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QUANTITATIVE DETERMINATION OF PLUTONIUM OXIDATION STATES
IN VARIABLE NITRIC ACID SOLUTIONS FOR CONTROL LABORATORIES --
SPECTROPHOTOMETRIC.

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QUANTITATIVE DETERMINATION OF PLUTONIUM OXIDATION STATES
IN VARIABLE NITRIC ACID SOLUTIONS FOR CONTROL LABORATORIES --
SPECTROPHOTOMETRIC

by

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May 4, 1965

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RICHLAND, WASHINGTON

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INTRODUCTION

Considerable information concerning the behavior of plutonium in solution has been obtained spectrophotometrically, due to the sharp-band absorption spectra exhibited by solutions of the various oxidation states.⁽¹⁾

The use of anion exchange units in separation facilities for the recovery and purification of plutonium⁽²⁾ has resulted in a need for rapid quantitative determinations of plutonium oxidation states. The data presented in this paper are designed to enable control laboratories to provide rapid quantitative oxidation state analyses in variable nitric acid solutions. This data will also find use in development work where plutonium oxidation state analyses are desired.

SUMMARY

Methods and data are presented which provide a rapid quantitative determination of plutonium oxidation states in variable nitric acid solutions.

Experience concerning practical use of a recording spectrophotometer when working with plutonium solutions is given.

The following are lower limits when using 1 cm absorption cells:

Plutonium(VI) - 0.01 g/l; Plutonium(IV) - 0.1 g/l; Plutonium(III) - 0.2 g/l.

The experimental material is presented in three parts as follows: Part I - the absorptivities of various plutonium ion absorption peaks in 2.0M HNO₃ solutions are given. These values should be used only as approximations in individual instrumental systems, since each spectrophotometer should be calibrated in order to obtain maximum accuracy. Part II - Factors are presented which when applied to the peak absorptivity at 2.0M HNO₃ will yield the absorptivity at the listed

↓

HNO₃ molarity. These factors may be used with any spectrophotometer. Part III - Formulas are given which will allow quantitative calculations of each oxidation state of plutonium.

DISCUSSION

Equipment

A Beckman Model DK-2A ratio-recording spectrophotometer was used. One cm rectangular cells were used throughout this work, since experience has shown these to be best for plutonium work in a control laboratory.

Control of Plutonium

Due to the highly toxic nature of plutonium, extreme precautions must be taken to avoid contamination of the environment with plutonium. Only those thoroughly trained and experienced in the handling of plutonium solutions should consider using this method.

Besides experienced personnel, the following items are essential:

(1) Detection instruments which will readily detect 500 disintegrations per minute must be at hand to monitor every step; (2) a hood designed to confine radioactive materials should be adjacent to or in conjunction with the recording spectrophotometer; and (3) emergency equipment such as assault masks, protective clothing, and cleaning materials must be available.

For the Chemical Processing Department, 1 cm rectangular cells designed for glass stoppers are used. The filled cells are not stoppered, however, since experience has shown better control without the stoppers. It is the shoulder on this type of cell that is desirable in plutonium control. The cells are filled and emptied while out of the cell holder. Cells are filled only as high as necessary. After the outside and lip of the cell have been found free of plutonium, it is placed in the holder. The holder is then transported to the

recording spectrophotometer which is in a plutonium-free environment. Care must be taken to read the sample and return it to the plutonium hood without undue delay. It has been found to be advantageous to use two people while reading samples, one to work with the plutonium solution and the other to operate the instrument.

Cells are cleaned after use with a solution of 50% 3M HCl and 50% ethanol, rinsed with water, and dried with ethanol.

Basic Technique

The following recommendations are for control laboratory use and were used in gathering this data:

- (1) The reference cell should contain nitric acid solution as close as feasible to that of the sample solution being read.
- (2) Zero the instrument at approximately 800 mu (wavelength not critical), with reference solution in both cells. If a series of different acidities are to be read between one and eight molar HNO_3 , it is not necessary to re-zero the instrument for each acidity as long as the same cells are used. The nitric acid in the reference cell must be changed accordingly, however.
- (3) A small amount of the sample to be read should be used to rinse the cell before final filling.
- (4) Align the cells properly in the cell holder (this step is important in old cell holders).
- (5) Scan the spectrum from 1350 mu to 400 mu.

