Determination of traces of radionuclides by hyphenated techniques coupled to inductively coupled plasma mass spectrometry (ICP-MS)
Determinació de traces de radionúclids emprant tècniques acoblades a l'espectrometria de masses i plasma induït per alta freqüència (ICP-MS)

Laura Aldave de las Heras,[1] Miguel Sandow,[1] Grzegorz Olszewski,[1,2] Daniel Serrano-Purroy,[1] Stefaan van Winckel[1] and Jean-Paul Glatz[1]

[1] European Commission. DG Joint Research Centre. Institute for Transuranium Elements, Karlsruhe, Germany

[2] University of Gdansk. Faculty of Chemistry. Analytics and Environmental Radiochemistry Chair, Gdansk, Poland

Abstract: An overview is given of the current state of the art for the determination of radionuclide traces in the environment and the separation of fission products and actinides in nuclear samples by techniques like flow-injection (FI)/sequential injection analysis (SIA) and chromatography hyphenated to inductively coupled plasma mass spectrometry (ICP-MS).

Keywords: Hyphenation, ICP-MS, radionuclides, ultratraces, actinides.

Resum: En aquest treball es fa una revisió dels aspectes més innovadors de la determinació de traces de radionúclids en el medi ambient i de la separació d'actínids i dels productes de fissió en mostres nuclears mitjançant tècniques com ara la injecció en flux (FI) / anàlisi per injecció seqüencial (SIA) i la cromatografia acoblades a l'espectrometria de masses mitjançant plasma induït per alta freqüència.

Paraules clau: Acoblament, ICP-MS, radionúclids, ultratraces, actínids.

Introduction

The determination of element concentrations at the trace (pg g^{-1}) and ultratrace level (fg g^{-1}) and the precise and accurate determination of isotope ratios of natural and artificial radionuclides are required for many purposes. The fields of application are environmental monitoring and health control, the study of radionuclide migration, age dating, determination of isotope ratios of radiogenic elements in the nuclear industry, quality assurance and determination of fuel material burn-up in nuclear power plants and reprocessing plants, nuclear material accounting and radioactive waste control. A large number of analytical methods have been developed and applied for the determination of natural and anthropogenic radionuclides in environmental and nuclear samples. Nuclear measuring techniques like α, β, γ, and X-ray spectrometry and neutron activation analysis as well as inorganic mass spectrometric methods are currently used.

For the determination of many specific radionuclides, both radiometric and mass spectrometric methods can be used. Se-

lection of the method is directly related to detection limits, analytical accuracy and capacity, and accessibility of the method. In addition, the sample preparation procedure in terms of duration, complexity, counting time, interferences, labour and cost are parameters considered in the choice of the analytical method. Due to the high sensitivity and accuracy and the easy access of radioactive measurement equipment in ordinary radiochemical laboratories, the determination of short-lived radionuclides (t½ < 10 years) and especially of those with γ-ray emissions is carried out only by radiometric methods. Figure 1 plots the specific radioactivity (Bq/g) vs. half-life of some radionuclides of interest in environmental and nuclear applications. As may be seen in figure 1, the shorter the half-life of the radionuclides, the higher their specific radioactivity. This means that compared to a mass spectrometric method, a radiometric method is more sensitive when the radionuclide's half-life is shorter. Radiometric methods are generally more sensitive for short-lived radionuclides, while mass spectrometric methods are more appropriate for long-lived radionuclides. The majority of radionuclides with half-life under 10 years are determined by using radiometric methods alone [1].

Inorganic mass spectrometry and especially inductively coupled plasma mass spectrometry (ICP-MS) as the foremost method today, possess excellent sensitivity, precision and good accuracy for isotope ratio measurements and practically

Contact address: Laura Aldave de las Heras
European Commission. Joint Research Centre. Institute for Transuranium Elements
PO Box 2340 D-76125. Karlsruhe, Germany
Tel.: +49 7247 951 357
E-mail: laura.aldave-de-las-heras@ec.europa.eu

no restrictions on the ionisation potential of the element investigated. Thermal ionisation mass spectrometry (TIMS), which has been used as the foremost analytical technique for precise isotope ratio measurements of long-lived radionuclides for many decades, is being increasingly replaced by ICP-MS. In the last few years, instrumental progress has been achieved in improving figures of merit for determination of isotope ratio measurements of long-lived radionuclides in ICP-MS by the application of a multiple ion collector device (MC-ICP-MS) and the introduction of the collision cell interface. They allow the dissociation of disturbing argon-based molecular ions, the reduction of the kinetic energy of ions and the neutralisation of disturbing noble gas ions (e.g., of $^{129}Xe^+$ for the determination of ^{129}I) [2].

