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DETERMINATION OF NEPTUNIUM USING CONTROLLED POTENTIAL COULOMETRY

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A method for controlled potential coulometric determination of neptunium by titration with internally electrolytically generated iron(II) has been developed. The method involves oxidation of Np to Np(VI) by Ce(IV), destruction of excess of Ce(IV) by $NaNO_2$ followed by determination of neptunium by reduction of Np(VI) to Np(IV) by internal generation of Fe(II). The method was employed for various neptunium solution samples and a precision of ±0.25% at 2–5 mg level of neptunium was obtained.

Introduction

Neptunium, like its neighboring actinides, exhibits a number of oxidation states ranging from + 3 to + 6 in aqueous acidic solutions.[1] The existence of the element in different oxidation states facilitates the use of redox methods for its determination. As Np(III) is unstable, no redox method involving Np(III) is reported. Redox methods for the determination of neptunium are, therefore, based on either Np(VI)/Np(V) or Np(VI)/Np(IV) couple. As compared to the redox methods available for the determination of uranium and plutonium, very few methods have been reported so far for the redox determination of neptunium.[2–4] Among these methods, the potentiometric method reported by MOSS[2] and the controlled potential coulometric method reported by STROMATT[3] are based on Np(VI)/Np(V) reversible couple. The other potentiometric method reported,[4] makes use of the Np(VI)/Np(IV) irreversible couple. A secondary coulometric method reported[5] for the determination of plutonium is advantageous in the presence of impurities like organic matter, polymeric species, complexing ions etc. Moreover, unlike primary coulometry, this method does not require accurate information of the formal potentials of redox couples involved in the determinations. It was, therefore, considered useful to develop a secondary coulometric method for the determination of neptunium.

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Experimental

Apparatus

Coulometer: Coulometer supplied by Princeton Applied Research Center (PARC) consisting of a potentiostat (Model 173) and current integrator (Model 179) was used.

Electrolytic cell: Three-compartment electrolytic cell with Pt electrode as described by CHITNIS et al.[5] was used.

Reagents

Cerium (IV) solution: About 8 g of ceric ammonium nitrate was dissolved in 1M $HClO_4$ and made up to 50 ml.

Sulfamic acid (1.5M): About 15 g of sulfamic acid was dissolved in 100 ml of distilled water.

Sodium nitrite (1M): About 7 g of sodium nitrite was dissolved in 100 ml of distilled water.

Sulfuric acid (1M): About 55.6 ml of concentrated sulfuric acid was diluted to 1000 ml using distilled water.

Iron solution (0.5M): About 20 g of ferric nitrate was dissolved in 100 ml of 1M sulfuric acid.

All reagents used were of A.R. or G.R. grade.

Purified neptunium stock solution

Neptunium was purified by anion exchange technique from 7M nitric acid.[6] Neptunium in nitric acid medium was evaporated to almost dryness and redissolved in 0.35M nitric acid. It was then allowed to react with hydrazine at room temperature for half an hour to convert all neptunium to Np(IV). The nitric acid concentration of the mixture was adjusted between 7 and 8M after adding sulfamic acid to it and the resulting solution was then passed over ion exchange column containing resin Dowex 1 X 4 supplied by Sigma Chemical Company, U.S.A. Neptunium adsorbed on the column was washed with 3 to 4 bed volumes of 7M nitric acid and neptunium was then eluted with 0.35M nitric acid. Neptunium thus purified was then fumed repeatedly with concentrated $HClO_4$ to destroy organic matter and was stored in 1M $HClO_4$. This stock solution was analyzed by primary coulometry[3] to determine its neptunium content. Weighed aliquots were drawn from this stock solution and used in this work.

Purification of argon

Argon was purified from oxygen impurity by passing through a solution of vanadous chloride.[7] Oxygen free argon was used for purging the electrolytic cell.

Analytical procedure

(1) Add 2–3 mg of Fe(III) and 6–7 mg of Ce(IV) to the aliquot containing 2–3 mg of neptunium. Stir the mixture intermittently for 5–6 minutes.

(2) Destroy the excess of Ce(IV) by adding a few drops of 1M $NaNO_2$. The destruction of excess Ce(IV) is indicated by disappearance of Ce(IV) color.