Interference

The absorbance spectrum and absorptivity of plutonium in solution are influenced by anionic environment, acid concentration, and temperature. It is assumed that all measurements will be made at approximately the temperature of

calibration as the net absorbance decreases about 0.3% for every degree centigrade increase in temperature.(3) Extraneous ions which have absorbance characteristics near plutonium spectra will interfere when present in sufficient amounts.

The possible presence of colloidal plutonium polymer(4) must be considered when analyzing plutonium solutions spectrophotometrically. Also when plutonium(IV) is present, the possible formation of polymer must be avoided by using weak acid rather than water when making dilutions. Generally, an acid value of at least 0.5M should be maintained when analyzing solutions of plutonium(IV).

Absorbance Determination

Net absorbance is determined from the chart scan by reading the absorbance at the peak and subtracting the absorbance reading of the first trough at a higher wavelength. It is important to note that the same wavelengths have been used throughout this work for determining absorbance even though, in one case, change in acidity shifted the wavelength of a trough and in another case, a peak became a slope due to oxidation state mixtures.

Nomenclature

$$\text{Absorptivity} = a = \frac{A}{bc}$$

where:

A = absorbance

b = concentration of substance (in g/l)

c = sample path length (in cm)

$$\text{Molar absorptivity (formerly molar extinction coefficient)} = \epsilon$$

= absorptivity x molecular weight of substance.

EXPERIMENTALPart IAbsorptivities of plutonium in
2.0M HNO₃ solution

	<u>Wavelength</u>	<u>Absorptivity</u>
Plutonium(VI)	(peak at 956 mu)-(trough at 978 mu)	0.0739
	(peak at 833 mu)-(trough at 841 mu)	1.03*
Plutonium(IV)	(peak at 475 mu)-(trough at 494 mu)	0.265
	(peak at 658 mu)-(trough at 686 mu)	0.0763
	(peak at 1070 mu)-(trough at 1274 mu)	0.114
Plutonium(III)	(peak at 565 mu)-(trough at 586 mu)	0.0853**

* The sharp absorption peak at 833 mu does not obey Beer's Law; however, in practice, linearity may be assumed below 0.4 net absorbance. A lower limit and greater accuracy will thus be obtained than if attempting to use the 956 mu peak.

** The absorptivity for plutonium(III) was determined on a different instrument (DK-2A) than were the values for plutonium(VI) and (IV).

Part II Effect of nitric acid concentration on absorptivity

Absorptivity at given HNO_3 = Factor (listed below) x
 absorptivity at 2.0M HNO_3

<u>HNO_3 (Molar)</u>	<u>Factor</u>					
	<u>Pu(VI) 956 mu</u>	<u>Pu(VI) 833 mu</u>	<u>Pu(IV) 475 mu</u>	<u>Pu(IV) 658 mu</u>	<u>Pu(IV) 1070 mu</u>	<u>Pu(III) 565 mu</u>
0.15	1.00					1.036
0.25	1.00					1.025
0.50	1.00		.853	.970	.936	1.017
0.75	1.00		.948	.990	.973	1.008
1.00	1.00		.984	1.000	.993	1.003
1.25	1.00		.992	1.000	.997	1.003
1.50	1.00		.997	1.000	.986	1.000
1.75	1.00		1.003	1.000	.986	1.000
2.00	1.00	1.00	1.000	1.000	1.000	1.000
2.25	1.00		.997	1.000	1.007	1.000
2.50	1.00		.992	1.000	1.014	1.000
2.75	.996		.987	1.000	1.020	1.000
3.00	.991		.979	1.000	1.024	1.003
3.25	.983		.972	1.000	1.027	1.003
3.50	.970		.962	1.000	1.031	1.006
3.75	.957		.950	.992	1.034	1.008
4.00	.943		.937	.987	1.041	1.011
4.25	.930		.917	.982	1.044	1.011
4.50	.917		.896	.972	1.047	1.008
4.75	.900		.873	.962	1.051	1.006
5.00	.883		.841	.947	1.058	1.003
5.25	.861		.807	.929	1.058	1.003
5.50	.839		.769	.912	1.058	1.000
5.75	.817		.728	.889	1.051	1.000
6.00	.791		.679	.853	1.044	.997
6.25	.765	.729	.629	.821	1.037	.997
6.50	.735		.572	.778	1.034	.997
6.75	.704		.509	.732	1.027	
7.00	.670		.445	.679	1.024	
7.25	.630		.371	.618	1.017	
7.50	.591		.293	.543	1.014	
7.75	.543					
8.00	.491					

