

Sequential analysis of Sr, Pu, Am and Cm: Low-level liquid radioactive effluents

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Abstract. A new sequential procedure for the analysis of Pu, Am, Cm and Sr in low-level liquid radioactive effluents is presented. The proposed method utilises an actinide specific extraction chromatographic resin (TRU-Resin) for the isolation and separation of the actinides. ^{90}Sr determination is accomplished via analysis of its progeny ^{90}Y , which is purified with TBP extraction. The proposed method is simpler, faster and more robust than traditional ion exchange, extraction and precipitation methods used in routine analysis of actinides and ^{90}Sr . The chemical yield of all analytes, when analysing 200 ml low-level effluent, is between 80-95%.

1. INTRODUCTION

The operation of nuclear power plants undesirably leads to the formation of liquid and solid radioactive waste containing activation and fission products. While the solid waste is suitably stored in repositories, the low-level liquid waste is normally discharged to appropriate surroundings, after decay of the shortest living radionuclides. Before such an operation can be undertaken the radionuclide content of the liquid must be examined. The Environmental Monitoring Section (EMS) of The Institute for Energy Technology (IFE), performs surveillance of discharges originating from IFE's nuclear activities to ensure that the discharge limits given by the Norwegian Radiation Protection Authority are not exceeded. The liquid effluents are analysed for gamma emitters (including ^{241}Am), ^3H , ^{35}S , uranium, ^{90}Sr , ^{238}Pu and $^{239,240}\text{Pu}$. The gamma analysis is performed directly on the liquid samples using HPGe detectors with low-energy windows. Analysis of ^{90}Sr , ^{238}Pu and $^{239,240}\text{Pu}$ is performed using standard separation procedures

The low-level liquid waste at IFE originates from the operation of a small (thermal output 2 MW) research reactor and the production of radiopharmaceuticals. The waste from different locations at IFE is collected in large drums to allow the decay of the shortest living radionuclides before an evaluation on the discharge of the liquid is undertaken. Representative samples from the drums are then analysed for α -, β - and γ -emitters. The composition of the liquid and the radionuclide content varies with the activities at the specific time. The general level of some radionuclides in the liquid is shown in Table 1.

Table 1: Activities of some radionuclides in the low-level waste from IFE.

Radionuclide	^{60}Co	^{90}Sr	^{134}Cs	^{137}Cs	$^{239,240}\text{Pu}$	^{241}Am
Activity (Bq/l)	1-230	0-150	0.5-10	1-150	0-240	0-5

In our lab ^{90}Sr is analysed using the traditional "fumic nitric acid method" [1,2]. Several nitrate, chromate, hydroxide and carbonate precipitations are used to pre-concentrate Sr and to eliminate interfering elements as Fe, Y, actinides, Ba, Ca and K. Sr-recovery is then determined by gamma analysis of the ^{85}Sr -spike and the solution is set aside for the ingrowth of ^{90}Y . Y is then precipitated several times as $\text{Y}(\text{OH})_3$ before a final precipitation as Y-oxalate. The oxalate is collected by filtration and the ^{90}Y -activity determined using a low-level beta GM multicounter (Risø GM-25-5). Y-recovery is

then determined using EDTA titration. $^{239,240}\text{Pu}$ analysis is done on a separate sample using traditional anion exchange procedure before the activity on electroplated discs is determined using PIPS detectors.

In an effort to optimise these analyses the use of extraction chromatography coupled with liquid-liquid extraction to develop a sequential procedure for the analysis of ^{90}Sr and α -emitters was studied. Since the gamma detection limit of ^{241}Am is quite high, an alpha analysis of ^{241}Am was also desired. The wastewater is normally stored for at least a month before radiochemical separations are undertaken. ^{90}Sr activity in the water therefore equals the activity of its progeny ^{90}Y . In the proposed procedure the more favourable separation chemistry of Y(III) is utilized to determine the activity of ^{90}Sr via ^{90}Y . An additional advantage in analysing ^{90}Y is its short half-life ($t_{1/2} = 64.1$ hours), which enables a simple check of chemical purity of the final source by just following its decay.

