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The Spectrophotometric Determination  
of Vanadium in Plutonium-Vanadium Alloys

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by

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# THE SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM IN PLUTONIUM-VANADIUM ALLOYS

by

W. J. Baughman and G. R. Waterbury

## ABSTRACT

Vanadium, when present in concentrations between 120 ppm and 5% in plutonium-vanadium alloys, is measured spectrophotometrically as the vanadium(V) - N-benzoyl-N-phenylhydroxylamine (BPHA) complex following separation from 100 mg of plutonium by extraction of the complex into chloroform. The vanadium and plutonium are first oxidized to their (V) and (VI) oxidation states, respectively, with fuming perchloric acid. The vanadium(V) is extracted from 2.8 $\times$ 10<sup>-2</sup> to 4.2 $\times$ 10<sup>-2</sup> M hydrochloric acid into chloroform containing BPHA, and the absorbance of the organic phase is measured at a wavelength of 530 m $\mu$ . At this wavelength, the molar absorptivity of the vanadium-BPHA complex is 4,260. Based upon 14 determinations each of 12, 30, 60, 120, and 225  $\mu$ g (120, 300, 600, 1200, and 2250 ppm) of vanadium, the relative standard deviations of the method are 3.5, 2.3, 1.7, 1.2, and 0.9%, respectively. Of 58 ions tested, 26 interfere when present in 100-mg quantities; at the 1-mg level, only Cr<sup>3+</sup>, Mn<sup>2+</sup>, Nb<sup>5+</sup>, Pt<sup>2+</sup>, Sn<sup>4+</sup>, Ta<sup>5+</sup>, Ti<sup>3+</sup>, and WO<sub>4</sub><sup>2-</sup> interfere.

## INTRODUCTION

A method was needed for measuring vanadium when present in concentrations between 120 ppm and 5% in plutonium-vanadium alloys. A literature survey revealed several spectrophotometric methods that would apply to the measurement of vanadium in this concentration range. Included among the reported chromogenic reagents were phosphotungstate,<sup>(9)</sup> 6-hydroxy-1,7-phenanthroline,<sup>(3)</sup> 8-quinolinol,<sup>(11)</sup> xylenol orange,<sup>(5)</sup> 1-(2-pyridylazo)-2-naphthol (PAN),<sup>(10)</sup> 4-(2-pyridylazo)-resorcinol (PAR),<sup>(2)</sup> N-benzoyl-N-phenylhydroxylamine (BPHA),<sup>(6, 0)</sup> N-cinnamoyl-N-phenylhydro-

xylamine,<sup>(7)</sup> and N-benzoyl-N-(p-chlorophenyl) hydroxylamine.<sup>(4)</sup> Several of these reagents were not tried because of unsuitable selectivity, poor sensitivity, or undesirable side reactions. Some of these, such as 6-hydroxy-1,7-phenanthroline, 8-quinolinol, xylenol orange, PAN, and PAR, were not attractive because they would require the quantitative separation of the vanadium from the plutonium and impurity elements prior to the formation of the colored complex. Vanadium-phosphotungstate had a low molar absorptivity. N-Cinnamoyl-N-phenylhydroxylamine and N-benzoyl-N-(p-chlorophenyl) hydroxylamine were not readily available commercially and did not seem to offer any

real advantage over the other reagents. The most logical choice was BPHA, which, in strong acid solutions, reacts with only a few metal ions to form water-soluble, highly colored complexes that can be extracted into chloroform.

This report describes the use of BPHA in the development of a selective, rapid method for the spectrophotometric determination of vanadium in plutonium-vanadium alloys. The method is insensitive to small changes in experimental variables, such as acidity, ionic strength, temperature, volume of aqueous phase, and amount of BPHA reagent. The reliability is adequate for measuring vanadium when present as a minor constituent in plutonium alloys.

#### APPARATUS AND REAGENTS

##### Apparatus:

Beakers, 20-ml, borosilicate glass.

