



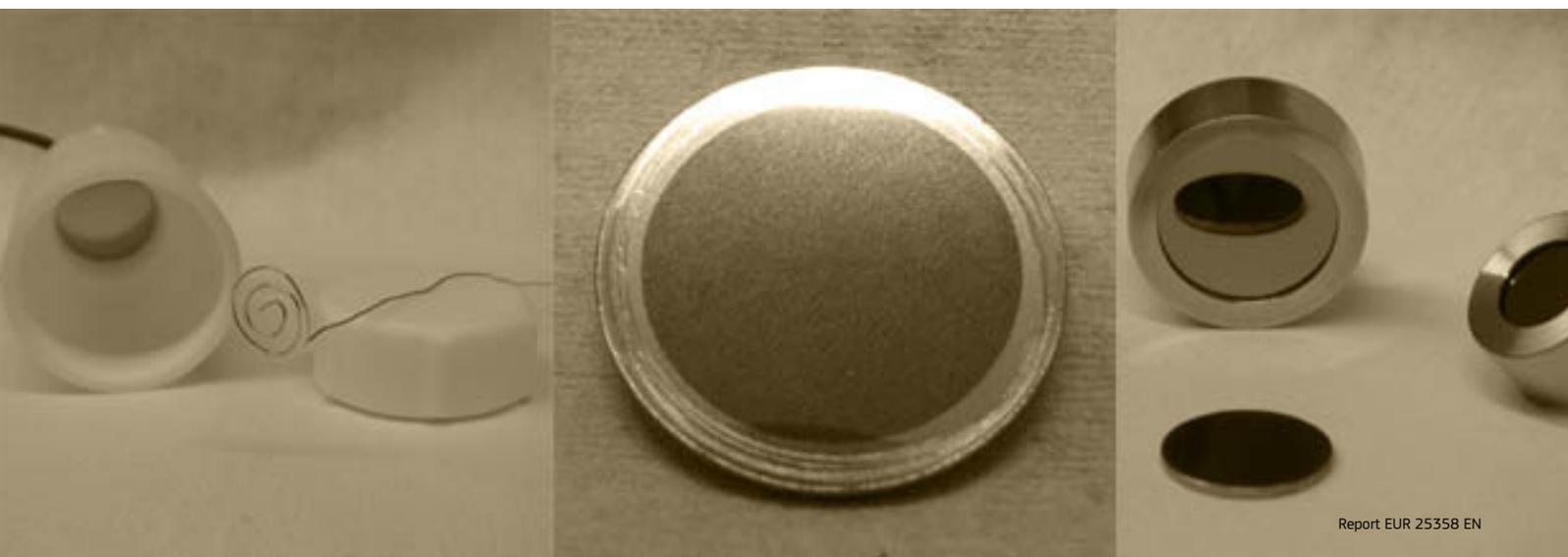
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Preparation of high resolution ^{230}U α -sources by electrodeposition from aqueous solution

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1. Introduction

Alpha-particle emitters are promising for the treatment of various types of cancer as well as infectious diseases [1]. Due to the short range and high linear energy transfer of alpha particles in human tissue, Targeted Alpha Therapy (TAT) offers the potential of delivering a highly cytotoxic dose to targeted cells while minimizing damage to the surrounding healthy tissue. The ^{230}U decay series, coupled to target-selective carrier molecules, has been identified as a candidate tool for TAT [2, 3].

As shown in Figure 1, ^{230}U is a pure alpha emitter with a half-life of about 20 days and its decay chain continues through a subsequent cascade of four alpha-emitting daughter nuclides with relatively short half-lives ranging from 30.70 (3)min (^{226}Th) to 164.2 (6) μs (^{214}Po) as presented by Pommé et al. 2012 and; Suliman et al., 2012 [4, 5].