2. EXPERIMENTAL

2.1 Reagents and apparatus

Seven different low-level liquid waste solutions were analysed for Sr, Pu, Am and Cm. ^{242}Pu (0.163 Bq/ml) and ^{243}Am (0,086 Bq/ml) were used as tracers for Pu and Am (Cm) yield determination, respectively. Y-carrier (10 mg/ml) was prepared from pa grade $\text{Y}_2(\text{NO}_3)_3 \cdot 6 \text{H}_2\text{O}$ purified by TBP-extraction [1]. The extraction chromatographic resin used for the separation of Pu, Am and Cm was TRU-Resin SPS (50-100 μm) (Eichrom Ind.). All chemicals were of analytical reagent grade.

An i.d. 5 mm glass column with a glass wool fitting at bottom and top was used to make an extraction chromatographic column of 0.50 gram TRU-Resin. 0.1 μm polypropylene membran filters (25 mm) fitted in a 50 ml polysulfone filter funnel (Gelman Sciences) were used to collect the fluorides when preparing the α -sources.

^{90}Y -beta activity was determined using a low level beta GM multicounter (Risø GM-25-5). The alpha-activities were measured with 450 mm^2 PIPS detectors placed in multichamber racks (Canberra). The vacuum in the chambers was kept under 10 torr and the distance between the source and the detector at 1 cm, giving a counting efficiency of 17 ± 1 %. Data treatment was done with the Canberra Alpha Analyst software.

2.2 Procedures

200 ml effluent water was acidified with 10 ml 65% HNO_3 and 0.2 ml each of ^{243}Am - and ^{242}Pu -tracer and 1 ml of Y-carrier solution added before the sample was evaporated to dryness. The salts were then treated twice with 10 ml 65% HNO_3 .

The salts were dissolved with 15 ml 3 M HNO_3 and Na_2SO_3 added to 0,2 M. The solution was left for 20 minutes for the complete reduction of Pu to Pu(III). NaNO_2 was added to 0,2 M and the solution left for 20 min for the oxidation of Pu(III) to Pu(IV). The solution was then loaded on a TRU-Resin column pre-treated with 3 M HNO_3 and the column washed with 10 ml 2 M HNO_3 and 10 ml 2 M HNO_3 -0,1 M NaNO_2 (Flow: 1-2 ml/min). All effluents were kept for Y-analysis. After washing the column with 2 ml 9 M HCl , Am was eluted with 10 ml 4 M HCl and Pu with 10 ml 4 M HCl -0,02 M TiCl_3 directly into two different 20 ml scintillation vials. The Am and Pu-fractions were added 50 μg Ce and 1 ml 40% HF and the fluorides allowed to develop for at least 30 min. The fluorides were then collected by filtration through 0,1 μm membrane filter pre-treated with 80% ethanol and the vials and filter washed with 5 ml H_2O followed by 5 ml 96% ethanol. The filters were then attached to planchets with double sided tape, dried at 60 $^\circ\text{C}$, and the alpha-activity determined using PIPS detectors.

The Y-fraction from TRU-Resin was evaporated to dryness, treated once with 5 ml 65% HNO_3 and the salts picked up with 30 ml 14 M HNO_3 . Y was then extracted twice with 30 ml TBP preconditioned with 14 M HNO_3 and the separation time between Sr and Y noted. The TBP phases were combined, washed with 30 ml 14 M HNO_3 , and Y stripped twice with 30 ml H_2O . NH_3 was then added to pH 2-3 and Y-oxalate precipitated with the addition of saturated oxalic acid solution. The solution was heated for approximately 1 hour at 90 $^\circ\text{C}$, cooled, and the oxalate collected on a 25 mm Whatman 42 ash less

filter paper. ^{90}Y -activity was then determined using a GM-counter. After β -counting the Y-oxalate was ashed at $900\text{ }^\circ\text{C}$ for 90 minutes and the Y_2O_3 picked up with 3 ml 65% HNO_3 . The solution was evaporated to dryness and the salts dissolved with 20 ml acetate buffer at pH 4,4. 1 drop of 0.5% xylene orange indicator was then added and Y titrated with 0.01 M EDTA until a color change from red to yellow was observed. Y-recovery was then determined by comparing the EDTA consumption of the analyte solution versus that of a reference solution containing 10 mg Y [4].

