Comparative Study of Three Sample Preparation Approaches for the Fast Determination of Americium in Urine by Flow Injection ICP-MS*

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Abstract

A flow injection (FI) on-line preconcentration/matrix separation method, using TRU resin as ion-exchanger, was applied for the determination of americium (^{241}Am) in human urine by ICP-MS. Three different approaches of sample preparation were developed and compared. Also, a fast procedure was developed for urine analysis without digestion of the urine sample. Total time of this analytical procedure was 11 min per sample or 110 min per 10 samples, with detection limit of 0.8 pg L^{-1} using a 10 mL sample volume. However, a better detection limit, 0.046 pg L^{-1}, was obtained when the sample was digested and a two-step sample evaporation was applied prior to on-line preconcentration. Total analysis time for the last procedure including sample preparation was 100 min per sample or 200 min per 10 samples. ^{205}Tl and ^{175}Lu were used as an internal standard and yield tracer, respectively.

Keywords: americium, inductively coupled plasma – mass spectrometry (ICP-MS), urine, microwave digestion, on-line chromatographic separation.

Résumé

Une technique d'analyse par injection en flux continu (FIA), utilisant une résine échangeuse d'ions, TRU , a été developée et appliquée pour la pré-concentration et détermination de l'américium (^{241}Am) dans l'urine humain par la technique de spectrométrie de masse à plasma à couplage inductif (ICP-MS). Trois différentes méthodes de préparation d'échantillons ont été mises au point et comparées. Une méthode rapide est obtenue si l'échantillon urinaire ne subit aucun pré-traitement avant son chargement dans la colonne. Dans ces conditions, le temps total nécessaire est de 11 min par échantillon ou de 110 min par10 échantillons. Cependant, on atteint de meilleures limites de détection, de l'ordre de 0.046 pg L^{-1}, en faisant subir aux échantillons une digestion suivie de deux étapes d'évaporation avant de soumettre l'echantillon à l'analyse par FIAS. Cette dernière approche est accomplie en 100 min par échantillon ou en 200 min par 10 échantillon. ^{205}Tl and ^{175}Lu ont été utilisés comme standard interne et indice de rendement, respectivement.

Introduction

The main isotope of americium which is of particular environmental interest is ^{241}Am (half-life = 458 years). It is a decay product of ^{241}Pu and has both α and γ emissions. Both ^{241}Am and its parent are released into the environment via atmospheric weapons testing, nuclear power production and spent fuel reprocessing. Activation products like ^{241}Am may contribute to human exposure to radiation in cases of accidental or other release into the environment. Therefore, the measurement of ^{241}Am in environmental samples is important in order to monitor its release and presence in the environment.

The control and minimization of human exposure by radionuclides is an important issue, and urine is considered as the best medium to assess any human contamination, through food chains or occupational exposure. The maximum acceptable concentration of ^{241}Am in drinking water, as recommended in the Guideline for Canadian Drinking Water Quality, is 0.2 Bq L^{-1} (or 1.6 pg L^{-1}) (1).

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Several different techniques have been developed for the determination of ^{241}Am in urine (2-7). Most of the methods require labour- and time-consuming sample preparation, such as precipitation, mineralization, extraction and ion-exchange chromatography etc.

γ-Spectrometric techniques (8, 9) allow direct determination of ^{241}Am without sample preparation but are limited to samples in excess of Bq/g levels, and correction for attenuation of the low energy γ photon by the sample matrix must be applied. For lower level analyses, chemical separation and α spectrometry are required prior to detection (10, 11). The later being the most commonly used technique, it is still limited by its low throughput and complicated procedures of sample preparation such as precipitation, evaporation, elution or filtration (12).

ICP-MS is one of the fastest methods for the determination of long-lived radionuclide and particularly americium (13, 14). Lately, several techniques for the determination of ^{241}Am in environmental samples, i.e. in sediments (15), in spent nuclear fuel (14, 16), in mosses (17), have been developed. Most of these studies have demonstrated that there are two main issues for the measurement of americium in environmental samples, the main one being the high concentration of matrix constituents, such as Na, Ca, Mg, Si, and organic matter. and the low level of Am in environmental samples. Therefore, the preconcentration and separation of Am from matrix is required prior to ICP-MS analysis.

The aim of the present study was to develop a rapid and accurate on-line technique for the determination of low levels of ^{241}Am in urine by ICP-MS.

