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Review

Use of ion chromatography for the determination of fission products and actinides in nuclear applications

Maria Betti

European Commission, JRC, Institute for Transuranium Elements, Postfach 2340, 76125 Karlsruhe, Germany

Abstract

The application of ion chromatography (IC) for the determination of trace radioisotopes and ion impurities, as well as for the separation of fission products and actinides in applications of nuclear concern is reviewed. Particular attention is given to the on-line coupling of IC with nuclear and non-nuclear detection modes. Recent results obtained employing a coupled IC–inductively coupled plasma mass spectrometry (ICP-MS) for the characterization of the complete inventory of fission products and actinides in spent nuclear fuel and high-level liquid waste samples are discussed in terms of isobaric interference elimination and isotope determination. © 1997 Elsevier Science B.V.

Keywords: Reviews; Nuclear applications; Actinides; Fission products

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1. Introduction

Ion chromatography (IC) is a versatile, selective and sensitive method for the determination of a variety of anions and cations at trace and ultra trace

levels. It has been applied to numerous problems in various fields involving ionic analysis in clinical, food, pharmaceutical, industrial, plating solution and environmental samples [1–6]. Perhaps the major reason for the rapid growth in popularity of IC is its

usefulness in the environmental field. The enhanced separating powers of the method also permits speciation.

In the last decade theoretical and practical development of IC for the analysis of metal ions and rare earths have been achieved mainly by the exploitation of metal complexation [1–4,7–9]. The complexation reactions can take place in either the mobile or stationary phase and sometimes simultaneously in both. Chromatographic separation of complexes formed before chromatography and detection by post-column complex-forming reactions are also within the scope of complexation IC.

Cation-exchange ion chromatography is the most obvious and therefore the most common method for the determination of metal ions and rare earths. Silica [10,11] or polymer-based sulphonated [12] ion-exchange stationary phases can give selective and efficient separation of polyvalent metal ions if complexant agents are added to the eluent media. The effect of the complexant is to decrease in a differentiated way the effective charge of the metal ions and, therefore, the retention on the stationary phase. When chelating chemically bonded phases (such as iminodiacetic acid functional silica-bonded material [13]) are employed instead of a cation exchangers, reactions of complexation on the stationary phase take place and are responsible for the separation.

Another promising method for the ion chromatographic separation of rare earths is their pre-column conversion into negatively charged chelates and successive anion-exchange chromatographic separation [14]. The separation of the same type of metal chelates on dynamically coated anion-exchange columns, i.e., in the ion-pairing mode, introduces additional possibilities for the improving the resolution.

The ability of ion chromatographic separation for the rare earths has increased, in the last few years, the interest in its application to the characterization of samples of nuclear concern. In particular, for the determination of 'non-gamma'-emitting radionuclides.

In our laboratory an ion chromatographic system has been on-line coupled with an inductively coupled plasma mass spectrometer (ICP-MS) [15] used for the characterization of nuclear samples [16–18] for more than 6 years. This review points out the

importance of the use of ion chromatographic separation for the determination of traces, fission products and actinides applied to samples of nuclear concern. Particular relevance is given to the coupling on-line of the IC with an ICP-MS detector, which has become a valuable tool for the determination of long-lived radionuclides.

2. Results and discussion

2.1. Determination of radionuclides and ion traces in a water reactor coolant

The determination of individual radionuclides in water reactor coolant and associated waste, effluents, and environmental samples is an important component of safeguards at nuclear power plants. Gamma-spectroscopy can be efficiently and accurately employed for radionuclides emitting gamma rays. Other radionuclides, such as 'non-gamma' emitters, like the pure beta emitters, e.g., ^{14}C , ^{63}Ni , $^{89,90}\text{Sr}$, ^{99}Tc and ^{129}I , radionuclides that decay by electron capture, e.g., ^{55}Fe and ^{59}Ni , and many transuranics and other actinides, have been determined by radiochemical methods. The separation procedures can be very tedious and time consuming. Some authors [19], have proposed the coupling of IC and on-line liquid scintillation counting for the analysis of the non-gamma-emitting radionuclides as an alternative to the traditional separation techniques. Modern high-performance chromatography systems with automated special features appear to be well suited to the problem of separating the small molar quantities of radionuclides in typical samples. Liquid scintillation counting is attractive because it offers high detection efficiencies for both α particles (ca. 100%) and β particles (>90% for $E_{\text{max}} > 156$ keV) and can detect X- and γ -rays, although at lower efficiencies.

