atomic physics, geochemical sciences, cosmochemistry and biomedical investigations. Depending on the individual applications, an overall efficiency of up to 10^{-3} in combination with an isotopic selectivity of as high as 10^{13}, which is mandatory, for example, for applications using ^{41}Ca, can be realized.

X ray fluorescence

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Problem

A method is needed to measure the element composition of materials such as soil, rock, scrap metal, painted surfaces, dust and more.

Why nuclear analytical techniques?

X ray fluorescence (XRF) spectroscopy is recognized as a very accurate non-destructive testing method for measuring the element composition of a material by irradiating a sample with high energy photons such as γ rays and observing the resulting XRF radiation emitted by the sample.

Handheld devices can be used for lead detection in painted surfaces, dust and soil, or for general analysis of soil (Fig. 1) or rock. The most important elements are lead, arsenic, chrome and cadmium.

How to solve the problem?

XRF spectrometers (Fig. 2) consist of a source of excitation radiation (an X ray tube for fixed systems or a radioisotope for portable systems), a radiation detector to detect the stimulated radiation from the sample and a display of the spectral output. In portable systems, built-in isotope identification software helps in comparing the wavelength of the stimulated X rays with known data. For further analysis, computers often are used.

Bibliography

JANSSENS, K.H.A., ADAMS, F.C.V., RINDBY, A. (Eds), Microscopic X-Ray Fluorescence Analysis, Wiley, Chichester (2000).

FIG. 1. Use of a handheld XRF device for analysis of soil (photo courtesy of NITON Inc.).

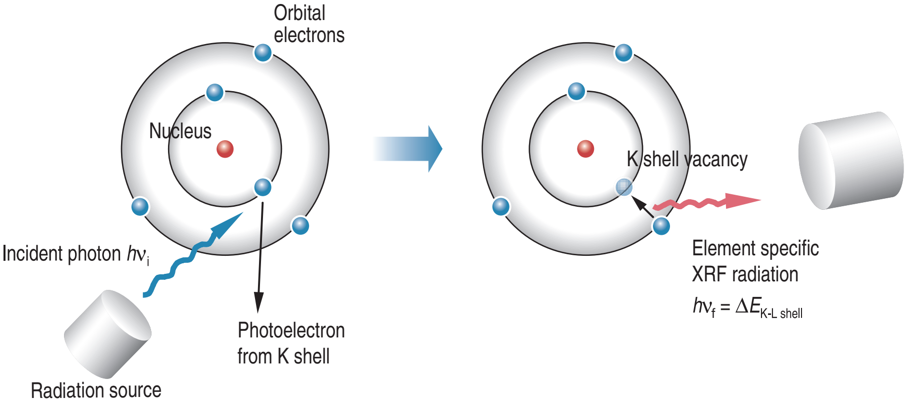

FIG. 2. XRF spectrometer.

Advanced X ray fluorescence techniques

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Problem

One of the goals of analytical techniques is to obtain in a non-destructive way the chemical composition and physical characteristics of individual particles, for example airborne particles or particles from soil dust or from a specific emission source. Detailed information on the composition and physical characteristics of individual particles is of importance in environmental pollution studies and forensic investigations, and it can be helpful in solving many other analytical problems. In a similar way, analyses of minute samples are carried out to quantify the degree of heterogeneity of the material with respect to element concentration, determination of porosity and identification of regions with the highest accumulation of the essential elements.

Another goal that is difficult to achieve is to carry out a bulk chemical composition analysis not under laboratory conditions but in situ. For various reasons, there is very often a need to identify and quickly evaluate the chemical composition of a material in the field or to monitor an area in search of the places with the greatest abundance of an element. The aim is to carry out the analytical process outside the laboratory with minimal or no sample preparation.

Why nuclear analytical techniques?

The X ray fluorescence (XRF) technique in the energy dispersive mode (EDXRF) has been used to deal with these analytical problems. XRF spectrometry is a well established instrumental analytical technique used for chemical composition analysis. XRF is a non-destructive multielement technique capable of determining elements with atomic number $Z \geq 11$ (sodium) in different matrices. The samples to be analysed require minimal or no preparation, and the technique is regarded as non-destructive. Typical relative detection limits vary from about 0.1 to 10 mg/kg, and in special configurations they can reach values as low as 1 μg/kg.

The technique is based on measurements of the characteristic X ray radiation emitted by atoms following their de-excitation to the ground electronic state. The excitation of the atoms is achieved by means of a photoelectric effect in which primary photons from an external source, for example photons emitted by an X ray tube or by a radioisotope source, illuminate the specimen and interact with inner atomic shell electrons. In this process an electron is expelled from its position in an atom, leaving a vacancy in the atom's shell. In a subsequent process the electronic configuration of the atom is rearranged, resulting in emission of the characteristic X ray photons. The energy of the emitted photons is specific for a given element, and their intensity depends on the concentration of that element in the sample. The range of photon energies covered by the XRF technique is from 1 to 50 keV for typical applications and may reach 150 keV for specific applications. This energy corresponds to a wavelength interval from about 0.25×10^{-10} m to about 12.4×10^{-10} m in a typical case.

An advanced EDXRF laboratory spectrometer utilizing a focused X ray beam has been used for the identification of individual particles. Microbeam XRF is a unique technique that can provide information on the distribution of elements within a heterogeneous specimen. This method is also suitable for the determination of elements in minute samples such as individual particles. It has capabilities similar to those of electron probe micro X ray analysis (EPMXA), with an inferior spatial resolution of about 10 μm (versus 0.1 μm for EPMXA) but much better detection limits for heavy metals. The microbeam XRF technique has been used to obtain spatially resolved images of element distribution in samples. Using the same spectrometer, the computerized tomographic (CT) imaging measurements are carried out with a spatial resolution of better than 20 μm. The CT imaging is performed with two detectors simultaneously in absorption and emission mode, providing information about the density and element distribution within the object.

The XRF technique has also been selected to perform in situ chemical composition analysis. XRF spectrometry is usually used for the field applications owing to its several advantages over other chemical or spectrophotometric methods. The XRF technique is a non-destructive method, it requires a minimum of sample preparation, it has the capability to analyse solid and liquid samples, it is a multielement technique and there are portable battery operated XRF spectrometers available. For the successful application of XRF for in situ measurements, dedicated instruments are constructed and robust quantitative analytical methods have been developed.

How to solve the problem?

The microbeam XRF technique was used to investigate the presence of depleted uranium (DU) rich particles in air and soil particulate matter. A schematic view of the microbeam XRF spectrometer is shown in Fig. 1.

The particles were deposited on a polycarbonate filter and the filter was scanned with an X ray beam focused down to a diameter of about 10 μm. Several DU rich particles were identified, and the distribution of uranium around the particles was obtained. Figure 2 shows an image of a uranium rich particle overlapped by an image of an iron rich particle. This type of analysis can only be achieved with a very few other analytical methods, e.g. secondary ion mass spectrometry (SIMS), electron probe microanalysis (EPMA), proton induced X ray emission (PIXE) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). Of the available analytical methods, only the XRF technique is fully non-destructive. All the methods are regarded as nuclear analytical techniques (NATs), and at present there is no alternative non-nuclear method to compete with them.

For in situ applications, two portable X ray spectrometers have been constructed. They are shown in Figs 3 and 4. The radioisotope source based spectrometer, shown in Fig. 3 being employed for in situ soil sampling, has been designed for element determination in surface soil. A robust quantification procedure has been developed and tested. In Fig. 5 a very good correlation between the known trace and minor element concentrations and those determined by the spectrometer is shown for selected standard reference materials.

The X ray tube based spectrometer, shown in Fig. 4, is aimed at archaeometry applications, including pigment identification and provenance studies. It has been found very useful in supporting the restoration work on cultural heritage resources.

The main advantage of the XRF technique over non-NATs, especially in archaeometry applications, is its non-destructiveness, portability and multielement capability. Also of importance are the very good detection limits of elements.

Recent developments in the X ray detector technology (the availability of liquid-nitrogen-free detectors) have made the in situ systems truly portable, relatively cheap and requiring a minimum of maintenance. Also important is the fact that XRF applications are receiving better recognition in national and international standards and analytical protocols.

Bibliography

JANSSENS, K.H.A., ADAMS, F.C.V., RINDBY, A. (Eds), Microscopic X-Ray Fluorescence Analysis, Wiley, Chichester (2000).

KALNICKY, D.J., SINGHVI, D.R., Field portable XRF analysis of environmental samples, J. Hazard. Mater. **83** (2001) 93–122.

Report of the First Research Coordination Mtg under the Coordinated Research Project on In Situ Applications of XRF Techniques, IAEA, Vienna, 2001.

VAN GRIEKEN, R.E., MARKOWICZ, A.A. (Eds), Handbook of X-Ray Spectrometry, Dekker, New York (2002).

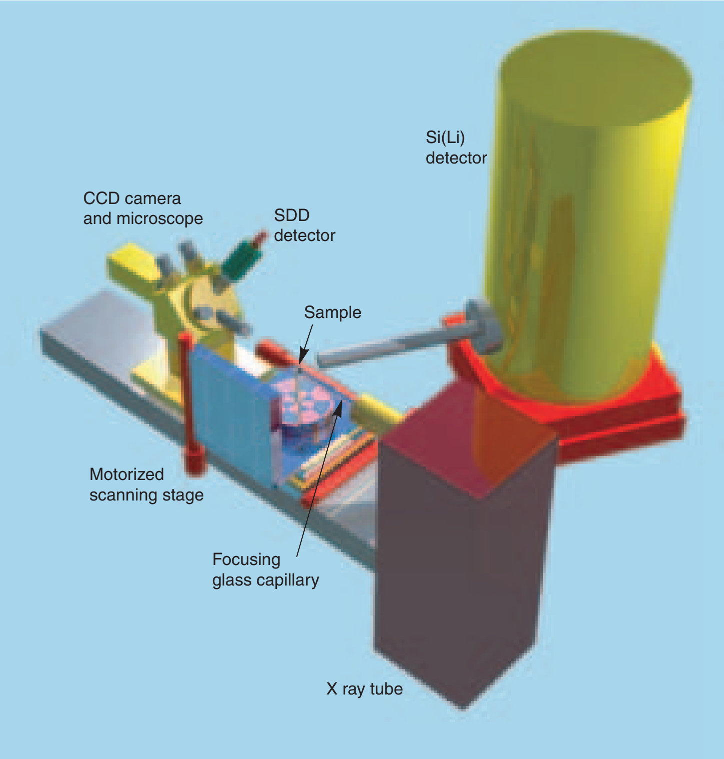

FIG. 1. *Schematic view of the microbeam XRF system.*

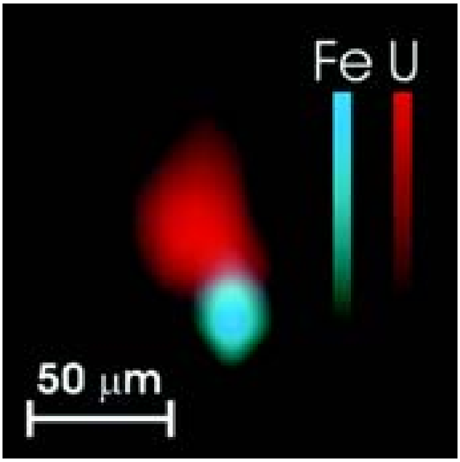

FIG. 2. *Uranium rich and iron rich particles.*

FIG. 3. In situ element determination in soil by XRF spectrometry.

FIG. 4. Pigment analysis with portable XRF spectrometer.

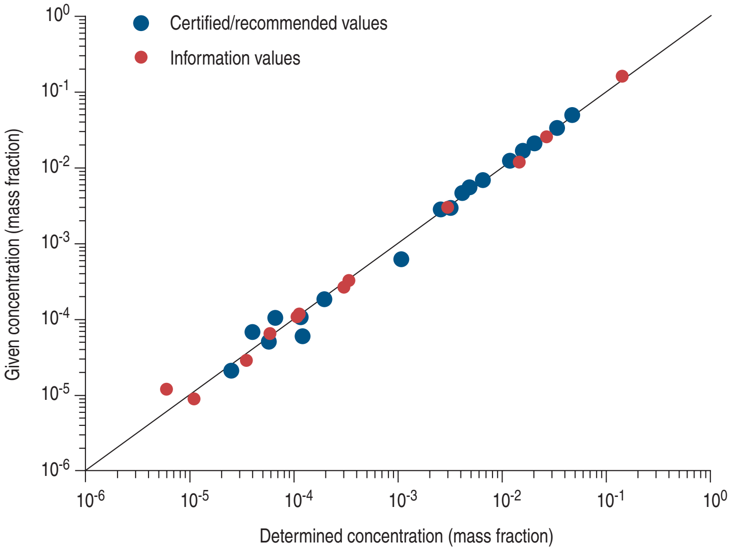

FIG. 5. Correlation between given and determined concentrations of elements.

Radioisotopes for method validation

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Problem

Validation of analytical methods is an obligation laid down in ISO Standard 17025, which provides general requirements for the competence of testing and calibration laboratories. The entire analytical process — from sampling, sample preparation and storage to the final determination of concentrations — is subject to quality control and validation. Particularly if legal, forensic, commercial or diagnostic purposes are involved, a protocol of the validation of the whole process for deriving analytical results might be needed to convince the customer, be it a judge, a medical doctor or a vendor of goods, of the trueness of the results.

Why nuclear analytical techniques?

Radionuclides are unique as a probe for method validation, since very minor quantities can be measured through their radioactive decay and, being isotopes, the nuclides behave chemically exactly like the parent element in a sample. To add a radionuclide of high specific activity to a sample virtually does not alter the sample composition, but it probes the sample and allows detection of small quantities of the material by counting the emitted radiation. Provided a good mixing of radionuclides with the sample matrix was achieved, the measured radioactivity is indicative of the amount of original material.

How to solve the problem?

There are numerous examples where radionuclides have been successfully used to detect analytical errors and pitfalls, some of which would never have been discovered by other means. Contamination or losses during sampling can be easily discovered by employing radionuclides. Sampling of aerosols for the determination of acidic compounds using a thermodenuder was investigated using $H_2{}^{35}SO_4$. As a function of the temperature, the ^{35}S activity was counted in the coating, and so the collection process could be optimized. Contamination of blood and serum samples collected by stainless steel puncture was shown to be too high for low level Cr and V determination using neutron activated stainless steel needles. Contamination by radioactive ^{51}Cr and ^{52}V was found in the sample in concentrations exceeding the natural concentrations.

Losses of trace elements in solution to the container walls have been detected using radionuclides; for example, ^{203}Hg migrating through polyethylene, or various metal ions absorb on SiOH groups, forming stable SiOMe groups. Losses of elements have also been detected during storage, drying and/or volatilization. Valuable knowledge to improve analytical methodology has emerged through the application of radionuclides for method validation.

Graphite furnace atomic absorption spectrometry (GFAAS) is widely used for trace analysis in a variety of matrices. In situ trapping of hydrides in the graphite furnace and subsequent atomization enhances the sensitivity and eliminates unwanted interferences. However, complete trapping of the analyte depends largely on the experimental parameters, the interface and the furnace design. ^{75}Se, ^{76}As and ^{122}Sb were used to investigate the analyte behaviour after hydride generation under various conditions [1]. The experiments suggest that optimal conditions for Se trapping are equally suitable for As and Sb. Radiotracer studies provided convincing proof that in situ trapping of Se, As and Sb in graphite furnaces is complete when performed under optimized conditions, and the method is relatively stable for application under routine conditions.

Analysis of contaminants in high purity refractory metals such as W or Mo is a difficult analytical task and cannot be accomplished by dissolution methods owing to high contamination risk. A slurry sampling AAS method was developed and validated using a large number of reactor irradiated nuclides [2]. In the radiotracer experiments, an aliquot of 50 μL of molybdenum oxide slurry was mixed in a graphite cup with an aliquot of 10 μL of concentrated ammonium molybdate solution and spiked with aliquots of 10–20 μL of the appropriate tracer solution containing 0.1–1 μg of each element. After the measurement of the initial activity, the cup was inserted into the atomizer head. The mixture was carefully dried and then pyrolized. After each step the cup was removed for radioactivity counting. Finally the cup was heated in the atomizer at various vaporization/atomization temperatures and the residual activity counted. Volatilization yields were determined for temperatures of between 1900 and 3000°C. For Na, K, Rb, Cu and Zn, volatilization was close to 100% at 2300°C. For Cs and Sr, a temperature of 2700°C, and for Ba the maximum temperature, must be applied to achieve the same result. For Co, Cr, Fe and Ni, a residue of more than 10% remained in the cup after treatment at the maximum temperature. This procedure can be adapted to electrothermal vaporization techniques used in atomic spectroscopy for the separation of analyte and matrix and the direct analysis of powders of high purity Mo and molybdenum oxide after its reduction to metal.

The disadvantage of AAS being a single element determination method is overcome by applying modern inductively coupled plasma optical emission spectrometry (ICP-OES) or inductively coupled plasma mass spectrometry (ICP-MS) instruments. However, owing to possible contamination or losses during digestion/nebulization, the determination of low analyte concentrations, as in the case of impurities in high purity materials, is limited. Direct solid sample injection methods, such as powder insertion, slurry nebulization, laser or spark source ablation, and electrothermal vaporization using filaments and graphite furnaces, have been developed to overcome these constraints. The transport losses of eight selected analytes in the individual segments of the GF-ETV-ICP-OES instrument were determined by means of the radiotracer technique. The results obtained from the study were the basis for further improvement of the interface design, leading to a considerable increase in the total transport efficiency, which was found to be between 26% for Cr and 57% for Ga [3]. Absolute detection limits of between 0.1 and 3.2 ng were determined for the elements investigated.

References

[1] DOCEKAL, B., DEDINA, J., KRIVAN, V., Radiotracer investigation of hydride trapping efficiency within a graphite furnace, Spectrochim. Acta, Part B At. Spectrosc. **52** (1997) 787–794.

[2] DOCEKAL, B., KRIVAN, V., FRANEK, M., Separation of analyte and matrix for the direct analysis of high-purity molybdenum-based materials by electrothermal atomic spectrometry methods, I. Radiotracer investigation of thermal extraction of impurities in a graphite cup, Spectrochim. Acta, Part B At. Spectrosc. **49** (1994) 577–582.

[3] SCHAEFFER, U., KRIVAN, V., A graphite furnace electrothermal vaporization system for inductive coupled plasma atomic emission spectrometry, Anal. Chem. **70** 3 (1998) 482–490.

Determination of element contents in large samples by prompt γ activation analysis

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Problem

How can we obtain the element concentration of large and valuable samples, such as archaeological samples or samples of art, which it is impermissible to destroy and whose surface it is not permissible even to scratch for the purpose of analysis? Since the shape of unearthed articles is an important item of information, archaeologists do not like even small scratches to be made on the articles. Non-destructive analysis is therefore preferable. There are several instruments that can be employed to analyse large samples using X ray fluorescence analysis (XRF). However, essentially XRF can analyse only the surface of samples, so it is unsuitable for bulk analysis. In addition to the field of archaeology, there are other areas of demand for non-destructive analysis of large samples, for example in cosmochemistry for the initial analysis to classify meteorites before their detailed study, and in biology for the measurement of element distribution in an animal's body (for example a rat) without killing it, in order to study metabolism.

Why nuclear analytical techniques?

In order to carry out bulk analysis of large samples, a probe going deep inside the sample is needed. One of the candidates to serve as such a probe is the neutron. The neutron seems to be a unique probe for practical analysis, but conventional instrumental neutron activation analysis is unsuitable because normally the amount and size of the sample are limited owing to the need to insert the sample into a reactor.

Recently the method of neutron capture prompt γ activation analysis (PGAA) has been more widely studied, with the installation of sophisticated neutron guide tubes at various nuclear reactors. Use of the extracted neutron beam provides the advantage that there is no stringent restriction on the size and shape of the sample.

How to solve the problem?

A comparison method using an external standard sample is generally used in PGAA as well as in the usual instrumental neutron activation analysis (INAA). The standard sample has to be prepared by matching its element content, size and shape, and has to be placed with the same geometry with respect to the neutron beam and to the detector as the samples to be analysed, in order to avoid the effect of neutron absorption and scattering, and γ ray absorption within the sample. For small and/or thin samples it is easy to prepare standard samples satisfying these conditions. However, it is difficult to prepare standards for large and bulky samples. Therefore we have proposed the internal monostandard method, which is similar to k_0 methods for PGAA.

A sensitivity ratio of the elements to be studied to a normalized element, which is a physical constant, was determined in advance from the analysis of standard samples of known contents. Element ratios are calculated with this constant and a relative efficiency. Silicon was selected as the normalizing element for an item of earthenware, a rock and a meteorite, and Cu and H were selected for an item of bronze and an organism, respectively. It is noted that this internal method determines only element content ratios to the element selected for normalization, thus the absolute content of one element must be determined by other methods for obtaining absolute contents.

Irradiations were performed at the prompt γ ray analysis (PGA) system installed at the neutron beam tube extending from a research reactor, JRR-3M, at the Japan Atomic Energy Research Institute. The procedure consists of a sample in an FEP foil bag being set in the sample box in the PGA system and prompt γ rays being measured during neutron irradiation. Solid and solution samples, samples with irregular shape and large samples can all be analysed. (Of course, the sample must be smaller than the sample box dimensions.) We applied PGAA using the internal monostandard method to archaeological bronze mirrors, archaeological Sueki ware and china pottery, large meteorites and living rats. For example, we found that it was possible to identify the area of production of archaeological items of china pottery by correlation of element content ratios, as shown in Fig. 1. Boron is one of the most sensitive elements in

PGAA. PGAA is an effective tool for identifying the area of production of archaeological earthenware samples.

Bibliography

NAKAHARA, H., et al., Some basic studies on non-destructive elemental analysis of bulky samples by PGA, J. Radioanal. Nucl. Chem. **244** (2000) 405–411.

OURA, Y., et al., Completely non-destructive elemental analysis of bulky samples by PGAA, Czech. J. Phys. **49/S1** (1999) 311.

SUEKI, K., et al., Nondestructive determination of major elements in a large sample by prompt γ-ray neutron activation analysis, Anal. Chem. **68** (1996) 2203.

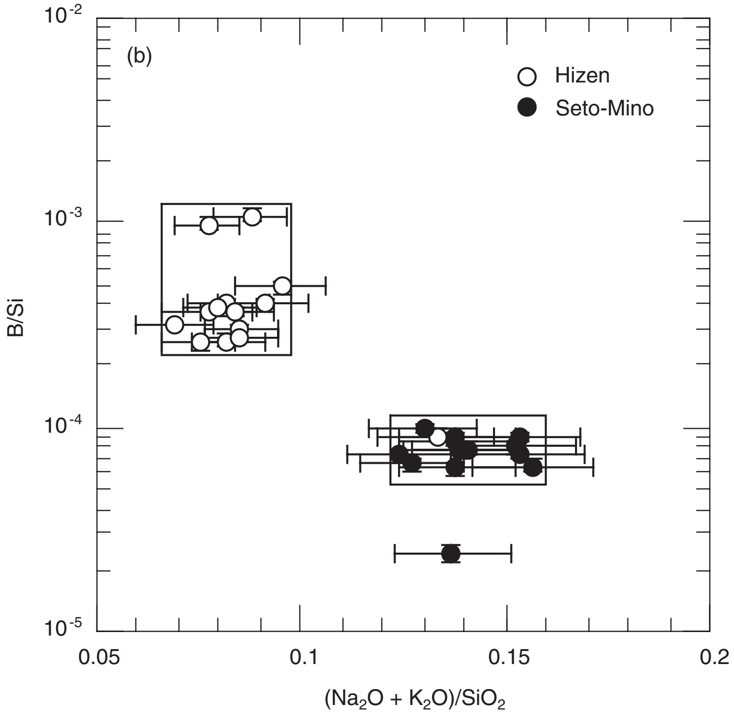

FIG. 1. Examples of correlation plots of the element contents of two kinds of china pottery that clearly show differences in the raw materials used and different areas of production.

Part III

ENVIRONMENTAL APPLICATIONS

Environmental impact assessment of illegal gold mining in the Amazon region

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Problem

Intensive gold exploration activities started in Brazil in the 1980s in the Amazon region. Ever since that time, awareness of the dangers of environmental contamination posed by the disposal of the metallic mercury used for the extraction of gold by amalgamation has been increasing among the general public and the authorities [1]. It is estimated that around 2000 t of mercury have been released in the Amazon in the last 20 years as a consequence of these mining activities. Several studies have been conducted by researchers from Brazil and other countries of the environmental impact of mercury pollution in the Amazon basin and of the health effects on the riverine populations, but much work remains to be done. On the basis of a comprehensive evaluation of many published scientific papers concerning the presence of mercury in several compartments of the Amazon region, it can be concluded that, instead of acute signs of contamination, the main impact of the gold mining activities will be to increase the general background of mercury in the soils, sediments and biota of the region, with long term consequences for the local population and for the fauna that are not yet known.

Why nuclear analytical techniques?

In the framework of a project developed in the Radiochemistry Division of the Instituto de Pesquisas Energéticas e Nucleares, Brazilian Nuclear Energy Commission (IPEN/CNEN-SP), and with support from the IAEA, a nuclear analytical technique, instrumental neutron activation analysis (INAA), was applied to the study of mercury contamination in Brazilian Indian populations living in the Xingu Park Indian Reservation, located in the Amazon region. Hair samples from the Indians and from a control population were analysed for total mercury, and very high concentrations of mercury were found in the Indians, with means of up to about 20 times that of the control population [2, 3]. The advantage of

INAA is that this method is non-destructive, avoids the need for chemical treatment of the samples, and is very accurate and sensitive, allowing determination of many other elements, such as aluminium, antimony, arsenic, cadmium, chromium and selenium, in these hair samples [4].

How to solve the problem?

Following this work on analysis of hair samples of Brazilian Indians, where the application of a nuclear technique allowed the analysis of mercury in about 400 samples, it is necessary to make a more complete study of this area, analysing samples of fish and other foodstuffs consumed by the Indians, as well as soils and sediments of the region, in order to assess the sources of contamination. In this project the hair samples of the Indians have also been analysed for methylmercury, a very toxic compound of mercury that is able to pass through biological barriers like the placenta and cause severe damage to the nervous system of the foetus. With the collaboration of the Jožef Stefan Institute, Ljubljana, Slovenia, methylmercury was analysed in many of the hair samples using another technique, cold vapour atomic absorption spectroscopy, and it was concluded that most of the mercury in the hair was present as methylmercury. It is already known that the most probable source of methylmercury for humans is fish, owing to the fact that fish can concentrate methylmercury to very high levels. Since the Amazon Indians consume fish on a daily basis, this could be the reason for the presence of very high amounts of mercury in their hair and also in their blood, as shown by other studies.

