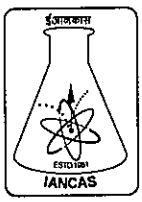

INDIAN ASSOCIATION OF NUCLEAR CHEMISTS
AND ALLIED SCIENTISTS

Neutron Activation Analysis

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Editorial

The most appealing property of a radioisotope is the feasibility of its detection at an extremely low level. As low as a few thousands of atoms of a radioactive isotope can be detected by using an appropriate instrument. This property has been harnessed in a big way for the development of a number of sensitive analytical techniques such as isotope dilution analysis (IDA) and radioimmunoassay (RIA). In all these techniques, the radiation emitted from an externally added tracer is measured for quantification of the analyte.

Activation analysis is another important technique that takes advantage of the high detection sensitivity of a radioisotope. In this method, the induced radioactivity in the sample is measured to quantify the analyte. The sensitivity of the technique depends on the particle (mostly neutrons) flux and the nuclear reaction cross section. Though primarily used for the measurement of elements, it could also be extended to include different chemical species by having appropriate chemistry during sample preparation. The availability of high flux research reactors together with modern gamma counting systems has helped in improving the sensitivity and ease of this technique.

Neutron activation analysis (NAA) is applied in several areas such as material science, earth science, environmental monitoring, trace metal analysis in medicine, forensic science and criminology. The present issue of the IANCAS Bulletin is on "Neutron Activation Analysis". This issue is brought out to coincide with a 'Workshop on utilization of Kamini Research Reactor' which will be held in IGCAR, Kalpakkam in August. Dr. A.V.R. Reddy, Guest Editor of this issue has done an excellent job in identifying authors, relevant topics and editing the articles. I am thankful to Dr. Reddy and the authors who contributed to this issue.

I am glad to inform the members that IANCAS bulletins are now regarded as 'collector's pride' by many of our valued readers. I thank all the readers who have expressed appreciation for our earlier issues

M.R.A. Pillai

CONTENTS

Neutron as an Analytical Probe

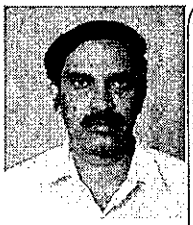
Dr. S. Gangadharan graduated from Madras University in 1959 and has been with DAE (BARC) since 1960 following graduation from the BARC Training School. He obtained his Ph.D. from University of Pittsburg, USA. He is currently Chief Executive, Board of Radiation and Isotope Technology, DAE and the Project Director, National Centre for Compositional Characterisation of Materials, Hyderabad. He is an expert in nuclear analytical chemistry and ultra-trace elemental analysis for applications to materials science, environmental and life sciences, forensic science and archeology. Dr. Gangadharan has been IAEA technical expert to Thailand and Zaire and has been associated with important assignment of IAEA, Vienna.

The use of neutron as an analytical probe has two major components: one, prompt measurements involving elastic or inelastically scattered neutrons, prompt gamma rays, x-rays or charged particles such as proton, neutron, alphas; the other approach is based on the activation process involving measurement of radioactive recoil product, either directly using high-resolution gamma ray spectrometry or preceded by physio-chemical separation to enhance the selectivity. Investigation of scattering has been of great interest in the study of texture of materials, while the detection of prompt gamma rays has enabled achieving very high sensitivity, particularly when the measurand of interest has been separated in ultra clean room conditions. The measurement of charged particles, using well thermalised neutron beams as probe, has been responsible for near non-destructive (very low dpa) depth profiling of several impurities, albeit near the surface.

Activation analysis using the measurement of recoil radioactive product has been by far the most exploited, thanks primarily to the combination of the high flux of neutrons from the reactor, good quantitative clean chemistry and high resolution large efficiency detectors with matching electronics. This last combination has enabled simultaneous, multi-element, quantitative, high sensitivity, large dynamic range analysis of a variety of samples in different disciplines. The near non-destructive nature of the method, not only enables to preserve the integrity of the sample before the excitation, but also preserves the sample for both re-examination and archival storage. The applications of activation analysis have been manifold, in material science for development of new materials and compositional characterisation, earth sciences for understanding the basic processes, in the environment for monitoring and ensuring the quality, in life sciences to study the role of trace elements in health and disease and in criminalistics and archaeology for establishing commonness of origin or authenticity. The use of neutrons in matters of national security, is of particular interest, as for example, in the case of detection of explosives earlier by thermal neutron activation and later by INGRIS.

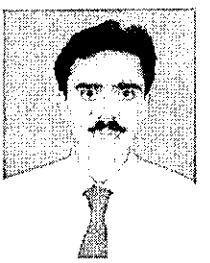
There is a need for proper validation of the experimental data in different disciplines to enable homogenisation and the use of the database for solving the problems. The medium flux reactor like KAMINI can be put to very good use if we make a judicious combination of high efficiency detectors and some good chemistry whenever required.

Neutron Activation Analysis



Dr. A.V.R. Reddy graduated from BARC Training School in 1976-77 and joined Nuclear Chemistry Section, Radiochemistry Division in 1977. His main areas of research are Nuclear fission, nuclear reactions, radiochemical separations and neutron activation analysis. He has obtained his Ph.D. in 1986 and has about 100 publications to his credit. He is one of the co-authors for the books (i) Principles of Radiochemistry, (ii) Experiments in Radiochemistry and (iii) Introduction to Radiochemistry. At present, he is Head, Nuclear Chemistry Section. He is a very active member of IANCAS. He is a member of IUPAC's (International Union of Pure and Applied Chemistry) Commission on Radiochemistry and Nuclear Techniques for the last three years.

Shri R.N. Acharya obtained M. Sc. in Chemistry from Utkal University in 1992. After graduating from Training School, he joined Radiochemistry Division, BARC in 1994. Since then he is engaged in research and development work on neutron activation analysis (NAA). He has about 30 publications to his credit.



Introduction

Fermi [1] first reported that radioactive product can be produced by neutron activation. In 1936, Prof. George de Hevesy and Hilde Levi [2] described the determination of dysprosium in the yttrium samples by irradiating the sample with neutrons from a radium-beryllium source and thus demonstrated the analytical utility and capability of neutron irradiations. In fact, they were investigating the effects of neutron irradiations on the rare earth elements and stumbled upon 'Neutron Activation Analysis' (NAA). NAA as a method of analysis has to wait until the construction of nuclear reactors as they provided high neutron flux and thus enhanced the capability of NAA. Due to relative simplicity, inherent selectivity and sensitivity, NAA occupies an important position among various analytical methods[3,4]. Advent of high resolution high purity Germanium (HPGe) detectors and online computer analysis techniques provide the possibility for simultaneous multielement analysis. Due to this, NAA finds applications in various areas of research. The advances in the development of methodology and applications are well documented [5].

Principle

Neutron being a non-charged particle interacts with the nuclei of all isotopes and may result in nuclear reactions. The product formed in such a nuclear reaction most probably will be a radioisotope. By measuring the radioactivity formed, concentration of the isotope that underwent nuclear reaction can be measured. Using the isotopic abundance, elemental concentration can be calculated. This is the principle of Neutron Activation Analysis (NAA). Therefore, NAA is based on irradiation of a sample with neutrons, preferably in a nuclear reactor and subsequent counting of the induced radioactivity, most frequently employing high resolution γ-ray spectrometers with a HPGe detector. Multi element analysis is carried out by measuring gamma rays corresponding to different radioisotopes (elements) using a multi channel analyser. For a limited number of applications isotopic neutron sources based on either the spontaneous fission of ^{252}Cf or nuclear reactions, such as the (α,n) reactions (e.g. ^{241}Am-Be) or the (γ,n) reaction (e.g. ^{124}Sb-Be) may be sufficient, although they provide a neutron fluence rate which is of several orders of magnitude lower compared to that obtained in nuclear reactors.

NAA can also be performed using 14 MeV neutrons produced by the (d,t) reaction in neutron generators, or with fast neutrons produced in several nuclear reactions of deuterons or protons accelerated in a cyclotron.

Activity formed in Neutron Activation

The absolute activity of the radionuclide, formed when an element is subjected to neutron activation, is given by,

$$A = N.\sigma.\phi.S.D$$
$$= (N_A\,\theta\,w/M)\,\sigma.\phi.S.D \qquad (1)$$

where, N_A = Avogadro number, θ = isotopic abundance, w = weight of the element, M = atomic mass, σ = capture cross section, ϕ = neutron flux, $S = 1-e^{-\lambda t}$ = saturation factor, $D = e^{-\lambda T}$ = decay factor, λ = decay constant, t = duration of irradiation and T = cooling time.

Radioactivity of activation product is assayed by gamma-ray spectrometry and in some cases by counting and is related to the concentration of the analyte

Sensitivity

About 70 elements can be measured using NAA with a sensitivity better than 10^{-7} g. For elements like In, Eu and Dy, achievable sensitivity is about 10^{-12} g whereas for Mn it is 10^{-11} g. Sensitivity is between 10^{-8} g and 10^{-7}g for elements like K, Sc, Ni, Rb and Cd. These calculations are based on the assumption that the neutron flux is of the order of 10^{12} $n.cm^{-2}.s^{-1}$ and a minimum of 100 Bq is the lower limit for activity measurement

Different methodologies of NAA

There are different modes of approach of NAA depending upon sample matrix and elements to be analysed. These are:

- Instrumental neutron activation analysis (INAA)
- Radiochemical neutron activation analysis (RNAA)
- Chemical neutron activation analysis (CNAA)
- Prompt gamma neutron activation analysis (PNAA)
- Derivative neutron activation analysis (DNAA)
- Cyclic activation analysis (CAA)

Neutron activation technique is divided into mainly three categories. If no chemical treatment is done, the process is called instrumental neutron activation analysis (INAA). After irradiation if radiochemical separation is carried out to remove interferences or to concentrate the radionuclide of interest, the technique is called radiochemical neutron activation analysis (RNAA). If preirradiation chemical separations are employed, the procedure is called chemical neutron activation analysis (CNAA). A different form of NAA called PGNAA is also used, where it is the prompt γ-rays emitted by the excited intermediate nucleus that are monitored. Derivative activation analysis (DAA) is a novel composite analytical approach that is used for elements that are poorly determined using conventional NAA. In DAA the poorly determined element is chemically exchanged for, or complexed with, an element that is amenable to NAA. Cyclic activation analysis (CAA) is based on the concept of enhancing the sensitivity of the activation method for the determination of elements with short-lived indicator radionuclides by use of repeated short irradiation and counting periods and summing of the γ-ray spectra obtained.

Another way to group NAA methods is according to the energy of incoming neutrons. They are categorised in three types:

- Thermal neutron activation analysis (TNAA)
- Epithermal NAA (ENAA)
- Fast NAA (FNAA)

Chemical Separations in NAA

NAA in principle is a non-destructive instrumental analysis (INAA). However, when certain elements like Na, K and Br if present as major constituents, the gamma rays from activation products formed would complicate the measurements. Additionally, if the sample contains uranium, it undergoes nuclear fission and the products formed would be between Z=35 and 70 and therefore, estimation of these elements would be erroneous. In such situations, it is essential either preconcentrate and/or remove elements like U prior to irradiation. This procedure is known as Chemical Neutron Activation Analysis (CNAA). In

Radiochemical NAA (RNAA), the sample is irradiated and the higher abundant matrix elements are removed by chemical methods In CNAA, gamma spectrum becomes simpler because matrix elements are removed before irradiation, sensitivity becomes higher and results in minimum radiation exposure. However, blank correction is often required. On the other hand, in RNAA gamma spectrum becomes simpler and blank correction for reagents is not needed. Radioactive samples have to be handled as the radiochemical separations are carried out after the irradiation.

Stadardisation Methods of NAA

NAA is carried out, in principle, by three methods : (i) Absolute method, (ii) Relative method and (iii) Single comparator method.

Absolute Method

Sample is irradiated in a neutron flux (ϕ) for a period of time (t). Radioactivity of the activation products is measured by gamma ray spectrometry. Using the nuclear and reactor data the amount is obtained from the intensity of the characteristic gamma rays. Since unacceptable uncertainties are associated with the values of nuclear parameters, namely activation cross sections σ_0, resonance integrals I_0, γ-ray emission probabilities γ, and isotope abundances θ (in order of decreasing importance), the absolute standardization is seldom used.

Relative Method

In the relative method, a chemical standard with a known mass of the element is co-irradiated with the sample of a known mass and both are counted, usually in the same geometrical arrangements with respect to the HPGe detector, so that the absolute detection efficiency of the detector need not be determined. When short-lived radio nuclides are employed both the standard and sample are irradiated separately in the same conditions, with a monitor of the neutron fluence rate. The ratio of activities of an isotope in sample and standard is related to the concentration of that isotope and hence the element. Though the relative method is simple and precise, prior knowledge of the elements present in the sample is necessary and standards for all the elements in similar matrices to be analysed are difficult to prepare.

Single Comparator Method (k_0 NAA)

The concept of the k_0-standardization in NAA, single-comparator method, is based on coirradiation of the sample and of a neutron fluence rate monitor and on using an experimentally determined composite nuclear constant k_0 [6-8]. In the case of k_0-standardisation, the analysis results are linked to the k_0-factors, absolute detection efficiency and neutron spectrum characteristics. k_0 is a ratio of four constants : average atomic weight, isotopic abundance, thermal neutron capture cross section and gamma ray abundance

As the factor k_0 is used for the calculation of the concentration of the element the method is referred as k_0 NAA method. Further details of the calculations and input parameters like f and α are given elsewhere [8]. The accuracy and consistency of the nuclear data play a significant role in the standardisation of reactor neutron activation analysis. Out of the these nuclear constants, data on cross sections and gamma ray emission probabilities are sometimes reported with large uncertainties. Therefore, the accuracy and consistency with respect to the above mentioned constants should be judged individually, consistency being the prime concern

Experimental Methodology in NAA

In k_0 NAA the following steps are involved : (1) Collection of the bulk sample, (2) Preparation of the sample for irradiation, (3) preparation of the standard, (4) Preparation of the sample and standard separately for irradiation, (5) Irradiation in a neutron source such as reactor, (6) Preparation of the counting sample from the irradiated sample, (7) Measurement of the activity in the irradiated sample and standard, (8) Calculation of the concentration of the elements present in the sample from the measured activities, (9) Evaluation of errors and (10) Interpretation of the results.

Experimental

Sampling

Sampling is an important aspect in the analysis. The results obtained for a portion (sample) forms the

basis of assessing the value of a material from which the sample is made. Care should be taken to ensure that the sample used for analysis is a true representative of the whole material. It is true for sampling of multi element reference standards as well as single comparators.

Irraditions

Appropriate amounts of samples and standards are either sealed in polypropylene tubes or quartz containers or aluminium depending on the requirement of the experiment, placed in a standard bottle and irradiated in a suitable irradiation position of a nuclear reactor, for a suitable period depending on the half life of the nuclide of interest

Radioactive Assay

After providing necessary cooling time, sample and standard / comparator are washed under running tap water, wiped and mounted on a standard perspex plate. Samples are normally assayed for gamma activity of the activation products using a high resolution gamma ray detector coupled to a PC based 4K channel analyser in an efficiency calibrated position with reproducible sample to detector geometry. The sample to detector distance is maintained between 8 and 15 cm depending upon the level of activity to avoid pile-up and coincidence effects.

Calculations

Peak areas corresponding to different gamma lines were obtained either by using the SAMPO programme in the case of complex gamma ray spectra or summing the counts under the peak and subtracting the linear Compton background in relatively simple spectra. Peak areas are used to arrive at the concentrations of corresponding isotopes (elements).