Experimental

Instrumentation

In order to optimize the chemical and flow injection variables for the on-line preconcentration/separation of americium from a urine matrix, a quadrupole ICP-MS mass analyzer ELAN-5000 (Perkin-Elmer SCIEX, Concord, Canada) was used. The quantification of Am was performed using an ICP-MS mass analyzer with dynamic reaction cell (DRC) ELAN-DRCII (Perkin-Elmer SCIEX, Concord, Canada). A highly-sensitive APEX-Q desolvation system (Elemental Scientific Inc., Ohama, NE, USA) was used as sample introduction. The instrumental conditions were optimized to achieve maximum analyte sensitivity (Table 1).

On-line preconcentration was performed with a Perkin-Elmer Model FIAS-400 flow injection system equipped with a Perkin-Elmer 2×4 channel, 16-port double layer rotary injector valve. The pH of the eluent was adjusted with an Accumet® pH-meter (from Fisher Scientific, Canada). A microwave sample preparation workstation (Ethos, Milestone, Monroe, CT, USA) was used for sample digestion and evaporation.

Materials and reagents

Trace metal grade nitric acid (from Fisher Scientific, ON, Canada) was used to acidify samples. Hydrogen peroxide, 30% (from J.T. Baker, Phillipsburg, NJ, USA) was used to assist sample digestion. High-purity water (18 MΩ cm^{-1}) was prepared with a Millipore Milli-Q-Plus water purification system (MQW). Americium samples were prepared using the long-lived isotope ^{241}Am, which was purchased from NIST (Gaithersburg, MD, USA). A 1000 µg mL^{-1} Tl standard solution and 1000 µg mL^{-1} Tm standard solution (both from SCP Science, ON, Canada) were used as an internal standard and a yield tracer, respectively. Ethylenediamine tetraacetic acid, diammonium salt hydrate (EDTA) 97% (Sigma-Aldrich, Germany) was used to prepare the eluent solution. For the separation of americium from the sample matrix, TRU Resin (Eichrom Technologies Inc, Darien, IL, USA) was used.

Table 1. Parameters for ICP-MS instrument (ELAN-DRCII) with APEX as introduction system.

Parameters	
Parameters from Optimization File	
Torch Position	Change daily to maximize sensitivity for analyte
RF-power	1200 W
Auxiliary Gas Flow Rate	1.2 L min^{-1}
Plasma Gas Flow Rate	15 L min^{-1}
Nebulizer Gas Flow Rate,	1.04 L min^{-1}
Lens voltage	9
Quadrupole Rod Offset [QRO]	-6
Cell Rod Offset [CRO]	-21.5
Discrimination Threshold	50
Cell Path Voltage [CPV]	-21
Parameters from Method File	
Sweeps per Reading	10
Readings per Replicate	1
Estimated Time of Analysis	11 min.
m/z Monitored	169, 205, 241
Dwell Time	50 ms

Urine samples were collected from twelve volunteers who had no known exposure to Am. The samples were analyzed following the procedure described below.

Procedures

Procedure optimization was performed using the flow-injection (FI) system coupled to a Meinhard concentric nebulizer with cyclonic spray chamber and to the ELAN-5000 ICP-MS instrument. The americium recovery measurements in urine samples were performed using a flow-injection system, an APEX desolvation system and an ELAN-DRCII instrument.

On-line flow injection preconcentration of Am

The operation sequence of the FI on-line system for the on-line preconcentration of americium is schematically presented in Figure 1. The preconcentration procedure consists of four steps including (i) column conditioning (ii) sample loading (preconcentration and matrix separation) (iii) column rinse and (iv) elution. A pre-fill stage is used when a new sample is introduced in order to flush the sample line. In this step, with the valve in fill position and pump 1 active, the tubing before column 1 is filled with the sample. Figure 1 (a) shows the column preconditioning, where 4 ml of 0.5 M HNO_3 is passed through the column when pump 1 is active and the valve is in inject position. During the sample loading step in Figure 1 (b), the valve is in fill position and pump 1 active, 10 mL of the urine sample in 0.5M HNO_3, spiked with 1 ng L^{-1} of Tm, flows through the TRU resin column. Am and Tm are retained on the resin, whereas the majority of the constituents of the sample matrix is eliminated to waste. Simultaneously, the nebulizer, the torch and the ICP-MS cones are rinsed with 2% HNO_3 at a flow rate of 1 mL min^{-1} to eliminate any residues from the previous sample. Figure 1 (c) shows the column rinsing stage with the valve still in fill position and pump 2 active. In this step, 6.25 mL of the rinse solution (8M HNO_3) is passed through the column to wash out all non-retained matrix and is directed to waste. During the elution step, Figure 1(d), with the valve in inject position and pump 2 still active, 3 mL of eluent (0.02 M EDTA spiked with 10 ng