Traditional methods of quantification of radioactive isotopes including radioactivity counting and TIMS call for radiochemical procedures which are often quite sophisticated to remove major and minor components from the sample. These techniques require extensive matrix separation and sample purification methods before unequivocal identification of specific isotopes and their relative abundance is possible. Counting techniques become highly time-consuming when the half-life of the target analyte is very long or the concentration of the analyte low. Atom counting using ICP-MS meets the nuclear industry requirements for many radionuclides and their daughter products. Recent improvements in ICP-MS signal-to-background have resulted in attogram mass detection capability and improved analysis of shorter half-life isotopes (see figure 1).
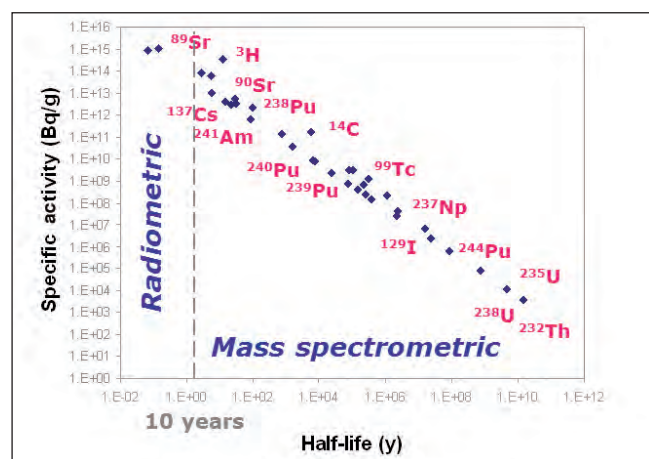
Currently, the most common techniques for trace element analysis and speciation include a combination of a separation technique coupled with a more sensitive detection technique. Earlier, such hyphenated techniques were based on the coupling of a separation of a special sample preparation offline, subsequently adding a detection technique. At present, the online coupling of the two techniques is more common. These hyphenated techniques provide a shorter analysis time, a higher degree of automation and sample throughput, better reproducibility, a reduction of contamination because they are closed systems, and an enhanced combined selectivity and therefore higher degree of information. Hyphenated techniques involving ICP-MS are among the fastest growing research and application areas in atomic spectroscopy. This is because ICP-MS on its own does not provide information on the chemical or structural form of the analytes present since all forms of the analytes are converted to positively charged atomic ions in the plasma. However, it is an excellent elemental analyser that performs well as a detector for chromatography. Hyphenated ICP-MS is achieved through the coupling of the ICP-MS to a separation technique, which is usually a chromatographic separation. In this way, target analytes are separated into their constituent chemical forms or oxidation states before elemental analysis (see figure 2). The most common separation techniques are gas chromatography (GC) and high-performance liquid chromatography (HPLC), which includes ion chromatography (IC), but other separation techniques such as capillary electrophoresis (CE) and field flow fractionation (FFF) are also used.

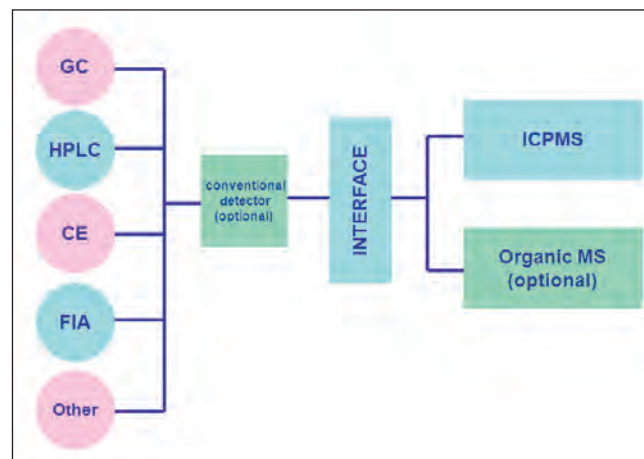FIGURE 1. Radiometric versus mass spectrometric methods.

