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Development of separation procedures for determination of uranium and thorium in the ^{82}Se source of the SuperNEMO experiment: first steps

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Abstract

Two methods have been tested for separation of uranium and thorium from selenium using UTEVA and anion exchange resins. The average yield for separation of uranium, thorium and selenium was determined to be for the UTEVA method 91 ± 9%, 79 ± 8% and 96 ± 8%, respectively, and 96 ± 10%, 88 ± 9% and 94 ± 8%, respectively, in the case of the anion exchange resin. The methods will be used in consequent development of analytical procedures for determination of ^{238}U and ^{232}Th content with mass spectrometric techniques in ^{82}Se source materials of the SuperNEMO experiment.

Keywords Uranium · Thorium · Selenium · UTEVA resin · Anion exchange resin · SuperNEMO

Introduction

Large-scale experiments which have been or are being established in order to answer some fundamental questions of nuclear physics, such as the SuperNEMO experiment [1], have been recently arising the need for radiopurity measurements on the nBq g^{-1} or even sub-nBq g^{-1} levels. The isotope source deposited on a foil to be used in the SuperNEMO experiment, which shall be exclusively devoted to the search for the neutrinoless double beta-decay, is made of enriched and purified ^{82}Se powder. From the point of view of internal contamination, there are two beta-emitters, ^{214}Bi ($T_{1/2}$ = 19.7 min) and ^{208}Tl ($T_{1/2}$ = 3.05 min), which are especially undesirable as energy of beta-electrons of these short-lived radionuclides is above the double beta-decay energy of the ^{82}Se source (~ 3 MeV) [2]. While ^{214}Bi is part of the uranium decay chain, ^{208}Tl is a progeny of ^{232}Th.

In recent years, several methodologies have been developed which could be utilized for radiopurity determination of ^{82}Se source and constructing materials of the SuperNEMO experiment. These methods can be intuitively divided into non-destructive—gamma-spectrometry, neutron activation analysis (NAA)—and destructive ones—inductively coupled plasma mass spectrometry (ICP-MS) and accelerator mass spectrometry (AMS). On top of that, the SuperNEMO collaboration successfully put in operation a dedicated BiPo-3 detector which is capable of determination of alpha and beta-emitters on a surface material at ultra-low levels [3].

If the SuperNEMO experiment is expected to reach the half-life of 10^{26} y, then the limits for radiopurity demands are very high. For ^{208}Tl and ^{214}Bi in the ^{82}Se source of the detector, the limits were set below 2 and 10 nBq g^{-1}, respectively [2]. As the short-lived thallium and bismuth progenies are expected to be in the secular equilibrium with their parents, the aforementioned detection limits can also be applied for ^{232}Th and ^{238}U. Screening of materials, including ^{82}Se source, has been already conducted using low-level HPGe γ-spectrometry, however, only detection limits of about 1 µBq kg^{-1} could be reported due to intrinsic contamination of gamma-spectrometers and surrounding materials of underground facilities by ^{238}U and ^{232}Th decay chain products [4]. Another approach to background constraints of the SuperNEMO experiment

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was introduced by Kučera et al. [5] who exploited radiochemical neutron activation analysis (RNAA) for determination of primordial radionuclides in the ^{82}Se source. In this case, pre-irradiation chemistry was not applied at all, which can be considered as the greatest advantage of the technique, though the authors were able to improve detection limits for radionuclides of interest by using chemical separation after irradiation; the detection limits of 4 μBq g^{-1} and 12 μBq g^{-1} have been reached for thorium and uranium, respectively.

Mass spectrometry techniques, such as ICP-MS and AMS are more sensitive if compared to radiometric methods, especially in the case of long-lived radionuclides with low specific activity. On the other hand, any mass spectrometry method is destructive as it requires the sample to be atomized. LaFerriere et al. [6] used ICP-MS for determination of ^{232}Th and ^{238}U in copper and lead shielding materials of the MAJORANA DEMONSTRATOR, which searches for the neutrinoless double-beta decay of ^{76}Ge. Removing unwanted matrix elements and pre-concentration of uranium and thorium was achieved with the use of a novel sample preparation method based on anion exchange. As a result, detection limits of 0.03 nBq g^{-1} and 0.1 nBq g^{-1} for ^{232}Th and ^{238}U, respectively, have been reported for analysis of copper samples.

