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A STUDY OF SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM

G. Goldstein

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Analytical Chemistry Division

A STUDY OF SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF OSMIUM

G. Goldstein

Submitted as a thesis to The Graduate Council
of The University of Tennessee in partial fulfillment
of the requirements for the degree of Master of Science.

DATE ISSUED

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ACKNOWLEDGEMENT

The author wishes to express his appreciation to the Graduate School of the University of Tennessee, and the Analytical Chemistry Division, Oak Ridge National Laboratory, for their cooperation in making possible the carrying out of this research through the Oak Ridge Resident Graduate Program.

His deepest appreciation is expressed to Professor J. A. Dean and Dr. Oscar Menis without whose earnest encouragement and guidance this dissertation would not have been possible. The author also gratefully acknowledges the editorial assistance of Mr. H. P. House in the preparation of this thesis.

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CHAPTER I

INTRODUCTION

Osmium has only a limited utility in the laboratory and in industry. Its chief uses are as a catalyst, and in the manufacture of pen points and bearings for small instruments. The analytical chemistry of this element, therefore, has not been extensively developed. Primarily, interest has centered on the separation of osmium from ores and alloys containing other platinum group metals. The classical method for accomplishing this is by the oxidation of osmium followed by distillation of the volatile osmium tetroxide.[1] Numerous studies have been made of oxidizing agents, distillation conditions, and absorbing solutions for the osmium tetroxide,[2,3,4] and the evolution method has been applied to the separation of osmium from various sample types. Following the distillation, osmium was commonly precipitated hydrolytically as the hydrated dioxide, ignited to the metal in a reducing atmosphere,[1] and weighed as such. More recently, several organic compounds were proposed by Hoffman and others[5] and by Wilson and Baye[6] as precipitants for osmium in the distillates. However, gravimetric methods are obviously not suitable for the determination of microgram quantities of osmium.[7]

Probably the most widely utilized approach to the determination of trace quantities of an element is the colorimetric method.[8] As a rule, few colorimetric methods are sufficiently specific to allow the

direct determination of an element in the presence of associated elements, and therefore more or less extensive separations are necessary. Colorimetric methods for osmium have been reviewed by Sandell[9] and by Beamish and McBryde.[10]

In 1944 Sandell[11] reported a spectrophotometric method for the determination of osmium after a distillation separation, which utilized thiourea as the chromogenic reagent. In this procedure, which has been utilized with some modifications[2,12,13] for many years, osmium is separated by distillation, following which the thiourea is added to the distillate. A red color is developed, the intensity of which is measured photometrically. Very few elements interfered in this method because of the efficiency of the distillation separation and, for that reason, samples of many different types have been analyzed by this procedure. It is not, however, an especially sensitive method. The molar absorbancy index is only about 2900, so that the optimum quantity of osmium which can be determined is within the range of about 0.2 to 1 mg. in the sample taken for analysis.

Several colorimetric methods have been recently proposed for the estimation of osmium in which the chlorosmate ion ($OsCl_6^{=}$) is reacted with o,o'ditolylthiourea,[14] 1,4-diphenylthiosemicarbazide[14] or tetraphenylarsonium chloride.[15] These methods are more sensitive than the thiourea method because the molar absorbancy indexes of the osmium complexes are about 20,000. They are, therefore, suitable for the determination of microgram quantities of osmium in the osmium tetroxide distillates.

Studies have also been made of the reaction of osmate ion ($OsO_4^{=}$) with various naphthylaminesulfonic acids[16] and spectrophotometric methods have been published utilizing 1-naphthylamine-3,5,7-trisulfonic acid[17] and 1-naphthylamine-4,6,8-trisulfonic acid[18] as the chromogenic reagents. These methods have the disadvantage of requiring that the osmium be initially present in the sexavalent state so that it is difficult to obtain solutions suitable for reaction with these reagents without resorting to the distillation of osmium tetroxide into a sodium hydroxide receiving solution. Numerous other elements also form colored products with the naphthylaminesulfonic acids and therefore the separation of osmium is necessary.

A second important method for the isolation of osmium which was first pointed out by Yost and White[19] in 1928, was based on the extractibility of osmium tetroxide from aqueous solutions by organic solvents. Sauerbrunn and Sandell [20] studied the extraction of osmium tetroxide with chloroform and carbon tetrachloride. In 1953 they proposed a method[21] in which osmium was oxidized to the octavalent state, extracted with chloroform and then re-extracted into an aqueous thiourea solution. The intensity of the red color which was formed was measured spectrophotometrically. They also established a procedure for eliminating the interference of ruthenium in the determination of osmium.