FIGURE 2. Scheme of a generic hyphenated system.

In our laboratory different separation techniques have been coupled online with an ICP-MS for the analysis of radionuclides in environmental and nuclear samples [3-8]. This paper points out the importance of the use of separation techniques for the determination of fission products and actinides applied to nuclear and environmental samples. Special importance is attributed to online chromatography ICP-MS coupling, which has become a valuable tool for determining radionuclides.

Results and discussion

Simultaneous and sequential actinide separation and preconcentration at ultra-low (fg g^{-1}) concentrations

In standard methods for the determination of actinides in very low concentrations, the target radionuclides have to be preconcentrated and separated before measurement because of their low activities in environmental samples and the presence of interfering elements and radionuclides. Actinide separations are required since a number of major actinide isotopes have unresolved alpha energies (e.g., ^{241}Am/^{238}Pu). The determination of all actinide elements by mass spectrometry is hindered by several isobaric interferences, namely those isotopes of various elements with the same mass number, which cannot be corrected (e.g., ^{241}Am/^{241}Pu, ^{238}U/^{238}Pu). Figure 3 sums up the potential polyatomic and isobaric interferences on actinide masses.

Polyatomic interferences like uranium isotope hydrides (^{238}UH$^+$ and ^{235}UH$^+$), which are relevant for the determination of ^{239}Pu and ^{236}U at ultra-low concentrations, can be minimised by using different types of nebulisers (cross flow, MicroMist,
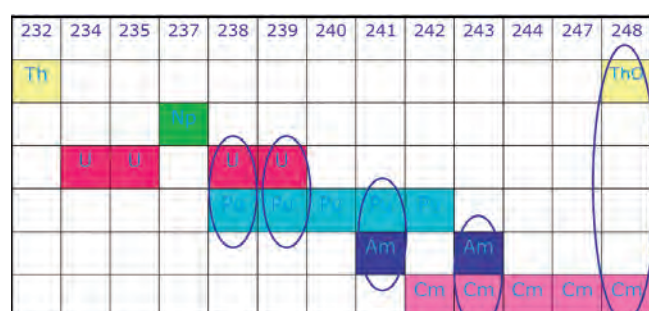
Aridus, and APEX). Moreover, some of these long-lived radionuclides occur at extremely low concentrations, especially in environmental samples. Matrix separation and/or preconcentration, which are performed offline or online, is needed to avoid possible isobaric interferences and matrix effects and to reduce detection limits. A procedure for the simultaneous and sequential separation and determination of major and minor actinides based on extraction chromatography coupled to an ICP-MS has been developed. Classical radiochemical separation for actinide separation by α-spectrometry is replaced by three consecutive chromatographic columns connected and coupled to an ICP-MS detector (figure 4).

This new approach allows the effective reduction of the laboratory time associated with each analysis, the reduction of the cost per analysis and the minimisation of the waste produced in the laboratory. The chromatographic phases that are used consist of actinide-specific extraction on commercially available resins (TRU, TEVA and UTEVA resins, Eichrom Industries, Inc., USA). TRU, TEVA and UTEVA resins can be used for a number of analytical purposes. In this method, they are applied for the separation of the actinides as a group from a sample matrix (based on the valence state), for the individual separation of Am/Cm and Pu from other actinides; and possibly the sequential separation of individual actinides on a single column. Actinides in 2.5 mol l^{-1} HNO$_3$ are sequentially retained depending on their oxidation state. In the load phase, tetravalent (Th, Np, Pu), hexavalent (U) and trivalent (Am, Cm) actinides are retained respectively in TEVA, UTEVA and TRU columns connected in tandem (see figure 4). The elution pro-