Characterisation of Neutron Spectrum

Sub-cadmium to epi-cadmium neutron flux ratio (f) is a measure of low energy neutron flux. It is determined for the irradiation position using cadmium cut off method or multi isotope foil method [7]. Another important parameter, the extent of deviation from ideal shape of neutron spectrum for each irradiation position is determined using multi isotope / element method. Details of measurements and calculations are given elsewhere [9]. Extent of contributions from the interfering reactions is often determined in each position for corrections. e.g., in the manganese estimation ^{56}Mn is the activation product. It is also formed by $^{56}Fe(n,p)^{56}Mn$ reaction. Therefore it is essential to estimate the extent of contribution.

Validation by Analysis of Standard Reference Materials

Since there is a large variation in the nature of the samples and the concentration of the elements present, it is essential to validate this analytical technique. A variety of the standard reference materials like AGV-1 and W-1, NOD-A-1, SOIL-7 and SRM-1571 are routinely analysed to validate the method in terms of precision and accuracy [10].

Quality assurance of NAA results is usually performed using certified reference materials which are available for various matrices as well as element levels.

Errors

In NAA, one has to account for both random and systematic errors. Random errors are mainly contributed by counting statistics. Depending on the level of activity and half-life of the nuclide, random errors can be brought down to reasonable level. Another important contribution to the random error is from background contribution, both due to ambient background as well as from the Compton contribution. Thus improvements in S/N ratio have to be made depending on the experimental conditions.

Systematic errors in NAA are more serious. Some of the important sources of systematic errors are:

(i) preparation of standards,

(ii) interference from nuclear reactions and nuclear fission,

(iii) self-shielding during the irradiation,

(iv) γ-ray interferences and

(v) in the various steps of chemical separations.

Advantages and Limitations of Neutron Activation Analysis

Neutron activation analysis is being used due to the following advantages : sensitivity and applicability for minor and trace elements in a wide range of matrices, the virtual absence of an analytical blank, the relative freedom from matrix and interference, nondestructive in nature (INAA), high specificity, the capability of multi-element determination and an inherent potential for accuracy compared to the other analytical techniques. Additionally the theoretical basis of NAA is simple and well understood, the sources of uncertainty can be modelled and well estimated. In some cases radiochemical separation (RNAA) provides interference-free detection limits close to the theoretical ones, though it is a destructive method

NAA has some disadvantages as well. NAA needs a neutron source. Nuclear reactor is the best neutron source, however, its maintenance is an economical constraint. Use of isotope and other neutron sources does not often meet the sensitivity required. Determination of elements forming long-lived isotopes is time consuming. NAA is insensitive to the nature of chemical species present unless pre-irradiation separation is carried out. For certain elements like Pb, and many elements with low Z NAA does not provide sufficient sensitivity .

Applications of Neutron Activation Analysis

The inherent potential of NAA for both accuracy and precision plays a very important role in quality assurance of chemical analysis, namely in the certification of reference materials of chemical composition, including homogeneity testing, and in checking of results of other trace element analytical techniques [11]. It appears that the share of NAA in the certification of element contents, and especially in homogeneity testing, exceeds that of any other analytical techniques. NAA has found extensive applications in many science and technology fields for macro, micro and trace element analysis in the samples corresponding to the following fields [12]: Archaeology; Biomedicine, animal and human tissues; Environmental science and related fields; Forensics; Geology and geochemistry; Industrial products; Nutrition; Quality assurance of analysis and reference materials .

Since the applications are varying and large in number, to describe even one from each area of interest is out of the scope of this article. However, a few applications that have been carried out in Radiochemistry Division, BARC are cursorily described here. We have mainly used k_0 NAA to determine the macro, micro and trace element concentrations in a variety of matrices. e.g., sediments [13], ferromanganese encrustations [14], nodules, dolomites, dolerites and serpentines [15], soil, plant materials [16, 17] etc. A few of the applications are described.

Sediments from Nainital Lakes

The knowledge of sedimentation rates and the elemental concentration levels in sediments from lakes and other water bodies might provide clues to unfold the chronology of the input of pollutants to the water bodies. Eight sets of sediments from Nainital lake corresponding to depths from 6 to 51cm were analysed. The IAEA lake sediment standard SL-3 was analysed as a control of the method. The data from different sections of the sediment core [13] represent the history of natural absorption/ desorption pattern of the previous 160 years. The elemental concentration of As, Cr, Br, Zn and Cs are found to be more or less constant from bottom to top which could be taken as an indication that there is no anthropogenic pollution of trace elements to Lake Nainital.

Ferromanganese encrustations from Indian Ocean

Ferromanganese oxide encrustations are common depositional features on exposed rock outcrops in the deep sea. They are mostly found on mid-oceanic ridges, seamounts and raised areas of sea floors of world oceans and significantly differ in their composition and mineralogy. Multielemental analysis together with a varying Mn/Fe ratio is relevant in understanding their distribution in Mn and Fe phases. Three ferromanganese crusts from different locations of the Indian Ocean and another crust from the Lau basin of the Pacific Ocean were analysed by K_0 NAA method for studying the influence of different oceanic conditions on the trace element distributions in ferromanganese crusts. The precision and accuracy of the method were confirmed by measuring the elemental

concentrations in a USGS nodule standard NOD A-1. The measured concentrations of elements ferromanganese oxide encrustations [14] were analysed to understand the hydrogenous properties. The rare earth elements were found to be highly enriched in the crust of the Afanasiy Nikitin seamont and elevated region compared to the crust from MIOR. The thorium content was remarkably high for hydrogenous crusts. A Co-Sb correlation was observed particularly in seamount crust.

Ferromanganese Nodules from Indian Ocean

The ferromanganese nodules are mostly found at the interface of Ocean waters and the underlying sediment on the ocean bed and are associated with minor and trace constituents of alkali, alkaline earth metals, transition metals, REEs and other heavy elements. A total of five ferromanganese nodules from different locations and water depth of Indian Ocean were analysed alongwith SRM NOD P1 to obtain information on physical, chemical and biological activities taking place in the ocean. A few elements, namely, Sc, Sb, Hf, W and Th have been estimated for the first time in the Indian Ocean nodules.

The Fe enriched hydrogenous nodules were associated with higher concentration of most of the minor and trace elements. Slow growth rate, high retention time and favourable depositional environment are attributed to their enrichment. Hydrogenous nodules characterised by low Mn/Fe ratio, found at shallow region of the Indian Ocean, indicates lower mobility of Fe component compared to the Mn in the oceanic environment, leading to the precipitation of Fe as its oxyhydroxide. Cobalt was found to have strong affinity towards Fe. Tungsten and thorium are found positively correlated with iron and are reasonably enriched in the hydrogenous nodules compared to the diagenic one. Rare earth elements are probably incorporated on iron oxyhydroxide phase by adsorption processes. The REE abundance increases with the increase in the Fe content and is in good agreement to the earlier reports on the nodules of Pacific Ocean. It has been shown that the rare earth elements (REEs) are adsorbed but not co-precipitated with the iron oxyhydroxide phase.

Future Outlook

Although NAA is a powerful analytical technique, the future position of NAA among alternative trace element analysis techniques will depend strongly on further development and exploitation of the advantages and reduction of the drawbacks. Applications of NAA should be selective, exploiting the specific advantages of the technique and avoiding application where NAA is clearly not the method of choice. NAA can be used advantageously when high accuarcy is required (i.e., as reference method), for the analysis of materials that are difficult to destruct, for large inhomogeneous samples and for samples that have to be preserved after irradiation. Use of clean laboratories (Class 100) and quality chemicals to avoid contamination via pre-irradiation separation in CNAA would help in enhancing sensitivity. Judicious use of relative and k_0 standardisation of NAA may be of considerable help in analysing all the elements in a sample. Prompt γ neutron activation analysis (PGAA) is important for determination of low Z (H, Li, B, C, N P, S, Si) and other elements (Gd, Pb, Hg, Cd, etc.) elements in biological and environmental materials [18]. PGNAA takes much less time compared to classical NAA and so that one can reduce the turn around time. To improve signal to noise ratio, special counting techniques, such as coincidence and anticoincidence, namely Compton suppression spectrometry is considered useful.

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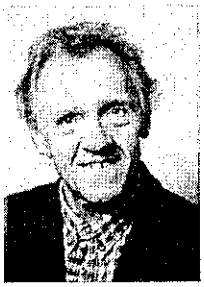
Epithermal Neutron Activation Analysis



Dr. Eiliv Steinnes is currently Professor in Environmental Science at University of Trondheim, Norway. Following his Masters degree in Nuclear Chemistry from University of Oslo, he did his Doctorate in Analytical Chemistry from the same University. He was with Institute of Atomic Energy, Norway, during 1963-79 in various capacities. Prof. Steinnes is a member of Norwegian Academy of Sciences and Letters, the Royal Norwegian Society of Science and Celtors and Norwegian Academy of Technical Sciences and various other professional bodies. Since 1971, he has been serving the IUPAC commission on Radiochemistry and Nuclear Techniques under various capacities and he was the Chairman of the Commission during 1981-83. He has also been President of Norwegian Society of Soil Science during 1982-91. Prof. Steinnes has about 365 publications out of which 196 are in International Journals.

Introduction

Neutron activation analysis (NAA) is one of the most powerful and widely used techniques based on the use of radioactivity in analytical chemistry. With the advent of nuclear reactors NAA soon became a very useful tool in trace analysis. For many years NAA was in fact the only means of studying many elements present at low concentration levels in materials such as silicate rocks, meteorites, high-purity metals and biological tissue.

The detection limits that can be achieved by INAA depend strongly on the elemental composition of the sample in question. Most often one or more of the matrix elements give rise to activities strongly interfering with the analysis by providing a high background in the γ-spectrometry measurements. In cases where the major interfering radionuclides have shorter half-lives than those of interest in the analysis, the problem can partly be overcome by appropriate delay of the measurements. In some cases purely instrumental means such as Compton suppression [1] can yield significant improvement in the detection limits. Another approach sometimes providing very significant improvement in the INAA determination of trace elements is selective activation with the epithermal neutron spectrum in the reactor, using a suitable filter to shield the thermal neutron component. This variant, which has become known as epithermal neutron activation analysis (ENAA) is the subject of the present article.

The neutron energy spectrum in a nuclear reactor ranges from very low energy to as high as 15 MeV. The thermal neutrons can be efficiently removed by means of a filter consisting of cadmium or some other material with very high thermal neutron absorption cross-section, allowing selective activation with the epithermal neutron flux in the reactor (resonance + fast neutrons). The practical 'cut-off' value of the thermal neutron filter depends on the character and thickness of the filter material. For a 0.7 mm cadmium foil, for instance, the effective 'cut-off' value is about 0.4 eV.

Most nuclear reaction with thermal and resonance neutrons leading to radioactive products are (n,γ) reactions. The neutron activation cross-section as a function of energy, however, shows great variation among different stable nuclides. In the thermal neutron region the activation cross-section of most nuclides follow the 1/v law (inversely proportional to the neutron velocity). Some nuclides continue to follow the 1/v law in the epithermal region, while others show strong resonances in their excitation function in that region. Therefore the ratio of thermal to epithermal activation shows large variation between different target nuclides, a fact which may be conveniently illustrated by looking at the ratio of resonance activation integral/thermal neutron cross-section (I_0/σ_0) for the nuclides concerned. While this ratio is of the order of 0.5 for nuclides following the 1/v law in the epithermal region, it may approach 100 for others. This means that the radionuclide distribution originating from epithermal activation may deviate strongly from that apparent when the whole reactor

neutron spectrum is employed. That forms the basis of ENAA.

The three main reasons for using epithermal activation [2] are (1) Improvement of precision and detection limits in INAA, (2) Reduction of high matrix activity and (3) Reduction of fission interference. In the following these three topics are discussed separately.

Improvement of Performance in INAA

Many of the nuclides giving rise to high activity in samples frequently studied by INAA, such as silicate rocks and soft biological tissue, show relatively low activation by resonance neutrons ($I_0/\sigma_0 \leq 1$). That concerns e.g. ^{23}Na, ^{27}Al, ^{31}P, ^{41}K, ^{45}Sc, ^{50}Cr, ^{55}Mn, ^{58}Fe, ^{139}La. Many trace element isotopes often studied in INAA, however, originate from target nuclides with I_0/σ_0 ratio of 10 or more. Epithermal activation has, therefore, been found useful in large number of cases.

Brune and Jirlow [3] showed that the relative activity enhancement by epithermal activation of a desired radionuclide (d) over an interfering radionuclide (D) may be expressed in terms of the cadmium ratio R of the two target nuclides concerned, as follows:

$$F_a = \frac{R_d}{R_D}$$

where, F_a is termed 'advantage' factor.

It appears that the practical improvement of detection limits is often considerably less that what is indicated by the F_a value, which does not take into account the fact that following ENAA, the activity of the desired radionuclide is also reduced by a factor R_D, meaning that statistical counting errors may increase [4,5]. Parry [4] defined an "improvement" factor (F_i) taking this into account:

$$F_i = \frac{F_a}{\sqrt{R_d}}$$

and concluded on that basis that nuclides with F_a of 5.5 or less would not show any improvement in sensitivity relative to ^{46}Sc.

Tian and Ehmann [6], however, realised that the F_i factor assumes counting of activated samples with or without Cd shielding, in the same geometry. In practise, after epithermal activation, the gross activity of the sample is dramatically reduced and the irradiated sample may be counted much closer to the detector without problems associated with high dead time. Tian and Ehmann [6] therefore, defined a new generalised advantage factor:

$$F = \sqrt{G} \cdot \frac{\sqrt{R_d}}{R_D}$$

where G is the increase in counting efficiency obtained by moving to a closer position. If samples are counted in the same position, then G = 1 and F = F_i. However, if the counting efficiency for ENAA can be increased such that the total sample counting rate is equal to that of the sample irradiated with the whole reactor spectrum, then G = R_d (assuming that most of the activity is from D) and F = F_a.

In ENAA long lived nuclides ($t_{1/2} > 15$ h) are produced for elements like Ga, As, Se, Br, Rb, Sr, Zr, Mo, Ag, Cd, Sn, Sb, Cs, Ba, Sm, Eu, Gd, Tb, Ho, Tm, Ta, W, Re, Au, Th and U [7] and elements like F, Br, Rh, In, Sn, I, Lu, Th and U from short-lived nuclides [7]. Relative nuclear data are given in ref. 7.

Reduction of High Matrix Activity

The practical limit of detection in NAA is sometimes limited by the total amount of activity that can be handled safely rather than by the activity produced of the radionuclide of interest. In geological samples, for example, ^{56}Mn and ^{24}Na most often represent problems of this kind. As both these nuclides have low resonance activation rates, however, the high-activity problem can be considerably reduced by epithermal activation, provided that the elements to be determined have isotopes with high F_a values. Epithermal activation may be advantageous even in cases where the concentration of an element to be determined is below the detection limit of purely instrumental ENAA and therefore, requires radiochemical separation, such as in the case of Cd in rocks.

Reduction of Fission Interference

Fission product interference, in most cases from thermal neutron fission of ^{235}U, is a well known source of error in neutron activation analysis, causing serious problems in the case of elements

such as Zr, Mo, Ru, La and Ce. The determination of molybdenum in rocks, for example, is subject to large interference from uranium. While the fission cross-section of ^{235}U follows the 1/v law closely, however, the I_0/σ_0 of ^{98}Mo is about 50. Thus epithermal activation was found to reduce the interference of ^{235}U fission [8] by a factor of 30. Still, however, a correction was necessary.

It should be noted that the possible interference of fission products from fast-neutron induced fission of ^{232}Th becomes more significant in ENAA, and therefore needs to be considered.

Choice of Filter Material

Although a few other elements are theoretically possible as thermal neutron filters in ENAA, cadmium and boron have been used almost exclusively. The effective cut-off energy using different filters was discussed by Parry [9]. For Cd, in which case the thermal neutron absorption is strongly affected by the huge 0.178 eV resonance, the cut-off is at 0.55 eV for 1 mm thickness, with little increase in energy beyond this. For B, which is a 1/v absorber, the effective cut-off depends on the boron thickness, and may be extended into the resonance region. A combination of Cd + B will raise the cut-off value compared to an equivalent thickness of B atoms, but at cut-off energies above 10 eV there is no advantage in using the additional Cd.

