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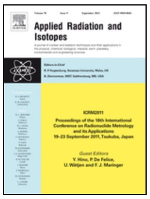

Investigation of key factors in preparation of alpha sources by electrodeposition

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ABSTRACT

The electrodeposition for alpha source preparation, using several electrolyte solution-cathode material combinations, is investigated and evaluated. The investigated factors focused on the electrodeposition time, the applied current, electrolyte volume and anode-cathode distances for the conventional electrodeposition cell (with no external stirring or cooling system). The conditions (temperature and the solution pH) during the electrodeposition process were also studied and discussed. The optimized parameters for each system are provided, and evaluated for the usage in determination of actinides (uranium, plutonium, americium and curium radioisotopes) in various samples.

1. Introduction

Preparation of high-quality alpha sources for determination of alpha-emitting radionuclides by alpha-particle spectrometry is the final step of the radiochemical analysis. The radiochemical separation methods used prior to the source preparation should be highly selective and sensitive to produce solutions of analytes as free as possible from any spectral or chemical interferences, and the source preparation itself should be quantitative and reproducible, giving homogenous, stable sources suitable for measurements at all source-detector distances. Many different source preparation techniques for alpha-particle spectrometry have been developed over the years to meet these necessary requirements (Aggarwal, 2016; Crespo, 2012; Lally and Glover, 1984; Sibbens and Altzitzoglou, 2007), but electrodeposition is certainly the most studied and still one of the most frequently used methods for determination of alpha-emitters in a variety of samples: environmental (Carvalho and Oliveira, 2009; Jia et al., 2002), geological (dos Santos et al., 2004), biological (Gaburo et al., 2006; Rzemek et al., 2015), industrial (Carvalho and Oliveira, 2009; Zarki et al., 2003), etc. Optimization of the electrodeposition method usually focuses on the usage of different aqueous and/or organic electrolyte solutions (Hallstadius, 1984; Ingelbrecht et al., 1997; Jobbágy et al., 2013; Kressin, 1977; Lee and Lee, 2000; Puphal and Olsen, 1972; Talvitie, 1972; Torrico et al., 2015) or on the improvements made on the system itself (e.g. the usage of rotating disc cathodes (Tsoupko-Sitnikov et al., 2000), semipermeable membranes to prevent platinum precipitation (Ferrero Calabuig et al., 1998), introduction of external equipment to improve the stirring of the electrolyte solution in a conventional electrodeposition cell (Jobbágy et al., 2013; Panta et al., 2010)). All the parameters that influence the electrodeposition yield and the source quality (chemical composition of the electrolyte solution, applied current/voltage, electrodeposition time, pH of the electrolytic solution, distance between the electrodes, electrolyte volume) need to be adjusted whenever such modifications are made. Furthermore, the process should enable (semi)quantitative deposition for various radionuclides under the same initial electrodeposition conditions (Aggarwal, 2016).

Several electrolyte solution-cathode material combinations were characterized and compared in our previous study for a conventional electrodeposition system used in order to obtain quantitative sources of americium isotopes with optimal spectral resolution for alpha-spectrometric measurements (Krmpotić et al., 2017; Trdin et al., 2012). This study is the extension of the reported findings, and focuses on the optimization of each proposed electrolyte solution-cathode material combination (for which ^{241}Am and ^{243}Am radioisotopes were again used as model solutions), and their implementation for the source preparation in determination of actinides (uranium, plutonium, americium and curium radioisotopes) in environmental samples.

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2. Materials and methods

2.1. Chemicals, reagents, equipment and instrumentation

The ^{241}Am and ^{243}Am standard solutions used in the study were purchased from Eckert & Ziegler Analytics (codes 76217-482 and 82708-482, respectively). The working solution for electrodeposition (ED) experiments, containing a mixture of ^{241}Am and ^{243}Am, was prepared by diluting aliquots of the above standard solutions to obtain approximately 1 Bq/g of each radioisotope.

. For ^{241}Am and ^{244}Cm determination in the samples, the ^{243}Am tracer solution (approximately 0.5 Bq/g) was also prepared by dilution of ^{243}Am standard solution. For determination of uranium and plutonium radioisotopes, standard solutions of ^{232}U (Eckert & Ziegler Analytics, code 76225-482), diluted to approximately 0.3 Bq/g, and ^{242}Pu (NIST, code 4334I), diluted to approximately 0.5 Bq/g, were used. All other chemicals and reagents used were of analytical grade.

The investigated electrolyte solutions were prepared by direct dilution of salts in deionised water, with the solutions' pH being adjusted by addition of concentrated H_2SO_4 or NH_4OH when needed (see Table 1). Their compositions and concentrations are presented in Table 1, and were chosen based on the fact that there is no need to manipulate with sample solutions in any way before the final source preparation step, as will be explained further in the procedures described in Sections 2.2 and 2.3.

