

# Development of Flow Electrolytic Strategies for Separation and Radiometric Analysis of Radionuclides

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**Abstract:** Radionuclides are used and produced for a variety of applications, such as in the framework of energy production and nuclear medicine. This requires appropriate monitoring which in turn translates into the analysis of a variety of radionuclides in demanding sample matrices. Radionuclide analysis is a challenging task and often requires complex chemical processing of the samples prior to radiometric measurements. This requirement arises due to interfering radionuclides as well as matrix elements, which typically prevent a direct measurement by  $\alpha$ - and  $\gamma$ -spectrometry, liquid scintillation counting or mass spectrometry. Despite offering promising possibilities, electrochemical approaches have been rarely used so far for the separation and analysis of radionuclides. Here, we present the development of fast flow-through electrolytic separation approaches for the analysis of carrier-added/-free radionuclides in fundamental and applied research.

**Keywords:** Flow electrolysis · Radiometric analysis · Radionuclides · Separation



**Paul Dutheil** obtained his MSc in chemistry from the University of Bordeaux (France) in 2020. During this time, he carried out his Master's thesis at the University of Helsinki, where he worked on the analysis of Pu and U isotope ratios in environmental archives to identify sources of past radionuclide contamination in Russian Arctic regions. In November 2020, he joined the groups of Prof. Patrick Steinegger &

Dr. Martin Heule at the Paul Scherrer Institute and ETH Zürich. His research has focused on the development of novel flow electrolytic separation approaches for the separation and analysis of radionuclides.

## 1. Introduction

Radionuclides are routinely produced and used in nuclear research and in industry. To comply with regulatory boundary conditions, their accurate identification and quantification is critical in support of these activities. Depending on their decay properties, the analysis of trace amounts of different radionuclides is carried out by means of radiometric or inorganic mass spectrometric techniques.<sup>[1,2]</sup> Whereas radiometric counting techniques, such as  $\alpha$ - and  $\gamma$ -spectrometry or liquid scintillation counting (LSC), are more applicable toward shorter-lived radionuclides (half-lives  $t_{1/2} < 100$  years), mass spectrometry techniques, in particular inductively coupled plasma mass spectrometry (ICP-MS), are commonly used to address longer-lived ones ( $t_{1/2} > 100$  years).<sup>[1]</sup> In complex matrices of industrial, environmental or biological origin, the presence of many stable or radioactive isotopes can hamper measurements carried out by said approaches. The presence of various  $\alpha$ - and  $\beta$ -emitters may lead to direct interferences during LSC or  $\alpha$ -spectrometry measurements, whereas large amounts

of high-energy  $\gamma$ -emitters can cause a significant increase of the Compton background during  $\gamma$ -spectrometric measurements and thus hinder the identification and quantification of less prevalent  $\gamma$ -emitters.<sup>[1]</sup> In addition, general chemical impurities in the sample matrix have the potential to trigger color and chemical quenching during LSC measurements or may prevent the preparation of appropriately thin  $\alpha$ -sources for  $\alpha$ -spectrometry. Consequently, the analyte must be systematically purified from matrix components and radionuclidic impurities prior to any analytical measurement. Suitable chemical separations are usually carried out by means of ion-exchange chromatography, extraction chromatography, coprecipitation, solvent extraction, or galvanic displacement.<sup>[1]</sup>

Although reported in literature, electrochemical approaches are rarely used for radioanalytical separations. Nevertheless, such methods provide a different chemical selectivity based on the electrochemical properties of the analyte, affording separations which may otherwise be more difficult to achieve by traditional means. In addition, they come with many other advantages such as excellent preconcentration properties as well as good matrix tolerance and removal.<sup>[3]</sup> Furthermore, electrolysis offers the possibility for the direct preparation of high-quality sources for  $\alpha$ -spectrometry or  $\beta$ -counting.<sup>[4,5]</sup> The use of solid inert electrode materials as a source of electrons avoids the introduction of chemical impurities from reagents or chromatographic materials and may provide generally higher resistance to radiation damage, as needed, for example, during the separation of large amounts of radioactivity (e.g. radionuclide generators). The implementation of flow-through electrolysis with porous electrodes featuring a high surface area further enables fast separations,<sup>[6,7]</sup> easy automation, and coupling with other separation or measurement techniques.<sup>[3]</sup> Lastly, the combination of electrolysis with the high sensitivity of radiometric detection offers a unique opportunity to study electrochemical properties of radionuclides at ultra-trace concentration levels. This is especially relevant for the electrochemical