The feasibility of B-based filters in ENAA has been discussed by several authors [9-12]. Generally speaking B provides higher F_a values than Cd for nuclides with high-energy resonances, and is also advantageous if fast-neutron induced reaction products are to be measured, whereas Cd is preferable for nuclides for which the epithermal activation depends mainly on low-energy resonances (<10eV).

Boron-based containers for ENAA are in most cases made from B_4C or BN. These materials are more difficult to deal with in the production process than metallic Cd, which is easily formed into the desired shape. Another problem associated with B is the heating associated with the $^{10}B(n,\alpha)^7Li$ reaction [12]. On the other hand boron does not become radioactive, while neutron activation of Cd gives rise to several radioactive isotopes which altogether may represent a radiation exposure problem. Moreover Cd is a very toxic material. Some of these problems are solved if a permanent epithermal activation facility can be installed in the reactor [11].

Fast-Neutron Induced Reaction in ENAA

Nuclear reactions induced by fast neutrons is of significance in ENAA and has been discussed in detail by Gladney and Perrin [13] and Tian and Ehmann [6]. The most important aspect is the interference caused by (n,p) and (n,α) reactions producing radionuclides that are at the same time products of (n,γ) reactions used in the analysis. On the other hand there are a few reactions that offer possibilities for determination of elements otherwise difficult to deal with by NAA, such as F, Ti, Si [11] and Ni [14]. Alfassi and Lavi [15] indicated that (n,n') reactions may also be used in ENAA in a few specific cases.

Application of ENAA

Although the first application of epithermal activation, dealing with the determination of Mn in blood plasma, occurred as early as 1961 [16], no great interest was evident from the literature before the early 1970's, after the feasibility of ENAA had been demonstrated for trace elements in geological material [3,17,18]. Since then a steady stream of papers has been published. A comprehensive literature survey is beyond the purpose of this paper. However, some trends apparent in three of the most important areas of application, i.e. geological, biological and environmental, will be discussed in the following.

Analysis of Geological Material

INAA has been used extensively for the last 30 years for the determination of trace elements in silicate rocks and similar geological materials, in most cases using medium- and long-lived nuclides. It appeared that ENAA offered considerable improvement in the determination of some of these elements, in particular As, Rb, Sr, Sb, Cs, Ba, Sm, Tb, Ta, W, Th and U [17,18], the main reason being that the major interfering nuclides ^{24}Na, ^{140}La, ^{46}Sc and ^{59}Fe are all produced from nuclides with low I_0/σ_0 values, By introduction of low-energy photon

detectors [19] for the measurement of X-rays and γ-rays below 150 keV, additional elements (Se, Mo, Nd, Gd, Tm, Yb, Hf) were favourably determined. Parry [20] extended the systematic study of geological material to short-lived nuclides, and reported improved detection limits in the case of 26 elements. The most obvious improvement in the use of silicate rocks was demonstrated in the case of Hf. The main advantage of ENAA in the case of short-lived activities in geological material is the strong reduction of ^{28}Al, and partly ^{56}Mn.

Analysis of Biological Material

In the case of biological material, the following problems are often faced.

(i) Many elements with favourable epithermal activation properties are present at extremely low levels in biological tissue.

(ii) One of the major interfering nuclides in INAA of biological material, ^{82}Br, is produced from a nuclide with a high I_0/σ_0 ratio.

(iii) Biological samples generally require more space during irradiation, and are more sensitive to high temperature.

The interference of ^{38}Cl, ^{24}Na, ^{42}K (plant material) and ^{32}P will be strongly reduced by introducing ENAA. Elements suitable for determination by ENAA may vary somewhat among different kinds of biological tissue. In general the improvement to conventional INAA seems to be greatest for elements such as Ni, As, Se, Sr, Mo, Ag (21) and I.

Analysis of Environmental Samples

INAA has been extensively used in air pollution studies related to trace elements. One early application of ENAA was the analysis of coal and fly ash [22,23] using short and long irradiations. Following a short irradiation, ENAA was preferable to thermal NAA for twelve elements (Ga, As, Br, Sr, In, Cs, Ba, La, Sm, Ho, W, U) whereas eighteen elements (Ni, Zn, As, Se, Br, Rb, Sr, Mo, Sb, Cs, Ba, Sm, Tb, Hf, Ta, Th, U) were determined favourably by ENAA following a long irradiation. A recent application reported from the environmental field is the multi-element analysis of mosses used as monitors of atmospheric deposition [24].

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Chemical Separation in Neutron Activation Analysis

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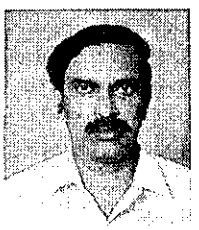

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Introduction

Chemical separations play an important role in Neutron Activation Analysis. The first radiochemical separation of an activation product was carried out by Curie and Joliot. They separated the activation product ^{30}P as PH_3 from the nuclear reaction of alpha particles on aluminium target [1]. A large number of separation methods were developed in NAA in order to achieve the required selectivity and sensitivity for trace element assay. Neutron Activation Analysis technique can be divided into three categories: (1) Instrumental Neutron Activation Analysis (INAA), (2) Radiochemical Neutron Activation Analysis (RNAA) and (3) Chemical Neutron Activation Analysis (CNAA) [2,3]. If the sample is irradiated and its activity is directly measured without any chemical separation step, it is called Instrumental Neutron Activation Analysis (INAA). If separation is done after irradiation to remove interference or to concentrate the radionuclide of interest, the technique is called Radiochemical Neutron Activation Analysis (RNAA). Pre-irradiation chemical separation (serves as pre-concentration) when employed is termed as Chemical Neutron Activation Analysis (CNAA). This can in some cases separate the molecular species involved according to their chemical state. The procedure is then called Molecular Activation. Invariably the basic purpose of these methods is to achieve maximum sensitivity and selectivity. The importance of radiochemical separations in RNAA and CNAA are discussed in brief.

Sample Preparation

In the case of RNAA the sample size is in the range of a few milligrams to grams. In the case of CNAA, the element to be analysed is preconcentrated by chemical separation thus allowing larger sample size and thus increasing the sensitivity.

Sample Mineralization

Sample dissolution in appropriate solvent mostly acids or combination of acids is very well known. Organic samples of biological origin are dissolved in nitric acid, perchloric acid mixtures. They can be also fused with $NaOH+NaNO_3$ for dissolution. Most of the geological samples are dissolved in HNO_3+HF mixture or fused with fusion mixture. Different schemes can be worked out for mineralization including the microwave digestion technique, which is now frequently used.

Carrier Addition

The actual amount of radioactive material produced after activation (in RNAA) being extremely small, a chemical carrier is required to be added to the dissolved solution. Care must be taken that the carrier equilibrates with the chemical species of the analyte present in the sample. Since the carrier added is chemically identical to the analyte, it provides a manageable amount of the sample for analytical separation and as well serves the purpose of determining the efficiency of separation process. The efficiency of separation can also be estimated by the use of appropriate radioactive tracers.

Chemical Separation

RNAA or CNAA are most often applied on samples that have complex matrices producing radionuclides from many elements. Geological and biological samples fit into this category. Rare earth elements, noble metals and uranium are frequent targets in geological samples, whereas, As, Cl, Cu, Hg, Se, Zn are of interest in biological samples. A brief review of some of the procedures reported and as well developed in our laboratory especially with reference to the analysis of rare-earths, noble metals, uranium and chemical separation schemes as applicable for Derivative Neutron Activation Analysis are discussed in this article.

CNAA has obviously more sensitivity, since one can start with a large amount of sample for chemical processing as compared to RNAA, where there is a limitation on the total amount that can be irradiated. In the former case, the total activity being less (activity due the element of interest only), one can afford to count the sample in a close geometry and obtain higher count rate. Since the major matrix elements are removed in the pre-concentration step we achieve higher signal to noise ratio. Some of the main advantages of CNAA are: (1) Higher sensitivity, improved detection limit of several folds are attainable. (2) Minimum radiation exposure as chemical separation is done before irradiation. (3) Gamma spectrum becomes simpler because matrix elements are removed before irradiation. However, in chemical processing, reagents, which are used, can add impurities. Advantages of RNAA are: (1) Gamma spectrum becomes simpler, (2) Blank correction for reagents is not needed as chemical procedures are applied only after irradiation, (3) During chemical process, carriers can be used without blank correction which improve the separation and minimize the loss of elements of interests. The disadvantages of this method are: (1) Samples are more radioactive at the beginning and reduces to very low level only after separation. This limits the amount of the sample to be handled. (2) During separation procedure short-lived nuclides may decay and their detection is not possible. This demands use of fast and simple radiochemical separation methods.

Separation Schemes Commonly Applied

Separation of Rare-earth Elements

Analysis of Rare Earth's Elements (REE) is important in many geological samples. REEs have been frequently analysed by Neutron Activation Analysis (NAA) and is considered to provide the most accurate results among the other analytical methods. The REE concentration in many geological samples are at μg/g (ppm) or below and their determination by NAA is difficult because of the high Compton background and other spectral interferences produced by the activation of other major elements. Apart from this, the presence of uranium causes interference at ^{140}La, $^{141,143}Ce$ and ^{147}Nd activities due to nuclear fission of uranium,

and at ^{153}Sm due to the gamma-ray spectral interference from ^{239}Np formed as an activation product of ^{238}U. The correction becomes significant if the REE concentration is low. For 1 ppm of U these correction factors are of the order of 0.3 ppm in the case of Ce and 0.018 ppm in the case of La. To overcome these difficulties CNAA is used. The difference in chemical properties of U/Th is used to achieve complete separation of REEs from U/Th. A typical procedure developed for the determination of REEs in high purity ThO_2 makes use of retention of REEs on a Chelex-100 resin to preconcentrate and thereby remove the Th [4]. Later the REEs were eluted with dil. HNO_3 acid to be followed by irradiation and assayed by gamma-ray spectrometry. This method also obviates the need for any correction from REEs produced by fission. Detection limits of the order of a few ppb could be achieved. We have recently developed a procedure to separate REEs from quartzite ores, which was suspected to contain traces of uranium [5]. Samples were dissolved in $HF/HClO_4$. The solution was taken in 9 M HCl. The REEs were co-precipitated with Ca^{++} as oxalate at pH 2 in presence of boric acid. The precipitate was centrifuged and dissolved in conc. HNO_3. The solution in 9 M HCl was loaded on an anion exchange (Dowex-1x8,100-200 mesh) resin column which effectively adsorbed all the uranium. The effluent containing REE was made up and known aliquot was irradiated in Apsara reactor and REEs estimated by gamma-ray spectrometry.

Uranium Determination

Uranium can be determined by assay of the immediate activation product ^{239}U, or its beta decay product ^{239}Np, or by any of the fission products formed (from ^{235}U) and by delayed neutron counting [6]. Uranium and Th are determined simultaneously using an ion exchange separation on Dowex-1 from nitrate medium, which allows separation of the activation products, ^{239}Np and ^{233}Pa, and thus improving detection limits. Uranium has been determined in high purity Al used in electronic component with detection limit of 0.05 ppb following a radiochemical neutron activation method. There is a 10-fold improvement in detection limit by adopting the RNAA procedure.

Platinum Group Elements and Gold

Separation and measurement of platinum group elements (PGEs) and gold have attracted much attention in view of their economic interest [7]. Since they occur in trace levels, various analytical methods based on solvent extraction, ion exchange, precipitation procedures and the classical fire assay technique have been applied to preconcentrate these elements. They are later analysed by spectroscopic or nuclear techniques to arrive at the concentration values. Occurrence of PGEs and gold have been noticed along with uranium bearing minerals, especially in the south west of Nogu valley in Himachal Pradesh, India and also in some of the sulphide rich flotation products of uranium mining. Estimation of Pd and Au in the presence of large amounts of U, Fe and Cu becomes complicated both by spectroscopic and nuclear techniques due to their interference.

The PGEs in general and Au in particular form very strong anionic complexes with moderate molarity of HCl. The method is based on selective separation and preconcentration by adsorbing Au and Pd on an anion exchange resin. The distribution co-efficient values range between 100 and 10000 in 1-4 M HCl solution. Gram amount of sample is dissolved in aqua regia or any such proper acids. Known aliquot of the sample in 1M HCl is passed through 100-200 mg of Dowex-1x8 resin taken in a polypropylene tube. The resin in which Pd and Au are adsorbed is irradiated with neutrons and the activation product ^{109}Pd is assayed through its daughter product ^{109m}Ag, which is in secular equilibrium, and Au assayed through its activation product ^{198}Au. We have used a Si (Li) detector and a thin window HPGe detector to assay the low energy photons of ^{109m}Ag (22.1 keV) and 88 keV and 412 keV of ^{198}Au. A typical spectrum of a neutron activated Pd separated from an ore sample containing major amount of uranium, copper and iron is given along with a standard Pd activated with neutrons (Fig.1). Under an ideal interference free condition we deduced a detection limit of 0.12 ng for Pd and 0.05ng for Au [8].

Separation of Sodium

Many naturally occurring samples, including most of the biological, mineral, sea-water and glassy

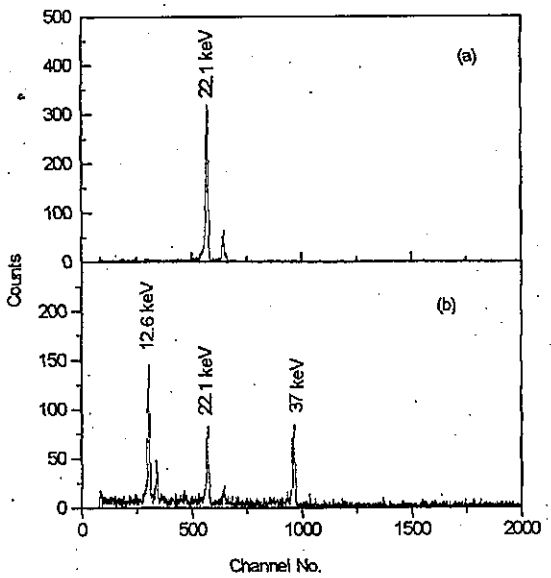

Fig. 1 Low energy photon spectrum of (a) neutron activated Palladium standard and (b) separated Palladium

types, contain a large quantity of Na and Br as compared with those of other elements. However, the detection and determination of trace elements are often made difficult or impossible by the presence of radio-sodium background. The elimination of radio-sodium (^{24}Na) without affecting the concentration of other cations would in many cases permit the determination of trace elements. Hydrated Antimony Pentoxide (HAP) has been frequently used due to its selectivity for removal of sodium. The exchange behaviour of HAP varies with its preparation and the selectivity depends on the surface structure, loading of the exchanging cations, co-ions present, and temperature and on the packing of HAP in the column. The selectivity of retention of cations on the amorphous HAP increases in the order, Li < Na < K < Rb < Cs. On the crystalline exchanger in nitric acid medium the selectivity order is Li < K < Cs < Rb < Na. Exchange of cation also depends on the strength of acid. Known amount of irradiated sample is dissolved in conc. HNO_3 and con. $HClO_4$ in the presence of hold back carriers like Zn, Fe, Sr, Mo, Ca, Mn and Mg. A few drops of Ce^{4+} are added to oxidize the bromide. The sample solution is prepared in 8M HNO_3 and is passed through a HAP column conditioned with 8M HNO_3. Sodium is quantitatively removed from the sample using 8M HNO_3. The estimation of ^{64}Cu is difficult or erroneous, as it is determined through the 511 keV annihilation radiation. This radiation is non-specific as this can theoretically arise from any gamma ray of energy higher than 1.02 MeV. In a typical case when ^{64}Cu is to be estimated, the contribution from higher energy gamma rays from ^{24}Na (2754 keV and 1369 keV) is considerable. After removing Na, Cu could be determined with an improved accuracy [9].