First successful attempts on ultra-sensitive radiopurity measurements of copper samples by AMS have been carried out by Famulok et al. [7] who refrained from application of the pre-concentration chemistry in order to avoid a possible contamination. Formation of actinide-copper clusters in sputter ion sources has been investigated to avoid environmental contamination with uranium and thorium oxides [7, 8]. The first detection limits for thorium and uranium on the level of tens of nBq g^{-1} (Cu) have been obtained using 10 MV accelerator [7].

As it is clearly obvious from the aforementioned paragraphs, the mass spectrometry methods are capable of reaching the lowest detection limits in radiopurity measurements. However, both ICP-MS and AMS generally require pre-concentration of the radionuclide of interest and its almost complete separation from the original sample matrix. Selenium, uranium and thorium can be separated from each other exploiting various techniques and sorbents, e.g. solid phase extraction (SPE) or anion exchange chromatography [9, 10]. In this study, we present results of testing of straightforward and simple procedures for separation of uranium and thorium from modelled selenium samples using UTEVA resin and anion exchange resin (Cl^- form). The radiochemical yields of the developed methods were traced with the use of ^{232}U and ^{229}Th, whose activities were determined by alpha-spectrometry. On top of that, qualitative evaluation of content of impurities in high-purity elemental selenium powder was conducted using low energy mass scanning.

Experimental

Reagents and materials

All chemical reagents were of analytical grade at minimum and all dilute solutions were prepared with deionized water (DI). The UTEVA (100–150 μm) and Anion Exchange (Cl^- form, 1 × 8, 100–200 mesh) resins were supplied by Eichrom Technologies (Lisle, USA). The radiochemical yield of uranium and thorium separations was monitored with the certified solutions of ^{232}U (A150051) and ^{229}Th (A160970) with the specific activity of 1.020 and 1.025 Bq g^{-1}, respectively, both supplied by the National Physical Laboratory (Teddington, UK). The elemental Se powder (Alfa Aesar, Karlsruhe, Germany) used in the mass scanning experiments had declared purity of 99.999% (metal basis). Modelled Se samples with the enhanced uranium and thorium activity were prepared from the acidic leachate of soil sampled at Novoveská Huta site (Spišská Nová Ves, Slovakia) and processed in a similar way as samples in the previous study [11], with the known ^{238}U and ^{232}Th activity concentration of 20.8 ± 1.6 and 0.4 ± 0.1 Bq g^{-1}, respectively.

Separation on UTEVA resin

Two types of modelled samples (without and with the addition of the soil leachate with the defined uranium and thorium content of natural origin) were prepared for separation experiments. Regardless the type, each sample was spiked with 52 mBq of ^{232}U and 49 mBq of ^{229}Th, followed by its mixing with 10 mg of selenium (p.a.). The sample was evaporated to dryness and dissolved with 15 mL of 3 M HNO_3. Approximately 0.5 g of UTEVA resin was packed into a chromatography column (15 × 1 cm), which was afterwards conditioned with 15 mL of 3 M HNO_3 (Fig. 1). After loading the sample onto the column, it was washed two times with 5 mL of 3 M HNO_3 to pass Se through the column, which was collected for further processing. For elution of thorium, 5 mL of 9 M HCl and subsequently 25 mL of 0.05 M $C_2H_2O_4$-5 M HCl were used. Uranium was eluted by 35 mL 0.01 M HCl at the flow rate of 2 mL min^{-1} [12], while the eluate containing uranium was gathered in 5 mL separate fractions to obtain the elution profile. Targets for determination of U and Th by alpha-spectrometry were prepared as described below. Selenium fraction was evaporated to dryness and diluted to 15 mL with 4.5 M HNO_3. Finally, Se in the solution was reduced to its