The polypropylene ED cells used in this study were designed and manufactured at Jožef Stefan Institute (Ljubljana, Slovenia), as presented in our previous work (Krmpotić et al., 2017). The cells, with a total volume of 25 mL, contain a closing lid and anode insertion opening at the top, a metal backing for the cathode at the bottom, and no cooling or stirring system. The active area for ED is 2.01 cm^2 for 19 mm cathode discs. A spiral shaped platinum wire was used as the anode, while stainless steel (SS), copper (Cu) and silver (Ag) discs were used as the cathodes. All ED experiments were performed using an HY3005D-3 DC Power Supply.

For the detection and measurement an alpha-spectrometer (CANBERRA Alpha Analyst™, Genie-2000) with passivated implanted planar silicon semiconductor detectors (450 mm^2 active area) was used. Energy and efficiency calibration of the detection system was made using a standard electroplated radionuclide source, containing ^{238}U, ^{234}U, ^{239}Pu and ^{241}Am (Analytics, Inc. code 66601-508). All measurements were conducted at 9 mm detector-source spacing, with 13% detection efficiency.

Measurements of the pH and temperature were conducted using a Mettler Toledo pH-meter SevenCompact™ with InLab Expert Pro-ISM combined pH electrode containing a temperature probe with ISM (Inteligent Sensor Management). The pH measuring range for the used electrode is from 0.00 to 14.00 (resolution 0.01, accuracy ±0.01), in the temperature range from 0.0 °C to 100.0 °C (accuracy ±0.1 °C).

Table 1
Electrolyte solution mixtures and cathode materials.

Electrolyte designation	Solution composition and concentration	Cathode material
AO-Cl	0.5 M $(NH_4)_2C_2O_4$/0.3 M HCl (no pH adjustment)	Stainless steel (SS)
ASO	0.2 M $(NH_4)_2SO_4$/0.05 M $(NH_3OH)_2SO_4$/0.1 M $(NH_4)_2C_2O_4$ (pH adjusted to 1.7)	Silver (Ag)
NS	0.3 M Na_2SO_4 (pH adjusted to 2.0)	Copper (Cu)

For the purpose of method validation, the selected samples for analyses consisted of a groundwater sample collected in the vicinity of a former uranium mine in Žirovski vrh (Slovenia), a Baltic Sea sediment (IAEA-300 reference material) and a PT water sample (environmental radioactivity proficiency test exercise, aqueous solution in 2 M HNO_3, sample code: B150415, National Physical Laboratory, UK).

2.2. Alpha source preparation from the working solution

After the cathode discs were thoroughly cleaned with ethanol, and fixed at the cell bottom, the cell was checked for leakage. The appropriate volume of the electrolyte solution was added to the cell, along with approximately 0.2 Bq of each americium radioisotope. The investigated electrolyte volumes ranged between 7.5 mL and 20 mL. Lower volumes were not investigated since they were not sufficient for the cell geometry and the anode could easily stay dry during the ED process, while volumes larger than 20 mL were inappropriate due to cell size. The investigated range of the electrode distances, due to the cell geometry and the electrolyte volume, was between 5 mm and 10 mm. The investigated applied current intensities ranged from the minimum of 300 mA to the maximum of 900 mA, in 100 mA increments, while the investigated times ranged between 30 min and 150 min, in 30 min increments. While varying each of the mentioned factors, others were kept constant based on the conducted preliminary experiments, i.e. the applied current at 600 mA, ED time at 120 min, electrolyte volume at 10 mL, and the distance between the electrodes at 10 mm. The prepared sources were subsequently heated on a hot plate at approximately 500 °C to fix the americium deposit on the cathode surface and remove any remaining volatile substances that could contaminate the detector in the alpha-spectrometer vacuum chamber.

For the pH and temperature measurements the ED was carried out with no tracers present in the electrolyte solutions (blank ED). The measurements were conducted every 30 min since these time intervals were taken for yield determinations.

2.3. Radiochemical separation and alpha source preparation techniques in determination of uranium, plutonium, americium and curium radioisotopes in various matrices

A groundwater sample and a marine sediment sample have been analysed to obtain the uranium concentration and isotopic composition by alpha-particle spectrometry. For determination of uranium isotopes, a standard solution of ^{232}U was used as a yield tracer. Uranium was pre-concentrated with $Fe(OH)_3$ co-precipitation from the water sample, while it was extracted from the sediment sample by total dissolution using a mixture of nitric, hydrofluoric and perchloric acids. Subsequent separation was performed using UTEVA resin (Eichrom Technologies, LLC) in 3 M HNO_3 solution, as described in (Eichrom Technologies, 2001).