Sequential separation followed by substoichiometric activation analysis is frequently used in biomedical research for elemental analysis. Elaborate chemical procedures based on solvent extraction, precipitation etc. have been used, designed and successfully worked out to separate more than 18 elements in biological samples. Similar separation schemes have also been applied in nutritional studies to separate and estimate major, minor and trace elements of interest.

Derivative Neutron Activation Analysis (DAA)

Derivative Neutron Activation Analysis is a pre-irradiation chemical process applied to enhance the sensitivity of nuclear activation analysis for the more elusive elements that are not easily amenable to INAA because of the one or more of the following reasons: (1) low activation cross-section or isotopic abundance, (2) the radioactive nuclide produced is of too short half life or (3) the radioisotopes produced do not have good gamma-ray emission [10]. Elements like Li, Be, Ni, B, P, Nb, Rh, Si, Sn, Tl, Pb and Bi come under these categories. One of the added advantages of DAA is that it allows separating the elements according to their chemical states (speciation) by adopting suitable chemical procedures, which is species specific. The principle of the method is to allow the element of interest, X to exchange or react with a surrogate element M and estimation of X is carried out through the activity of the surrogate element M. The surrogate element has superior nuclear properties with respect to neutron activation. The main advantage in this case is the absence of correction due to interference reaction. The compound formed should have known stoichiometry, the ratio of M: X should be preferably being 1 or greater. The final chemical compound

should be stable and easily separable quantitatively or with reproducible chemical yield.

DAA finds very innovative and versatile applications. Both solvent extraction and paper chromatography techniques can be applied to separate the compound of interest from excess reagent. In our laboratory we have developed a very sensitive method to determine phosphorous by this technique making use of one of the heteropoly acids of phosphorus, namely Molybdo Vanado Phosphoric Acid (MVPA). In this method the sample solution is allowed to complex with excess amount of Mo and V at about pH ≤ 1 and the yellow complex formed is extracted into known volume of methyl isobutyl ketone (MIBK). Known aliquot of the organic phase is irradiated. The 1434 keV gamma line of ^{52} V is correlated with the amount of P with a correlation coefficient of 0.995. A typical gamma-ray spectrum of the MVPA complex separated and irradiated is shown in Fig.2. The stoichiometry and quantitative extraction by MIBK is established for this compound. The stoichiometry is derived as 1:8:2 among the elements of P, M, and V respectively. The method is found suitable for P determination in water and biological samples. A detection limit of 0.07 ng is derived in the present case. DAA finds lot other applications not only in purely elemental concentration determinations, but also in several functional group determinations, which include the carboxylic acid, amino acids, keto acid etc. This chemical derivative technique explained is relatively unexplored and offers opportunity for innovative radiochemists when there is an increasing trend to adopt more and more instrumental methods.

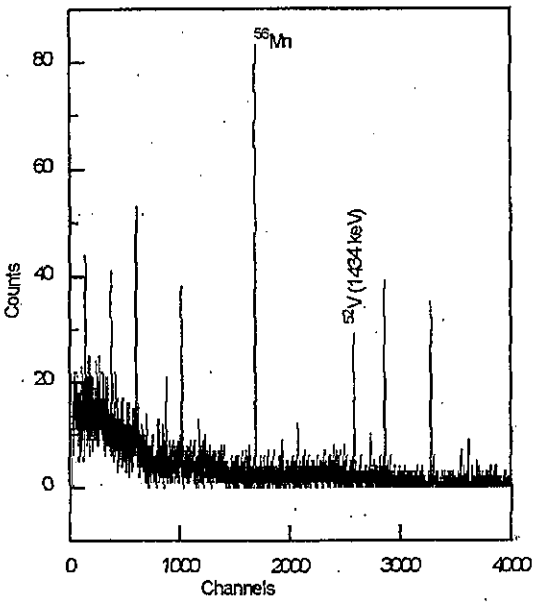

Fig. 2 Gamma-ray spectrum of neutron irradiated MMPA complex separated from 100 mL water sample.

Conclusion

Radiochemical Neutron Activation Analysis (RNAA) and Chemical Neutron Activation Analysis (CNAA) can be applied to improve the sensitivity and selectivity as compared to Instrumental Neutron Activation Analysis (INAA). Though the absence of blank correction due to the reagents is an obvious advantage in the case of RNAA, minimal handling of radioactivity coupled with higher sensitivity are added advantages in the case of CNAA provided the extraneous reagent contamination is taken care of. Conventional chemical separation techniques are considered to be the backbone of any analysis. The tedious nature involved in any radiochemical separation is a discouraging factor for many a new entrants in this field. But the higher sensitivity attainable is of paramount importance.

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Charged Particle Activation Analysis

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Introduction

Charged particle activation analysis (CPAA) is one of the most sensitive analytical techniques for the determination of low Z elements, e.g., Li, Be, B, C, N, O, at ppm to sub ppb levels. In addition to these light elements, CPAA can be applied to other elements such as S, P, Cl, transition metal elements, rare earth elements and heavy metals such as Pb, Bi and Tl, for their determination at trace and ultra trace levels. Although neutron activation analysis (NAA) has been exhaustively studied for the last 50 years, CPAA has become important in the last two decades. In fact, CPAA supplements NAA in order to make activation analysis a versatile analytical technique enabling the determination of almost all the elements in the periodic table. The developments in CPAA have been reviewed in specialised articles [1,2] and reviews [3,4] in scientific and technical monographs. The international conferences [5] on modern trends in activation analysis held every four years since 1968 bring out the latest works in the various aspects of CPAA. The applied works using CPAA are introduced as a topic nowadays in the international conferences of accelerators and their applications.

Basic Formalism of CPAA

The activity, D, of a suitable isotope produced from the analyte element in CPAA in a thick target is given by,

$$D\ (dps) = In \int \sigma_x\, dx \qquad (1)$$

where, I = intensity of the charged particles per sec, n = no. of target atoms per g, σ_x (cm^2) = the cross section at depth, x (g/cm^2). The integral in the above eqn. (1) represents the total cross section over the range (R_E) of the charged particles. The value of integral cross section (ICS) depends upon the nuclear reaction and the target matrix. When the excitation function is known, the numerical integration can be applied to determine ICS. Since it is not possible to know the excitation function of a particular reaction in different type of matrices, several methods [3] of approximation have been proposed to obtain the value of ICS, namely (1) Average cross section method, (2) Equivalent thickness method and (3) Average stopping power method. The average cross section method [6], proposed by Ricci and Hahn in 1965, is most commonly used. In this method, the average cross section, $\%_{av}$, is defined as follows,

$$\sigma_{av} = \frac{\int \sigma_x\, dx}{\int dx} \qquad (2)$$

It has been shown that σ_{av} does not vary much with the nature of target matrix for a particular nuclear reaction. Thus,

$$D = In\ \sigma_{av} \int dx = In\ \sigma_{av}\, R_E \qquad \text{---------- (3)}$$

Since σ_{av} is approximately independent of the target material, comparator technique can be applied to determine the concentration of the analyte element. The range of the charged particles, R_E, which gives the penetration depth in the sample, in different materials are available in published literatures [7]. The product isotope will not be produced beyond the threshold energy of the reaction of interest and hence an effective range, R_{eff}, is defined by,

$$R_{eff} = R_E - R_{th} \qquad (4)$$

where, R_{th} = Range corresponding to threshold energy, for computational purpose (Eqn.3). Ranges of the α-particles, R_E, R_{th}, R_{eff}, in some matrices are shown in Table 1.

Table 1. Range of α-particles in different matrices. Reaction : $^{16}O(\alpha,d)^{18}F$, Threshold energy = ~20 MeV

Matrix	Range of 40 MeV α-particles (μm) R_E	Range of 20 MeV α-particles (μm) R_{th}	Effective range (μm) R_{eff}
Silicon	718	231	487
Copper	198	84	114
Iron	267	92	175
Quartz	590	188	402
GaSb	404	132	272

Characteristics of CPAA

The most commonly used charged particles and its energies are (1) triton (4 MeV), (2) proton, deuteron and ^{3}He (5 to 20 MeV) and α-particles (20 - 45 MeV). Charged particles can undergo numerous nuclear reactions from a target atom and the reaction leading to a product, with high yield, reasonable half life and convenient γ-ray, is the most suitable one. The analytical possibility of getting a suitable nuclide is more in CPAA, compared to NAA, for the determination of an element. The choice of the charged particles in CPAA is based on (1) bombarding energy, (2) cross section of the reaction, (3) production of suitable isotopes free from interferences, (4) availability of the charged particles with the required energy from the accelerator.

^{3}He is the most suitable one due to its low binding energy which enables bombardment well below the coulomb barrier of major component elements. Triton activation is best suited from the consideration of sensitivity with minimum interferences due to its low bombarding energy (4 MeV). However, this low bombarding energy poses a problem in determining the bulk concentration. Both ^{3}He and triton are not so readily available in the accelerator centres. The sensitivity of the determination with proton, deuteron and α-particles are also very good and at the same time these charged particles are easily accessible in most of the accelerator centres.

The detection limits have been reported [1] for almost all the elements in the periodic table corresponding to the best reaction on each element under the irradiation conditions feasible in practice. The nuclear interferences in CPAA, compared to NAA, are likely to be more probable because of possibility of more number of reaction channels mostly from the neighbouring elements (within ±2) of the element of interest. A proper selection of the charged particles and its energy can reduce the order of interferences. The studies of excitation functions and activation curves [8] for a radioactive product from the analyte element are a prerequisite for the selection of the nuclear reaction in CPAA. The excitation functions and the yield curves already studied [9,10] for the transition elements, e.g., Fe, Ni, Cr, V, Zr, may be consulted for the selection of the nuclear reactions for the detemination of these elements.

Analytical Determination by CPAA

CPAA can have both instrumental and radiochemical approaches depending on (1) nature of impurity and matrix and (2) level of impurity. CPAA can be either single element or multi element determination depending on the analytical problem. All the classical chemical separation techniques, such as ion exchange chromatography, solvent extraction, distillation, precipitation, etc. are used in the radiochemical approach.

Single Element Determination

The light elements, O, C, N, B, can be determined by both instrumental and radiochemical approaches in CPAA. ^{18}F (110 min) is a suitable nuclide for the determination of oxygen whereas ^{11}C (20 min) and ^{13}N (10 min) nuclides are suitable for the determination of C, N and B depending on the nature of projectiles. We have reported the determination of oxygen in Si, Cu, Fe samples using 40 MeV α-particles [11]. Si samples, produced from rice husk for solar energy programme in IIT,

Table 2. Determination of oxygen in different samples by CPAA using 40 MeV α-particles, Radiochemical approach

Sample	Beam current (μamp)	Time of irradiation (h)	Oxygen content (ppm)
Silicon A	0.8	2.0	16.7 ± 2.8
Silicon B	0.8	1.9	13.1 ± 2.7
Silicon C	0.9	2.0	22.6 ± 1.9
Silicon (p-type)	1.2	2.5	2.3 ± 0.3
	1.1	2.5	2.5 ± 0.4
Silicon (n-type)	1.1	2.5	3.1 ± 0.4
	1.1	2.5	2.8 ± 0.3
Copper (OFHC)	1.0	2.0	2.3 ± 0.3
	1.0	2.0	2.6 ± 0.3
Copper (Magnet)	0.5	0.3	380 ± 12
	0.5	0.3	370 ± 15
Stainless Steel	1.0	1.5	20.8 ± 2.8
	1.1	1.5	23.4 ± 2.6
Stainless Steel	0.5	0.5	151 ± 15
	0.5	0.5	162 ± 12

Kharagpur, West Bengal, with oxygen content ~100 ppm was suitable for instrumental determination. ^{18}F was separated by (1) distillation of H_2SiF_6 followed by precipitation of PbClF and (2) precipitation of KBF_4 followed by solvent extraction. Both the methods are quite fast with chemical yield >90%. Oxygen determined in various samples using radiochemical approaches are shown in Table 2. Carbon was determined [12] in Si, Cu, Fe samples at ppm levels using $^{12}C(\alpha,\alpha n)^{11}C$ by 40 MeV α-particles. The isotope ^{11}C was separated by oxidative fusion of the sample in the stream of oxygen gas followed by fixing of CO_2 as Li_2CO_3.

Several studies are already reported [5,13] particularly in the last two decades for the determination of the light elements by CPAA in ppm to sub ppb levels in high purity semiconductor materials and metals of technological interest. The unique features of freedom from blank and the post irradiation surface etching in CPAA make it possible for the accurate determination of O, C, N, at sub ppb levels with minimum systematic error. CPAA is routinely used [14] nowadays to determine these elements in different laboratories. In addition to this, CPAA is highly useful for the determination of other elements. Sulphur [15] can be determined in a variety of organic and inorganic matrices at trace levels. Constantinescu et.al. [16] reported the determination of P and Cl using proton and α-particles. Heavy metals, like Pt, Pb, Bi, Tl, can be determined [17,18] at trace and ultra trace levels by CPAA.

Multi Element Determination

The multi element determination by CPAA are so far reported based on instrumental approach. Proton has the inherent potential for matching the requirements of multi element analysis, like coverage of large number of elements, sensitivity and selectivity. Moreover, for instrumental analysis, discrimination of impurity against matrix activation is possible based on the differences in the threshold energies for proton induced reactions. Proton, 10 - 15 MeV, is most advantageous yielding high specific activities for (p,n) reactions. The other reaction

channels, like (p,2n), (p,pn), (p,α) etc. may be energetically possible but with low cross sections and do not yield high specific activities. Several works have been published on proton activation [19-22] for the instrumental determination of trace impurities in high purity technologically important metals, like silicon, aluminium, gold, cobalt, silver, irridium, niobium, rhodium and tantalum. Deuteron [23] and α-particles can also be used for the determination of trace elements instrumentally in CPAA. We have reported [24] the instrumental determination of transition elements, like V, Cr, Mn, Fe, Ni, Zn, Cu, Ga in crude petroleum oils using 20 - 40 MeV α-particles.

Multi element determination by radiochemical approach [25] by CPAA are not reported much till date. We have reported [26] the determination of rare earth elements (REE) in geological samples by CPAA. NAA is widely used for the determination of REE in geological samples but is suitable only for the determination of La, Ce, Nd, Sm, Eu, Tb, Yb And Lu. However, it is preferable to know the concentration of as many REE as possible for a complete picture of the mineral melt system in the petrogenic study. CPAA can be applied to determine the other elements and thus CPAA supplements NAA in providing the full knowledge of REE. We have developed and standardised a radiochemical separation of the REE as a group from the matrix with international geological standards like SY2 and SY3. The determination of REE elements such as Eu, Pr, Ho, Sm, Tm, Er at ppm levels were reported. The total time taken for the chemical separation was 10 hrs and the chemical yield was obtained 60-70% using ^{152}Eu tracer.

Conclusion

CPAA is one of the best sensitive analytical technique for the determination of the low Z elements at ppm to sub ppb levels in high purity metals and semiconductor materials. In addition, it has been shown that CPAA can be applied for the determination of the other elements at trace and ultra trace levels. Although, the sensitivity is quite high for the determination of the trace impurities, not much voluminous work has yet reported. In fact, the accelerator became available for the analytical works from late sixties and even after that availability of the accelerators with required projectiles and its energies are also very limited. Therefore a wide scope still remains for the application of CPAA in different analytical problems.