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characterization of radioelements which are present only in minute amounts, such as heavy actinides and transactinide elements ( $Z \geq 104$ ). These can only be investigated at the so-called carrier-free concentration levels, whereas radioisotopes of elements up to Bi (apart from Tc and Pm) can be studied under carrier-added conditions (*i.e.* with the addition of a stable isotopic carrier). In the case of transactinide elements, fast electrolysis methods could be implemented to study the chemical properties of the thus far unexplored chemical elements meitnerium (Mt,  $Z = 109$ ), darmstadtium (Ds,  $Z = 110$ ) and roentgenium (Rg,  $Z = 111$ ). However, their exclusively short-lived isotopes with half-lives ranging from a few minutes down to single seconds pose a significant experimental challenge.<sup>[5,8]</sup>

Here, we present fast electrochemical techniques for the separation and analysis of radionuclides at trace to ultra-trace scales, for both, fundamental investigations of model systems as well as for applications with complex systems, such as encountered in industrial, environmental, or biological samples. Specifically, separations based on flow-through electrolysis are explored by (1) electrodeposition/-stripping or (2) electrolysis in combination with the adsorption on functionalized electrode surfaces.

## 2. Experimental Approach for Flow Electrolysis of Radionuclides

### 2.1 Flow Electrolysis Setup

The potential at the working electrode (WE) was controlled by means of a conventional 3-electrode cell configuration and potentiostat. The general layout of a typical flow-through electrolysis cell is shown in Fig. 1. In such a cell, the counter electrode (CE) and the reference electrode (RE) are separated from the WE by a nanoporous separator, enabling the analyte solution to be in contact only with the porous WE. The high surface area of carbon fiber felt WEs allows for quantitative electrolysis upon a single pass through the cell and a fast exchange to avoid memory effects and cross-contamination.

### 2.2 Separation Strategies

Many radionuclides can be electrodeposited as metals by cathodic electrodeposition in aqueous electrolytes. The reduction potential associated with electrodeposition is described by the Nernst equation and depends largely on the element considered. As a result, analytes or interfering radionuclides/elements can be electrodeposited on the WE and retained selectively upon application of the appropriate potential before being recovered by anodic stripping after a subsequent potential switch (mechanism A in Fig. 1). This approach is particularly convenient for the separation of carrier-added radionuclides (*i.e.* measurable electrochemical response), which allows a careful control over all experimental parameters to ensure a good selectivity during separation.

Under carrier-free conditions, the concentration of radionuclides can be extremely low (Table 1). If these conditions are reached, the amount of radionuclide is not sufficient to fully cover the electrode surface. In the case of these sub-monolayer amounts, the Nernst equation is not valid anymore and the electrodeposition potential is strongly dependent on the electrode material and the adsorption energy of the electrodeposited element on said surface. A strong interaction between the electrode substrate and the deposited atom can considerably shift the reduction potential to higher values. This effect is known as underpotential deposition (UPD),<sup>[9]</sup> and has long been observed to impact the electrodeposition of carrier-free radionuclides.<sup>[5,10,11]</sup> If the substrate-analyte bonding is weak, the inverse effect occurs with the electrodeposition being largely affected by crystallization or nucleation overpotentials (overpotential deposition, OPD). Therefore, the choice of electrode materials introduces an additional parameter for tuning the separation of different carrier-free radionuclides.

Table 1. The radioactivity, mass, and number  $N$  of atoms of typical radionuclides with different half-lives  $t_{1/2}$ , as encountered in some representative samples.

	<sup>242</sup> Pu	<sup>238</sup> Pu	<sup>210</sup> Po	<sup>134</sup> Te
$t_{1/2}$ <sup>a</sup>	$3.73 \cdot 10^5$ a	87.7 a	138.38 d	41.8 m
$A$ [Bq]	0.05	0.05	0.05	200
$m$ [pg]	$3.42 \cdot 10^2$	$7.89 \cdot 10^{-2}$	$3.01 \cdot 10^{-4}$	$1.61 \cdot 10^{-4}$
$n$ [pmol]	1.41	$3.31 \cdot 10^{-4}$	$1.43 \cdot 10^{-6}$	$1.20 \cdot 10^{-6}$
$N$	$8.50 \cdot 10^{11}$	$2.00 \cdot 10^8$	$8.62 \cdot 10^5$	$7.25 \cdot 10^5$

<sup>a</sup>with a: year (annum), d: day, and m: minute.

However, *s*- and *f*-block elements as well as early transition metals cannot be electrodeposited from aqueous electrolytes. Therefore, other strategies must be utilized for their electrochemical separation. One of them is the control of their oxidation state and the selective adsorption on an electrochemically modified electrode surface. The coating of the electrode with a functional layer containing moieties, which are selective towards only one oxidation state of the analyte, allows for its retention and release by concomitance of electrolysis and adsorption/desorption (mechanism B in Fig. 1).