Plutonium, americium and curium have been analysed in a proficiency test water sample (Table 4). Solutions of ^{242}Pu and ^{243}Am were used as yield tracers. The analysed water sample was evaporated to dryness and the residue was dissolved in 2 M HNO_3. For plutonium oxidation state adjustment, freshly made 1.25 M $FeCl_2$ solution was added to the sample to reduce Pu^{6+} to Pu^{3+}, followed by the addition of 1 M $NH_2OH{\cdot}HCl$. For oxidation of Pu^{3+} to Pu^{4+} 1 M $NaNO_2$ was added to the sample solution. After the oxidation state adjustment, the separation of plutonium, americium and curium radioisotopes was performed on tandem anion-exchange and extraction chromatographic resins according to the procedure described in detail in (Benedik, 2013).

For the preparation of the alpha sources by ED, the purified analyte fractions from the chromatographic columns were evaporated to dryness, dissolved in a small volume of concentrated HNO_3 and H_2O_2 (to remove any eluted organic compounds), and again evaporated to dryness. The dry residues were dissolved in 2 mL of the selected electrolyte solution and quantitatively transferred to the ED cell up to final volume of 10 mL. The current was adjusted depending on the electrolyte used, and the sources prepared in the time ranges between 60 min and 120 min, as described in Table 2. The ED process was finished as described in the previous section.

The alpha sources from these matrices were also prepared by the micro co-precipitation method (MPC) with NdF_3 (Hindman, 1983; Sill and Williams, 1981) for the comparison and evaluation purpose of the proposed ED method(s).

3. Results and discussion

3.1. Time and current optimizations

The chosen time and applied current ranges for the investigation of americium electrodeposition were based on preliminary experiments, which are given in Section 2.2. Additionally, ED times above 150 min were not investigated since they proved too long and inconvenient (due to decrease of the ED yield), while the 30 min time intervals were chosen to reduce the number of experiments needed to reach the satisfying conclusions, while also producing less chemical and radioactive wastes. Despite the fact that the ammonium sulphate/oxalate based electrolyte with diethylenetriaminepentaacetic acid (DTPA) as a chelating agent, used in our previous study (Krmpotić et al., 2017), was reported to give the sources of highest quality on Ag cathode, further experiments for method optimization were made on the solution without DTPA since its presence proved to significantly decrease the electrodeposition (ED) yield while not improving the source quality drastically.

The time dependent ED yields obtained for americium radioisotopes from the working model solution of the electrolytes are presented in Fig. 1a. Under the experimental conditions of 600 mA, 10 mm anode-cathode distance and 10 mL electrolyte volume, quantitative ED was obtained in 120 min when using AO-Cl electrolyte with SS cathode, and in only 60 min when using NS electrolyte in combination with Cu cathode. Slight yield decrease was observed as the electrolysis continued (150 min) for the AO-Cl/SS system (95%), while the usage of sodium sulphate did not exhibit any activity loss as the electrolysis continued after the americium was quantitatively deposited on the cathode surface. As for the ASO electrolyte mixture in combination with Ag cathode, the maximum deposition yield was also obtained in 120 min, but reaching only 88%, and slightly decreasing (to 74%) as the process continued further (150 min), indicating that higher currents are needed for the quantitative deposition to occur in this medium.

Table 2
Optimized parameters for the conventional electrodeposition cell (25 mL).

Electrolyte solution	AO-Cl	ASO	NS
Cathode material	Stainless steel	Silver	Copper
Current (mA)	600/700–900	700	600–700
Time (min)	120/90	120	60
Anode-cathode distance (mm)	10	10	10
Electrolyte volume (mL)	10–15	10–15	10–15

Looking at the deposition yields with respect to the applied currents (Fig. 1b) (semi)quantitative results were obtained in each case under the experimental conditions (120 min). The sodium sulphate electrolyte (NS) yielded quantitative results in the whole investigated current range, even under lower currents (300 mA and 400 mA). However, these lower currents are not recommended since lower spectral resolution was observed (around 40 keV) below 500 mA, most probably due to the fact that no stirring equipment was being used and that the gas evolution at the two electrodes was too low under these conditions (along with the temperature rise, see Fig. 3) to enable appropriate natural convection of the solution and thus uniform mass distribution. But it is very interesting that for the NS system the quantitative source preparation can be obtained in a fairly broad range of applied currents, making the process highly susceptible to any possible fluctuations that can easily occur during the electrolysis. The AO-Cl and ASO electrolytes yielded quantitative results at higher currents compared to NS, being 600 mA for AO-Cl/SS system and 700 mA for ASO/Ag system (Fig. 1b). Furthermore, no yield decrease was observed for the NS/Cu system when applying higher currents (just as when prolonging the electrolysis time), while slight yield decrease was observed with the other two electrolytes. The AO-Cl/SS system exhibited no significant actinide loss in the range between 600 mA and 800 mA (under 120 min time period), while it was observed for the ASO/Ag system above 700 mA.