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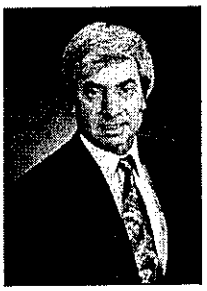
Preconcentration Neutron Activation Analysis for Simultaneous Multielement Determination in Water Samples



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Neutron activation analysis (NAA) can be performed in a variety of ways depending on the element and its levels to be measured as well as on the nature and the extent of interference from other elements present in the sample. The NAA techniques can be broadly classified under two categories based on whether any chemical separations are employed in the analytical procedure. Under favourable conditions, the experimental parameters such as irradiation, decay and counting times can be simply optimized so that the elements of interest can be determined without the need for physical destruction of the sample by chemical treatments, the process is called non-destructive NAA which is more commonly known as instrumental NAA (INAA). It is the most widely used form of NAA. On the other hand, interferences from the sample matrix and/or from the other elements present in the sample can be so severe that the element of interest cannot be reliably determined by INAA. Furthermore, if the concentration of the element of interest is lower than the detection limit of the non-destructive technique, then also INAA cannot be used. Under such circumstances, chemical separations are often employed in conjunction with NAA; the process is then referred to as destructive NAA. This type of NAA can be further classified into two categories. If the irradiation is followed by a chemical separation then the technique is called radiochemical NAA (RNAA). In an opposite situation, the element can be chemically separated prior to irradiation; this technique can be further sub-classified to preconcentration NAA (PNAA) and derivative NAA (DNAA). In DNAA, the element of interest that has a poor sensitivity for NAA is either replaced or complexed with another element which can be determined by NAA with higher sensitivity. All other pre-irradiation chemical separations are included in PNAA.

During the early stages of development, the NAA technique was mainly used in conjunction with radiochemical separations. Jervis [1,2] has recently reviewed the development of radiochemistry over the last 50 years or so. The advantages of RNAA over other analytical techniques include freedom from

reagent blanks, improvement of detection limits, precision and accuracy, and non-requirement of a clean room. In some cases, the number of elements determined can be considerably extended using RNAA, as well as the recovery of each element can be calculated and corrected for at the end of the measurement. In RNAA, however, competing nuclear reactions cannot be eliminated, large volumes of sample cannot be easily irradiated in most reactor facilities, and short-lived nuclides cannot be conveniently used. The RNAA methods are generally time-consuming and there exists a potential for radiation hazards. Alternatively, PNAA can be employed. In fact, PNAA is being increasingly applied for the determination of single as well as groups of elements in a variety of complex sample matrices where neither INAA nor RNAA can be conveniently used. Various advantages of PNAA have been described by Minczewski *et al.* [3] and Chatt [4,5].

An ideal preconcentration method should be a simple procedure, involve a few steps, use small amounts of a few reagents which are available in high purity, give no or minimum contamination from handling and reagents, allow simultaneous isolation of several metals, employ media which must not become too active and interfering, generate a low background noise, and give low detection limits. The most commonly used preconcentration techniques are coprecipitation, cocrystallization, solvent extraction, ion exchange, chelating ion exchange, adsorption, various types of chromatography, distillation, sublimation, electrodeposition, and flotation.

The improvement of detection limits in PNAA can be achieved by increasing the amount of the element of interest per unit mass or volume of the sample (expressed as enrichment or concentration factor, E), by eliminating interferences caused by either sample matrix or major elements in the sample (given as separation or decontamination factor, S), and by increasing the yield of the element in the separated fraction (termed as recovery or yield factor, R). An ideal PNAA method should have very high values for all three factors, which are not always achievable in practice. A number of preconcentration methods in conjunction with NAA have been used in the past [6]. These include absolute preconcentration methods such as oven-drying (E<2, S=0, R=100% except for the volatile species, VS), evaporation (E<1,000, S=0, R=100% except for VS), lyophilization (E=10, S=0, R=100% except for VS), dry-ashing (E<2, S=0, R<100% and VS are generally lost unless trapped). The commonly used relative preconcentration methods are: liquid-liquid extraction (E=100, S>10, R>98%), distillation E<100, S=1, R>95%), sorption (E=100, S=10,000, R>95%), coprecipitation (E=100, S>10,000, R>95%), cocrystallization (E<100, S>1,000, R>95%), and ion exchange (E=100, S>1,000, R>95%). Both single and multielement concentrations have been measured using some of these techniques [7-9].

Reagent blanks must be kept to a minimum in all trace elemental analyses. This is particularly important when preconcentration methods are employed. It is necessary to select ultrapure reagents and non-contaminating apparatus as well as to maintain an ultra-clean environment for obtaining reliable results. With the increasing availability of highly pure reagents and clean rooms, preconcentration of trace elements is becoming popular among analytical chemists. When preconcentration is done using ion exchange resins, inorganic adsorbents, or activated charcoal, the elements of interest are eluted prior to their determinations by techniques such as atomic absorption, inductively coupled plasma-atomic emission, and polarography where measurements are generally carried out in sample solutions. In NAA, however, the solid exchanger or sorber can be directly irradiated for determining elemental concentrations; therefore, distinct possibilities of contamination by an eluent and incomplete as well as irreproducible elution of certain elements can be avoided.

We have developed a number of PNAA methods in our laboratory for the determination of trace elements in a variety of complex sample matrices. Due to the lack of space, it will not be possible to describe all of these methods here. In all our work, we used the Dalhousie University SLOWPOKE-2 Reactor (DUSR) and a neutron flux of either 5 or 10×10^{11} cm^{-2} s^{-1}. At the beginning we employed a simple lyophilization method for the determination of Al, As, Au, Br, Ca, Ce, Cl, Cr, Cu,

K, Mg, Mn, Na, Sb, Sm, V and Zn in atmospheric wet precipitation by INAA [10]. Then we developed a PNAA method using Chelex-100 for the measurement of low levels of Al, Au, Ba, Ca, Cd, Cr, Cu, Hg, La, Mg, Mn, Sc, Se, Sm, V and Zn in the soluble fraction of acid rain [11]. We observed that only a fraction of As and Sb were retained by this cation exchange column indicating that large fractions of these two elements were present as anionic species. This method was later extended for the speciation studies of certain elements.

One of the main advantages of PNAA can be ideally exemplified by the determination of Al in environmental (such as acid rain, estuarine and sea water) and biological materials (such as food, liver and blood). Aluminum can be rapidly determined by NAA through its 2.24-min half-life nuclide ^{28}Al. However, the same nuclide is also produced through two competing nuclear reactions: ^{31}P(n,α)^{28}Al and ^{28}Si(n,p)^{28}Al. It becomes essential, therefore, to separate P and Si from the samples prior to irradiations if reliable measurements of Al are desired. Elements such as Br, Cl, and Na also need to be separated from samples of sea and estuarine water, blood, urine, *etc.* not only for eliminating interferences but also for reducing radiation hazards. Chelex-100 ion exchange resins have been used to develop PNAA methods for the determination of low levels of Al in aqueous samples [8,9,11].

Hydrated antimony pentoxide (HAP) is well known for its usage in RNAA for the efficient removal of Na and Cl. We have attempted to use HAP to remove Na and Cl from seawater prior to NAA for trace elements. Although this method was eventually successful, Sb was observed to leach from the HAP column. Antimony had to be separated using either acid alumina oxide (AAO) or tin dioxide (TDO) exchangers before most of the trace elements in seawater can be reliably determined [12].

We developed a number of cocrystallization and coprecipitation methods for the determination of trace elements in water samples. For example, we measured the levels of Mo in sea and estuarine water with β-naphthoin oxime and NAA [13]. This method is superior to the commonly-used α-benzoin oxime method for Mo because β-naphthoin oxime, unlike α-benzoin oxime, does not concentrate U and Th along with Mo; thus no interference from fission to ^{99}Mo was evident.

We developed a PNAA method for the determination of very low levels of V in seawater [14]. In order to achieve the minimum reagent blank requirement of PNAA, we decided to advantageously use one of the major ions of seawater in a coprecipitation scheme. Magnesium(II) is the fourth most abundant ionic constituent of seawater, and it forms highly insoluble $Mg(OH)_2$ which can be precipitated from seawater by simply adding ammonia. The PNAA method thus developed involved coprecipitation of V with $Mg(OH)_2$. We carried out radioactive tracer studies to evaluate various factors that can influence the recovery of V. In the optimized procedure, we added 1 mL of carrier-free ^{48}V with known activity to 100-mL seawater, stirred for 5 min, raised pH to 10.2 with ULTREX ammonia, and shook for 1 h. We allowed the mixture to settle for 15 min prior to filtration under suction, dried the precipitate, and irradiated it in DUSR at a neutron flux of 5×10^{11} cm^{-2} s^{-1} for 3 min, counted in a high-resolution Ge(Li) detector for 10 min after a decay period of 3 min. We used the 1434.1-keV photopeak of ^{52}V (half-life = 3.76 min) for assaying the V content of seawater, and the 983.5-keV gamma-ray of ^{48}V (15.98 d) for calculating the recovery of the element which was >98% in almost all cases. No reagent blank correction was required because no V was detected in ULTREX ammonia, ultrapure water, Whatman No. 1 filter paper, polyethylene bag used for irradiation, and ^{48}V tracer. Reductions of Na and Cl concentrations by a factor of 3×10^4 made the determination of V by NAA a lot simpler. We investigated the precision of the PNAA method by analyzing 3 portions of a seawater sample collected from a depth of 50 m, and obtained a value of 1.12 ± 0.06 μg L^{-1}. The accuracy of the method was also excellent. The detection limit was 0.38 μg V L^{-1} of seawater. We applied the PNAA method to a number of surface and deep ocean water samples with concentrations between 1.10 and 1.75 μg L^{-1}. We later extended the PNAA method for V to include the determinations of 15 additional elements in seawater [15]. We also developed an independent method for the determination of V in seawater using Chitosan and again further developed it to include Co, Mn, and Zn [15].

Coprecipitation of trace elements with organic chelating agents is one of the most attractive preconcentration techniques that can be used in conjunction with NAA because of the relatively high purity of the organic reagents, their general lack of affinity for alkali and alkaline earth metal ions, and of their low induced radioactivity. We developed a method for the simultaneous preconcentration of Cd(II), Co(II), Cu(II), Hg(II), Mn(II), Th(IV), U(VI), V(IV) and Zn(II) from 0.5-1 L of water samples by coprecipitation using a combination of 1-(2-thiazolylazo)-2-naphthol (TAN), ammonium pyrrolidinedithiocarbamate (APDC) and ammonium salt of N-nitroso-phenylhydroxylamine (Cupferron) followed by NAA [16]. We studied the effects of various parameters such as pH (4-10), temperature (25, 80°C), time for coprecipitation (5-60 min), type of surfactant (lauryl sulfate, sodium dodecyl sulfate, Triton X-100), amounts of coprecipitating agents and potentially interfering ions. on the quantitative recovery of these elements. The recoveries of all elements were better than 95%; precision and accuracy of measurements were between ±10%; detection limits were in the ppb range; and enrichment factors for most of the elements were of the order of 10^4. We applied this PNAA method to several surface and seawater samples.

We developed a preconcentration method for Cd(II), Co(II), Cu(II), Mo(VI), U(VI), V(V) and Zn(II) ions from water using coprecipitation with APDC in presence of Bi^{3+} ions as carrier [17]. The method involved the addition of 10 mL of a 0.05 M acetate buffer (pH 4.0), 30 mg of Bi^{3+}, and 165 mg of APDC to 300-500 mL water. We adjusted the solution pH to 4.0, stirred for 5 min, and then allowed it to stand for 30 min at room temperature. We filtered the precipitate through 0.45 µm pore-size Gelman filters under vacuum suction. The recoveries of all elements were >95%. The precision and accuracy were between ±2 and 10%. The enrichment factors were of the order of 10^3. The detection limits were in the ppb range varying between 0.04 ng mL^{-1} for V and 5 ng mL^{-1} for Zn. We applied this PNAA method for the analysis of drinking water samples.

The use of adsorption and reversed-phase extraction chromatographic techniques for trace metal determination has increased substantially in recent years. Chelating ligands have been immobilized by either chemical bonding or adsorption on various substrates such as diatomaceous earth, silica gel, glass, alumina, cellulose, polytetrafluoroethylene (Teflon), polyurethane foam and copolymers of polystyrenedivinylbenzene, and used extensively in extraction chromatography. Functional groups such as dithiocarbamate on polyacrylamidoxime resin; thiol groups, 1-(2-pyridylazo)-2-naphthol, TBP-diethyldithiocarbamate, dithiozone, diethyldithiocarbamate and ethanedithiol on polyurethane foam; thiothenoyltrifluoroacetone on divinylbenzene beads; arsonic acid on macroporous resin; MIBK and TOPO and ferroin-type ligands on Amberlite XAD-2 resin; 8-hydroxyquinoline-5-sulfonic acid on Bio-Rad AGI-X2 and AG MP-1; 8-hydroxyquinoline on XAD-2 resin, silica gel and glass beads; and 7-dodecenyl-8-quinolinol on macroporous resins have been immobilized and tailored to specific needs.

We developed a PNAA method involving reversed-phase extraction chromatography (RPEC) on 8-hydroxyquinoline-loaded Amberlite XAD-2 resin for the simultaneous determination of selected trace elements in acid rain and natural water samples [18]. We selected Amberlite XAD-2 resin as the inert support because of its exceptional stability to chemical reagents and solvents. It readily retains a layer of organic extractant that forms the stationary phase. Unlike the inorganic supports which require a special pretreatment to render them hydrophobic, XAD-2 is strongly hydrophobic and ready for use as is. Moreover, when a final quantitation of solid samples by NAA is contemplated, the inert support should be free from halides, Na and other highly activable elements which can cause potential interferences in NAA. In this aspect, XAD-2 is more advantageous and preferred over the commonly used supports such as teflon, alumina, silica and Kieselguhr. For the preparation of ligand-impregnated chelating resins, the ligand should possess the following characteristics: it should (i) be chemically stable, (ii) be strongly adsorbed onto the substrate, (iii) have sufficiently low solubility in aqueous solution, and (iv) be capable of forming complexes with as many metals as possible at near neutral pH of most natural waters.

8-Hydroxyquinoline is one of the ligands which satisfies such conditions.

We studied in detail the various factors that can influence the preconcentration procedure [18]. We achieved quantitative retention for Co, Cu, Hg, V and Zn at pH 6.0 and for Cd at pH 7.0. We obtained an enrichment factor of 500, detection limits between 0.01 and 3 ppb, and high precision and accuracy by the direct irradiation of the resin. We found that it is more convenient to concentrate trace elements onto a solid phase if their quantitation by NAA is desired. Our method is superior to other procedures where the elements of interest are eluted from the resin for their subsequent determinations. Further, the possibility of additional reagent blanks and incomplete and/or irreproducible recoveries, commonly encountered in elution studies, are eliminated here. The bleeding of the impregnated chelating agent from the solid support is often considered a problem in RPEC; however, we observed that the loss of oxime can be kept to a negligible amount (~0.01%). Hence, the columns can be reused 10-15 times, if needed, after elution of the elements with 2 M HNO_3 and reconditioning them to the desired pH.

In another RPEC method, we used TAN impregnated on Amberlite XAD-4 resin for the extraction of Cu from aqueous samples [19]. We cleaned the XAD-4 resin by successive washings for 1 h each on a wrist action shaker with 2M HNO_3, distilled deionized water (DDW), 1M NH_3, DDW, 3M HNO_3, and finally rinsing with DDW. We washed the product with acetone and dried it at 100°C overnight, and stored. We determined the elemental impurities of the cleaned resin by NAA, and found no detectable elements of interest. We designed a column apparatus for use in this study [19]. It consisted of a Bio-Rad Econo-Column of 10 cm length; the bottom of the column was fitted with a fluoropolymer frit and the top with a Luer lock connector. We controlled the flow rate using a removable Teflon stopcock. A 100-mL Nalgene polyethylene separatory funnel served as the reservoir for feeding the aqueous solution to the column. We prepared the TAN-impregnated XAD-4 (TAN-XAD-4) resin by equilibrating 10 g of the precleaned resin with 500 mL of 0.05 M TAN solution in methanol on a wrist-action shaker for 2 h. After equilibration, we filtered the TAN-XAD-4 resin, washed with DDW, and stored under DDW. We slurry-packed the TAN-XAD-4 resin into the columns to a height of 5 cm. After each extraction, we drained the column, dried it by passage of forced air, transferred the resin beads to a polyethylene vial, and heat-sealed the vial for irradiations. We assayed the Cu levels through the 1039-keV gamma-ray of ^{66}Cu after a 10-min irradiation, 1-min decay, and a 10-min counting period.

