Radiochemistry: inconvenient but indispensable

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Abstract

Radiochemistry has always been and still is a crucial tool in the field of radionuclide determination, both for high and low level works; this holds particularly in the case of alpha and beta emitters. Requests to the analyst are increasingly demanding in terms of performance (detection limit, reliability, accuracy, precision,\ldots), but also of economy (cost, time,\ldots) and of flexibility with respect to sample types. In general, chemical and radiochemical analyses consist of four main steps: sample pre-treatment including pre-concentration, dissolution and/or digestion, separation of analytes from the matrix and from each other, transformation of the separated fraction into a source suited for measurement, determination of the amount or the activity of the analytes. The required combination of sub-procedures is determined by the analytes under investigation, their absolute and relative amounts, the matrix composition and by the performance required. IRMM's Analytical Chemistry Unit started several years ago to develop, adapt and/or validate various radiochemical methods and procedures, and apply these to different measurement tasks. This paper gives an overview on recent and ongoing activities. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Traditionally, the main task of the Analytical Chemistry Unit at IRMM (IRMM-ACH) was the preparation and elemental certification of Nuclear Reference Materials such as uranium and plutonium pure metals or oxides, relatively concentrated solutions of these elements or matrix materials with relatively high concentrations (e.g. ores). The principal clients of such materials are Safeguards Authorities and the laboratories related thereto, nuclear industry and on a somewhat lower scale, research institutions who apply them because of their very high purity. Another significant part of the work were analyses on request from third parties, also mainly dealing with U, Pu and Am.

During the recent decade, on the one hand the need for nuclear materials has been decreasing due to both a general decrease of nuclear activities in Europe and a saturation of the respective market. On the other hand, more and more requests for low level radioisotope analyses under various scopes were expected for different reasons:

- There is a general lack of matrix reference materials certified for radionuclide content.

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• There is an increase of anthropogenic radionuclide sources, or rather of the revelation thereof.
• Occupational exposure regulations or dose calculation models have been/are being adapted, possibly leading to more stringent requirements for analysis, particularly, in the case of materials present in workplace environments.
• Often official or recommended methods for radionuclide determination are rather lengthy and/or cumbersome, or create a lot of (expensive) radioactive waste.

Therefore, a need was felt to direct resources into this field. According to the acquired expertise in nuclear and particularly in actinoid chemistry, and to the detection equipment available or already planned to be purchased (Fig. 1), the decision was taken to concentrate on the development, adaptation and validation of analytical methods for low level actinoid determination, with emphasis on Th, U, Pu, Am and Cm, the elements which are presently the most important ones with respect to analysis requests. Np, which during recent years has gained importance, is foreseen to be included in this list in the near future.

In general, radiochemical analyses (of samples in the laboratory) consist of four main steps: sample pre-treatment including pre-concentration, dissolution and/or digestion, separation of analytes from the matrix and from each other, transformation of the separated fraction into a source suited for measurement, determination of the amount or the activity of the analytes. Since alpha spectrometry and ICP-MS are our workhorses in actinoid detection, the first necessity was a rapid and reliable actinoid separation procedure. Shortly afterwards, projects were started to couple this procedure with various sample pre-treatment steps, determined by the nature of the matrices under investigation, and to adapt/simplify it for particular requirements concerning the analytes. In parallel, specially occurring problem areas which, when neglected, may lead to serious analytical errors were tackled.

The present paper gives an overview on recent and ongoing works in these areas within IRMM’s Analytical Chemistry Unit (ACH).