The so called ANABET (Bradtec-US, Roswell, GA) system has been extensively employed and investigated [20]. It consists of an ion chromatographic and a flow-cell scintillation counter along with a software package and proprietary eluents for the analysis of both cations and anions in aqueous solutions. Ionic radionuclides, in aqueous solutions, are concentrated on an ion-exchange pre-concentration column and subsequently removed to a

separation column with the appropriate eluents to achieve the elemental separation of the different radioisotopes. The effluent stream then passes through a flow-cell scintillation counter which detects the analytes. In this way prolonged sample handling can be avoided and the monitoring of the radioisotopes in the sample can also be performed continuously. The ANABET elution program was originally developed specifically for anionic (e.g., ^{14}C , ^{99}Tc , ^{129}I) and cationic (e.g. ^{55}Fe , ^{60}Co , ^{63}Ni , $^{89,90}\text{Sr}$, ^{90}Y and $^{134,137}\text{Cs}$) activation/fission products. Recently, a program for separation of actinides has been also made available. The separations were found to be consistent and reliable with reproducible elution times and resolution. Detector response was found to be linear from approximately 4–2000 Bq (100–80 000 pCi) and the detection limits ranged from approximately 4 Bq (100 pCi) for α emitters and high-energy β emitters to 40 Bq (1000 pCi) for low-energy β -emitters. Corresponding minimum detectable concentrations (MDCs), based on 1-l samples, were on the order of 4–40 kBq m^{-3} (10^{-7} to 10^{-6} $\mu\text{Ci}/\text{ml}$).

The ANABET system works well when applied to aqueous samples containing few potential radiological or chemical interferences. However, when the actinide separations program was tested on simulated and actual surface water samples, interferences were observed due to sulfate and humic acid. Thus, the applicability of the technique to actual reactor-related samples, which could contain a variety of potential chemical and radiological interferences, is an open question that needs to be studied. The ANABET system has been extensively studied [20] with regard to its application for the monitoring of a reactor coolant from a pressurized water reactor (PWR). The chemical and radiological interferences that would be encountered in a PWR coolant have been investigated. The detection efficiency as a function of β particle endpoint energy was determined and the detection limits for ^{14}C , ^{55}Fe , ^{63}Ni , ^{90}Sr , ^{99}Tc and ^{129}I estimated. Moreover, the potential chemical and radiological interferences on the cation radionuclides ^{55}Fe , ^{63}Ni , $^{89,90}\text{Sr}$, ^{90}Y were identified.

During the past decade, IC has been the primary analytical method for monitoring trace ionic impurities such as chloride, sulfate, organic acid and, recently, manganese in a power water plant [21,22].

The on-line monitoring of soluble manganese can be used as an indicator of feed water corrosion product transport in nuclear power plants [22], and the required detection limit and limit of quantification must be 5 and 50 pg/ml, respectively. In order to achieve these limits, a method based on IC has been recently proposed for the on-line monitoring of manganese [23]: the concentration of the sample on a chelating resin selective for manganese. Separation is then accomplished on a carboxylate ion-exchange stationary phase which allows elution of Mn and other alkali metal and alkaline earth cations with a simple acid eluent. The detection mode involves post-column derivatization followed by visible detection to obtain pg/ml Mn detection limits. The use of a cation suppressor after the separator column and before the post-column system allowed the use of a weak complexing agent to improve manganese separation from other interfering transition metals. The detection limit obtained for manganese in ammonium matrix is approximately 2 pg/ml and the limit of quantification is 10 pg/ml with 100-ml samples.

2.2. Separation of fission products

The determination of the complete fission product inventory by mass spectrometry is hindered by several isobaric interferences (namely those isotopes of different elements having the same mass number) that cannot be corrected for. These isobaric interferences arise from β -decay of the short- and medium-lived radionuclides (e.g., ^{147}Pm , half-life 2.62 years, which decays to ^{147}Sm), from neutron capture reactions during fuel irradiation (e.g., ^{149}Sm forms ^{150}Sm by neutron capture and the latter interferes with ^{150}Nd formed directly by fission) or from the presence of natural elements (e.g., in the analysis of vitrified waste or contaminated environmental samples ^{135}Cs is subject to interference by naturally occurring ^{135}Ba). The elimination of the above mentioned isobaric interferences requires a chemical separation of the interfering nuclides. IC on-line coupled to the detector, can be chosen to perform such a separation, avoiding tedious and time-consuming procedures [15,33].

