



Development of cadmium/silver/palladium separation by ion chromatography with quadrupole inductively coupled plasma mass spectrometry detection for off-line cadmium isotopic measurements

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ABSTRACT

A separation method was investigated to perform off-line cadmium isotopic measurements on a ^{109}Ag transmutation target. Ion chromatography (IC) with Q ICPMS detection (quadrupole inductively coupled plasma mass spectrometry detection) was chosen to separate cadmium from the isobarically interfering elements, silver and palladium, present in the sample. The optimization of chromatographic conditions was particularly studied. Several anion and cation columns (Dionex AG11[®], CS10[®] and CS12[®]) were compared with different mobile phases (HNO_3 , HCl). The separation procedure was achieved with a carboxylate-functionalized cation exchange CS12 column using 0.5 M HNO_3 as eluent. The developed technique yielded satisfactory results in terms of separation factors (greater than 5) and provides an efficient solution to obtain rapidly purified cadmium fractions (decontamination factors higher 100,000 for silver and palladium) which can directly be analyzed by multi collection inductively coupled plasma mass spectrometry (MC ICPMS). By applying the proposed procedure, accurate and precise cadmium isotope ratios were determined for the irradiated ^{109}Ag transmutation target.

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1. Introduction

In the framework of long-term management and recycling of nuclear wastes, the transmutation process has been identified as a promising option to decrease the radiotoxicity of radionuclides [1]. The French Atomic Energy Commission (CEA) is involved in transmutation experiments to validate neutron calculation codes and to obtain neutron databases useful for the design of future fast neutron reactors and transmutation of nuclear wastes [2,3]. Among these investigations, the experiments named PROFIL-R consisted in the irradiation of pure isotopic samples of actinides and fission products in fast neutron Phenix reactor until 2005 [4]. 44 different natures of transmutation targets (around 2–5 mg of isotopically enriched powders) were enclosed in small steel containers and assembled in pins before irradiation. The behaviours of the transmutation targets are characterized from the determination of their accurate and precise elemental and isotopic compositions after irradiation. To provide useful data for the validation of neutron calculation codes, isotope ratio measurements are performed with mass spectrometric techniques (multi collection inductively coupled plasma mass spectrometry, MC ICPMS; thermal ionization

mass spectrometry, TIMS) with accuracy and uncertainties of a few permil [5,6].

A sample containing around 5 mg of ^{109}Ag metal powder is one of the fission product transmutation targets which were irradiated. This sample was initially enriched in ^{109}Ag (>99%). After irradiation, the theoretical evolution scheme predicts respectively the formation of 366 μg of cadmium and 1 μg of palladium compared to 4636 μg of silver. Determination of cadmium isotopic compositions is of prime interest to validate neutron calculation codes and to obtain the integral capture cross section of ^{109}Ag . The measurements of Cd isotope ratios have generally been investigated in terrestrial, marine, anthropogenic and extraterrestrial samples [7–11]. Due to the high ionization potential of cadmium and due to the high sensitivity required for isotopic analysis, MC ICPMS displays a strong potential for our issue. But, as it can be observed from Table 1, isobaric interferences occur at mass 108 between cadmium and silver, and at mass 110 between cadmium, silver and palladium respectively. The mass resolution required to overcome $^{110}\text{Cd}/^{110}\text{Ag}/^{110}\text{Pd}$ interference is about 100,000 which is beyond actual possibilities of mass spectrometers. Recent works have shown the interest of collision-reaction cells introduced in ICPMS instruments for in situ resolution of isobaric interferences [12–14]. However, up to now, no collision-reaction gas has been identified to achieve Ag/Pd/Cd separation. Thus, a chemical separation step must be completed to isolate cadmium in a purified fraction before off-line isotopic measurements by MC ICPMS [5,6,12]. From Table 1, it

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Table 1
Quantities of silver, cadmium and palladium (in μg) predicted from neutron calculation codes for the irradiated ^{109}Ag transmutation target.

Predicted quantity (μg)	107	108	109	110	111	112
Ag	11	0.1	4625	0.1	<0.1	<0.1
Cd	<0.1	1	<0.1	360	5	0.1
Pd	<0.1	<0.1	<0.1	0.1	<0.1	<0.1

can be deduced that the separation method must guarantee decontamination factors (which correspond to the ratio of interfering element mass before and after separation procedure) higher than 100 and 5, respectively for silver and palladium, in order to obtain accurate cadmium isotope ratios with uncertainties of a few %.

Purification procedures on anion exchange resins are particularly developed for geological and cosmochemical applications to separate cadmium, silver and palladium [7,15–20]. In the case of radioactive materials, the chemical separations performed with gravity flow on ion exchange resins induce drawbacks for analysts, such as increased handling time on samples. Moreover, in most proposed procedures [7,17,18], cadmium is generally eluted after silver, which lowers the separation factor between silver and cadmium and decreases decontamination factors because of silver peak tailing in cadmium fraction.