(3) Destroy the excess of $NaNO_2$ by adding about 10–15 drops of 1.5M sulfamic acid.

(4) Transfer an aliquot to the electrolytic cell, using 4–5 ml of 1M H_2SO_4 and deaerate the cell solution by passing the purified argon through electrolytic cell with the rate of 1–2 liter per minute for 5 minutes.

(5) Pre-oxidize the Np(V) formed, during the destruction of excess Ce(IV), to Np(VI) at 1.05 V vs. SCE till the cell current approaches 10–15 μA and set the current integrator to zero.

(6) Reduce Np(VI) to Np(IV) by electrogeneration of Fe(II) at 0.270 V vs. SCE for 200 seconds and record the current integrator output (Q_r).

(7) Back-oxidize the excess of Fe(II) produced in the earlier step to Fe(III) at 0.730 V vs. SCE till cell current decreases to 10–15 μA. Record the current integrator output (Q_o).

(8) Calculate the difference between the charge collected in steps 6 and 7 ($Q_s = Q_r - Q_o$).

(9) Repeat steps from 1 to 8 in the absence of neptunium and determine electrolyte blank (Q_b).

(10) Calculate the amount of neptunium as follows

$$\text{Amount of neptunium} = \frac{(Q_s - Q_b) \times 118.5}{96.487}\ \text{mg}$$

Results and discussion

Determination of neptunium using the Np(VI)/Np(IV) couple

The most important step in this method is the conversion of all neptunium in the aliquot to Np(VI). Neptunium in aqueous acidic solution can occur as Np(IV), Np(V) and Np(VI). Np(VI)/Np(V) being reversible, conversion of Np(V) to Np(VI) can be carried out electrolytically, whereas, due to irreversibility of Np(VI)/Np(IV) couple, electrolytic oxidation of Np(IV) to Np(V) or Np(VI) is rather difficult. Therefore, oxidation of Np(IV) has to be carried out chemically using a suitable strong oxidizing reagent. Fuming with concentrated $HClO_4$ or use of Ce(IV) has been tried for quantitative oxidation of Np(IV) to Np(VI) in coulometric methods. However, it has been observed that the use of Ce(IV) is more convenient as compared to oxidation by fuming it with $HClO_4$.

In coulometric methods, destruction of excess of Ce(IV), is normally carried out electrolytically.[3] During initial experiments it was observed that electrolytic reduction of excess of Ce(IV) is somewhat time consuming. Moreover, it also affects the performance of platinum electrode leading to longer time for subsequent electrolytic pre-oxidation of Np(V) to Np(VI). Therefore, destruction of excess of Ce(IV) was carried out using a chemical reagent. Sodium nitrite reduces Ce(IV) rapidly and quantitatively while it does not reduce Np(VI) to Np(IV). Moreover, excess of $NaNO_2$ can be easily destroyed by sulfamic acid and hence it was selected for destruction of excess Ce(IV).

While destroying excess of Ce(IV) by $NaNO_2$, it was observed that nearly 60–70% of Np(VI) was also reduced to Np(V). Since neptunium determination is based on the Np(VI)/Np(IV) couple, it was necessary to back-oxidize the Np(V) thus formed to Np(VI) before its reduction to Np(IV) by electrogeneration of Fe(II). The pre-oxidation of Np(V) to Np(VI) at 1.05 V vs. SCE was therefore carried out.

During the reduction of Np(VI) to Np(IV) by electrogenerated Fe(II), it is beneficial to know the completion of Np(VI) reduction, in order to avoid the generation of too much excess of Fe(II). Preliminary experiments showed that, in the presence of 2–3 mg of iron, reduction of 2–5 mg of Np(VI) is complete without much excess of Fe(II) if electrogeneration of Fe(II) is carried out for 200 seconds at 0.270 V vs. SCE.