All of these activities require the direct application of “radiochemistry”. This term has been used for many different meanings, reaching from the very tight definition of “application of radioactive decay phenomena to chemistry” (e.g. activation analysis, dilution analysis, labelling, Szilard-Chalmers reactions) to the wider sense of “chemistry of the radioactive elements and/or nuclides”. In the present paper the latter meaning is considered. It should be emphasised that some special problems exist, which are not usually considered as important in “conventional” chemistry, e.g. the behaviour of analytes in extremely low (mass) concentrations (adsorption effects, non-exceeding of solubility products, etc.) Conversely, detection advantages exist in comparison to inactive analytes due to the high sensitivity of nuclear radiation detection. Hence, the expertise and experience of the radiochemist is crucial during each step of the total analysis in order to generate reliable results. This will be outlined in more detail in the course of this paper.

2. Actinoid detection

Alpha spectrometry with Particle Implanted Planar Silicon (PIPS) detectors and quadrupole Inductively Coupled Plasma Mass Spectrometry (ICP-MS) are used as the detection methods. In the former case, the (activity) detection limits depend to a large extent on the measurement time. In the latter, they lie in the region of 10–50 pg/ml of measurement solution without an ultrasonic nebuliser, i.e. in terms of activity (which most often is the quantity of interest in these kind of measurements) they depend on the half life of the nuclide under investigation. Considering a sample brought to 10 ml would contain 100 pg the detection limit corresponds, e.g. to 0.4 μBq of 232Th, 790 μBq of 229Th and to 12.7 Bq of 241Am. This shows clearly that the two methods are complementary rather than competitive with respect to detection limits. While short lived nuclides can be determined only by radiometric methods, ICP-MS offers some advantages for long lived ones: faster measurement and the avoidance of tedious sample preparation prior to measurement. The borderline lies somewhere in the half life region of several 10^3 to 10^5 years.

The application of alpha spectrometry requires extremely good control in the chemical preparation of
the measurement sample sources, which consist either of electrolysed steel platelets or lanthanoid fluoride co-precipitates on filters. Many sources of error must be eliminated in order to obtain quantitative deposition/precipitation and sufficiently homogeneous area distribution of the nuclide on the sample. Procedures have to be completely under control with respect to solution pH, carrier concentrations and reaction times in the co-precipitation case. For electrolysed samples, extreme care must be taken with respect to pH, solution composition, voltage, current and time of deposition.

In the case of ICP-MS measurement these parameters are less crucial. However, there are other possible pitfalls, mainly due to the extremely low mass concentration of the radionuclides. Adsorption effects onto lab vessels and within the solution-carrying parts of the instrument (tubing, nebuliser, spray chamber) start to play an important role. As an example, Fig. 2 shows the wash-out behaviour of Th, U and Pu in the ICP-MS instrument. After measurement of a fairly high concentrated solution (100 ng/ml) of each element, the washing solution was pumped through the system (as usually performed between different sample measurements) and the analyte signal measured every 30 s. It is obvious that the different elements exhibit different adsorption within the system and it is clear that respective measurement procedures have to take account of this difference. To complicate the matter, such effects are actually not due to the different elements but to the different species (oxidation states, complexes, colloids etc.) present in the solution, which, therefore, have to be known with a high degree of certainty.

The only way to enable control of all such parameters is radiochemical expertise and experience combined with proper validation of each single step of the respective procedures.

### 3. Actinoid separation

At the start of the low-level programme, various methods were tested and applied to separate the actinoids from each other and from the respective matrix, primarily the well known combinations of precipitations (Fe(OH)_3), redox reactions, ion exchange (DOWEX) and solvent extraction techniques. Although the official or recommended methods usually work well, it soon became obvious that improvements were needed, especially with respect to the time required and to the waste produced. As an example, the German recommended procedure for the determination of Pu in sea water, as handed out in 1987 (Leitstellen, 1987) consists of one acid–base titration, four extraction or washing steps, four ion exchanger column steps, seven evaporation or fuming steps, and produces 390 ml of liquid waste, even without considering any pre-concentration or sample preparation steps. Procedures for more nuclides or other matrices are sometimes even more cumbersome.