In the last few years ICP-MS has been increasingly applied for the determination of long-lived radio-

isotopes in irradiated samples [37–39], and its coupling with IC can be a good choice for the elimination of isobaric interferences in the determination of fission products and actinides in samples of nuclear concern. Fig. 1 shows a diagram of the system described in detail elsewhere [12,40], installed in a glove-box for the handling of active and/or contaminated samples. The chromatographic pump (Dionex 4500i) is situated outside the glove-box, but the chromatographic column as well as the injection valve are located inside.

2.2.1. Separation of ^{90}Sr

The biologically hazardous radionuclide ^{90}Sr , produced in nuclear fission, was released into the environment during the nuclear weapons testing in the 1950s and 1960s and, more recently, as a result of the accident at Chernobyl in 1986. Once in the environment it can easily and quickly enter the food chain and be rapidly incorporated into the inorganic matrix of bone mass, as its chemical behavior is similar to calcium. Strontium-90 is a pure β -emitter and in 28.8 years decays to ^{90}Y that, in turn, in 64.1 h produces the stable ^{90}Zr . For the determination of ^{90}Sr , very complicated chemical separations from ^{90}Y are necessary before β -counting.

The classical method for ^{90}Sr involves the precipitation of strontium nitrate from fuming nitric acid solution, followed by subsequent ingrowth and separation of the ^{90}Y daughter [24,25]. Other methods based on liquid–liquid extraction [26,27], ion-exchange [28] and chromatography [29,30] have been proposed. More recently analytical methods based on IC have been also reported [31,32]. Both methods use IC as the separation step prior to subsequent β -counting.

Yttrium-90 could be extracted from the sample solution on to a Dionex Metpac CC-1 column containing a high-capacity iminodiacetate resin. This resin, under specific pH conditions retains transition metals and rare earths, whilst having a low affinity for alkali and alkaline earth metals, which can be easily removed from the resin by elution with ammonium acetate [31]. The retained metals can be then eluted from the resin in dilute nitric acid for further separation. The separation of transition metals and rare earths is achieved by complexation IC. In particular for rare earths and ^{90}Y , an oxalate–

diglycolate eluent is proposed for their separation on a mixed-bed anion–cation-exchange column (CS5, Dionex). Others have exploited a pure cation-exchange mechanism [32] using a CS3 (Dionex) column for the separation of $^{90}\text{Sr}^{2+}$ in nuclear fuel reprocessing samples.

A method based on an on-line coupling of a chromatographic system with inductively coupled plasma mass spectrometry as detector [15] has also been employed for the separation of Sr from Y and other fission products in spent nuclear fuel solutions. The separation was performed on a CS10 column [16], using as eluent 1 M nitric acid. Under these conditions, the elution order for the fission products is Rb, Cs, Sr and Y. The resolution between Rb and Sr and the differences in isotope abundances from the natural elements allows natural elements to be used as spikes for the isotope dilution procedure. The determination of Y, which has only one stable isotope, was performed with the method of the standard addition. The separation of ^{90}Sr from ^{90}Zr was also achieved by using this method. In Fig. 2 an example of a such separation in a spent nuclear fuel solution is given.

2.2.2. Separation of Cs and Ba

Caesium-137 is readily detected in the environmental samples but its origin cannot normally be attributed to reactor operations or to atmospheric weapons tests. It may be possible to use ^{137}Cs to ^{135}Cs ratio as an indicator as to the source of radioactivity in the environment. The mass 135 isobaric chain has a 6.7-h ^{135}I precursor for the formation of ^{135}Xe which shunts the chain by n,γ reaction to ^{136}Xe . In a weapons device, if significant chemical fractionation does not take place, relatively more ^{135}Cs should be formed since there is very little ^{135}Xe present at the time of high neutron flux. Therefore unfractionated weapons material should have a relatively low ^{137}Cs to ^{135}Cs ratio. Correspondingly, the long exposure to neutron fluxes in a reactor should burn most of the ^{135}Xe and decrease the ^{135}Cs yield. Measurements of environmental samples could confirm this prediction. While ^{135}Cs is difficult to measure by radiochemical methods because of its long half-life and low-energy β -decay, modern ICP-MS instruments have reported detection limits of pg/ml for Cs. Moreover a separation

