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SPECTROPHOTOMETRIC DETERMINATION OF PLUTONIUM WITH CHLOROPHOSPHONAZO III IN n-PENTANOL

by

N. M. Saponara and S. F. Marsh

ABSTRACT

Microgram amounts of plutonium are measured spectrophotometrically as the plutonium-chlorophosphonazo III complex after extraction into n-pentanol from 1.5*M* HCl. The relative standard deviation is 1.5% for the range of 2.5 to 17.5 µg. The tolerance is excellent for many metals and nonmetals present in nuclear fuel-cycle materials. A preceding anion-exchange-column separation increases tolerance for certain metals and nonmetals.

I. INTRODUCTION

Chlorophosphonazo III (3,6-bis-[(4-chloro-2-phosphonophenyl)azo]-4,5-dihydroxy-2,7 -naphthalenedisulfonic acid), termed CPA, has been used for spectrophotometric determinations of many elements including thorium,[1] uranium,[2,3] and plutonium.[4] The present method has been developed for determining microgram amounts of plutonium using the Los Alamos automated spectrophotometer[5] or a similar instrument in which all operations, from addition of reagents through the absorbance measurements, are done in a single tube. Extraction of the Pu(IV)-CPA complex into a water-immiscible alcohol improves selectivity and simultaneously increases the complex absorbance. A two-wavelength absorbance measurement improves precision by correcting for base-line shifts in a single-beam instrument, such as the Los Alamos automated spectrophotometer. The method as presented, however, provides a selective determination of plutonium suitable for a manually operated spectrophotometer.

II. EXPERIMENTAL

A. Spectra in Hydrochloric Acid and n-Pentanol

In dilute HCl solution, plutonium(IV) and CPA form a green complex having absorption peaks at 630 and 685 nm. The peaks of the extracted complex in n-pentanol are shifted to shorter wavelengths of 625 and 673 nm with a four-fold increase in absorbance (Fig. 1), similar to the effect reported by Yamamoto for the U(IV)-CPA complex extracted into 3-methyl-1-butanol.[6]

Various pairs of wavelengths, one wavelength representing the peak and the other the valley, were evaluated for absorbance measurement. The pair giving best precision was 680 and 710 nm.

B. Effect of Solvent

A reliable extraction system requires a solvent that has low viscosity, low volatility, and effective phase disengagement. Of five water-immiscible alcohols evaluated, color intensity was higher and phase disengagement better for n-pentanol, isopentanol, and hexanol than for cyclohexanol and p-methylhexanol. N-pentanol best met the stated requirements and was selected as the extractant.

C. Effect of Hydrochloric Acid Concentration

The absorbance of the Pu(IV)-CPA complex in n-pentanol is essentially constant when extracted from 1 to 2*M* HCl. The solubility of hydrochloric acid in n-pentanol increases at higher acid concentrations to lower the absorbance. A concentration of 1.5*M* HCl was selected.

D. Effect of Plutonium Oxidation State

The extraction of plutonium, initially in the (III), (IV), and (VI) oxidation states was measured under the conditions of the recommended procedure. The Pu(III) had been prepared by drying the HI-HCl eluate from an anion exchange column, Pu(IV) by oxidizing Pu(III) with sodium nitrite, and Pu(VI) by evaporating Pu(III) to dryness with $HClO_4$ and a trace of HNO_3. Extraction was measured in each case by liquid scintillation counting the aqueous phase. Extractions of Pu(III), Pu(IV), and Pu(VI) were 98.0, 99.6, and 99.4%, respectively, indicating conversion to Pu(IV), which is strongly complexed by CPA. To ensure constant extraction, sodium nitrite is added in the recommended procedure to oxidize Pu(III) to Pu(IV).

E. Effect of Chlorophosphonazo III Concentration

The effect of CPA concentration on the formation of the complex was established by extracting 10-µg (0.042 µmole) portions of Pu(IV) with increasing quantities of 0.04% ($5.3 \times 10^{-4}M$) CPA solution from 1.5*M* HCl into n-pentanol. The absorbance, relative to a reagent blank, increased to 0.6 mℓ (0.32 µmole) of CPA and was constant thereafter. A volume of 1 mℓ of 0.04% (0.53 µmole) CPA solution was selected.

