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ABSTRACT

Potentiometric method is employed by using memotitrator coupled with combined electrode for the estimation of plutonium. The estimations are carried out on the process samples and the acid dissolved samples for auditing, in the concentration range of 5 g/l to 20 g/l. The chemical procedure is i) oxidising plutonium to higher oxidation state by silver oxide ii)reducing the same by adding excess ferrous and iii)titrating potassium dichromate against the unreacted ferrous. The plutonium content is computed from ferrous consumed in the reaction. The average percentage error of the method is +/-0.27.The values obtained are in close agreement with those obtained by coulometry. (1)

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I INTRODUCTION

Several instrumental methods (1-5) for the determination of plutonium have been studied in recent years. The process lot samples have to be estimated within reasonable accuracy for the fissile material. It should also be accounted for at each stage of operation in the reconversion laboratory. At present the radiometry and coulometry methods are in use for these estimations. However, an attempt was made to estimate the plutonium from the process and audit samples by potentiometry methods using an instrument - memo titrator. This analytical instrument facilitates the determination of plutonium quantitatively by measuring the potential at equivalence point. The method involves the oxidation of plutonium to sixth valency by AgO and subsequent reduction of the same by adding excess ferrous. The unreacted ferrous is then determined by titrating against potassium dichromate standard. The actual ferrous reacted with plutonium is thus computed. The values obtained by this method are in close agreement with those of coulometry. One of the major advantages of the potentiometric method is that the estimation of plutonium can be carried out in less than an hour. In this method samples can be directly pipetted unlike in other methods where extensive sample preparation is required.

II INSTRUMENTAL

Memo titrator is a microprocessor controlled compact instrument used for individual titrimetric analysis. It is simple to use in routine operations. The instrument provides the possibility for automatically performing individual and combined titrations.

Being a microprocessor controlled unit each titration can be carried out by selecting the proper programme and feeding the appropriate parameters. These titration methods can be stored in the memory, replaced or deleted at any time. The results can be obtained with the GA-40 printer in the print out form.

Suitable modifications were made in the set up to use the system for the estimation of plutonium in the process sample. For this purpose the cables of the electrode and delivery end of the burettes were extended by attaching a capillary tube. The glass container with the electrode assembly was kept in the fumehood. The electromechanical stirrer supplied by the manufacturer was replaced by a magnetic stirrer. The combined electrode used for this estimation was platinum electrode DM-140.

III STANDARDISATION OF REAGENTS

i Standard potassium dichromate 0.025 N soln.

3 g of finely powdered AR grade K2Cr2O7 was heated in an oven at 140-160 degree centigrade for an hour. It was cooled in a

desiccator. 1.266g was weighed and quantitatively transferred into one litre standard flask and made upto volume by distilled water. It is necessary to prepare the standard before use (at least once in 15 days).

ii 1M Sulfuric Acid

56 ml of AR sulfuric acid was taken in one litre standard flask containing some distilled water and it was made upto one litre by adding distilled water.

iii Argentic Oxide

7.5 g of potassium persulphate was dissolved and made upto 250 ml in a standard flask.

2.5 g of silver nitrate crystals were dissolved and made upto 25 ml in a standard flask.

Both the solutions were mixed in a beaker and allowed to stand for an hour. Afterwards the black ppt. thus formed was filtered and washed with water. The ppt. (argentic oixde) was kept in a desiccator for dryness and used for analysis.(4)

iv 1.5 M sulphamic acid

15 g of sulphamic acid crystals were dissolved in hot water and made upto 100 ml after cooling.

v 0.2M ferrous ammonium sulphate in 1M H_2SO_4.

3.9214 g of $(NH_4)_2Fe(SO_4)_2$ was dissolved in 1M H_2SO_4 and made upto 50 ml in 50 ml flask.This ferrous ammonium sulphate was standardised daily with standard potassium dichromate.

IV ANALYTICAL PROCEDURE

a. Blank Titration-

Standard ferrous ammonium sulphate solution was prepared daily to carry out blank titration as follows:

Argentic oxide (slightly in excess of stoichiometric amount) was added to 2 ml of 1M sulphuric acid. For destroying the argentic oxide 1 ml of sulphamic acid was added followed by 10 ml of 1M sulphuric acid and the solution was stirred . 500 micro litres of 0.2 M ferrous ammonium sulphate was added and titrated against 0.025 N solution of potassium dichromate in such a way that the results were obtained in terms of milliequivalence.

This procedure was repeated thrice to obtain an average milliequivelence value.

b. Sample Titration

An aliquot of the sample(containing 4-5 mg Pu) was transferred to a titration beaker and stirred after the addition of 2ml of 1M H_2SO_4. Argentic oxide was added till the solution turned dark brown. The stirring was continued for 5 minutes and 1ml of 1.5M sulphamic acid was added to destroy the excess argentic oxide. When the dark colour disappeared, 10ml of 1M sulphuric acid was added and stirring was continued for 5 minutes. Similar to the blank titration 500 micro litres of 0.2M ferrous ammonium sulphate were added to carry out the titration of the unreacted ferrous.