The alpha branching ratios, half-lives and energies for the major peaks of ^{230}U and its progenies have been deduced from only few experiments performed more than three decades ago. It was necessary to up-date these fundamental nuclear data and perform more accurate radiometric measurements that needed high quality ^{230}U alpha sources.

A uranium source for nuclear data measurement by alpha-particle spectrometry must have a thin uranium layer uniformly distributed over the target area in order to achieve high energy resolution spectra and avoid low energy tailing. To meet these requirements, electrodeposition is a commonly used and suitable method.

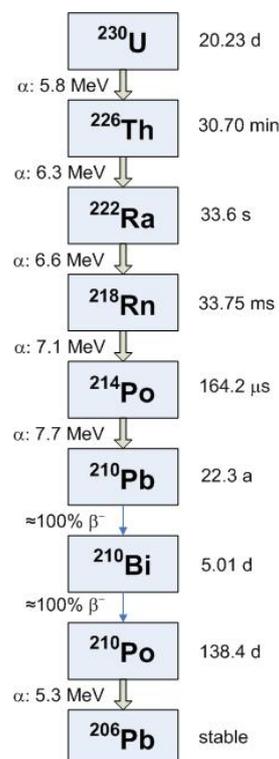


Figure 1. The ^{230}U decay chain

2. Objectives

The objective of this work was to prepare ^{230}U alpha sources with excellent spectral properties - high resolution, low tailing - and relatively high specific activity in order to accurately determine the relative alpha emission probabilities and half-lives via high-resolution alpha-particle spectrometry. The demands for source quality in radionuclide metrology are much higher than in applied spectrometry, e.g. for environmental analysis or geological studies. To achieve this, very thin and uniform ^{230}U alpha sources have to be prepared.

3. Experimental procedure

For our purposes, two different types of electrolyte preparation procedures were tested. One of them was based on Talvitie's and Hallstadius' methods [6, 7] modified according to Tome and Sanchez [8] where uranium is deposited from $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ electrolyte. The other procedure was developed at CIEMAT where alpha sources are prepared from a saturated NH_4NO_3 solution [9].

Each procedure consists of a sample preparation and an electrodeposition step. An overview of the different steps in the procedures is presented in Figure 2 and discussed in more details below.

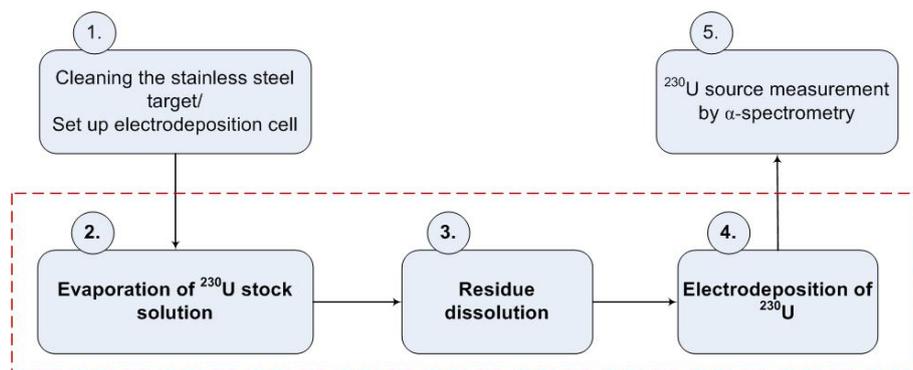


Figure 2. Flow chart of the procedure

3.1. Chemicals

Two $^{230}\text{U}^{\#}$ stock solutions, one with and another without carrier, were used. They were prepared by dissolving uranium in 1M HCl.

- 1) ^{230}U solution with natural U as carrier (0.6 mg/g) had an activity concentration of 5 MBq/ml (reference date: 27/10/2010).
- 2) ^{230}U solution without carrier had an activity concentration of 3.75 MBq/ml (reference date: 27/10/2010).

[#]The specific activity of the ^{230}U isotope is $\sim 9.99 \times 10^{14}$ Bq/g.