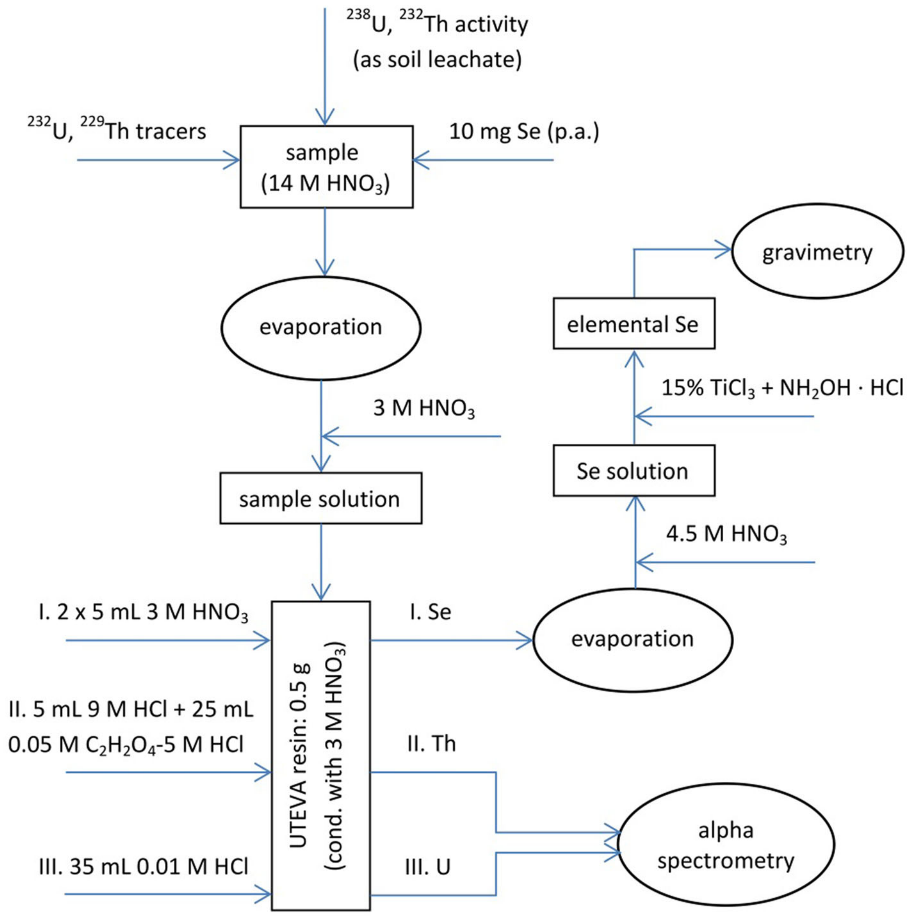

Fig. 1 Schematic diagram of separation of uranium and thorium from selenium matrix using UTEVA resin

elementary form by addition of 1 mL of 15% $TiCl_3$ and 1 g of hydroxylammonium chloride to gravimetrically determine its chemical yield.

Separation on anion exchange resin

A modelled sample, prepared the very same way as described earlier, was first evaporated to dryness. The obtained residue was then dissolved in 10 mL of 4 M HCl. Preceding the loading of the sample, a chromatography column (15 × 1 cm) was packed with roughly 0.7 g of anion exchange resin and washed with 15 mL of 4 HCl (Fig. 2). Next, selenium and thorium (together with radium isotopes) were eluted using 3 × 5 mL of 4 M HCl. Stripping of uranium from the column was achieved by 35 mL of deionized water [13]. To construct the elution profile of uranium, the eluate was gathered in 5 ml separate fractions, which were then evaporated to dryness and converted into the alpha spectrometry sources. The fraction containing Se and Th was evaporated to dryness and dissolved with 8 M HNO_3, then it was loaded on another column (15 × 1 cm) with fresh anion exchange resin (0.7 g) conditioned with 8 M HNO_3. While selenium passed through as a part of the eluate and wash (2 × 5 mL of 8 M HNO_3), thorium retained on the resin was eluted with 25 mL of 0.05 M HNO_3 at the flow rate of 2 mL min^{-1}. In the end, an alfa counting source was prepared from the Th fraction and the Se fraction was processed similarly as in the case of the UTEVA separation experiment.

