

# Characterisation of plutonium species in alkaline liquors sampled from a UK legacy nuclear fuel storage pond: Electronic Supplementary Information (ESI)

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## 1. Pu recoveries from ultrafiltration

A <sup>239</sup>Pu standard solution (99+% as <sup>239</sup>Pu traceable to the National Physical Laboratory, UK) was prepared to a concentration of 2.8e-9 M (1.54 Bq.cm<sup>-3</sup>) in 1 M HNO<sub>3</sub>. A series of dilutions were then carried out on this solution at different pHs. The dilution concentrations were chosen so that the final Pu concentration remained below the solubility limit for the pH under investigation. All solutions were prepared in polypropylene volumetric flasks to minimise surface sorption on to vessel walls. During preparation of the dilution series, care was taken to minimise colloid formation by dilution prior to pH adjustment (using dilute carbonate free volumetric caustic solution). Small aliquots of both the Pu standard solution and the dilution series were placed in a Vivaspin 2 ultracentrifuge cartridge (5 kDa molecular weight cut-off (MWCO), 1 nm pore size, polyethersulphone membrane). The centrifugal tubes were then placed in a centrifuge and spun for 30 minutes at 2000 rpm. An aliquot of the filtrate was taken and flame fixed onto a stainless steel planchet. Aliquots of the unfiltered solutions were also taken and flame fixed for direct comparison. All samples were analysed by  $\alpha$ -spectrometry (Canberra Quad Alpha Spectrometer model 7404). Detector efficiencies were calculated using the standard solution as reference. A summary of the results is tabulated below (Table S1). For the dilute solutions, recoveries were calculated against unfiltered samples. All determinations on both unfiltered and filtered solutions were carried out in triplicate. All results were background corrected.

Table S1: Summary of ultrafiltration results on standard Pu samples (\*indicates that the Vivaspin cartridge was conditioned by passing a 2 ml portion of the standard solution through the cartridge prior to filtering the solution again; for all other determinations one cartridge was used per determination without prior conditioning)

Sample Details	pH	Expected Activity (Bq.cm <sup>-3</sup> )	Measured Activities (2 $\sigma$ ) filtered solutions (Bq.cm <sup>-3</sup> )	% recovery compared to unfiltered solution
Pu239 standard	0	1.54	1.46 (0.04)	95
Pu239 standard	0	1.54	1.79 (0.04)	116
Pu239 standard	0	1.54	1.54 (0.04)	100
Pu239 standard *	0	1.54	1.46 (0.04)	95
Pu239 standard *	0	1.54	1.61 (0.04)	105
Pu239 standard *	0	1.54	1.56 (0.04)	101
Pu239 standard 1/27.8 dilution	1.4	0.0554	0.0462 (0.0056)	94
Pu239 standard 1/27.8 dilution	1.4	0.0554	0.0487 (0.0052)	99
Pu239 standard 1/27.8 dilution	1.4	0.0554	0.0550 (0.0060)	112
Pu239 standard 1/27.8 dilution	10	0.0554	0.0253 (0.0020)	58
Pu239 standard 1/27.8 dilution	10	0.0554	0.0223 (0.0022)	51
Pu239 standard 1/27.8 dilution	10	0.0554	0.0237 (0.0020)	55
Pu239 standard 1/55.6 dilution	10	0.0277	0.0299 (0.0050)	108
Pu239 standard 1/55.6 dilution	10	0.0277	0.0300 (0.0054)	108
Pu239 standard 1/55.6 dilution	10	0.0277	0.0307 (0.0024)	111
standard 1/556 dilution Pu239	10	0.00277	0.0022 +/- 0.00062	95
standard 1/556 dilution Pu239	10	0.00277	0.0030 +/- 0.00072	129
standard 1/556 dilution Pu239	10	0.00277	0.0022 +/- 0.00080	95

From the results in Table S1, it is seen that ~100 % recoveries are obtained for ultrafiltered solutions. The exceptions are the solutions at an activity of  $0.0554 \text{ Bq.cm}^{-3}$  ( $1.01\text{e-}10 \text{ M Pu}$ ) at pH 10 where recoveries against the unfiltered samples were only 51-58 % suggesting that either sorption or colloid formation had occurred in this solution. This concentration corresponds to the top of the uncertainty range for the solubility limit reported by Neck and Kim<sup>1</sup> at pH 10.