F. Effect of Time

The development and extraction of the Pu(IV)-CPA complex is not instantaneous. After 10 min of phase

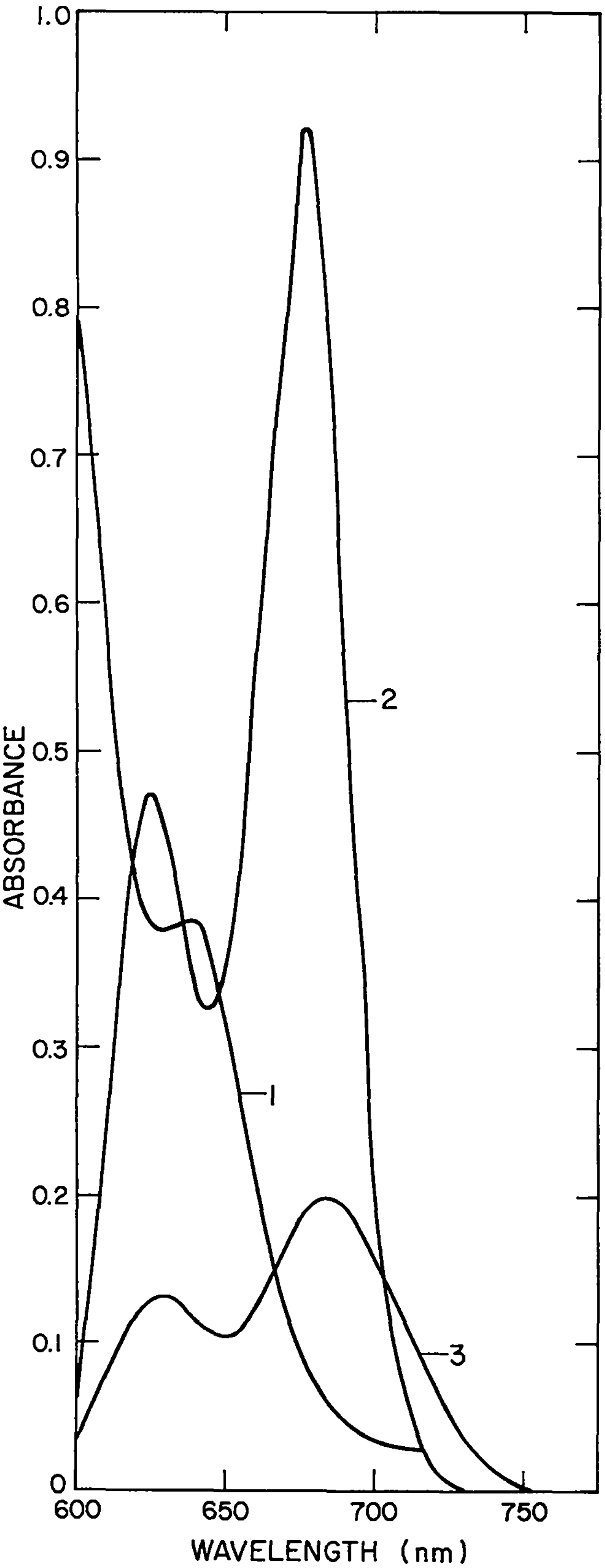

Fig. 1. Absorption Spectra. (1) 0.04% CPA in n-pentanol relative to air. (2) 15 µg Pu(IV)-CPA in n-pentanol relative to reagent blank in n-pentanol. (3) 15 µg Pu(IV)-CPA in 1.5*M* HCl relative to reagent blank in 1.5*M* HCl.

mixing and a 2-min period of phase disengagement, the absorbance is 93% of maximum, increasing to 97% in 2 h and to the maximum in 12 h. This is not critical for an automated instrument operation in which the timing of all steps is highly reproducible. For manual operation, however, a 2-h color development time is recommended.

G. Measurement Reliability

Measurement precision and linearity of absorbance were determined for the range of 0 to 20 μg of plutonium. As shown in Table I, the response is linear through 17.5 μg and the relative standard deviation is better than 1.5% for the range of 2.5 to 17.5 μg.