A powerful way to reduce analysis time and to improve selectivity is high performance ion chromatography [21–23]. However, no detector classically associated with a HPIC system can measure Ag, Cd and Pd with high specificity and sensitivity [24,25]. The ICPMS can tackle those specifications: it can be used to detect trace elements at the exit of the chromatographic column. Ion chromatography-inductively coupled plasma mass spectrometry (IC-ICPMS) has demonstrated a strong potential in environmental [26,27] and biological [28] fields. This hyphenated technique minimizes sample pretreatment and shortens analysis time, which is of prime interest for nuclear applications [29–34]. The application of IC-ICPMS provided a solution for the separation of transition metals (Mo, Ru, Pd) in spent nuclear fuels [34]. But, no separation procedure based on IC-ICPMS has been developed to separate cadmium, silver and palladium. Consequently, given the potential of this approach for our issue, IC was chosen to separate cadmium from silver and palladium with quadrupole inductively coupled plasma mass spectrometry (Q ICPMS) detection. Because of the fast mass scanning ability of the quadrupole in peak jumping mode, this kind of spectrometer enables an easy handling of transient signals associated with high sensitivity [35].

The aim of this work was to develop a procedure based on IC technique with Q ICPMS detection to separate Cd/Ag/Pd and to collect purified cadmium fractions in order to determine their off-line isotopic compositions in an irradiated ^{109}Ag transmutation target. Since the 3 elements displayed different chemical behaviours in solution, the speciation of these elements was first discussed in the paper so as to guarantee their stability in solution. The choice of the suitable column and chromatographic conditions was then studied to maximize decontamination factors towards cadmium and to obtain high resolution factors (R_s greater than 5). Several anion and cation stationary phases were compared with different mobile phase concentrations. Moreover, as the separation procedure had to be transposed in glove-boxes to handle the radioactive ^{109}Ag target, the use of concentrated acids, especially HCl, was minimized in order to prevent corrosion. The use of complexing agents was also limited due to the constraints linked to radioactive effluent management. After the optimization of chromatographic conditions, the method was applied to the separation of non-radioactive solutions simulating the composition of the irradiated sample. The cleanup procedure was particularly described and decontamination factors of collected cadmium fractions were

determined. Afterwards, the analytical procedure was validated for the irradiated ^{109}Ag target. The developed method yielded to obtain purified cadmium fractions which were off-line analyzed by MC ICPMS.

2. Experimental

2.1. Reagents and solutions

All solutions were prepared using ultra-pure water (resistivity 18.2 $\text{M}\Omega/\text{cm}$) obtained from a Milli-Q system (Millipore, France). Nitric and hydrochloric acids (Suprapur) from Merck were used. Anhydrous oxalic acid was obtained from Fluka (purity $\geq 99\%$). Preliminary investigations on non-radioactive solutions were made with Ag, Pd, Cd SPEX certified standards with a concentration of 1 mg/L. After the optimization of chromatographic conditions, synthetic solutions simulating the irradiated ^{109}Ag target were prepared from SPEX certified standards. Given the concentration necessary for cadmium isotopic analyses by MC ICPMS, the synthetic solution to be injected had the following concentrations: Ag 400 mg/L, Cd 31 mg/L and Pd 90 $\mu\text{g}/\text{L}$ respectively. For the validation of the analytical procedure, separations were performed with natural and isotopically enriched solutions. The ^{109}Ag solution was obtained from a metallic powder enriched at $99.75\% \pm 0.01$ (Eurisotop, France) dissolved in 14 M HNO_3 using an open-vessel microwave digestion oven (Ethos, Milestone, USA). To determine isotopic compositions of the collected cadmium fractions, a SPEX solution of cadmium was used as a standard based on IUPAC reference values [36].

2.2. ^{109}Ag transmutation target

The PROFIL-R transmutation experiments involved the irradiation of 110 samples enclosed in a steel inner container (190 mg). Among these targets, 5 mg of ^{109}Ag metallic powder (Eurisotop, France) were irradiated. After irradiation, the steel container was opened in hot cell facilities (CEA Cadarache, France) to recuperate all the powder. Several developments were conducted to optimize the powder recovery procedure in order to minimize the impact of steel in the final dissolution solution [4]. After its recuperation, the irradiated ^{109}Ag powder was dissolved in 14 M HNO_3 using an open-vessel microwave oven (Ethos, Milestone, USA) which was installed in hot cell facilities. Finally, the radioactive solution was supplied to the Isotopic and Elementary Nuclear Analysis Laboratory (LANIE, CEA Saclay, France) for isotopic measurements.