Therefore, it was decided to seek a faster, cheaper but still reliable method based on extraction chromatography, to be performed in the course of a thesis. The resulting basic method for the separation of Th, U, Pu, Am and Cm is shown in Fig. 3 details of development and validation (Pilvioä, 1996, 1997; Pilvioä and Bickel, 1997; Pilvioä, 1998; Van Tigchelt et al., 1999) and of application to the certification of a reference material (Pilvioä and Bickel, 1998a, 1998b; Pilvioä et al., 1999) are described elsewhere. The method has proven to be reliable through experiments with certified refer-

![Fig. 2. Washout behaviour from the ICP-MS system of Th, U and Pu with 2% nitric acid. No error bars are given because each dot relates to a single measurement. The expected errors lie in the order of 5–10% relative.](image1)

![Fig. 3. Basic separation procedure for actinoids used at IRMM.](image2)
ence materials. It exhibits high recoveries (> 80%), low waste volumes (< 80 ml/sample) and the separation is achieved within less than a working day, starting with a HNO₃ solution and ending with platelets or filters ready for the alpha measurement. No disturbing crossover of different analytes between fractions is observed.

Since the completion of this work, various simplifications and/or adaptations to different measurement problems (Th only, U and Th only, U and Pu only in a ratio of 10⁸, impurities in U) were performed (Holmes and Pilviö, 1999a, 1999b; Slowikowski and Bickel, 1999; Slowikowski et al., 1999).

Again, although the overall procedures exhibit very good performance, many possible sources of error have to be excluded or minimised, and proper method validation is crucial to enable complete control.

4. Sample pre-treatment

The goal of the development of pre-treatment methods is twofold: to transform the sample into a solution directly applicable for the basic separation procedure, and to ensure that unavoidable solution constituents (introduced by the pre-treatment) would not interfere with it nor with detection procedures. Again, carefully validated radiochemical procedures are required in order to find the appropriate combination of steps to assure reliability of analysis. Some examples of ongoing projects are presented below.

4.1. Large water volumes

Many European seas, lakes and rivers exhibit elevated radionuclide concentrations caused mainly by anthropogenic sources. For their determination reliable pre-concentration methods for volumes up to several hundreds of litres are required, in order to achieve the required detection limits. Many different methods have been and are being used for this purpose, mainly based on co-precipitation (e.g. Fe-hydroxide, Ca-phosphate) or adsorption (e.g. Mn or Ti oxides) processes (Kouldiris, 1998). To enable the use of such processes, together with our separation procedure, they must be characterised and possibly adapted. Preference was given here to MnO₂ adsorption and organic ion exchanger methods because, the former was assumed to comply better with the separation procedure (Mn in comparison to Fe or phosphate) and the latter would introduce less additional ions into the sample. Systematic investigations involving XRD, SEM and adsorption studies on various MnO₂ phases, the ion exchanger Hyphan (Van Britsom et al., 1995), some Russian made exchangers based on fibrous polymeric materials (Molochnikova et al., 1997; Myasoedova et al., 1988; Myasoedova, 1991) and a molecular sieve are being performed for Th, U, Pu and Am. Detailed results are given elsewhere at this conference (Kouldiris et al., 1999).

4.2. Thorium in workplace materials

In the workplace environment, thorium is found in starting materials such as zircon sand for ceramics production, monazite for production of refractories, zirconia for the production of special glasses etc., but also as working tools (e.g. tungsten welding electrodes) or waste (e.g. welding dust). The European Directive (EURATOM 80/836) laying down the basic safety standards for the health protection of the general public and workers, requires that materials exceeding 100 Bq/g must be reportable; this limit is expected to be set significantly lower in the near future. However, it has been shown recently, in the course of an interlaboratory exercise (Dean et al., 1996) that there is a strong need for reference materials and validated methods for thorium analysis. Therefore, a network of expert laboratories has been set up for this purpose by DG XII of the European Commission (Modna et al., 1999).

