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EUROPEAN ATOMIC ENERGY COMMUNITY — EURATOM

THE DETERMINATION OF FREE ACIDITY IN PLUTONIUM CONTAINING SOLUTIONS AND THE SEMI-QUANTITATIVE ACIDIMETRIC ESTIMATION OF PLUTONIUM

by

K. BUIJS, B. CHAVANE DE DALMASSY and M.J. MAURICE

1968

Joint Nuclear Research Center
Karlsruche Establishment — Germany

European Institute for Transuranium Elements

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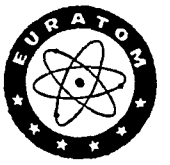

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Summary

A fast method for the analysis of free acid in plutonium solutions has been developed. An ammonium fluoride solution provides the medium in which hydrolysis of plutonium is prevented.

KEYWORDS

PLUTONIUM COMPOUNDS
SOLUTIONS
ACIDITY
DETERMINATION
AMMONIUM COMPOUNDS
FLUORIDES
STABILITY
HYDROLYSIS

CONTENTS

The determination of free acidity in plutonium containing solutions and the semi-quantitative acidimetric estimation of plutonium (+)

INTRODUCTION

The analysis of free acid in plutonium solutions, as in all heavy metal solutions, is hampered by the hydrolysis of the plutonium ions, which occurs at a pH of about 1 - 2. If no precautions are taken, the acidity values found are inevitably high.

Various procedures have been developed to eliminate excess alkali consumption due to hydrolysis. Methods most frequently used are elimination of plutonium from the solution by precipitation prior to analysis or complexation of the metal. Potassium iodate is often used for precipitation (1). It is known that this method introduces a negative bias. Moreover, it involves a time-consuming separation step and causes difficulties with the concentrated iodate solutions during waste treatment. For complexation, a solution of sodium citrate (2) has been used. This procedure, however, introduces a positive bias due to the fact that the plutonium citrate complex is not stable over the entire pH range of the titration. The resulting waste solution still requires special attention.

In view of this situation we decided to study a new method for the free acid analysis, which has to be accurate, fast, without separation step, and leads to acceptable waste solutions.

(+) Manuscript received on March 24, 1968.

Experimental part

The complexing or precipitating agent should be a neutral salt or a salt of a relatively strong acid and a weak base, to avoid any positive bias. The plutonium complex or precipitate sould be stable over the whole pH range of the titration. A series of experiments were conducted with ammonium fluoride which fulfills these requirements.

On solutions of plutonium nitrate in nitric acid three determinations were performed :

a) An aliquot of the sample solution (1 ml for acidities higher than 4 N or 2 ml for acidities lower than 4 N) was added to 10 ml of 1.5 M ammonium fluoride solution. The solution was titrated potentiometrically with 1 N sodium hydroxide solution to the original pH of the ammonium fluoride solution with disregard of the plutonium fluoride precipitate which was formed. A glass electrode and a saturated calomel electrode were used. In this way, the free acidity, x, (see table 1), was determined.

b) For each sample solution a determination of total acidity, y (table 1), was also made in the absence of fluoride by potentiometric titration of a suitable aliquot with 1 N sodium hydroxide solution.

c) In each sample solution the plutonium content, z, was determined according to Corpel and Regnaud (3).

When all results are expressed in mequivs, the following equation holds :

$$x = y - z \qquad (I)$$

The results are given in table 1.

Table 1

sample	free acid x	total acid y	plutonium z	plutonium z'	free acid calculated y - z	difference Δ = x-(y-z)
1	1.74 N	2.00 N	0.26 N	15.3 g/L	1.74 N	0 N
2	3.34	3.65	0.26	15.3	3.39	-0.05
3	1.36	1.73	0.39	23.2	1.34	+0.02
4	1.22	1.83	0.52	31.0	1.31	-0.09
5	3.67	4.15	0.54	32.1	3.61	+0.06
6	1.50	2.10	0.58	34.8	1.52	+0.02
7	1.85	2.65	0.65	38.8	2.00	-0.15
8	1.34	1.97	0.66	39.4	1.31	+0.03
9	1.14	1.80	0.72	42.7	1.08	+0.06
10	2.30	2.93	0.72	42.7	2.21	+0.09
11	1.74	2.37	0.73	43.5	1.64	+0.10
12	0.92	1.77	0.86	51.2	0.91	+0.01

average, $\bar{\Delta}$ = +0.012 N

standard deviation of Δ, s_{Δ} = 0,07 N

Discussion

It cannot be detected that the Δ-values of table 1 contain outliers and, therefore, all values can be used for further calculations. The average difference between the results of the two types of measurements, $\bar{\Delta}$, does not differ significantly from zero on the 0.05 level, which follows from application of the t-test. This means that the method has no detectable bias. A correlation between the Δ_i-values and the plutonium concentrations, z_i, cannot be detected with a modified sign test.

From $\Delta = x - y + z$ (II)

it follows $s_\Delta^2 = s_x^2 + s_y^2 + s_z^2$ (III)

where: s_x = standard deviation of a single free acidity determination

s_y = standard deviation of a single total acidity determination

s_z = standard deviation of a single plutonium determination.

Since s_z^2 is negligible with respect to s_x^2 and s_y^2, and moreover, s_x^2 may be put equal to s_y^2, it is seen that

$$s_\Delta^2 = 2s_x^2$$
$$\text{or } s_x = 1/2\, s_\Delta\sqrt{2} \quad \text{(IV)}$$

Substitution of $s_\Delta = 0.07$ in (IV) gives :

$$s_x = s_y = 0.05 \quad \text{(V)}$$

As results are unbiased, it can be said that

$$z = y - x \quad \text{(VI)}$$

This means that in a solution of pure plutonium nitrate in nitric acid the plutonium concentration can be estimated very rapidly by carrying out an acidity determination in the absence and one in the presence of ammonium fluoride.

From (VI) it follows, that

$$s_z^2 = s_y^2 + s_x^2 = 2\, s_x^2 \qquad \text{(VII)}$$

Substitution of $s_x = 0.05$ in (VII) gives

$$s_z = 0.07 \text{ equivs/L} \qquad \text{(VIII)}$$

or $s_z' = 4.2$ g/L

From eq.(VIII) is follows that this plutonium determination is essentially a semi-quantitative estimation.

CONCLUSIONS

1. The method gives unbiased results for solutions containing 15 to 50 g of plutonium/liter and having acidities between 0.9 and 4 N.

2. The standard deviation of a single determination of the free acid concentration is 0.05 N.

3. Since results are unbiased (conclusion 1), plutonium can be estimated in a solution of its nitrate in nitric acid as the difference between total acidity and free acidity.

4. The standard deviation of a single plutonium estimation, mentioned under 3, is 4.2 g/L, which means that this estimation is a semi-quantitative one.

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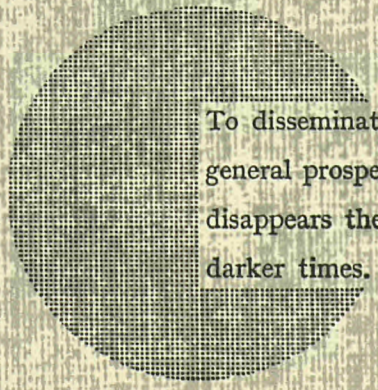

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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