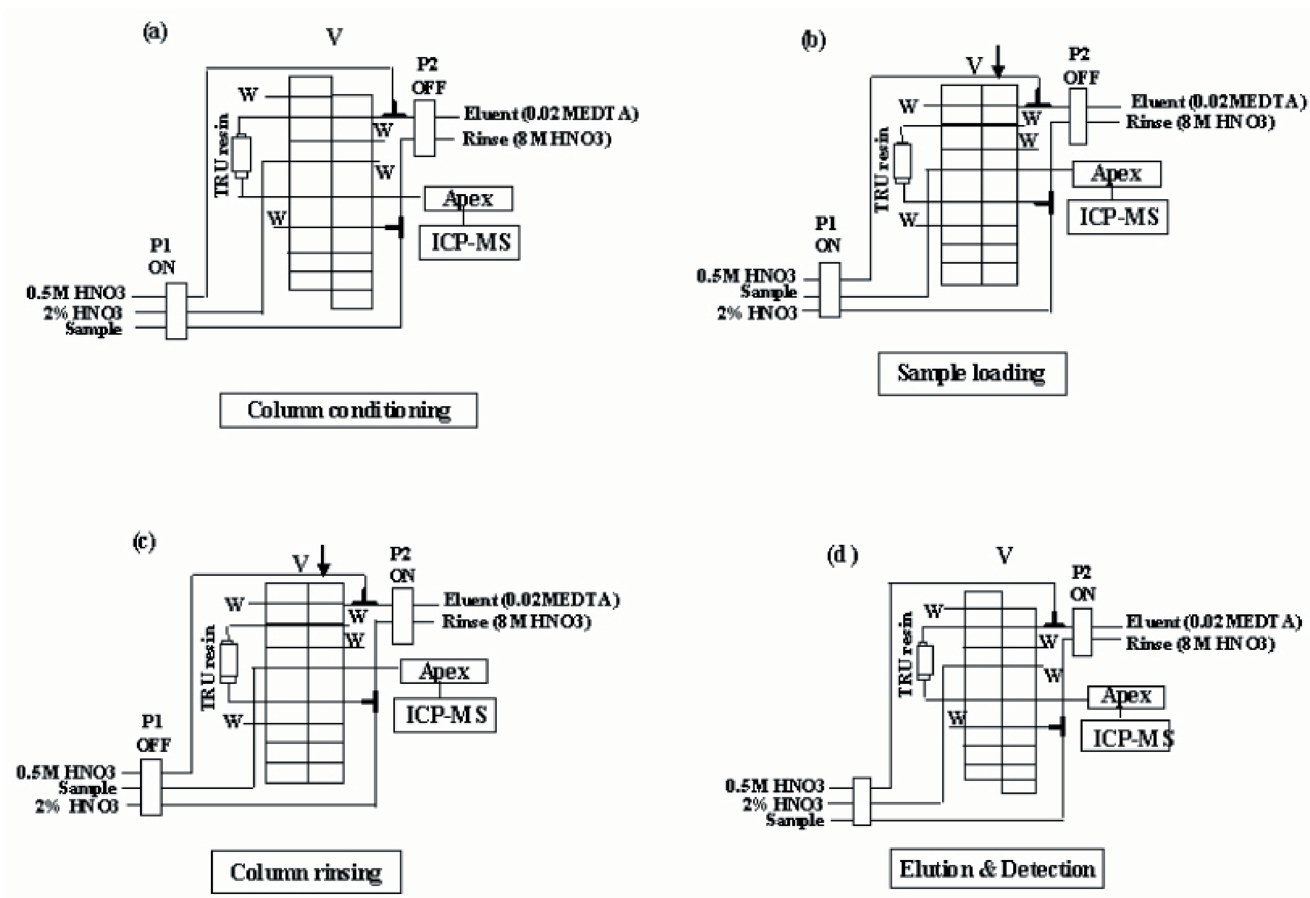

Figure 1. Diagram of flow-injection on-line separation of Am from urine using ICP-MS.