This project will continue, with analysis of fish samples from the region of the Xingu Park, as well as of soils and sediments, in order to better understand the cycle of mercury in this region. INAA will be utilized throughout the project.

References

[1] PFEIFFER, C., LACERDA, D., Environ. Technol. Lett. **9** (1998) 325.

[2] VASCONCELLOS, M.B.A., et al., in Proc. NIMD Forum '99, Minamata City, Japan, 1999, Natl Inst. of Minamata Disease, Minamata (2000) 10.

[3] VASCONCELLOS, M.B.A., et al., J. Radioanal. Nucl. Chem. **244** 1 (2000) 81.

[4] VASCONCELLOS, M.B.A., et al., J. Radioanal. Nucl. Chem. **249** 2 (2001) 491.

Environmental monitoring programmes: Protecting the community

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Problem

Because of the occurrence of the natural radioactive series of thorium and uranium in the Brazilian soil, and consequently the occurrence of ^{232}Th, ^{228}Th, ^{230}Th, ^{238}U, ^{226}Ra, ^{228}Ra and ^{210}Pb, it is important to determine such radioisotopes in several matrices. Some of these radioisotopes are α emitters and others β emitters. From a radiological protection point of view and depending on the concentration or activity present in a matrix, they may cause health damage. In order to know, for instance, if underground water is suitable for drinking, one of the parameters is to determine the radioactivity level and verify if this value is within the limits recommended by the relevant legislation.

Samples from industries and mining, such as aqueous and organic effluents from leaching, solid and liquid waste, industrial residues and precipitates, are also analysed.

Why nuclear analytical techniques?

To determine radioisotopes at very low concentrations or activities in a matrix, the best method is to apply nuclear techniques that are based on nuclear characteristics of the radioisotope. One technique applied is the gross α and gross β technique, a very fast procedure in which the sample is not submitted to a chemical process. The sample is simply evaporated — aqueous samples, for instance — or dried and powdered, if the sample is solid. The other techniques are those specific for each radioisotope: neutron activation analysis, coprecipitation plus radiometry, α spectrometry and γ spectrometry. All of them are specific for each radioisotope, with low detection limits that are suitable for very low activity.

How to solve the problem?

Owing to the high demand for analysis — many samples from diversified matrices and from all over the country must be analysed — the first step is to know the radioactivity level of the sample. In this step the technique applied is the gross α and gross β technique. These measurements show the total

α activity level and the total β activity level but do not show which radionuclide is responsible for such activity or its contribution to the total measurement. The result is compared with the limits recommended and a decision is made. If the limits foreseen are not exceeded, the sample does not present activity of a dangerous level, but if the limits are exceeded, the radionuclides mentioned above should be determined by a specific method. This is the second step. The new results will be compared with the radioisotope specific limit. Concerning water from a mine shaft, for instance, if the measurements exceed the limits this water should not be used as potable water. Nowadays the matrices analysed are surface water, drinking water and groundwater, aqueous and organic effluents from leaching, soil, sediment, ore, pasture, biomaterial, air filters, mud, solid and liquid waste, industrial residues, precipitates and others. To determine ^{228}Th and ^{230}Th, water and air filter samples are analysed. The monitoring programmes have been applied at the clients' request. These clients are from mining industries, nuclear facilities and governmental institutions such as the National Health Foundation, and they must ensure the quality of the water distributed to communities.

Bibliography

COMISSÃO NACIONAL DE ENERGIA NUCLEAR, Basic Directives for Radioprotection, CNEN-NE-3.01, CNEN, Rio de Janeiro (1988).

MELO, M.A.M.O., in Proc. 3rd General Conf. on Nuclear Energy, Rio de Janeiro, 1990, Associação Brasileira de Energia Nuclear, Rio de Janeiro (1990) 20.

MENEZES, M.Â.B.C., et al., Determination of ^{232}Th in Water by Instrumental Neutron Activation Analysis via ^{233}Pa, RT(AT4) CDTN-0233, Internal Report, Nuclear Technology Development Centre, Belo Horizonte, 1995.

MENEZES, M.Â.B.C., SABINO, C.V.S., "Thorium: Determination by CDTN, Brazil", Proc. Radiochemical Conf. Mariánské Lázně, 1998, Czech. J. Phys. **49** Part 1, Spec. Issue (1999) 359–365.

SABINO, C.V.S., et al., Alpha Spectrometry, Implementation of the Technique, DETQ.CN-001/88, Internal Report, CDTN/Nuclebrás, Belo Horizonte, 1988.

Persistent organic halogens in environmental materials

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Problem

Nowadays there are innumerable chemicals in commercial and domestic use. Huge masses of such chemicals are manufactured and used in various industrial processes and in the everyday life of the public. For the past few decades, environmental chemists have been detecting innumerable chemicals which are polluting the environment. These pollutants are ubiquitous — present everywhere on the globe, even in the Antarctic environment. However, in spite of the detection efforts, only a limited proportion of the chemicals in the environment have been detected and listed as pollutants.

Because of their persistence in the environment and biota and their toxic effects on organisms, organohalogen compounds are considered as one of the most toxic pollutants of concern. They have been given enormous attention by the policy makers of several countries, the United Nations and many non-governmental agencies. It should also be noted that, apart from these organohalogen compounds, many other toxic and persistent chemicals exist in the environment that are yet to be detected and listed as pollutants.

Why nuclear analytical techniques?

How are the levels of occurrence of unknown halogen compounds polluting the environment to be measured? The answer is very simple. First the total organically bound halogen compounds should be measured with the technique known as neutron activation analysis (NAA). Environmental chemists call this fraction the extractable organohalogens (EOX). It is possible to detect the individual halogens — chlorine, bromine and iodine — using NAA. The concentration of the organohalogen compounds of known constituents, which can be measured by instruments like the gas chromatograph mass spectrometer (GCMS), should be subtracted from the EOX values to obtain the concentration of organohalogen compounds of unknown constituents. NAA is a preferred technique because of its sensitivity, its capability to detect individual halogens and its simplicity of analytical procedure, as well as the fact that it is easier to analyse any chemical substance through this method. Apart from EOX, all the analytical procedures developed so far for estimating organohalogen compounds have several problems in terms of sensitivity, simplicity and capability to analyse individual halogens. Consequently NAA is the most suitable technique for the quantification of organohalogen compounds in environmental samples.

How to solve the problem?

It is possible to analyse the individual organically bound halogens existing in any chemical structure with high sensitivity and simplicity. For the analysis of individual halogen compounds using the NAA technique, prior chemical treatment of the samples is not necessary. The results so far obtained in various environmental samples suggest high concentrations of EOX.

Figure 1(a) shows the per cent compositions of known extractable organochlorine (EOCl) in adipose tissue of the brown booby (Fig. 1(b)). It is clearly evident that the concentration of unknown EOCl exceeds that of known EOCl in the total EOX. Known halogen compounds such as polychlorinated biphenyls (PCBs) and DDTs contribute only a small fraction of EOX. This shows that the environment is relatively more contaminated by the organohalogen compounds of unknown constituents. It is also possible that some natural halogen compounds also contribute to EOX. Identification of such EOX, be they natural or anthropogenic, still remains a challenge for environmental chemists. This is a problem that needs to be solved in view of the possible threat to human and animal health, because of the possible widespread occurrence of such compounds in our environment.

Bibliography

BERNES, C., Persistent Organic Pollutants: A Swedish View of an International Problem, Swedish Environmental Protection Agency, Stockholm (1998) 152.

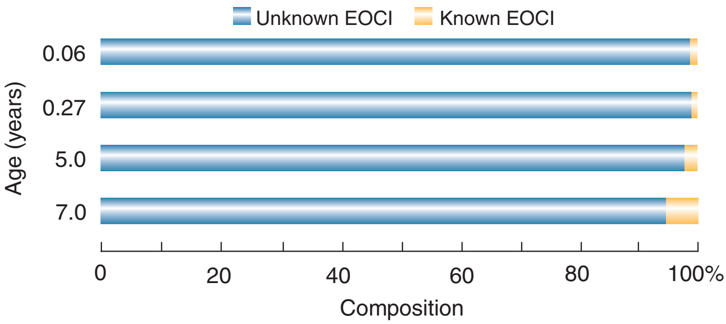
BOTTARO, C.S., KICENIUK, J.W., CHATT, A., Spatial distribution of extractable organohalogens in northern pink shrimp in the North Atlantic, J. Biol. Trace Elem. Res. **71–72** (1999) 149–166.

KANNAN, K., KAWANO, M., KASHIMA, Y., MATSUI, M., GIESY, J.P., Extractable organohalogens (EOX) in sediment and biota collected at an estuarine marsh near a former chloralkali facility, Environ. Sci. Technol. **33** (1999) 1004–1008.

KAWANO, M., KOHNO, H., FALANDYSZ, J., WAKIMOTO, T., Extractable organohalogens (EOX) in brown booby (*Sula leucogaster*) from Nakanokamishima Island, South Ryukyus, Japan, Organohalogen Compounds **52** (2001) 104–107.

KAWANO, M., YOSHIOKA, H., TEJIMA, Y., TATSUKAWA, R., "Occurrence of organic halogens in marine mammals", Naturally-Produced Organohalogens (GRIMVALL, A., LEER, W.B., Eds), Kluwer, Dordrecht (1995) 333–337.

(a)



(b)

FIG. 1. (a) EOCl composition in adipose tissue of the brown booby collected on Nakanokami Island, South Ryukyus, Japan. (b) Brown booby (Sula leucogaster) *(photo by H. Kohno).*

Neutron activation analysis for organohalogen pollutants in milk and other foodstuffs

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Problem

The halogen elements, when they exist as organohalide compounds (chlorinated pesticides, polychlorinated biphenyls (PCBs), dibenzo-p-dioxins/dibenzofurans, etc.), have long been known as persistent environmental pollutants. Their toxic effects are generally undisputed. Huge amounts of organochlorinated compounds (OCs) are continuously being released into the environment with the extensive use of organochlorinated pesticides (OCPs) and herbicides, and the discharge of wastewater from the bleaching of pulp and municipal wastewater treatment. PCBs and OCPs, such as hexachlorocyclohexanes (HCHs), dichlorodiphenyl trichloroethane (DDT) and its metabolites, are well known among the OCs for their persistence, toxicity and bioaccumulation. Although human exposure to this type of pollutant comes from air, water and diet, many studies have shown that about 95% of the intake of OCs comes from food, and that OC intake by the general population depends greatly on the geographical area and food structure. A number of reports have indicated that chlorinated pesticide contamination in food is a serious problem in many countries, because of the extensive use of these pesticides in agriculture, in forestry and for other purposes. Further, information about the overall pollution status of organohalide compounds and their impact on human health is not complete. Thus it is imperative to critically evaluate the pollution status of organohalide compounds in food and other environmental samples and to study the biological effects of these compounds on human beings at epidemiological and molecular levels.

Why nuclear analytical techniques?

The traditional analytical techniques, such as gas chromatography (GC), gas chromatography mass spectroscopy (GCMS) and high performance liquid chromatography (HPLC), cannot reflect the overall pollution status of organohalide compounds. Many reports have indicated that the contents of OCs given by GC amounted to only about 10–20% of the actual contents, or even less. Owing to the advantageous nuclear properties of Cl, Br and I, neutron activation analysis (NAA) can easily evaluate the whole pollution status of the halogen elements, when combined with organic extraction techniques. An additional merit of instrumental neutron activation analysis (INAA) is the ease of simultaneously measuring Cl, Br and I in one sample.

How to solve the problem?

Since OCs may accumulate in organisms through the food chain as a result of their lipophilic property, food is considered the main source of human exposure to these compounds. Milk can serve as one of the convenient indicators for measuring the extent of persistent residues that may originate from contaminated animal feed. Therefore it is recommended by the United Nations Environment Programme as an indicator of persistent organic pollutants and has been studied in recent surveys as an indicator of OCP exposure. However, there is still insufficient information on the OC concentration in milk. The nuclear analytical techniques (mainly NAA) can be applied to analyse total halogens, extractable organohalide and persistent organohalogens in milk and other foodstuffs via $^{37}Cl(n,\gamma)^{38}Cl$, $^{79}Br(n,\gamma)^{80m}Br$ and $^{127}I(n,\gamma)^{128}I$, which are short lived nuclides and are easily determined (Fig. 1).

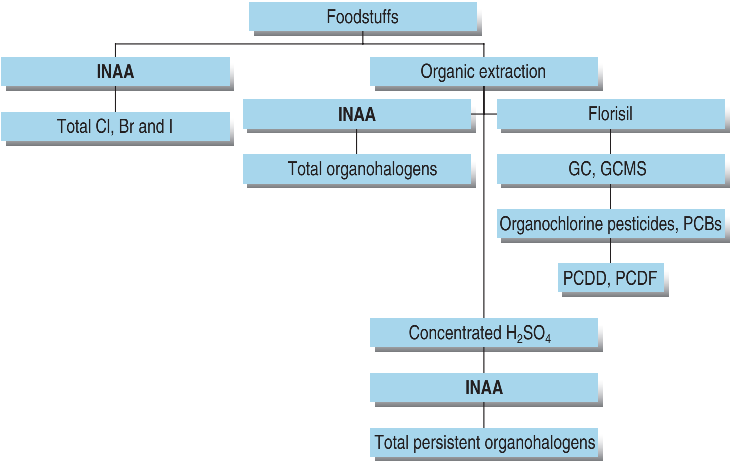

FIG. 1. Flow chart of nuclear analytical techniques for the determination of organohalogens in foodstuffs. PCDD: polychlorinated dibenzo-p-dioxins; PCDF: polychlorinated dibenzofurans.

Bibliography

MUKHERJEE, G., MADHUBAN, G., Organochlorine pesticide residue in dairy milk in and around Delhi, J. Assoc. Off. Anal. Chem. **76** (1993) 283–286.

RIVA, C., ANADON, A., Organochlorine pesticides in cow's milk from agricultural regions of northwestern Spain, Bull. Environ. Contam. Toxicol. **46** (1991) 527–533.

UNITED NATIONS ENVIRONMENT PROGRAMME, Persistent Organic Pollutants, http://www.chem.unep.ch/pops/default.html.

Environmental evaluation of estuarine sediments

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Problem

A number of estuarine areas around the world have undergone significant industrial, residential and leisure development during the past hundred years. With increasing human dependence on estuarine areas, the environmental monitoring of these areas now receives much attention. However, an estuary is a very complicated system where fresh water and sea water are mixed. Accordingly, the distribution and migration of chemical elements, especially trace elements, in estuarine sediments are not well understood. Although the distribution of metals in sediment cores has been used to reconstruct past environment, few studies on post-depositional migration of elements in the sediments have been conducted to check the validity of such reconstructive studies.

Why nuclear analytical techniques?

We applied neutron induced prompt γ ray analysis (PGA) and instrumental neutron activation analysis (INAA) to estuarine sediments. These simultaneous multielement analytical methods are both non-destructive, which is advantageous because they can save much labour in sample preparation and avoid contamination or loss of some constituents due to chemical destruction. In addition, PGA is characterized by its capability for analysing light elements, such as boron, hydrogen, sulphur and silicon, which cannot readily be analysed by INAA. By using these methods to complement each other, many elements, including trace elements, whose distribution in estuarine sediments has not been well understood, can be determined simultaneously.

How to solve the problem?

We describe here a case study of the Tama River, which is located in the southwestern part of Tokyo and which has been heavily polluted with municipal sewage. The vertical distributions of elements in the Tama River estuarine sediments and in the sediment of Lake Okutama were determined by

INAA and PGA. Lake Okutama is the most upstream water reservoir of the Tama River and its sediment is regarded as the least polluted among the Tama River sediments. Figure 1 shows general trends in the depth profiles of 40 elements in the Tama River estuarine sediments and the Lake Okutama sediment. The elements which increased and decreased with depth are shown in red and green, respectively. The elements that were independent of depth are shown in blue. The intensity of the colours indicates the relation between the Tama River sediments and the Lake Okutama sediment, with the most intense colours showing cases where the content in the estuarine sediments was greater than the content in the Lake Okutama sediment, the palest colours indicating cases where the content in the estuarine sediments was less than the content in the Lake Okutama sediment, and the medium colours indicating cases where the content was about equal.

The distribution of major elements is affected by weathering. Sulphate reduction coincides with the weathering processes, resulting in an accumulation of sulphides in the deeper layers. Cadmium is also highly concentrated in these layers, where the sulphate ion is reduced to hydrogen sulphide. The cadmium content in this layer is significantly higher than the average content in the soil of Japan. Some elements are more abundant in the Lake Okutama sediment than in the estuarine

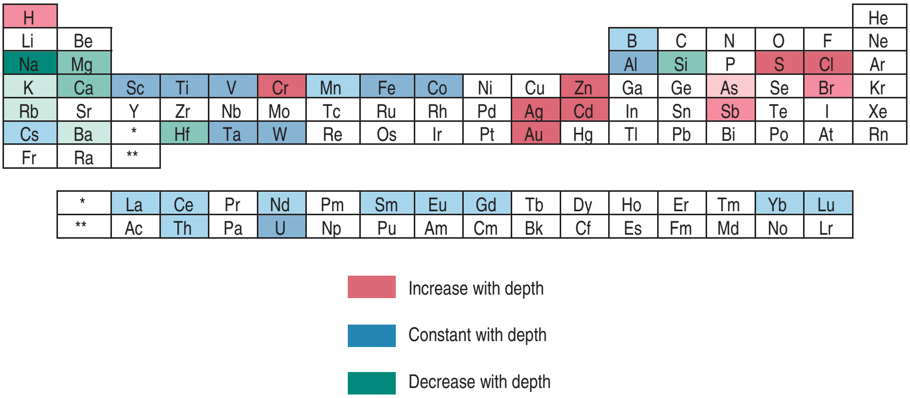

FIG. 1. General trends in the depth profiles of 40 elements in the Tama River estuarine sediments and the Lake Okutama sediment.

sediments, presumably owing to adsorption by clay minerals. The behaviour of rare earth elements and boron in the sediments, which has not been well known, was investigated in this study.

Finally, PGA and INAA were successfully applied to the Tama River estuarine sediments so as to investigate the distribution and migration of chemical elements under such conditions. PGA is a relatively new analytical method and gives data complementary to those of INAA. Being simultaneous multielement analysis methods, PGA and INAA are quite useful techniques for the basic study of environmental samples.

Bibliography

KUNO, A., et al., Neutron induced prompt gamma-ray and instrumental neutron activation analyses of urban estuarine sediments, J. Radioanal. Nucl. Chem., Articles **218** 2 (1997) 169–176.

— Vertical distribution of elements in non-polluted estuarine sediments determined by neutron induced prompt gamma-ray and instrumental neutron activation analyses, J. Radioanal. Nucl. Chem., Articles **239** 3 (1999) 587–590.

Neutron capture radiography to determine the concentration of natural boron in leaves using the nuclear reaction $^{10}B(n,\alpha)^{7}Li$

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Problem

Boron was recognized long ago as an essential element for plants. The exact mechanisms involved in boron metabolism are still a matter of discussion. From a practical point of view, boron deficiency may cause a significant decrease in the yield of crops. This is especially the case with coffee plants in Central and South America. A common way to treat such boron deficiencies in the field consists of spraying a boron containing solution onto the plants at the appropriate time (especially before blooming).

Why nuclear analytical techniques?

Neutron capture radiography (NCR) is a nuclear analytical imaging method. It is based on using thermal neutron induced nuclear reactions, such as (n,p), (n,α) or (n,f). Clearly NCR can be used for the detection of only those nuclides whose cross-section (σ) for one of these nuclear reactions is not too low. With σ being indicated in barns (1 barn = 10^{-28} m^2) in brackets, this is the case especially with ^{14}N (1.83), ^{35}Cl (0.48), ^{40}K (4.4) for (n,p) reactions; ^{6}Li (941.4), ^{10}B (3836), ^{17}O (0.24), ^{35}S (0.14), ^{40}K (0.39) for (n,α) reactions; and ^{235}U (583) and ^{239}Pu (742) for neutron induced fissions (n,f).

Some of these nuclear reactions are characteristic of stable isotopes (^{14}N, ^{6}Li, ^{10}B, ^{17}O) of chemical elements that are highly relevant for biology but have no radioactive isotope usable in practice. It is possible to use these stable isotopes for the labelling and analytical imaging of the corresponding elements almost as easily as with radioactive tracers when they exist.

In conventional NCR studies, the biological specimen (a histological section in most cases) is laid against an appropriate detector (most often a film of cellulose nitrate or polycarbonate), and then this whole assembly is irradiated with thermal neutrons. The impact of the ionizing particles (p, α, fission fragments) emitted by the nuclear reactions creates latent tracks in the detecting film. Using an appropriate chemical treatment (most often by dipping the detectors in a strong alkaline solution), the latent tracks are enlarged to the size of tracks visible with an optical microscope. The features (especially the size) of these tracks are characteristic of the nuclides involved in the neutron induced nuclear reactions, thus rendering their discrimination possible.

NCR is used in Costa Rica as a nuclear analytical technique to determine the boron concentration in vegetal samples, boron being a stable isotope whose concentration is difficult to evaluate by chemical methods.

How to solve the problem?

(a) Leaves

After the superficial density (g/cm^2) of fresh and dried leaves is measured, the dried leaves are incinerated carefully (in order to preserve their structure) by heating them to 380°C between a quartz slide and a copper frame. The spodogram obtained from the leaf has an appropriate thickness to permit the α particles to reach the detector. After removing the copper frame, the spodogram is covered with a solid state detector (Kodak LR 115, Type I, 6 μm in thickness, or CR-39, 500 μm in thickness), which records the tracks produced by the α particles. The leaves also could be lyophilized, if the laboratory has the necessary equipment. Table 1 shows the results for boron content in coffee leaves.

(b) Fruits

Fruit fragments composed of the skin (approximately 3 cm^2 surface area) and the flesh (12–17 mm thickness) are frozen in liquid nitrogen, and cryosections 50 μm in thickness are cut perpendicular to the skin with a cryotome. The frozen section is placed on a CR-39 polycarbonate sheet, freeze-dried and covered with another CR-39 sheet.

TABLE 1. TYPICAL BORON CONTENTS OF COFFEE LEAVES

Type of leaf	Ranges of boron concentrations (ppm, dry material)		
	Suboptimal	Optimal	Above optimal
Young	<25	25–75	>75
Adult	<40	40–75	>75

(c) Calibration drops

Three drops of ^{10}B boric acid solution (97%) of the same concentration (82 mmol and 2% in gelatin for coffee leaves) and of 3–5 µL volume are sampled and deposited on a solid state detector which is dried in open air.

The solid state detectors (LR 115, Type I, 6 µm, and CR-39, 500 µm) with the biological samples and the detectors containing the calibration drops are irradiated simultaneously in the thermal flux from a neutron source or a nuclear reactor. Under the bombardment by thermal neutrons, the ^{10}B nuclei are split into ionizing particles, an α particle and a ^7Li nucleus, according to the nuclear reaction

$$^{10}B(n,\alpha)^7Li \tag{1}$$

When these ionizing particles reach the detector, they leave a latent track in it. After an appropriate time of irradiation the detectors are dipped into an etching solution (NaOH, 2.5M at 60 ± 0.1°C for 110 min if using LR 115, or NaOH, 6M at 70 ± 0.1°C if using CR-39). The ideal fluence for irradiations is 10^{13} n/cm^2, in order to change the latent tracks into holes with a diameter of 1 µm, so that they become visible with an optical microscope. The number of tracks per vision area of the microscope is proportional to the concentration of boron in the biological sample. In all cases it is necessary to count several areas for the purpose of obtaining good statistics.

Bibliography

LORÍA, L., et al., Neutron-capture-radiography study of the distribution of boron in the leaves of coffee plants grown in the field, J. Trace Microprobe Tech. **17** 1 (1999) 91–99.

LORÍA, L., JIMÉNEZ, R., BADILLA, M., Complementary study of boron absorption by coffee leaves using the neutron-capture-radiography method, Rom. J. Physiol. **35** 1–2 (1998) 169–177.

LORÍA, L., JIMÉNEZ, R., BADILLA, M., MARTINI, F., Neutron-capture-radiography study of boron absorption by leaves of coffee plants, J. Trace Microprobe Tech. **15** 3 (1997) 335–340.

MARTINI, F., et al., Biological applications of neutron capture radiography, J. Trace Microprobe Tech. **13** 3 (1995) 321–323.

Large sample instrumental neutron activation analysis for chemical analysis of large quantities of materials in environment related studies

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Problem One of the basic functions of chemical analysis is to provide quantitative element compositions for materials under investigation. The combined uncertainty of analytical results consists of two parts: uncertainty in sampling and uncertainty in analysis. When sampling is performed incorrectly, the sampling uncertainty may be orders of magnitude higher than the analysis uncertainty, and a false conclusion may be drawn.

Uncertainty in sampling is related to the homogeneity of the material being sampled, which depends on the grain size and the components of the material. To yield representative analytical results for material like that shown in Fig. 1, the sample size should be of the order of kilograms, namely large enough to be homogeneous. On the other hand, for technical or practical reasons the sample size in chemical analysis is

FIG. 1. Example of waste received from an incineration plant.

largely restricted, as seen in Table 1, which shows the sample size and analytical portions which can be handled by several analytical techniques. It is clear that, for the techniques often used in environment related studies, such as atomic absorption spectroscopy (AAS) or graphite furnace AAS (GFAAS), inductively coupled plasma atomic emission spectroscopy (ICP-AES) or ICP mass spectroscopy (ICP-MS), and X ray fluorescence (XRF) spectroscopy, the maximum sample size is no more than 50 g, and the analytical portion which can be handled in one determination is much smaller still.

To resolve this problem, homogenization is needed before determination. However, it is well known that homogenization is time consuming, tedious and a potential source of uncertainties due to contamination or loss of components. Furthermore, for many materials encountered in environment related studies, homogenization can be too difficult to perform. As an example, Fig. 1 shows waste received from an incineration plant. Most of the waste consists of large fragments and chips with different shapes and sizes, and mixed with tiny grains and fine powders. Some of the large fragments can be distinguished as various metallics, ceramics and pottery, glass with different colours, and fused lumps. The others cannot be recognized visually. The average size of the large fragments is about 2–5 cm. For determination of the components of the waste, such as the metals and the elements essential in environment related studies, a sample size of a few kilograms is needed. It would be very difficult, if not impossible, to perform homogenization of such material to yield a homogeneous sample to satisfy the requirements of analysis by the techniques listed in Table 1. A similar situation pertains for the many diverse materials encountered in environment related studies. These materials include, among others: contaminated soil/sediment, municipal and industrial sludge, plants and trees (roots, stalks, leaves, fruits), electronics waste (discarded TVs, PCs, cellphones, etc.), air particulate matter (aerosols, dust, fly ash, etc.), domestic waste, discarded plastics and compost from biodegradable waste. Obviously an ideal solution would be direct determination of a kilogram of sample. Large sample instrumental neutron activation analysis (LS-INAA) is the only technique which can be used to perform such analysis.