2.3. IC-ICPMS system

The IC separation procedure with Q ICPMS detection was first optimized on non-radioactive apparatus. For ^{109}Ag transmutation target analysis, the system was transposed in a glove-box to work safely on the radioactive samples.

2.3.1. Chromatographic system

For the optimization of separation conditions (choice of column and eluents), the chromatographic system includes an ICS 3000 gradient pump and an AS 50 auto-sampler (Dionex, Sunnyvale, USA) equipped with a six-way Rheodyne injection valve. The volume of the sample loop is 25 μL . The columns used, namely Dionex AG11, CS10 and CS12, have respectively the functional groups of alkanol quaternary ammonium, sulfonic acid and carboxylic acid. The eluent flow-rate is set at 1 mL/min. For the analysis of radioactive samples, only the injection valve and the analytical column are located inside the glove-box whereas the ICS 3000 pump and the eluent bottles are placed outside the glove-box. The eluents are supplied to the chromatographic system with a

PEEK (polyetheretherketone) tubing (Upchurch, USA) which goes through the glove-box. To collect purified cadmium fractions for off-line isotopic measurements by MC ICPMS, the eluent flow-rate was divided in 2 ways using a tee and PEEK tubings of different internal diameters at the exit of the column: 10% of the flow-rate eluent was used for Q ICPMS detection whereas 90% of the resulting flow-rate eluent was dedicated to the collection of purified cadmium fractions.

2.3.2. ICPMS systems

A quadrupole ICPMS XSeries^{II} instrument (Thermo Electron, UK) equipped with a quartz concentric nebulizer (1 mL/min) and a quartz bead impact spray chamber (thermostated at 3 °C) was used as a detector for IC separation. A modified ICPMS X7 instrument was used to handle radioactive materials. The details of its installation in glove-box have been previously given [37]. The Q ICPMS instrument (nebulizer, spray chamber, coil, torch, injector, cones) is inside the glove-box. The skimmer cone is located at the interface while the mass spectrometer is outside the glove-box. Instrumental and operating conditions were optimized daily with the factory-suggested tune solution and were formerly detailed [37].

Isotopic measurements were carried out with a single focusing sector field MC ICPMS Isoprobe (GV Instruments, Manchester, UK) which was previously modified in order to work on radioactive samples in safe experimental conditions [6,13,14,38]. It is equipped with a standard ICP source, a Radio-Frequency-only hexapole collision-reaction cell, a magnetic sector and a multicollector system with nine Faraday cups and one Daly electrode implanted in the axial position. Sample introduction is performed with a micro-concentric nebulizer (0.1 mL/min) and a cyclonic spray chamber.

2.3.3. Coupling IC and Q ICPMS, automation and data acquisition

The coupling between IC and Q ICPMS was achieved by connecting directly the column effluent to the Meinhard nebulizer with a PEEK or PFA HP (perfluoroalkoxyalkane high purity) tubing (Upchurch, USA). For the development of the separation method on non-radioactive samples, all the system was completely automated using the Q ICPMS PlasmaLab software and an external trigger accessory card. Data acquisition was performed with PlasmaLab software in the transient mode. The isotopes were monitored in peak jumping mode using a single channel per mass and a dwell time of 10 ms. No isobaric interference is present in the non-radioactive samples, so ¹⁰⁵Pd, ¹⁰⁹Ag and ¹¹⁴Cd were used. For the irradiated ¹⁰⁹Ag transmutation target, 108 and 110 isotopes were monitored but no more 105, 109 and 114. ¹⁰⁵Pd and ¹¹⁴Cd were not useful since they were not present in the irradiated sample (see Table 1). Moreover, ¹⁰⁹Ag was not monitored to avoid the saturation of Q ICPMS detector due to its high quantity in the sample.

3. Results and discussion

3.1. Speciation

The development of Cd/Ag/Pd separation first requires the speciation characterization of these elements. Their chemical properties are strongly different in acid medium (hydrochloric and nitric acids) [30], which is generally used as eluent for chromatographic separations and ICPMS analyses in the inorganic speciation field. The study was performed for a solution simulating the irradiated ¹⁰⁹Ag target in concentration (Ag 400 mg/L, Cd 31 mg/L and Pd 90 µg/L respectively) by applying Chess speciation code [39]. The stability constants introduced in Chess [39,40] and the results obtained are detailed in Table 2. In acid medium, silver (I), cadmium (II) and palladium (II) are respectively the most stable valence forms of silver, cadmium and palladium. In nitric acid, the predominant