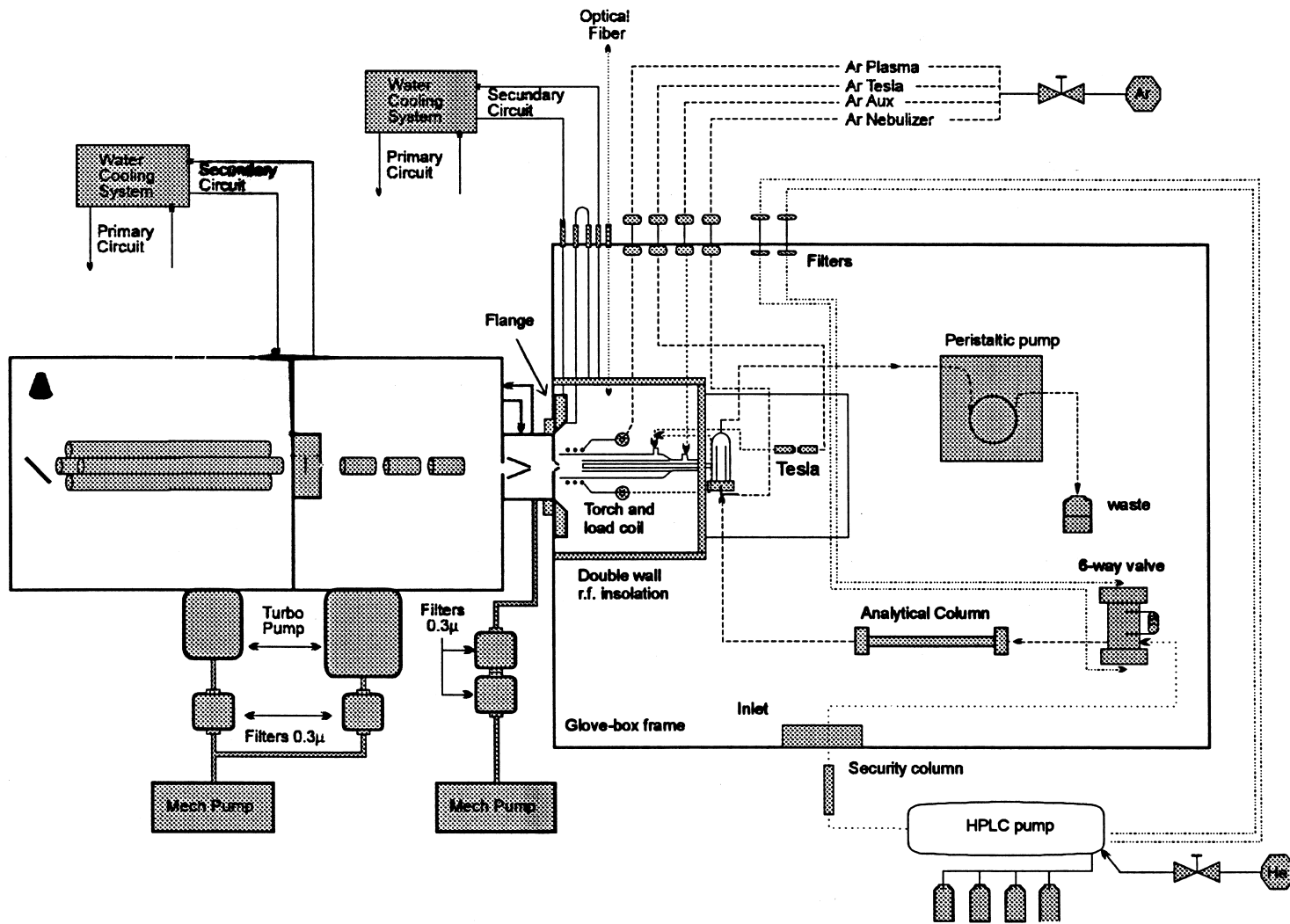


Fig. 1. Schematization of the IC on-line coupling with ICP-MS for the handling of active and/or contaminated samples.