Beaker tongs

Extraction vessel, consisting of a 150- x 27-mm test tube that is tapered at the bottom and sealed to a 1-mm-i.d. capillary tube. The capillary tube is bent upward along the side of the test tube as shown in Fig. 1.

Flask, volumetric, 10-ml, borosilicate glass.

Heat lamps, infrared, Pyrex, red-end, 250-W, or similar.

Hot plate, electric, thermostatically controlled, 4-in. diam, 0 to 700° F temperature range.

"Handi-plate", Precision Scientific Co., or equivalent.

Normal laboratory glassware, including beakers, volumetric flasks, pipets, and centrifuge cones.

Spectrophotometer, Beckman, model DU, with a set of four matched fused-silica cells having 1-cm light paths.

Stopcock, Teflon plug, 1-mm bore.

Stoppers, rubber, No. 6, one-hole.

Syringe, Luer, 10-ml, glass.

Tubing, borosilicate glass, 2-in. long, 8-mm i.d.

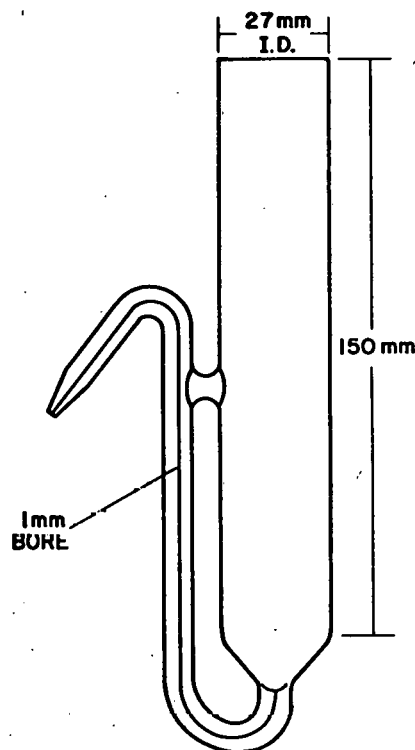


Fig. 1. Extraction vessel.

Timer, interval, spring-wound, in plastic case. General Electric, or similar.

Wash bottles, polyethylene, 30-ml, 100-ml, and 500-ml volumes.

Watch glass, beaker, borosilicate glass, 40-mm.

##### Reagents:

Acetone, reagent grade.

Chloroform, reagent grade.

Hydrochloric acid, 12M, reagent grade.

Hydrochloric acid, 3M. Dilute 125 ml of 12M hydrochloric acid to 500 ml with distilled water.

Hydrofluoric acid, 48%, reagent grade.

N-Benzoyl-N-phenylhydroxylamine (BPHA), 0.5% solution. Dissolve 2.5 g of N-benzoyl-N-phenylhydroxylamine, Eastman Organic Chemicals Distillation Products Industries, or equivalent, in 500 ml of chloroform. The solution should be stored in the dark. (8)

Nitric acid, 15.7M, reagent grade.

Perchloric acid, 70%, reagent grade.



Vanadium solution, 20  $\mu\text{g}/\text{ml}$  of vanadium. Dilute 4 ml of the vanadium stock solution to 200 ml with 17 ml of 12M hydrochloric acid and distilled water.

Vanadium stock solution, 1 mg/ml of vanadium. Dissolve 1 g of high purity vanadium metal in 12M hydrochloric acid and 15.7M nitric acid, and dilute to 1 l with distilled water. (The total of the detected impurities in the vanadium metal was less than 300 ppm.)

#### SAMPLE PREPARATION

Samples of plutonium metal or alloys are usually received as turnings or small pieces. Carefully inspect each sample and remove any extraneous material, such as lint or foreign metal chips, that may have been introduced in the sampling or machining operation. Accurately weigh duplicate 0.5- to 1-g portions, transfer the samples to 40-ml centrifuge cones, and cover with watch glasses. To each sample add 1 ml of water; then add drops of 12M hydrochloric acid to dissolve the sample. Wash the watch-glass cover and walls of the tube with distilled water, centrifuge the solution for 5 min, and inspect to determine if the dissolution is complete. If there is no insoluble residue, transfer the solution to a volumetric flask having a volume such that the vanadium concentration will be in the range between 4 and 120  $\mu\text{g}/\text{ml}$  when the solution is diluted. Dilute the solution to volume with 3M hydrochloric acid.