All chemicals used (Na_2SO_4 , NH_4NO_3 and H_2SO_4) were analytical grade reagents. The saturated NH_4NO_3 solutions were always freshly prepared by dissolving 19.2 g NH_4NO_3 in 10 cm^3 of deionised water. Commercially available mirror polished stainless steel discs were used as source backing.

3.2. Preparation of the electrolytic cell and the target

Mirror polished stainless steel discs were used as targets. To make them ready for use, the protective plastic tape was removed from the target surface of the disc. Then it was cleaned with acetone and placed into the electrodeposition cell. The electrodeposition cell was initially a polyethylene plastic scintillation vial, later replaced by a Teflon vial. The stainless steel target disc was fitted in the cap on the top of a wire (electrical connection) as is shown in Figure 3. The thread of the polyethylene vial was covered with Teflon tape in order to make the cell leak tight. The Teflon vials were leak tight by themselves. The top side of the vial was cut off.

Before using it, the cell was checked for tightness by filling it with 15 mL of distilled water. It was left standing for 10-15 minutes and checked visually for any signs of leakage.

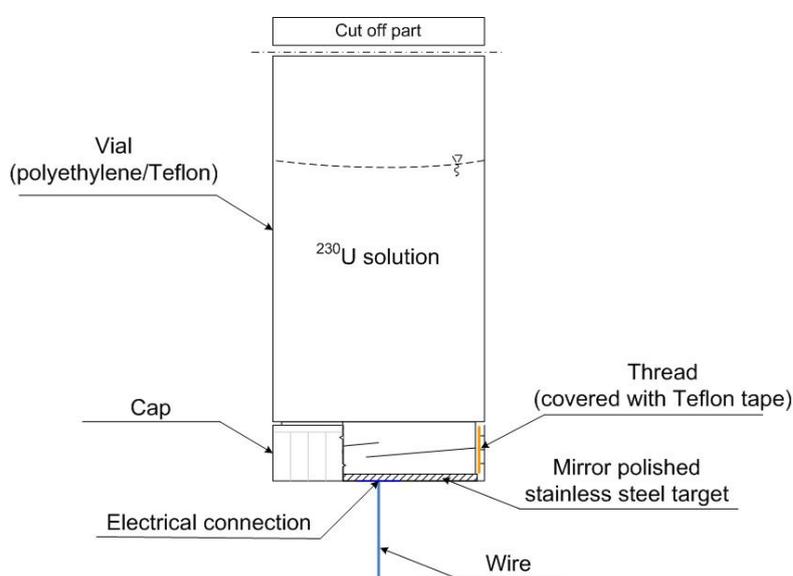


Figure 3. Experimental setup of the electrodeposition cell

3.3. Sample/Electrolyte preparation

Two different electrolyte solutions were used for the electrodeposition:

- A) A conventional solution containing Na_2SO_4 , H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$ [5 – 8].
- B) A saturated NH_4NO_3 solution [9].

A) Na_2SO_4 , H_2SO_4 and $(\text{NH}_4)_2\text{SO}_4$

- 1) An aliquot of ^{230}U stock solution (20-100 μL) was transferred into a 50 mL glass beaker and 0.2 mL of 0.3M Na_2SO_4 was added to prevent the uranium from being adsorbed into the glass wall.
- 2) The solution was evaporated very carefully to dryness.
- 3) The dry residue was dissolved in 300 μL concentrated H_2SO_4 . When necessary, the solution was warmed up in order to dissolve the residue completely. Any loss of H_2SO_4 was avoided.

- 4) 4 mL of distilled water was carefully added (heat production), followed by 2 drops of 0.1 % thymol blue indicator.
- 5) The pH was adjusted to 2.1-2.4 with 25 wt% NH₄OH. This was done slowly as the reaction was exothermic and the solution needs to cool to room temperature. At pH 2.1-2.4, the colour of the solution changes from red to salmon pink (yellow/yellow orange).
- 6) The solution was transferred into the electrodeposition cell and the glass beaker was washed with 5 mL of distilled water.
- 7) If necessary, the pH was readjusted to 2.1-2.4.