TABLE 1. SAMPLE SIZES AND ANALYTICAL PORTIONS HANDLED BY SEVERAL ANALYTICAL TECHNIQUES

Analytical technique	Mass of solid material used in analysis	Volume of solution used as analytical portion
AAS and GFAAS	Max. 10 g, to be processed to make solution; typically 1–2 g	10–20 μL to 1–2 mL
ICP-AES and ICP-MS	Max. 10 g, 50 g for fire assay, to be processed to make solution; typically 1–2 g	Approximately 500 μL
XRF	Max. 10 g, to be analysed directly; analysis yields surface information only	—
Conventional instrumental neutron activation analysis (INAA)	Sample mass typically up to 0.5 g, in some cases up to 20 g, to be analysed directly	Sample volume typically 1 mL, in some cases up to 20 mL
Large sample instrumental neutron activation analysis (LS-INAA)	Sample mass typically up to 1 kg, max. 50 kg, to be analysed directly	Sample volume analysed typically 250 mL, in some cases up to 500 mL

Why nuclear analytical techniques?

Conventional INAA involves two basic procedures: neutron irradiation of the sample followed by γ ray spectroscopy of the activated sample. INAA can be extended to LS-INAA to analyse kilograms of sample simply, owing to the high penetration of neutrons and of γ rays into the sample.

Despite the fact that the principle is the same as in conventional INAA, applying LS-INAA in practice should resolve some inherent theoretical and technical problems. Among these are the evaluation of spatial neutron flux distribution in a large sample during irradiation, the evaluation of the γ ray counting efficiency of a large sample, standardization and analysis validation for diverse materials.

How to solve the problem?

In order to understand these problems and to investigate the feasibility of LS-INAA, a preliminary LS-INAA was carried out. Three different wastes, including that shown in Fig. 1, were analysed. The analysis was performed by irradiation of 1 kg of sample in the FRM-I reactor in Garching, Germany, followed by γ ray spectroscopy with high purity germanium (HPGe) detectors. Standardization was performed by applying the k_0 method. The analytical results of two determinations for the waste shown in Fig. 1 are given in Table 2.

TABLE 2. LS-INAA RESULTS (ppm) FOR THE WASTE SHOWN IN FIG. 1

Group/ element	First INAA	Second INAA	Average	rstdev (%)[a]
I/Ba	2 365	2 719	2 542	10
Br	4.06	4.00	4.03	1
Ca	122 042	147 656	134 849	13
Ce	36.7	39.4	38.1	5.1
Cr	797	846	821	4
Eu	0.448	0.521	0.484	11
Hf	7.30	6.62	6.96	7
K	6 508	7 500	7 004	10
La	14.8	16.7	15.8	9
Lu	0.276	0.279	0.278	0.8
Na	24 277	28 244	26 261	11
Rb	40.0	37.7	38.8	4
Sc	3.92	4.42	4.17	8
Sm	2.68	2.82	2.75	4
Ta	1.58	1.74	1.66	7
Tb	0.344	0.280	0.312	15
Th	5.51	6.07	5.79	7
U	2.52	2.56	2.54	1
W	18.0	19.5	18.8	6
Yb	0.961	0.892	0.926	5
II/As	27.8	40.6	34.2	26
Ag	8.22	23.1	15.7	67
Au	0.362	0.997	0.680	66
Co	23.4	41.5	32.4	40
Cu	8 755	34 831	21 793	85
Fe	97 709	152 498	125 103	31
Mo	23.7	32.9	28.3	23
Ni	776	1 201	989	30
Sb	111	212	161	44
Zn	2 193	11 798	6 996	97
III/Cd	<5.5	<8		
Nd	10.5	10.8	10.6	2
Sr	435	<250	435	

[a] Relative difference between two determinations.

Cadmium and other heavy metals in plastics

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Problem

Cadmium is generally considered to be a hazardous element for humans and the environment. The metal and its compounds are being used, for instance, in rechargeable nickel–cadmium batteries, as pigments and as stabilizing agents in certain polymers. Many of the plastic products in which Cd is applied are disposables and thus have a relatively short life cycle. Approximately 400 000 t of plastic products end up annually in the domestic waste in the Netherlands. Only a minor fraction of the plastic is separated, recovered and prepared for recycling. The major part is incinerated together with the domestic waste. To limit and to control eventual environmental consequences, the European Community issued directives for the permissible levels of Cd in plastic products. Following these directives, a 1989 Cadmium Decree in the Netherlands prohibits the use and marketing of plastic products containing more than 50 mg/kg of Cd. Some exceptions are allowed for products in which the presence of Cd does not have a significant environmental impact, or in which the Cd is present for safety reasons.

The term ‘plastic’ comprises a wide variety of polymers, such as polyethylene, polypropylene, polystyrene and polymethyl methacrylate. Often the analyst does not know beforehand which polymer is present, and will face difficulties in selecting the proper protocol for dissolving the plastic

product, a usual step in many common analytical techniques. Moreover, these techniques also require standards of the same composition as the unknown sample. A standard for 'Cd in plastic' was not available in the 1980s.

The Dutch National Institute of Public Health and Environmental Protection approached the Interfaculty Reactor Institute in Delft to assess whether instrumental neutron activation analysis (INAA), being a non-destructive technique, would have the proper characteristics for an inventory study of the levels of Cd in various types of plastic.

Why nuclear analytical techniques?

INAA has very good prospects for the determination of Cd in plastics. Plastic is composed primarily of the elements carbon, hydrogen, oxygen and nitrogen, and sometimes it contains chlorine. The first four elements are rarely converted into γ emitting radionuclides, which thus makes the material 'transparent' for the detection of the γ radiation of the activation products of contaminants such as Cd. Moreover, the technique is non-destructive, which overcomes the cumbersome problems — and costs — that can arise with alternative techniques when samples have to be brought into a solution prior to analysis. In addition, the original sample is not lost when using INAA, which allows a second opinion analysis if doubts should occur afterwards. Simultaneously a large number of elements other than Cd can be determined by INAA, and it has thus been observed that, even if the material satisfies the Dutch Cadmium Decree, other potential environmental contaminants, such as bromine, antimony (both present as flame retarding agents) and mercury may be determined.

For a non-destructive analysis, wavelength dispersive X ray fluorescence (XRF) spectroscopy may be an alternative. However, since information is obtained on concentrations in surface layers, much attention has to be paid to sample homogeneity, quality control and standardization. XRF is suitable if the material to be analysed can be pelletized, and it thus has good opportunities for use in routine process control. The advantages of XRF are the very fast analysis time and the absence of interference of elements such as antimony and bromine. But if the material has an irregular shape or possibly coatings, or if it is composed of different materials, as may occur in the analysis of parts of final products, INAA is the preferred technique.

The Cadmium Decree recommends the use of INAA as the analytical method for the enforcement of the Decree, with XRF and atomic absorption spectroscopy as alternatives. The laboratory for INAA at the Interfaculty Reactor Institute has been involved in inventory studies on the levels of trace elements in plastics as well as in analyses related to the enforcement of the Decree. The analytical capabilities of INAA for the determination of trace elements in plastics have resulted in similar studies in, for example, Canada, the United States of America and Brazil.

How to solve the problem?

Soft plastics are cut with titanium scissors; hard plastics are embrittled after immersion in liquefied nitrogen gas. A subsample of approximately 200 mg is collected and weighed in a small capsule made of a very pure type of polyethylene. The sample is then, together with standards and quality control reference samples, irradiated with neutrons near the core of a nuclear research reactor. In Delft, the irradiation typically takes 1–2 h. The radioactivity is subsequently measured by γ spectroscopy.

One of the performance indicators of the analysis is the turnaround time. The common turnaround time is 5–6 days for a regular flow of samples, which is acceptable for the customers. For a limited number of samples the analysis may be performed under a different protocol, allowing reporting

1–2 days after receipt of the samples. Difficulties are sometimes encountered if products contain flame retarding antimony and/or bromine-containing substances, resulting in unexpectedly high induced activities. This can interfere with the selected counting conditions. In extreme cases, the antimony and bromine levels reach the 5–10% range, resulting in a detection limit for Cd of the order of 1000 mg/kg.

During the first inventory study in the mid-1980s as well as in the first years after the issue of the Cadmium Decree, the samples were collected by the National Institute of Public Health and Environmental Protection. At that time the sampling focused on products with a relatively short life cycle, with a preference for red, orange and yellow colours. In 1992 the Ministry of Public Health, Planning and Environmental Protection started to coordinate the sampling with a view to enforcement, and since 1991 the samples have been collected by the Dutch Customs Laboratory. The Dutch Consumers' Union also became interested in the potential environmental impact of the presence of Cd in plastic products. In order to carry out comparative tests, they also provide samples for analysis, and the results are included in the test results.

Since the early 1990s the laboratory for INAA in Delft has been analysing approximately 2000–2500 samples a year for the presence of Cd, and sometimes for other trace elements as well. In recent years several companies have been

directly presenting their (new) products to the laboratory for testing by INAA.

A large variety of plastic types have been sampled, PVC being of principal interest. The upper limit of Cd in PVC is of the order of 1000–1500 mg/kg, with an extreme case of 40 000 mg/kg or 4%. In polypropylene and polystyrenes, for example, levels of 3000 and 5000 mg/kg , respectively, are no exception. Very high Cd levels, up to 1%, have also been regularly found in polyamides.

As early as the first inventory study in 1986–1988 it was found that there is a high probability that red, orange or yellow coloured plastics will have a high Cd content (up to 4%) because of the use of pigments such as cadmium sulphide and cadmium selenosulphide. However, because of the use of Cd as a stabilizer in PVC, it cannot be excluded that PVC of other colours also contains Cd. This applies especially to products that are exposed to certain environmental conditions (e.g. UV radiation), for example inflatable boats or products used at beaches and swimming pools. Perhaps the most remarkable finding of recent years is that black, and also transparent, PVC products have high Cd levels, which resulted in selective sampling. The transparent products are often label windows and parts of packaging material.

Most of the products discussed so far have been made of 'new' raw material. Parallel to this, part of the plastic in the waste stream is being recycled to new, durable products such as pickets and picnic furniture for use at recreation areas. Such products from recycled plastic may have elevated Cd levels, and concentrations varying between 50 and 200 mg/kg have been found.

Bibliography

BODE, P., The use of INAA for the determination of trace elements, in particular cadmium, in plastics in relation to the enforcement of pollution standards, J. Radioanal. Nucl. Chem. **167** 2 (1993) 361–367.

BODE, P., DE BRUIN, M., AALBERS, T.G., MEYER, P.J., Plastics from household waste as a source of heavy metal pollution: an inventory study using INAA as analytical technique, Biol. Trace Elem. Res. **26** 7 (1990) 377–383.

HOGEWONING, S.J., BODE, P., Sampling studies of plastics and its recycling process using normal and large sample INAA, J. Radioanal. Nucl. Chem. **244** (2000) 589–594.

NOMURA, D.H., SAIKI, M., BODE, P., Characterization of inorganic components in plastic materials, J. Radioanal. Nucl. Chem. **244** (2000) 61–65.

Part IV

MEDICAL APPLICATIONS

Trace elements in fingernails and toenails for use in cancer research and other health related studies

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Problem

Ecological studies and animal tests in the 1980s indicated a relation between the element selenium and the risk of cancer. A selenium deficiency could be correlated with various types of cancer. This observation was supported by the hypothesis that low selenium levels would reduce the role of glutathione peroxidase, an enzyme that neutralizes free radicals in the body. Prospective studies were needed to obtain more insight into the role of selenium and the impact of nutrition. Such studies, organized and interpreted by epidemiologists, involve large groups of a population in order to obtain statistically sound evidence. It is not uncommon for 50 000 to 100 000 people to be examined and re-examined over time for case control studies. The first such studies dealt with breast and colon cancer. Later on such studies were extended to, for example, gastrointestinal, bladder and prostate cancer.

Studies dealing with other diseases and hypotheses on the role of trace elements in metabolism resulted in interest in the elements mercury, chromium, iron and zinc in connection with myocardial infarction, chromium in connection with diabetes, calcium and magnesium in connection with osteoporosis, and selenium and copper in connection with pre-eclampsia.

If it were possible, epidemiologists would like to study the element status of persons in case and control studies by analysing blood samples, in particular serum and red blood cells. However, this is an impossible task from a logistical and financial point of view. Not only will there be resistance to providing blood, but there is also the problem of sample storage and conservation. Hence several other bioindicators have been investigated, and finally nail clippings were selected for the work presented here. Like hair, nails consist mainly of keratin, a material that contains sulphur. Selenium, the first element of study, is chemically very similar to sulphur. Nail clippings are easy to collect, the material is stable over time and the clippings can simply be preserved in bags in cooled rooms. Moreover, since the average fingernail grows 0.01 cm/day (the average toenail less than this), nail clippings also provide a time window.

The organization of such a cohort study, including sample collection and data interpretation, is a rather expensive activity. Since the material is collected only once, non-destructive analytical techniques are strongly preferred over techniques in which precious collected material might, through analytical errors, be completely lost, for example by dissolution.

In addition, it often occurs that epidemiologists cannot obtain initial funding for a full multielement scan, so that only the elements of highest immediate priority are selected for determination. However, new funding for the determination of other trace elements might be obtained in subsequent years. This is an additional reason why collected material should not be lost after the first round of analyses. The analytical technique should have adequate sensitivity, should be under strict quality control with a high degree of reproducibility, and should allow for easy automation and high throughput, i.e. the analysis of a large number of samples in a short time.

Why nuclear analytical techniques?

Instrumental neutron activation analysis (INAA) and X ray fluorescence (XRF) spectroscopy are the only analytical methods in which the material is not destroyed but can be preserved for other applications after the measurement has been completed. For this type of analysis the sensitivity of INAA makes it superior to XRF, since the amount of selenium, the element to be studied, is very small (of the order of several nanograms — billionths of a gram) owing to the relatively small samples provided (of the order of 20–50 mg). In addition, the results in INAA are not influenced by chemical matrix effects, so any type of reference material with a well known amount of selenium that is measurable under the same conditions as the real samples can be applied for quality control. A large throughput of samples can be attained by determining selenium via the measurement of ^{77m}Se (half-life 17.5 s).

The multielement character of INAA also allows the simultaneous determination of other elements which may turn out to be of unanticipated importance.

How to solve the problem?

Toenail clippings were collected by the participating epidemiologists, often in collaboration with medical centres. In several case control studies other material (such as blood) was also collected from selected persons. Extensive questionnaires were used to obtain background information on the persons' living habits (food intake, smoking, etc).

The clippings were cleaned in the laboratory using a quartz knife. Washing procedures were initially not applied since insufficient information was available on possible leaching effects. Later on it was shown that cleaning by rinsing in turn with water and acetone does not affect the selenium present in the keratin.

The clippings were transferred in small polyethylene vials. The standard reference material NIST 1572 (trace elements in bovine liver) was used for quality control in the selenium determination. The analytical procedure consisted of irradiation for 17 s and measurement for 30–60 s carried out as quickly as possible (typically 15–20 s) after completion of the irradiation. Thus approximately 25 samples and standards could be processed per hour, which met the requirements of the epidemiologists.

Routine approaches were applied for the determination of the other trace elements (e.g. chromium, iron, zinc and mercury). These consisted of irradiations for 4 h and countings 2–4 weeks after irradiation. Various quality control materials were applied.

In the development of the analytical protocols, much attention was given to obtaining the best possible counting statistics, in order to facilitate the comparison between cases and controls. This required irradiation in the highest neutron flux available and the use of high efficiency counting equipment (such as well-type semiconductor detectors).

Bibliography

GUALLAR, E., et al., Mercury, fish oils, and risk of myocardial infarction, N. Engl. J. Med. **347** (2002) 1746–1753.

VAN DEN BRANDT, P.A., et al., A prospective cohort study on selenium status and the risk of lung cancer, Cancer Res. **53** (1993) 4860–4865.

— A prospective cohort study on toenail selenium and the risk of gastrointestinal cancer, J. Natl. Cancer Inst. **85** 3 (1993) 224–229.

— Predictors of toenail selenium levels in men and women, Cancer, Epidemiol., Biomarkers, Prevention **2** (1993) 107–112.

— Toenail selenium and the risk of lung, gastrointestinal and breast cancer: A prospective study, Am. J. Epidemiol. **138** (1993) 626–627.

ZEEGERS, M.P.A., GOLDBOHM, R.A., BODE, P., VAN DEN BRANDT, P.A., "Prediagnostic toenail selenium and risk of bladder cancer", Congr. of Epidemiology, Toronto, 2001, Cancer, Epidemiol., Biomarkers, Prevention **11** (2002) 1292–1297.

Breath test to diagnose the presence of *Helicobacter pylori,* the causative agent of active chronic gastritis and ulcers

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Problem

In Brazil almost 80% of the population presents the bacterium *Helicobacter pylori,* considered to be the causative agent of active chronic gastritis and ulcers. This does not mean that all of these people will suffer gastritis or ulcers, but it is highly probable. The usual diagnostic procedure used a microbiological culture in mucus biopsy specimens collected during gastroscopy, an invasive method. The problem was to find a non-invasive, easy, fast and efficient procedure to diagnose this bacterium.

Why nuclear analytical techniques?

The nuclear technique applied was liquid scintillation, a suitable technique to measure the low energy β emission of ^{14}C. This was the best method available at the time to develop and establish the test.

How to solve the problem?

In order to develop a non-invasive test to diagnose *H. pylori,* research was carried out with doctors from the Department of Gastroenterology at the School of Medicine of the Federal University of Minas Gerais. This research applied a radiochemical method using ^{14}C, a radioisotope of carbon. The patient's control breath sample was obtained after a 12 hour fast. Then a standard meal was offered to delay gastric emptying, after which the patient drank a determined amount of urea labelled with ^{14}C in water. Breath samples were collected at 10, 15, 30 and 60 minutes in a hyaline–ethanol solution with a pH (acid) indicator. If the bacteria were present, the labelled urea would be metabolized and the ^{14}C would be eliminated as $^{14}CO_2$ by exhalation; otherwise the ^{14}C would be eliminated through the faeces. This ^{14}C urea breath test was applied in around 5000 participants and the results were compared with results obtained through culture. The urea test was a simple, inexpensive, sensitive and reliable method to detect *H. pylori* colonization, a useful test for epidemiological and therapeutic trials.

At present this test is still being applied, but ^{13}C rather than ^{14}C is used to label the urea, and the technique employs infrared radiation, with the advantage that it can be applied to children. The nuclear technique was useful and very important to the establishment of the procedure.

Bibliography

COELHO, L.G.V., et al., *Campylobacter pylori* in the oesophagus antrum and duodenum, Dig. Dis. Sci. **34** (1989) 445–448.

— Test respiratoire à l'urée marquée au carbone-14 pour le diagnostic de la colonisation gastrique par *Helicobacter pylori,* Gastroenterol. Clin. Biol. **14** (1990) 801–805.

MARSHALL, B.J., SURVEYOUR, I., Carbon-14 urea breath test for the diagnosis of *Campylobacter pylori* associated gastritis, J. Nucl. Med. **29** (1988) 11–16.

Evaluation of metal concentration in bovine tissues from a region potentially contaminated by metals

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Problem

The Brazilian daily diet is usually composed of vegetables, rice, beans and meat. Beef is the main protein source for Brazilians, because it is abundant and cheap. Minas Gerais state has the largest number of cattle of any state in Brazil. Kidney and liver are widely consumed by Brazilians. Their consumption is a cultural habit and these meats are cheap. However, some animals are raised in a region potentially contaminated by metals, for example Curvelo City and its surrounding areas. The interest in analysing bovine tissues from this region arose because of the intensive mining activities along the Das Velhas River. The Das Velhas is the second largest river in Minas Gerais state and flows through this region, carrying with it industrial residues, which had previously been detected in local water, soil and forage samples.

Veterinarians were interested in chromium, copper, sodium, potassium, iron and zinc element concentrations in bovine tissues — kidney, liver and muscle — from animals raised in a region potentially contaminated by metal through mining activities, and doctors were interested in knowing the quality of the meat with respect to these elements.

Why nuclear analytical techniques?

The k_0 instrumental neutron activation analysis (INAA) technique was chosen because it was the most suitable technique for these materials. The samples do not have to be chemically processed, avoiding the risk of contamination. They only have to be dried. Besides, this technique was able to determine all the elements of interest to the veterinarians in only one aliquot of the sample, almost simultaneously.

How to solve the problem?

To perform this study, cattle specimens — muscle, kidney and liver — were analysed. The beef cuts and bovine organs used as samples were chosen at random and purchased at butcher shops located in downtown Curvelo. The source of the animal product purchased was checked. Approximately 200 g of each specimen was frozen at –70°C and lyophilized. Each freeze-dried sample was powdered, homogenized and accurately weighed. After the analysis, the values of the Brazilian data were compared with data from international organizations and it was found that they were compatible. It was possible to conclude that the samples were not contaminated, but the cattle should be continuously monitored.

Bibliography

AVELAR, A.C., MENEZES, M.Â.B.C., VEADO, J.C.C., Study of essential elements in cattle tissues from a tropical country using instrumental neutron activation analysis, Food Nutr. Bull. **23** 3 Suppl. (2002) 237–240.

ISTITUTO NAZIONALE DI RICERCA PER GLI ALIMENTI E LA NUTRIZIONE (INRAN), Banca Dati Interativa Composizione degli Alimenti, http://www.inran.it.

IYENGAR, G.V., Elemental Analysis of Biological Systems, CRC Press, Boca Raton, FL (1992).

SUBCOMMITTEE ON MINERAL TOXICITY IN ANIMALS, Mineral Tolerance of Domestic Animals, National Academies Press, Washington, DC (1980).

UNITED STATES DEPARTMENT OF AGRICULTURE, http://www.nal.usda.gov.

How much iodine is in our diet?

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Problem

Even at very low concentrations, many elements have important roles for the optimal functioning of biological systems and for human health. Such elements are termed essential trace elements. Their absence or deficiency produces either functional or structural abnormalities. The abnormalities are related to, or a consequence of, specific biochemical changes that can be reversed by the presence of the essential element. One such element is iodine, which forms an indispensable part of thyroid hormones. Iodine deficiency is a worldwide public health problem and is the single most important preventable cause of brain damage and mental retardation in the world today. The clinical and subclinical manifestations of iodine deficiency are collectively called iodine deficiency disorders (IDDs) and affect all stages of human growth and development. Severe iodine deficiency causes cretinism, and even mild deficiency can cause a significant loss in learning ability. Other effects include goitre and, in women, a higher risk of stillbirth and miscarriage. In 1990 the World Health Organization (WHO) estimated that 1570 million people, i.e. about 30% of the world's population, were at risk of IDD [1].

The major part of essential iodine enters the human organism via the food chain. Iodization of salt (with an iodine content of 25–100 μg/g) is the most effective measure to control and prevent IDD. Many industrialized countries started large scale iodization before 1960. Nevertheless, reliable knowledge of the iodine levels in foods is still of great importance, because even today only approximately 70% of the populations in countries affected by IDD have access to iodized salt.

Why nuclear analytical techniques?

Information on iodine levels in foods is largely lacking in many countries, mainly owing to the analytical difficulties associated with the use of non-nuclear techniques, such as colorimetry based on catalytic reactions, gas chromatography, ion selective electrodes and inductively coupled plasma mass spectrometry. Most of these methods are not sufficiently sensitive for iodine determination at low levels, and most of them are also not very selective and free from various kinds of interference. On the other hand, nuclear analytical methods, such as isotope exchange and neutron activation analysis (NAA), appear to be the techniques of choice for the accurate determination of iodine in trace amounts. NAA is especially suitable for this purpose owing to its inherent sensitivity, selectivity and freedom from reagent blank and matrix interferences. There are several approaches to the use of NAA for iodine determination. The possibilities of non-destructive instrumental NAA (INAA) with thermal neutrons are rather limited because of the high background formed by neutron activation products of sodium, potassium, manganese, bromine and chlorine, which are present in appreciable quantities in most biological materials. Activation with epithermal neutrons (ENAA) improves the signal to background ratio significantly, and its combination with Compton suppression counting in particular provides a detection limit in the range of tens of nanograms per gram, which is sufficiently low for many types of biological materials and foods. An even better detection limit, down to nanograms per gram, can be achieved using radiochemical separation in radiochemical NAA (RNAA).

How to solve the problem?

Samples of diets from six Asian countries were analysed using ENAA and RNAA within the framework of the IAEA project Reference Asian Man, which aims at obtaining data on daily intake of nutrients and trace elements, including iodine [2]. It has been found [3] that, in most of the countries, consuming staple foods (cereals, rice, vegetables, etc., with iodine contents in the range 7–40 ng/g, dry mass) without the addition of iodized salt cannot yield the recommended daily intake of iodine, which amounts to 150 µg/d during adolescence and adulthood and 200–300 µg/d during pregnancy and lactation [4]. Exceptions are populations that frequently consume seafood rich in iodine (e.g. up to 21.7 µg/g, dry mass, in duplicate diet samples from Japan). In addition to iodine determination in foods, ENAA and RNAA were also used to analyse a number of food reference materials in which the iodine content was not known or was known only with a large uncertainty [3]. The newly obtained reference values will help other laboratories in optimizing their analytical procedures to be able to arrive at reliable values of iodine in foods in future studies.

It can be concluded that more effort on the part of national governments and the salt industry is needed to achieve universal salt iodization in the countries where there still exist groups at risk of IDD.

References

[1] WORLD HEALTH ORGANIZATION NUTRITION UNIT, Global Prevalence of Iodine Deficiency Disorders, MDIS Working Paper 1, WHO, Geneva (1993) 1–80.

[2] IYENGAR, G.V., et al., Food Nutr. Bull. (in press).

[3] KUČERA, J., IYENGAR, G.V., ŘANDA, Z., PARR, R.M., in Proc. 7th Int. Conf. on Nuclear Analytical Methods in the Life Sciences (NAMLS-7), Antalya, Turkey, 2002, J. Radioanal. Nucl. Chem. **259** (2004) 505–509.