To eliminate sorption of Pu as the cause of poor recovery, a solution was prepared at a concentration of  $5.4\text{e-}11 \text{ M}$  ( $0.0277 \text{ Bq.cm}^{-3}$ ). This concentration was closer to the theoretical solubility limit.<sup>2</sup> Following ultrafiltration of this solution and subsequent analysis the filtered Pu concentration was again found to recover ~100 % Pu, confirming that sorption of Pu was not the problem and the most likely cause of the poor recoveries at the higher concentration was Pu colloid generation. Further ultrafiltration and analysis of a solution at a concentration of  $5.4\text{e-}12 \text{ M}$  ( $0.00277 \text{ Bq.cm}^{-3}$ ) again confirmed that sorption on these particular filters was not a problem.

## 2. Separation scheme used in $\alpha$ -spectrometry of U, Pu and Am solutions

The aqueous fractions (samples P1-3, HT1-3) obtained after respective ultra-filtrations were subjected to a chemical separation procedure to provide sources for  $\alpha$ -spectrometry. The scheme employed is illustrated in Fig. S1. The fractions generated were then either electrodeposited or flame fixed in the standard manner prior to analysis by conventional  $\alpha$ -spectrometry (Canberra Quad Alpha Spectrometer model 7404).

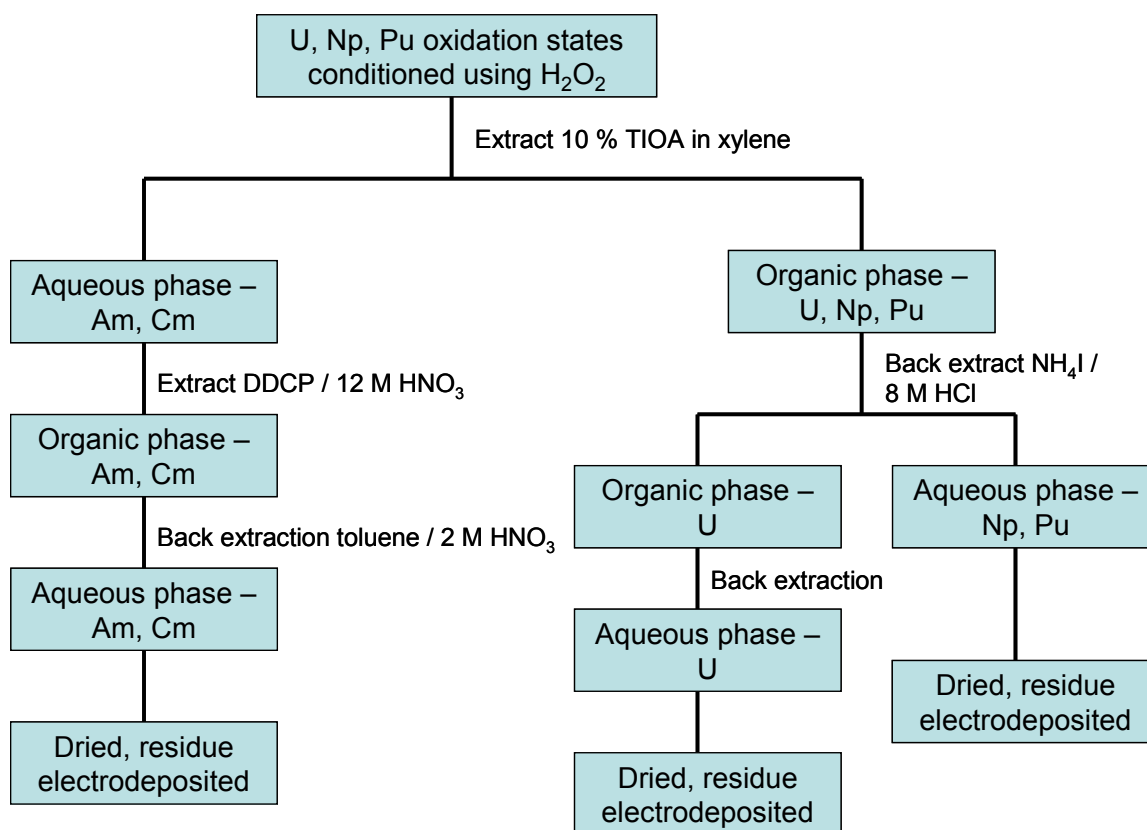


Fig. S1: Separation scheme used to provide U, Pu and Am fractions for  $\alpha$ -spectrometry (TIOA = Triisooctylamine, DDCP = di-n-butyl-di-ethyl-carbamyl-phosphate)

## 3. Sampling and analysis of Main Pond samples

22 samples from three deployments of the Bell Jar sampler in the Main Pond area plus two additional near-surface samples have been analysed in this project for their Pu concentrations. Sampling is described elsewhere<sup>3</sup> but involves either mild or vigorous agitation of the sludge deposits, which are comparatively shallow in the Main Pond area. Characterisation of the particulates from sludges has been described elsewhere also<sup>4</sup>. This paper reports the analysis of the Pu- $\alpha$  in the supernate (liquor) samples using a modified TTA (thenoyltrifluoroacetone) extraction as illustrated in Fig. S2. The aim of this method was to try and obtain values for total [Pu], [Pu(III+IV)], [Pu(V+VI)] and [Am] efficiently from relatively small samples within a single scheme. The first extraction should lead to a determination of the [Pu(III+IV)]. The second extraction on the  $\text{H}_2\text{O}_2$  conditioned sample should lead to the total Pu concentration. [Pu(V+VI)] is then the difference between the two values.