B) Saturated NH₄NO₃

- 1) An aliquot of ²³⁰U stock solution (20-100 μL) was transferred into a 50 mL glass beaker and evaporated to dryness.
- 2) The dry residue was dissolved in 5 mL of saturated NH₄NO₃ (1920 g/L; T = 20 °C) solution and transferred into the electrodeposition cell.
- 3) The beaker was rinsed with saturated NH₄NO₃ little by little (with 1-2 mL portions or 3 times 5 mL).
- 4) The total volume of the electrolyte in the electrodeposition cell was 15 mL.

3.4. Electrodeposition

The set-up used for the electrodeposition procedure, presented in Figure 4, was the same for the two types of electrolytes. The electrolytic cell and the wire were introduced in a water tight plastic foil and the screw cap side part of the electrodeposition cell (approximately 2 cm) was immersed into a water bath before loading the uranium bearing solution into it. Water conducts the ultrasonic waves and cools the cell; it keeps the solution homogeneous and stabilises the electrodeposition process.

The distance between the platinum anode and the stainless steel target cathode was set between 0.5 – 1 cm. The cut off part of the vial was put tightly on the top of the electrodeposition cell and it was fixed with tape.

- 1) The platinum anode was rotating during the electrodeposition (~ 10-12 rpm).
- 2) The following settings were used for the electrodeposition:

I = 1 A	t = 20 min	for "A" type electrolyte.
I = 0.5 – 0.6 A	t = 60 min	for "B" type electrolyte.
- 3) 1 ml of 25 wt% NH₄OH was added 1 minute before switching off the current.
- 4) The disc was rinsed with distilled water and then with acetone.
- 5) The electrodeposition cell was disassembled.
- 6) The disc was rinsed with acetone and dried at ambient temperature.