These results are consistent with the previously published data for similar ED systems (electrolyte compositions used) and radionuclides (Hallstadius, 1984; Oh et al., 2014), while also showing that fast source preparation of actinides can be achieved under significantly lower applied currents for the conventional ED cells when using higher concentrations of sodium sulphate in the diluted sulphuric acid medium than initially proposed (Hallstadius, 1984), and also frequently used.

As the AO-Cl electrolyte exhibited certain degree of robustness to the electrolysis conditions for americium quantitative deposition, especially for the applied currents, further investigations were made in order to potentially reduce the ED time for this medium. From Fig. 2a, in which the ED yields with time for different applied currents in the mentioned medium are presented, it can be seen that the currents higher than 700 mA are needed for the quantitative deposition to occur under 120 min. To be able to produce quantitative sources in 60 min, as

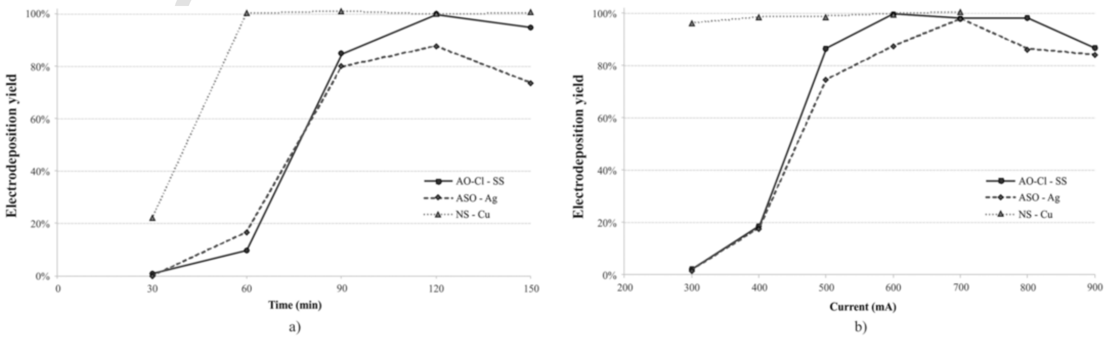
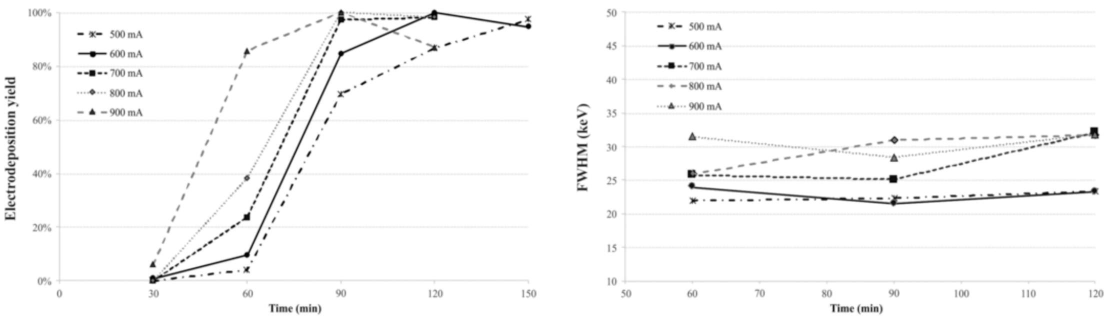


Fig. 1. Americium isotopes electrodeposition yields in dependence of the three electrolyte solution-cathode material systems investigated ($l = 10$ mm; $V = 10$ mL) with a) time ($I = 600$ mA), b) the applied current ($t = 120$ min).



a)

b)

Fig. 2. a) Electrodeposition yields of americium isotopes with time under different applied currents for the AO-Cl/SS system (l = 10 mm; V = 10 mL), and b) the corresponding spectral resolution of the prepared sources.

with the NS electrolyte, currents higher than 900 mA should be applied for this electrolyte, but were inconvenient to use with the power supplies available in this study. Additionally, as presented in Fig. 2b, the increase in the applied current decreases the spectral resolution (FWHM), most probably due to higher gas evolution, and degrades the source quality (> 30 keV). The ED time also increases the spectral resolution but to a lesser extent (Fig. 2b). Also, special care on ED conditions must be taken when preparing the counting sources in environmental sample analysis, especially as the obtained solutions of radionuclides to be determined are not entirely free from all interferences after the purification and separation steps.