FIGURE 3. Potential polyatomic and isobaric interferences on actinide masses in mass spectrometry.
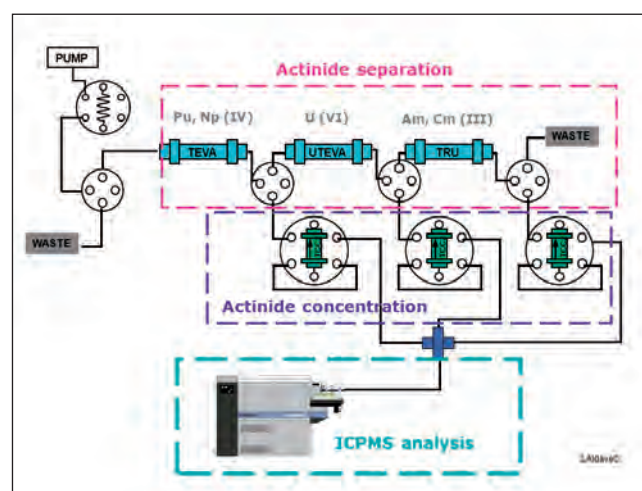

FIGURE 4. Complete chromatographic system coupled to ICP-MS for the determination of actinides at ultra low concentrations.

file for all the actinides obtained with an ICP-MS coupled on-line to the three columns is given in figure 5. By using this arrangement, good detection limits are achieved for long-lived radionuclides. However typical α-spectrometry detection limits are not reached (10^{-3}-10^{-4} Bq/ml). The use of an IonPac Cation Concentrator Column (TCC-2) as an additional concentration step is necessary to improve detection limits. In the concentration phase, the actinide analytes are eluted from each analytical column and loaded into their respective cation concentration column. Subsequently, the actinide analytes are backpressure-eluted from each cation concentration column to the ICP-MS with an APEX spray chamber (Elemental Scientific) for their determination. The use of cation concentration columns before ICP-MS determination allows the improvement of the shape and width of the chromatographic peaks that are collected (see figure 5), enhancing the sensitivity and detection limits of the method down to the fg g^{-1} level. The use of extraction chromatography coupled to an ICP-MS system reduces considerably the analysis time, enabling the complete determination of the six actinides in about 2 hours with detection limits similar to those obtained by α-spectrometry, which can take several weeks.

Fast analysis of some radionuclides by flow-injection (FI)/sequential injection analysis (SIA). Determination of ^{90}Sr at ultratrace levels