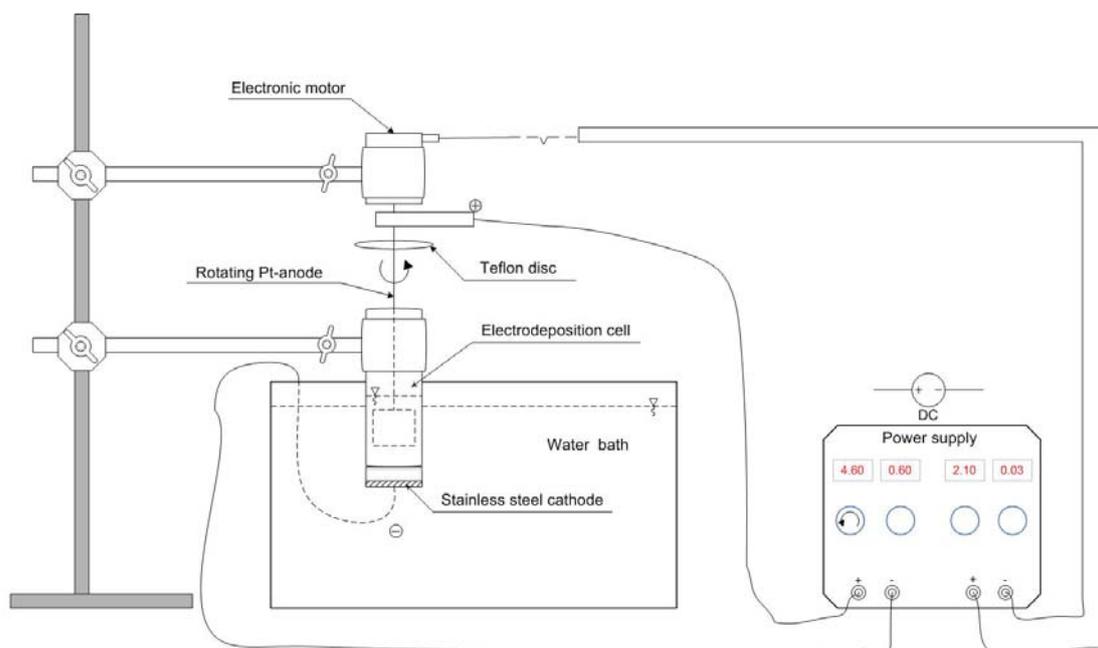


Figure 4. Set-up for the electrodeposition procedure

3.5. Instruments

For the electrodeposition an Aim & Thurlby Thandar Instruments EL 302 TV power supply was used.

The measurements at IRMM were performed in a vacuum chamber equipped with an ion implanted Si detectors, having an active area between 50 and 150 mm². A set of internal baffles prevented the scattering of α -particles from the counter walls into the detector. The solid angle subtended by the detectors was between 0.39 – 1.77 % of 4π sr.

The electronic chain was composed of a temperature stabilised preamplifier, an amplifier, a single channel analyser, a dead time unit, an ADC and a clock. The data were acquired using the DAQ2000 computer software package developed at IRMM [10].

The energy resolution of the measured spectra was determined by fitting the alpha peaks with the DAQ2000 software.

4. Results and discussion

For the electrodeposition, we first used polyethylene vials and later the chemically more resistant Teflon vials. The main observations are detailed below.

4.1. Polyethylene electrodeposition cell

Four sources were prepared by using a polyethylene vial as an electrodeposition cell. The quality of the first two sources - U230SS1004 and U230SS1005 - was reasonable, even the one (U230SS1004) prepared from the ²³⁰U solution with natural uranium carrier. In case of these sources procedure "A" was applied for the electrodeposition.

For the two other sources (U230SSB01 and U230SSB02) procedure "B" was used. After electrodeposition, polymer traces on the discs were observed. The discs were rinsed with

distilled water and acetone, but the polymer traces remained on the surface. We assumed that it was organic origin i.e. either the polyethylene vial or the glue from the tape that was dissolved in the electrolyte solution itself or in the condensed acidic fumes. Therefore the polyethylene electrodeposition cell was replaced by chemically more resistant Teflon.

4.2. Teflon electrodeposition cell

For the first source (U230SSB03) the cut off part was fixed on the top of the vial with tape. The quality of the source was poor with the apparent presence of polymer traces on the surface. Furthermore metal dust was observed on the top of the cut off cover. Therefore no Teflon tape was used later and a Teflon disc – thin and flexible – was fixed on the Pt wire in between the cut off part and the electronic contact in order to avoid falling of metal parts from the electrical contact into the cell. The same procedure was used for source U230SS1006 (procedure "A") and U230SS1007 (procedure "B") as well. The quality of these sources was better than the previous sources as shown in Figures 5 and 6. No polymer traces and impurities were observed, only some tiny light white spots.



Figure 5. ^{230}U source electrodeposited from "A" type electrolyte with polymer traces



Figure 6. ^{230}U sources electrodeposited from "A"(U230SS1006) and "B" type electrolyte (U230SS1007)

The settings of the electrodeposition, main observations and the properties of the ^{230}U alpha sources are summarized in Table 1.

As far as the spectral properties (resolution, peak to valley ratio) are concerned, there is no significant difference between the sources deposited from the two different electrolyte solutions. The resolutions were in the same range, while the peak to valley ratio (P/V) was

slightly higher ($P/V = 200$) for the ^{230}U source prepared in sulphate electrolyte compared to the saturated ammonium nitrate electrolyte ($P/V = 150$).

The ^{230}U source with carrier has lower peak to valley ratio most likely because of the co-deposited natural uranium layer that can absorb part of the energy of the emitted alpha particles.