## 3. Applications to Analysis of Radionuclides

### 3.1 Selective Electrodeposition Under Carrier-Added Conditions

A selective flow electrolytic deposition approach was investigated for the separation and analysis of various  $\gamma$ -emitters.<sup>[12]</sup> The investigated radionuclides are formed by neutron activation of

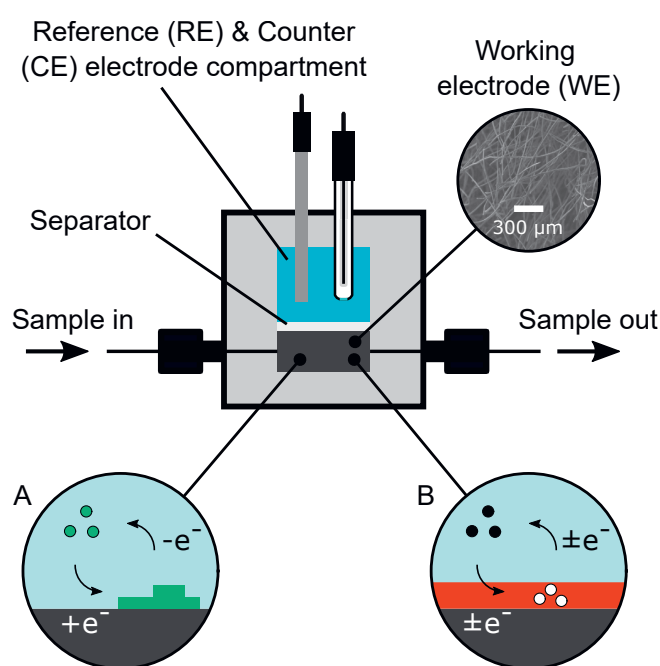


Fig. 1. Cross-section of a typical flow-through electrolysis cell including a close-up of the carbon fiber working electrode as retrieved by means of a scanning electron microscope; the lower part of the figure illustrates the two mechanisms used for the separation of radionuclides with A the cathodic electrodeposition/-stripping, and B the selective adsorption/desorption on a functional layer (red) by electroreduction/-oxidation of the analyte.

various core components in the primary circuit of a nuclear power plant (e.g.  $^{110\text{m}}\text{Ag}$ ,  $^{124,125}\text{Sb}$ ,  $^{113}\text{Sn}$ , and  $^{123\text{m}}\text{Te}$ ). Using flow-through electrolysis, radioisotopes of electroactive elements could be readily separated from non-electroactive ones. The approach was then successfully tested with radioactive tracers after the addition of stable isotopic carriers (Fig. 2).

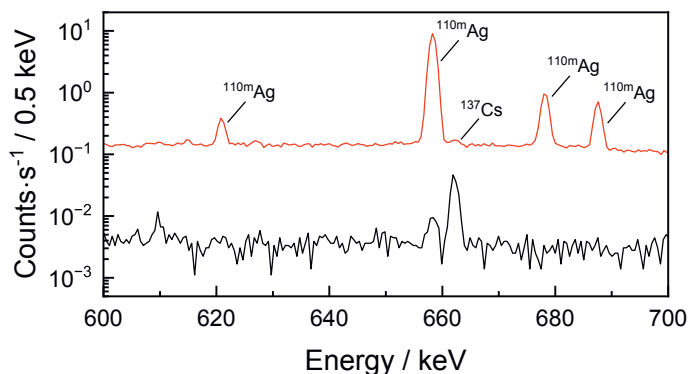


Fig. 2.  $\gamma$ -spectra of a sample measured before (red) and after (black) separation of  $^{110\text{m}}\text{Ag}$  (143 Bq) from  $^{137}\text{Cs}$  (0.5 Bq) by flow-through electrolysis in 1M  $\text{HNO}_3$  at  $-0.3$  V vs.  $\text{Ag}/\text{AgCl}/\text{KCl}$  sat. Adapted from ref. [12].

A reduction of the radioactivity of  $^{110\text{m}}\text{Ag}$  by 4 orders of magnitude (1) enabled an overall more accurate  $\gamma$ -spectrometric measurement of  $^{137}\text{Cs}$  and (2) led to an improved detection limit for  $^{137}\text{Cs}$ . Experiments with digested wipe tests from the primary circuit of a nuclear power plant demonstrated that this approach is applicable to complex sample matrices.<sup>[12]</sup> The electrolytic elimination of dominating  $^{60}\text{Co}$ , afforded significant analytical benefits. Besides enabling a more accurate measurement of  $^{123\text{m}}\text{Te}$ , the flow electrolytic separation procedure led to the detection and quantification of radionuclides  $^{103}\text{Ru}$  and  $^{110\text{m}}\text{Ag}$ , which were previously below the detection limit.