species of the three elements are mostly cations: respectively Ag⁺ for silver, Cd²⁺ and CdNO₃⁺ for cadmium and PdNO₃⁺ for palladium. In hydrochloric acid, cadmium and palladium are mainly present as anion complexes: CdCl₃⁻ and Pd(Cl)₄²⁻ respectively. For high HCl concentrations, the predominant species of silver are anions: Ag(Cl)₃²⁻ and Ag(Cl)₄³⁻. However, the predominant species of silver is a precipitate of AgCl_(s) in 1 M HCl and only 0.2% of silver remain in solution. From the Chess predictions, the formation of anion complexes is only expected in concentrated HCl medium for all the studied elements. This property can be applied to separate Ag/Pd/Cd with HCl eluent, as it is reported in the literature for anion exchange resins [7,15–19]. It can be deduced from this speciation study that only concentrated HCl media should be used as eluent to separate Ag/Pd/Cd so as to guarantee the stability of the three elements in solution. Moderate HNO₃ concentration could also be applied as mobile phase in order to form cations as predominant species of the elements of interest.

3.2. Optimization of chromatographic conditions

3.2.1. Ion Pac AG11 column

From the method published by Bruzzoniti et al. [27], the anion guard AG11 column was first investigated for Ag/Pd/Cd separation with HNO₃ as eluent. Whatever the HNO₃ concentration used, cadmium and palladium were co-eluted at dead time. This result is in agreement with the speciation of both elements in nitric acid (see Section 3.1). The predominant species are cations for cadmium and palladium and consequently they might have a similar behaviour and are not retained by an anion exchanger column using HNO₃ as eluent. On the contrary, the behaviour of silver was strongly different from cadmium and palladium. Silver was retained on AG11 column by applying HNO₃ as mobile phase. Although the predominant species was a cation, it can be assumed that silver might interact with the pellicular-coated beads of the anion exchange column, which induced its retention on AG11 column.

A complexing agent, the oxalic acid, was then added in HNO₃ mobile phase to modify the speciation of the studied elements [40,41]. The experiments were first performed using the mobile phase composition (0.14 M HNO₃ and 18 mM oxalic acid) given by Bruzzoniti et al. [27]. The introduction of oxalic acid both in eluent and in sample enabled to separate cadmium from palladium. Furthermore, the retention time of palladium was very close from the one reported by Bruzzoniti et al. [27]. However, the peak resolution between cadmium and palladium (calculated at 0.8) was not sufficient. The increase of oxalic acid concentration in the mobile phase (0.1 M) improved the separation selectivity between palladium and cadmium: palladium retention time was 20% higher whereas cadmium was still eluted at dead time. But, the use of oxalic acid did not change the behaviour of silver: this element remains strongly retained on the anion column. Concentrated HNO₃ and HCl media were applied as eluent but no elution was observed for silver. So, silver is expected to accumulate and saturate the column capacity when high concentrations are injected, as it is the case of the irradiated ¹⁰⁹Ag sample. This result was not satisfactory for our application, consequently the AG11 column was not chosen.

3.2.2. Ion Pac CS10 column

Given the behaviour of silver on anion columns, experiments were carried out with two types of cation exchange columns: CS10 and CS12 (sulfonate and carboxylate functional groups respectively). First, studies on the influence of HCl eluent concentrations were performed on CS10 column whereas a Ag/Cd/Pd solution was injected in 2 M HCl medium. The retention factors *k'* of the three elements and peak resolutions were measured as a function of HCl mobile phase concentrations. As it can be noticed in Table 3, silver was practically unretained and the retention factor of cadmium did

Table 2
Predominant species of Ag, Cd and Pd in HNO₃ and HCl media (predicted from Chess speciation code) for a solution simulating in composition the irradiated ¹⁰⁹Ag transmutation target (Ag 400 mg/L, Cd 31 mg/L and Pd 90 μg/L respectively).

Element	HNO ₃ medium			HCl medium		
	Stability constant β(1:1)	0.5 M HNO ₃	8 M HNO ₃	Stability constant β(1:4)	1 M HCl	11 M HCl
Ag	-0.2	Ag ⁺	AgNO ₃	3.8	AgCl _(s) is predominant, only 0.2% of silver is in solution	Ag(Cl) ₃ ²⁻ , Ag(Cl) ₄ ³⁻
Cd	2.4	Cd ²⁺ , CdNO ₃ ⁺	CdNO ₃ ⁺	–	Cd(Cl) ₂ , Cd(Cl) ⁺	Cd(Cl) ₂ , Cd(Cl) ₃ ⁻
Pd	1.5	PdNO ₃ ⁺	PdNO ₃ ⁺	15.0	Pd(Cl) ₄ ²⁻	Pd(Cl) ₄ ²⁻

Table 3
Retention (*k'*) factors and peak resolution (*R_s*) obtained with cation CS10 column as a function of HCl eluent concentrations.

