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

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

1. INTRODUCTION: GENERAL THESIS

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

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

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

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

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

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

2. PROMISING TRENDS IN NAA

2.1. Instrumental NAA (INAA)

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

The use of k_0-INAA continues to spread and extensive experience with this technique has revealed few problems and good accuracy. The present status of the technique and typical applications are summarised in the Proceedings of the 2nd Workshop on k_0-INAA, held in Ljubljana [3]. Heydorn and Damsgaard [4] also showed how k_0-factors can be used to validate and check relative standards in NAA. Recently, Bossus and Van Sluijs reviewed the range of applications for k_0-INAA in a Dutch chemicals and materials group [5]. The major applications are for panoramic analyses of solids and organic liquids, analysis of catalysts (solids and slurries), the analysis of industrial slurries, the determination of halogens, analysis of samples for which no other in-house technique has yet been calibrated, and finally as a check or referee method for a second opinion.

2.2. Quality assurance/Quality control

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

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

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

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

2.3. Radiochemical NAA

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

In the case of multi-element RNAA, k_0-factors can be combined with chemical yields to perform k_0-RNAA independently of the relative standard method.

2.4. Speciation analysis

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

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

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

3.1. General

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

3.2. Radioecology

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

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

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

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

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

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

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

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

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

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

3.4. Other studies

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

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

4. COLLABORATION WITH OTHER NUCLEAR-BASED TECHNIQUES

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

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

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

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

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

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

5. COLLABORATION WITH OTHER NON-NUCLEAR ANALYTICAL TECHNIQUES

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

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

6. SYNTHESIS AND STRATEGY

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

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

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

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

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