[4] WORLD HEALTH ORGANIZATION, Trace Elements in Human Nutrition and Health, WHO, Geneva (1966) 49–71.

Instrumental neutron activation analysis as an analytical tool supporting the establishment of guidelines and databases for workers' health awareness programmes

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Problem

Belo Horizonte and its surrounding areas are an important industrial centre, the third largest industrial centre in Brazil, where many industries in several fields are concentrated. Considering the hazards that can arise from some chemical elements, contamination by metals is a health hazard for workers at different plants. However, there are no records of the level of metal concentration in the environmental air in industry, nor even any records of the level of contamination of factory workers. In Belo Horizonte alone there are more than 20 galvanizing factories, ranging from home factories to well equipped ones. The galvanization industry was chosen as the object of the present project because it is responsible for the majority of patients who seek medical assistance because of metal contamination.

Galvanization is an electroplating process whereby a coating is deposited on a form by means of electrolysis. It is a kind of industrial process that does not demand a complex structure to be installed, and that involves only low maintenance costs and an inexpensive and readily available labour force. The term 'hard chromium' is applied to factories where the main industrial process is to plate chromium, usually over very large items such as car parts. 'Decorative chromium' means that various kinds of electrodeposition are applied involving chromium, zinc, nickel, brass, gold, silver and copper plating. In general the plating is over small items such as taps, trays and decorative items.

In this kind of industry, chromium is among those elements that are responsible for the great majority of harmful health effects caused to workers in the short term. The toxicity of chromium is well known: the oxidizing agent chromic acid and the dichromate salts cause various injuries, in some circumstances, for example, perforation of the septum. But exposures in the workplace are registered only when the occurrence of a disease is obvious or probable, that is, in the case of dangerous diseases that are easily identified. The main problem is that the majority of workers are exposed to low levels of toxic chemicals that can be lethal in the long term, owing to chronic diseases. Most often the onset of the diseases goes unnoticed, and the presence of a lung cancer or heart disease is attributed to non-occupational causes. As a result, these cases of illness do not become part of the compiled data. Besides, there is no specialized and complete literature concerning occupational aetiology, nor is there an evaluation of the onset of disease linked to long term exposure to low levels of toxic agents.

With the aim of giving support to the Workers' Health Awareness Programme of the Secretaria Municipal de Saúde (Municipal Department of Health) of Belo Horizonte, capital of Minas Gerais state, an assessment was done in galvanizing factories by means of airborne particulate matter collected in air filters and in hair and toenails as biomonitors. This project was approved by the Ethics Committee of the Federal University of Minas Gerais, COEP-UFMG. All research involving human beings has to be submitted to this committee in order to protect the population studied.

Why nuclear analytical techniques?

The k_0 instrumental neutron activation analysis (INAA) technique was chosen to be applied for the determination of elements in air filters and in hair and toenail samples, as it can determine several elements in the same sample almost simultaneously, with a low detection limit and without any chemical procedure as is required in the majority of non-nuclear techniques, and also because it requires only a small amount of sample for the analysis. The k_0 method was applied to all samples, demonstrating its quality as a versatile technique, and it was confirmed to be one of the most advantageous and suitable nuclear analytical techniques.

How to solve the problem?

Stationary air sampling was carried out in order to evaluate the level of element concentration in the indoor environment of three plants randomly chosen in downtown Belo Horizonte. As the primary objective was to obtain information regarding worker exposure, the samples collected came from places that would reflect as much as possible the indoor environment: near the polishing activities, as close to the chrome and copper baths as possible, in the office and at the items reception desk. According to the sampling strategy, the Workers' Group sampling was carried out after the participating physicians had explained to the workers the aims of the project and how it would be performed. Volunteers from among the workers donated their toenail clippings and also hair samples. The scalp hair samples were collected according to IAEA instructions and were washed following the IAEA procedure. After being washed, the samples were dried and weighed in the irradiation container. The toenail samples were washed using the procedure described in the literature. After being washed, the samples were air-dried and weighed in the irradiation container. The same procedures for collecting and preparing the biomonitors were applied to the Comparison Group samples.

The high concentrations of elements such as aluminium, arsenic, chromium, copper, gold, iron and silver in the workers' samples as well as in air filters surprised the physicians because, while many studies concerning this industrial process had considered various aspects, including the consequences of chromium and nickel contamination, none had so far detected and measured other elements, such as antimony, arsenic, gold and silver — elements not considered essential for human beings. Other elements considered essential had been determined, but in high, perhaps toxic, concentrations. This first assessment indicated the need to assess the influence of long term exposure and will support the establishment of guidelines and databases for the next occupational programme for this specific type of workplace. Concerning the elements determined in air filters, 92.3% of them were also determined in hair and toenail samples: aluminium, antimony, arsenic, chlorine, chromium, copper, gold, iron, manganese, silver, sodium and zinc. These results point out that hair and toenails reflect the influence of the polluted environment on workers' health and can be useful as bioindicators in epidemiological studies as well as in individual studies.

Bibliography

MENEZES, M.Â.B.C., et al., "Workplace and occupational health: The first metal evaluation using nuclear and analytical techniques in the State of Minas Gerais, Brazil", Report of the First Research Co-ordination Mtg on Assessment of Levels and Health Effects of Airborne Particulate Matter in Mining, Metal Refining and Metal Working Industries Using Nuclear and Related Analytical Techniques, Vienna, 1997, IAEA, Vienna (1998).

— "Galvanizing industry: Evaluation of contamination level using biomonitors", Proc. General Conf. on Nuclear Energy, Belo Horizonte, 1999, Brazilian Assoc. for Nuclear Energy, Belo Horizonte (1999) CD-ROM.

MENEZES, M.Â.B.C., MAIA, E.C.P., ALBINATI, C.C.B., SABINO, C.V.S., BATISTA, J.R., "How suitable are scalp hair and toenail as biomonitors?", Proc. 7th Int. Conf. on Nuclear Analytical Methods in the Life Sciences (NAMLS-7), Antalya, Turkey, 2002.

MENEZES, M.Â.B.C., SABINO, C.V.S., AMARAL, A.M., MATTOS, S.V.M., FILHO, S.B.S., "k_0-NAA applied to certified reference materials and hair samples: Evaluation of exposure level in a galvanising industry", Proc. Conf. on Modern Trends in Activation Analysis, Bethesda, MD, 1999, J. Radioanal. Nucl. Chem. **245** 1 (2000) 173–178.

SILVA, C.S., Um Estudo Crítico sobre a Saúde dos Trabalhadores de Galvânicas, por Meio das Relações entre as Avaliações Ambientais, Biológicas e Otorrinolaringológicas, PhD Thesis, Chemical Inst. of São Paulo Univ. (1998) 196 pp.

Part V

INDUSTRIAL APPLICATIONS

Analysis of industrial material with X ray fluorescence

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Problem

The content of selenium in a calcium carbonate based fodder additive was determined by X ray fluorescence (XRF) analysis using radionuclide excitation. The aim was to develop a fast and uncomplicated technique that could be used on-site, for example in a factory or in other places of industrial scale production of material. The selenium contents to be determined were around 4–5 mass per cent in the additive, which is produced in tonne quantities; hence emphasis was placed upon the mobility and simplicity of the device rather than upon the possibility of analysis of small traces.

Why nuclear analytical techniques?

Most of the analytical techniques usable for selenium determination require a chemical pretreatment of the material and/or a separation of the element from the matrix analysed. An analysis without chemical treatment steps included can be carried out only by radiation methods, e.g. activation analysis or XRF spectrometry. The advantage of the former is the extremely low limit of detection. However, on the one hand, the instrumental and procedural effort required is great, and on the other hand, as mentioned above, a trace determination was not required in this case.

In addition, activation analyses usually cannot be performed on-site. Therefore an XRF spectrometer was used that can be installed and run on-site quickly (Figs 1 and 2). Moreover, it can be used without an external power supply, since fluorescence excitation is carried out by using a radionuclide (^{241}Am, activity 0.5 GBq), and the spectrometer can be powered by battery. The lifetime of the radiation source is conveniently long (half-life 430 years), so a practically constant source strength can be assumed.

How to solve the problem?

The samples to be analysed were pressed into pellets of 20 mm diameter and about 2 mm thickness. The pellets were placed in a sample changer and exposed to the γ emission of

FIG. 1. X ray spectrometer.

the americium source (energy 59.6 keV) at a favourable incident angle (Figs 1 and 2). The characteristic selenium X rays were measured with a spectrometer which consisted of a small silicon PIN diode and a small and highly integrated pulse processor controlled by notebook computer. The spectra thus produced were processed by appropriate PC programs. The quantification was performed using synthetic calibration materials with well known selenium contents. The analyses could be carried out quickly (exposure period about 5 min). The total time required for the complete analysis on-site is dependent upon several additional parameters (rapidity of sampling, pellet pressing, transfer to the spectrometer, etc.).

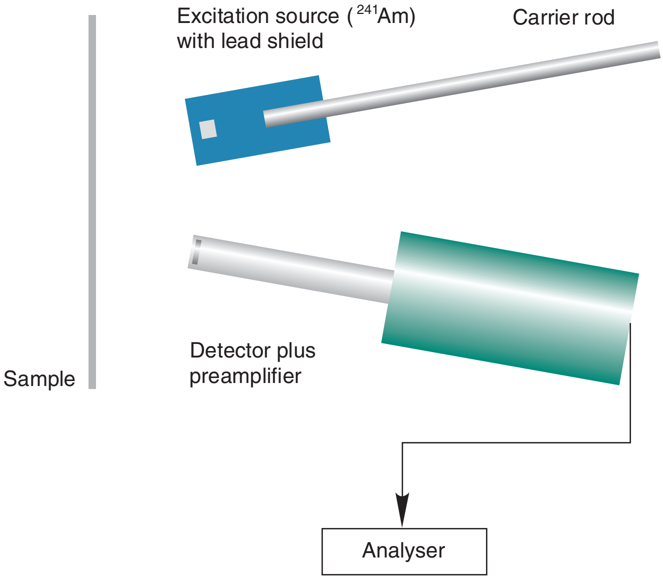

FIG. 2. Schematic drawing of the X ray spectrometer.

Bibliography

KEMPENAERS, L., VINCZE, L., JANSSENS, K., Spectrochim. Acta Part B **55** (2000) 651–669.

Trace contamination in pure high-tech materials

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Problem

High purity refractory metals and their oxides are widely used in advanced technology, for example in microelectronics or parts of turbines and aircraft. The purity requirements are extremely high, as mobile ions may alter the materials' mechanical and electrical properties to a large extent. Additionally, α emitters such as Th and U can produce defects in data storage cells. Control of these impurities in raw materials as well as during the production process and in the final product requires the greatest sensitivity and the virtual absence of blanks in the analytical process.

Why nuclear analytical techniques?

Neutron activation analysis (NAA) is a direct, non-destructive method with extraordinary sensitivity for some of the important elements in high purity materials. If, after irradiation, the samples are removed from the irradiation containers prior to counting, the method can be considered as basically blank free. The power of determination can be additionally increased by post-irradiation chemistry, where the concentration of the radionuclide produced during irradiation and used for counting will not be altered by the addition of the stable isotopes of its parent element. This makes radiochemical neutron activation analysis (RNAA) an ideal candidate for the sensitive quantification of trace contamination in high purity refractory metals and metal oxides. Competing analytical techniques, such as thermal ionization mass spectrometry (TIMS), inductively coupled plasma mass spectrometry (ICP-MS) or atomic absorption spectrometry (AAS), have to contend with the digestion of the materials, increasing the risk of contamination, or are confined to surface analysis, as in the case of proton induced X ray emission (PIXE) or laser and spark source mass spectrometry.

How to solve the problem?

Silicon nitride has become one of the most important non-oxide ceramic materials for use in high temperature parts of engines and gas turbines. In microelectronics, ultra-pure silicon nitride is used as a substrate and package material for integrated circuits. It was found that the presence of oxides of alkali and alkaline earth elements may lead to fracture and subcritical cracking at high temperatures. Other trace elements were investigated with regard to their influence on the dielectric properties. Comprehensive characterization of the starting materials as well as of the final product is needed, and instrumental neutron activation analysis (INAA) and RNAA proved to be the methods of choice for this delicate analytical challenge. Using optimized irradiation, decay and counting conditions, and owing to the fact that Si and N produce only short lived radioisotopes, up to 55 elements in several high purity Si_3N_4 materials could be determined quantitatively by INAA. Some of the concentrations determined instrumentally have been successfully validated by RNAA [1]. Excellent limits of detection have been achieved by INAA: 14 elements below 0.1 ng/g, 14 elements between 0.1 and 1.0 ng/g, 11 elements between 1 and 10 ng/g, and 8 elements between 10 and 100 ng/g; the 8 remaining elements were detectable only at >100 ng/g.

Naturally occurring α emitters are known to be responsible for changes in the potential of memory cell units by single-event phenomena causing the 'soft error effect'. The required purity of wafer silicon and package material used for integrated circuits with respect to Th and U is lower than 5 ng/g and 1 ng/g, respectively, and demands high accuracy and precision from the applied analytical technique. The most powerful techniques in this respect are mass spectrometry and activation analysis. NAA has proved to be a very suitable method for the determination of ultra-traces of Th and U via their daughter nuclides ^{233}Pa and ^{239}Np. The extremely low limits of detection that are required demanded the elaboration of an efficient separation procedure for RNAA. High purity quartz, silicon nitride, polyimide and aluminium oxide were investigated using the radiotracer technique for yield determination. Prior to counting the activity, an ion exchange procedure was used to purify the radioisotopes from the neutron irradiated sample after digestion. Depending on the purity grade of the materials, limits of detection of 10–100 pg/g for both elements were achieved. Comparison of the results with results obtained by ICP-MS agreed within 20–30%, which, considering the extremely low concentrations in Si_3N_4 (230 and 190 pg/g for Th and U, respectively) was excellent [2].

Aluminium oxide and aluminium nitride, the most important raw materials for advanced ceramics used in microelectronics and bioceramic endoprotheses, must be of the highest possible purity to ensure their mechanical and insulating properties. Oxides of Cr, Fe, Mg, Na and Ti affect the electrical resistivity of ultra-pure Al_2O_3, whereas the oxides of Ca, Fe, Mg, Na, Si and Zr reduce the thermal stability and shock resistance. Because of the refractory character of the two materials, direct determination methods using solid samples are of great interest for their analysis. A combination of INAA and RNAA was developed for the characterization of 56 elements in raw and high purity aluminium oxide and nitride powders [3]. Again the comparison with results of other laboratories using ICP atomic emission spectroscopy (ICP-AES) within a round robin study showed good agreement for elements above the limit of detection for the latter method. Although some of the important elements (B, Mg, V) could not be detected by NAA, it was shown that INAA and RNAA had sufficient detection power for most of the relevant elements interfering with the properties of high purity ceramic materials.

References

[1] FRANEK, M., KRIVAN, V., Multi-element characterization of silicone nitride powders by instrumental and radiochemical neutron activation analysis, Anal. Chim. Acta **264** (1992) 345–358.

[2] FRANEK, M., KRIVAN, V., Determination of sub-ng g^{-1} concentrations of thorium and uranium in microelectronic materials by radiochemical neutron activation analysis, Anal. Chim. Acta **274** (1993) 317–325.

[3] FRANEK, M., KRIVAN, V., Multi-element analysis of aluminium-based ceramic powders by instrumental and radiochemical neutron activation analysis, Anal. Chim. Acta **282** (1993) 199–207.

Trace element determinations for advanced material research

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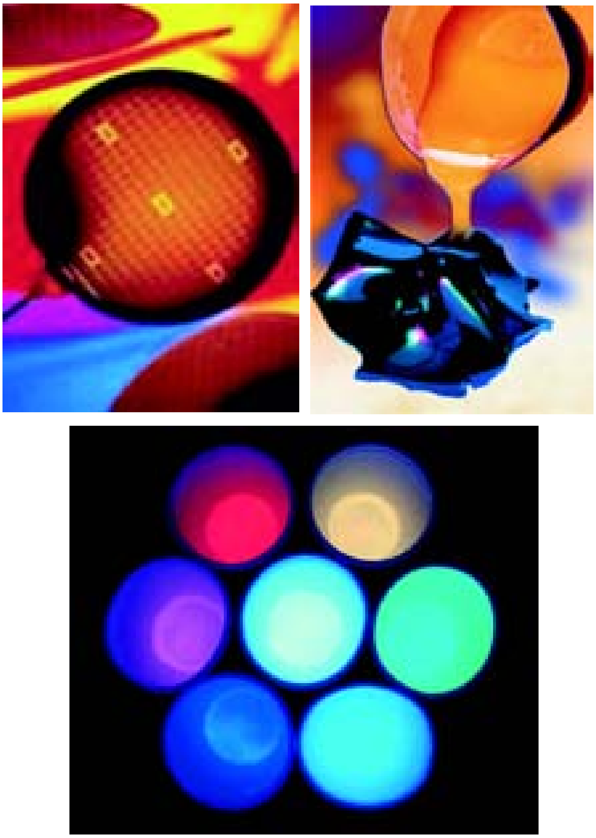
Problem

For many years, determination of the rare earth elements in trace element studies was limited to their role as indicator elements in geology and related fields. In recent years, these elements have acquired new interest. Currently the rare earth elements are being used in several rapidly expanding markets, for equipment and components such as:

— High performance catalytic converters for diesel engines (high purity Ce and La);
— Pigments (Ce) for plastics and paints to replace Pb, Cd and Hg based pigments;
— High luminosity lamps (Y, La, Ce, Eu, Tb);
— Phosphors for flat screen monitors (Y, Eu, Dy) as well as pigments;
— Critical components in mobile phones, fine ceramics, etc.;
— (Permanent) magnets (Ce, Sm, Nd) and batteries;
— Optical devices such as optical fibres (La, Lu, Nd).

The supporting research and development for such applications requires accurate information on the stoichiometry and purity of the rare earth compounds. Product quality control is typically done using X ray fluorescence (XRF) spectroscopy and atomic absorption spectroscopy (AAS). The industrial use of these products containing rare earth elements may eventually have impacts on the environment and on occupational health. In China, several studies have already been initiated on the ecotoxicity of the rare earth elements in view of their levels in phosphate rock based fertilizers produced and used in that country.

Materials based on skeletons of carbon atoms are increasingly being developed and applied because of their relatively low density and their high resistance to abrasion and chemicals. Graphite based ceramics have been developed, amongst others, to support the semiconductor industry, but they are also applied in chemical process industries, as



construction materials in nuclear fusion reactors, in aircraft components, etc. Examples are carbon–carbon composites, silicon carbides and graphite substrates coated by carbon vapour deposition. These materials are heated to temperatures well above 2000°C during the production process, which implies that many impurities vaporize. Typical total ash contents may vary from 30 to 300 mg/kg. The high purity is obviously of importance for applications in the production process of high purity silicon compounds.

Why nuclear analytical techniques?

The non-destructive character of instrumental neutron activation analysis (INAA) and the fact that it does not require matrix matching reference materials, together with the possibility of controlling contamination, make the technique very suitable for trace element assessments in a wide variety of new materials currently being applied

NAA faces several challenges when dealing with the analysis of rare earth element concentrates, in particular when dealing with final products of irregular shapes. Since the average atomic number of these materials may be much higher than in traditional materials analysed (soil, rocks, air filters), γ ray self-attenuation should be anticipated. Although there is no need for matrix matching calibrants — which make the analysis of these materials especially difficult in the case of other techniques — the availability of well characterized standards for calibration and material for internal quality control may be a problem. The European Union recently initiated the development of several (environmental sciences oriented) reference materials to be characterized for the rare earth elements, and this process is also under way in other countries.

With respect to the analysis of high purity silicon and carbon based compounds, the advantage of INAA lies in the possibility of minimizing and controlling contamination prior to the start of the analysis procedure (packing for irradiation). In other methods for element determination, the material has to be dissolved, resulting in a distinct risk of contamination.

How to solve the problem?

There is no standard recipe for the analysis of new, advanced materials [1]. An experienced NAA practitioner may use the technique to greatest advantage by extrapolating, for example, the neutron fluence (irradiation time × neutron flux) and/or the detection capabilities (detector efficiency × counting time).

Some of these materials may contain elements, e.g. B, Gd and Sm, with high neutron absorption characteristics. It is the responsibility of the NAA practitioner to acquire the necessary prescience concerning the samples to be analysed to decide on preventive actions in developing the analysis protocol. Therefore sample masses may often have to be kept small to limit the effects of neutron and γ ray self-attenuation. In such cases, well type Ge detectors are very useful to compensate for the small sample mass and to avoid the geometry effects that otherwise would occur in counting close to the end cap of a normal coaxial detector. A secondary spin-off is that NAA may serve to validate other analytical techniques should the latter still be preferred for such analyses.

The trace element levels in high purity silicon and carbon composites are extremely low, so the highest neutron fluxes and the highest counting efficiencies are needed (such as those available using well type detectors or large volume semiconductor detectors). A special irradiation facility was designed for silicon wafers [2]. In a clean laboratory the wafers (diameter up to 15 cm) were packed, up to ten in a batch, into special quartz containers consisting of two half-cylinders. The cylinders were moulded together. The entire container was rotated during irradiations in which the wafers were perpendicular to the fuel elements of the reactor core. The containers were opened after a sufficient cooling time. The wafers were counted on the end cap of a detector and were regularly etched so as to study the distribution with depth of the trace elements in the surface layer of the wafer.

References

[1] BODE, P., VAN MEERTEN, T.G., Challenges for INAA in studies of materials from advanced material research, including rare earth concentrates and carbon based ceramics, J. Radioanal. Nucl. Chem. **44** (2000) 497–500.

[2] VERHEIJKE, M.L., JASPERS, H.J.J., HANSSEN, J.M.G., THEUNISSEN, M.J.J., Applications of neutron activation analysis in the field of silicon technology for the modern electronic industry, J. Radioanal. Nucl. Chem. **13** (1987) 397–403.

(Trace) elements on catalysts in chemical technology

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Problem

Catalysts containing metal compounds are widely applied in the chemical industry. Scientific research on the properties, optimization, stability and consumption rate of the compounds requires determination of the relevant elements. Samples of the catalyst are taken, for example, at various stages of the chemical reaction or under different chemical reactor operating conditions (temperature, pressure, loading).

Why nuclear analytical techniques?

Often the catalysts are based on substrates such as polymer, alumina (aluminium oxide) and silica (silicium oxide). The active compounds are adsorbed onto these substrates and obviously cannot easily be removed for analysis. Thus the entire catalyst (substrate plus active compound) has to be analysed. The materials mentioned above all are difficult to dissolve, and control of complete digestion is very difficult. Moreover, there are no matrix matching reference materials for the compounds and elements applied (such as Rh, Pd, Te, Ce, La and Hf).

Nuclear analytical techniques such as instrumental neutron activation analysis (INAA) have ideal characteristics for the determination of metals on substrates such as polymer, alumina and silica. INAA is non-destructive, so cumbersome problems such as complete dissolution of the compound can be overcome. The major components of these materials do not produce interfering radioactivity for the determination of the elements of interest. There is no need for matrix matching standards. The elements of interest are often present in high concentrations, and very small amounts of catalyst are often sufficient. The high concentrations also result in a determination with a very good measurement uncertainty.

How to solve the problem?

The determination of trace elements on catalyst substrates does not follow a uniform protocol but has to be adapted to address each specific question. For instance, the determination of Rh on alumina and silica requires a measurement to be made rapidly after activation because the nuclide ^{104}Rh (half-life 42 s) has to be determined. For elements such as Ce, La and Hf, a longer decay time can be applied, although, if smartly designed, an analysis may be completed within one working day.

There are few or no certified reference materials in which the elements typically applied in catalysis are known to a high degree of accuracy. Quality control can, however, be performed using samples of pure element standards or aliquots of working standard solutions.

Controlling static charge

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Problem

When two insulators are brought into contact with and possibly rubbed against each other, electrons will move across the interface. When they are then separated, one material will be left with a positive charge and the other a negative charge. The static charge thus produced will not dissipate easily from the surface of such materials.

Although static charges are not visible, their effects are quite noticeable. The introduction of static electric charging in a manufacturing environment can lead to production problems such as material jams, misfeeding of product and programming errors in servo-controllers sensitive to an electromagnetic field, resulting in reduced product quality and increased production costs.

Additionally, a buildup of static charge can attract dust and dirt. Another concern is electrostatic discharge, which can ignite combustibles, shock personnel and destroy sensitive electronic components or other materials.

Industries that are particularly susceptible to static problems are paper production, plastics and film production, hard disk manufacturing, electronics manufacturing and assembly, wafer processing, packaging and many more. Also affected are many applications associated with the processing of photographic and radiological films, as well as analytical equipment used in scientific laboratories.

In moving web applications, static charges are frequently generated from the continuous friction of the material in process as it passes over and then separates from the rollers (Fig. 1).

Hence systems or devices that can neutralize static charges on processed materials or products can reduce product damage and loss, and can enhance product cleaning processes in the electronics, graphics, printing and converting industries.

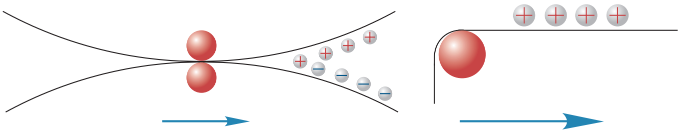

FIG. 1. Friction, pressure and separation are the major causes of industrial static electricity.

Why nuclear analytical techniques?

Alpha particle emitting ion sources totally eliminate static buildup, not just reduce it, as with other methods of static control. Alpha particle ionizers provide a balanced output without the need for periodic calibration or monitoring, resulting in higher productivity and reliability.

This type of ionizer does not require a high voltage power supply to produce ions. Therefore such ionizers are safe to use even in volatile or solvent laden environments, and, unlike electrical ionizers, they pose no risk of electrical shocks to people and components sensitive to electrostatic discharge.

How to solve the problem?

Alpha particles are emitted from, for example, ^{210}Po with sufficient energy to cause ionization of gas or air molecules, i.e. they can strip off electrons from gas atoms. Alpha particles are emitted at a rate of 2.2×10^{12} particles$\cdot$min$^{-1}\cdot$Ci^{-1} (1 Ci = 37 GBq) from the nucleus of the polonium atom at 5.3 MeV energy. Positive and negative ions are created as the α particle strips electrons from the surrounding air or other gas molecules. With each interaction the α particle loses about 34 eV of energy. The particle will travel about 4 cm in air before it loses sufficient energy to no longer generate new ions. At this point it will pick up two electrons and become a stabilized helium atom.