L^{-1} of Tl) is pumped through the column at a flow rate of 1 mL min^{-1} and directed to the Apex nebulizer and then to the ELAN-DRCII instrument for the on-line specific detection of Am. A complete preconcentration cycle including detection time lasts about 11 minutes.

Urine Digestion

Microwave digestion was used for digestion and evaporation of urine samples. A 40 mL urine sample was placed into a Teflon vessel along with 5 mL of concentrated HNO_3 and 3 mL of hydrogen peroxide. Samples were then sealed and digested using the Microwave Lab Station with the procedure and program described in Table 2 (step 1). When vessels were cooled and opened, samples were evaporated using the microwave evaporation programme also given in Table 2 (step 2). The sample was redissolved in 8M HNO_3 (Table 2, step 3) and analysed by ICP-MS (Table 2, step 4b). A preconcentration factor of 4 is achieved for Am using this procedure. Total time for this procedure is approximately 55 min, and a total of 10 samples can be processed simultaneously.

Preconcentration of americium was further enhanced using second step of microwave evaporation. In this case, 5 fractions of digested urine using the protocol described in (a) are combined into one Teflon vessel together with 3 mL of H_2O_2 and sample was evaporated (Table 2, step 4a). The final residue was re-dissolved in 8M of HNO_3 (Table 2, step 5), resulting in a total preconcentration factor of 20 by the successive evaporation steps. Total time for this procedure is approximately 70-80 min.

The digested samples were then measured using the on-line protocol, which is described above. The flow chart in Figure 2 summarizes the 3 different sample preparation procedures for ICP-MS analysis of ^{241}Am in urine.

Results and Discussion

Analysis of urine samples by ICP-MS with minimum sample preparation

In this part of our work we have studied the possibility of the determination of ^{241}Am in urine with a minimum sample preparation for a rapid measurement. Urine samples without any pre-treatment were acidified with HNO_3 to a final concentration of 0.5 M and analyzed by the developed protocol. We have investigated the reusability of TRU resin for the analysis of non-digested urine samples and the influence of the urine matrix on the retention properties of the TRU resin. The same TRU-resin column was used for loading 3 replicates of an acidified urine samples. In 80% of urine samples analyzed, the recovery of Am for the second replicate was lower than that obtained for the first replicate. Signal intensity for the third replicate of Am was found to be significantly

Table 2. Digestion procedures (A – digestion with one step of evaporation: steps 1, 2, 3, and 4b; B – digestion with two steps of evaporation: steps 1, 2, 3, 4a, 5 and 6)

Step	Operation	Sample	Reagents added per vessel/tube	Ramp temperature (°C) or power (W), time (min)	Hold temperature (°C) or power (W), time (min)	Cooling time (min)
1	Digestion	40 mL of urine	5 mL HNO_3, 3 mL H_2O_2	20 – 200°C, 10 min	200°C, 10 min	20
2	Evaporation	Samples after step 1	No	No	800 W, 10 min	No
3	Re-dissolving	Sample after step 2	5 mL HNO_3, 5 mL MQW	No	No	No
4a	Evaporation	5 fractions of the same sample prepared using steps 1-3 combined into one vessel	3 mL H_2O_2	No	800 W, 10 min.	No
4b	Analysis	Sample after step 3 transferred into 50 mL tube	No	No	No	No
5	Re-dissolving	Sample after step 4a	5 mL HNO_3, 5 mL MQW	No	No	No
6	Analysis	Sample after step 5 transferred into 50 mL tube	No	No	No	No