We investigated several factors, such as flow rate, pH, column height, presence of other trace elements and interference from major elements, which can affect the uptake of Cu onto the ligand-impregnated resin. The results showed that Cu was quantitatively recovered using a column containing 300-700 mg dry coated resin at a flow rate of 0.3-5 mL min^{-1} and at a pH 4.5-8.5. We also found that 0.4M NaCl, 0.005M Ca, 0.001M Br and 0.05M Mg ions had no effect on the uptake and quantification of Cu. We determined the uptake of Cu onto the column to be 100±2% using ^{64}Cu radiotracer. We made a detailed study on reagent blanks and found that no Cu as a contaminant in detectable amounts in the blank. The reproducibility of the method was within ±6%. The accuracy of the method was also good: we obtained a value of 19±1 µg Cu L^{-1} for the NIST SRM 1643-a (Trace Elements in Water) compared to the NIST value 0f 18±2 µg L^{-1}. We have further developed this RPEC method to include the simultaneous determination of Ag, Cd, Co, Cu, Hg, Mn, Ni, U and Zn in water samples [20]. The detection limits of the method ranged between 0.014 µg for U and 7.57 µg for Ni.

It will not be possible, due to the lack of space, to describe other preconcentration methods which have been either developed or are being developed in our laboratory. A few of these studies are briefly mentioned. We developed several methods for the determination of I. The first method involved preconcentration of total I, after reduction to iodide with hydrazine sulfate, by coprecipitation with bismuth sulfide [21]. The second PNAA method [22] consisted of two stages: first quantitative extraction of iodine in toluene, reduction to iodide and back-extraction to an aqueous phase, and then coprecipitation of iodide with bismuth sulfide. One of the RNAA methods involved the coprecipitation

of iodide with bismuth sulfide. Yet another method consisted of precipitation of iodide with bismuth sulfide, irradiation, dissolution of the precipitate in acid, followed by precipitation of iodide by palladium chloride and counting [22,23]. A PNAA method for U and Th involved coprecipitation with calcium oxalate [24]. Zinc was separated by an ion-exchange and a solvent extraction method [25]. We have determined As and Sb in natural waters by coprecipitation with Se [26] and Au by coprecipitation with Te [27] followed by NAA.

We have been interested in studying the speciation of Am, Tc and Np in simulated vitrified groundwater leachates of high-level wastes under oxic and anoxic conditions using a number of techniques [28-31]. We then used PNAA methods for studying speciation of trace-element analogues of radionuclides (*e.g.* trivalent lanthanides for trivalent actinides). We developed a synergic solvent extraction method consisting of 1-nitroso-2-naphthol and trioctylphosphine oxide in chloroform to study the carbonate complexes of Eu(III) under realistic total carbonate concentrations. We have been able to identify various europium carbonate species and to calculate their formation constants [32-34]. We have used similar methods for the characterization of other lanthanide species [35,36].

We have been able to apply biochemical techniques and NAA for the separation, preconcentration and characterization of metalloprotein and protein-bound trace element species in subcellular fractions of bovine kidneys. Much of our work focused on Se along with As, Br, Cd, Cu, Mn and Zn [37-43].

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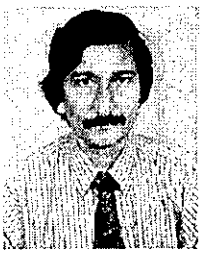
Neutron Activation Analysis for Forensic Studies - Indian Scene



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Introduction

Highly sensitive, specific and at the same time accurate Neutron Activation Analysis (NAA) technique having simultaneous multi element determination capability is a powerful analytical tool for trace element analysis of wide varieties of forensic case exhibit samples. Combination of NAA and other complementary analytical methods can help to arrive at reliable data which plays important role in crime investigation and detection. This approach is inevitable and very useful as corroborative evidence in criminal justice system, particularly in situations where conventional methods cannot yield proper solution to a particular problem. The outcome of visionary realisation of stalwarts like Dr. H.J. Bhabha, Shri B. N. Mullick and Dr. N.K. Iyenger ultimately culminated into a unique collaborative work programme between MHA and DAE; "Neutron Activation Analysis Unit of CFSL" which started more than two decades back in the Analytical Chemistry Division, BARC.

Table 1. NAA in Forensic Studies

1.	Forensic ballistics - (known group of elements)	(a)	Determination of gunshot residues (GSR) to opine whether a hole is really due to passage of a bullet.
		(b)	Firearm discharge residue detection in the hands of a suspect shooter to differentiate homicide / suicide cases and/or to identify the shooter.
		(c)	Estimation of the range of firing and to differentiate entry and exit shot hole
		(d)	Matching of bullet specimen with metal piece obtained from the scene of crime.
2.	Forensic toxicology (known specific element (s))	(a)	Analysis of biological materials to confirm toxic metals mainly As, Hg etc. in poisoning cases.
		(b)	Differentiation between slow and acute poisoning.
		(c)	Assessment of environmental pollution causing great concern in internal toxicity.
3.	Source correspondence-commonness of origin (multi element analysis may not be known before hand)	(a)	Identification of evidence materials [which might have originated from the suspect(s)] left at the scene of crime.
		(b)	Matching of specimens of different varities to connect the crime with the criminal.
4.	Customs and other related cases of white collar crime (one or two specific elements at low level)	(a)	Detection of a particular element, the presence of which can help solve the problem i.e. transfer of traces due to contact.

Reactor irradiation facilities of APSARA, CIRUS and DHRUVA are regularly utilised by the Unit for catering to the needs of different State/ Central forensic science laboratories in the country pertaining to the examination of real life crime exhibits. Apsara reactor at BARC is a versatile nuclear reactor with flexibility to handle odd size samples, ideally suited in criminalistics to help answer certain questions required by the investigating agencies. Application of NAA for forensic studies can be visualised in different disciplines. The major areas are indicated in Table1.

Ballistics

Forensic ballistics constitutes major part of work pursued in the utilisation of research reactors in India for NAA of evidence specimens. The application here itself is mainly four fold.

Analysis of Suspected Bullet Hole/Dent Samples for Evidence of Gun Shot Residues:

A forensic ballistician comes across problems in shooting incidents to ascertain whether a hole/dent has been caused due to passage of bullet or lead shot. When a bullet or shot pellets strike a target (cloth, leather or any other object) transfer of material in the form of residues is bound to happen on the targets arising from primer, core metal / jacket and propellant powder discharges. Most cartridge primers contain barium nitrate, antimony sulphide, lead styphnate and some of the older ones contain mercury fulminate. Explosion of the primer causes the bullet to be coated with the elements in the primer. Lead bullets are commonly used in the revolvers while modern bullets are provided with jacket to withstand friction in barrel of the gun. The jacket material may either be of cupronickel (Cu 80%, Ni 20%), gilding metal (Cu 90%, Zn 10%) or

mild steel clad with cupro nickel or gilding metal. Thus, as a result of firearm discharge, groups of characteristic elements in different combinations from Ba, Cu, Sb, Hg, Ni, Zn, Pb etc. could be deposited in and around the hole/dent area at trace level or lower. Determination of these elements by employing NAA can be an indicator to provide answers to different questions asked by the investigating officers forwarding the case. Most of the exhibit samples in this class pertain to wearing apparels (cloth). However, Indian synthetic/blend cloth material itself contains high antimony making this important typical element of establishing GSR not useful whenever such materials are involved. An alternate element like tin (Sn) has been established to provide this type of information in place of antimony.

Shooter Identification via NAA of Swabs to Detect Firearm Discharge Residues

Firearm Discharge Residues (FDR) detection on the hand due to back blast after firing is of great importance in criminal cases involving death by shooting. Many a times, investigators and the laboratory are asked to decide with reasonable certainties whether a suspect has fired a gun a short time prior to apprehension. In suspected suicide cases, the detection of FDR on the hands of the deceased has importance to differentiate and rule out homicide or otherwise. The positive FDR in the form of two principal elements Ba and Sb at trace level can help to answer or support homicide/suicide discrimination and hence to identify the shooter. NAA by virtue of its effectiveness for detection of these two elements simultaneously, provides to come out with definitive opinions in such cases.

Estimation of the Range of Firing and to Differentiate Entry and Exit Hole

It is sometimes important to estimate approximate range of firing and differentiate entry and exit hole in certain cases for forensic experts to preclude innocent from being accused and also to search for truth. Amounts and concentrations of a group of characteristic elements are normally expected to be higher in entry point than those at the exit point. Quantitative trace elemental data can thus help to differentiate entry and exit shot holes which have more relevance in wound ballistics. Estimation of range of firing (for shot muzzle to target distance) can also be applied in forensic ballistics to reconstruct factual circumstances in the scene of crime. NAA, because of its good degree of sensitivity, allows to derive relative ascending/descending magnitudes of GSR with respect to increase/decrease of range taking into account one or two typical elements into proper consideration.

Bullet Lead and Matching Against Metal Piece

It is often necessary in forensic investigation involving firearms to compare trace elemental composition of small pieces of lead from shot gun pellets or from bullets found at the scene of crime or its vicinity or inside the body of the victim with the lead bullets taken for the suspect weapon for the establishment of commonness of origin. Commercially available bullets are generally made from either soft lead (usually 99.8% or better) or from lead that has been hardened by adding specified quantity of antimony. In most cases, antimony alone can be used as a discrimination for classifying bullet lead. But in those cases involving overlap of antimony concentrations, data for additional element(s) is required. Various trace elements (Au, As, Bi, Cr, Fe. Mg, Si, Se, Zn etc) are reported to be present in bullet lead, but these are not detected by instrumental NAA. A radiochemical procedure has been developed here for determining some of the elements like Sb, As, Cu, Se, Cr, Zn and Ag. This increases number of identification points for better characterisation. Another radiochemical procedure has also been developed for the determination of Sn, As, Cu and Sb for bullet lead specimen which proved to be useful in solving a case referred to the Unit related to Rhinoceros killing to decide guilt or innocence in search of truth.

Trace Elements in Forensic Toxicology

From forensic point of view, the most common toxic metals are arsenic, mercury and lead. In the human organism, a number of trace elements are present because they are essential for life processes. The levels of essential elements are maintained constant in the organism. These are hardly the ones which can result in death if taken in excess. But if there is any exposure to the elements such as arsenic, mercury exceeding toxic limits for homicidal

reasons such as deliberate poisoning or accidental ingestion, then the amount of the particular element will be abnormally high. These elements also possess high sensitivity by NAA. Analysis of hair is more useful for this purpose because hair growth allows to calculate an approximate record of time by element exposure, as reflected by the blood stream. Cases of heavy metal poisoning are referred to the NAA Unit of CFSL for detection and estimation of As, Hg, Se, Sb, Pb etc. The exhibits cover both biological (hair, nail, bones, body tissues etc) and non biological e.g. ayurvedic drug samples. These are analysed by a judicious combination of INAA/RNAA for As, Hg, Se, Sb. As lead is not easily amenable to be analysed by NAA, an alternate method like AAS or DPASV technique is utilised. The combination of NAA/AAS or DPASV proved to be useful for detection and estimation of these elements even for very low concentrations. In a case, a person continuing ayurvedic medicine supposed to have Hg in it, showed symptoms of Hg poisoning. NAA of corresponding hair and nail showed considerable amount of Hg (~200 ppm).

Though there is a lack of data on Hg content with respect to Indian population, it seems to be very high. Similarly deliberately administered arsenic over a period of time enhanced the level of As (250-300 ppm) in hair and nail as observed by NAA.

Environmental Pollution

In an interesting study to assess environmental pollution, chronic case of arsenic toxicity was confirmed by analysis of a large number of hair, nail, and liver samples for arsenic. A large number of people in one part of the country who were exposed to subsoil water contaminated with arsenic, showed all clinical features of arsenic toxicity called arsenicosis. The symptoms were more or less similar to liver damage disease.

The results interestingly show fairly higher contents of arsenic (2-100 ppm) in hair and nail from only aresenicosis cases. The level in liver tissue varied from zero (below detection limit) to about 6 ppm. Analysis of arsenic by NAA, thus, confirmed arsenic toxicity as suspected by medical officers based on their clinical observations.

Table 2. Trace element patterns in the form of parameter (information) established and reported for different types of forensic exhibit samples.

Type of exhibit	Trace elements
Transmission Copper wire	Ag, Au, Sb and Se (Discriminating)
Transmission Aluminium wire	Mn, Cr, Hf, Sc and Fe (Discriminating)
Glass	Eu, Ce, Co, Fe, Th, Sb and Sc
Cannabis	Mn, Cu, K, Cl, Br, Fe, Sc, Hf and Zn
Animal Hair	Mn, Cl, Na, K, Cu, Br, Au and Zn
Ornamental Gold	Cd, Zn, Cu, As and Ag

Nuclear Evidence for Source Correspondence

Another area of application of NAA in forensic science is the possibility of trace element characterisation of specimens in an effort to establish probability of commonness of origin (COO) or Source Correspondence (SC) as they are commonly known in forensic science. Criminalists are often called upon to identify the evidence material(s) left at the scene of crime originating from suspect(s). Trace element profile is a method to establish this. Cases of pilferage or theft of electrical transmission wires or cables used for telephones are regularly referred for NAA for the purpose to arrive at trace element data to establish source correspondence between control and questioned sample. Examination based on morphological properties of the sample can at best establish similarity between the samples but no definite opinion regarding commonness of their origin can be given. Trace elements profile by NAA is very useful in the comparison of copper and aluminium wires particularly because of simultaneous multielement determination capability and non destructive approach in the analysis. Results of some of the cases involving Cu and Al wire theft cases helped to derive definitive inferences. Apart from transmission wires, other types of exhibit samples examined for SC/COO are paints, glass, cannabis, hair etc. The

Table 3. Radioisotopes in Forensic Applications

Sl. No.	Element	Isotope	Abundance %	Cross-section in barns	Radioisotope (Radionuclide)	Half-life	γ-energy in keVused for calculation
1.	Sc	^{45}Sc	100	23	^{46}Sc	84 d	889
2.	Cr	^{50}Cr	4.31	16	^{51}Cr	27.8 d	321
3.	Mn	^{55}Mn	100	13.3	^{56}Mn	2.6 d	847, 1811
4.	Fe	^{58}Fe	0.33	1.23	^{59}Fe	45 d	1099
5.	Cu	^{63}Cu	69.1	4.5	^{64}Cu	12.8 h	511
6.	Zn	^{68}Zn	18.6	0.1	^{69m}Zn	13.9 h	439
7.	Ga	^{71}Ga	39.6	5.0	^{72}Ga	14 h	630, 834
8.	As	^{75}As	100	4.3	^{76}As	26.5 h	559, 657
9.	Se	^{74}Se	0.87	30	^{75}Se	120 d	136, 264
10.	Ag	^{109}Ag	48.6	3.2	^{110}Ag	253 d	657, 763, 884, 937
11.	Sn	^{120}Sn	33	0.14	^{121}Sn	27 h	β-counting
12.	Sb	^{121}Sb ^{123}Sb	57.2 42.8	6.2 3.45	^{122}Sb ^{124}Sb	67.2 h 60.3 d	564, 692 603
13.	Ba	^{138}Ba	71.2	0.35	^{139}Ba	1.38 h	166
14.	La	^{139}La	99.9	9.5	^{149}Ka	40.2 h	329, 487, 1596
15.	Sm	^{152}Sm	26.7	210	^{153}Sm	47 h	103
16.	Hf	^{180}Hf	35.4	12.6	^{181}Hf	42.5 h	133, 482
17.	Au	^{197}Au	100	98.8	^{198}Au	64.6 h	412
18.	Hg	^{196}Hg ^{202}Hg	0.15 29.8	31.0 4.9	^{197}Hg ^{203}Hg	64.1 h 46.5 d	67, 77, 279

discriminating elements in the form of parameters (information) which could be developed employing NAA for copper and aluminium wires are unique. Additionally, the trace element patterns established and reported for other type of exhibits are given in Table 2. Individualisation of hair by trace element analysis has been attempted but found extremely uncertain owing to factors influencing variation of trace element contents even in different parts of the same individual. However, the NAA data on hair has opened up the possibility of picking out the criminal amongst a restricted number of suspects in specific and restricted circumstances. For example, a clump of hair in the clenched fist of the victim or collected from the automobile in a hit and run crime can be compared and possibly matched with the hair of suspect(s).