A single α particle creates more than 100 000 ion pairs. Ions can move towards a charged surface by two means: passive (no air movement) or forced (with a blower or compressed air). The passive means takes advantage of the electric field and basic electrostatic attraction principles. Forced air picks up the ions and propels them towards the charged surface. Passive neutralization will always yield a faster decay time than the forced air method owing to the dilution and dispersion of the ions in the air stream. Grounding the source holder will intensify the electric field and produce secondary ions. In many cases this effect can double the number of ions in the field. To achieve this effect the distance between the ionizer and the charged surface must be increased to allow more interactions with air molecules. The proper distance can be determined experimentally and is affected by factors such as the strength and density of the electric field, ion mobility and ground positioning.

As can be seen in Fig. 2, a positively charged surface attracts negative ions and repels positive ions. At the surface the two charges recombine and the surface becomes neutral.

Commercially produced α energy devices are available in many configurations, including ionizing guns, blowers, fans, in-line cells, spot sources and bars. The α emitting foils in these devices are produced as 'sealed sources' where the polonium is sealed between layers of a precious metal. Owing to the 138 day half-life of polonium, the ionizing cells must be replaced every 12 months.

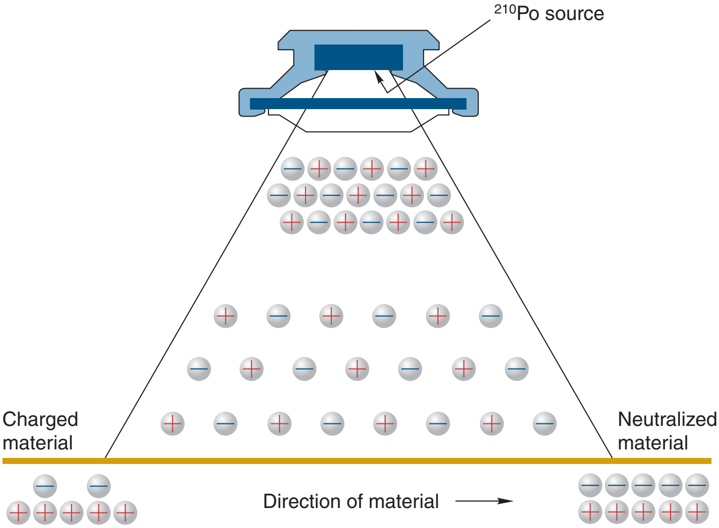

FIG. 2. Alpha particles interact with air molecules, and ionized air is generated to neutralize static charges on a non-conducting surface.

Is it safe to use recycled paper and board packaging in contact with food?

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Problem

We were asked by the United Kingdom Food Standards Agency whether it was safe to use recycled paper as food packaging in contact with dry food. We carried out an extensive search on the extent of use of recycled paper in contact with food, and collected a wide range of samples of recycled and virgin papers, including products such as egg boxes, pasta boxes, cake wrappers, salt drums and sugar bags. We needed to first determine the concentrations of major and trace elements in these two types of paper, to establish whether recycled paper contained elevated concentrations of potentially toxic elements. Secondly, if these elements were concentrated in the recycled paper, we needed to investigate whether they migrated from the packaging into food, and thus posed a risk to human health.

Clearly an analytical technique was required that could determine a large range of elements at trace concentrations in the complex paper matrix. Paper contains a range of major elements such as aluminium, calcium and sodium, and trace elements such as zinc, chromium, barium and iron. These elements or 'inorganic contaminants' relate to various compounds used in the paper making process, such as fillers and additives, or printing inks used on the paper surface. Dissolution of the complex matrix of paper is not easy and so analytical techniques requiring the sample in solution (such as inductively coupled plasma mass spectrometry (ICP-MS)) could be quite difficult.

Once the paper packaging material had been characterized, the problem that faced us was how to determine any migration of potentially toxic elements from the paper product into the food. If a technique like ICP-MS were used, one would first need to know very accurately and precisely the concentration of an element in the food to be tested, and to know the degree of variation of that element within the food. On migration, any changes in the concentration of the element of interest would have to be determined, which would be difficult to carry out with extreme accuracy. For example, it would be difficult to detect migration of one part per billion of zinc into a sample of rice containing one part per million of zinc. A more accurate and repeatable method was required that would ensure that any inorganic contaminants in the food due to migration from the packaging were easily identified and quantified.

Why nuclear analytical techniques?

Neutron activation analysis (NAA) was used for the determination of major and trace elements in virgin and recycled paper and board packaging because it is a highly sensitive multielement analytical technique, capable of determining over 60 elements in a solid sample. NAA is a particularly adaptable method with reference to sample form, sample size, sample shape and sample preparation. The paper sample can be in the form of a solid, requiring no dissolution stage, where volatile elements such as mercury can be lost. The sample can weigh anything from micrograms to hundreds of grams, although in this case about one gram was used. One of the major advantages of the method is that preparation of the paper is limited to tearing the sample into small pieces before packing it into a polyethylene container for irradiation. The sample shape together with size is, however, significant, as geometry will affect the activity produced and care must be taken to reproduce the geometry with a suitable standard.

The most appropriate neutron source, with the highest flux, is a thermal nuclear reactor. A suitable reactor will have a high proportion of thermal neutrons, in conjunction with a component of epithermal and fast neutrons. The Imperial College Research Reactor, CONSORT, was used for this purpose. It is light water moderated and cooled, and has a neutron flux of up to $2.5 \times 10^{16} \cdot m^{-2} \cdot s^{-1}$. Detection limits were demonstrated to be sufficiently low to provide adequate assurance of the quality of the packaging for all of the toxic elements determined.

Neutron activation was also used to develop a radiotracer method to evaluate the migration of trace elements from recycled paper and board into food. It was based initially upon work carried out by Thompson et al. which looked at the migration of toxic metals from plastic packaging into liquids. This method has the key advantage over traditional methods that it can be applied to real food. The main concept of the test relies upon the fact that if any elements migrate following activation, they will be revealed as radioactivity in the food. With this method, samples of recycled paper and board are irradiated in duplicate and counted to establish homogeneity of element distribution. Then the samples are placed in contact with food products for storage periods of up to three months. Finally the food samples are counted using γ ray spectrometry to determine if any radionuclides have migrated from the paper and board into the food. The method differentiates between the radioactive element that has migrated from the packaging and the stable elements already present in the food. This is not the case for other non-nuclear analytical techniques, where any element that has migrated from the packaging will be indistinguishable from the 'natural' element in the food.

How to solve the problem?

Work has shown that the recycling of waste paper increases the concentrations of elements in the recycled paper product. Using NAA, common elements such as sodium, magnesium, aluminium, chlorine, potassium, calcium, scandium, titanium, vanadium, manganese and iron were detected. Fifteen other elements were revealed, including chromium, copper, nickel, zinc, gallium, arsenic, selenium, molybdenum, cadmium, antimony, barium, mercury, thorium and uranium. These elements were generally present at extremely low concentrations (<1 mg/kg). However, some of these elements, e.g. chromium, zinc and barium, were seen to increase on a larger scale than the others. To give just a few examples, since over 60 elements were analysed for: chromium concentrations were between 1 and 15 mg/kg, whilst zinc ranged from 8 to 50 mg/kg and barium from 15 to 75 mg/kg. Once element levels in these samples had been established, we could see that there could be a potential problem of migration from the recycled packaging into the food.

Ten examples of packaging with the potential for migration were selected for the study, with products including salt, rice, oats, tea, fruit, pasta, French fried potatoes and pizza. The migration measuring technique consisted of neutron irradiation of the paper packaging sample to activate the radionuclides of elements of interest. The food was then placed in contact with the radioactive packaging to provide a packaging to food ratio. The food was removed at regular intervals (1, 8, 21, 30, 60 and 90 d) and counted on a high purity germanium semiconductor detector to check for any signs of radioactivity, since activity detected in the food sample could only be due to migration from the packaging. One example of fatty food (French fried potatoes) had been included, and for this sample a 2 h test at 100°C was applied. The technique is very sensitive because it is not affected by the presence of a stable element of interest in the food itself.

This was the first time that the radiotracer method had been applied to a real food situation. It was a particularly sensitive method, revealing that migration did occur, but only in very small amounts. The only elements to be detected during the migration test were iron and zinc, and the only foods to show appreciable migration were rice, oats, custard powder and mushrooms. Migration levels ranged from a minimum level of 0.001 mg/dm^2 zinc migration into French fried potatoes to 0.022 mg/dm^2 zinc in mushrooms. Detection limits ranged from 0.001 to 0.1 mg/dm^2, with elements such as zinc giving a detection limit of around 0.002 mg/dm^2. The maximum migration determined in this study was 4.8 μg of zinc and 2.6 μg of iron, which is negligible when compared with the recommended daily intakes of 15 and 14 mg, respectively.

Bibliography

CASTLE, L., OFFEN, C.P., BAXTER, M.J., GILBERT, J., Migration studies from paper and board food packaging materials, 1. Compositional analysis, Food Addit. Contam. **14** 1 (1997) 35–44.

PARRY, S., Activation Spectrometry in Chemical Analysis, Wiley, New York (1991).

— Neutron activation analysis of recycled paper and board in contact with food, J. Radioanal. Nucl. Chem. **248** 1 (2001) 143–147.

PARRY, S.J., ASTON, D.S.J., "Inorganic contaminants in recycled packaging: Potential impact for consumer safety", Proc. Int. Conf. on Nuclear Science and Technology: Supporting Sustainable Development Worldwide, Trans. Am. Nucl. Soc. **83** (2000) 485–486.

THOMPSON, D., PARRY, S.J., BENZING, R., A novel method for the determination of migration of contaminants from food contact materials, J. Radioanal. Nucl. Chem. **213** 5 (1996) 349–359.

Treating wood with chemical preservatives

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Problem

The Canadian softwood lumber industry produces several billion dollars worth of construction lumber each year. Most of this wood is treated with chemicals to protect it against fungi. Some is treated to preserve its appearance until it is installed in a building, while other wood, used for windows, doors and outdoor furniture, is treated more extensively to protect it from decay for many years, and also from insects. Wood is treated by spraying or dipping, and sometimes pressure–vacuum treatment is used to improve the penetration of the treatment solution into the wood. Some of the chemicals used are: IPBC — 3-iodo-2-propynyl butyl carbamate; TBTO — tributyltin oxide; and CCA — chromated copper arsenate.

The problem facing the lumber industry was quality assurance: how to ensure that the correct amount of chemical was applied. The required amounts were well known from previous studies, but application of the correct amounts was not always achieved at the lumber mill. On one occasion, improperly treated lumber began showing mould after crossing the Pacific and the entire shipload had to be returned to the mill. Too little chemical gives inadequate protection while too much increases costs and may be harmful to the environment if it leaches out. The answer was to take samples regularly at the lumber mill and to measure the amount of chemical in them. The problem then became how to measure the amounts of the chemicals in large numbers of wood samples quickly and reliably.

Why nuclear analytical techniques?

Classical methods of chemical analysis, which require dissolving the sample, could not be used for two reasons. First, they are not reliable, because the chemical may form insoluble species in the wood; even if the chemical is soluble, it is still necessary to dissolve the whole piece of wood to be able to measure it. Second, they are too labour intensive and costly. Even modern instrumental techniques that shine light or charged particles onto the piece of wood will not do the job, because they only see the chemicals at the surface, not what has penetrated.

The answer is a nuclear technique. Only neutrons and high energy γ radiation can easily penetrate a piece of wood several millimetres thick to probe what is inside. In neutron activation analysis (NAA) the sample is bombarded with neutrons from a nuclear reactor. The neutrons cause nuclear reactions in the atoms of heavy elements (but not of the light elements carbon, hydrogen and oxygen found in wood) and turn them into radioactive isotopes. After a few seconds the sample is removed from the reactor and placed in front of a γ ray detector. The radioactive heavy elements emit β rays of variable energy and γ rays at specific energies characteristic of the element. The γ rays are detected with a germanium semiconductor spectrometer and the number of γ rays detected at an element's energy gives the amount of the element.

How to solve the problem?

At École polytechnique in Montreal we have a small nuclear reactor called SLOWPOKE (only 5 kg uranium) that is easy to use and that is routinely used for NAA. It produces enough neutrons to easily activate the iodine in IPBC, the tin in TBTO or the arsenic in CCA. We needed to optimize our NAA method for the fast and reliable analysis of large numbers of wood samples.

The sample of wood, typically 20 mm × 20 mm × 4 mm thickness, is placed in a polyethylene vial and sent to the reactor in a pneumatic tube using compressed air. We automated our pneumatic system so that it could be programmed to send up to 100 samples to the reactor one after another and then to the detector, storing all the γ ray spectra on computer disk. We then developed computer software to quickly convert the γ ray spectra into the amounts of the chemical in the samples of wood.

Even though Canada is a big country, wood samples can be sent from the west coast, where the biggest trees are found, to arrive in Montreal the next morning. We have staff ready to analyse the samples as soon as they arrive and send the results the same day. This one day service is necessary because the lumber mills need the quality assurance results before their products can be shipped. The availability of this service is ensured by redundant γ ray spectrometers and the very reliable SLOWPOKE nuclear reactor (only one day unscheduled reactor downtime in 26 years). When the reactor was refuelled in 1997 over a one month period, the service was set up at an alternative reactor.

The NAA technique is accurate and reliable because it is simple and direct. The expertise we have developed in this field has made us the authority in several disputed cases. When wood in windows and doors begins to rot prematurely, the buyer may sue the supplier for falsely declaring that the wood had been given adequate chemical protection. Samples of the decaying wood are sent to us, and our measurements prove whether the chemical is present as claimed or not.

Bibliography

BARNES, H.M., Wood protecting chemicals for the 21st century, Document 93-30018, International Research Group on Wood Preservation, Stockholm (1993).

CSERJESI, A.J., JOHNSON, E.L., Mould and sapstain control: Laboratory and field tests of 44 fungicidal formulations, For. Prod. J. **32** (1982) 10, 59–68.

École polytechnique de Montréal, http://www2.polymtl.ca/nucl/.

EDEN, D., WAKELING, R., CHITTENDEN, C., VAN DER WALLS, J.G., Field performance of novel anti-sapstain formulations, Document 97-30125, International Research Group on Wood Preservation, Stockholm (1997).

Part VI

NON-DESTRUCTIVE TESTING, AND ANALYSIS OF ART OBJECTS

Radioisotope applications for troubleshooting and optimizing industrial processes

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Problem

Though radioisotope technology is applicable across a broad industrial spectrum, the petroleum and petrochemical industries and the mineral processing and wastewater treatment sectors are identified as the most appropriate target beneficiaries of radioisotope applications. These industries are widespread internationally and are of considerable economic and environmental importance.

The petroleum industry is one of the main users and beneficiaries of radioisotope technology. Chemical and petrochemical plants are generally continuously operating and technically complex establishments where radioisotope techniques are very competitive and are largely applied for troubleshooting inspection and process analysis. Mineral processing plants are to be found in one form or another in practically every country in the world, and in many cases they are major contributors to national economies. Though the range of minerals that are extracted and processed is extremely wide, there are certain processes found throughout the industry that involve multiphase flow and are notoriously difficult to control. Radioisotope technology is of proven benefit in optimizing mineral resource recovery. Radiotracers are tools of choice for efficiency testing of wastewater treatment installations, aiding in both their design and their performance optimization.

Benefits derived from troubleshooting: Radioisotope technology is used to diagnose specific causes of inefficiency in plants or process operations. In very many cases the benefit is derived in the form of savings associated with plant shutdown minimization and loss prevention.

Benefits derived from process optimization: Radioisotope measurements provide information that facilitates improvements in either the throughput or the product quality.

The economic and employment benefits from the use of radioisotopes in industry are estimated at several billion US dollars per year, which indicates the important and competitive role of radioisotopes in industrial growth.

Why nuclear analytical techniques?

Radiotracer and sealed source technology in the petrochemical industry: Radiotracers and radioisotope sealed sources are commonly applied to the solution of problems in petrochemical plants and oil refineries.

Gamma scanning technique for troubleshooting inspection of columns: To carry out an internal inspection of any process equipment without interrupting production, γ scanning is the best technique. A collimated beam of penetrating γ rays (^{60}Co or ^{137}Cs) passing through a vessel, column or pipe is recorded by a NaI probe. Without affecting the processing unit, this reliable and accurate technique can be used to determine the liquid level on trays, as well as the presence or absence of internals, such as trays, demister pads, packing and distributors, and other anomalies.

Radiotracers in oilfield production (Fig. 1): The enhancement of oil production through the investigation of secondary recovery processes by radiotracers is estimated at 10–15% of the residual oil for each oilfield, which in terms of economic benefit means several million dollars per year.

Radiotracers for testing the efficiency of wastewater treatment plants: Radiotracers are very competitive and sometimes uniquely valuable in troubleshooting diagnosis of wastewater treatment plants (Fig. 2). Such a diagnosis helps end users to improve the performance and efficiency of existing installations and to design better water purification systems. The basic radiotracer methodology consists in the accurate formulation of the residence time distribution (RTD) experimental curve and its utilization for system analysis. This is a well established methodology with universal applications. The trend is towards standardization and simplification through customization of software and hardware, which will make RTD safer, more cost effective and more competitive.

Flowmeter for water, oil or gas based on multiple energy γ ray absorption (MEGRA) measurement: A multiphase flowmeter nucleonic gauge (Fig. 3) can be used to measure the individual flow rates of water, oil and gas during oil production. The ultimate aim for multiphase flowmeter technology is to replace the measurement function of the large, expensive,

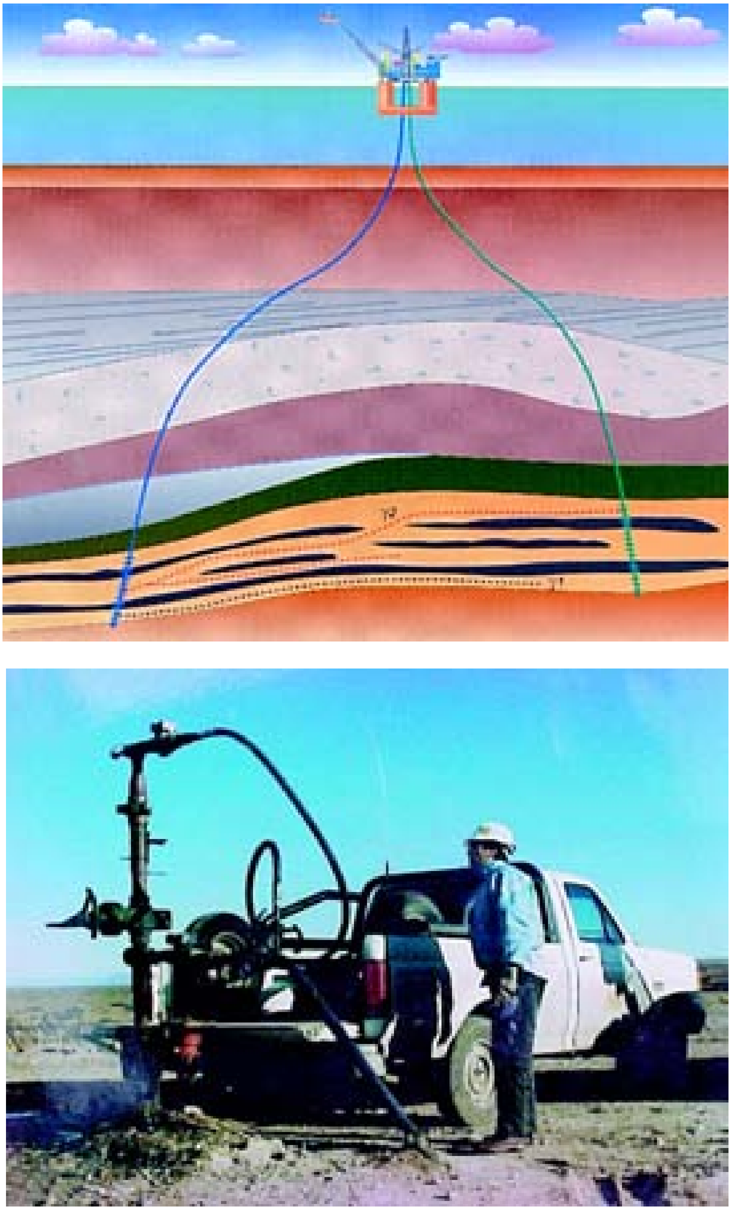


FIG. 1. Radiotracer technology as applied to oilfields.

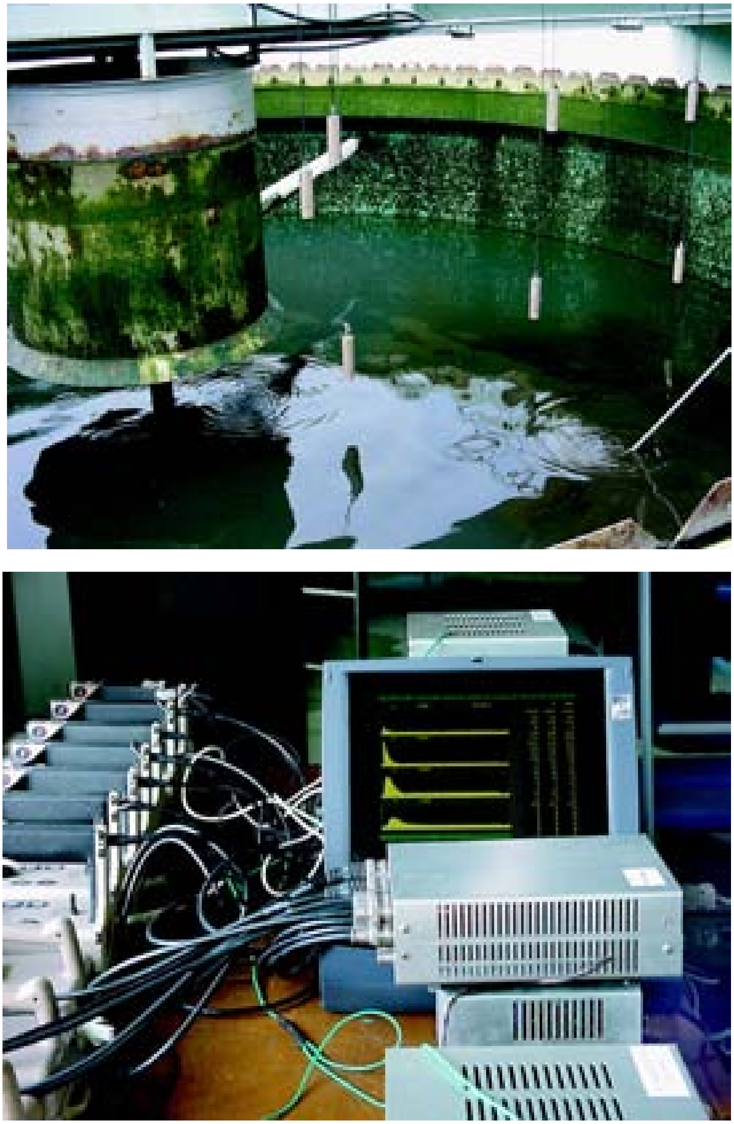


FIG. 2. RTD measurement in wastewater treatment in the Republic of Korea.

maintenance intensive test separator. Using a multiphase flowmeter to replace a test separator can save several million dollars in a single oilfield.

Prompt γ neutron activation analysis (PGNAA) technique: PGNAA is a very efficient and accurate technique for

FIG. 3. Nucleonic gauge for oil, water and gas flow rate measurement during oil production in an oilfield.

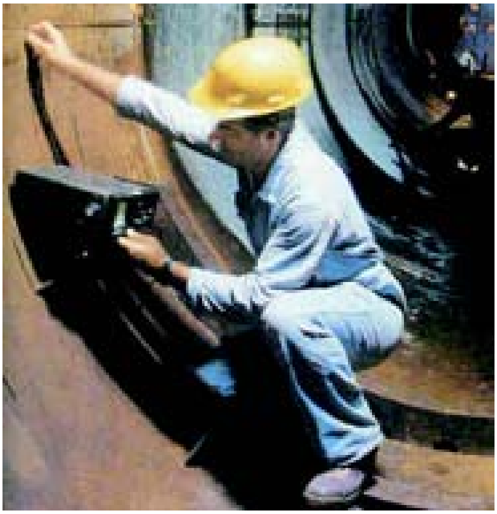
optimization of industrial processes through improved in situ, off-belt and online bulk analysis. PGNAA is used for coal and mineral exploration and exploitation.

Low activity nucleonic gauges for coal mining: A low radiation intensity (1.1 MBq) γ spectrometric borehole logging probe for coal delineation and determination of raw coal ash content utilizes single-scattered γ rays to provide information about the bulk density of the formation, and utilizes multi-scattered γ rays of lower energies to determine raw coal ash content. A low activity portable coalface ash analyser for differentiating between coal and sediments of a similar appearance permits selective mining and is applicable to the production phase in opencut pits and underground mines. The analyser works as a backscatter γ ray type gauge.

How to solve the problem?

In one application of radioisotopes, radioisotope techniques were used to investigate production limitations as part of a de-bottlenecking exercise. Gamma ray scans on the overhead line from a stripper column revealed the presence of a serious liquid carry-over. Design changes made on the strength of these studies resulted in a production increase of $400 000 per year.

Attempts to operate the plant at higher rates were frustrated by a bottleneck in a fractionation column. Production staff believed that the problem was caused by damage to the



trays. Gamma ray transmission scanning revealed that there was no internal damage and that the column functioned well at normal rates. However, scans at different feed rates revealed that the column was operating close to its upper limit of liquid capacity. Its design was such that it was not capable of handling the higher throughput. As a result of the study, a new column was designed and was ready for installation at the next scheduled shutdown.

Prior to the γ ray scans, a special shutdown of seven days' duration had been planned for the purpose of conducting a visual inspection of the column internals. The scans removed the need for this course of action, thereby saving seven days of lost production.

Pre-shutdown γ ray transmission scans on the suction catch-pot of a compressor unexpectedly revealed that the internal filter was damaged. As a result, an additional maintenance effort was programmed to effect the repairs. Had the damage been discovered only after bringing the plant off-line, the shutdown would have been extended by half a day, equivalent to production losses of $50 000.

In another case, the formation of deposits in the flare system on the amine units was a potentially hazardous occurrence, since such deposition could restrict the route for flammable gases to be safely vented to the atmosphere in the event of plant malfunction. Recognizing this, the plant operators periodically shut down the units to visually inspect, and if necessary clean out, the pipework. The total shutdown time was typically ten days per year.