Concentration of HCl eluent (M)	<i>k'</i> (Ag)	<i>k'</i> (Cd)	<i>k'</i> (Pd)	<i>R_s</i> (Cd/Pd)	<i>R_s</i> (Cd/Ag)
1	0.5	1.5	4.9	4	3
1.25	0.4	1.6	3.3	3	4
1.5	0.3	1.7	2.5	1	5
2.5	0.2	1.7	1.1	2	6
5	0.1	0.7	0.4	2	5

not depend significantly on the concentration of HCl eluent within the range of 1–2.5 M HCl. As illustrated in Fig. 1, the separation of the three studied elements can be achieved in less than 10 min using 1.25 M HCl eluent in isocratic mode with satisfactory peak resolutions. Nonetheless, a relatively low concentration of HCl eluent cannot guarantee the stability of silver in solution for the irradiated ¹⁰⁹Ag transmutation target, as it was described in Section 3.1 (see Table 2). Silver is expected to precipitate while using low HCl concentration, which might hinder the separation step on CS10 column. So, HCl eluent was not appropriate for Ag/Pd/Cd separation in our case.

In the same way, the effect of HNO₃ eluent concentration was investigated on CS10 column with a Ag/Cd/Pd solution prepared in 1 M HNO₃. The retention factors *k'* of silver, cadmium and palladium are given as a function of HNO₃ eluent concentrations in Table 4. Whatever the concentration of HNO₃ mobile phase, the retention factor of palladium was higher than 15: palladium was strongly retained and was not eluted in a reasonable time. As demonstrated in Table 3, palladium elution can be achieved with concentrated HCl eluent. From Table 4, it can also be highlighted that the retention factors of silver and cadmium reached the highest values for the lowest HNO₃ concentrations. The separation between silver and cadmium can be completed with satisfactory peak resolutions (greater than 5) using HNO₃ eluent concentration lower than 0.3 M. The chromatogram obtained on CS10 column with 0.25 M HNO₃ eluent is reported in Fig. 2. Cadmium can be separated from silver and palladium in 20 min in isocratic mode using CS10 column. It

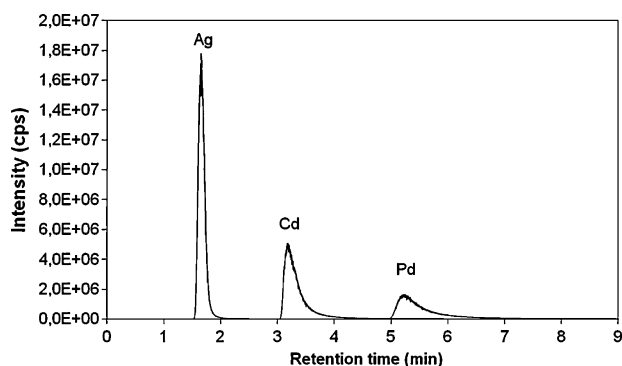


Fig. 1. Chromatogram obtained from natural Ag, Pd, Cd 1 mg/L solution in 2 M HCl medium; CS10 column; 1.25 M HCl eluent in isocratic mode.

Table 4
Retention (*k'*) factors and peak resolution (*R_s*) obtained with cation CS10 column as a function of HNO₃ eluent concentrations.

Concentration of HNO ₃ eluent (M)	<i>k'</i> (Ag)	<i>k'</i> (Cd)	<i>k'</i> (Pd)	<i>R_s</i> (Cd/Ag)
0.14	5.2	>15	>15	Not determined
0.25	2.3	10.5	>15	7
0.3	1.6	5.4	>15	5
0.5	1.0	1.7	>15	2
1	0.5	0.4	>15	0
4	0.1	0.1	>15	1
8	0.1	0	>15	1

can also be noticed that silver was eluted before cadmium, which can induce a decrease of peak resolution and decontamination factor for cadmium in the case of concentrated silver solutions, as for the irradiated ¹⁰⁹Ag target.

3.2.3. Ion Pac CS12 column

Further investigations were performed on CS12 column to reverse the selectivity between cadmium and silver by changing the functional group nature of the column stationary phase compared to CS10 column. Given the potential of the separation method proposed on CS10 column, only the influence of HNO₃ eluent concentrations was studied. The resulting elution patterns obtained with HNO₃ eluent are displayed in Fig. 3. By choosing HNO₃ as eluent, palladium had the same behaviour using CS10 and CS12 columns. Palladium was retained on cation exchange columns whatever the HNO₃ concentration, but it can be eluted with HCl eluent with gradient mode. For silver and cadmium, a change in selectivity was observed with CS12 column in comparison to CS10 column. Cadmium was eluted at dead time whatever the HNO₃ eluent concentration. But, the increase of HNO₃ eluent concentration induced the enhancement of silver retention factor. Whatever the concentration of HNO₃ eluent between 0.5 M and 2 M, cadmium and silver can be separated on CS12 column in isocratic mode with a peak resolution value about 6–7, which is particularly satisfactory for our issue.