Some problems were encountered with the Am data which thus are not described within this paper. Also, the low concentrations of soluble Pu in these samples made the speciation data (III+IV vs. V+VI split) rather unreliable. This is discussed in the main paper.

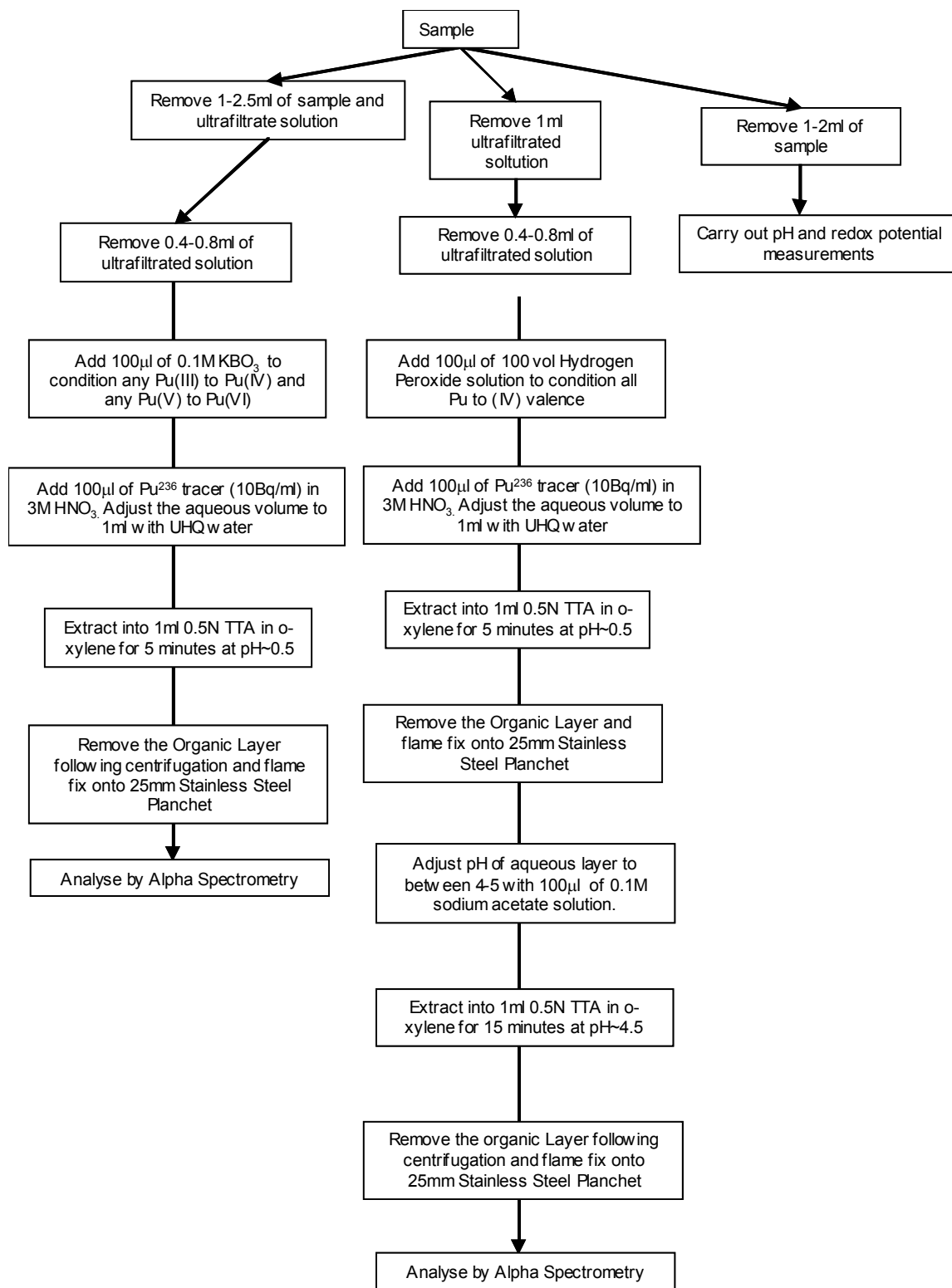


Fig. S2: Separation scheme adopted for Pu and Am analysis on Main Pond samples

#### 4. Composition of sampled pond liquors

The pond liquors contain a wide range of inorganic and organic species, including U, actinides and fission products from corroded fuel, Mg and Al from corroded cladding and corrosion products from other pond items. The major analytes in solution were analysed as part of the pond sampling campaigns. Typical ranges of some of these major analytes are given below in Table S2.