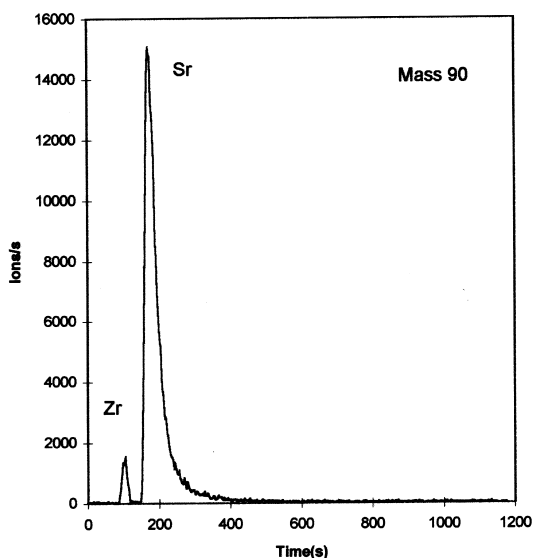


Fig. 2. IC separation for Sr and Zr at mass 90.

procedure to remove isobaric interferences from natural ^{135}Ba is required for the identification and the quantification of ^{135}Cs .

Exploiting the coupling of IC–ICP–MS, the separation of Cs and Ba has been carried out on-line to measure the concentration of radioactive Cs isotopes

(134, 135 and 137) in the presence of the Ba decay products or natural Ba isotopes. The separation of these two elements can be easily performed using cation-exchange chromatography exploiting their different valence state. Using a Dionex CS3 cation-exchange column and 1 M nitric acid as eluent, a complete separation and elution of both the analytes could be obtained in 10 min [17]. In Fig. 3 an example of the separation of Cs/Ba for the mass 137 is shown. As can be seen, the monovalent Cs elutes first and at the same time the other masses, 134 and 135, are also found. Moreover, its isotopes can be quantified by means of the technique of isotope dilution analysis, spiking the sample with natural Cs.

2.2.3. Separation of lanthanides (Ln)

The lanthanides La, Ce, Pr, Nd, Pm, Sm, Eu, and Gd are fission products that are found in spent fuel solutions and can easily be detected by mass spectrometric techniques instead of radiometric methods. However, their determination is also affected, as already mentioned, by isobaric interferences and separations have to be performed before instrumental mass spectrometric measurements can be performed. Also for this class of elements, the IC separation has been investigated and successfully applied [15,33,34].

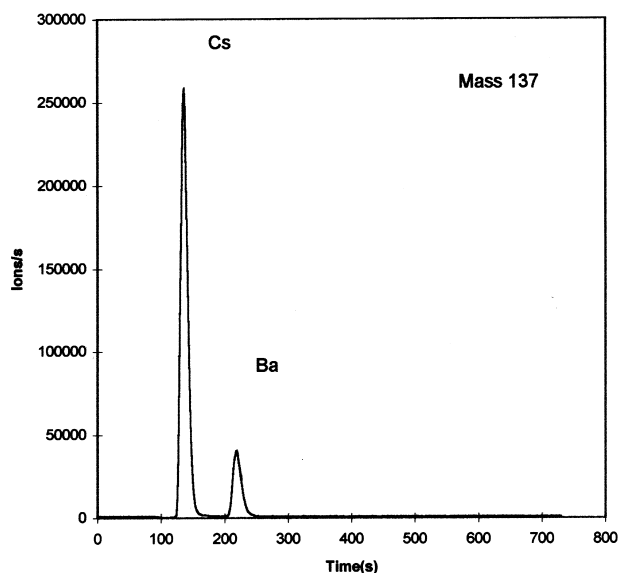


Fig. 3. IC separation for Cs and Ba at mass 137.

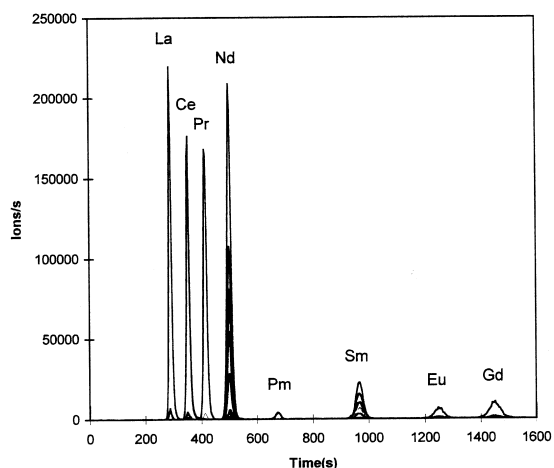


Fig. 4. IC separation for lanthanides in a spent nuclear fuel solution (Ref. [17]).