Measurement precision of the method was obtained over a 3-month period. The relative standard deviation for 60 analyses of 10 μg of plutonium reference material was 1.7%.

H. Diverse Ion Tolerances

Diverse ion tolerances were established by adding individual ions to 10 μg of plutonium and comparing the absorbances to that of plutonium alone. The initial molar ratio tested was 1000. If a result was significantly different at the 95% confidence level relative to plutonium alone, lower amounts were tested until there was no significant difference. The results, summarized in Table II, show high tolerances for many impurities present in plutonium materials characteristic of the nuclear fuel cycle.

Additional tolerance to diverse ions is difficult to obtain with masking agents because they also form highly stable complexes with Pu(IV).[7] Additional selectivity is gained by an ion exchange separation preceding the extraction, described in Sec. III, Recommended Procedure. The tolerances for selected ions, following the anion exchange separation, are given in Table III.

The anion exchange separation does not lower precision significantly; however, plutonium recovery decreases about 2%. Occasionally a set of samples and reference materials yield low recovery for all members of the group. This bias is caused by a residue of fine particles or degradation products of the resin that accompanies the eluted plutonium. Wet sieving of the resin to remove fine particles usually eliminates the interference; however, it occasionally recurs. This residue resists oxidative chemical treatments including fuming with perchloric and nitric acids. It can be decomposed by ignition, a treatment not recommended for routine plutonium analyses.

III. RECOMMENDED PROCEDURE

A. Reagents

- Hydrochloric Acid (saturated, $6M$, $1.5M$). Distill $\sim 6M$ HCl in a quartz still. Using polyethylene apparatus, pass HCl gas into the distilled acid while cooling in an ice bath. Verify that the molarity of the gas-saturated hydrochloric acid is at least $12M$ by titrating with a standard NaOH solution. Dilute as necessary with distilled water to obtain $6M$ and $1.5M$ HCl.
- Hydriodic Acid-Hydrochloric Acid Mixture ($0.1M$ HI-$12M$ HCl). Dilute 1 mℓ distilled $7.4M$ HI to 74 mℓ with saturated HCl. Prepare this reagent fresh before use. The HI is distilled, preferably in quartz apparatus, to remove H_3PO_2, the holding reductant in AR grade HI. Store the distilled HI in flame-sealed ampoules or in plastic containers under inert atmosphere.
- Nitric Acid ($15.6M$). Use quartz-distilled HNO_3.
- Perchloric Acid ($6M$). Mix 50 mℓ $12M$ $HClO_4$ with 50 mℓ distilled water.
- Anion Exchange Resin, Bio-Rad AG MP-1, 50-100 mesh, chloride form. Separate the fines by backwashing with distilled water.
- Chlorophosphonazo III (0.04% solution in $0.5M$ HCl). ICN Pharmaceuticals, Inc., Plainview, NY 11803. Dissolve 40 mg CPA in a 100-mℓ volumetric flask using 96 mℓ distilled water and 4 mℓ $12M$ HCl. This solution is stable in the absence of strong oxidizing or reducing agents.
- n-Pentanol. Kodak Laboratory Chemicals, Rochester, NY 14650. Use without further purification.
- Sodium Nitrite ($1M$). Dissolve 6.9 g of the reagent in 100 mℓ distilled water.

TABLE I. Linearity of Absorbance and Measurement Precision[a]

Plutonium (μg)	Absorbance	Absorbance Relative to Reagent Blank per μg Plutonium	Rel. Std. Dev. (%)
0.	0.037	0.000	11.4
1.	0.091	0.054	2.8
2.5	0.170	0.053	0.7
5.	0.310	0.055	1.5
7.5	0.439	0.054	1.0
10.	0.579	0.054	0.7
12.5	0.709	0.054	1.4
15.	0.842	0.054	0.8
17.5	0.962	0.053	0.5
20.	1.056	0.051	2.0

[a]Based on 6 determinations at each level.