Alpha-spectrometry

The activity of uranium and thorium in the extraction and anion exchange chromatography elutes was determined using two-chamber alpha-spectrometer EG&G Ortec 576A equipped with the ULTRA ion-implanted silicon detectors (600 mm^2 active area) at the Department of Nuclear Chemistry, Faculty of Natural Sciences of the Comenius University in Bratislava [14]. The spectra were processed using the Alpha-Vision emulation software from the EG&G Ortec company. Alpha-counting sources, measured for 60,000 s, were prepared by neodymium fluoride microprecipitation; for uranium fraction, a reduction step with 0.7 mL of 15% $TiCl_3$ solution was applied before microprecipitation. The detection limit of alpha spectrometry measurements for ^{238}U and ^{232}Th was 2 mBq, with the

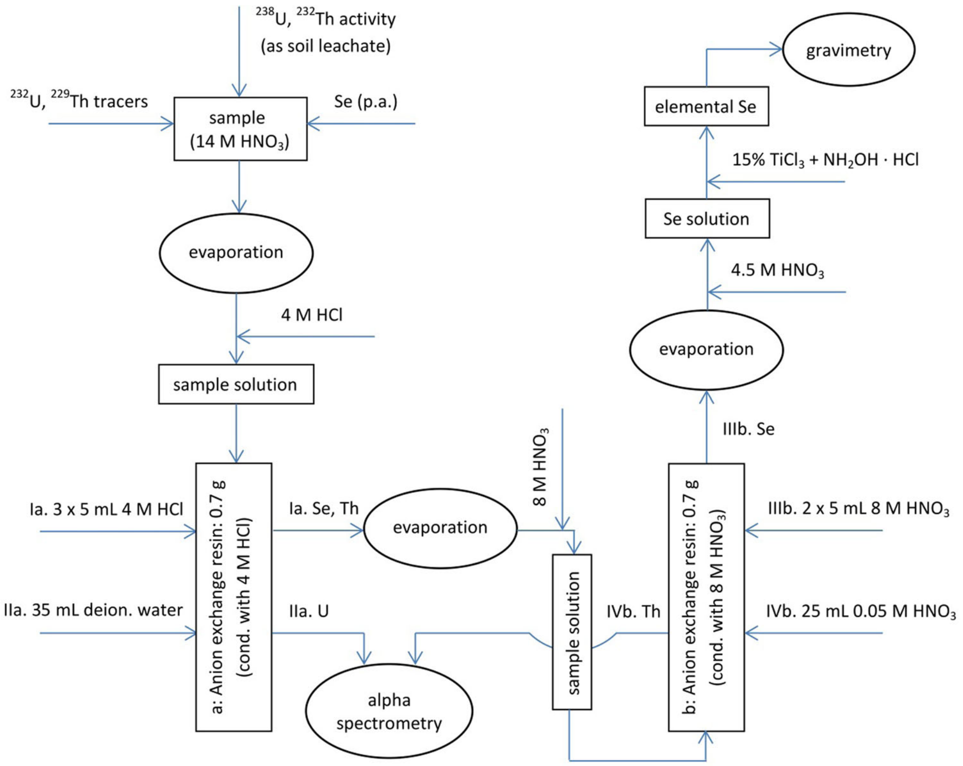

Fig. 2 Schematic diagram of separation of uranium and thorium from selenium matrix using anion exchange resin

overall detection efficiency of 19%. Typical uncertainty of the measurements was in the range of 7–10%.

Mass scanning

In order to evaluate its pureness by qualitative analysis, low energy mass scanning of high purity elemental selenium (99.999%) was carried out at the Centre for Nuclear and Accelerator Technologies (CENTA) in Bratislava [8, 15]. Selenium powder material was pressed into an aluminum cathode which was placed in the ion source for solid targets. The produced ion beam was pre-accelerated to 61.0 keV and analyzed with a 90° bending magnet, leading to the mass separation of ions between 0 and 180 amu. Ion detection, up to 10^{-10} A of the ion current, was performed by a Faraday cup [16].