After reduction of Np(VI) by electrogeneration of excess Fe(II), excess Fe(II) was subsequently back-oxidized electrolytically at 0.73 V vs. SCE. Since formal potentials of Fe(III)/Fe(II) and Np(V)/Np(IV) couples in 1M $HClO_4$ are almost the same during oxidation of excess Fe(II) in 1M $HClO_4$ medium oxidation of Np(IV), though the Np(V)/Np(IV) couple is irreversible, was observed to take place at slow rate. This can cause a negative error in neptunium values determined. However in sulfuric acid medium, due to preferential complexing of Fe(III) and Np(IV), difference in formal potentials of Fe(III)/Fe(II) and Np(V)/Np(IV) couples increases to almost 0.3 V and then quantitative oxidation of Fe(II) to Fe(III) without any significant oxidation of Np(IV) to Np(V) or Np(VI) is possible. Moreover, during the reduction of Np(VI) by Fe(II) as represented by the following equation

$$NpO_2^{2+} + 2Fe^{2+} + 4H^+ \rightleftharpoons Np^{4+} + 2Fe^{3+} + 2H_2O$$

Table 1
Secondary coulometry: blank analysis runs

Date	Amount of total iron in the aliquot, mg	Charge collected during the reduction of Fe(III) (A), coulomb	Charge collected during the back oxidation of Fe(II) coulomb	Difference in the readouts of (A) and (B), coulomb
15–7	1.5	2.317	2.298	+0.019
	1.5	2.249	2.232	+0.017
	1.5	2.461	2.444	+0.017
19–7	3.0	5.018	4.992	+0.026
	2.5	3.597	3.574	+0.023
	2.0	2.941	2.917	+0.024
	2.5	3.978	3.955	+0.023
20–7	3.0	4.195	4.153	+0.042
	3.0	4.864	4.825	+0.039
	3.0	4.321	4.275	+0.046
	3.0	4.227	4.180	+0.047
21–7	2.5	3.747	3.732	+0.015
	3.0	5.296	5.280	+0.016
	2.5	3.747	3.734	+0.013
	3.0	5.105	5.092	+0.013

the preferential stabilization of Np(IV) and Fe(III) by H_2SO_4 helps to drive the reaction in the forward direction. Hence 1M H_2SO_4 was chosen as electrolysis medium during the reduction of Np(VI) and back-oxidation of excess Fe(II).

In this method, the amount of neptunium is calculated from the difference in charges collected during the reduction of Np(VI) to Np(IV) by electrogenerated Fe(II) and the back-oxidation of excess Fe(II) generated, to Fe(III). It is, therefore, necessary that the charge equivalent to the amount of excess Fe(II) produced in the reduction step and the charge collected in back oxidation of this excess Fe(II) should match. In case if it differs, then the difference should be well established beforehand to apply due corrections in the neptunium results. In order to verify this, a few experiments containing only iron were carried out and the results obtained are summarized in Table 1. It is seen from the results that, under the experimental conditions, the readouts of reduction of iron and its back-oxidation differ somewhat over the period of a week. However, this difference (referred to as blank) remains almost constant throughout the day and is unaffected by the small variation in the amount of iron in the aliquot. So, blank runs were carried out every day in the beginning and at the end of neptunium analysis, and the neptunium results were corrected by subtracting the mean blank from the charge collected during the neptunium determination.

A few aliquots of purified neptunium stock solution were analyzed using the present method and the results are given in Table 2. The method was also employed for the determination of neptunium in solution before purification and after purification but before fuming with $HClO_4$ and the results are summarized in Table 3. It is observed from all of these results that the method is capable of giving precision within ±0.2% for neptunium in 2–5 mg range. The results also agree with those obtained by primary coulometry within the precision limit.

Table 2
Secondary coulometry: determination of neptunium in purified neptunium solution using Np(VI)/Np(IV) couple

Sample	Aliquot weight, g	Amount of Np in the aliquot, mg	Concentration of Np in the solution, mg/g
1	0.21970	3.174	14.447
2	0.26128	3.767	14.417
3	0.29288	4.226	14.429
4	0.29417	4.252	14.454
5	0.24230	3.494	14.420
6	0.24655	3.555	14.419
7	0.23322	3.362	14.416
8	0.22194	3.212	14.472
9	0.24351	3.512	14.422
10	0.24267	3.505	14.443
11	0.24256	3.512	14.479
12	0.25353	3.660	14.436
13	0.24129	3.476	14.406
14	0.25544	3.691	14.450
15	0.29014	4.204	14.490
16	0.24188	3.494	14.445
17	0.24769	3.568	14.405
18	0.25309	3.646	14.406
19	0.24972	3.605	14.436
20	0.24643	3.571	14.491
21	0.24635	3.548	14.402
22	0.29206	4.200	14.401

Mean concentration: 14.436 mg/g. R. S. D.: ±0.19%. Concentration determined using primary coulometry[3] = (14.445±0.029) mg/g.