Since the memotitrator was pre-programmed the blank value in milli-equivalence was fed to the programmer for sample titration

(as described in the procedure for blank titration)to obtain the result in mg/aliquot.

c. Interference studies:-

In order to study the interference of uranium on the estimation of Pu, two sets of samples (samples I&II) were prepared where the percentage of U with respect to Pu was varied from zero to hundred percent. The details of this study are discussed later on in this paper.

The chemical reaction involved in the above are as follows:

$$PuO_2^{++} + 4H^{+} + 2Fe^{++} \longrightarrow Pu^{+4} + 2Fe^{+3} + 2H_2O$$

The excess Fe^{++} is titrated against standard $K_2Cr_2O_7$

$$6Fe^{++} \longrightarrow 6Fe^{+3} + 6e^{-} \qquad Eo\ (Fe) = -0.771$$

$$Cr_2O_7^{-2} + 14H^{+} + 6e^{-} \longrightarrow 2Cr^{+3} + 7H_2O \qquad Eo\ (Cr_2O_7) = +1.359$$

$$6Fe^{++} + Cr_2O_7^{-2} + 14H^{+} \longrightarrow 6Fe^{+3} + 2Cr^{+3} + 7H_2O \qquad E = 0.588$$

V. RESULTS AND DISCUSSION

Estimations of plutonium in the process samples and audit samples using memotitrator were found to be quite rapid and the reproducibility was very good. Since there is no step of sample preparation the result can be given quickly to speed up the

processing of plutonium nitrate to oxalate. With aliquots containing 4 to 5 mg of Pu the results are reproducible. The impurities present in the tail-end product do not interfere in the estimation of plutonium. Uranium interference in the estimation of plutonium was checked. It was found that Uranium does not affect the estimations. Since the sensitivity of this system is more than 2 mg the aliquot samples used in the estimation should contain 4 to 5 mg of plutonium.

Table 1 shows the results obtained in the estimation of plutonium in process lot samples. Here the aliquots for the analysis were taken on volume basis. The standard deviation was +/- 0.13 and the error is well within +/- 0.25% .

Table 2 shows the results obtained in the estimation of plutonium in Audit lot samples. Here also the aliquots were taken on volume basis. The standard deviation was found to be +/- 0.18% is well within +/- 0.77% error.

A number of estimations were carried out on weight basis also. The results are shown in Table 3. The standard deviation was +/- 0.07 & is well within +/- 0.60% error.

From Tables 1,2,&3 it can be deduced that plutonium in either process samples or audit samples can be estimated within an error of +/-1%. From Table IV it is clear that uranium does not interfere in the estimation of plutonium. Samples containing 20 to 100% of U with respect to Pu were analysed and it was found that presence of uranium did not affect the estimation. The results were within the limits of accuracy.

VI. CONCLUSION

Since potentiometric titration methods were found to be very simple, precise and accurate this method can be employed in the routine analysis of plutonium in process samples. The results can be reported within half an hour. In comparison with radiometric method, this method has the advantage of speed.

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TABLE 1

Process lot samples
(Analysed on volume basis)

Lot No.	Con. by present method g/l	Coulometry g/l	Std. dev.	% error
409	15.63	15.67	0.13	-0.25
410	16.94	16.94	0.05	0.00
411	14.64	14.66	0.05	-0.14
412	9.20	9.20	0.00	0.00

TABLE 2

Audit Lot samples
(Analysed on volume basis)

Sample No.	Conc. by present method g/l	Coulmetry g/l	Std. dev.	% error
1.	8.34	8.32	0.09	+0.24
2.	8.26	8.29	0.07	-0.36
3.	8.02	7.99	0.04	+0.37
4.	8.67	8.62	0.08	+0.58
5.	10.26	10.22	0.05	+0.42
6.	10.30	10.28	0.03	+0.24
7.	5.26	5.30	0.18	-0.77
8.	8.60	8.62	0.07	-0.23
9.	8.61	8.62	0.13	-0.09
10.	10.54	10.53	0.03	+0.14

TABLE 3

Audit samples (analysed on weight basis)

Sample No.	Con. by present method g/l	Coulometry g/l	Std. dev.	error %
1.	6.26	6.30	0.04	-0.50
2.	7.76	7.81	0.07	-0.60
3.	7.80	7.82	0.05	-0.23

TABLE 4

Pu estimation in presence of U*

Sample No.	% U added	Con. by present method g/l	Coulometry** g/l	Std. dev.	error %
1.	20	16.94	16.94	0.08	0.00
	100	16.94	16.94	0.06	0.00
2.	20	15.94	15.92	0.04	+0.13
	100	15.93	15.92	0.05	+0.06
	40	15.93	15.92	0.07	+0.06

*U:Pu ratio maintained as one.

** Without addition of uranium

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