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SECTION 2: RADIO ANALYTICAL CHEMISTRY AND SERVICES

2.1 Chemical analysis of plutonium

2.1.1 Analysis of plutonium in PuO_2

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In continuation of the auditing of PuO_2 lots from the Fuel Reprocessing Division (FRD) samples of plutonium were analysed for their Pu content by potentiometric titration[1,2]. A secondary standard maintained at FRD was analysed along with each set of Pu samples in order to keep a check on the accuracy of the analysis results obtained. This secondary standard was in turn checked against the NBS Pu metal standard for the Pu content. The potentiometric analysis results were in agreement with the corresponding coulometric values at FRD within $\pm$ 0.5%.

Dissolution of sintered PuO_2

The work on dissolution and analysis of sintered PuO_2 samples from Radiometallurgy Section for the purpose of auditing of this material was continued. The dissolution of the sintered oxide with conc. HNO_3-HF-mixture, was modified by adding a drop of conc. HF directly to the oxide powder before adding the acid mixture. It was found that 500 mg of the oxide could be dissolved in 5 hours. The composition of the acid mixture was maintained at 0.1M HF in conc. HNO_3. Thus, each sintered oxide sample was analysed both by HNO_3-HF dissolution and by H_2SO_4-$(NH_4)_2SO_4$ refluxion methods[2,3,4]. The results from both the methods for the same sample agreed within $\pm$ 0.3%. Some typical results are given in Table 10. Though the H_2SO_4-$(NH)_2SO_4$ dissolution technique was faster it has the disadvantage of introducing sulphate ions in the solution which may be troublesome during the recovery and purification of Pu from analysis wastes. However, it was established that by corresponding increase of the quantity of the reagents required, 5 g of sintered PuO_2 could be brought into solution by refluxing it with 9M H_2SO_4-$(NH_4)_2SO_4$ mixture for 8 hours. Thus the refluxion method has the ability to bring the difficultly soluble sintered PuO_2 into solution in a comparatively short time without having to resort to drastic steps of heating the material with acid mixtures under high pressure in an autoclave[5].

TABLE 10

Comparison of analysis results on sintered PuO_2 samples by HNO_3-HF and H_2SO_4-$(NH_4)_2SO_4$ dissolution methods

Sample No.	Analysis results by HNO_3-HF dissolution		Analysis results by H_2SO_4-$(NH_4)_2SO_4$ dissolution	
	Wt. of PuO_2 taken (mg)	(%) Pu	Wt. of PuO_2 taken (mg)	(%) Pu
1	279.23	87.05	236.77	87.26
2	271.00	87.19	189.40	87.43
3	149.92	87.71	209.58	87.50
4	224.41	87.43	195.40	87.88
5	247.54	88.02	140.24	87.61
6	140.52	87.46	127.02	87.72
7	300.00	87.69	169.04	87.55
8	201.90	87.64	195.20	87.14
9	343.22	87.51	165.82	87.17
10	280.24	87.88	203.94	87.57

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2.1.2 Estimation of plutonium in UO_2-PuO_2 mixture, Pu-Al alloy and Pu-Ga alloy by potentiometric titration

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Plutonium content of various materials like UO_2-PuO_2 mixture, Pu-Al alloy

and Pu-Ga alloy from Radiometallurgy Section was determined by the potentiometric titration method. UO_2-PuO_2 was dissolved by heating in conc. HNO_3. The high concentration of uranium present in the solution was found to have no effect on the analysis of plutonium by potentiometric titration as was established earlier[1, 2]. Several samples of UO_2-PuO_2 mixture containing PuO_2 in the range of 2-4% were analysed by this method. Some results are given in Table 11.

TABLE 11

Analysis results on UO_2-PuO_2- mixed oxide samples

Sample Number	Wt. of the sample dissolved (g)	Pu content from analysis (mg)	$\left(\frac{PuO_2}{UO_2 + PuO_2}\right)\%$
1	3.4427	78.73	2.59
2	3.4685	79.72	2.61
3	3.6262	83.11	2.59
4	3.1200	108.74	3.95
5	3.2012	111.62	3.95
6	3.0465	105.63	3.93
7	3.7015	149.85	4.59
8	3.2306	127.48	4.47
9	3.7170	147.08	4.49
10	3.1140	125.32	4.56

Pu-Al alloy was dissolved in HNO_3 in presence of 0.02M $Hg(NO_3)_2$. Presence of aluminium ion or mercuric ion was found not to interfere in the subsequent potentiometric estimation of Pu in the solution[3]. Several samples of Pu-Al alloy containing 14-16% of Pu were analysed in this way. Results are given in Table 12.