Nuclear Methods for Customs and Other Related Cases

Determination of one or two specific elements at very low levels can help solve customs or other related cases. The confiscated material (cloth or

leather) suspected to be in contact with gold or any other precious metal can be examined for the determination of the metal at trace /sub trace level by NAA. Comparison of trace/sub trace abundance of the element in the area, suspected to be in contact with the metal object and that in the control surface can help to give definitive opinion whether the metal was actually concealed inside the article sent for examination. In a typical case, a jacket/belt suspected to have been used for carriage of gold was referred to the Unit and non-destructive NAA of cloth along the periphery of the zipper pocket lining showed gold contents 100 times more than that of control. This confirmed the use of the jacket for carrying the gold, consistent with the allegations.

In connection with another case, compositional characterisation was necessary to identify two seized solid(white crystalline) samples i.e. whether these were drugs of abuse/explosives or any other compound. Here again, NAA findings in conjunction with conventional chemical tests gave rise to the clue that the composition of the material could be potassium gold cyanide $KAu(CN)_2$. This type of study can help investigating agencies to unravel the mystery of gold carriage in this way.

A list of radioisotopes, one usually comes across in forensic applications through NAA technique, is given in Table 3.

Apart from the above categories, there are many other vital areas where NAA can be useful for crime detection purposes, viz, forensic biology, authentication of antiques, detection of explosives, environmental contamination, occupational exposure, electrocution, forgery of documents and other related problems. Although, one can enumerate an impressive list of analytical techniques, neutron activation analysis is the one which fulfils the requirement of many elements within the framework of specialised national facility. Some of the other notable advantages of NAA are the absence of reagent blank, matrix effect and minimal sample handling prior to neutron irradiation. Efforts are always made to develop/standardise proper methodologies following either non-destructive (INAA) or radiochemical separation approaches (RNAA) or by judicious combination of both depending on situation and requirement. It is in this context that the work on forensic activation analysis (FAA) has been pursued in this country and elsewhere.

Training

Regular short duration Workshops / Training courses mainly for working forensic scientists are conducted in the Centre for generating awareness, technical application and appreciation of nuclear methods in crime cases. These courses consist of series of lectures and hand on practicals to primarily highlight NAA technique, both instrumental and radiochemical, using high resolution gamma-ray spectrometry. In addition, necessary exposure is also provided to other useful complementary techniques, viz., AAS, DCPAES, XRF electroanalytical techniques etc. employed in forensic investigations. The curriculum also emphasises the art of collecting clue materials from scene of crime, sample preparation and interpretation of data with illustrative examples to demonstrate application to real life case samples.

Conclusion

The present scenario of nuclear techniques to aid crime investigation is illustrated in the foregoing paragraphs. The level of applications in thrust areas though still growing by continued availability of research reactors in India, can be enhanced further with the technology development commensurate with need based requirements to apply in forensic samples. With the present trends of efforts to create proper awareness about the potentialities of the facility, one can safely look forward towards the development and exploitation of new methods (particularly nuclear based) for compositional characterisation and for providing validation support to programmes using other analytical techniques and also in the interpretation of data for forensic studies.

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NAA for the Analysis of Big Samples

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Introduction

All routine multi-element analysis techniques employ rather small amounts of material varying from only microliters and milligrams to a few grams. Often the amount of collected material is larger by orders of magnitude, not only because it may be inconvenient to sample at the 0.2 to 2 gram scale, but also because of the requirement of representativeness. Homogenization and sub-sampling is, therefore, required to obtain a final representative analytical portion. Problems arise when

(i) homogenization is impossible, or cumbersome due to material properties. Examples are electronic circuits on printed boards, household waste, scrap from recycled electronics, automobiles, plastics. A solution to this problem is to sort the material and to perform individual homogenization and, subsequently, analyses; thereby increasing the total project costs.

(ii) the homogenization step results in contamination of the sample, or in incidental cases losses of the analyte. Often the contamination due to crushing or milling is not controlled on every sample type. When processing large series of samples, careful interim cleaning may get the less attention since it is time-consuming and thus expensive.

Testing the degree of homogeneity is a common practice in the preparation of reference materials, but for routine operations the requirement of analysis and statistical evaluation of at least five test portions of each sample would raise the cost of an analysis considerably.

These considerations indicate that for some applications, direct analysis of the large (solid) sample as it has been collected might have advantages, both analytically and economically.

A method for the analysis of large samples has been developed on the basis of Instrumental Neutron Activation Analysis (LS-INAA) at the Interfaculty Reactor Institute in Delft, The Netherlands. The method does not require any a-priori knowledge on the composition of the sample and does not imply any disturbance of the collected material. The facilities allow for the processing of samples with maximum sizes of 15 cm diameter and 1 m length, which corresponds for e.g. a geological material with masses of approximately 50 kg.

Materials and Methods

The method for LS-INAA and the facilities have been described in more detail elsewhere [1-5]. Only a brief summary is given here.

Irradiation facility

The LS-INAA irradiation facility [5] is located in the reactor's thermal column (Figure 1) which has been customized to obtain a well-thermalized neutron flux. In the irradiation facility, water is used as a shielding against neutrons and gamma-rays. The large sample, surrounded by flux monitors, is packed in a polyethylene container. The sample can be rotated around its vertical axis during the irradiation whilst the holder with flux monitors is immobilized. The neutron flux is approximately 3×10^{12} m^{-2} s^{-1}

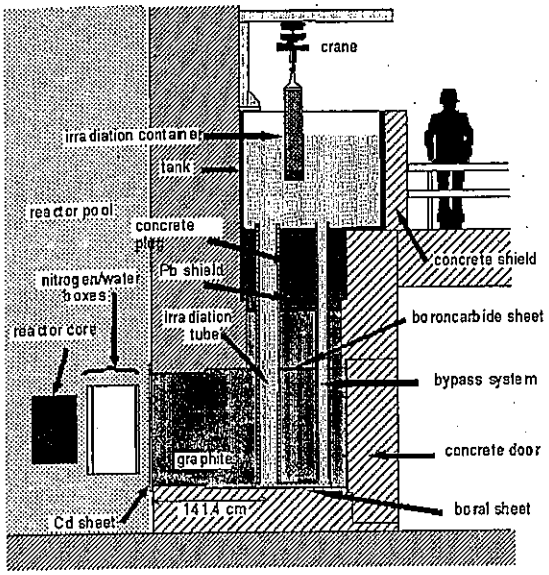

Fig. 1 Schematic vertical cross section of the relevant part of the reactor, showing the thermal column and the large sample irradiation facility.

(cadmium-ratio > 10^4), which is a factor 10^4 - 10^5 lower than in the other irradiation facilities of the reactor. The product of neutron flux and sample mass is about the same as in conventional INAA.

Measuring facility

The measurement of the induced gamma activity is performed with a gamma-ray spectrometer integrated in a scanning device [5]. The detector is a large-volume HPGe semiconductor (relative efficiency 96% for the 1332 keV gamma ray of ^{60}Co). Both the spectrometer and the scanner are connected to the laboratory's local area computer network. The scanner allows for rotation around the vertical axis of the sample during counting. Vertical displacement with respect to the detector is also possible e.g. for longitudinal (collimated) scanning.

Methods to correct for neutron- and gamma-ray self attenuation phenomena

Correction for neutron self-attenuation is based on the neutron flux depression as measured just outside the large sample, compared to the situation of large sample of pure graphite. From measurements at three positions around the sample the parameters can be derived (neutron diffusion length, neutron diffusion coefficient and undisturbed neutron flux) which are needed to describe the neutron flux inside the sample [3]. Since these calculations follow from the fitting of the results of several flux monitor measurements, the final uncertainty in the estimate of the neutron flux is smaller than the uncertainty of each individual measurement and typically less than 1%.

The flux monitors can be positioned at different vertical levels around the sample in order to account for the vertical flux gradient in the thermal column, and to inspect for neutron self-attenuation variations along the sample. This approach was preferred above measuring the neutron flux via inserting flux monitors inside the sample, which is impractical and sometimes even not feasible, e.g. when the monitors have to be precisely positioned at different levels or because of sample characteristics.

Correction for gamma-ray self-attenuation is based on the effective linear attenuation coefficients determined via the transmission of gamma-rays from a reference source. The gamma-ray self-attenuation correction is integrated with the calculation of the detector's photopeak efficiency for a sample with finite dimensions, where usually 'point' sources are assumed [2].

Combination of both correction algorithms yields an 'overall correction factor'. This overall correction factor reflects the difference in actual detector response for a given gamma energy compared to the theoretical detector response if the sample would have been a massless point-source located in the large sample's centre, without any neutron and gamma attenuation [4].

It should be noted that in the determination of the overall correction factor, no assumptions whatsoever are made on the composition of the sample; nor is a priori information required on the composition, and all measurements are carried out non-invasively.

Additional Corrections

Since large samples of quite a few materials also display gamma lines originating from natural radioactivity, a spectrum of this natural radioactivity

is recorded prior to irradiation for correct interpretation of the gamma spectrum after activation. When required, also levels of natural radioactivity are given as result of the element analysis.

Quantitative Analysis

Quantitative analysis is carried-out via the k_0 single comparator approach [6], using a zinc metal foil as neutron flux monitor and comparator element. Zinc was selected since the two activation products ^{69m}Zn and ^{65}Zn can be used for internal quality control. The k_0 approach is facilitated by the well-thermalized neutron flux. The k_0 method enables the determination of concentrations and detection limits of about 60 elements.

Validation

Validation of the LS-INAA method has been done by the analysis of homogeneous materials, different in neutron and gamma-ray attenuation characteristics. Gamma-ray spectra of both large samples and small samples of each material. The overall correction factors matched, within limits of uncertainty, the corresponding ratios of the peak areas of the small sample and large sample analysis [4].

Use of Large Sample INAA

In several fields of applied research the analytical problem could be approached by large sample INAA [7]. Typical for those cases was that sample size reduction to a representative analytical portion for conventional analysis was considered to be rather difficult or even practically impossible. Examples of applications are:

- Construction waste: mixtures of stone, concrete, sand, and metal fragments;
- Compost from biodegradable household waste;
- Shredded plastics: chips of ca 10 x 10 mm^2 of different origin and composition, serving as raw material for recycling;
- Shredded electronics: remainders of printed circuit boards and components from television sets; also to serve as raw material for recycling;
- Ferrous and non-ferrous fractions of household waste, separated directly from collected waste

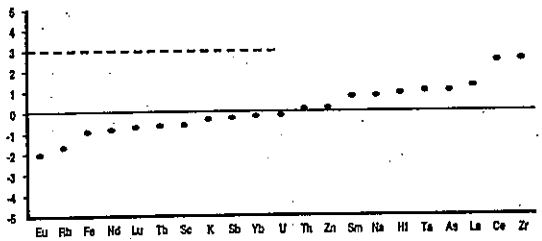

Fig. 2 Comparison of INAA results of large, 1.6 kg sample of a uranium waste rock pile, and of 200 mg sample derived after sample size reduction and homogenisation [8]. The z-score represents the difference between the individual result, weighted on basis of the uncertainty of this difference. Scores between –3 and + 3 indicate that there is no statistically significant difference at the 99.7 % confidence level

- Rocks and deposits containing Pt-group elements;
- Uranium mine waste rock pile material, before and after homogenisation; see Figure 2 [8]
- Soil, containing an inhomogeneously distributed contamination by Hg.

Large sample INAA offers the opportunity to validate sub-sampling procedures and to verify experimentally aspects of the sampling theory. This is also useful for materials of which the natural radioactivity has to be assessed. The Interfaculty Reactor Institute currently operates a laboratory intercomparison program for verification of the sub-sampling procedures in measurements of natural radioactivity in construction waste. To this end, large samples have been composed and characterised utilising the algorithms for gamma-ray self-attenuation and spatial detection efficiency. These large samples are subsequently distributed amongst the participants. The participants measure small sub-samples following a national standard procedure for sample size reduction and sub-sampling of this type of material. Comparison of the results will be indicative for potential problems in this standard procedure, which are almost impossible to detect elsewise.

Inhomogeneity Studies

It has been demonstrated that extreme inhomogeneities in matrix or in trace element composition may result in inaccuracies in the analysis [9]. Inhomogeneities of trace elements affecting the gamma-ray detection efficiency have the largest effect in this respect. Tools have been developed to monitor and to identify the existence of such extreme inhomogeneities [10]. Several constraints exist: the total induced radioactivity is typically less than 100 kBq and the total counting time should be restricted to 4 h. The identification method should also allow for multi-element determinations. The method shows some similarities with waste barrel scanning. Gamma-ray spectroscopy is carried out with a scanning collimated detector, resulting in voxels with sizes of a few tens of cm^3. First the 'raw' spectra are monitored for measurable inhomogeneities using a z-score test: a tool to decide whether a sample is extremely inhomogeneous such that the localisation and quantification of the inhomogeneities is necessary. In that case, the spectra are analysed as individual INAA measurements, corrected for cross talk by a Least-Squares matrix inversion of the detection efficiency matrix. The pixel size is relatively large compared to those used for Single Photon Emission Computing Tomography. However, a relatively quick 3D screening is obtained. If extreme inhomogeneities are observed, more detailed pictures can be reconstructed by scanning a small fraction of the sample around the inhomogeneity with a smaller collimator opening and a longer measurement time.

Discussion

The quantitative determination in large sample NAA is based on the same principles as conventional NAA and traceable to primary standards. The corrections for neutron flux distribution, source geometry during counting and overall correction for neutron and gamma ray self-attenuation may reduce the degree of accuracy compared to conventional NAA, and will increase the uncertainty.

The traditional approach of internal quality control via (certified) reference materials cannot be followed. Even if a suitable internal quality control material would be available in sufficient large quantity, the question remains to what extent the results of such a material -close to 'ideal' with respect to sample homogeneity- would reflect the quality of an analysis of a sample with unknown, and most likely not 'ideal' degree of homogeneity. Indications on the homogeneity can be obtained from the calculated values of the neutron diffusion length and diffusion coefficient and of the linear attenuation coefficient for gamma-radiation. These parameters should all have physically realistic values, with constraints that can be derived from tabulated values of the pure elements. Another indication on extreme inhomogeneities absorbing gamma rays is obtained by scanned measurements, as shown in the above.

In all cases the analyst should be prepared to the effect of extreme inhomogeneities in large sample analysis and, as with other types of chemical analysis, a certain degree of pre-science is required. As an example, for any type of INAA it is important to know if the sample contains significant amounts of boron, lead, thallium, bismuth etc. Similar questions are needed for LS-INAA

Conclusion

LS-INAA offers the possibility to analyse materials of which the sample size reduction step, sub-sampling and/or preparation of the analytical portion raise difficulties. Since the neutron and gamma ray doses in the irradiation position are a factor of 10^4 lower than in the irradiation facilities for conventional INAA, the radiolysis of water can be neglected and pressure build-up is not a matter of concern. This enables direct analysis of materials that contain water and in which drying raises difficulties with respect to volatile components to be determined, like mercury in soil.