Table 1. Summary of the ^{230}U source preparation

Source I.D	^{230}U stock solution [μL]	^{230}U stock solution	Electrolyte	Source quality	Other observations	FWHM [keV] at 5888 keV	Peak to valley ratio
U230SSB01	50	1)	B	Poor quality; Polymer on the surface	After drying polymer traces on the disc	n.d.	n.d.
U230SSB02	50	2)	B	Poor quality; Polymer on the surface	Polymer traces on the disc	n.d.	n.d.
U230SSB03	100	2)	B	Poor quality; Polymer on the surface	Polymer traces on the disc	n.d.	n.d.
U230SS1004	100	1)	A	Uniform deposit	Light grey coloured deposit	12.5(5)	~50
U230SS1005	100	2)	A	Uniform deposit		12.5(5)	~90
U230SS1006	40	2)	A	Very thin deposit	Some transparent white spots on the surface	11.5(5)	~200
U230SS1007	40	2)	B	Very thin uniform deposit/hardly to see		12.4(5)	~150

- 1) ^{230}U solution with carrier
 2) ^{230}U solution without carrier
 n.d. – not defined

The ^{230}U spectra obtained from alpha-spectrometry measurements are presented in Figure 7. The two most intense peaks of ^{230}U are indicated as $^{230}\text{U}_{p1}$ and $^{230}\text{U}_{p2}$, while the rest of the peaks belong to the short-lived ^{230}U daughter products.