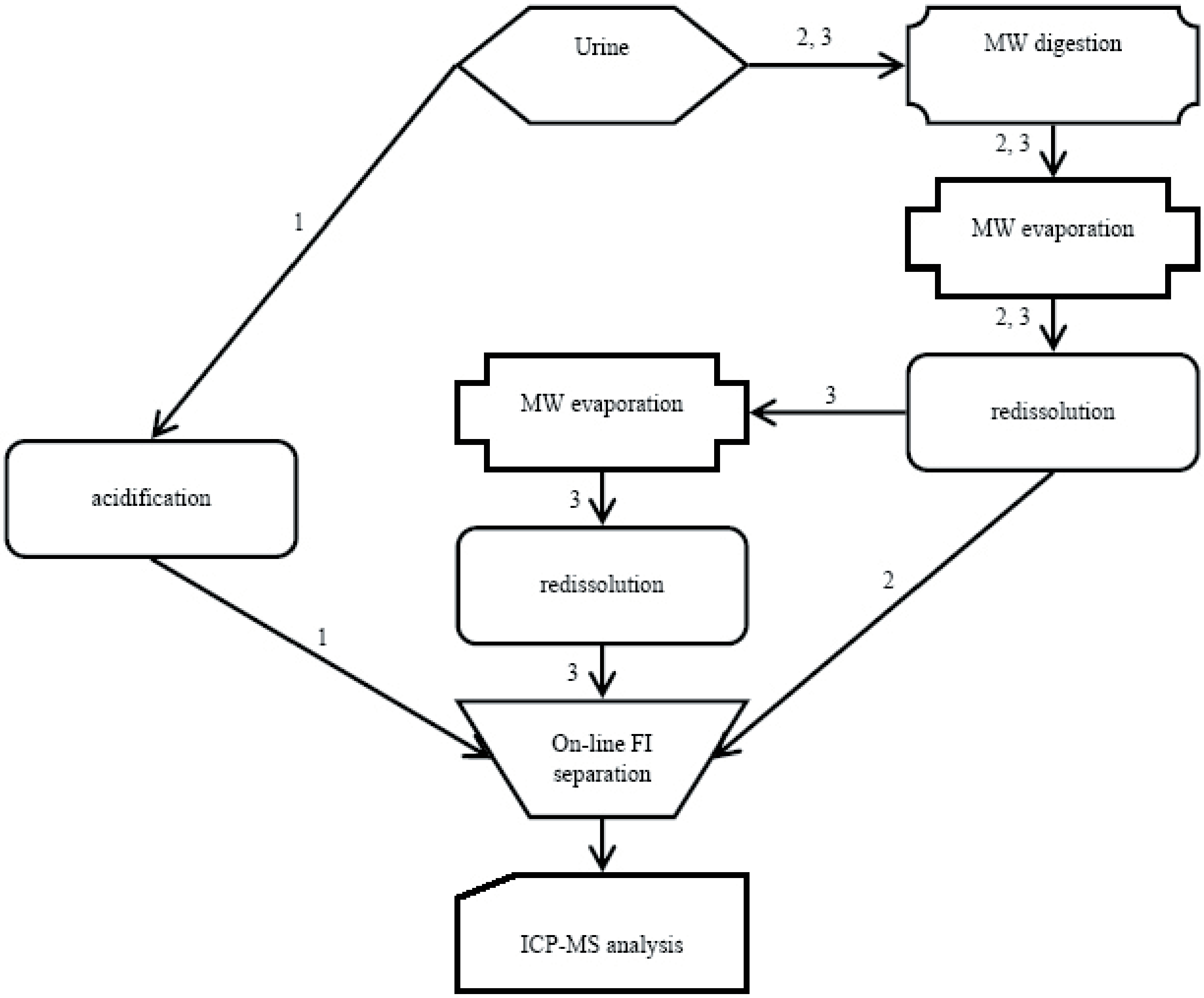

Figure 2. Flowchart illustrating the sample treatment operations for the determination of ^{241}Am by ICP-MS. MW – microwave, FI – flow injection.

lower. We can conclude that for the rapid determination of Am in urine, the same TRU-resin column cannot be used for more than 2 replicates of the same sample, and in most cases only for 1 replicate. Nine different urine samples were spiked with 10 pg L^{-1} of ^{241}Am and analyzed to study its recovery measurements. Thallium was determined to be a good internal standard for Am. All the results described below were calculated using 10 ng L^{-1} of Tl which was added to the eluent solution. Calculations of the recoveries were made using peak maximum of Am transient signals, as depicted in the elution profiles (Figure 3). For the first replicate of the measured samples, the analytical intensities were found to vary from 26 to 40 counts-per second (cps), while for the second replicate, signals varied from 18 to 38 cps with average background equal to 0.25 cps (varied from 0 to 2 cps). Figure 3 shows a comparison of the elution profiles for the first replicate of two different urine samples with their respective minimum and maximum intensities obtained. As can be seen from this figure, sizes of both peaks are very similar. Intensities measured for both replicates of pure standard of ^{241}Am were found to be 40 cps, which illustrates that urine matrix influences the sorption/retention/elution of americium onto/from the column. Accordingly, recoveries for first and second replicates varied from 65 to 100 % and from 45% to 95%, respectively. These results demonstrate that better precision for measurement of urine samples can be obtained if a TRU column is used for a single Am measurement. Recovery data for both replicates of Am measurements are presented in Table 3.