### 3.2 Selective Electrodeposition Under Carrier-Free Conditions

Carrier-free conditions are typically encountered for the analysis of radioelements such as Po or heavy actinides as well as transactinide elements. These exclude the addition of an isotopic carrier. Therefore, the electrochemical separation must be carried out at a sub-monolayer coverage, thus being strongly impacted by UPD.<sup>[5,9–11]</sup> However, UPD can also be directly utilized to design dedicated separation strategies for the analysis of specific radionuclides by simply selecting the right electrode material. So far, flow electrolytic approaches for the separation of carrier-free radionuclides have only been explored under OPD conditions.<sup>[7]</sup> Electrodeposition approaches were considered as fast batch separation and measurement methods for ultra-low amounts of lighter homologs of transactinide elements,<sup>[5,11]</sup> whereas flow-through electrolytic approaches with chemically modified electrodes were used for the electrochemical characterization of heavy actinides.<sup>[8]</sup>

However, no electrodeposition studies of transactinide elements nor their lighter homologs have been carried out in-flow to date and it remains unclear if this approach can indeed be used for their electrochemical characterization. Therefore, new electrochemical experiments are needed to advance to more comprehensive models for the study of flow electrolytic electrodeposition under carrier-free conditions. Further efforts in this direction are now being pursued using the SINQ Gas-Jet facility at the Paul Scherrer Institute where carrier-free radionuclides can be readily retrieved in the form of thermal-neutron-induced fission products of  $^{235}\text{U}$ .<sup>[13]</sup>

### 3.3 Electrolysis and Adsorption

In the past, modification of the electrode surface by impregnation with ion-exchange polymers<sup>[8]</sup> or organic extractants<sup>[14]</sup> yielded fast and efficient separation of ultra-trace amounts of radionuclides by flow-through electrolysis. However, strategies which are based on covalently strongly bound functional groups to the electrode surface are more attractive since these prevent the leaching of any organic material into the analyte solution. Simple procedures based on the *in situ* electrochemical modification by anodization of carbon surfaces have been shown to induce selective adsorption or desorption of U and Pu upon their reduction and oxidation.<sup>[15]</sup>

This approach was adapted for the separation and analysis of U and Pu isotopes by  $\alpha$ -spectrometry. The prior anodization of the carbon fiber felt WE allowed the adsorption of, e.g. U in its U(IV) oxidation state at low potential ( $-0.15$  V vs.  $\text{Ag}/\text{AgCl}/3\text{M KCl}$ ). U was subsequently released from the anodized carbon surface by oxidation to U(VI) upon switching the WE potential ( $1.2$  V vs.  $\text{Ag}/\text{AgCl}/3\text{M KCl}$ ). This mechanism affords the separation of U from other actinides (Fig. 3). These results are particularly interesting for the separation of U isotopes from interfering transuranic elements prior to  $\alpha$ -spectrometry (e.g. separation of  $^{232}\text{U}$  from  $^{243}\text{Am}$  with similar  $\alpha$ -energies). A similar mechanism could also be used for the separation of Pu isotopes from other actinide elements.

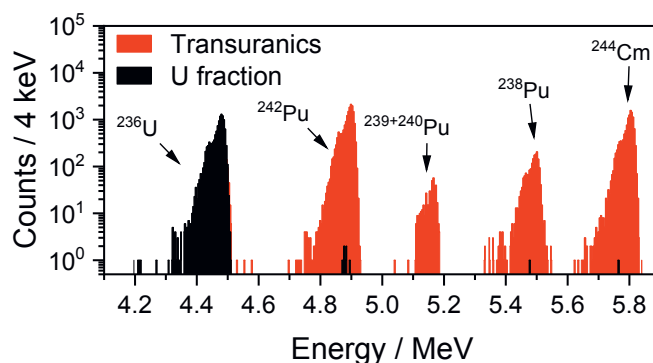


Fig. 3.  $\alpha$ -Spectra of the two fractions obtained after flow-through electrolytic separation of  $^{236}\text{U}$  (0.5 Bq; black) from  $^{242}\text{Pu}$  and  $^{244}\text{Cm}$  (0.5 Bq) as well as traces of  $^{238}\text{Pu}$  and  $^{239+240}\text{Pu}$  (red). A counting time of 24 h was used for both fractions (live time).

### 4. Conclusion and Outlook

The presented results highlight the applicability of flow-through electrolytic approaches for the separation of carrier-added/-free radionuclides. The proposed separation strategies provide clear analytical benefits for subsequently conducted radiometric measurements such as  $\alpha$ - and  $\gamma$ -spectrometry. The high tolerance toward complex sample matrices enables the direct employment of the developed procedures for the routine analysis of radionuclides in complex industrial, environmental, or biological matrices.

Further work will address the electrodeposition of short-lived, carrier-free radionuclides under the influence of UPD and will target lighter homologs of transactinide elements in the ultra-trace domain, down to single atoms.

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