Results and discussion

Although selenium can be separated from other elements using different procedures [10], testing of the methods developed in this study showed that techniques based on the extraction and anion exchange chromatography have undeniable potential. The chemical behavior of Se is rather complex, mainly due to the coexistence of the large number of oxidation states. Selenium solubility is generally controlled by its oxidation state. In the tetravalent and hexavalent oxidation states, selenium prevails as aqueous oxo-ions. Hexavalent Se(VI) occurs over a wide pH range as SeO_4^{2-}, while for Se(IV), the dominant species are H_2SeO_3 (aq) below pH 3, $HSeO_3^-$ between pH 3 and 8, and SeO_3^{2-} above pH 8 [9, 17]. Unlike uranium and thorium, selenium does not form nitrate complexes at all [18] and because the active component of UTEVA resin is diamyl amylphosphonate, which specifically extracts nitrate complexes, selenium is not retained and passes through the column. Similar deduction can be applied in the case of anion exchange resin (Cl^- form) method, though formation of chloride selenium complexes was indeed observed. However, distribution coefficient of Se on strong anion exchange resin in HCl is very low [19]. As selenium is washed away together with thorium, which does not create chloride complexes as well, another column is needed to separate these two elements.

The chemical yields for selenium and radiochemical yields for uranium and thorium for the UTEVA resin and anion exchange resin methods are summarized in Table 1. The given values were calculated as an average of several experiments (n = 3), which were separately conducted in the case of the modelled samples with and without the addition of the soil leachate. As we can see from the results, (radio)chemical yields are quite comparable for both methods and only slight differences in favor of the anion exchange resin method were obtained for uranium and thorium. Interestingly, both methods showed a bit

Table 1 Average separation yields ($n = 3$) for uranium, thorium and selenium

Sample type[a]	UTEVA resin			Anion exchange resin		
	^{232}U (%)	^{229}Th (%)	Se (%)	^{232}U (%)	^{229}Th (%)	Se (%)
I	95 ± 9	83 ± 8	97 ± 9	98 ± 10	90 ± 9	95 ± 8
II	87 ± 8	75 ± 7	95 ± 8	94 ± 9	86 ± 8	93 ± 7

[a] I = modelled samples without addition of the soil leachate; II = modelled samples with addition of the soil leachate

lower yields for all three elements in the case of the modelled samples prepared from the acidic soil leachate. This may be due to the fact that these samples had more complicated matrices, as the soil sample contained not only uranium and thorium but also other elements, e.g. iron and arsenic. Nevertheless, obtained results suggest that the developed methods are highly effective in separation of uranium and thorium from selenium.

From the practical point of view, the tested extraction and anion exchange chromatography procedures are comparable, though the UTEVA resin method might seem to be more advantageous because it requires a single column to extract uranium and thorium from selenium (Fig. 1). Another aspect to consider is that the procedure based on the anion exchange needs an additional evaporation step and consequent dissolution of the residue in nitric acid; this way formed nitrate complexes of thorium are retained on the second column, while Se is not extracted and passes through as the effluent (Fig. 2). This means that the method is definitely more laborious, thus more time-consuming and demanding on material, especially chemical reagents and resins.

Figure 3 shows elution profiles of uranium for both the UTEVA and anion exchange methods, using 35 mL 0.01 M HCl and deionized water, respectively. While slightly more or similar amounts of U are recovered in the first two fractions, i.e. first 10 mL, much more uranium was obtained in the third fraction in the case of the anion exchange method than for the UTEVA method. Content of uranium in the remaining eluates was more or less comparable. The respective recoveries of U in the very last fractions were almost negligible (0–2%), thus documenting that the selected volumes of the eluting reagents in both methods were sufficient to desorb all uranium from the resins.