In this context, IRMM participates with the development of analysis methods based on alpha spectrometry and ICP-MS. Measurements on well-characterised reference samples have shown promising results up so far.

The crucial point here is the validation of the necessary digestion procedures, which have to be quantitative (particularly important for refractories) and must comply with our basic separation method. Presently, most activities here are directed towards microwave digestion and, if necessary, fusion. Details of this project are presented elsewhere (Holmes and Pilviö, 1999a, 1999b, 1999c).

4.3. Certification measurements on biological reference materials

Several alpha emitting radio-elements, e.g. Pu, accumulate in bone. Until recently, there were no reference materials available for the calibration of measurement equipment and methods used for this particular matrix. Therefore, the National Institute of Standards and Technology (NIST), USA, prepared a bone ash RM and organised an international comparison to certify it for the radioactivity concentrations of 15 radionuclides.

Several stringent requirements existed in this case: a difficult matrix (high Ca and phosphate), necessity of determination of Sr from the same sample, limited availability of sample material and the maximum performance in terms of precision and accuracy. Therefore, a special pre-treatment procedure (based on
perchloric acid digestion and extraction chromatography) was developed during this exercise in order to separate actinoids, as a group, from Sr and the matrix, was then coupled to the basic separation method, and validated. Details on this project are given elsewhere (Pilvio and Bickel, 1998a; Pilvio et al., 1999). The next project of this kind will be a similar exercise with a future shellfish reference material.

5. Considerations on uncertainty budgets

The proper budgeting of the uncertainty attached to the analysis is a basic requirement for the delivery of reliable results. According to the presently accepted way of doing this (ISO, 1993), the overall procedure is divided into relatively simple steps, and for each of these the Type A and Type B uncertainties are calculated or reasonably estimated before combining them according to the rule of error propagation. To correctly identify and evaluate all these single uncertainty contributions, again, the whole procedure must be under complete control of the responsible analyst, and proper validation of methods is an absolute requirement.

In the case of ICP-MS measurements by standard addition, for example, the evaluation leads to the following uncertainties to be considered:

Type A uncertainties
- Dilution of mother solution including all weighings. Balance used as a comparator only. Effect of temperature and other influences are considered by the metrologist.
- Dilution of working solution (See weighing above.)
- Preparation of standard solution. Precision of pipette.
- Analysis of standard addition samples. Uncertainty on slope and intercept arising from counting statistics, precision of sample preparation and instrument drift. Changes in nebulisation rates, and factors which may affect the instrumental parameters are taken into account by the internal standard. Short term drifts uncorrected for by the internal standard, but will be taken into account in the uncertainty on the slope and intercept.

Type B uncertainties
- Combined uncertainty on the volume of the prepared sample for analysis, arising from inaccuracies of the pipettes.
- Inaccuracy of pipetting sample.
- Inaccuracy of pipetting standard.
- Uncertainty in the concentration of the standard, includes combined uncertainties from the stock solution, and possible sequential dilutions (pipetting and volumetric uncertainties).
- Conversion from volume (mg/ml) to mass based (mg/g) result. Uncertainty on density of solution.
- Conversion from mg/g to Bq/g, if required. Uncertainty on half-life of nuclide.

Uncertainties considered to be negligible
- Uncertainty arising from changes in the climatic conditions within the laboratory (e.g. temperature, pressure, humidity) which may affect sample/standard volumes or instrument performance. These are regulated within the laboratory and held constant.
- Uncertainty arising from the competence of the analyst. Includes taking correct notes (e.g. weighing readings), correct use of the apparatus (e.g. pipettes), use of the correct reagents (e.g. internal standard), performing the correct calculations of the results, correctly following the validated procedures, correct interpretation of observations in the event of any atypical behaviour.

A very similar budget is constructed in the case of alpha spectrometry. Particularly, the last point of the above list is the same, virtually for all analytical methods. Gross errors (taking notes, using equipment, etc.) can be largely minimised or almost excluded, by proper training of staff. However, for the correct interpretation of observations, the expertise and experience of the radiochemist are absolutely essential.