3. RESULTS AND DISCUSSION

In normal routine operations where the analysis of Sr and actinides is desired for a sample the analyses are performed on different sample aliquots. One aliquot is analysed for Sr and another for Pu and Am. This requires the pre-treatment of two different sub samples. Since the pre-treatment step for many matrixes is the most time consuming step a considerable gain in throughput can be achieved by using the same sample for both Sr and actinide analysis. In a two-step sequential procedure the time used for the analysis of the second analyte can additionally be reduced as many interfering elements are eliminated in the first step.

In the proposed procedure tri-, tetra- and hexa-valent actinides are extracted by TRU-Resin while most other elements pass right through. Some Y(III) is also extracted, but this is washed out of the column with 2 M HNO_3 [3]. When the column is washed with HNO_3 containing NaNO_2 any remaining traces of Pu(III) are oxidised to Pu(IV). Since trivalent actinides are not extracted by CMPO (the active extractant in TRU-Resin) from HCl solutions, 4 M HCl is used to elute Am and Cm. As Cm(III) resembles Am(III) the recovery of ^{243}Am equals the recovery of Cm and the activity of other Cm isotopes can also be calculated. After the removal of trivalent actinides plutonium can be reductively eluted with 4 M HCl – 0,02 M TiCl_3 . The α -sources are then made by micro co-precipitation with CeF_3 . The alpha spectra of the Am and Pu fraction can be seen in Figure 1. As seen both fractions are very clean and do not contain any interfering α -emitters.

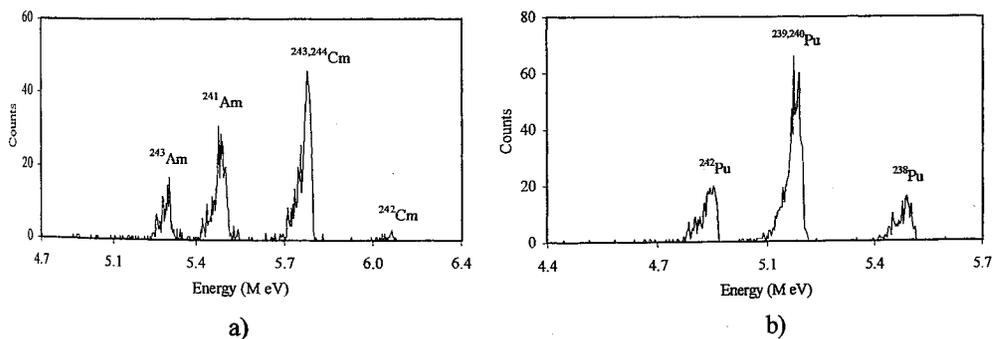


Figure 1: Alpha-spectra of the americium (a) and plutonium (b) fraction.

TBP extraction is here used to extract Y and separate it from Sr and other mono and divalent cations. Only those elements that are not extracted by CMPO from 2-3 M HNO_3 but extracted by TBP from 14 M HNO_3 and form sparingly soluble oxalates at pH 2-3 can interfere in the determination of ^{90}Y . The possible co-precipitation of radionuclides interfering in the determination of ^{90}Y can easily be checked by following the decay of the Y-source. In none of the seven samples analysed did the decay deviate from that of ^{90}Y . The chemical yield of Y is traditionally checked by gravimetric methods. This however can give a too high yield estimate as other elements also can precipitate together with Y-oxalate. In our lab we have found pH-controlled EDTA titration to be more reliable than gravimetric methods for the determination of Y-recovery [4]. The chemical yield of Pu, Am, Y and Sr for the proposed and traditional methods is shown in Table 2.

Table 2: Chemical yields of Pu, Am, Y and Sr using the proposed and the traditional methods.

Element	Pu	Am	Y	Sr
Yield (Proposed method)	94 ± 9%	87 ± 12%	79 ± 7%	n.d.
Yield (Traditional methods)	24 ± 12%	n.d.	80 ± 12%	67 ± 27%

While the recoveries of both Sr and Y are high using the tradition method, the recovery of Pu is very low. Using the proposed method the recoveries of all analytes are very high. In addition the new method allows a simple α -analysis of Am and Cm. The traditional method requires the use of about one week for Pu analysis and 3 weeks for Sr-analysis. The proposed method offers significant time reduction as separation and source preparation of Pu, Am and Y can be achieved in one day.

4. CONCLUSION

A simple, rapid and reliable method for the analysis of Pu, Am, Cm and Sr in low-level liquid effluents is proposed which offers higher chemical yields, is less time consuming and more environmentally friendly than traditional methods.

References

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