To improve accuracy and determine Am recovery, ^{169}Tm was used as yield tracer. It was found that Tm has recovery and elution characteristics similar to those of

Am, when spiked in urine and analyzed by ICP-MS, as can be seen from Figure 4. Recoveries for first and second replicates of Am measurements were recalculated using corresponding peak maximum measured for ^{169}Tm. It was demonstrated that for both replicates, the quantification of concentrations were significantly improved. Recoveries for new values obtained after correction were 92–108% and 88–115% for the first and second replicate, respectively, as shown in Table 3. Relative standard deviation (RSD) values, presented in Table 3, were calculated for different urine matrices spiked with the same concentration of ^{241}Am. A higher value of RSD demonstrates higher fluctuation of results from the average value. Relative error values show how close the average value of measured intensities is to the expected value, which was measured for a pure standard of Am using the same experimental conditions. Both RSD and relative error values indicated better results for the first replicate of non-digested urine and significant improvement in calculation when Tm was used as a yield tracer.

Detection limits for ^{241}Am in non-digested urine samples were determined and compared using a standard addition approach. Urine samples were spiked with 1, 3, 10 and 30 pg L^{-1} of ^{241}Am and a calibration curve was plotted. Detection limits were determined on the basis of 3σ (n=7) of the blank in the procedure. Under optimum conditions of preconcentration and nebulization, detection limits obtained were in the range 0.7 – 1.2 pg L^{-1} corresponding to 0.089 – 0.152 Bq L^{-1}, depending on the specific urine sample.

Analysis of digested samples

The influence of the volume of reagents used for the digestion of urine on the recovery of americium was studied. Different amounts of HNO_3 (1 – 5 mL) and H_2O_2 (0 – 5 mL) were added to 40 mL of urine spiked with 10 pg L^{-1} of ^{241}Am. The final volume was digested using a microwave program presented in Table 2 (steps 1, 2, 3 and 4b). It was found that the best analytical performances