3.2. pH and temperature conditions during the electrodeposition

For the investigation of the changes occurring in the working model solution during the electrolysis in terms of the solution pH and temperature, the measurements for AO-Cl and ASO electrolytes were conducted for the applied currents of 400 mA, 600 mA and 900 mA since significant differences in yields and source qualities were observed at these conditions. The measurements for the NS electrolyte were conducted under slightly lower currents (300 mA, 400 mA and 600 mA) due to significant differences in source qualities, despite the quantitative depositions that were observed at these conditions. The obtained results are summarized in Fig. 3.

When looking at the conditions during the ED in the AO-Cl medium (Fig. 3), the pH of the solution rises drastically to 8 in the first 30 min, and drops below 2 in the time frame that depends on the applied current. When applying only 400 mA it takes at least 120 min for the pH to drop (below 2) into the region where hydroxide precipitation occurs (Hansen, 1959), which is the reason that yields were so low under these conditions (Fig. 1b). On the other hand, the pH drops fairly quickly (in 60 min' time) when applying 900 mA, which is again consistent with the yields obtained (Fig. 1b).

As for the sulphate based electrolytes, ASO and NS, the initially adjusted pH (Table 1) does not change significantly throughout the whole process (with time or the applied current), as presented in Fig. 3, and is highly susceptible to hydrogen evolution at the cathode surface due to sulphate ion buffer properties. This is probably an additional reason, along to the occurrence of Pt dissolution in a sulphate medium which contributes to improvements in the ED yields (Beesley et al., 2009), for such fast precipitation in the NS electrolyte under both low and high currents, while the usage of a more complex system (ASO), that contains both sulphate and oxalate ions with chelating properties, inhibits the ED process to a certain degree.

The observed temperatures under the all investigated ED conditions did not reach boiling points of the investigated solutions. The highest temperatures observed were around 65 °C and 70 °C for the ASO and AO-Cl media, respectively, under high applied currents (900 mA), indicating that no significant electrolyte loss should occur as long as the process is not too long and the cell is covered with a lid to prevent excessive solution evaporation. In general, slightly lower temperatures (about 5–10 °C) evolved in the sulphate based electrolytes (ASO and NS), compared to the oxalate-chloride medium (AO-Cl) under the same electrodeposition conditions (Fig. 3).

3.3. Effect of the electrolyte solution volume and the distance between the electrodes

The investigation of the dependence of ED yield with respect to the electrolyte solution volume and the distance between the electrodes was performed under the applied current of 600 mA, and 120 min electrodeposition time. The anode-cathode distance was fixed at 10 mm for the investigation of the solution's volume influence, while 10 mL solution volume was used for investigation of the effect of the distance between the two electrodes in the cell.

The obtained results, presented in Fig. 4, indicate that the volumes of the electrolyte solution between 10 mL and 15 mL enable (semi)quantitative deposition of americium radioisotopes, with the highest spectral resolutions obtained. Lower volumes (5 mL) also yielded satisfying results, but with the high risk of the pH being changed and/or anode staying dry, these volumes were not considered as optional for regular use. Either way, the system is fairly robust in a fairly wide range of electrolyte volumes, between 5 mL and 15 mL for the used cell. Larger volumes (20 mL) gave extremely low deposition yields (Fig. 4a), as low as only a few percent of the initial activity. Time of the electrodeposition, or the applied current, should, in that case, be significantly increased.

Similar results were obtained for the anode-cathode distance investigations, where quantitative yields were obtained in the whole investigated range, between 5 mm and 10 mm, with a slight improvement of the spectral resolution when 10 mm spacing was employed (Fig. 4b). For this reason, the 10 mm distance between the electrodes was chosen as optimal.

3.4. Application of the optimized electrodeposition method for alpha source preparation in determination of actinides in various samples

The proposed optimal conditions for source preparation by electrodeposition (Table 2), using the selected cathode materials as source backings in combination with the chosen electrolyte solutions, were tested for application in determination of actinides (uranium, plutonium, americium and curium radioisotopes) in different types of samples.