Besides (radio)chemical yields, there are other important factors for evaluation of the developed methods, i.e. contamination and concentration of uranium and thorium in the procedural blank. It is not audacious to expect that the amount of ^{232}Th and ^{238}U in the purified Se material is at the level of detection limits of mass spectrometric techniques, or in other words, at the level of their concentration in blanks. In order to solve this problem, one possibility is to significantly increase the initial amount of Se material, e.g. from 10 mg to 1 g, while keeping or even lowering the amounts of other reagents. Further option is to prepare blanks containing as low as possible concentrations of uranium and thorium. However, due to the high

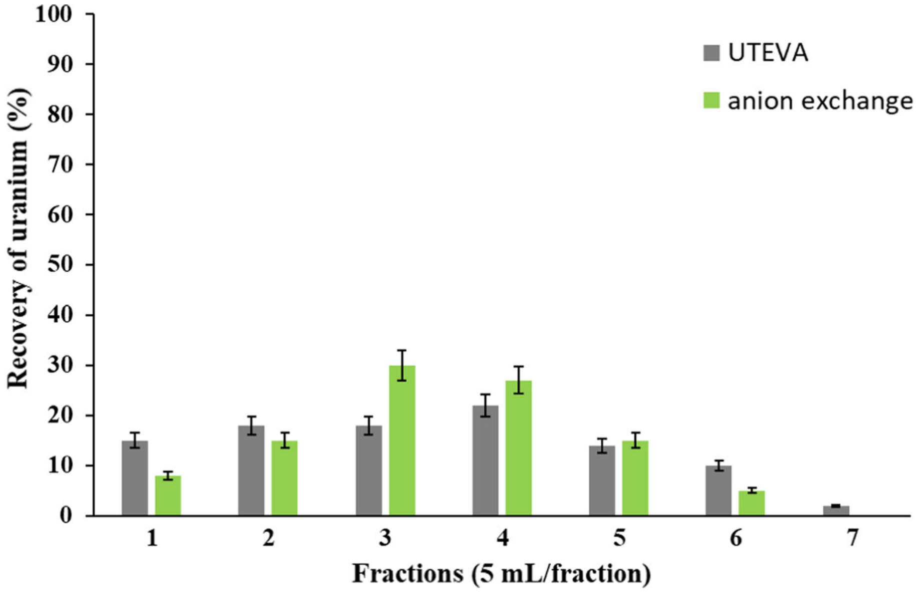

Fig. 3 Profiles of uranium elution from UTEVA and anion exchange resin

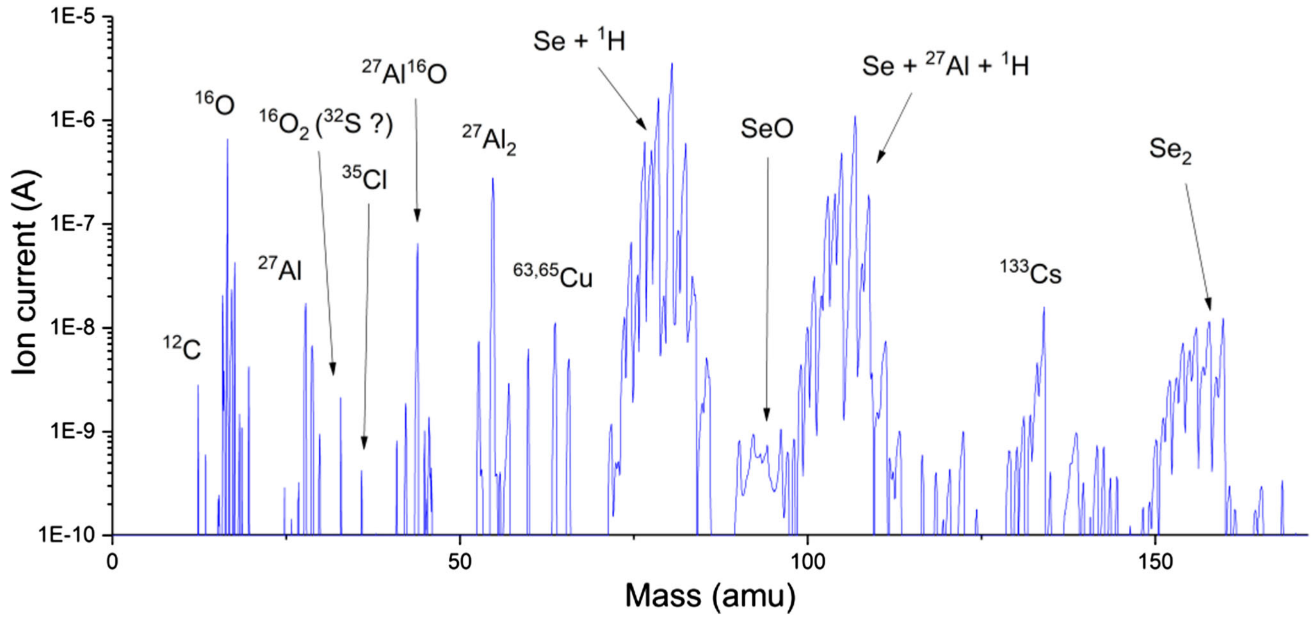

Fig. 4 Spectrum of the high-purity elemental selenium material determined by low-energy mass scanning

detection limit of the alpha-spectrometry (2 mBq), we focused in this work on the yields of tracers and selenium measurable with alpha-spectrometry and gravimetry, respectively. After mastering the separation methods, we plan to carry out ultra-sensitive ^{238}U and ^{232}Th measurements in selenium samples using ICP-MS and AMS. This will require further development in terms of determination of the maximum processable amount of selenium sample and optimal amounts of ultrapure chemical reagents, whose quality can be increased, e.g. by distillation of acids, and resins to obtain the limit of detection on the nBq g^{-1} level.

A mass spectrum obtained by qualitative low-energy mass scanning of the high-purity elemental selenium is depicted in Fig. 4. All naturally occurring selenium isotopes, which are either stable or decay via very rare processes (e.g., double beta decay), including ^{82}Se, were difficult to distinguish one from another due to minimal mass differences and possibility of formation of molecular ions with hydrogen. As expected, the highest ion current was observed for ^{80}Se, which is the most abundant isotope of selenium in the environment [20]. The presence of some of the highlighted ions was anticipated, e.g., ^{12}C, ^{16}O, ^{27}Al, $^{27}Al_2$, ^{27}Al^{16}O, ^{133}Cs. Oxygen is ambiguous and formation of its ions is practically unavoidable. Two aluminum peaks ^{27}Al and $^{27}Al_2$ most