If a residue is present, decant the supernatant solution into a volumetric flask having an appropriate volume. Transfer the residue to a 30-ml platinum dish, add a few drops of 70% perchloric acid, and heat the dish until the hydrochloric acid is evaporated. Then add 4 ml of 15.7M nitric acid, 5 drops of 48% hydrofluoric acid, and 0.5 ml of 70% perchloric acid to the dish. Heat the solution under an infrared heater and on a hot plate until dense fumes evolve. Cool the solution, add a few drops of hydrochloric acid and of water, and warm to dissolve any solids. Decant this solution into the volumetric flask, and repeat the fuming operation until all the residue is in solution. Dilute the solution to volume with 3M hydrochloric acid.

#### RECOMMENDED PROCEDURE

Caution: Health safety rules for the handling of plutonium must be rigidly followed, and adequate protection for the operator must be ensured by use of suitable dry boxes and protective clothing.

1. Pipet two aliquots, each containing 12 to 225  $\mu\text{g}$  of vanadium and not more than 0.1 g of plutonium, from each solution prepared as described under Sample Preparation, and transfer each aliquot into a 20-ml beaker.
2. Add 0.5 ml of 15.7M nitric acid and 1 ml of 70% perchloric acid to each 20-ml beaker and to each of two additional beakers to prepare the reagent blanks. Evaporate the solutions to fumes of perchloric acid under infrared heat lamps, and perform the following steps on each solution.
3. Place a 40-mm watch glass on the beaker and set the beaker on a hot plate at 225°C (450 dial setting) under an infrared heat lamp. Heat the solution so that it fumes very strongly until almost evaporated.
4. Remove the beaker from the hot plate with beaker tongs and cool the beaker quickly in a water bath. As soon as it is possible to do so without causing the solution to spatter, add 1 ml of distilled water from a wash bottle through the beaker pouring spout.
5. After about 1 min, remove the watch glass and wash it with distilled water. Add the washings to the beaker.
6. Allow the solution to cool; then wash it into an extractor using 3 ml of 12M hydrochloric acid, and add water to make the final volume 10 ml.
7. Add 5 ml of 0.5% BPHA in chloroform, and insert a one-hole, No. 6, rubber stopper in the top of the extraction vessel.
8. Insert a 2-in. length of 8-mm-i.d. glass tubing in the stopper, and connect to vacuum through a stopcock. Adjust the stopcock to cause a flow of air through the extraction vessel to mix the layers.
9. Extract for 5 min; add chloroform, as needed, through the 1-mm capillary tube to maintain the volume of the organic phase about constant.
10. Remove the glass tube from the stopper and insert the end of a 10-ml Luer syringe. Withdraw the syringe plunger to the 10-ml mark to draw all the liquid from the capillary tube. Let the solution stand for 5 min to allow the phases to separate.
11. Push the syringe plunger to force the organic phase into a clean, dry 10-ml volumetric flask. (Watch the meniscus between the two phases and stop the liquid flow just as the last of the organic phase is forced from the capillary side arm.)

12. Add 3 ml of 0.5% BPHA in chloroform to the extraction vessel, and repeat Steps 8 through 11; mix the phases for only 3 min in Step 9.
13. Repeat Step 12, adding only 2 ml of 0.5% BPHA in chloroform.
14. Dilute the combined organic phases in the volumetric flask to 10 ml with chloroform, and mix well.
15. Measure the absorbance of the BPHA-vanadium complex at a wavelength of 530 m $\mu$ , using acetone or chloroform as a reference solution.
16. Subtract the average absorbance of the reagent blanks from the absorbance of the sample to obtain the corrected absorbance. (If the absorbance of the reagent blank is greater than 0.015, prepare fresh reagents and repeat the determination.)
17. To prepare a working curve, pipet aliquots containing 12 to 225  $\mu$ g of vanadium from the standard vanadium solution into 20-ml beakers, perform Steps 2 through 16, and plot the absorbance as a function of the quantity of vanadium. Make at least four determinations of each of five quantities of vanadium in preparing the working curve. (Each time the samples are analyzed, make at least two measurements of known quantities of vanadium to determine if the method is working properly.)
18. Read from the working curve the micrograms of vanadium (V,  $\mu$ g) corresponding to the corrected absorbance for the sample, and calculate the vanadium concentrations, using Eq. (1).