The activity concentration results for uranium radioisotopes in water and sediment samples (Table 3) were mutually in good agreement, and with the assigned values (in the case of the sediment sample), for

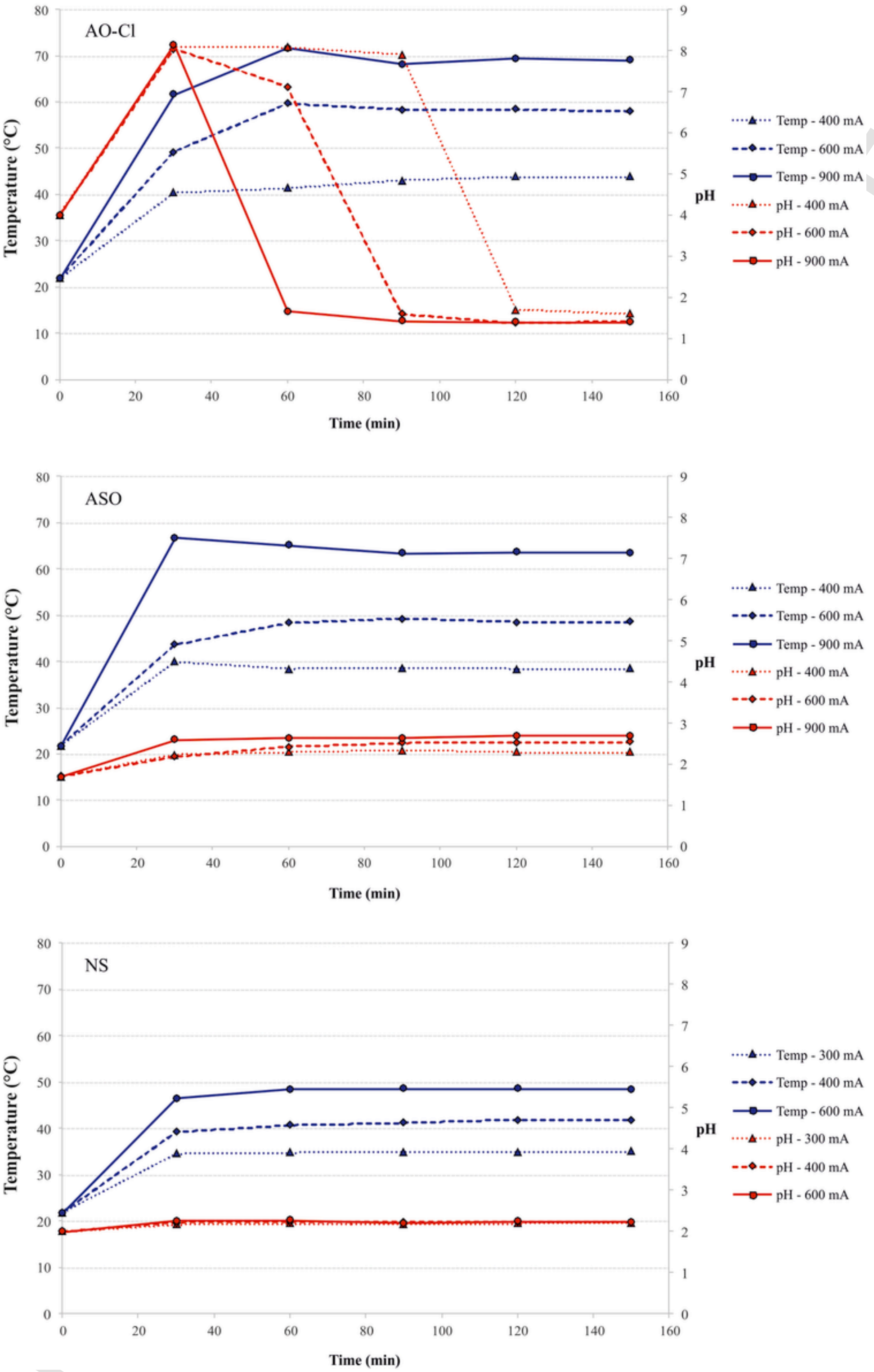
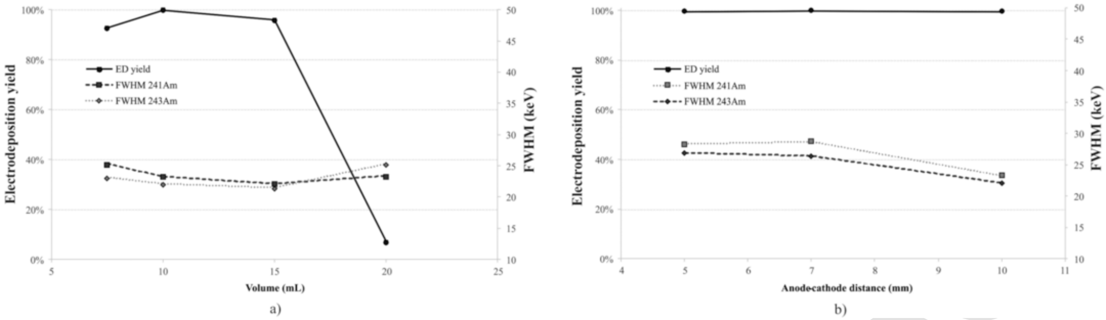


Fig. 3. Variations of pH and temperature with respect to the applied current during the electrodeposition process for the three types of electrolytes ($l = 10\,\text{mm}$; $V = 10\,\text{mL}$).

every source preparation method used. The obtained overall radiochemical yields for uranium suggest that its deposition on the cathode surface could be (semi)quantitative for every investigated system (cathode material-electrolyte solution combination), ranging from 57% to 82% (total), which is comparable to yields obtained for source preparation by MPC. As can be seen, both the lowest and highest yields were obtained when using the same source preparation conditions for different samples (in the NS/Cu system), indicating that sample type and/or handling process could have a greater influence on the overall result, rather than the source preparation (step) itself.