The radioisotope applications team developed a neutron backscatter technique that was used to identify the location of any deposits and to measure their thickness. The measurements were performed with the plants online and without any interruptions. By eliminating unnecessary shutdowns, production losses estimated at $1 million per year were avoided.

In a third application, γ ray scanning, carried out in conjunction with radiotracer residence time measurements, was used to measure the buildup of catalyst on the walls and pipework of aniline reactors. By conducting the measurements at intervals over the plant's operating cycle, significant progress was made towards understanding the mechanisms responsible for catalyst deposition. Corrective actions taken on the basis of the findings of the radioisotope studies extended the life of the catalyst by approximately 30%, resulting in cost savings of $400 000 per year.

In another case, the engineering group at the research centre of a major oil company was asked to investigate the performance of a malfunctioning separation train on an oil production platform in the North Sea. The separators were unable to dehydrate the oil to the level required for export through the company's pipeline. The effect of this was to restrict production to 70 000 barrels per day rather than the targeted 80 000 barrels per day. Attempts had been made to improve matters by injecting various chemical agents, but the problem still persisted.

Radiotracer studies of the residence times of the organic and the aqueous phase were therefore carried out using a standard impulse injection measuring technique. The results showed that the mean residence times of both the oil and the water were approximately 60 seconds, as opposed to the four minute residence times for which the vessels had been designed. In essence, the process material was short circuiting the vessel, allowing insufficient time for the oil and water phases to become fully separated. Installing baffles in the lower section of the separator to increase the mean residence time solved the problem. This made it possible to increase production to the targeted 80 000 barrels per day and subsequently, with further modifications, to 100 000 barrels per day. With crude oil costing approximately $25 per barrel, the resulting benefit was, and continues to be, enormous.

Radiotracers were also applied in the case of a reservoir in Colombia that was naturally and heavily compartmentalized. Information about fluid flow across faults, and therefore the effect of water injection, could only be obtained by the use of radiotracers. Several wells were uniquely labelled, and the exercise showed that there was an unexpectedly good communication across a fault that originally was a suspected barrier. The reservoir engineer in charge stated that "the first two points on the tracer production curve saved me the cost of two new wells!" The cost of two wells in this particular area would be approximately equivalent to $10–15 million. The whole tracer operation was carried out at a cost of approximately $150 000, giving a benefit/cost ratio of between 70 and 100.

Bibliography

BLET, V., BERNE, P., TOLA, F., VITART, X., CHAUSSY, C., Recent developments in radioactive tracers methodology, Appl. Radiat. Isot. **51** (1999) 615–624.

INTERNATIONAL ATOMIC ENERGY AGENCY, Guidebook on Radioisotope Tracers in Industry, Technical Reports Series No. 316, IAEA, Vienna (1990).

— Emerging New Applications of Nucleonic Control Systems in Industry, IAEA-TECDOC-1142, IAEA, Vienna (2000).

Traces of Albrecht Dürer: Non-destructive analyses of Renaissance silverpoint drawings

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Problem

Silverpoint drawings are among the most precious and rarest treasures of graphic art collections. They date from the Renaissance and are characterized by a brownish colour and a very fine and precise line. Art historical investigations of silverpoint drawings generally allow the determination of the drawings' origin. However, some drawings cannot be attributed to a certain artist or school. Further information on provenance and authenticity can only be gained from chemical analysis. A database containing chemical composition data of clearly attributed drawings from different artists would be helpful for carrying out such analyses.

Silverpoint drawings from the sketchbook that Albrecht Dürer kept during a journey through the Netherlands in 1520–1521 were analysed. They are drawn on both sides of the sheets with silverpoint on a white preparation layer. The uniqueness of this sketchbook, filled with Dürer's impressions, is that it is accompanied by a personal diary [1], which allows us to reconstruct Dürer's travels nearly completely. However, this sketchbook was divided in the late 19th century. About 15 sheets are now conserved in different art collections, among them the Musée Condé in Chantilly, France, and the Kupferstichkabinett in Berlin, Germany.

This study aims to reconstruct and confirm the art historical coherence of the sketchbook and to obtain reliable data for comparison with other drawings of uncertain origin.

Why nuclear analytical techniques?

Until the late 1990s, analysis of the chemical composition of these silverpoint drawings was impossible owing to the high analytical performance required. As these drawings are precious and fragile, sampling and measurements in a vacuum are out of the question. Therefore investigations have to be carried out fully non-destructively, without any contact or any harm to the drawing. In addition, the applied technique must allow the determination of major and minor elements in the silver alloy and be very sensitive because of the extremely thin silver layers deposited on the paper. The sample mass does not exceed 0.1 mg/cm^2. That is why only nuclear analytical techniques are generally applicable for this task, and among these, external micro proton induced X ray emission (micro-PIXE) and spatially resolved synchrotron radiation induced X ray fluorescence (SR-XRF) are the most suitable. With these techniques the sample is irradiated with protons or X rays and the X ray emission lines characteristic for the individual elements are detected.

How to solve the problem?

The investigations of the Dürer silverpoint drawings from the Musée Condé were successfully performed by A. Duval at the research laboratory of the French museums in Paris using external 3 MeV micro-PIXE [2, 3]. An SR-XRF method was applied at the hard X ray synchrotron beamline at BESSY II [4] to allow the determination of major and minor element contents in the silver lines of the drawings conserved in Berlin.

The results obtained in Paris and Berlin show a similar composition of the silverpoint used for the drawings in Dürer's sketchbook, corresponding to a silver alloy containing between 4 and 12 wt% of copper, except in the partial drawing of the man with a fur cap (Fig. 1), which had a chemical composition of 13.0 wt% of copper, 5.3 wt% of zinc and 81.7 wt% of silver [5].

The origin of this drawing cannot at present be determined. During restoration and fixing of the drawings in the mount, glues containing trace amounts of zinc are applied to strengthen or link the paper. Therefore high zinc concentrations are found in the backing at the border of the drawings. However, this particular drawing was analysed at different points presenting the same zinc amount, which was significantly different from that of the backing determined in

FIG. 1. Albrecht Dürer drawing, "Thronender Bischof; Brustbild eines Mannes mit Pelzmütze" (probable date March 1521), from the Kupferstichkabinett, Staatliche Museen zu Berlin (Inventory No. KdZ 34r).

positions next to the drawing and far from the border between drawing and mount. This led us to conclude that all drawings in the sketchbook except this one were realized with the same point or at least with silverpoints having the same chemical composition.

On some drawings lead was detected together with silver. The detection of this element can be explained by the presence of lead point strokes, which are visible under the microscope. These strokes are either a residue of a preliminary leadpoint sketch which was erased after the final silverpoint drawing was executed or correspond to some extra strokes added intentionally to the drawing in order to intensify its contrast.

Mercury was also detected in all drawings and is only located in strokes; this element had already been observed in silverpoint drawings of Italian and Flemish origin. Experiments showed that silver amalgam could not have been used for drawing, implying that mercury was probably not included in the silverpoint when the drawing was made. Therefore the only convincing explanation for its presence is an uptake due to exposure to the atmosphere during the last 500 years. Indeed, a large quantity of mercury has been released to the atmosphere mainly since the beginning of the industrial period, and silver has a strong tendency to form a very stable amalgam with mercury. This formation seems to be a general alteration of the silver alloy used in drawings, as it was observed on different drawings that were kept at various places. This observation has important consequences for the conservation of these drawings and also makes it possible to distinguish original drawings from recent ones.

Acknowledgements

We gratefully acknowledge the help of H. Bevers, M. Roth, E. Alex, C. Severit, R. Fricke and R. Wittich (Kupferstichkabinett, Staatliche Museen zu Berlin), as well as N. Garnier (Musée Condé, Chantilly), for providing and accompanying the drawings for analysis. The reproduction of the Dürer drawing “Thronender Bischof; Brustbild eines Mannes mit Pelzmütze” was provided by courtesy of the Kupferstichkabinett, Staatliche Museen zu Berlin. We are indebted to the accelerator team of the Centre de recherche et de restauration des musées de France for their valuable assistance. This work is supported, in the framework of the French–German project PROCOPE, by the German Academic Exchange Service (DAAD) under contract D/0122896, and by the French Foreign Office.

References

[1] RUPPRICH, H., Dürer Schriftlicher Nachlass, Vol. 1, Verlag Deutscher Verein für Kunstwissenschaft Berlin (1956) 146–204.

[2] DUVAL, A., "PIXE analysis of metalpoint drawings", Proc. 6th Int. Conf. on Non-destructive Testing, Microanalytical Methods and Environmental Evaluation for Study and Conservation of Works of Art, Rome, 1999, 1007–1022.

[3] CALLIGARO, T., et al., Ion beam analysis with external beams: Recent set-up improvements, Nucl. Instrum. Methods Phys. Res. **B188** (2002) 135–140.

[4] GÖRNER, W., et al., BAMline: The first hard X ray beamline at BESSY II, Nucl. Instrum. Methods Phys. Res. **A467–468** (2001) 703–706.

[5] REICHE, I., et al., "Non-destructive investigations of Dürer's silverpoint drawings by PIXE and SR-XRF", Proc. 7th Int. Conf. on Non-destructive Testing and Microanalyses for the Diagnostics and Conservation of the Cultural and Environmental Heritage, Antwerp, 2002.

Part VII

FORENSIC APPLICATIONS

Bomb pulse radiocarbon dating

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Problem

Modern forensic science has to deal not only with homicides and other traditional crimes but also with more global threats such as the smuggling of nuclear materials, clandestine production of weapons of mass destruction, stockpiling of illicit drugs by state controlled groups and war crimes. Forensic applications have always benefited from the use of advanced analytical tools that can characterize materials found at crime scenes. In this paper we will discuss the use of accelerator mass spectrometry (AMS) as an ultrasensitive tool for the crime laboratories of the third millennium.

An important objective in forensic science is to order past events chronologically by analysing materials associated with criminal actions. Radiocarbon dating is known to the general public for its application to historical and prehistorical investigations. Examples of forensic significance include the assassination of the Inca Atahualpa by Francisco Pizarro in the early 1530s [1], the possible murder of the Tyrolean Ice Man (Ötzi) 5300 years ago [2] and the analysis of the burial cloths allegedly associated with the crucifixion of Jesus Christ [3]. Recent murders, including those associated with war crimes in the Balkans during the 1990s, can be studied using ^{14}C bomb pulse dating. This method has other forensic applications, including investigation of frauds related to food and wine counterfeiting, dating of opium crops and dating of substances used in biological warfare. AMS extends the applicability of the radiocarbon method, allowing the analysis of ^{14}C in submilligram organic samples. Specific molecular compounds extracted from bones, hair, skin and other carbon bearing substances of forensic significance can now be dated, enhancing the sensitivity and reliability of chronological determinations. AMS can also be used to analyse rare actinide isotopes released into the environment during the clandestine production of nuclear weapons or associated with the smuggling of nuclear materials. In the following discussion we will first review the basic principles of AMS analysis and radiocarbon dating and then we will present some case studies of forensic significance, often drawing from the experience of the AMS laboratory (Fig. 1) of the Australian Nuclear Science and Technology Organisation (ANSTO) [4].

Why accelerator mass spectrometry?

Twenty-five years have passed since it was first demonstrated that AMS could count radiocarbon atoms directly in natural organic samples, overcoming the fundamental limitations of decay counting and conventional mass spectrometry. Since then, AMS systems have been developed at more than forty laboratories and the analysis capabilities of AMS have been extended to a wide range of low abundance radionuclides, for applications in archaeology, environmental sciences, biomedicine and other disciplines based on the use of long lived tracers and chronometers [5]. The majority of radioisotopes with half-lives in the range 10^3–10^7 years have been detected by AMS. This includes a number of radioisotopes that exist only as a result of the nuclear age, such as plutonium and other actinide isotopes.

AMS systems are still evolving, with a trend towards smaller accelerators and lower voltages. A spectrometer based on a 500 kV accelerator has been developed by the PSI/ETH group [6] using thick gas stripper to destroy the molecules in the 1+ charge state. The same group is presently testing the analysis of ^{14}C at 250 kV, opening the way to the construction of table-top AMS systems (Fig. 2).

Carbon-14 is formed in the atmosphere by nuclear reactions of secondary cosmic neutrons with nitrogen and is quickly distributed throughout the atmosphere as $^{14}CO_2$. In pre-industrial times, the atmospheric isotope ratio $^{14}C/^{12}C$ was about 1.2×10^{-12}. In a simplified model that is often used to introduce the basic idea, living organisms participating in the carbon cycle via metabolic processes are characterized by this radiocarbon concentration. When a living organism dies, the carbon exchange stops. Hence by measuring the residual ^{14}C concentration in organic samples, it is possible to calculate the time elapsed since the material was originally formed. Ages up to about 50 000 before present (BP) can be determined by radiocarbon dating. Calibration curves [7] determined with high precision for all of the Holocene by radiocarbon

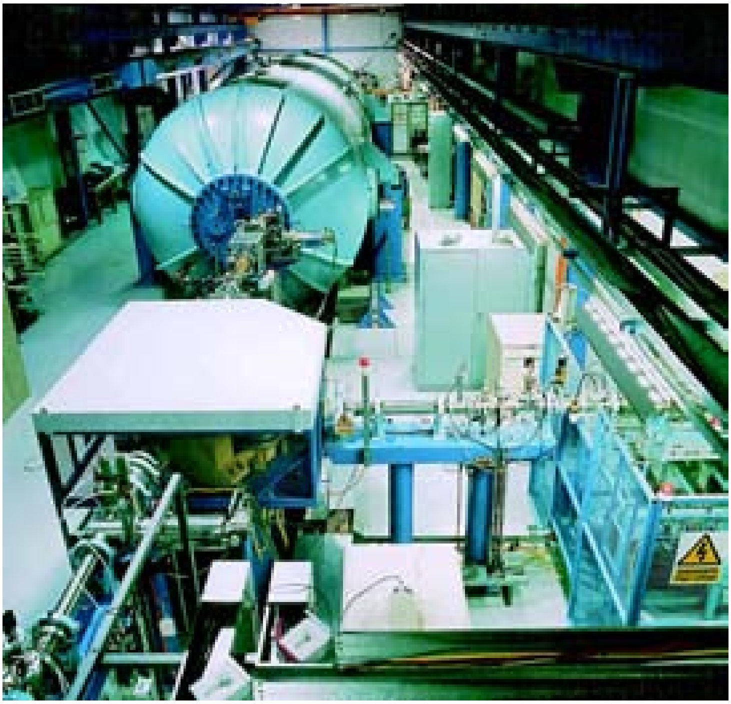

FIG. 1. Accelerator at ANSTO.

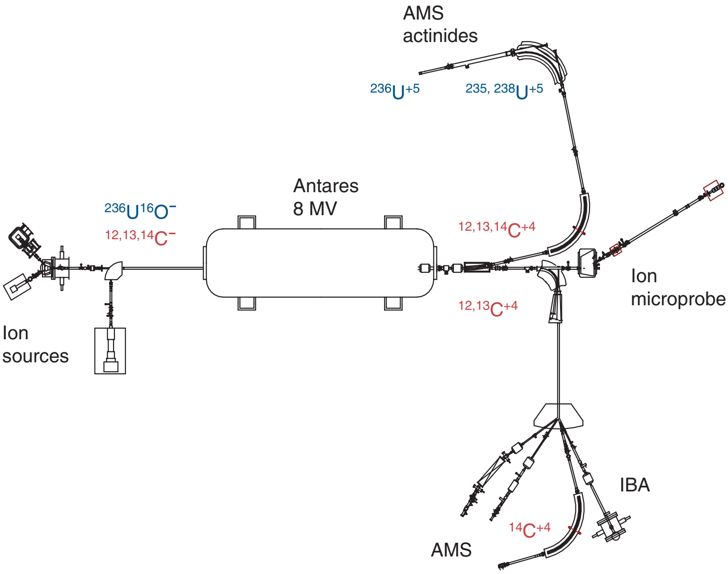

FIG. 2. Layout of the AMS set-up at ANSTO.

measurements on tree ring samples, which are independently and precisely dated by dendrochronology, are used to correct for variations of ^{14}C production rate in the atmosphere due to geomagnetic and heliomagnetic effects and global variations in the parameters of the carbon cycle.

How to solve the problem?

Bomb pulse dating

Atmospheric nuclear weapon tests during the 1950s and early 1960s produced a rapid increase in ^{14}C. In the northern hemisphere, the 1963–1964 ^{14}C concentration reached a level nearly double the pre-bomb level. Since the Nuclear Test Ban Treaty came into effect in 1963, the atmospheric ^{14}C concentration has been decreasing owing to exchange with the biosphere and the oceans. Presently the ^{14}C level has declined to a level about 10% higher than the pre-bomb level. The shape and intensity of this bomb pulse have been determined by measuring ^{14}C in atmospheric CO_2, tree rings and ice cores (Fig. 3) [8–13].

This well determined temporal change of ^{14}C since 1955 provides a clock for dating recent biological materials and leads to interesting forensic applications. Unfortunately the atmospheric $^{14}C/^{12}C$ ratio is decreasing exponentially with a half-life of approximately 15 years. In a few years the seasonal variations will overcome the magnitude of this decreasing trend, and dating to the nearest year of newly formed biological materials will become impossible.

Archaeo-forensics: Who killed Ötzi?

Ötzi, the mummified Copper Age corpse found trapped in a glacier in the Öztaler Alps on the Austrian–Italian border on 19 September 1991, is a well known forensic case studied by AMS. The corpse was well preserved and the first hypothesis was that it was that of a mountaineer who had died ten or twenty years before. Carbon-14 analyses of the bones and tissues revealed that the person had died sometime between 5300 and 5100 years ago. Similar ages were obtained for the grass from his shoes and for wood samples from his bow and axe shaft. A flurry of forensic studies were later developed to pinpoint Ötzi's origins and to understand what happened in

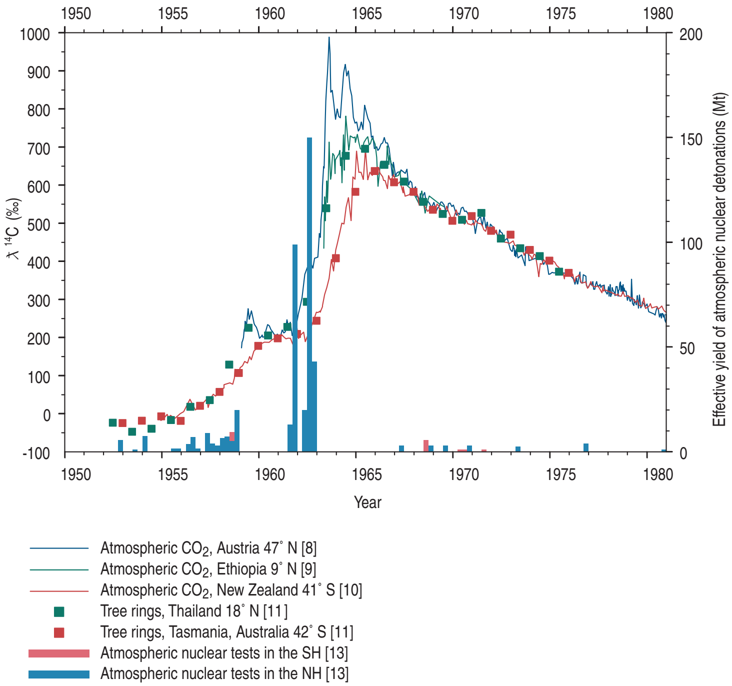

FIG. 3. Carbon-14 concentrations 1950–1980 and effective yield of atmospheric nuclear detonations. SH: southern hemisphere; NH: northern hemisphere.

the last days of his life. Recent computed tomography scans have revealed what looks like an arrowhead planted in Ötzi's left shoulder, implying that he may have been a victim of foul play [2].

The assassination of Atahualpa

In August 1533, Francisco Pizarro, conqueror of the Inca empire of South America, executed the Inca god-king Atahualpa, charging him with the assassination of his own brother Huascar, his rival for the title of Inca. A letter dated 5 August 1533 and written by Francisco de Chaves, chronicler on the Conquistador's expedition, has cast Pizarro's actions in a new and murderous light [14]. This letter was meant for the eyes of King Carl V of Spain but never reached its destination. It reports that Atahualpa had agreed to go to Spain and honour the King but that Pizarro, fearing Atahualpa would reveal Pizarro's atrocities, condemned the Inca to death and poisoned his generals with arsenic laced wine. The letter ended up in the family papers of the Neapolitan historian Clara Miccinelli. Our AMS radiocarbon dating provided a date between 1429 and 1483 for the sealing wax from de Chaves's letter [1], providing evidence for the authenticity of the letter.

The Turin Shroud: the burial cloth of Jesus Christ?

One of the most fascinating forensic studies involving AMS has been the analysis of the Turin Shroud [3]. This textile shows the image of what appears to be a crucified man and is considered by some to be the burial cloth of Jesus Christ, an object of devotion for many Catholics. The historical record of this cloth dates back to the 1300s. Willard Libby, the father of radiocarbon dating, proposed some forty years ago the use of his method for determining the age of the shroud, but conventional counting techniques would have required the destruction of an unacceptable fraction of the textile. Finally, with the advent of AMS, the nearly 'non-destructive' dating of the shroud became possible, and the test was carried out in 1988 under the coordination of the British Museum. Three laboratories (at the University of Oxford, the Institut für Mittelenergiephysik, Zurich, and the University of Arizona) made independent measurements on samples prepared from 10–15 mg of linen, obtaining a date of 1260–1390 with 95% confidence. There are still groups that do not believe these results and invoke contamination by microorganisms as the explanation for the measured radiocarbon age of the shroud.

Forensic applications

An important problem for forensic anthropologists and homicide investigators is to evaluate the post-mortem interval from the analysis of human remains. Traditional methods include the use of flies or other insects feeding on the decomposed corpse. The succession of insects found on a body provides a measure of time since death. Moreover, the exoskeletons of the different insect species provide the time of death even years after the event. An alternative method for determining the time of death is based on the radiocarbon bomb pulse. The $^{14}C/^{12}C$ ratio of a suitable material taken from human remains is very close to the atmospheric $^{14}C/^{12}C$ ratio at the time when the carbon uptake of the organism ceased. Hence the ^{14}C content of this material can be used to estimate the time of death. The most suitable human materials for obtaining reliable estimates for the time of death are those having a fast turnover time of carbon, such as lipids from bone, bone marrow and hair. The bone collagen always yields older ages than lipids or hair. Its age, combined with that of the materials with rapid turnover, can be used to discriminate between the period corresponding to the increasing or decreasing part of the bomb pulse [15].

The bomb pulse method has also been applied to war crimes. The victims of these crimes are often buried in mass graves that are hidden to conceal the evidence. The radiocarbon bomb pulse has been used for investigations of the mass killings allegedly carried out by the Nazis at the end of the Second World War in Serniki (Ukraine). In 1990, forensic archaeological excavations unearthed a mass grave containing several bodies. Holocaust deniers often attribute mass murders to Stalin or the Soviet KGB. Therefore it was vital to date the event and identify the killers. Parabellum handgun ammunition used by the Nazis was stamped with the place and year of manufacture, and the most recent found in the grave was dated 1941. Radiocarbon dating of hair samples showed the absence of the radiocarbon bomb pulse signal [16]. Therefore ignoring all eyewitness statements and using only archaeological techniques, it was possible to date the killings between 1941 and 1952. On the basis of all the collected evidence, Ivan Polyukhovich, the only Australian to face trial for war crimes, was arrested and charged with murdering Jews and of being involved in the deaths of up to 850 others in Nazi occupied Ukraine in 1942 and 1943.

The ^{14}C bomb pulse dating method is also being considered for the investigation of more recent war crimes, such as those perpetrated in the former Yugoslavia in the 1990s.

Counterfeiting of food and wine

Most food additives are obtained from materials derived from mineral oils. Such materials are 'dead' in terms of radiocarbon activity. On the other hand, natural products contain ^{14}C concentrations characteristic of modern materials. Hence the concentration of ^{14}C in specific foods can be used to identify the addition of small amounts of synthetic additives.

For example, our laboratory was involved in the analysis of radiocarbon in mustard oil for an Australian company to show that their product was derived from natural materials. This company specializes in the production of flavours and essences, and it wanted to expand its overseas markets, particularly in Japan, by demonstrating that its mustard essence was derived from recently harvested plants and was therefore a natural 'young' product. Mustard essence can be produced synthetically as a by-product of petroleum, the derivative going by the name of allylisiothiocynate. Both the source and derivative of these materials are so old that no radiocarbon is present. The subtle, delicate trace flavours present in the natural mustard essence are missing in the synthetic product. This is important in Japanese cooking, for instance in the making of wasabi, the green horseradish paste that is a companion of raw fish dishes.

The ^{14}C bomb pulse can also be used to detect the use of unauthorized additives to wines or other winemaking frauds, a process of major interest to the wine industry. As part of a cooperative project with the Department of Horticulture, Viticulture and Oenology at the University of Adelaide, we have recently analysed the radiocarbon concentration in a number of authenticated single label vintage red wines from the Barossa Valley, South Australia (Fig. 4). The results of this pilot study performed on alcohol separated by distillation show that radiocarbon dating can be used to determine wine vintages accurately and therefore to reveal the addition of unrelated materials of natural and synthetic origin.

Counterfeiting of works of art and artefacts

A common problem in the antiques market is forgery of works of art and artefacts. Thanks to the very limited

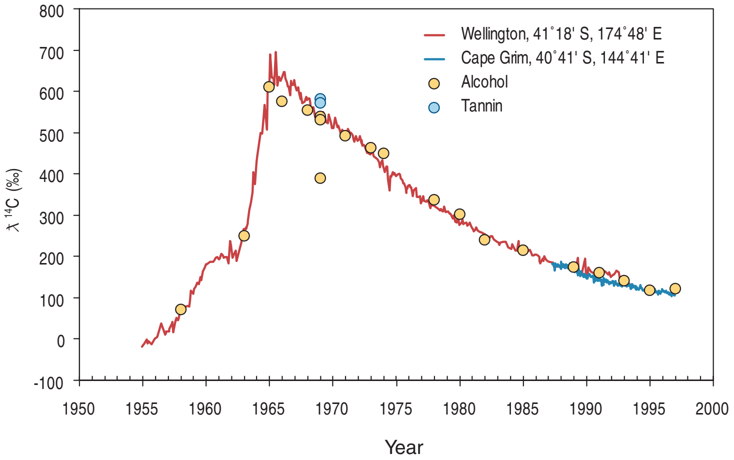

FIG. 4. Radiocarbon concentration in vintage red wines.

invasiveness of AMS, rare artefacts can be sampled for dating without undue damage. For example, tiny pieces of charcoal extracted from inclusions in ceramics can directly date the object of interest. Microsamples of wood, textiles (see the paragraph on the Turin Shroud above), ivory or other materials can be removed from the archaeological objects or the works of art. Canvas is often dated to obtain the age of precious paintings. Our laboratory, like many other AMS laboratories, receives authentication requests from antiques shops, art galleries and private individuals. We have had to deal with Egyptian works of art supposedly of the third millennium BC that showed a ^{14}C concentration characteristic of the early 1960s, and chess pieces supposedly found in Roman tombs with radiocarbon ages corresponding to 1000 years ago.