TABLE II. Tolerances of Metals and Nonmetals without Anion Exchange Separation (Mole Ratio, Relative to 10 μg Pu)

1000:1		100:1	50:1	10:1	1:1
Cd II	Pt IV	Cu II	Fe III	Sb III	Cr III
Co II	Re IV	Mn II		Mn VII	Cr VI
Hg II	Se IV	Mo VI			
Pd II		Ru III			
acetate	iodate	V V			
borate	nitrate	Zn II			
bromide	nitrite	sulfide			
bromate	perchlorate	thiocyanate			
chloride	peroxide				
citrate	sulfamate				
EDTA	sulfate				
fluoride	sulfite				
formate	tartrate				
iodide	thiosulfate				

Ce III, Ir III, Rh III, phosphate not tolerated at molar ratio of 1.

TABLE III. Tolerances of Metals with Anion Exchange Separation (Mole Ratio, Relative to 10 µg Pu)

100:1		10:1
Ce III	Fe III	Rh III
Cr III	Mn VII	
Cr VI	Sb III	
Ir III	U(VI)	

Phosphate not tolerated at molar ratio of 1.

B. Apparatus

- A double-beam recording spectrophotometer with 1-cm cells was used for absorbance measurements.
- An inversion rotator, 48 rpm, Scientific Industries, Inc., Springfield, MA 01103, was used for extracting the Pu(IV)-CPA complex into pentanol.

C. Ion Exchange Separation (optional)

1. **Column Preparation.** Prepare the columns from disposable 1.6 mℓ polyethylene droppers having 2 mℓ reservoirs (Cole-Parmer Instrument Co., Chicago, Il 60648, No. C-6096-00 or equivalent). Cut off the top of the dropper to form an open reservoir and insert a small wad of quartz wool in the tip. Transfer a water slurry of the ion exchange resin into the column until the settled height is just below the reservoir. Immediately before use, pass 6 mℓ of the specially prepared, saturated HCl through the column. Keep the column wet with saturated HCl until use.

2. Column Separation.

(a) To an aliquot containing between 1 and 17.5 µg of plutonium in a 10-mℓ Teflon ™ beaker, add 2 drops of 6*M* $HClO_4$ and 1 drop of concentrated HNO_3, then evaporate to dryness.

- All Pu(III) oxidizes.

(b) Dissolve and transfer the residue with a polyethylene dropper to the anion exchange column with three 0.5-mℓ portions of saturated HCl.

- Americium, thorium, and many interfering elements elute.

(c) Pass 8 mℓ saturated HCl through the column in 2-mℓ increments.

- This completes the elution of many interfering elements.

(d) Place a 15-mℓ glass test tube under the column and elute the plutonium fraction with two 2-mℓ portions of 0.1*M* HCl mixture, then wait 10 min.

- Plutonium reduces to Pu(III).

(e) Pass four 2-mℓ portions of the 0.1*M* HI-12*M* HCl mixture through the column to complete the reduction and quantitative elution of plutonium.

(f) After allowing the saturated HCl eluate from step (e) to outgas overnight, gently evaporate the solution to dryness.

(g) Add one drop of concentrated HNO_3 to the residue and heat to remove the residual HI.

(h) Convert the residue to a chloride salt by heating to dryness with one drop of 6*M* HCl.

(i) Redissolve the salt in 4 mℓ of 1.5*M* HCl.

D. Extraction and Absorbance Measurement

- Using the recommended procedure and standard reference material, establish a calibration curve in the range of 0 to 17.5 µg of plutonium.

1. Deliver a 4-mℓ aliquot containing between 1 and 17.5 µg of plutonium in 1.5*M* HCl into a glass test tube.

2. Add 0.1 mℓ 1*M* $NaNO_2$ and warm the solution in a 60°C water bath for 10 min.

- Pu(III) oxidizes to Pu(IV).

3. After cooling, add 1 mℓ 0.04% CPA solution and briefly agitate the mixture.

- Pu(IV)-CPA complex forms.

4. Add 10 mℓ n-pentanol. Seal the test tube with a hollow polyethylene stopper using masking tape and mix the two phases for 10 min using a 48-rpm inversion rotator.

- Pu(IV)-CPA complex extracts into n-pentanol.

5. After phase disengagement, measure absorbance at 680 and 710 nm. For manual operation, a 2-h wait is recommended before absorbance measurement.

- The difference between the two absorbance measurements is proportional to the plutonium concentration.

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Technical guidance and editorial suggestions of J. E. Rein are appreciated.

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