For the separation of lanthanide elements a method based on the use of 0.1 M oxalic acid in 0.19 M LiOH [33] as eluent on a Dionex CS5 mixed-bed column has been applied to spent fuel solutions [16,17]. Using inductively coupled plasma (ICP-MS) as the detector, the fission product mass ranges from 139 to 160 a.m.u. can be scanned. The elution order observed is La, Ce, Pr, Nd, Pm, Sm, Eu and Gd, as expected on the basis of the separation mechanism

exploited, with increasing atomic number and is accomplished in 25 min. In Fig. 4 the chromatogram obtained for the elution of lanthanides from a spent nuclear fuel sample is shown. All the isobaric interferences present in the original sample between Ce and Nd, Nd and Sm, Pm and Sm, and Sm, Eu and Gd were resolved. Moreover, the oxide polyatomic ions from ^{139}La , ^{140}Ce , ^{141}Pr and ^{142}Ce , which interfere with most of the Gd isotopes measured are observed in the chromatogram at the retention time corresponding to the metal. Fig. 5 shows the separation obtained at mass 154 for the relevant isotopes of Sm, Eu, and Gd. As can be seen, even for low signals the peak shape is well defined. The isobars at mass 142 of Ce and Nd are also very well separated and their peaks do not present any tails (Fig. 6). The separation obtained between ^{148}Nd and ^{148}Sm can be exploited for the measurement of the ^{148}Nd concentration from which the fuel burn-up can be determined.

2.3. Separation of actinides (An)

Separation of actinide ions such as NpO_2^+ , Pu^{4+} , Am^{3+} and Cm^{3+} is particularly important to reduce the long-term potential hazards of high-level liquid

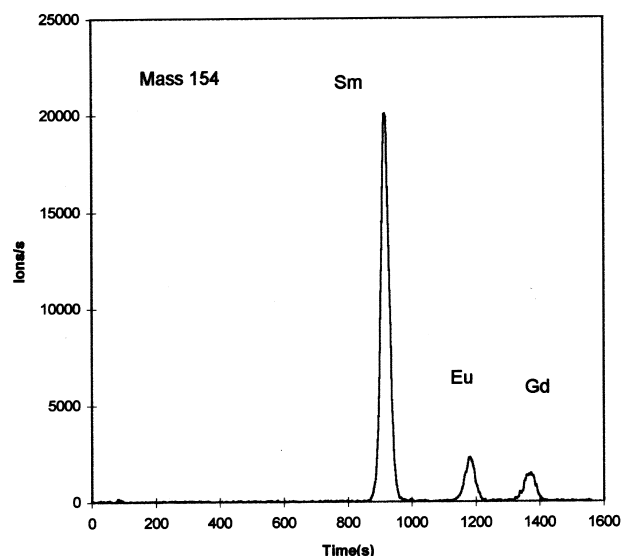


Fig. 5. IC separation for Sm, Eu and Gd at mass 154.

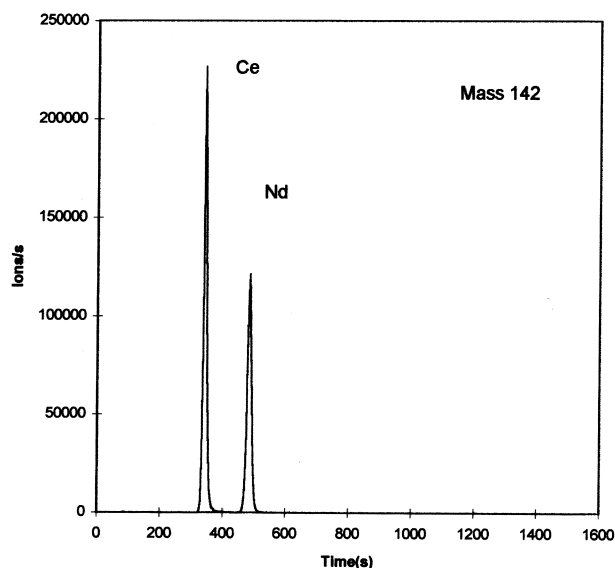


Fig. 6. IC separation for Ce and Nd at mass 142.

waste (HLW). Since the chemical properties of trivalent actinides (An) are very close to those of lanthanides (Ln), it is difficult to separate An from a large amount of Ln [35]. Solvent extraction and ion-exchange methods with the aid of complexing agents have generally been used for mutual separation [36] and different inorganic exchangers have also been synthesized [18].

Using a method based on IC-ICP-MS [17], the actinides could be selectively separated from the Ln by elution on cation-exchangers [16–18] where actinides are not retained. Moreover, a chromatographic separation among the actinides themselves was performed.