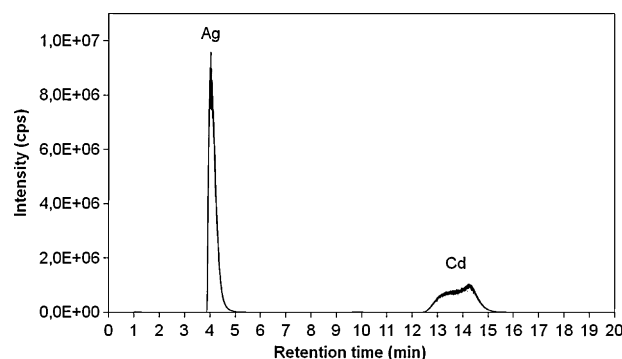


Fig. 2. Chromatogram obtained from natural Ag, Pd, Cd 1 mg/L solution in 1 M HNO₃ medium; CS10 column; 0.25 M HNO₃ eluent in isocratic mode.

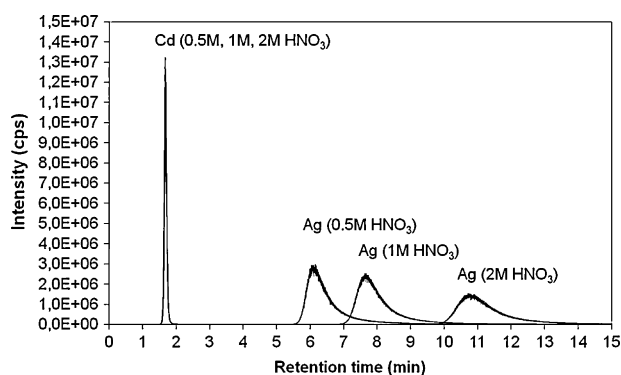


Fig. 3. Chromatograms obtained from natural Ag, Pd, Cd 1 mg/L solution in 1 M HNO₃ medium; CS12 column; HNO₃ eluent in isocratic mode.

3.2.4. Choice of chromatographic conditions

Whatever the cation CS10 and CS12 columns used, a separation between cadmium and silver can be achieved in isocratic mode with HNO₃ mobile phase with satisfactory peak resolutions (greater than 5). In such chromatographic conditions, palladium is retained but can be eluted with HCl mobile phase in gradient mode. The elution of cadmium in HNO₃ acid enables to collect purified fractions in a medium directly compatible with MC ICPMS analysis. It is of prime interest, especially for nuclear applications: handling time on samples is limited and natural contamination risks of the collected fractions are minimized. Compared to separation procedures on ion exchange resins with gravity flow, the developed method reduces time analysis: purified fractions of cadmium can be obtained in less than 20 min. The elution order is particularly more satisfying with CS12 column. Collections of purified cadmium fractions can be carried out in less than 5 min. In addition, as silver is eluted in second, the silver decontamination factor is expected to be higher in the collected cadmium fractions. This result implies a better potential for the separation method when strong Ag concentrations have to be injected, as it is the case for the irradiated ¹⁰⁹Ag transmutation target. Consequently, the cation CS12 column was chosen for further experiments. Moreover, the HNO₃ eluent concentration was fixed at 0.5 M for isocratic mode elution which is directly compatible with MC ICPMS analysis without any dilution or treatment.

3.3. Method validation

3.3.1. Applications to non-radioactive natural and enriched ¹⁰⁹Ag samples

3.3.1.1. Blank and cleanup procedure. For the choice of chromatographic conditions, separation experiments were conducted on a natural solution containing 1 mg/L of Ag, Pd and Cd in HNO₃ medium. Further studies were carried out with a non-radioactive isotopically enriched sample which had the following composition: 0.5 mg/L of natural Spex Pd and Cd and 1 mg/L of ¹⁰⁹Ag respectively in 0.5 M HNO₃ medium. Optimized chromatographic conditions were applied: column CS12, eluents: (A) 0.5 M HNO₃, (B) 1 M HCl; gradient mode, 0–15 min eluent A, 15 min to 17 min from A to B, 17–20 min eluent B. As demonstrated by the chromatogram reported in Fig. 4, the separation procedure gave satisfactory results in terms of peak resolution for a solution containing the elements of interest in equivalent concentrations around 1 mg/L.