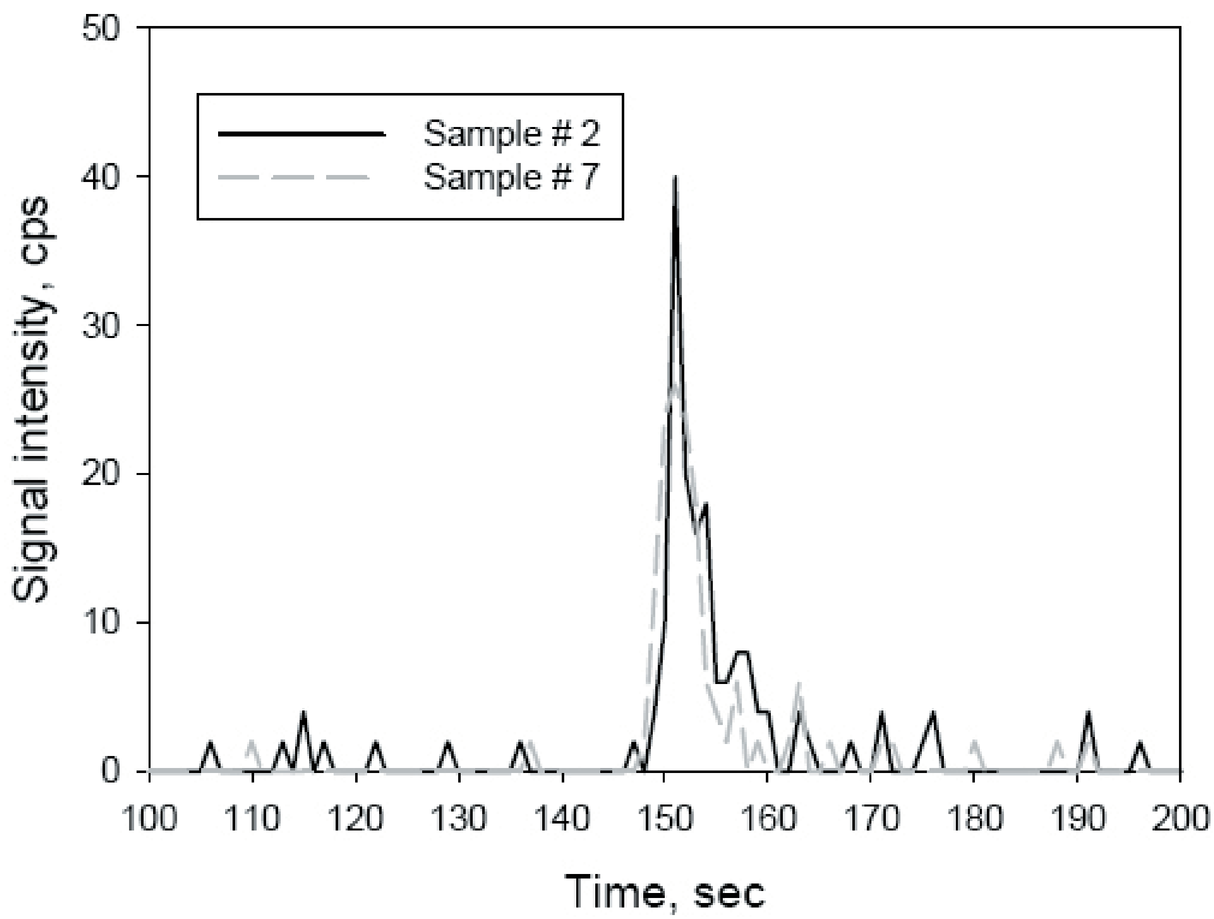

Figure 3. Elution profiles of 10 pg L^{-1} of ^{241}Am for two different non-digested urine samples.

Table 3. Signal intensities obtained for 1 ng L^{-1} solutions of ^{241}Am spiked with different urine samples compared with the signal of 1 ng L^{-1} solution of pure ^{241}Am standard.

	Measured signal of ^{241}Am, cps									RSD	Relative error	Expected signal
	S-1	S-2	S-3	S-4	S-5	S-6	S-7	S-8	S-9			
1st replicate	36	40	36	30	35	26	26	40	26	16.9%	18.1%	
2nd replicate	22	36	38	26	26	32	28	20	18	25.9%	31.7%	
1st replicate calculated with yield tracer	39.4	42.2	36.7	39.0	41.7	37.5	43.2	43.1	37.0	6.5%	0.04%	40 cps
2nd replicate calculated with yield tracer	35.2	45.9	42.1	35.9	37.1	38.7	36.9	34.5	35.9	9.8%	4.91%	