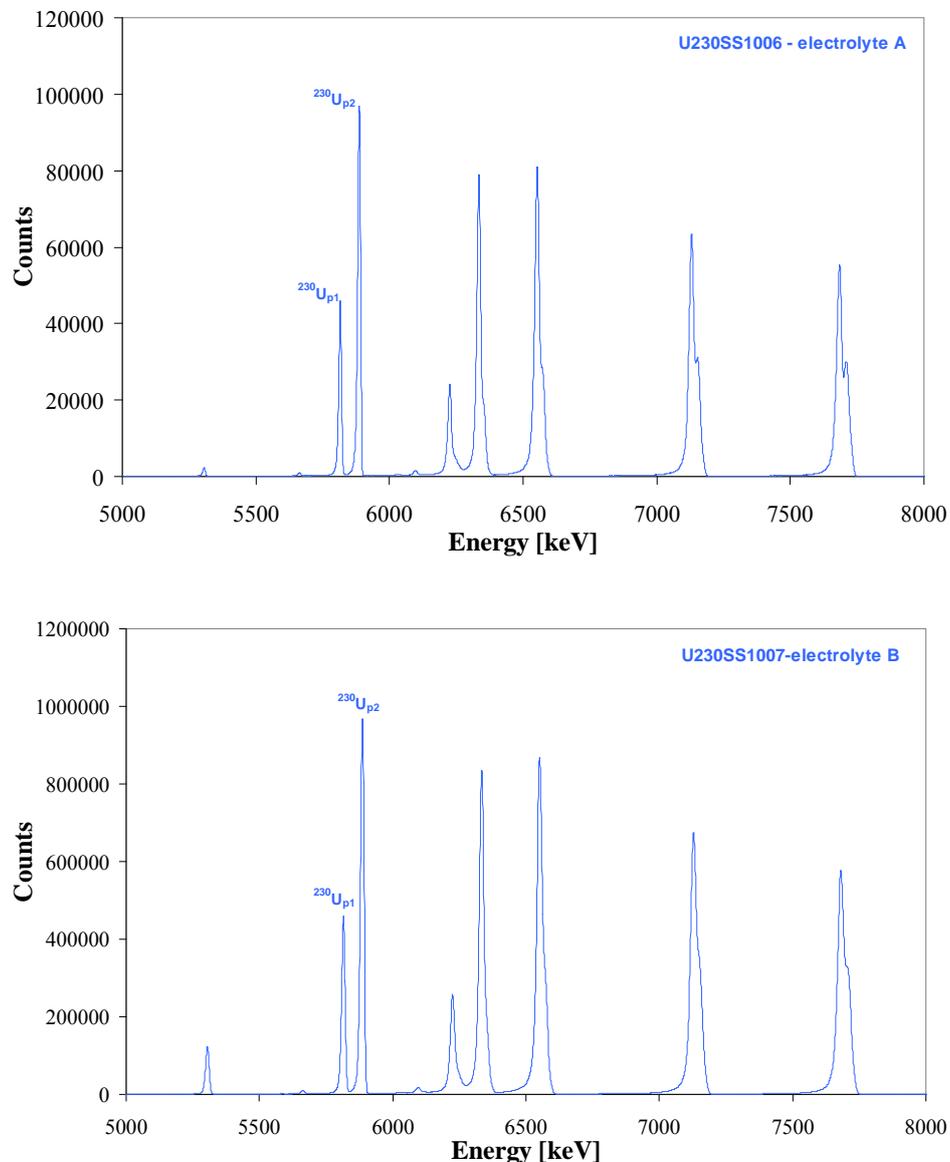


Figure 7. ^{230}U spectra of electrodeposited sources from electrolyte "A"(U230SS1006) and "B" (U230SS1007)

The fitted alpha-particle spectrum of the ^{230}U decay chain measured with a 50 mm^2 PIPS[®] detector is shown in Figure 8. The residuals represent the difference between measurements and fit in units of one standard deviation of the channel contents.

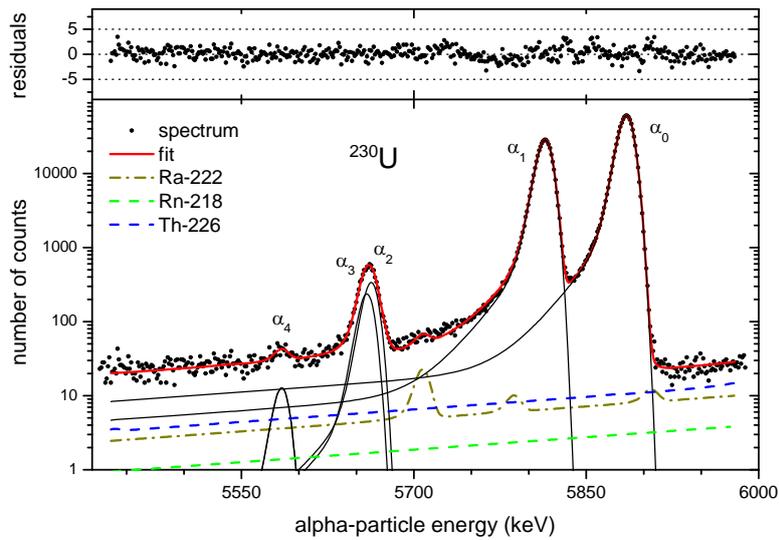


Figure 8. Fitted alpha-particle spectrum of ^{230}U and the fitted contributions from its daughter nuclides.

5. Conclusions

The electrodeposition procedures for the production of ^{230}U sources to be measured for high-resolution alpha-particle spectrometry were optimised. Two different electrolytes were tested with respect to attainable resolution for sources of 150 - 500 kBq, corresponding to 1.5 - 5 ng of deposited ^{230}U . According to our results, good energy resolution and peak to valley ratio were obtained with sources produced in saturated NH_4NO_3 and in the conventionally used $\text{H}_2\text{SO}_4/(\text{NH}_4)_2\text{SO}_4$ electrolyte as well. Our best sources had a diameter of 18.6 mm with a resolution of 12 to 16 keV and the peak to valley ratios varying from 46 to 222.

Both electrolytes using the optimized electrodeposition method are suitable to make high resolution ^{230}U sources. These sources can be used to determine more accurately the nuclear data of ^{230}U .

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Abstract

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