Flow-injection (FI)/sequential injection analysis (SIA) has been widely used for the determination of trace elements since its introduction in 1975 [9] and has made significant progress not only in terms of efficiency but also in reliability, speed and robustness [10]. However, this technique was not applied for the determination of radionuclides until 1996 [11]. With the demands for rapid analysis of radionuclides for emergency purposes and the increased application of ICP-MS, the automated analysis of radionuclides by hyphenation of flow injection/sequential injection for online separation with ICP-MS measurement has become more attractive for waste and environmental radioactivity analysis. Automated analysis using FI online separation is usually composed of a multi-port valve, an eluent distributor which can divert a solution in a different direction, a peristaltic pump, and one or more chromatographic columns. The operation of the system is controlled by a PC and an automated autosampler. Figure 6
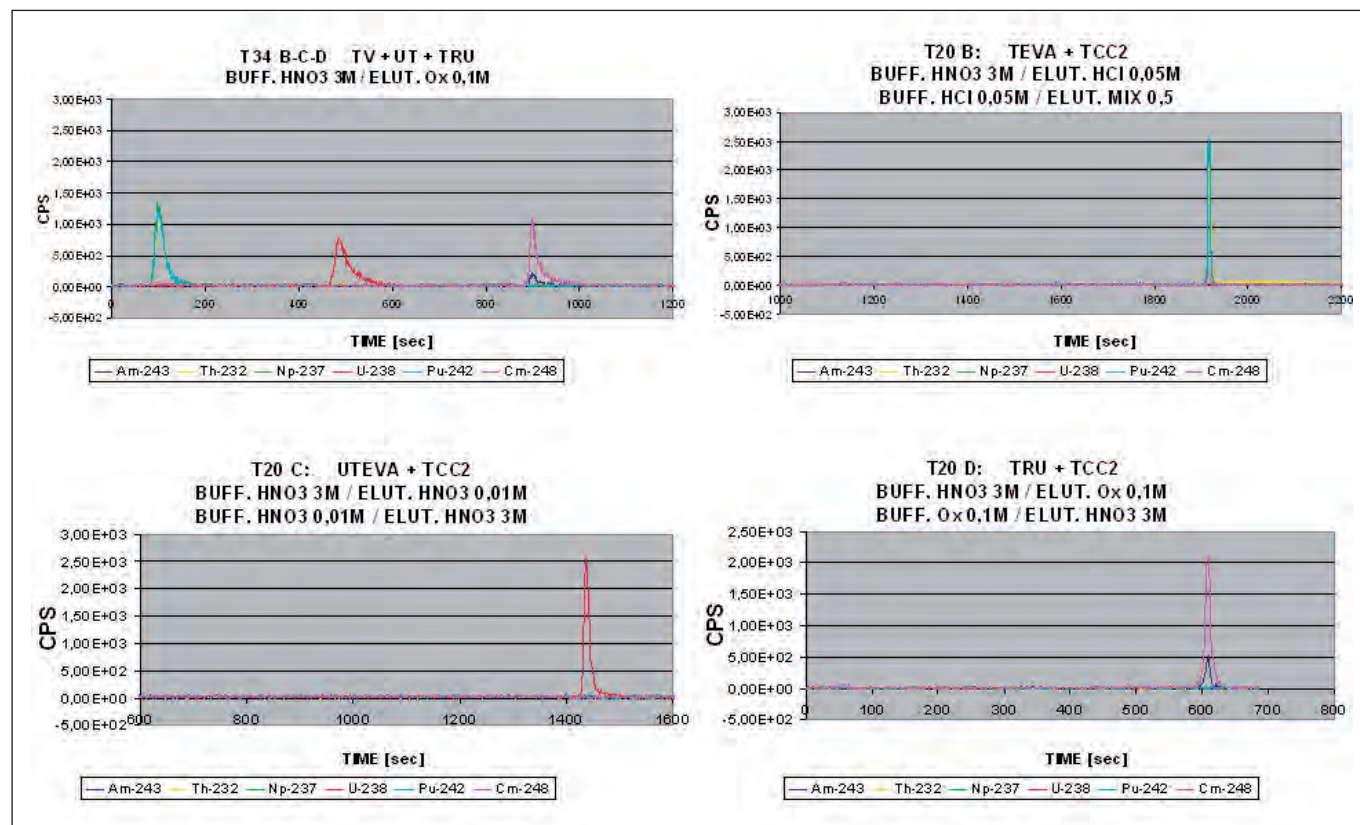

FIGURE 5. Actinide elution profiles on TEVA, UTEVA and TRU columns.

shows a schematic diagram of this system. The prepared sample in a suitable solution is first loaded to a loop, which is then loaded to the column. The column is subsequently washed with a different eluent to remove the interfering elements and radionuclides. The target radionuclide is finally eluted from the column, which can be introduced directly into the detector or gathered by a fractionation collector for measurement later. The main advantages of the sequential injection system compared to the traditional separation method include: 1) rapid separation, 2) direct connection to the ICP-MS for measurement, 3) automated operation, 4) lower consumption of chemical reagents, 5) less cross contamination, and 6) lower risk of exposure of chemicals. In recent years, this method has been used for the determination of fission products and actinides.

Radionuclide strontium (^{90}Sr) has been released into the environment by global fallout following atmospheric nuclear explosions, by nuclear waste discharges and by fallout from nuclear accidents. In environmental monitoring, it is desirable to detect radionuclides at very low levels. This helps to establish a baseline value that can be used to evaluate the impact of an accidental release of radionuclides into the environment. In addition, the ability to determine their activity at low environmental levels should help to achieve a more accurate estimate of the dose received by the population.