The separation of actinides has to be carried out in order to eliminate isobaric interferences at masses 238 (U–Pu), 241 (Pu–Am) and 244 (Pu–Cm). The peak at mass 237, corresponding to the Np could be subjected to interference by a large excess of ^{238}U in the spent fuel and in HLW samples.

The dissolution of spent fuel or reprocessing sample specimens in nitric acid can give rise to different species of actinide elements: Cm and Am basically will form An^{3+} ions; U will give UO_2^{2+} and Np NpO_2^+ ions; Pu is found in four different oxidation states, of which the most stable is Pu^{4+} . For the separation of An the use of a mixed-bed

column, such the Dionex CS5 used for Ln separation, was found to be inadequate [17]. The use of a pure cation-exchanger, such as the Dionex CS3 column, gave better resolution for the separation of Np and U, but the Pu was uncompletely resolved. Further, the Dionex CS10 column, which has a high capacity and high efficiency was investigated in detail, and successfully employed for An separations [16,18].

In Fig. 7 the separation obtained between Np, Pu and U in two samples containing 10 ng/ml (a) and 50 (b) ng/ml of the three elements is reported. The chromatographic separation was obtained on a CS10 column simply using nitric acid as eluent. In Fig. 8 the separation has been performed on an environmental sample to detect traces of Pu in the presence of a high amount of U. As can be seen, Np also was present in the sample. The masses 235 and 238 for the U and 239 and 240 for Pu are clearly visible in the figure. Pu could be quantified by isotopic dilution analysis, spiking the sample with ^{244}Pu .

In Fig. 9 Fig. 10 the separation obtained at mass 241 and 238 for the isobars of Pu and Am, and Pu and U are given. In less than 4 min ^{238}Pu and ^{238}U can be efficiently separated by pure cationic exchange (in this example the CS10 column has been used) at low concentration levels. In only 10 min the

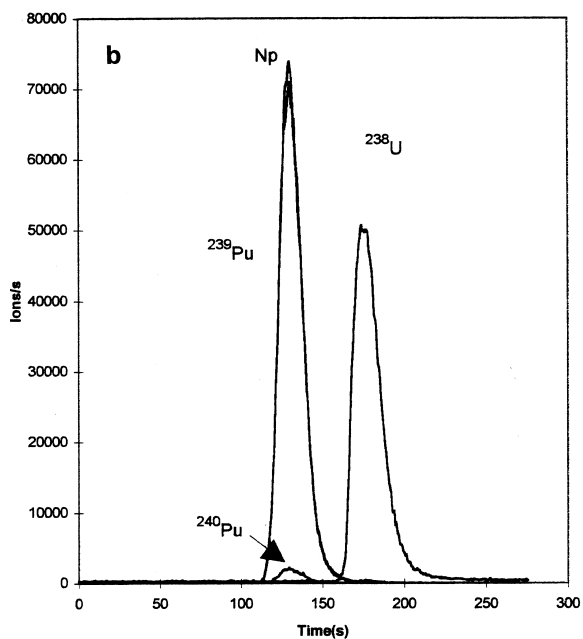
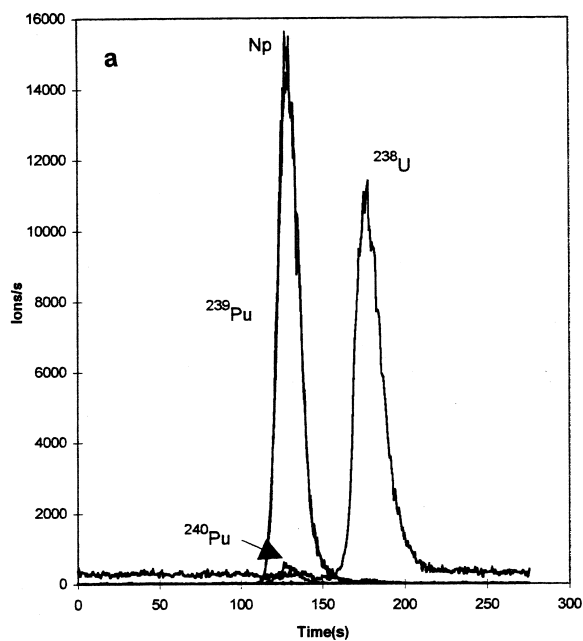


Fig. 7. IC separation for U, Pu and Np at two different concentration levels: (a) 10 ng/ml; (b) 50 ng/ml.

separation between ^{241}Pu and ^{241}Am can be accomplished allowing determination by isotope dilution analysis.