The best spectral resolution for uranium radioisotopes (23–25 keV FWHM) was obtained on stainless steel cathodes in combination with ammonium oxalate-chloride medium (AO-Cl), which is significant improvement in comparison with the resolution obtained if source is



a)

b)

Fig. 4. Electrodeposition yields and spectral resolutions (FWHM) of the electroplated americium sources for the AO-Cl electrolyte with respect to a) the electrolyte volume, and b) the anode-cathode distance ($I = 600\,\text{mA}$, $t = 120\,\text{min}$).

Table 3
Activity concentrations of uranium radioisotopes in water and sediment samples.

Sample type	Source preparation method	A (mBq L^{-1})		Radiochemical yield (%)
		^{234}U [FWHM (keV)]	^{238}U [FWHM (keV)]	
Water collected in the vicinity of a former uranium mine	ED[a] (AO-Cl/SS)	65.7 ± 5.8[*] [25]	24.3 ± 2.4[*] [23]	68 ± 5[*]
	ED (ASO/Ag)	67.3 ± 5.3 [26]	25.4 ± 2.3 [30]	74 ± 5
	ED (NS/Cu)	61.8 ± 5.2 [41]	23.1 ± 2.3 [35]	82 ± 6
	MPC[b] (NdF_3)	64.2 ± 4.5 [54]	25.3 ± 2.0 [50]	54 ± 4
		A (Bq kg^{-1})		
IAEA-300 (Baltic Sea sediment)	ED (NS/Cu)	73.0 ± 4.7[*] [40]	69.7 ± 4.1[*] [31]	57 ± 5[*]
	MPC (NdF_3)	69.0 ± 6.8 [55]	70.0 ± 6.9 [63]	72 ± 6
	Assigned value	69.0 ± 5.0	64.7 (61 – 68.7)	–

[a] Electrodeposition.
[b] Micro co-precipitation.
[*] Expanded measurement uncertainty with k = 2 (95% significance level).

prepared by MPC method (50–63 keV FWHM). The lowest resolution for ED source preparation (from 31 keV to 41 keV FWHM) was obtained when using the sodium sulphate medium (NS), which is in agreement with the results obtained for electrodeposition of americium radioisotopes in the previous study (Krmpotić et al., 2017).

The activity concentration results for ^{239}Pu, ^{241}Am and ^{244}Cm in a PT water sample (NPL 2015) also showed very good agreement comparing the obtained results by using different source preparation methods, and with the assigned values provided by the organizer (Table 4). The total radiochemical yields for plutonium determination were very high for the counting sources prepared with NS/Cu and AO-Cl/SS systems, being 85% and 97%, respectively. Very low yield (only 28% total) was obtained when using the ASO electrolyte for ED, which in this case cannot be attributed to the radiochemical procedure used, due to the fact that all the samples were treated with the same radiochemical procedure up to the source preparation step, but suggests that the parameters for ED in this medium (Table 2) are most probably not optimal for Pu deposition. This was somewhat expected and is in accordance with the previous reported studies (Lee and Pimpl, 1999; Oh et al., 2014), but was tested nevertheless due to the fact that lower concentrations of the chosen electrolyte's components were studied here, which previously proved to give higher deposition yields under lower currents (Krmpotić et al., 2017). To be able to quantitatively prepare plutonium sources in this medium, higher currents would be necessary.

Very high overall radiochemical yields were obtained for americium and curium radioisotopes for every source preparation method used, ranging from 87% to as high as 97% when sources were prepared by ED, compared to also very high 89% when using the MPC method. These results suggest, as in the case of uranium radioisotopes determination, that major discrepancies in total recovery are most probably due to the whole process and not the source preparation step alone, indicating that the electrodeposition should be (semi)quantitative for the investigated radioisotopes, and that the optimized and proposed parameters obtained in this study for the ED source preparation could be applicable to real sample measurements of actinides.

Table 4
Activity concentrations (Bq/g) of plutonium, americium and curium radioisotopes in a PT water sample (NPL 2015, number B150415).