Part III

Formulas for calculating quantitative
plutonium oxidation states

Formula #1: For use if the Pu(VI) concentration is greater than 0.4 g/l.

$$\text{g/l Pu(VI)} = (\text{net absorbance at } 956 \text{ mu}) \times \frac{1}{\text{absorptivity}} \times \text{dil'n F.}$$

Formula #2: For use if the plutonium(VI) concentration is less than 0.4 g/l. The lower limit is 0.01 g/l, using 1 cm cells.

$$\text{g/l Pu(VI)} = (\text{net absorbance at } 833 \text{ mu}) \times \frac{1}{\text{absorptivity}} \times \text{dil'n F.}$$

Formula #3: Utilizes the most sensitive peak for plutonium(IV), which is also the only practical peak to use when the solution also contains plutonium(III). Evidence indicates, however, that this peak is not as consistent as that used in Formula #4. The net absorbance is measured as the absorbance between the peak at 475 mu and the trough at 494 mu. It is important to note that the trough at 494 mu ceases to be a trough at approximately 5M HNO₃. Calculation should still be made from 494 mu. The following corrections must be applied when samples contain mixed oxidation states.

- (a) If plutonium(III) is present, subtract the following value from the 475 mu peak: (net absorbance of the 565 mu peak - plutonium(IV) correction*) x 0.14.

* Note: see Formula 6.

- (b) If plutonium(VI) is present, subtract the following value from the 475 mu peak: net absorbance of the 956 mu peak x 0.45.

The lower limit is 0.1 g/l, using 1 cm cells.

$$\text{g/l Pu(IV)} = (\text{net absorbance at } 475 \text{ mu} - \text{above corrections}) \times \frac{1}{\text{absorptivity}} \times \text{dilution factor}$$

Formula #4: Utilizes the most consistent peak for determining plutonium(IV) when only Pu(IV) or Pu(IV) and (VI) are present. Do not use if Pu(III) is present.

$$\text{g/l Pu(IV)} = (\text{net absorbance at } 658 \text{ mu}) \times \frac{1}{\text{absorptivity}} \times \text{dil'n F}$$

Formula #5: Do not use if plutonium(III) is present.

$$\text{g/l Pu(IV)} = (\text{net absorbance at } 1070 \text{ m}\mu) \times \frac{1}{\text{absorptivity}} \times \text{dil'n F}$$

Formula #6: The net absorbance at the 565 mμ peak used in this formula must be determined and corrected as indicated below if plutonium(IV) is present.

Normally, the absorbance maximum is read at 565 mμ and the trough absorbance at 586 mμ is subtracted. When plutonium(IV) is present, the peak at 565 mμ becomes a slope. In this work, the absorbance is read on the slope at 565 mμ, the trough absorbance at 586 mμ subtracted as usual and correction made for plutonium(IV) as indicated below:

Correction: If plutonium(IV) is present, subtract the following value from the 565 net absorbance: net absorbance of the 475 mμ peak x 0.08.

The lower limit is 0.2 g/l, using 1 cm cells.

$$\text{g/l Pu(III)} = (\text{net absorbance at } 565 \text{ m}\mu - \text{above correction}) \times$$

$$\frac{1}{\text{absorptivity}} \times \text{dilution factor}$$

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