6. Considerations on traceability

Traceability of measurement results is a crucial requirement for their compatibility and comparability, which is becoming more and more important within the permanently increasing exchange of data throughout the world, affecting issues as diverse as health, legislation or international trade. For this purpose traceability chains from particular measurement results to internationally accepted standards, in last consequence to the SI units, are to be established. This is not always easy, particularly, when chemistry is involved. The pathway to the solution of this problem is usually the use of isotopic spikes or tracers which are assumed to exhibit exactly the same behaviour as the analyte during the overall procedure. This assumption must be thoroughly investigated and proven to be appropriate, again by the careful validation of all steps of the analytical procedure.

In recent scientific thinking, the possibility for isotope dilution mass spectrometry (IDMS) to achieve traceability is widely accepted. IDMS, together with gravimetry, titrimetry and coulometry is considered as having the potential to be a primary method of measurement. In the case of other methods, e.g. alpha spectrometry, this is not the case. However, Table 1
shows the (simplified) step-by-step procedures for both methods. Obviously, there are similarities, particularly in the pre-measurement (i.e. the “chemical”) steps. The establishment of the traceability chain, therefore, does not seem impossible for the latter method.

7. Conclusions

A certain radioanalytical know-how has been established within IRMM’s ACH unit over the last decade. The combination of a versatile separation procedure with compatible sample pre-treatment and detection methods, and the validation of the respective methods, have led to increased capabilities in actinoid analytics (Fig. 4). Without radiochemical treatment, most alpha (and beta) emitters could not be determined. This simple fact already renders the fostering of radiochemistry indispensable.

The radiochemistry applied consists of the development of multiple, different method developments depending on the natures of matrices, analytes and results requested. This is most often a very tedious and time consuming activity, involving a high number of single experiments, of drawbacks, pitfalls and one way streets. However, development is only the initial stage, with far more effort required for the validation process. These facts stand as the reason for making radiochemistry extremely inconvenient.

At the same time, the radiochemist’s expertise is needed throughout this overall process to

- be aware of all technical and scientific details of all steps involved in the analytical procedure,
- recognise the possibilities for pitfalls and compensate for them,
- exclude or minimise analytical errors leading to uncertainties,
- recognise and properly evaluate all contributing uncertainties of type A and particularly type B,
- control the chemistry involved in order to enable the establishment of the traceability chain.

This is the principal reason for making the radiochemistry expert as indispensable as the radiation physicist, the software engineer, the metrologist, the statistician, and often many others, within the multidisciplinary symbiosis required for the reliable application of low level radionuclide measurements.

Table 1
Comparison between the single steps of an isotope dilution mass spectrometric and an alpha spectrometric analysis

<table>
<thead>
<tr>
<th>IDMS</th>
<th>Common to both</th>
<th>AS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition of spike</td>
<td>Sample dissolution</td>
<td>Addition of tracer</td>
</tr>
<tr>
<td></td>
<td>Chemical treatment</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Aliquoting</td>
<td></td>
</tr>
<tr>
<td>Preparation of filament</td>
<td>Measurement of count ratios</td>
<td>Preparation of platelet or filter</td>
</tr>
<tr>
<td>Transformation of cts ratios into mole ratios</td>
<td>Transformation of cts ratios into activity ratios</td>
<td></td>
</tr>
<tr>
<td>Known: number of spike atomsequeation: ( \Rightarrow ) mass concentration of subsample</td>
<td>Known: tracer activity Equation: ( \Rightarrow ) activity concentration of subsample</td>
<td></td>
</tr>
<tr>
<td>( \Rightarrow ) Mass concentration of analyte in sample</td>
<td>Known: mass of subsample</td>
<td>( \Rightarrow ) Activity concentration of analyte in sample</td>
</tr>
</tbody>
</table>

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