In most analytical procedures and for a large number of samples in radioecological, environmental and oceanographic

studies, the determination of ^{90}Sr involves inefficient, time-consuming and expensive steps. In fact, to achieve low detection limits, large samples are generally required in conjunction with long counting times. Most radiochemical separations are designed around the concept of minimising the presence of spectral interferences and improving detection via sample pre-concentration.

Beta counting, liquid scintillation counting and Cherenov counting are the most common analytical techniques for determination of ^{90}Sr. However, radiometric determination of ^{90}Sr is hindered by its low energy beta emission, slow decay rate and interferences from others beta-emitters, particularly its daughter isotope ^{90}Y. Furthermore, accurate beta counting requires the separation of ^{90}Sr from other beta-emitter isotopes, followed by ingrowth of ^{90}Y (half-life 2.7 days), until secular equilibrium is reached (2-3 weeks), and a sufficiently long counting time to achieve acceptable measurement precision. The determination of ^{90}Sr in environmental samples by ICP-MS faces a different set of analytical challenges from those associated with beta counting. Depending on the matrix composition of the sample, isobaric interferences by molecular or atomic ions can be expected at m/z 90, decreasing the accuracy of the ICP-MS determination of ^{90}Sr. Complete removal of the stable isobar ^{90}Zr to below background intensity is necessary to quantify ^{90}Sr. Low instrumental detection limits (< pg g^{-1}) are required because the high natural abundance of stable Sr present in environmental samples limits pre-concentration possibilities. High concentrations of stable Sr in the final sample solution requires a sufficient abundance sensitivity to resolve the peak tail of ^{88}Sr. Both Zr and Sr are usually over six orders of magnitude more abundant than ^{90}Sr. In case of a radiological emergency where a faster response is needed, or environmental monitoring where a large number of samples have to be analysed, a more rapid, efficient and reproducible method is required. Mass spectrometric determination of ^{90}Sr becomes advantageous due to its short analysis time. In addition, the concentration of ^{90}Y is negligible even at secular equilibrium and does not interfere with the determination of ^{90}Sr.

A fast sensitive method for determining ^{90}Sr at trace levels in ground water, seawater and diluted nuclear spent fuel leachates by ICP-MS coupled to an automated flow injection system has been developed. This method uses an automated online system (see figure 6) for the determination of ^{90}Sr at
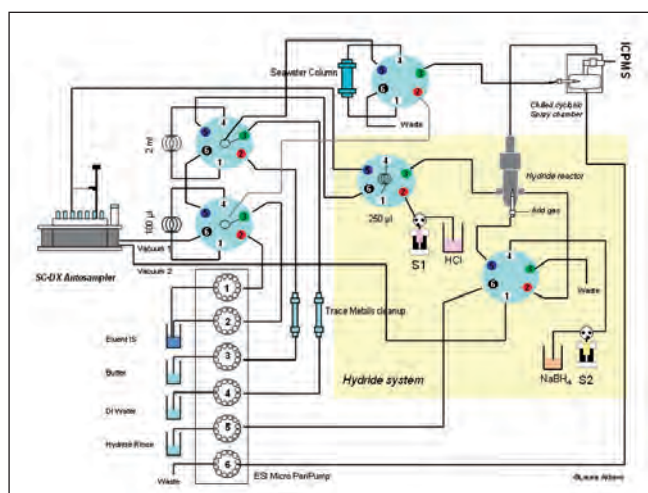

FIGURE 6. Sequential flow injection analysis system than can be used in direct, preconcentration and hydride mode. Analytical columns are chosen as function of the radionuclide to be determined.

ultratrace levels in natural samples by ICP-MS. The *FAST* system uses two high purity valves to take up an aliquot of sample and to retain and concentrate Sr, removing the matrix on a PFA column packed with Sr®-Spec resin. The preconcentrated Sr is eluted by backpressure into a PFA nebuliser attached to the ICP-MS spray chamber. Standard and matrix-matched aqueous standard solutions in 4 mol l^{-1} HNO$_3$ are vacuum loaded into a 250 µL sample loop on the *FAST* valve. The *FAST* valve switches to inject the sample into the column. The Sr®-Spec resin retains the Sr while the matrix is washed out of the column for 3 minutes with 4 mol l^{-1} HNO$_3$. After the matrix has been removed from the column, the second valve is switched, allowing Miliq water to pass through the column to elute the ^{90}Sr as a transient peak. The sensitivity of this peak and the concentration of ^{90}Sr in the samples are measured and calculated by the ICP-MS software. Once the ^{90}Sr has been eluted from the column, the second valve is switched to recondition the column before the next analysis. The total run time is less than 10 minutes sample-to-sample.