$$V, \% = \frac{(V, \mu\text{g})(10)}{(\text{Sample wt, mg})} \quad (1)$$

## EXPERIMENTAL

### Selection of Oxidant

Vanadium(V) is reportedly<sup>(6, 8, 12)</sup> the only oxidation state of that element forming a colored complex with BPHA that is extractable from an acid solution into chloroform. Plutonium(IV) can also be extracted.<sup>(1)</sup> Plutonium(VI), however, by analogy to the behavior of uranium(VI),<sup>(12)</sup> cannot be expected to form a chloroform-soluble complex with BPHA. An oxidant that simultaneously oxidizes plutonium and vanadium to their (VI) and (V) oxidation states, respectively, was needed to obtain suitable conditions for a clean separation. Bromine water and potassium permanganate, recommended oxidants for vanadium(IV),<sup>(8, 9, 12)</sup> were tried, but the results for vanadium found were low (Table I).

Fuming perchloric acid has advantages in that it quantitatively oxidizes either plutonium(IV) or vanadium(IV) to its highest oxidation state and does not introduce additional metal ions that might interfere. In the absence of plutonium, vanadium was oxidized quantitatively to the (V) oxidation state; the average for the vanadium found was 100%. In the presence of 100-mg of plutonium, the vanadium results were low (89%) and the reagent blank absorbances were high (Table I). The high blank absorbances were probably caused by incomplete oxidation of plutonium and by extraction

Table I  
Effect of Various Oxidants on Vanadium Recovery

V taken, $\mu$ g	Pu taken, mg	Number of determinations	Oxidation method	Absorbance at 530 m $\mu$	V found, %
96.9	0.0	5	Br <sub>2</sub> -H <sub>2</sub> O	0.096	12
38.7	0.0	2	KMnO <sub>4</sub>	0.297	92
0.0	100.0	4	Fuming HClO <sub>4</sub>	0.018	-
60.0	0.0	2	Fuming HClO <sub>4</sub>	0.510	101
60.0	100.0	2	Fuming HClO <sub>4</sub>	0.448	89
0.0	100.0	8	Fuming HClO <sub>4</sub> <sup>a</sup>	0.002	-
60.0	0.0	14	Fuming HClO <sub>4</sub> <sup>a</sup>	0.504	100
60.0	100.0	14	Fuming HClO <sub>4</sub> <sup>a</sup>	0.502	100

<sup>a</sup>Oxidation was accomplished by increasing the temperature of the fuming HClO<sub>4</sub> until it almost boiled.

of trace amounts of plutonium(IV) into the BPHA. The quantitative oxidation of plutonium and vanadium was accomplished by increasing the temperature of the fuming perchloric acid to near-boiling: the beaker was covered with a watch glass, the temperature of the hot plate was increased, and an infrared heat lamp was placed over the beaker. The reagent blank absorbance was reduced to 0.002, and the vanadium found was 100%.

#### Selection of N-Benzoyl-N-Phenylhydroxylamine Concentration

Priyadarshini and Tandon<sup>(6)</sup> have recommended 0.1% BPHA in chloroform for the extraction of vanadium(V) in the absence of uranium, and an unspecified higher concentration of BPHA in samples containing uranium. It was found, however, that 0.1% BPHA in chloroform would not quantitatively extract vanadium in the presence of plutonium. Quantitative extractions were obtained in the presence of plutonium when 0.5% BPHA in chloroform was used, and high results were obtained when 1.0% BPHA was used.