Source preparation method	^{239}Pu (Bq/g)	Radiochemical yield (%)	^{241}Am (Bq/g)	^{244}Cm (Bq/g)	Radiochemical yield (%)
	[FWHM (keV)]		[FWHM (keV)]	[FWHM (keV)]	
ED[a] (AO-Cl/SS)	1.351 ± 0.043[*] [29]	97 ± 3[*]	4.87 ± 0.19[*] [24]	10.42 ± 0.39[*] [23]	87 ± 4[*]
ED (ASO/Ag)	1.336 ± 0.109 [38]	28 ± 2	5.08 ± 0.23 [27]	10.27 ± 0.53 [26]	89 ± 5
ED (NS/Cu)	1.299 ± 0.081 [33]	85 ± 5	5.07 ± 0.22 [33]	10.48 ± 0.43 [31]	97 ± 4
MPC[b] (NdF_3)	1.394 ± 0.091 [42]	89 ± 5	4.64 ± 0.36 [41]	10.66 ± 0.78 [51]	89 ± 4
Assigned value	1.335 ± 0.003	–	5.03 ± 0.01	10.78 ± 0.04	–

[a] Electrodeposition.
[b] Micro co-precipitation.
[*] Expanded measurement uncertainty with k = 2 (95% significance level).

As for the quality of the electrodeposited sources, the highest spectral resolutions (29 keV for ^{239}Pu and 24 keV/23 keV for ^{241}Am/^{244}Cm, respectively) were obtained when using the AO-Cl/SS system, as was the case for uranium radioisotopes. The lowest resolutions were again obtained in the NS medium (33 keV for ^{239}Pu and ^{241}Am, and 31 keV for ^{244}Cm), which is in accordance with the results obtained on americium model solutions, additionally proving that this electrolyte is very good for fast and quantitative electrodeposition of actinides but on account of slight spectrum degradation (Vera Tome and Martin Sanchez, 1991). The lower spectral resolution of ^{239}Pu obtained in the ASO electrolyte (38 keV FWHM) is probably more a result of the low counting statistics due to low source activity (low radiochemical yield) than the true method capability.

4. Conclusion

The three electrodeposition systems (electrolyte solution-cathode material combinations) for the preparation of (semi)quantitative, high-quality alpha sources by electrodeposition, were investigated and their suitability for the routine usage in determination of actinides (^{234}U, ^{238}U, ^{239}Pu, ^{241}Am and ^{244}Cm) in various types of samples was evaluated.

This study showed that fast and quantitative source preparation can be obtained when using 0.3 M Na_2SO_4 aqueous solution (with pH pre-adjusted to 2.0) and copper as the source backing, in only 60 min, under relatively low current conditions (600 mA or higher). Despite the fact that the electrodeposition time prolongation, and the increase in the applied current degrade the source quality, optimal applied currents for this system are set between 600 mA and 700 mA (FWHM < 30 keV) since the usage of lower currents showed significant source degradation in this medium (FWHM > 40 keV). Slightly longer electrodeposition times are required for the usage of 0.5 M $(NH_4)_2C_2O_4$/0.3 M HCl aqueous solution in combination with the stainless steel backing, being 90 min under slightly higher applied currents (than for the Na_2SO_4 medium), between 700 mA and 900 mA, or 120 min for lower current conditions (600 mA). The longest time (120 min), and strictly defined current (700 mA), are needed to reach (semi)quantitative deposition when using a more complex electrolyte solution, 0.2 M $(NH_4)_2SO_4$/0.05 M $(NH_3OH)_2SO_4$/0.1 M $(NH_4)_2C_2O_4$ (pH pre-adjusted to 1.7) with silver cathode as the source backing.

The electrolyte volumes for the investigated ED cell proved to give satisfactory results as long as they are below 20 mL. With respect to the source quality the optimum volumes ranged between 10 mL and 15 mL. Similarly, all investigated electrode distances yielded quantitative results, but the 10 mm anode-cathode distance provided the highest quality of the prepared sources and the corresponding alpha spectra.

The proposed conditions for alpha source preparation by electrodeposition were evaluated through determination of actinides in different types of real (environmental and PT) samples. The high-quality sources for alpha-spectrometric measurements, with satisfyingly high overall yields and spectral resolutions, were prepared from the investigated electrolyte solutions, and on available source backings (cathode materials) for all determined radioisotopes (^{234}U, ^{238}U, ^{239}Pu, ^{241}Am and ^{244}Cm). The one exception was electrodeposition of plutonium from the sulphate/oxalate electrolyte solution (0.2 M $(NH_4)_2SO_4$/0.05 M $(NH_3OH)_2SO_4$/0.1 M $(NH_4)_2C_2O_4$), where very low yield was obtained.

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