In contrast to conventional approaches - sampling, sub-sampling, combining sub-samples, homogenization - a direct analysis of the large sample requires attention for, answers on and interpretation of the degree of inhomogeneity of the material.

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Neutron Activation Analysis : An Update

Shri R.N. Acharya obtained M. Sc. in Chemistry from Utkal University in 1992. After graduating from Training School, he joined Radiochemistry Division, BARC in 1994. Since then he is engaged in research and development work on neutron activation analysis (NAA). He has about 30 publications to his credit.

Neutron activation analysis (NAA) was originated by George de Hevesy and Hilde Levi, in Denmark, in 1936. Since then, NAA has a fascinating history of growth and has become a matured and reliable analytical technique [1]. Prior to this, no other analytical method was available that could detect and measure quantitatively a large number of elements present in variety of matrices at trace and ultra trace levels. The recent trends of NAA methodology are associated with the improvement of the quality of the instrumentation, especially for γ-ray spectrometry (more efficient high resolution high purity germanium (HPGe) detectors and use of Compton suppression spectrometry), spectrum analysis software in terms of its adaptability to PC, updated nuclear data library and the nuclear reactor as the intense source of neutrons. The NAA method has become a simultaneous multi-element and a powerful reference analytical technique. After the year 1970 extensive applications have been manifested in the determination of trace elements in the fields like environment, biology, geology, material sciences, nuclear technology and forensic sciences [1,2]. Relative and k_0 standardised methods of instrumental NAA (INAA) are capable analysing as many as 70 elements. However, radiochemical NAA (RNAA) and chemical NAA (CNAA) have their role for achieving high sensitivity in some cases. Epithermal NAA (ENAA), fast NAA (FNAA), neutron induced prompt gamma ray activation analysis (PGAA) along with specialised methods of NAA like derivative activation analysis (DAA) and cyclic activation analysis (CAA) have been developed to cater to the needs of different problems. In view of this an update on NAA viz., literature is included in this article.

Literature Update

A large number of publications, covering various areas that use either NAA or NAA in combination with other analytical techniques, are available in literature. Guinn [1] has dicussed various aspects of the growth rate of the NAA method during 1936-1991; Girardi [2] reviewed the cumulative number of publications on activation analysis in different journals during 1945-1980 and Bruin reported [3] the number of total publications in activation analysis for the last 25 years i.e., from 1970-1995. Recent trends in applications of NAA can be identified from the topics discussed in the last conferences on "Modern Trends in Activation Analysis" (MTAA) and "Nuclear Analytical Methods in the Life Sciences" [4, 5]. Similar trends can also be identified from the proceedings of two recent symposia organized by IAEA in these fields: "Applications of Isotopes and Radiation in Conservation of the Environment" in 1992 [6] and "Harmonization of Health-Related Environmental Measurements Using Nuclear and Isotopic Techniques" in 1996 [7]. Bruin has reported activation analysis and its future development in a historical perspective [8] and recently Spyrou [9] has reviewed the NAA challenges and its applications in biomedical and other areas.

An attempt is made to include a few publications using INIS-CDROM facility on neutron activation analysis that are mainly from the year 1995 onwards ensuring that each area is reported.

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Quality Management and Accreditation in NAA

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Introduction

Analytical laboratories are confronted with an increasing pressure to give objective evidence of formal certification or accreditation for their technical competence, reliability of results and performance. This pressure may be evoked by laboratory's customers (e.g., industry, but also national bodies) but may also result from scientific considerations, e.g., when striving to operate as a national reference laboratory for metrology in chemical measurements. To accomplish mutual (international) acceptance of such evidence, several protocols have been developed for quality assurance activities. The most widely recognized and used in chemical measurements and testing fall in three groups and are applied according to a laboratory's needs. The groups are (i) the ISO-9000 series of standards and its national equivalents; (ii) the ISO/IEC Guide 25 and its derived national and international standards and (iii) the OECD Guidelines for Good Laboratory Practice and its national and sectoral equivalents.

To comply with such requirements, the laboratory has to develop itself a quality system describing its quality assurance activities and the management thereof. Top-management may translate this into the need for a project resulting in a 'quality manual' and 'accreditation'. One of the mistakes that often follows is that the project leader starts with writing a quality manual, derived from the lists of requirements in the protocols mentioned in the above or from related guidance documents [1,2] in an attempt not to spend too much time and to continue laboratories' all normal activities. The laboratories' employees are suddenly confronted with this manual, new vocabulary, a new organizational and managerial structure, with a long list of (or demands for) standard operating procedures and requests for book keeping and other paperwork. Irritation and frustration will develop faster than the quality system which is needed.

Many laboratory managers and their superiors realize insufficiently that a quality system may only be self-sustainable and cost-effective when it is bottom-up supported by all employees. Since a quality system and its management often implies a drastic change of the everyday's culture at the laboratory and attitude to work, sufficient time is needed for awareness building. Time, patience and lot of tact are required to guide a process in which traditions have to be left which were build-up over many years, in which people have to understand that cross-checking is not a matter of mistrust but a need to prevent repetition of work. The employees need time to experience the benefits of full trackability, and to decide on harmonization of operations. And to become aware that there may be also internal considerations to improve the laboratory's performance, e.g., because of a high level of repetition of work. It is initially a slow process: awareness building easily may require many months. A realistic plan for implementation has to be made, a plan that can count on everyone's support and commitment. To this end, the laboratory manager should realize that the final goal, e.g. formal recognition of the quality system by certification or accreditation, should merely be seen as 'cosmetics'. The real objective of the entire operation is still to improve the reliability of the analytical and managerial performance of the laboratory and to be able to give objective evidence on this. The

international protocols provide guidance in this. When all of it has been accomplished, the quality system may be summarized and described in a quality manual.

So, the first questions and tasks to start with should be :

"What is known about

- the reliability, trackability and traceability of our results
- what are our sources of error?
- how can we monitor them? and
- how can we take them into account or ultimately eliminate them and how can improvement on all this be attained?"

Once these questions are answered and the underlying matter is understood, quality control measures can be taken and quality assurance may be designed-in in the laboratory's activities. Unfortunately, the terms 'quality control' and 'quality assurance' are frequently not correctly interpreted, and even abused. As an example, it sometimes occurs that the analysis of a sample of a reference material is considered to be the laboratory's 'quality assurance'[1].

Quality assurance on its own is not sufficient to ensure the proper and efficient operation of an analytical laboratory. There are many operational activities which may have an effect to the reliability of the analysis. Moreover, not all of the procedures for work and for the quality control/quality assurance actions have been written down. As a result, some will be known in detail only selectively by individuals; others are considered to be 'common knowledge'. This system is not self-sustainable when one day something goes wrong because not everyone was aware of the correct procedure, criteria, specifications or checkpoints. This stresses the necessity to harmonize and document *all* operations to make them unambiguous; to quantify the criteria for acceptance of data and to develop a system for internal inspection (auditing). This all leads to the importance of implementing aspects of total quality management (TQM).

Laboratory Accreditation

In a contractual situation it becomes rather impractical when the customer himself has to inspect the laboratory's 'objective evidence' on the quality of the produced data and the reported uncertainties. In many cases the customer does not have the technical and scientific abilities to do so. It marks the difficulty of mutual acceptance of data and trustworthy of laboratories. Often, the absence of this all might result in re-analysis or extensive disputes on the quality of the data.

Laboratory accreditation is the key to take away this mistrust, and the consequential expenditure of resources. National laboratory accreditation bodies have been formed, which verify the technical competence of a laboratory to carry-out specific tests, and the compliance of the laboratory's quality system with the ISO-25 guide or derived standard (like EN45001).

There are no paragraphs in the ISO Guide 25 and derived standard that would be insurmountable for a NAA laboratory, as has been demonstrated in Delft. The quality system at the laboratory for INAA of the Interfaculty Reactor Institute in Delft, The Netherlands has been accredited in February 1993 for its compliance with the EN45001 criteria [4, 5,6].

All the aspects of a routine NAA procedure can be laid down in documented procedures. Moreover, new NAA procedures, especially in INAA, are often

[1]Both terms are well defined in the document ISO 8402 (1994) 'Quality Vocabulary' [3] :

- Quality Control : The operational techniques and activities that are used to fulfill requirements of quality.
  Quality control procedures relate to ensuring the quality of specific samples or batches of samples and include - Analysis of reference materials, blind samples, blanks, spiked samples, duplicates and other control samples.
- Quality Assurance : All those planned and systematic actions necessary to provide adequate confidence that a product or service will satisfy given requirements for quality.
  Quality assurance describes the overall measures that a laboratory uses to ensure the quality of its operations. Typical items are: Quality control, suitable equipment, trained and skilled staff, documented and validated methods, requirements to calibration, standards and reference materials, traceability, proficiency testing, non-conformance management, internal audits, statistical analysis.
  The quality assurance activities should be embedded in a managerial quality system.

based on a different choice of irradiation and counting conditions which hardly require a new complete validation. The objective evidence of the performance can be given via participation in laboratory performance assessment schemes, control charts for internal quality control and analysis of blind duplicate samples.

Many methods for elemental analysis deal with chemical matrix effects and therefore need matrix matching reference materials. Laboratories employing such methods usually seek accreditation for specific tests, such as the determination of a few given elements in a given sample type. But in INAA, the scope of accreditation may cover multi-element determinations in a large variety of materials. A practical problem in obtaining an accreditation for NAA might be the availability of technical peer assessors. Such an assessor should not only be an expert in NAA, but also be well acquainted with the quality principles of the ISO guide and derived standards.

Strategic Considerations

Implementation of quality management in analytical laboratories, even at universities and at research facilities is possible, required and sometimes inevitable. This does not imply that every laboratory should pursue per-sé accreditation, since for this step other motives play a role. For NAA laboratories there are some strategic reasons that call for the introduction of some form of quality management. These are listed below.

To Remain Eligible for Commercial Services using NAA

Many nuclear research facilities need some form of commercial NAA to acquire extra funds to cover the running costs and to justify the existence of such an expensive facility. Industry needs measurement reports that will be internationally accepted. This can only be accomplished if the laboratory is formally accredited for its quality system complying with the relevant international standard, often derived from ISO-Guide 25.

To Participate in National Programmes for Metrology in Chemistry

Metrology systems are being increasingly established by various countries for the worldwide comparability of data related to trade, industrial products, health and the environment. This has in-turn led to an increased interest in methods that could be of the highest metrological order. INAA is useful for method validation, proficiency testing, development of reference materials and reference methods. Moreover, it can be demonstrated [7] that INAA may comply with the CCQM definition of a primary method, provided that the uncertainty in the results is reduced to a much lower level than currently common in NAA laboratories. It seems to be inevitable that a quality system and laboratory accreditation will turn out to be a prerequisite for a laboratory interested in participation in a metrology program.

To Preserve the Hitherto Undocumented knowledge of the Laboratory's Staff for Future Generations

Several NAA and radiochemistry laboratories deal with the ageing of their staff. Training new employees becomes easier and unambiguous if using documented procedures, based on the experience and skills of the existing staff.

Cost-Benefit Evaluation

This paragraph reflects, as a case study, the costs and benefits of the quality system as developed at the laboratory for INAA in Delft, The Netherlands.

Costs for Development of the Quality System

In the development stage between January 1990 and November 1992, no time keeping has been done; however, a resume learned that the effort invested by the 7 employees in the development of the quality system summed up to about 2 man-years. Assistance by an external consultant integrated to about 0.7 man-years. Miscellaneous costs came from small investments in the laboratory and stationary for the manual and forms. It all amounts to a total that is equivalent to approximately 25-30% of the laboratory's one years' running costs (salaries and other budget).

Costs for Maintaining the Quality System

Once accredited, returning annual costs[2] should be taken into account. The following contributions can be distinguished :

(i) Prevention costs are costs required to keep unacceptable data from being generated in the first place. They include costs associated with training of personnel, the necessary system calibrations, internal quality control and performance checks. Calibrations (equipment, element-standardizations, pipettes, balances) and performance checks integrate up to about 1 man-year.

(ii) Appraisal costs are costs required to sustain the system. These include the internal audits and alterations in the quality manual. These require attention of the quality coordinator (0.3 man-year) and the Institute's quality manager (0.05 man-year). Also the costs of the audit by the National Organisation for Accreditation should be accounted for.

(iii) Correction costs are those required to correct conditions that have been found to be out-of-control, or less than satisfactory. These include costs for trouble shooting, implementation of corrective and new preventive measures and reanalysis of samples.

The total of these annual costs amount approximately 20 - 25 % of the annual running costs of the laboratory; the prevention costs are the most dominant component in this all (approximately 75 % of the total).

Benefits of the Quality System

The costs for sustaining an accredited quality system are out-of-pocket costs. But the benefits are more difficult or even impossible to quantify and to turn into money since many of them are only measurable as an improved effectiveness of operations and a considerable reduction of non-conformance [6] :

(i) Less repetition of analyses and less corrections because of last moment discoveries of small mistakes and miscalculations. A conservative estimate is that every employee 'earns' approximately 10% of his time.

(ii) Trackability of analyses by the extensive documentation and registration of relevant parameters. The time savings are estimated at approximately 5% for every employee. Additionally, it works as a time-saver in the training of new personnel.

(iii) The documentation and assignment of deputies reduce the risk of 'single points of failure'. The benefit is with the continuation of operations, and not quantifiable.

(iv) The QA prevents the release of bad results and the possible forthcoming claims and other costs. On the basis of an evaluation of analyses since 1992 it is now known that on the average in 5% of all samples analysed wrong results may occur, the reporting of which is prevented by timely corrective actions prior the release of the reports. These samples would otherwise probably analysed again; thus an estimate of benefits can be made.

(v) The accreditation prevents discussions on the verification of results since this is implicitly covered by the accreditation; the gain in time is not quantifiable either.

(vi) Laboratory accreditation has become indispensable to be eligible for third party contracts.

The estimated total of the quantifiable benefits amounts approximately 15% of the annual running costs. When comparing with the costs of sustaining the quality system, the not quantifiable benefits (reduction of single-points-of failures, prevention of claims because of reported wrong results, no disputes on quality) and income from commercial INAA services should not be forgotten.

[2]The realization of the quality system has, in the respective years, been justified in the annual research and development program of the institute. Therefore, the cost-benefit evaluation does not include a proportional part of these costs of realization. It is in analogy with the cost analysis of INAA which also does not include the costs related to the development of the technique, but only the running costs.

Final Remarks

Managers of analytical laboratories are facing more requirements to quality assurance and organisation of their laboratories. These requirements may be different from what was learned in the past. It is, therefore, important to realise that the new requirements are no condemnation of the performance of the laboratories hitherto. The additional requirements come from new insights and beliefs to improve the performance of the laboratory in terms of effectiveness of operations, assurance of quality and uncertainty of the results and to prevent a waste of time and money. And to generate a basis for the customers for acceptance of and confidence in the results.

It is understandable -but not justifiable- that non-profit laboratories may put these new requirements aside assuming that the ideas about quality systems and laboratory accreditation is contemporary, and only a new 'gimmick' for industrial organizations to distinguish themselves in their economical competition. Non-profit laboratories -like universities and research institutes- may learn from the measured benefits of quality management. When the new requirements are not taken seriously, it may occur that the laboratory classifies itself as an academic curiosity thereby weakening its competitive position, nationally but may be even internationally. Moreover, universities have a mission to educate and train academics in an environment which is not too different from what society calls for; and society may increasingly call for academics which are capable and experienced to manage laboratories in which, for corporate objectives, quality management has been installed.

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