One interesting case related to glue used to repair a 15th century sculpture by Donatello. The Italian Ministry of Cultural Heritage wanted to know who had repaired the large cracks in the terracotta cherubs decorating the Annunciazione Cavalcanti in the Santa Croce church in Florence. Our radiocarbon date for the glue, 1331–1429, proved that the restoration had been performed during the lifetime of Donatello (1386–1466). Italian scholars theorize that because the statue was not hollowed out before firing — as the artist's later pieces were — it broke in the kiln.

Narcotics and drugs

Opium poppies and the coca shrub, the plants from which heroin and cocaine are produced, are generally cultivated in Asia and Latin America, respectively. In 1999, worldwide production of opium reached a record of 5778 tonnes, derived from 217 000 hectares of poppy. Global production of coca leaf mounted to 290 000 tonnes from 183 000 hectares of coca.

Since 1994 the United Nations International Drug Control Programme (UNDCP) has been carrying out ground surveys to monitor the extent of opium poppy cultivation in Afghanistan. The UNDCP estimates that in 1999 Afghanistan alone produced nearly 80% of all opium worldwide, and Colombia more than 65% of all coca leaf. Political interventions, for example the ban on opium cultivation in Afghanistan by the Taliban authorities in 2000, can affect the market and the distribution of drugs. The UNDCP has recently developed the Global Illicit Crops Monitoring Programme for Afghanistan, which is based on the use of advanced geographic information technologies, including the Global Positioning System (GPS) and satellite imagery. It would now be important to develop methodologies for establishing the age of the drug on the market to confirm the existence of stockpiles of opium or heroin. The ^{14}C bomb pulse is an effective tool for drug dating, and AMS allows the analysis of ^{14}C in milligram samples taken from the seized drug (Fig. 5). This information would support the action of law enforcement authorities against criminal organizations involved in drug trafficking.

Bio-terrorism

Anthrax is an acute infectious disease caused by the spore-forming bacterium *Bacillus anthracis*, cultivated for the first time in 1877 by Robert Koch, who showed that it produced anthrax when injected into animals.

Bacteriological weapons based on aerosol containing anthrax have allegedly been developed by some countries, in breach of legal commitments under the Biological Weapons Convention, which entered into force in 1975.

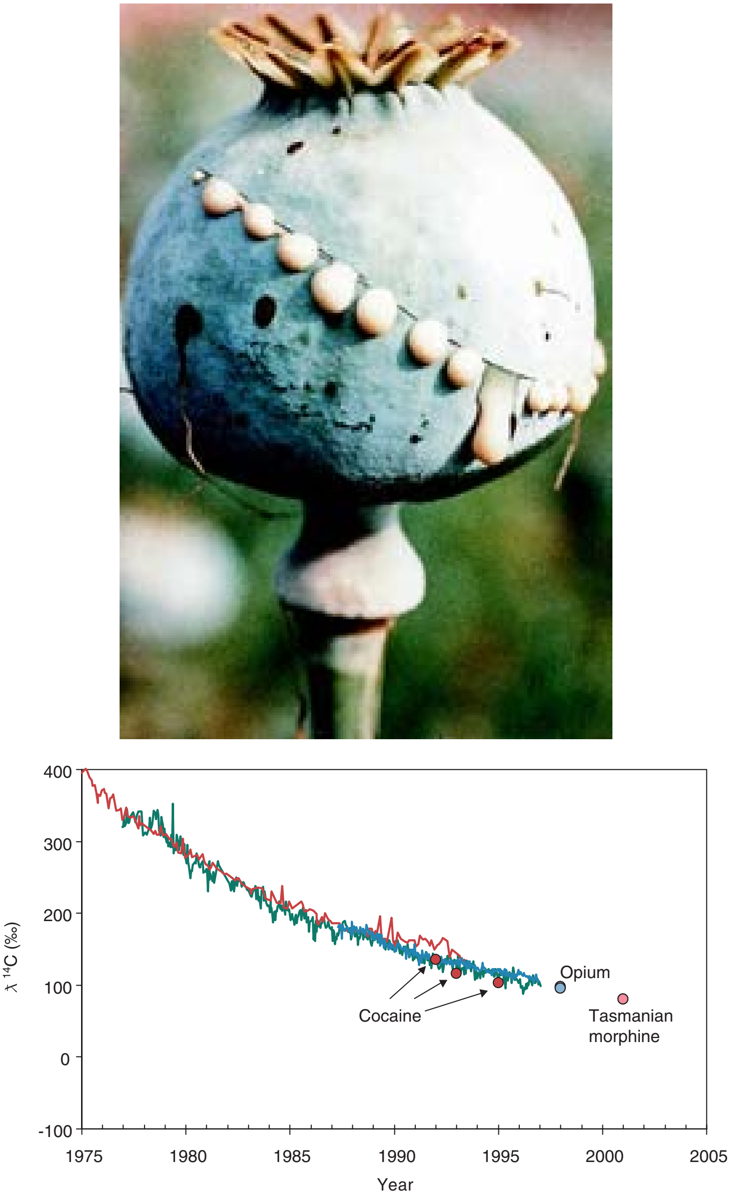

FIG. 5. Radiocarbon concentration in drugs.

Letters containing anthrax spores were sent through the mail in the United States of America in October 2001, causing the death of five people. The US Federal Bureau of Investigation has used the ^{14}C bomb pulse method to date the anthrax spores, determining that they had been in a state of suspended animation for two years. This finding rules out the previous theory that the anthrax spores had been obtained from laboratory samples prepared in the early 1980s. The investigators fear now that the terrorists have a microbiology laboratory available to them where they could produce more anthrax spores.

Nuclear forensics

Nuclear forensics is a special branch of forensic activities where evidence is required in civil or criminal court proceedings related to radioactive or nuclear materials. For example, smuggled radioactive material seized by customs and other police groups is analysed to provide clues to the origin of the material. AMS can be used to determine the isotope ratios of nuclear materials such as plutonium and uranium at very low concentrations. These ratios are sensitive indicators of the past history of the material. In particular, the isotope ^{236}U is useful for reconstructing the irradiation history of uranium samples. It can occur at very low levels which are only detectable by AMS [17]. Nuclear forensics is gaining prominence in a range of fields, including the assessment of environmental contamination from nuclear weapon testing, military use of depleted uranium and nuclear accidents, and litigation involving occupational, military and public exposure to uranium and plutonium.

Policing nuclear non-proliferation

Between the early 1960s and the beginning of the 1990s, the international safeguards system implemented by the IAEA was developed to provide assurance that nuclear material had not been diverted from declared nuclear activities. These traditional safeguards methods are based upon nuclear 'accountancy' complemented by containment and surveillance techniques. Since the early 1990s work has been under way to strengthen the international safeguards system by giving it a capability to provide assurance of the absence of undeclared nuclear material and activities. The IAEA has now assumed a more 'detective' role, with the task of verifying the correctness *and completeness* of declarations made by States.

As part of the strengthened safeguards system, environmental sampling and analysis have now been implemented by the IAEA. Plutonium or highly enriched uranium (HEU) is needed for the construction of nuclear weapons. Disturbance of uranium isotope ratios would be the most evident signature for uranium enrichment. The reprocessing of irradiated reactor fuel for the production of plutonium would have the effect of releasing a wide range of fission products and actinide isotopes into the surrounding environment. Iodine-129 and ^{236}U, both measurable by AMS in environmental samples, are key radionuclides for identifying the presence of clandestine nuclear activities [18].

References

[1] ZOPPI, U., et al., Nucl. Instrum. Methods Phys. Res. Sect. B **172** (2000) 756.

[2] SHOUSE, B., Science **293** (2001) 2373.

[3] DAMON, P.E., et al., Nature **337** (1989) 611.

[4] LAWSON, E.M., et al., Nucl. Instrum. Methods Phys. Res. Sect. B **172** (2000) 95.

[5] TUNIZ, C., BIRD, J.R., FINK, D., HERZOG, G.F., Accelerator Mass Spectrometry: Ultrasensitive Analysis for Global Science, CRC Press, Boca Raton, FL (1998).

[6] SUTER, M., JACOB, S.W.A., SYNAL, H.A., Nucl. Instrum. Methods Phys. Res. Sect. B **172** (2000) 144.

[7] STUIVER, M., et al., Radiocarbon **40** (1998) 1041.

[8] LEVIN, B., et al., in Trends 93 — A Compendium of Data on Global Change (BODEN, T.A., KAISER, D.P., SEPANSKI, R.J., STOSS, F.W., Eds), Carbon Dioxide Information Analysis Center, Oak Ridge Natl Lab., TN (1994) 203.

[9] NYDAL, R., LÖVSETH, K., Atmospheric CO_2 from Northern and Southern Hemisphere Sites, 1962–1993, Carbon Dioxide Information Analysis Center, Oak Ridge, TN (1996).

[10] MANNING, M.R. MELHUISH, W.H., ibid., p. 173.

[11] HUA, Q., BARBETTI, M., JACOBSEN, G.E., ZOPPI, U., LAWSON, E.M., Nucl. Instrum. Methods Phys. Res. Sect. B **172** (2000) 359.

[12] LEVCHENKO, V.A., et al., Nucl. Instrum. Methods Phys. Res. Sect. B **123** (1997) 290.

[13] ENTING, I.G., Nuclear Weapons Data for Use in Carbon Cycle Modelling, Div. of Atmospheric Physics Tech. Paper No. 44, Commonwealth Scientific and Industrial Organization, Canberra (1982).

[14] LAURENCICH MINELLI, L., MICCINELLI, C., ANIMATO, C., Studi e Materiali di Storia delle Religioni **64** (1998) 57.

[15] WILD, E.M., et al., Nucl. Instrum. Methods Phys. Res. Sect. B **172** (2000) 944.

[16] WRIGHT, R., director of the forensic archaeological excavations in Serniki (Ukraine), personal communication.

[17] HOTCHKIS, M.A.C., et al., Nucl. Instrum. Methods Phys. Res. Sect. B **172** (2000) 665.

[18] TUNIZ, C., et al., “Is accelerator mass spectrometry useful in non-proliferation and safeguards?”, Proc. 42nd Annu. Mtg of the Institute of Nuclear Materials Management, Indian Wells, CA, 2001.

Contents of arsenic, mercury and other trace elements in Napoleon's hair determined by INAA using the k_0 method

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Problem

Napoleon died on the island of St. Helena on 5 May 1821 at the age of 51. It was officially declared that his death was due to cancer of the stomach. This statement, however, was questioned even at that time by Napoleon's household physicians. Since then, extensive investigations have been conducted to clarify this issue.

In early 1960s, radiochemical neutron activation analysis (RNAA) made it possible for the first time to determine trace amounts of arsenic in hair. One of Napoleon's hairs was analysed and a high arsenic content of 10.38 ppm was reported. Accordingly it was suggested in 1961 that arsenic poisoning was the chief suspect in Napoleon's death. Later, two more of Napoleon's hairs, from another source, were analysed by RNAA. Uneven arsenic distribution along the length of the hairs was discovered. The growth rate of human hair is about 0.4 mm/d, so the arsenic distribution in the hair can be used to date arsenic intake. Since then, arsenic in more than 30 samples of Napoleon's hair has been analysed.

Nowadays a non-destructive method employing a germanium detector, instrumental neutron activation analysis (INAA), is used that is even more convenient. By INAA, it is possible to determine arsenic as well as other trace elements simultaneously in a single hair.

Why nuclear analytical techniques?

In this work an INAA procedure is applied to determine the contents of arsenic and mercury in two samples of Napoleon's hair. Three additional elements — chromium, antimony and zinc — are determined simultaneously and are reported as well. Mercury is a component of calomel, of which a great deal was consumed by Napoleon and which is considered to play an important role in the arsenic poisoning theory. Antimony is interesting because it was a component of many medications, particularly tartar emetic, which Napoleon frequently received during his last year. Chromium and zinc are essential elements.

How to solve the problem?

Two pieces of Napoleon's hair, hereafter referred to as hair 1 and hair 2, were sent by post by R. Maury, a professor at the University of Montpellier, France, in a special parcel sealed by G. Kaendel, the Curator of the Museum of History in Lausanne, Switzerland. These two samples were taken from a strand of hair cut the day after Napoleon's death. The weights were 0.1722 and 0.2151 mg, respectively. The INAA results are presented in Table 1.

Arsenic and other trace elements in Napoleon's hair

The arsenic contents found in this work are 1.85 ± 0.11 and 3.05 ± 0.18 ppm for the two hairs. These values are higher than the normal level nowadays.

The elevated content and non-uniform distribution of arsenic along Napoleon's hair are used as the main evidence to support the arsenic poisoning theory. The instigator for the murder was believed to be the Comte D'Artois, who was Louis XVIII's brother and later became Charles X. The Bourbon king wanted to be sure that Napoleon would not return to regain his throne. According to the arsenic poisoning theory, Napoleon did not directly die of arsenic toxicosis. Chronic arsenic poisoning was only the 'prelude', giving the public an impression that Napoleon was deteriorating in a normal and natural way from disease. According to the theory, his death was due to a lethal poisoning. Starting two months before his death, he frequently received tartar emetic (antimony potassium tartrate). The real purpose was to eventually inhibit vomiting, so that the patient was no longer able to expel poisons. Then calomel and orgeat were given to relieve his constipation and great thirst. Constipation and thirst were symptoms of arsenic poisoning. Calomel is mercury chloride and orgeat is an orange flavoured drink which contains the oil of bitter almonds. This oil can be hydrolysed in the stomach to hydrocyanic acid. When calomel and orgeat are combined in the stomach, mercury cyanide is formed, which is said to have been ultimately responsible for Napoleon's death. For this reason the elements

TABLE 1. ELEMENT CONCENTRATIONS (ppm) OF ARSENIC, CHROMIUM, MERCURY, ANTIMONY AND ZINC IN SAMPLES OF NAPOLEON'S HAIR

	Hair 1	Hair 2
Arsenic	1.85 ± 0.11	3.05 ± 0.18
Chromium	7.65[a]	10.5 ± 1.9
Mercury	1.84[a]	3.98 ± 0.29
Antimony	4.47 ± 0.27	4.32 ± 0.38
Zinc	35[a]	58 ± 13

[a] Information value.

mercury and antimony were determined in this work. The mercury content of 3.98 ± 0.29 ppm found in hair 2, however, is in the normal range of 0.5–10 ppm. However, the antimony contents in the two samples of Napoleon's hair, 4.47 ± 0.27 and 4.32 ± 0.38 ppm, as shown in Table 1, are much too high, regardless of whether they are compared with the reference concentration of 0.05–0.25 ppm or with the normal level of 0.016–1.3 ppm for the local population. The element antimony is not the only one found in Napoleon's hair in an unusual concentration. The concentrations of the two essential elements chromium and zinc are also not normal. The normal level of the two elements nowadays is less than a few parts per million for chromium and between 150 and 250 ppm for zinc. The concentration of chromium found in Napoleon's hair is too high (10.5 ± 1.9 ppm), while the zinc content, 58 ± 13 ppm, is too low.

While no one seems to deny the elevated arsenic content in Napoleon's hair, the extensive investigations that have been carried out result in two diametrically opposed opinions. One adheres to the chronic arsenic poisoning theory mentioned above, and the other insists that Napoleon died of cancer. The latter theory can be supported by the following arguments. The diagnosis of chronic arsenic poisoning should not be based on the elevated arsenic content in hair alone, but should include specific clinical features, which were not reported in

Napoleon's case. Regarding the elevated arsenic content, doubts exist whether the determined arsenic was really the endogenous/ingested one or was a result of contamination. Hair absorbs externally applied arsenic on its outer surface and/or in the core, and it has been reported that it is not possible to remove it completely by washing. Furthermore, because consumed arsenic is also deposited on the surface of the hair shaft and/or in the core, these two sources cannot be distinguished by examining the hair. Moreover, external contamination can also be unevenly distributed along the hair shaft. Attempts have been made to identify external contamination sources during the period of Napoleon's exile in St. Helena. The possible contamination sources, including wallpaper, coal smoke, drinking water, cosmetics containing arsenic, and the arsenic compounds used as preservatives, were critically examined. Besides external contamination, the elevated arsenic content might also result from ingestion of arsenic as an impurity in tartar emetic. Owing to the similar chemistry of antimony and arsenic, the tartar emetic produced in the 19th century might have contained arsenic. All of these sources are possible, but so far it has not been possible to positively determine what was responsible for the elevated arsenic content in Napoleon's hair.

The debate on the issue of who or what killed Napoleon will very likely continue. It is clear, however, that reliable analytical data from neutron activation analysis will be helpful in the course of clarifying this historic mystery.

Part VIII

ARCHAEOLOGICAL INVESTIGATIONS

Neutron activation analysis applied to archaeological problems

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Problem

During the last three decades, ceramic analyses have become central to archaeological investigations, partly owing to the concurrent advances in computer technology and instrumental chemistry, and partly owing to a recognition by archaeologists that archaeometry provides much more than mere measurement. The delineation of past systems of production and exchange lies at the core of these investigations.

Because of their abundance and variety, ceramics provide one of the fundamental tools used to derive archaeological information and to further the understanding of how different civilizations lived. Such studies are of utmost interest to archaeologists, anthropologists and ethnoarchaeologists, as well as to physicists, chemists and geologists. The characterization of ceramics involves numerous studies, such as sample typology, i.e. the study of shape, colour, texture, and the presence of drawings and decoration, and the determination of chemical composition.

Typology has been very useful when applied to whole or reconstructed objects. However, it has proven to be less helpful for materials in fragmented condition. Ceramic fragments make up a large portion of the materials recovered from excavations and can appear to be very similar even under microscopic examination, but the clay, sand and other natural materials from which they were fashioned can have a chemical composition that is unique and diagnostic for the local source from which they were taken (Fig. 1).

Therefore the chemical composition characteristics of ceramics play an important role in the study of ceramic provenance. The composition of any ceramic fragment depends on the types and proportions of the clay paste and mineral, rock, grog (e.g. crushed pottery or firebricks) and organic tempers used in its manufacture. It is well established that ceramics can be grouped on the basis of similarities or dissimilarities derived from chemical data. Chemical differentiation of

FIG. 1. Pottery vessel found at the Justino site, Canindé do São Francisco, Sergipe State, Brazil.

groups depends on the occurrence and measurement of discriminating elements within the clay matrix, i.e. those elements showing significant concentration differences between production centres.

There is generally no predictability as to which individual elements will be discriminating. One important point to note and which few researchers realize is that the elements useful in discriminating sources from one region may not be useful for another, and that a handful of grab samples from a road cut will rarely provide a sufficient explanation to characterize source variability.

For this reason, it is logical to aim for maximum discrimination by measuring the largest possible number of elements. It is also important to take into account the accuracy with which the elements can be measured, because if an element is measured with poor precision, it tends to reduce the discriminating effect of other, well measured elements. Thus, as well as providing a large number of elements, a satisfactory provenance procedure requires measurements with high accuracy and high precision.

Why nuclear analytical techniques?

Different techniques can be applied to determine the sample composition, including atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-

MS), X ray fluorescence (XRF) spectrometry, and neutron activation analysis (NAA) or instrumental neutron activation analysis (INAA). Among the various techniques, the main analytical methods used to characterize ceramics are undoubtedly XRF and INAA.

The principles of NAA differ from those of XRF in that samples are irradiated by thermal neutrons from a nuclear reactor. During irradiation, a few neutrons are captured by the nuclei of atoms in the specimen. This process, called activation, causes some of the nuclei to become unstable. During and after neutron irradiation, these unstable nuclei emit γ rays with unique energies at rates defined by the characteristic half-lives of the radioactive nuclei. Identification of the radioactive nucleus is possible by measuring the γ ray energies. Determination of their intensities permits quantitative analysis of the elements in the sample. The use of NAA in ceramics by a combination of two or three irradiation, decay and measurement strategies allows the determination of the elements Ba, Ce, Cl, Co, Cs, Dy, Eu, Fe, Hf, K, La, Lu, Mn, Na, Nd, Rb, Sb, Sc, Sm, Sr, Ta, Tb, Th, U, Yb, Zn and Zr, if necessary by changing the irradiation, decay and measurement schemes.

In general, XRF is more available, more rapid and less expensive than NAA. However, NAA offers a far greater number of elements, more sensitivity, superior precision and greater accuracy than XRF. On the other hand, NAA can be performed on extremely small samples (5–10 mg), meaning that only minor damage to valuable artefacts may be required.

How to solve the problem?

The main objectives of statistical analysis when applied to compositional data are data exploration, hypothesis generation, hypothesis verification and data summarization, which is provided by multivariate statistical methods.

The multivariate statistical technique is based on the idea that each specimen can be considered a point in multidimensional space (hyperspace), with the number of dimensions equivalent to the number of elements measured. In such a hyperspace, groups of specimens with similar compositions form a cloud of points surrounding a mathematically calculable ‘centre of mass’. An individual compositional group is characterized by the location of its centroids and by the unique hyperellipsoidal shape of the group distribution. The shape is due to the correlation between different elements. Distinct source groups are represented by two or more clouds that do not overlap. In general there are three multivariate methods used in archaeometry: cluster analysis, principal component analysis (PCA) and discriminate analysis.

Cluster analysis is often used in the initial inspection of ceramic source data because it is a rapid and efficient technique for evaluating relationships between large numbers of samples between which distance measures have been calculated. The results are commonly presented as dendrograms showing the order and levels of clustering, as well as the distances between individual samples. One of the most frequently employed distance measurements is the squared mean Euclidean distance between individual samples in the calculation of similarity or difference, in which it is assumed that the elements under consideration are uncorrelated (hyperspherical). Consequently, dendrograms may accurately represent the differences between members within a group but greatly distort the differences between clusters of samples. Thus the effectiveness of dendrograms as a means of providing a faithful illustration of differences between groups is questionable. Dendrograms can be used as an initial step in the identification of groups, but they are inadequate as a quantitative measurement of the ability to differentiate between groups. Fortunately, as is illustrated below, there are other procedures that allow a more reliable determination of both within- and between-group differences.

PCA is one of the most widely utilized techniques for exploring underlying relationships in multivariate data. PCA is employed when the main objective is to derive a set of uncorrelated linear combinations of the original variables that retain the original information. If the original variables are significantly correlated, a reduced number of PCs may be adequate to describe the significant features of the original data set.

In PCA, one performs a transformation of the data using eigenvector methods to determine the direction and magnitude of maximum variance in hyperspace. Computation of the eigenvectors is derived from either the variance–

covariance or correlation matrix of the original variables. The first PC is oriented in the direction of the maximum variance of the data. The second PC lies in the direction of the maximum remaining variance, with the additional constraint that it must be orthogonal to the first PC. The third PC is orthogonal to the first two PCs, again representing the direction of the maximum remaining variance. The procedure continues until the number of PCs is equal to the number of original dimensions. All resulting PCs are then linear combinations of the original axes, and loading factors (coefficients) used to construct the PCs can be used to identify attributes important to the individual components.

Discriminant analysis is a multivariate statistical technique that is concerned with separating previously defined groups. Each group consists of a number of specimens (group size), and a number of variables are determined for each specimen.

Canonical discriminant analysis consists of finding a linear combination (transform) which gives the maximum ratio of the variability between groups to the variability within groups. The linear combinations that maximize this criterion are called the first canonical discriminant. A second canonical discriminant is defined by the same criterion, subject to the restriction that it is correlated with the first canonical discriminant. Further canonical discriminants are defined in the same manner, i.e. with the restriction that they are uncorrelated with the previous canonical discriminants. Generally the first few canonical discriminants summarize the separation.

Bibliography

GLASCOCK, M.D., "Characterization of archaeological ceramics at MURR by NAA and multivariate statistics", Chemical Characterization of Ceramic Pastes in Archaeology (NEFF, H., Ed.), Monographs in World Archaeology No. 7, Prehistory Press, Madison, WI (1992) 11–26.

GLASCOCK, M.D., BRASWELL, G.E., COBEAN, R.H., "A systematic approach to obsidian source characterization", Archaeological Obsidian Studies: Method and Theory (SHACKLEY, M.S., Ed.), Advances in Archaeological and Museum Science, Vol. 3, Plenum Press, New York (1998) 15–65.

MUNITA, C.S., PAIVA, R.P., ALVES, M.A., OLIVEIRA, P.M.S., MOMOSE, E.F., Contribution of neutron activation analysis to archaeological studies, J. Trace Microprobe Tech. **18** 3 (2000) 381–387.

STARK, M.T., BISHOP, R.L., MIKSA, E., Ceramic technology and social boundaries: Cultural practices in Kalinga clay selection and use, J. Archaeol. Method Theory **7** 4 (2000) 295–325.

Contribution of nuclear analytical techniques to the rescue of Brazilian history through the analysis of ceramics

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Problem

The prehistory of the last two millennia in Brazil has been characterized by the coexistence of several cultures in each region. Some were competing — specialized agricultural societies in the alluvial plains — but other groups lived in a more isolated and probably peaceful way in the upper interfluvial region. It is difficult to determine what the level of integration was between the different tribes of the Proto-Gê, Proto-Tupi, Proto-Aruaque and Carib populations.

Otherwise, there was no urban civilization in Brazilian prehistory. Most of the inhabitants lived in tribes, perhaps with regional economic integration, as is suggested by recent ethnographic examples (e.g. in the Upper Xingu or Rio Negro areas). Only along the Amazon river may there have been chiefdoms. In this region, there may have been some specialized pottery makers, and it seems that fine ceramics were exported from one village or region to another. Outside Amazonia, pottery is generally plain, with the exception of the Tupiguaranis', which was partly decorated. In this particular case, each Tupiguarani family was able to produce its own traditional decorated pots, and some of them would even have been exchanged with the Gê people.

Archaeologists wanted to obtain more information concerning social behaviour through the chemical analysis of the ceramics. They had several questions: Were there populations (from different archaeological cultures in the Peruaçu region) that lived in a very small area (and were in contact), used the same regional raw materials and exchanged pottery or pottery makers (probably women)? Were there differences between the households of one village located in the Guara region? Did people from each clan have a raw material source? Were different clays used to make pottery for distinct functions?