cps – counts per second,
RSD – relative standard deviation

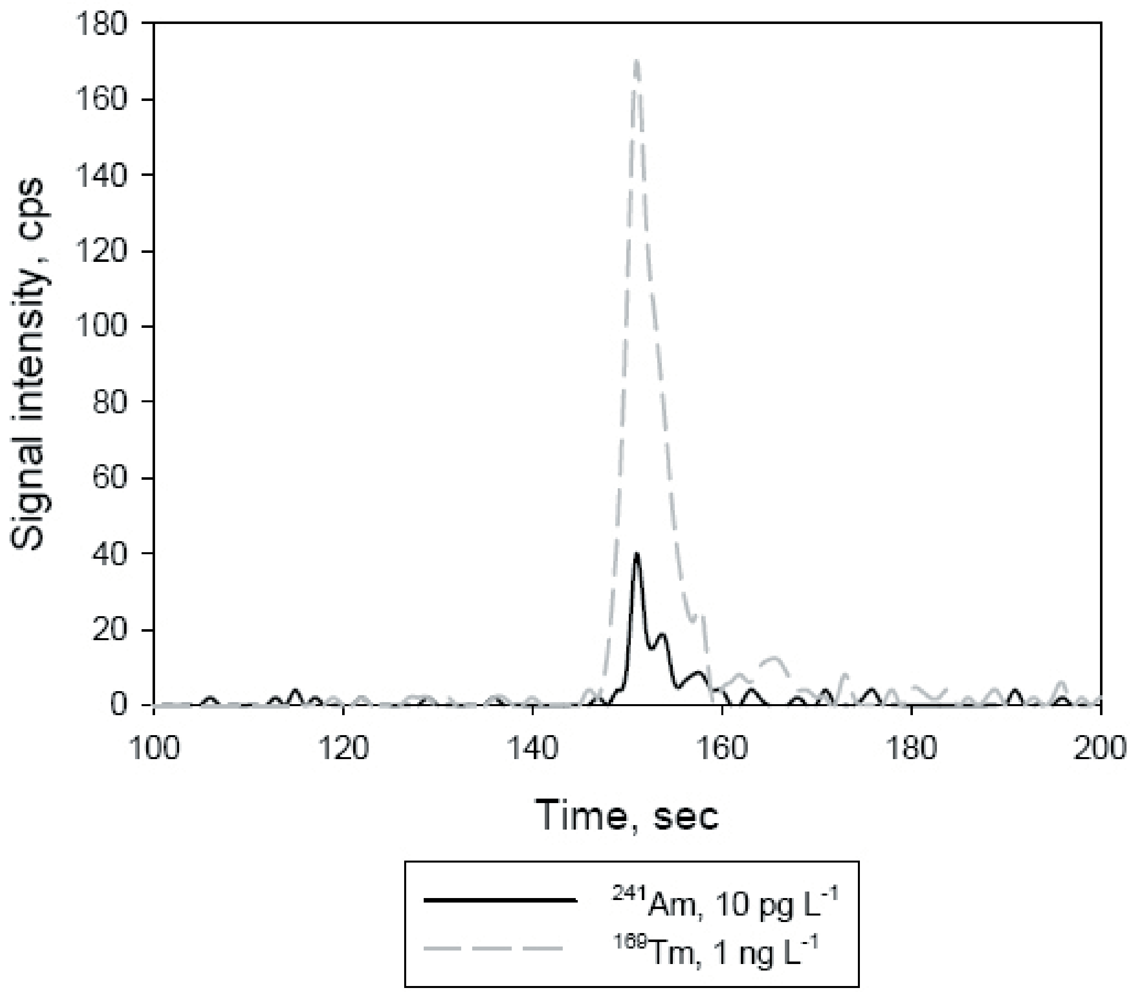

Figure 4. Elution profiles of ^{241}Am and ^{169}Tm using TRU resin.

were obtained for the following combination of sample and reagents: 40 mL of urine, 5 mL of HNO_3 and 3 mL of H_2O_2. After digestion, samples were evaporated and re-dissolved in 10 mL of 8 M HNO_3. For the evaluation of the analytical performances and the validation of the present method, urine samples were spiked with different Am concentrations, digested and analyzed using the protocol described above. It was found that the detection limit obtained for the digested, evaporated and re-dissolved urine samples (0.2 pg L^{-1}), is 4 times lower than that obtained for non-digested samples when a single measurement is made on the same column. In addition, the column can be reused for analysis of several digested replicates of the same or different urine samples without significant degradation of the packed resin.

The possibility of further improvement of Am detection limits for the analysis of urine samples were investigated using sample digestion followed by a double evaporation of the sample using the same microwave system. Two steps of evaporation proved to allow a 20 fold preconcentration of the sample. 200 mL of urine sample was digested and evaporated using the protocol presented in Table 2 (steps 1, 2, 3, 4a, 5 and 6), and resulted in a final volume of 10 mL of digested urine that was analyzed using the developed on-line method. The detection limit for ^{241}Am was improved by a factor of 17, when using a double evaporation after digestion (0.046 pg L^{-1} that corresponds to 0.0061 Bq L^{-1}) in comparison with the direct urine analysis. The present method resulted in a selective, sensitive and fast method for the on-line Am preconcentration and detection. The total time of analysis of 10 urine samples, including sample preparation, on-line preconcentration and detection is 110 min. 170 min. and 200 min. for non-digested, digested with single evaporation and digested with double evaporation, respectively.

Conclusion

Flow injection, on-line preconcentration, and matrix separation was developed for the rapid detection of ^{241}Am in urine by ICP-MS. Three different protocols for sample preparation were compared, evaluated and validated: (1) no sample preparation before the on-line preconcentration of urine onto TRU resin, (2) sample digestion with single evaporation, and (3) sample digestion with double evaporation.

Depending on special needs, the fastest analysis was obtained when no sample preparation was required. However, the best re-usability of column and best detection limits were achieved when digestion and digestion plus evaporation of urine were used.

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