likely originated from the cathode in which the selenium material was pressed, while relatively strong cesium signal is understandable due to production of negative ions in the source by Cs sputtering [8, 15, 16]. According to the manufacturer [21], the selenium material contains only trace amounts of Na and Si (also observed in our spectrum—^{28}Si), as all other determined elements had the concentration beyond the detection limit of the analytical technique. However, the qualitative mass scanning measurements suggest the presence of some other minor elements, such as carbon (^{12}C), sulphur (^{32}S), chlorine (^{35}Cl), chromium (^{52}Cr), iron (^{56}Fe), and copper (^{63,65}Cu). Heavier species might have been present as well, though their identification can be complicated due to production of plentiful molecular ions during the sputtering [22]. In conclusion, the matrix of the measured high-purity Se material, whose quality may be considered as an approximation of the quality of the ^{82}Se material used as the SuperNEMO source, seems to be less simple than declared.

Conclusions

Two chromatographic methods for separation of uranium and thorium from selenium using UTEVA and anion exchange resins were developed and tested on two types of samples with different matrices. Both procedures are similar in complexity and feasibility and showed very high separation efficiencies. The average yield for separation of uranium and thorium, obtained by alpha-spectrometry of ^{232}U and ^{229}Th tracers, was determined to be in the case of the UTEVA method 91 ± 9% and 79 ± 8%, respectively, and 96 ± 10% and 88 ± 9%, respectively, for the anion exchange method. Similarly, the chemical yield for selenium, which was determined by gravimetry, was very close to the ideal value, that is 96 ± 8% and 94 ± 8% for the for the UTEVA and anion exchange method, respectively. Mass scanning experiments imply somewhat complex matrix of the high-purity elemental selenium material, which can be taken as an approximation of the ^{82}Se material used as the SuperNEMO source for neutrinoless double beta-decay investigations. It is planned to conduct this type of analysis for the ^{82}Se material in a near future, as well as to exploit the developed methods for measurements of uranium and thorium content in this material by mass spectrometric techniques, such as ICP-MS and AMS.

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