To provide some clues to help the archaeologists find the answers, k_0 instrumental neutron activation analysis (INAA) was used to determine element concentrations in the ceramics.

Why nuclear analytical techniques?

The k_0 INAA technique was chosen to be applied to the determination of elements because it can determine several elements in the same sample almost simultaneously, with a low detection limit and without any chemical procedure, as is required in the majority of non-nuclear techniques.

This technique was the most suitable for this study because it did not entail the destruction of these important items of historical ceramics, it required only a very small piece of the materials to be analysed, and it was able to give the element concentration of more than 20 elements from just one small piece of precious ceramic.

The k_0 method was applied to all samples, demonstrating its quality as a versatile technique, and it was confirmed to be one of the most advantageous and suitable nuclear analytical techniques.

How to solve the problem?

Before carrying out the analysis, sample data were recorded and shards were prepared for irradiation. Each shard was recorded according to its physical and stylistic characteristics and archaeological sources. It was very difficult to sample some of the very small (1 cm^2) shards. They are considered precious by the museum curators and have to be sent back to their collection.

The results analysed using statistical procedures gave very important insights for the archaeologists. The results showed that nuclear analytical techniques can be used to differentiate Amazonian ceramics. It will probably be the most interesting area in Brazil to be studied by this method, because more complex societies lived along the banks of the great river. Exchanges or population migration probably occurred during the last two millennia, and pottery would have been easily carried by canoe.

Bibliography

BISHOP, R.L., NEFF, H., "Compositional data analysis in archaeology", Archaeological Chemistry IV (ALLEN, R.O., Ed.), Advances in Chemistry Series 220, American Chemical Soc., Washington, DC (1989).

PROUS, A., Investigations in the cave of Boquete, Minas Gerais, Brazil, J. Soc. Res. Am. Inhabitants **77** (1990) 77–109.

SHENNAN, S., Quantifying Archaeology, Academic Press, New York (1988).

WÜST, I., CARVALHO, H.B., New perspectives on studies developed by pre-colonial ceramists related to central and west Brazilian regions: Spatial analysis from Guará 1 site (GO-NI-100), Goiás, J. Museum Archaeol. Ethnol., São Paulo Univ. **6** (1996) 47–81.

Investigation of antiques with radiation methods

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Problem

The authenticity of three European medieval swords (Fig. 1) had to be proven. In addition, the production techniques used by the medieval smiths were studied. For the assessment of antiques and objects of art, both examination of the material and stylistic studies are required in nearly all cases.

Why nuclear analytical techniques?

In most of these cases, not only one but several essentially different investigation methods have to be applied during the study of the material. Nuclear and radiation techniques are favoured, primarily because these can frequently be carried out non-invasively, which is essential in the study of objects of high value, since taking samples from the objects might devalue them significantly. Theoretically this could be circumvented by taking samples in the microgram range. However, owing to the possibly inhomogeneous nature of the material, such samples may not represent the entirety of the object under study. This might then lead to misinterpretation of the

FIG. 1. One of the three swords investigated.

results obtained. Using nuclear techniques such as neutron activation analysis (NAA) or photon activation analysis (PAA), large volumes of material can be analysed in many cases, so it is possible to investigate the entire body of the object or large parts of it. Thus meaningful results with a high degree of representativeness can be obtained non-destructively.

How to solve the problem?

In activation analysis, the material under study is exposed to irradiation by subatomic particles — neutrons, photons, protons, etc. During bombardment with these, radioactive nuclides are produced through nuclear reactions. The radionuclides decay by emission of different types of radiation. Among these, photons (γ or characteristic X rays) are preferred for use in analytical evaluation. The energy distribution of X and γ rays is characteristic for each radionuclide. Measured with an appropriate spectrometer, the spectra can be used for simultaneous multicomponent analyses. Since the method is based upon nuclear reactions, only the element composition can be determined; normally no chemical speciation is possible.

Investigation of the swords

Among other methods, instrumental PAA was used for the investigation of the swords. Several parts of interest were irradiated with bremsstrahlung photons from an electron linear accelerator. The radioactivity induced thereby was measured with low energy photon spectrometers and with standard high resolution semiconductor detectors for high energy γ radiation. The element composition of the material measured could be obtained by evaluation of the characteristic signal lines in the spectra. Usually evidence of the genuineness or forgery of the object studied cannot be expected from analytical results only. However, these results provide useful fingerprints, and together with other investigations, including stylistic studies, they are indispensable for a final assessment in nearly all cases. Therefore the swords were also studied using optical and electronic microscopy, X ray diffraction, computer tomography and other methods. All the results of the material study and the assessment by weapons experts, military historians, etc., yielded authenticity for all the pieces under study with a high degree of probability. Moreover, some information about the production technique was also obtained. For instance, some details of the hardening method used by the medieval smiths were discovered through analytical and crystallographic findings. Finally it was found that two of the swords were pattern-welded, and the two metal phases used could be well characterized by computer tomography and in situ activation analysis.

Bibliography

MOMMSEN, H., Archäometrie, Teubner, Stuttgart (1986).

SEGEBADE, C., WEISE, H.P., LUTZ, G.J., Photon Activation Analysis, de Gruyter, Berlin and New York (1987).

Spectrometric Examination in Conservation (Proc. 18th Int. Symp. on Conservation and Restoration of Cultural Property, Tokyo, 1994).

Non-destructive analysis of historical silver coins

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Problem

A selection of 115 Roman silver denarii, minted during the period A.D. 128–194, have been examined in order to determine their silver and copper content. This work was carried out in cooperation with the Institute of Nuclear Chemistry and Technology, Warsaw, Poland. All these denarii were found at Romanów near Krasnystaw in Poland. Most of the surviving coins are in poor condition, as can be seen from the example shown in Fig. 1. It is supposed that they had been in circulation for a long time before they were deposited in Romanów. A common practice in the reign of various Roman emperors was the cutting of coins for debasement of their original value, but they still remained a medium of payment. We wished to prove the assumption of debasement with the help of prompt γ activation analysis (PGAA) [1].

Why nuclear analytical techniques?

Recently the chemical analysis of archaeological artefacts (metals, stone tools, sculptures, pottery, etc.) has gained more attention in view of the availability of new techniques.

FIG. 1. Obverse side of a Roman silver coin issued in A.D. 141 by Faustina I.

Knowledge of the element composition, including major and trace elements, may provide clues concerning the provenance, manufacturing process, raw materials and so on. The most commonly applied optical methods, such as polarizing microscope investigations, and the more widespread of the analytical methods, such as X ray fluorescence (XRF) analysis, instrumental neutron activation analysis (INAA) and inductively coupled plasma mass spectrometry (ICP-MS), are destructive, which is generally a serious obstacle in the case of valuable whole or fragmental artefacts. Although XRF can also be applied non-destructively, in this form it is usually restricted to the study of smooth surfaces of restored archaeological objects.

PGAA is one of the new candidates for coping with this problem. Its basis is a physical process, radiative capture of neutrons. Because of the low intensity of the external neutron beams employed (10^6–10^8 $cm^{-2} \cdot s^{-1}$), PGAA can be considered non-destructive and applicable to samples that must be preserved intact. After some days of cooling (i.e. decay of short lived radioactive products), the investigated objects can be returned to the owner (museums or collectors) in their original form. Another great advantage of PGAA is that it is a multielement method, i.e. in theory all of the chemical elements can be detected, albeit with different sensitivities, by virtue of the induced prompt γ radiation. With the help of PGAA, both the major components and many trace elements of objects can be identified from the same measurement.

Moreover, PGAA measurements do not require sample preparation; the artefacts can be positioned directly in the neutron beam. Thus the method can be regarded as fast compared with other analytical methods. Owing to the large penetration depth of the neutron, PGAA will give the average composition of the bulk material, i.e. of the object as a whole. If necessary, well defined parts of large archaeological objects, such as jugs, helmets, shields, arms or whole sculptures, can be investigated separately by irradiating only that part of the sample. This example is only one of the numerous interesting applications of PGAA in archaeology.

How to solve the problem?

The chemical elements are identified in a PGAA spectrum according to the energies of their characteristic γ ray peaks, while the quantitative analysis is based on the exact determination of γ peak intensities. The sensitivities for the most intensive prompt γ lines of all chemical elements were determined by internal standardization measurements at the Budapest Research Reactor.

In this study, two series of coins were investigated. The first 45 pieces are dated from A.D. 138 to 165, the second 70 pieces from A.D. 128 to 194. We decided to determine the Cu/Ag mass ratios of the objects with ten-minute-long measurements. The PGAA method had previously been checked on a set of Cu–Ag standard alloys obtained from the Hungarian Institute of Standards for Noble Metals, and a good agreement was found [2]. The Cu/Ag ratios of coins were investigated as a function of date during the historical period investigated. This ratio was found to increase with time from about 0.3 to about 0.5 in the first series of coins (Fig. 2). The significant increase of the copper content of the denarii at the expense of their silver content probably indicates the course of inflation at that time. This tendency was also reinforced by the measurements of the second series.

A set of Hungarian medieval and modern silver coins was also investigated in the same thermal neutron beam in order to verify the parallel XRF measurements [2, 3].

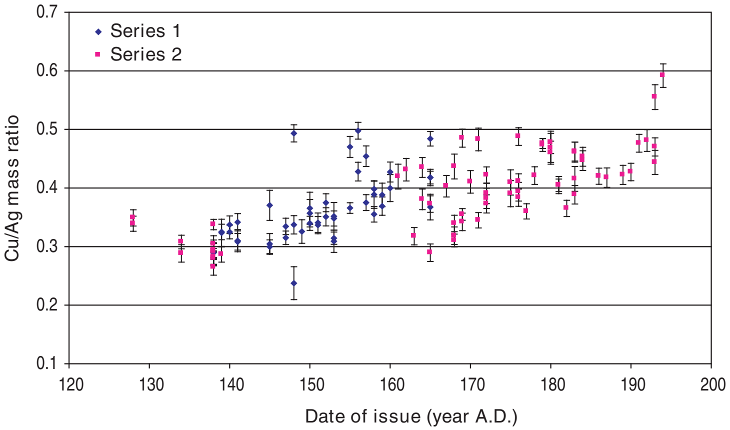

FIG. 2. Copper/gold mass ratio of Roman denarii in different periods.

We have to emphasize again that, owing to the neutrons' large penetration depth, PGAA gives information on the bulk material in a non-destructive way. We cannot distinguish, however, between 'bulk' and 'surface' sample composition. It can be important to take into consideration the different corrosion or weathering effects on the archaeological objects, which were buried for hundreds or thousands of years. It is highly recommended to perform complementary analytical investigations.

References

[1] KASZTOVSZKY, Z., PANCZYK, E., FEDOROWICZ, W., RÉVAY, Z., MOLNÁR, G.L. (in preparation).

[2] KASZTOVSZKY, Z., RÉVAY, Z., BELGYA, T., MOLNÁR, G.L., J. Radioanal. Nucl. Chem. **244** 2 (2000) 379–382.

[3] SÁNDOR, Z., TÖLGYESI, S., GRESITS, I., KASZTOVSZKY, Z., J. Radioanal. Nucl. Chem. **254** 2 (2002) 283–288.

Part IX

MISCELLANEOUS APPLICATIONS

Characterization of material difficult to homogenize and/or to subsample

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Problem

The continuous development and improvement of electronic products results in regular replacement by the public of their radios, television sets, telephones, etc. A new waste stream has developed, and technologies have been developed for recycling the components in this stream. However, regular control of the composition of the stream is necessary. Representative sampling of shredded electronics is a difficult task, since the shredded material is extremely inhomogeneous (consisting of wires, parts of printed circuit boards, parts of resistors, plastic, etc.) and has particle sizes that are equal to or larger than the average portion needed for analysis.

The waste rock pile of a decommissioned uranium mine in Brazil had to be characterized for its trace elements to assess the environmental impact of leaching by rain and drainage water. The first studies showed a high variability in the levels of lanthanides, uranium and thorium in samples collected very close to each other. Three possible causes had to be evaluated: (a) the quality control procedures, (b) the degree of homogenization, and (c) the local variation at the sampling site.

Many plastic products have a relatively short period of usage and end up in the waste stream, from which they may be collected for recycling. The plastics being recycled are cleaned of contaminating dirt and subsequently shredded, resulting in plastic scrap consisting of flakes of a few square millimetres in size. Although the use of cadmium-containing pigments and stabilizers in newly produced and imported plastic products has declined considerably in the Netherlands during the past ten years, cadmium-containing plastics may still be found in the waste stream. Some plastics may have cadmium concentrations ranging up to several thousands of milligrams per kilogram. Within one batch of flakes, the cadmium concentration may therefore vary by several orders of magnitude. Large variations in scrap constituents may in principle have consequences for inhomogeneous element distributions in the final product of the recycling process.

Why nuclear analytical techniques?

All routine multielement analysis techniques employ rather small amounts of material, varying from microlitres and milligrams to a few grams. For technical reasons, larger quantities are not handled. In atomic absorption spectroscopy and in

inductively coupled plasma spectroscopy, only small portions can be introduced, and since in X ray fluorescence spectroscopy information is derived from the surface layers, the use of quantities larger than required to prepare the target is meaningless. For both practical and sampling reasons, often more material is collected and presented for analysis than can be handled. Preparing a representative subsample — either by bringing the material into solution or by extensive homogenization procedures — requires a lot of effort, and the degree of homogeneity has to be verified via replicate analyses.

Instrumental neutron activation analysis is probably the only analytical technique capable of analysing samples of kilogram size. There is no need for digestion — which is advantageous, for example, in the case of electronic and plastic scrap — or for laborious sample size reduction and homogenization procedures. This makes possible the analysis of material collected in large quantities in an attempt to obtain a representative picture of the population under study.

How to solve the problem?

Large sample instrumental neutron activation analysis is operational at the Interfaculty Reactor Institute in Delft. A special irradiation and counting facility exists by which cylindrical samples with diameters of up to 15 cm and total lengths of up to 1 m can be handled.

Shredded electronics and plastic flakes were analysed in quantities of approximately 1.5 kg. The observed amount of copper in the shredded electronics could be verified with the amount of copper found by hand-picking and weighing the copper wires. Excellent agreement was found. The analysis of recycled plastic flakes has been turned into a routine activity.

Two samples of 2 kg each were collected directly next to each other at the waste rock pile mentioned above. One was sent to Delft for direct large sample analysis; afterwards it was sent back to Brazil, where both large samples were identically processed for sample size reduction and homogenization. Small subsamples of both sets were analysed in Brazil; small samples of the sample analysed previously as a large sample were analysed in Delft. The results eventually indicated that a very high local variation was the prime cause of the problem in analysing the material.

Bibliography

BODE, P., OVERWATER, R.M.W., Trace element determinations in very large samples: A new challenge for neutron activation analysis, J. Radioanal. Nucl. Chem. **167** 1 (1993) 169–176.

FERNANDES, E.A.N., BODE, P., Sampling and homogenization studies of uranium mining waste rocks using normal and large-sample INAA, J. Radioanal. Nucl. Chem. **244** (2000) 589–594.

HOGEWONING, S.J., BODE, P., Sampling studies of plastics and its recycling process using normal and large sample INAA, J. Radioanal. Nucl. Chem. **244** (2000) 531–535.

Inactive tracing using PGNAA

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Problem

The mixing of materials in industrial processes (furnaces, chemical reactors, etc.) is often investigated using radioactive tracing. The emitted radioactivity is characteristic of the homogeniziation and flow properties. When investigating large objects (e.g. melting furnaces of hundreds of tonnes), radioactive tracing cannot be applied because of the dangerously large activities needed. In this case an inactive tracer in a quantity which does not disturb the properties of the product must be added to the batch of raw materials. The concentrations of the tracer measured in the samples taken regularly at the working end of the furnace also reveal the flow properties.

Why nuclear analytical techniques?

Prompt γ neutron activation analysis (PGNAA) is a relatively young nuclear analytical technique. The samples are irradiated in a neutron beam, which is usually provided by a research reactor. After the neutron capture, the nuclides in the sample emit characteristic prompt γ radiation, which is detected by a semiconductor detector. After evaluation of the prompt γ spectrum, the qualitative and quantitative analysis can be performed. Owing to nuclear physical factors, the different nuclides (and also the elements) have extremely different neutron capture cross-sections, which affect the analytical sensitivities. The PGNAA method is ideal when trace elements having high cross-sections (such as B, Gd and Sm) are analysed in a low cross-section matrix (most light elements, such as C, O, N, Mg, Al and Si).

PGNAA is also advantageous from the point of view of the analysed volume. Since neutrons penetrate deeply into the sample, the composition obtained is averaged over the irradiated volume. The beam cross-section used during the irradiation in our laboratory is 2 cm × 2 cm, while the thickness of the glass samples was typically 1–2 cm; thus the active volumes were about 4–8 cm^3. This volume is large enough to eliminate

FIG. 1. PGNAA experimental layout.

the effect of local inhomogeneities. Figure 1 shows the experimental layout.

How to solve the problem?

Samples taken from different glass melting furnaces were investigated. In the case of borosilicate glass, gadolinia (Gd_2O_3) was added as a tracer. Its average concentration was 10 ppm. Gadolinia in this concentration does not change the properties of the glass product. In the case of other types of glass, boron was applied as the tracer, in the form of borax. Its average concentration was 30 ppm, while the measured boron background was 5 ppm in the raw material.

Samples were taken regularly (typically every 1–5 hours) at the working ends of the furnaces. The cooled glass pieces were transported to the Institute of Isotope and Surface Chemistry in Budapest and were measured with PGNAA in the thermal neutron beam at the Budapest Research Reactor.

The measurement times were typically 3 hours for borosilicate glasses and only 10 minutes in the case of other types. The compositions were obtained within a few minutes after the acquisition of the spectra, and the results were used in scheduling the sampling.

The test results were used in modifying the glass furnace design at the factory. Subsequent test series showed an improvement in the homogenization and flow properties of the melting furnace. In Fig. 2 the tracer concentration is

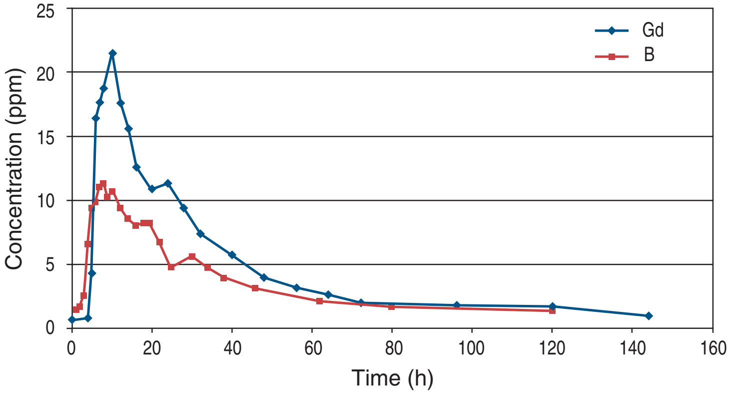

FIG. 2. Tracer concentrations in vitric glass samples as a function of time elapsed after feeding.

plotted as a function of time elapsed after feeding, for a furnace before and after the reconstruction.

Bibliography

MOLNÁR, G., RÉVAY, Z., VERES, Á., SIMONITS, A., RAUSCH, H., Cold neutron facility for prompt gamma neutron activation analysis, J. Radioanal. Nucl. Chem. **167** (1993) 133–137.

RÉVAY, Z., MOLNÁR, G.L., Standardisation of the prompt gamma activation analysis method, Radiochim. Acta **91** (2003) 361–369.

RÉVAY, Z., MOLNÁR, G.L., BELGYA, T., KASZTOVSZKY, Z., FIRESTONE, R.B., A new gamma-ray spectrum catalog for PGAA, J. Radioanal. Nucl. Chem. **244** (2000) 383–389.

Vino sin arsénico, por favor (Wine? *Yes please.* Arsenic? *No thanks*.)

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Problem

Until the 1970s lead arsenate was used as a fungicide in apple orchards and vineyards in many countries around the world. Both lead and arsenic are toxic at certain concentration levels. These two elements are considered persistent chemicals, meaning that they can stay in the soil for a number of years even after the usage has been stopped. Health Canada, the Canadian federal government health department, monitors many food items on a routine basis for toxic chemicals. These food items include those produced in Canada as well as ones imported to Canada from other countries.

Although Canada produces wine, much of the wine consumed in Canada comes from Europe, Australia and South America. Health Canada regularly tests wine for arsenic, among other possible contaminants. In the late 1990s laboratories of Health Canada and of a few provincial governments measured levels of arsenic in a shipment of wine from South America. They used different analytical techniques and methods, and obtained arsenic levels which did not quite agree with one another. They decided to seek the help of another laboratory in solving the problem. One of the laboratories knew about the expertise available at our laboratory in the determination of low levels of arsenic in food items by instrumental neutron activation analysis (INAA) and contacted us, which is how we became involved in the project.

Why nuclear analytical techniques?

Other laboratories were using various methods based on atomic absorption spectrometry (AAS), a well established and widely used analytical technique. Almost all AAS methods are destructive in nature. In simple terms, the samples must be dissolved first before any measurement can be done. Hot sulphuric acid, which is commonly used for the dissolution and oxidation of biological materials, is known to interfere with the arsenic signal in the AAS flame method. Matrix interferences are reported to occur in arsenic measurements by

AAS furnace methods (graphite furnace or electrothermal atomization). Incomplete reduction of various arsenic species by sodium borohydride is a possible source of error in AAS hydride generation methods. Moreover, all digestion methods are susceptible to contamination by chemical reagents and handling. Isotope dilution mass spectrometry (IDMS) is another reliable analytical technique. Apart from being a destructive technique, IDMS cannot be applied to the determination of monoisotopic elements such as arsenic (the natural isotopic abundance of ^{75}As is 100%).

One of the most important advantages of INAA, especially for the determination of arsenic in wine, is that the sample can be analysed directly without any need for its digestion, which can result in loss and/or contamination. Moreover, INAA is a very sensitive technique for the determination of arsenic at nanogram levels with high precision and accuracy.

How to solve the problem?

We developed an INAA method for the determination of arsenic in wine using the Dalhousie University SLOWPOKE-2 reactor (DUSR) facility. We have previously described the unique features of this small research reactor for NAA [1–3]. We took 1 mL of wine, placed it in a clean polyethylene irradiation vial, put the cap on and heat sealed it, and irradiated the sample in DUSR at a neutron flux of 5×10^{11} $\mathrm{cm}^{-2} \cdot \mathrm{s}^{-1}$ for 7 h. We waited for about 50 h and then counted the sample for about 8 h using a Compton suppression γ ray spectrometry system. This system consisted of a high purity germanium (HPGe) detector surrounded by a 10 in × 10 in[1] NaI(Tl) guard detector with a 3 in × 3 in NaI(Tl) plug. The peak to Compton plateau ratio of this system is about 590:1.

To be fair to the people who use other analytical techniques as well as to the people who want to use INAA, perhaps we should describe the special procedures we developed to determine low levels of arsenic.

Biological materials of complex chemical composition contain several elements, such as bromine, chlorine, sodium and potassium, that can produce high activities that result in poorer detection limits for arsenic. At the sub-ppm or ppb

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[1] 1 inch = 2.54 cm.

levels of arsenic commonly found in biological samples, the 559.1 keV peak of ^{76}As (half-life 25.9 h) could be especially susceptible to interference by the 554.3 keV peak of ^{82}Br (half-life 35.3 h) on one side and the 564.1 keV peak of ^{122}Sb (half-life 65.3 h) on the other. Modern HPGe detectors usually have sufficient resolution to resolve these three peaks. However, when the bromine content of the biological sample is high, which is often the case, the tailing of the 554.3 keV peak can mask part of the 559.1 keV peak of ^{76}As and can make the detection of the arsenic peak rather difficult. For this reason INAA methods can only be used to measure arsenic down to levels of a few parts per million in biological materials by conventional γ ray spectrometry. We have used epithermal neutrons to reduce the activities due to chlorine, sodium and potassium.

Owing to the longer half-life of ^{82}Br, the interference from the 554.3 keV peak cannot be eliminated by simply extending the decay period. The ^{76}As nuclide decays by β emission and two major γ rays, namely 559.1 and 657.0 keV, which are partially coincident. An anticoincidence (also called Compton suppression) counting technique can be beneficially used in such situations. We found that Compton suppression spectrometry not only reduces the 554.3 keV peak of ^{82}Br but also suppresses the background under the 559.1 keV peak of ^{76}As. Details of the determination of arsenic by NAA coupled to Compton suppression γ ray spectrometry can be found in Refs [4–7].

We analysed the samples of wine directly and also after evaporation to dryness. We found that the evaporated samples could be subjected to longer irradiation times without a danger of rupture of the irradiation vial due to the pressure buildup inside the vial from the radiolysis of water. While both types of sample gave comparable results of less than 100 ppb arsenic, the results of the analysis of dried samples were more reproducible owing to the better counting statistics. The detection limit is about 5 ppb of arsenic, and the accuracy is better than 95%. In a more recent study we found that we could keep the total uncertainty to less than 1.5%. We believe that the method is very good and can be applied to a variety of biological samples for the reliable determination of low levels of arsenic.

References

[1] RYAN, D.E., STUART, D.C., CHATTOPADHYAY, A., Rapid multielement neutron activation analysis using a SLOWPOKE reactor, Anal. Chim. Acta **100** (1978) 87.

[2] HOLZBECHER, J., CHATT, A., RYAN, D.E., SLOWPOKE epicadmium neutron flux in activation analysis of trace elements, Can. J. Spectrosc. **30** (1985) 67.

[3] RYAN, D.E., HOLZBECHER, J., CHATT, A., Analysis for trace elements with a SLOWPOKE reactor, Anal. Chim. Acta **200** (1987) 89.

[4] ZHANG, W.H., Studies on Anticoincidence Gamma-Ray Spectrometry in Neutron Activation Analysis, PhD Thesis, Dalhousie Univ., Halifax, Nova Scotia (1997).

[5] ZHANG, W.H., CHATT, A., Compton suppression spectrometry for arsenic in biological reference materials, Trans. Am. Nucl. Soc. **77** (1997) 11.

[6] LANDSBURGER, A., SWIFT, G., NEUHOFF, J., Nondestructive determination of arsenic in urine by epithermal neutron activation analysis and Compton suppression, Biol. Trace Elem. Res. **26–27** (1990) 27.

[7] LIN, X., LIERSE, C., WAHL, W., An innovative Compton suppression spectrometer and its capability of evaluation in multi-elemental neutron activation analysis, J. Radioanal. Nucl. Chem. **215 (**1997) 169.

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