Table 3
Secondary coulometry: determination of neptunium in different solutions using Np(VI)/Np(IV) couple

Sample, No.	Amount of Np in the aliquot, mg	Concentration of Np in the solution, mg/g	Mean concentration mg/g	Concentration determined by primary coulometry,[3] mg/g
Solution A				
1	3.144	8.922		
2	3.444	8.925		
3	3.707	8.923		
4	2.835	8.875		
5	3.641	8.899	8.909±0.24%	8.901±0.2%
Solution B				
1	2.977	6.642		
2	3.600	6.656		
3	3.484	6.663		
4	3.639	6.650		
5	3.263	6.662	6.655±0.13%	6.665±0.2%

Solution A: Before ion exchange purification.
Solution B: After ion exchange purification but before fuming with $HClO_4$.

Table 4
Determination of neptunium simultaneously using Np(VI)/Np(V) and Np(VI)/Np(IV) couple

Sample, No.	Using Np(VI)/Np(V) couple		Using Np(VI)/Np(IV) couple	
	Amount	mg/g	Amount	mg/g
1	2.658	7.565	2.666	7.579
2	2.712	7.560	2.718	7.577
3	3.011	7.576	3.014	7.583
4	2.483	7.572	2.493	7.602
5	2.496	7.575	2.504	7.601
6	2.894	7.563	2.906	7.585
7	2.090	7.564	2.096	7.586
8	2.854	7.568	2.864	7.594
Mean:		7.568		7.588
R. S. D.:		+0.08%		+0.13%

Concentration determined using primary coulometry[3] = (7.580±0.015) mg/g.

Determination of neptunium, simultaneously using Np(VI)/Np(V) couple and Np(VI)/Np(IV) couple

During the experiments on the determination of Np by secondary coulometric titration as given in the procedure, it was observed that, while excess of Ce(IV) was reduced to Ce(III) by $NaNO_2$, almost 60–70% of Np(VI) was also reduced to Np(V) and it was necessary to back-oxidize it to Np(VI) prior to electrogeneration of Fe(II). It was, therefore, felt that, along with destruction of excess Ce(IV), if Np(VI) is also quantitatively reduced to Np(V), then it may also be possible to determine neptunium using Np(VI)/Np(V) couple during its preoxidation to Np(VI) along with its determination based on Np(VI)/Np(IV) couple.

A few preliminary experiments had shown that, under the experimental conditions, 100 μl of 2M $NaNO_2$ reduces excess Ce(IV) as well as Np(VI) to Np(V) rapidly and quantitatively. So this modification was incorporated in the procedure described under 2.5 and neptunium was determined simultaneously in the preoxidation step using Np(VI)/Np(V) couple and in subsequent steps using Np(VI)/Np(IV) couple. The results of the analysis of neptunium using this modified procedure are given in Table 4. It is seen from the results that neptunium values obtained simultaneously using both couples in a single procedure, are reproducible and agree with their corresponding primary coulometric values.

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References

1. G. T. SEABORG, Man-made Transuranium Elements, Prentice-Hall Inc. 1963, p. 84.
2. J. H. MOSS, Report, AERE-R-3214.
3. R. W. STROMATT, Report, HW-59 447.
4. A. G. GODBOLE, S. K. PATIL, Talanta, 26 (1979) 330.
5. R. T. CHITNIS, S. G. TALNIKAR, R. G. BHOGALE, J. Radioanal. Chem., 49 (1979) 63.
6. J. A. WHEAT, Appl. Spectrosc., 16 (1962) 108.
7. L. MEITES, T. MEITES, Anal. Chem., 20 (1948) 984.