#### Selection of Wavelength

Although measurements of the absorbance of the vanadium-BPHA complex at wavelengths of 510 m $\mu$  and 530 m $\mu$  had been reported<sup>(6, 8)</sup> as being satisfactory, in the presence of plutonium, the 530 m $\mu$  wavelength was preferred. The plutonium imparted to the extracts a slight yellow color that absorbed more at 510 m $\mu$  than at 530 m $\mu$ .

#### Selection of Extractors

In the initial work, extractions were done in separatory funnels using electric-motor-driven glass paddles to mix the phases. When the organic phase was drained from the separatory funnel through the stopcock, some of the aqueous phase generally was entrained; the extracts were turbid and the absorbances were high. Extraction vessels (see Fig. 1) greatly improved separations of the phases because the organic phase could be forced through the capillary side arm with very little entrainment of the aqueous phase. Mixing of the phases by drawing in air through the side arm also was effective.

Table II

Effect of Plutonium on Vanadium Determination  
(96.9  $\mu$ g of vanadium in each determination)

<u>Pu, g</u>	<u>Number of determinations</u>	<u>V found, %</u>
0.0	9	100
0.1	13	98
0.5	4	114
1.0	4	120

#### Effect of Plutonium

The effect of plutonium was determined by measuring 96.9  $\mu$ g of vanadium, according to the Recommended Procedure, in the presence of different quantities of plutonium varying from 0.1 to 1.0 g. The high results obtained when more than 0.5 g of plutonium was present (Table II) were probably caused by the plutonium not being quantitatively oxidized to the (VI) oxidation state. In the absence of vanadium, the extract was a dark yellow which absorbed strongly at 365 m $\mu$ . This interference was not eliminated by washing the chloroform layer with various aqueous solutions, such as 8M hydrochloric acid, 3M hydrochloric acid plus 1% hydroxylamine, 3M hydrochloric acid plus 1.5% hydrogen peroxide, 3M hydrochloric acid plus 0.1M hydrofluoric acid, 3M hydrochloric acid plus 5N acetic acid, ascorbic acid in hydrochloric acid, or dilute sodium hydroxide, or by contacting the organic phase with hydrochloric acid containing zinc metal. Attempts to back-extract the vanadium from the organic phase into either dilute sodium hydroxide containing hydrogen peroxide or 1M iron(II), and then reextract with BPHA-chloroform also were ineffective. The interference was eliminated, however, by keeping the plutonium present to less than 0.1 g.

#### RELIABILITY

The reliability of the method was determined from data obtained from 14 measurements at each of five vanadium concentrations. Measured aliquots of a solution having a known vanadium concentration were added to aliquots containing 0.10 g of plutonium; the vanadium was determined according to the Recommended Procedure. The data (Table

Table III

The Spectrophotometric Determination of Vanadium in Plutonium  
(0.10 g of plutonium in each solution)

V taken, $\mu\text{g}/10\text{ ml}$	Number of determinations	V found, % <sup>a</sup>	Relative Std. Dev., %
0	12	-	28.0
12	14	95	3.5
30	14	98	2.3
60	14	99	1.7
120	14	100	1.2
225	14	99	0.9

<sup>a</sup>Based on the average absorbance per  $\mu\text{g}$  obtained for repeated determinations of vanadium in the absence of plutonium.

III) showed that the relative standard deviation was 3.5% in determining 12  $\mu\text{g}$  (120 ppm) of vanadium and ranged from 2.3 to 0.9% in determining 30 to 225  $\mu\text{g}$  (300 ppm to 0.225%). The molar absorptivity was calculated from these data to be 4,260. The measurements also showed that the absorbance of the vanadium-BPHA complex was a linear function of the vanadium concentration in the range between 12 and 225  $\mu\text{g}$  of vanadium in 10 ml of

solution.