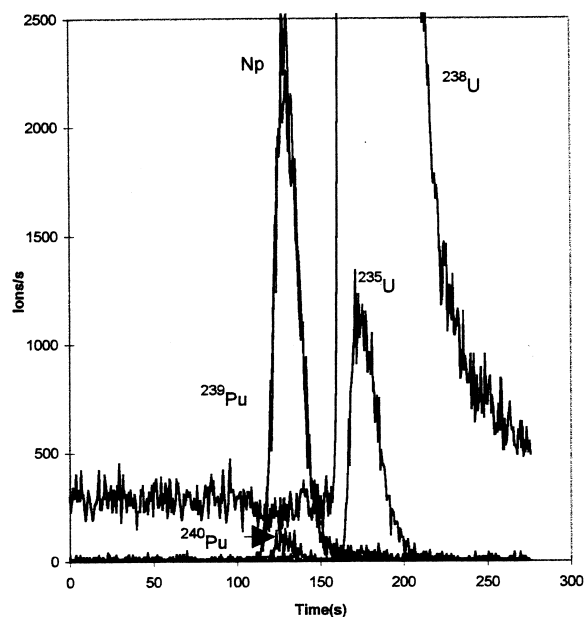


Fig. 8. IC separation for U, Pu and Np for the determination of traces of Pu (Ref. [18]).

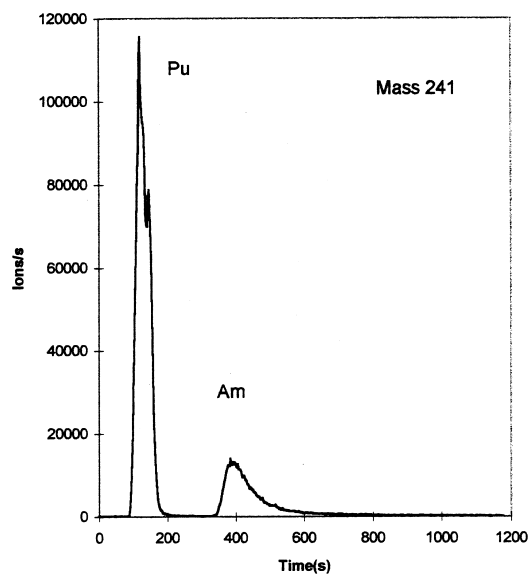


Fig. 9. IC separation for Pu and Am at mass 241 in a spent nuclear fuel solution.

3. Conclusions

The use of ion chromatographic separation has been found to be very useful for applications of

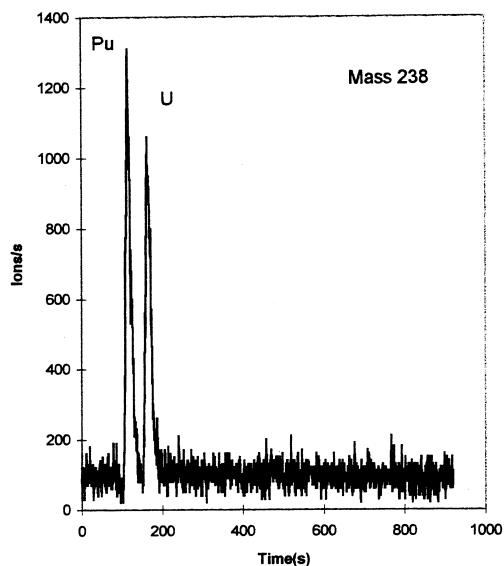


Fig. 10. IC separation for Pu and U at mass 238 in a spent nuclear fuel solution.

nuclear concern. Different types of detectors can be coupled on-line allowing the trace radionuclides of interest to be determined. In this way tedious and time-consuming chemical separation procedures can be avoided, and the handling of hazardous active and/or contaminated samples can be limited, with minimum exposure time for the analyst. The coupling of an ion chromatographic system with an ICP-MS has been found to be effective in obtaining a complete inventory of the fission products and actinides in nuclear samples. Moreover, owing to the low detection limit of an ICP-MS, which can be further reduced by the use of on-line pre-concentration techniques, the IC-ICP-MS coupling can be exploited for the characterization of environmental samples from contaminated areas and for routine environmental monitoring.

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