



Development of radiochemical analysis strategies for decommissioning activities

D. Zapata-García*, H. Wershofen

Physikalisch-Technische Bundesanstalt (PTB), Bundesallee 100, 38116 Braunschweig, Germany

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ABSTRACT

Radioactive waste generated in decommissioning activities need be classified according to their radioactive content. The radiological information required by national authorities includes diverse alpha and beta emitters, which can only be determined after a radiochemical separation process.

This paper presents the work on the development of radiochemical methods for the simultaneous separation of several radionuclides in concrete, steel and graphite samples, on the basis of individual sample treatments which merge in a common radiochemical separation procedure based on extraction chromatography.

1. Introduction

Currently there are 438 nuclear power plants in operation worldwide, and a further 149 that are shut down or are undergoing decommissioning, including 17 that have been fully decommissioned. These numbers become even bigger if fuel cycle facilities and research reactors are included (IAEA, 2015). Given that many of the nuclear facilities currently in operation will reach the end of their design lives within the next two decades, significant decommissioning activities are expected for several decades to come and these are one of the most challenging technological legacy issues that many countries will face in the near future.

Most of the waste generated during decommissioning is not radiologically restricted and can be released into the environment or sent for recycling, but the rest will end up in different repositories, classified according to their radioactive content. Classification and control need to be done accurately in order to optimise the use of the limited repository space, but also to ensure that both the personnel involved and the public are not needlessly exposed to radiation and to minimise the environmental impact of such work. Thus, the characterisation of the radioactive materials present in nuclear facilities is a key technical aspect in the development of any decommissioning plan, but which proceeds also during and after the decommissioning process. The information required by national authorities, especially in the early stages of the decommissioning process, includes a great number of radionuclides, and characterisation is generally done combining several strategies, which range from activation calculations to sample taking and analysis in the laboratory. Whenever direct measurements can be

made, these are preferred because they produce reliable results and are faster and cheaper. However, radiochemical analysis is the only alternative when the radionuclides of interest are difficult to measure, as is the case of alpha and beta emitters, which need to be separated from the matrix before measurement.

Although the costs involved in sample analysis are large, it is possible to make significant savings by the adoption of best available practices, such as the use of validated methods for on-site measurements and simultaneous determination of more than one radionuclide whenever possible (IAEA, 2014, 2010). In addition to this, the development of radiochemical methods which reduce the times of analysis from several to ideally one working day is one of the objectives many laboratories pursue nowadays, due to the time savings such improvements would entail.

The samples that need processing within decommissioning works are also challenging, as they combine a complex matrix with an unknown distribution of the radionuclides. Among the variety of matrices probably are concrete, steel and graphite the ones of greatest interest (Cross et al., 2012).

The present work deals with the development of procedures for the simultaneous determination of alpha and beta emitters in three matrices: concrete, steel and graphite. On the basis of individual sample treatment strategies based on the chemical properties of these matrices, the work focused in making these procedures merge in a common radiochemical analysis scheme based on extraction chromatography setups for the simultaneous separation of up to three radionuclides.

* Corresponding author.

E-mail address: daniel.zapata@ptb.de (D. Zapata-García).

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2. Materials and methods

2.1. Reagents and samples

High purity double deionised water and analytical grade reagents were used throughout this study.

Commercial solutions of ^{242}Pu (NIST), ^{232}U (NIST) and ^{85}Sr (PTB) were used as tracers. The activities added to each sample were 200 mBq in the case of actinides and 1 Bq in the case of ^{85}Sr .

Concrete samples were produced at National Physical Laboratory (NPL) using commercial components and commercial steel and graphite were used.

2.2. Equipment

A fully automated electric fluxer K1 Pime (Katanax, Canada) and a START 1500 closed vessel microwave system (MLS GmbH, Germany) were used in this study.

Radiometric measurements were done with alpha spectrometers Alpha Duo (Ortec) and high resolution gamma spectrometers IGC 34, PGT and GC5019-7500SL-R (Canberra).

2.3. Sample treatment

For the analysis of aqueous solutions, tracers were added to 20 ml of concentrated HNO_3 and evaporated to dryness on a sand bath. The final residue was dissolved with 10 ml of 6 M HNO_3 and 10 ml of 1 M $\text{Al}(\text{NO}_3)_3$.

Different sample treatment procedures were applied to the different matrices considered in this work. Ground concrete samples (0.5 g) were spiked with tracers and fused at 1000 °C in Pt/Au crucibles with a mixture of $\text{LiBO}_2/\text{Li}_2\text{B}_4\text{O}_7$ adding LiBr as a wetting agent. The fusion protocol lasted 10 min and the fused material was dissolved with diluted HNO_3 immediately after fusion. Silicates were removed by adding polyethylene glycol (PEG) and filtrating after leaving to polymerise for at least 12 h. The solution was then heated, concentrated HNO_3 and HF added to eliminate any rest of silicate, evaporated to dryness once more and redissolved in 40% HNO_3 . Alkali metals were removed by means of $\text{Ca}_3(\text{PO}_4)_2$ precipitation and the residue was dissolved with 10 ml of 6 M HNO_3 and 10 ml of 1 M $\text{Al}(\text{NO}_3)_3$.