Thereafter, the developed method was applied on a non-radioactive isotopically enriched sample simulating the irradiated transmutation target in concentration and isotopic composition. In order to recover sufficient quantities of cadmium for MC ICPMS analysis, the synthetic solution to be injected had the following concentrations: 90 μg/L of natural Spex Pd, 31 mg/L of natural Spex Cd and 400 mg/L of ¹⁰⁹Ag respectively. As it can be noted, high

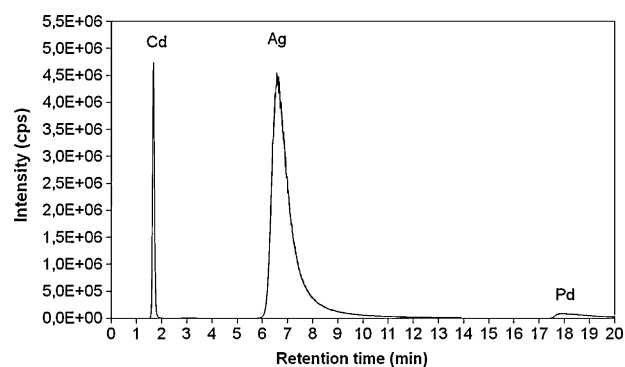


Fig. 4. Chromatogram obtained from a non-radioactive ¹⁰⁹Ag enriched solution in 0.5 M HNO₃ medium (natural Pd, Cd 0.5 mg/L and ¹⁰⁹Ag 1 mg/L); CS12 column; gradient mode: (A) 0.5 M HNO₃, (B) 1 M HCl; 0–15 min eluent A, 15 min to 17 min from A to B, 17–20 min eluent B.

silver concentrations had to be introduced in IC-ICPMS system, which implies potential pollutions for both the analytical column and the Q ICPMS instrument. To overcome those difficulties, caution was particularly taken towards the cleanup procedure of the column. Different cleanup methods based on a gradient of concentrated HNO₃ or HCl eluents were investigated. The injection of a blank solution proved the incomplete efficiency of these eluents in terms of decontamination. However, the cleanup procedure recommended to remove hydrophobic cations and organic contaminants by the column supplier [42] was adapted successfully. It consisted in repeated gradient programs using 1 M HCl and 90% acetonitrile in water. The monitoring of a blank solution between two injections of concentrated Ag samples demonstrated the relevance of the cleanup procedure. To prevent Q ICPMS pollution, a skimmer cone generally used for analysis of environmental matrices (which had a smaller orifice compared to the one applied for high sensitivity analysis) was installed to reduce the introduction of high analyte quantities in ion optics and mass spectrometer.

3.3.1.2. Decontamination factors. The efficiency of the procedures proposed to minimize IC-ICPMS pollution was then evaluated. For that purpose, natural solutions simulating in concentration the irradiated ¹⁰⁹Ag target were alternately injected after ¹⁰⁹Ag enriched samples of the same concentrations. Cadmium fractions were successively collected to determine the resulting decontamination factors towards silver and palladium. The chromatogram corresponding to the injection of a ¹⁰⁹Ag enriched sample is displayed in Fig. 5. No palladium was detected in the collected cadmium fractions. The silver decontamination factor (measured at around 100,000) was strongly sufficient to obtain cadmium fractions suit-

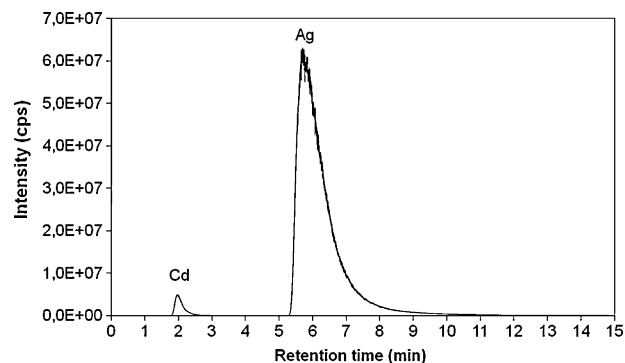


Fig. 5. Chromatogram obtained from a non-radioactive enriched ¹⁰⁹Ag solution simulating in concentration the irradiated transmutation target (natural Cd 31 mg/L and ¹⁰⁹Ag 400 mg/L in 0.5 M HNO₃ medium); CS12 column; 0.5 M HNO₃ eluent in isocratic mode.