Table S2: Typical chemical composition (major analytes) of filtered samples from the Main Pond area and Pond Bay (ND = not determined)

Element	Main Pond (filtered) (ppm)	Pond Bay (filtered) (ppm)
Al	4.9-2.14	<0.1
B	1.13-13.4	ND
Ca	0.7-2.3	<0.1-70
Cr	<1.5	<0.1
Cu	<1.5	<0.1-2
Fe	0.1-0.4	1-15
Hg	<1.3	<0.1
K	<2	7-9
Mg	<10	30-160
Na	70-97	9.1-10.6
Ni	1-2	<0.1
P	0.3-0.8	ND
Pb	<0.2	0.1-5
S	0.2-13	ND
Mn	ND	<0.1
Zn	<1	<0.1-7
U	<2	150-250

## 5. Soluble Pu concentrations in samples analysed directly compared with TTA and DBM extractions

Table S3: Total soluble Pu concentrations determined from various methods for samples P1-3 and HT1-6, (r) = replicate

Sample Code	Solubility / size fractionation experiments		TTA extractions		DBM extractions	
	Total Pu (M)	% error (2 $\sigma$ )	Total Pu (M)	% error (2 $\sigma$ )	Total Pu (M)	% error (2 $\sigma$ )
Unfiltered samples						
P1	5.57E-08	7.6				
P1 (r)	3.79E-08	3.5				
P2	9.78E-08	9.2				
P2 (r)	1.08E-07	9.9				
P3	2.19E-07	6.4				
P3 (r)	2.14E-07	6.7				
HT1	2.20E-07	5.4				
HT1 (r)	2.37E-07	4.2				
HT2	4.45E-07	5.5				
HT2 (r)	3.40E-07	6.2				
HT3	2.96E-07	7.4				
HT3 (r)	2.95E-07	5.9				
Ultrafiltered samples						
P1	3.13E-09	8.8	1.24E-09	2.6	1.48E-09	5.0
P1 (r)	3.01E-09	5.7	1.30E-09	3.7	1.23E-09	4.9
P2	2.17E-09	4.6	2.48E-09	2.2	2.62E-09	3.4
P2 (r)	1.81E-09	7.6	2.41E-09	2.2	3.07E-09	3.2
P3	1.59E-09	6.3	3.19E-09	2.4	3.42E-09	3.1
P3 (r)	2.14E-09	15.1	3.27E-09	2.6	3.53E-09	2.9
HT1	1.34E-09	18.0	5.56E-10	4.6	5.63E-10	7.1
HT1 (r)	1.23E-09	7.5	5.89E-10	4.5	7.63E-10	6.2
HT2	1.43E-09	1.7	2.98E-09	2.0	2.70E-09	4.0
HT2 (r)	1.47E-09	1.5	2.78E-09	2.1	2.73E-09	3.7
HT3	1.38E-09	2.0	2.98E-09	2.3	2.31E-09	9.5
HT3 (r)	1.51E-09	1.8	3.08E-09	2.3	2.77E-09	8.1
HT4			7.66E-11	8.3	4.77E-11	35.3
HT4 (r)			7.69E-11	15.2	4.94E-11	35.1
HT5			2.59E-10	6.4	1.06E-10	15.7
HT5 (r)			2.00E-10	7.0	1.10E-10	15.1
HT6			2.23E-10	4.0	4.65E-11	27.0
HT6 (r)			1.93E-10	4.6	4.55E-11	22.4

## Notes and references

- 1 V. Neck and J. I. Kim, *Radiochim. Acta*, 2001, **89**, 1.
- 2 H. Metivier and R. Guillaumont, *Radiochem. Radioanal. Lett.*, 1972, **10**, 27.
- 3 J. J. Hastings, *Release Behaviour of Sr-90 From Hydraulically Retrieved ILW Sludge*, MRS Conference, Sheffield, September 2007.
- 4 C. C. R. Gregson, D. T. Goddard, M. J. Sarsfield, R. J. Taylor, *J. Nucl. Mater.*, 2011, **412**, 145.