Steel samples (4.4 g) were dissolved with aqua regia to produce around 50 ml of solution. Tracers were added at this point and iron was removed by forming its complex with oxalate and coprecipitating the actinides and strontium with calcium oxalate at pH = 1.7, before the precipitation of $\text{Fe}(\text{OH})_3$ occurs. Oxalate precipitate was treated twice with 40 ml aqua regia and evaporated to incipient dryness to destroy the oxalates and then redissolved with HNO_3 and concentrated to dryness again. The final residue was dissolved with 10 ml of 6 M HNO_3 and 10 ml of 1 M $\text{Al}(\text{NO}_3)_3$.

Graphite samples (0.2 g) were digested with H_2SO_4 and HNO_3 at 260 °C for 30 min in a closed vessel microwave system. After digestion tracers were added and the solution obtained was concentrated to near dryness, 50 ml concentrated HNO_3 added and concentrated to dryness again. The final residue was dissolved with 10 ml of 6 M HNO_3 and 10 ml of 1 M $\text{Al}(\text{NO}_3)_3$.

2.4. Radiochemical separation method

Plutonium oxidation state in the solution was adjusted to Pu^{4+} before radiochemical separation by adding ferrous sulfamate followed by NaNO_2 . Radiochemical separation was performed using extraction chromatography cartridges (TrisKem International) on a vacuum box system. All cartridges were conditioned with 20 ml of 3 M HNO_3 before adding the samples.

TEVA resin cartridges were used for the extraction of plutonium. After charging the sample, media was switched to HCl by adding 4 ml of

9 M HCl and possibly interfering Th and Cm isotopes were stripped with 20 ml 4 M HCl. Finally, plutonium was stripped with 20 ml 0.1% NH_4OCl in 2 M HCl.

UTEVA resin cartridges were used for the extraction of uranium. After charging the sample, media was switched to HCl with 3 ml 9 M HCl and finally uranium was stripped with 20 ml 0.01 M HCl.

Sr resin cartridges were used for the extraction of strontium. After charging the sample, the resin was rinsed with 10 ml 8 M HNO_3 and strontium was stripped with 10 ml of 0.05 M HNO_3 .

Multielement separations were performed using a setup of all three cartridges (TEVA, UTEVA, Sr) in tandem. Once the samples had gone through all three cartridges, these were separated and elution of each radionuclide was performed individually by applying the procedures described above.

Plutonium and uranium were electroplated and measured by alpha-particle spectrometry while strontium was measured directly after elution without further treatment by high-resolution gamma spectrometry.

3. Results and discussion

The radiochemical separation scheme proposed in this work is based on the combined use of three extraction chromatography resins, each of them used for the separation of one single radionuclide. Methods used were developed in the laboratory on the basis of the multiple approaches found in the literature. (Eichrom Technologies, 2014; Maxwell et al., 2015, 2011; Tavcar et al., 2005; Wang et al., 2004) The radiochemical separation schemes described in this work were tested with spiked aqueous solutions, firstly with a single radionuclide using its specific resin, and afterwards with solutions spiked with all three radionuclides of interest using the tandem setup. Three replicates of each test were performed. Once the separation schemes had been tested with aqueous solutions, the work focused on the feasibility of such schemes for the analysis of matrices of interest in the field of decommissioning: concrete, steel and graphite.

The spectra corresponding to plutonium and uranium measured by alpha-particle spectrometry showed no crossed interference of these elements, which provides confirmatory evidence that the proposed separation scheme is adequate.

The results of the tests using aqueous solutions are presented in Fig. 1. Contrary to expectations, recovery values in the case of plutonium were higher for the multielemental tests than for the single radionuclide tests. Spectra were investigated for possible contamination of progeny present in the other tracer solutions, but no such effect was observed. Being TEVA the first cartridge in the tandem setup, this could not be attributed to the effect that other cartridges might induce and the results should be considered to show the variability in the performance of the resin applying the proposed separation scheme.

In the case of uranium, recovery values showed great variability in the case of multielemental tests, with values ranging from 23% to 91%. This variability does not correlate with the results of the other two radionuclides. The possible uptake of uranium by the TEVA resin, though unexpected, was investigated. The results showed that the amount being retained by TEVA resin was below 0.8%, so the variability on the uranium recoveries cannot be based on this phenomenon. No other reason for this performance could be found.

In the case of strontium, in contrast to actinides, the values of the two series of analyses do not show significant differences. Moreover, recovery values are the highest observed (ranging 85–95%), which can be explained on the basis of the specificity of this resin for strontium separations.

In order to apply the proposed radiochemical separation scheme to the matrices of interest in this study, it was necessary to introduce sample treatment strategies previous to the radiochemical separation. The different treatment strategies were decided taking into account the sample chemical features in order to obtain a solution in nitric acid

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