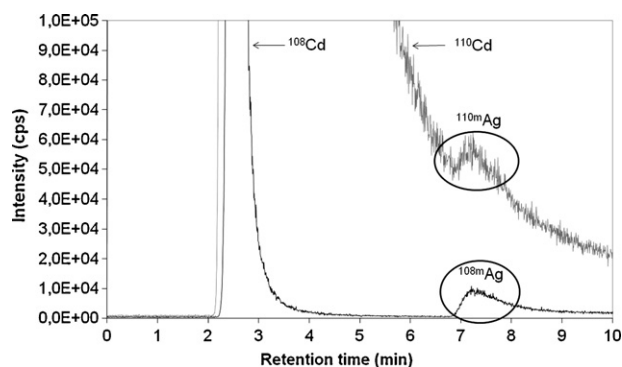


Fig. 6. Chromatogram obtained from the irradiated ^{109}Ag transmutation target; CS12 column; 0.5 M HNO_3 eluent in isocratic mode; monitored isotopes: 108 and 110, respectively in black and grey.

able for off-line MC ICPMS analysis. Actually, from the predictions of neutron calculation codes (see Table 1), the decontamination factor should be higher than 100 to eliminate isobaric interferences related to silver at masses 108 and 110. These results demonstrate that the collected cadmium fractions do not need further purification after IC separation step and validate the developed separation method.

3.3.2. Applications to irradiated ^{109}Ag transmutation target

3.3.2.1. Collection of purified cadmium fractions. The developed IC technique with Q ICPMS detection was applied to the irradiated ^{109}Ag transmutation target. The same experimental conditions as described in Section 3.3.1.1 for the analysis of non-radioactive synthetic samples were used. The chromatogram corresponding to the injection of the irradiated ^{109}Ag target solution was very close to the one reported in Fig. 5. The monitoring of 108 and 110 isotopes is proposed in Fig. 6 for the irradiated ^{109}Ag transmutation target. Despite the very low quantities of $^{108\text{m}}\text{Ag}$ and $^{110\text{m}}\text{Ag}$ present in the sample, both isotopes can be observed in the chromatogram. As illustrated in Fig. 6, purified cadmium fractions can be collected between 1 min and 5 min before the elution of silver. Two Cd fractions were obtained from the irradiated ^{109}Ag target solution and off-line isotopic measurements were performed by MC ICPMS.

3.3.2.2. Off-line cadmium isotopic analysis of the collected fractions. For the determination of cadmium isotopic compositions by MC ICPMS, a sample-standard bracketing method was employed and the mass bias was corrected by using the exponential law [43,44]:

$$R_{\text{true}} = R_{\text{meas}} \left(\frac{m_1}{m_2} \right)^{\beta} \quad (1)$$

where R_{true} and R_{meas} are the true and measured isotope ratios of the two isotopes 1 and 2; m_1 and m_2 are the respective atomic masses of these isotopes and β the mass fractionation factor.

Isotopic measurements were performed in static multicollection mode with Faraday cups. Each experiment consisted of 2 blocks, 10 cycles (10 s integration time). Cd sensitivity was 2 V per mg/L with Ar gas in the collision-reaction cell. The analytical procedure described above was applied for the isotopic measurements of the purified cadmium fractions collected after IC separation. The values of Cd isotope ratios are reported in Table 5. The results obtained for two independent measurements on cadmium isotope ratios present a difference less than 1% for isotope ratio values higher than 10^{-3} . Cd produced in the irradiated transmutation ^{109}Ag target has a very different isotopic composition in comparison to non-radioactive natural cadmium [36] or cadmium formed in spent nuclear fuels. These data are of prime interest for the val-

Table 5

Cd isotope ratio values determined for the irradiated ^{109}Ag transmutation target ($n = 2$).

Isotope ratio	Ranges of values
$^{108}\text{Cd}/^{110}\text{Cd}$	0.00236–0.00239
$^{111}\text{Cd}/^{110}\text{Cd}$	0.013486–0.013494
$^{112}\text{Cd}/^{110}\text{Cd}$	0.00103–0.00104

idation of nuclear calculation codes for fast neutron reactors and have not been measured experimentally up to now.

4. Conclusions

This study shows the development of a IC method with Q ICPMS detection to separate cadmium from silver and palladium with selectivity and sensitivity. The use of a carboxylate-functionalized cation exchange CS12 column with 0.5 M HNO_3 as eluent gave satisfactory results in terms of peak resolution and decontamination factors. This work demonstrates the possibility to obtain rapidly purified cadmium fractions which can directly be analyzed by MC ICPMS to determine isotopic compositions. By applying the developed procedure, accurate and precise cadmium isotope ratios were successfully measured for an irradiated ^{109}Ag transmutation target. Compared to procedures on ion exchange resins with gravity flow, this hyphenated separation technique provides an attractive solution to separate Cd/Ag/Pd by minimizing handling time on samples and time analysis. The developed method displays a strong potential for nuclear issues but also for geological and cosmochemical applications where high accuracy and precision isotopic analyses are also needed for cadmium, silver and palladium.

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