Pu-Ga alloys were dissolved in 6M HCl giving a blue solution typical of Pu(III). For potentiometric estimation of Pu the chloride ions were removed by repeated fuming with H_2SO_4. Nearly 2% of gallium present in the alloy was found not to interfere in the Pu estimation. Some typical results are given in Table 13.

TABLE 12

Potentiometric analysis results on Pu-Al alloy samples

Sample Number	Wt. of the sample dissolved (mg)	Pu content (mg)	Percentage of plutonium in the alloy
1	425.39	70.77	16.64
2	327.22	54.29	16.59
3	571.73	85.26	14.82
4	328.99	95.88	14.53
5	326.04	95.45	14.62
6	471.69	73.47	15.58
7	547.01	85.33	15.60

TABLE 13

Potentiometric analysis results on Pu-Ga alloy samples

Sample Number	Wt. of the sample dissolved (g)	Pu content of the alloy (g)	Pu content (%)
1	1.2777	1.2311	96.35
2	1.3577	1.2991	95.69
3	0.8292	0.7980	96.24
4	1.0209	0.9836	96.35

References

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2. C.L. Rao, G.M. Nair, N.P. Singh, M.V. Ramaniah and N. Srinivasan, Z. anal. chem., 254, 126 (1971).
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2.1.3 Accuracy of the potentiometric method of estimation of plutonium

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The accuracy of the potentiometric titration method for plutonium estimation was checked by using standard solutions prepared from anhydrous $Pu(SO_4)_2$ made in this laboratory[1, 2]. It was found that the accuracy of the result was within the limits of the precision which was in the range of ± 0.2%. In order to confirm this result the method was checked against NBS plutonium metal primary standard recently procured by FRD. Nearly 0.5 g of the sample of exactly known weight (No. 949C) in argon atmosphere supplied by the National Bureau of Standards, U.S.A. was carefully dissolved in a calibrated, weighed 50 ml standard flask in 6M HCl at room temperature. The solution was made up with 6M HCl and aliquots of this solution were used for the standardisation of coulometric method[3] of estimation of Pu at FRD and the potentiometric[4] and mass spectrometric methods at RCD.

The chloride ions in the solution were removed by fuming with H_2SO_4 before the estimation of Pu. 500 µl and 250 µl aliquots were separately fumed with conc. H_2SO_4 three or four times to ensure complete removal of the chloride ions and then diluted with 1M H_2SO_4. Ten analyses with 250 µl aliquots and six analyses with 500 µl aliquots were carried out and the results are given in Table 14. The results confirm the earlier observation that there is no bias in this method and that the mean values obtained agree with the expected value within the precision limits (± 0.2%).

References

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TABLE 14

Potentiometric analysis results on NBS plutonium metal standard (No.949C)

Weight of the metal supplied by NBS = 566.16 mg
Volume of the solution made up = 49.9413 ml
Medium = 6M HCl
Atomic weight of plutonium = 239.08

No.	Plutonium analysis results with 250 µl aliquots (mg/ml)	Plutonium analysis results with 500 µl aliquots (mg/ml)
1	11.338	11.347
2	11.329	11.336
3	11.325	11.338
4	11.355	11.318
5	11.299	11.338
6	11.329	11.327
7	11.338	-
8	11.372	-
9	11.363	-
10	11.359	-
Mean	11.341 ± 0.0216	11.334 ± 0.010
Std.Deviation	± 0.190%	± 0.089%
Deviation from expected value	+ 0.039%	- 0.022%
Total Pu from analysis	566.384 mg	566.035 mg

2.2 Mass Spectrometry

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2.2.1 Calibration of the instrument

Isotopic standards of uranium (SRM U-015, U-030, U-050, U-100, U-200, U-500) and plutonium (SRM 948) obtained from the National Bureau of Standards were analysed in triplicate to find out the overall mass discrimination factor (m.d.f.)