In figure 7 the elution profiles obtained for solutions of 4 mol l^{-1} HNO$_3$ containing 1, 2.5, 4 and 5 pg g^{-1} of ^{90}Sr are reported. As may be seen, ^{90}Sr is eluted in a total time of 120 s. A calibration curve is obtained by applying the peak area of ^{90}Sr versus the total ^{90}Sr concentration. Linear regression is calculated by the least squares linear regression method. A fit for
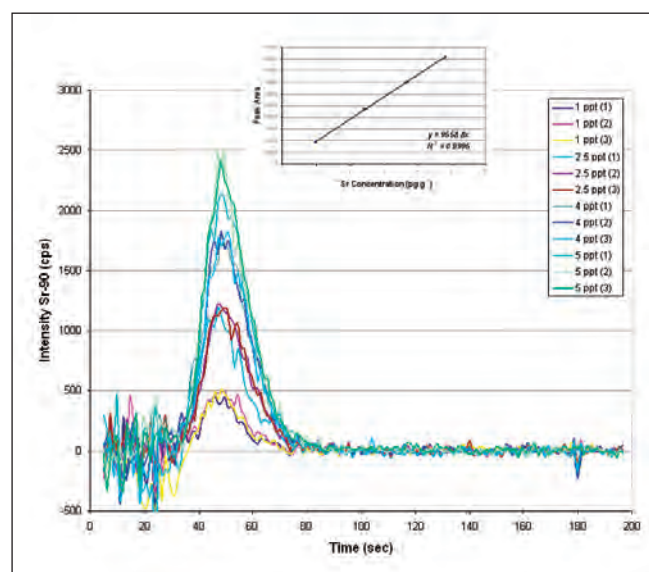
purpose curve is obtained which does not introduce an additional uncertainty component.

The detection limit of ^{90}Sr is calculated by means of repeated measurements of the blank, according to Currie [12]. The detection limit is 36.4 fg g^{-1} (0.2 Bq g^{-1}), taking into account that the injection volume is 250 µl, which represents an absolute amount of 9 fg (46 mBq) of ^{90}Sr. The repeatability of the method, based on the relative standard deviation of the peak area calculated on the basis of three repetitions, is always less than 1% at this concentration interval.

Conclusions

The application of hyphenated techniques, principally flow-injection (FI)/sequential injection analysis (SIA) and chromatography coupled to ICP-MS, has been found very useful for determining trace radionuclides in environmental or nuclear samples. Different types of columns can be coupled online, allowing the trace radionuclides of interest to be determined. Tedious and time-consuming chemical separation procedures can be avoided. With the demands for rapid analysis of radionuclides for emergency purposes and the increased application of ICP-MS, the automated analysis of radionuclides by hyphenation of flow injection/sequential injection or chromatography for online separation with ICP-MS measurement has become more attractive for waste and environmental radioactivity analysis.

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FIGURE 7. ^{90}Sr elution chromatograms of solutions containing 1, 2.5, 4 and 5 pg g^{-1} of ^{90}Sr and calibration curve.

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L. Aldave

Dr Laura Aldave de las Heras obtained her PhD in Chemistry at the Autonomous University of Madrid. Since 1998 she has been working for the European Commission at the Joint Research Centre of the Institute of Transuranium Elements (ITU). Dr Aldave is an expert on the development of analytical methods for the detection of trace and ultratrace elements in nuclear materials and environmental samples, mainly using mass spectrometry and radiometric methods. Dr Aldave is specialised in hyphenated techniques involving the use of ICP-MS both in collision/reaction cells and with high-resolution equipment.