The effects of 58 different ions on the determination of 30  $\mu\text{g}$  of vanadium were investigated by adding known quantities of each ion to solutions containing the vanadium and analyzing the solutions for vanadium as described in the Recommended Procedure. As shown in Table IV, 32 of the ions tested did not interfere at the 100-mg level. The

Table IV

Quantities of Various Ions<sup>a</sup> Tolerated in the  
Measurement of 30  $\mu\text{g}$  of Vanadium

100 mg	50 mb <sup>b</sup>	10 mg <sup>b</sup>	5 mb <sup>b</sup>	1 mg <sup>b</sup>
Al <sup>3+</sup> , AsO <sub>3</sub> <sup>3-</sup> , Ba <sup>2+</sup> , Be <sup>2+</sup> , Bi <sup>3+</sup> ,	Co <sup>2+</sup>	Au <sup>3+</sup>	Fe <sup>3+</sup>	MoO <sub>4</sub> <sup>2-</sup>
Br <sup>1-</sup> , Ca <sup>2+</sup> , Cd <sup>2+</sup> , Ce <sup>3+</sup> ,	Pb <sup>2+</sup>	Rn <sup>3-</sup>		Pd <sup>2+</sup>
Cl <sup>1-</sup> , Cs <sup>1+</sup> , F <sup>1-</sup> , Ga <sup>3+</sup> ,	TeO <sub>4</sub> <sup>2-</sup>	Cu <sup>2+</sup>		SbO <sub>3</sub> <sup>3-</sup>
Ge <sup>4+</sup> , Hg <sup>2+</sup> , I <sup>1-</sup> , In <sup>3+</sup> ,	Th <sup>4+</sup>	Hf <sup>4+</sup>		SiO <sub>3</sub> <sup>2-</sup>
K <sup>1+</sup> , La <sup>3+</sup> , Li <sup>1+</sup> , Mg <sup>2+</sup> ,	UO <sub>2</sub> <sup>2+</sup>	PO <sub>4</sub> <sup>3-</sup>		SO <sub>4</sub> <sup>2-</sup>
Na <sup>1+</sup> , NO <sub>3</sub> <sup>1-</sup> , Ni <sup>2+</sup> ,				Tl <sup>3+</sup>
Pu <sup>4+</sup> , Rb <sup>1+</sup> , Re <sup>2+</sup> , Ru <sup>4+</sup> ,				Zr <sup>4+</sup>
Sc <sup>3+</sup> , Sr <sup>2+</sup> , Y <sup>3+</sup> , Zn <sup>2+</sup>				

<sup>a</sup>The ions were added in the oxidation states shown, but oxidation of many of the ions probably occurs during the analysis. The weights given are for the quantity of the element added rather than that of the ion.

<sup>b</sup>Quantities greater than the amount shown cause a change greater than 5% in the results for vanadium.

remaining ions changed the absorbance of the vanadium-BPHA complex by more than 5%. Smaller quantities of these ions, plus enough plutonium to make a total of 100 mg, were then tested. At the 1-mg level, eight ions interfered: titanium ( $Ti^{3+}$ ) and niobium ( $Nb^{5+}$ ) extracted with the vanadium, and the absorbances were high; tantalum ( $Ta^{5+}$ ), tungsten ( $WO_4^{2-}$ ), and tin ( $Sn^{4+}$ ) formed insoluble precipitates that inhibited the formation of the vanadium-BPHA complex; platinum ( $Pt^{2+}$ ) inhibited the extraction of vanadium; chromium ( $Cr^{3+}$ ) and manganese ( $Mn^{2+}$ ) oxidized during the initial fuming with perchloric acid to higher oxidation states that reacted with the BPHA and caused the extracts to be yellow-brown. (7) Only very small amounts of sulfate (< 2.5 mg) could be tolerated because larger quantities prevented the quantitative oxidation of plutonium to the (VI) oxidation state by perchloric acid.

It was concluded that the method is sufficiently reliable, selective, and sensitive for measuring vanadium when present in concentrations between 120 ppm and 5% in binary alloys with plutonium.

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