In the catalytic method,[22] submicrogram quantities of osmium were determined by the accelerating effect of Os(VIII) on the reaction between As(III) and Ce(IV). The osmium was first extracted as osmium tetroxide and then re-extracted into a sulfuric acid-arsenious acid

solution. Ceric sulfate solution was added and the rate of the reaction was determined spectrophotometrically by measuring the absorbancy of the remaining ceric ion. However, in this method even trace quantities of other elements as contaminants in the glassware are serious interferences. Small temperature fluctuations also affect the measurements.

Procedures for the separation of osmium by extraction with organic reagents dissolved in an immiscible organic solvent have been suggested by Geilman and Neeb.[23] In these methods the extraction was combined with a distillation separation. Although small quantities of osmium can be efficiently separated and determined, the proposed methods do not appear to offer any advantage over procedures in which either the distillation or extraction of osmium tetroxide is utilized.

It is extremely difficult to dissolve solid samples without oxidation and loss of the volatile osmium tetroxide. For solid samples, therefore, the evolution method is of particular value since the sample can be decomposed and the osmium oxidized and separated simultaneously. Following the distillation, sensitive spectrophotometric methods are available for the determination of microgram quantities of osmium. The distillation procedure is, however, time-consuming and special apparatus is required. For liquid samples, therefore, a simple, rapid extraction procedure is of more value in the separation of osmium.

A direct determination of osmium without prior separations would be preferable. Other methods for the direct determination of osmium were not sufficiently selective and required that the osmium be present in a single valence state.[9,10]

The purpose of this work, therefore, was to develop rapid, selective, and sensitive methods for the determination of osmium in liquid samples. The specific application of primary interest was the estimation of microgram or milligram quantities of osmium in homogeneous reactor fuel solutions which contain uranyl sulfate as the major component and corrosion products of stainless steel as minor components.

CHAPTER II

REAGENTS AND APPARATUS

A. Reagents

1. Acetic Acid, Glacial, Analytical Reagent Grade.

2. Chloroform, Analytical Reagent Grade.

3. Diphenylcarbazide, (DPC) 0.2-per cent.

Dissolve 100 mg. of diphenylcarbazide in 50 ml. of analytical reagent grade ethanol. Since this reagent solution is not stable for more than one day it should be prepared daily. An excellent discussion of the quality and stability of this reagent is given by Allen.[24]

4. Ethanol, Analytical Reagent Grade.

5. Osmium Tetroxide, approximately 0.4 mg. of osmium per ml., in 0.1 M. sulfuric acid.

Weigh a vial containing 0.5 g. of analytical reagent grade osmium tetroxide. Then break the vial under 500 ml. of 0.1 M. sulfuric acid and allow the osmium tetroxide to dissolve completely. Filter the solution into a 1-liter volumetric flask and dilute to volume with 0.1 M. sulfuric acid. Dry and weigh the broken glass collected on the filter, calculate the weight of osmium tetroxide in the vial by difference, and determine the concentration of osmium

in the standard solution. The concentration of osmium in the solution may also be verified by the gravimetric 1:2:3-benzotriazole method suggested by Wilson and Baye,[6] or by any of the standard gravimetric[7] or volumetric[25] methods.

B. Apparatus

1. Beckman Model DU Spectrophotometer, equipped with ultraviolet accessories.

2. Warren Spectracord.

CHAPTER III

EXPERIMENTAL: EXTRACTION OF OSMIUM TETROXIDE AND MEASUREMENTS OF ITS ULTRAVIOLET ABSORBANCY

A. Extraction of Osmium Tetroxide

Solutions were prepared which contained from 0.4 to 2.7 mg. of osmium as the tetroxide in 10 ml. of 30-per cent (V/V) nitric acid. These solutions were transferred to 60-ml. separatory funnels and extracted successively with 10-, 10-, and 5-ml. portions of chloroform. The three extracts were drained into a second separatory funnel containing 10 ml. of 0.1 M. sulfuric acid and washed with this solution in order to remove any traces of nitric acid which may also have been extracted. The chloroform phase was then drained into a 25-ml. volumetric flask containing about 1 g. of anhydrous sodium sulfate and diluted to volume.

B. Ultraviolet Absorption Spectrum of Osmium Tetroxide

An aqueous solution of osmium tetroxide was prepared that contained 1.52 mg. of osmium. The osmium tetroxide was extracted as previously described (Section A). The ultraviolet absorption spectrum of the extract was determined versus a chloroform blank, and is presented in Figure 1.

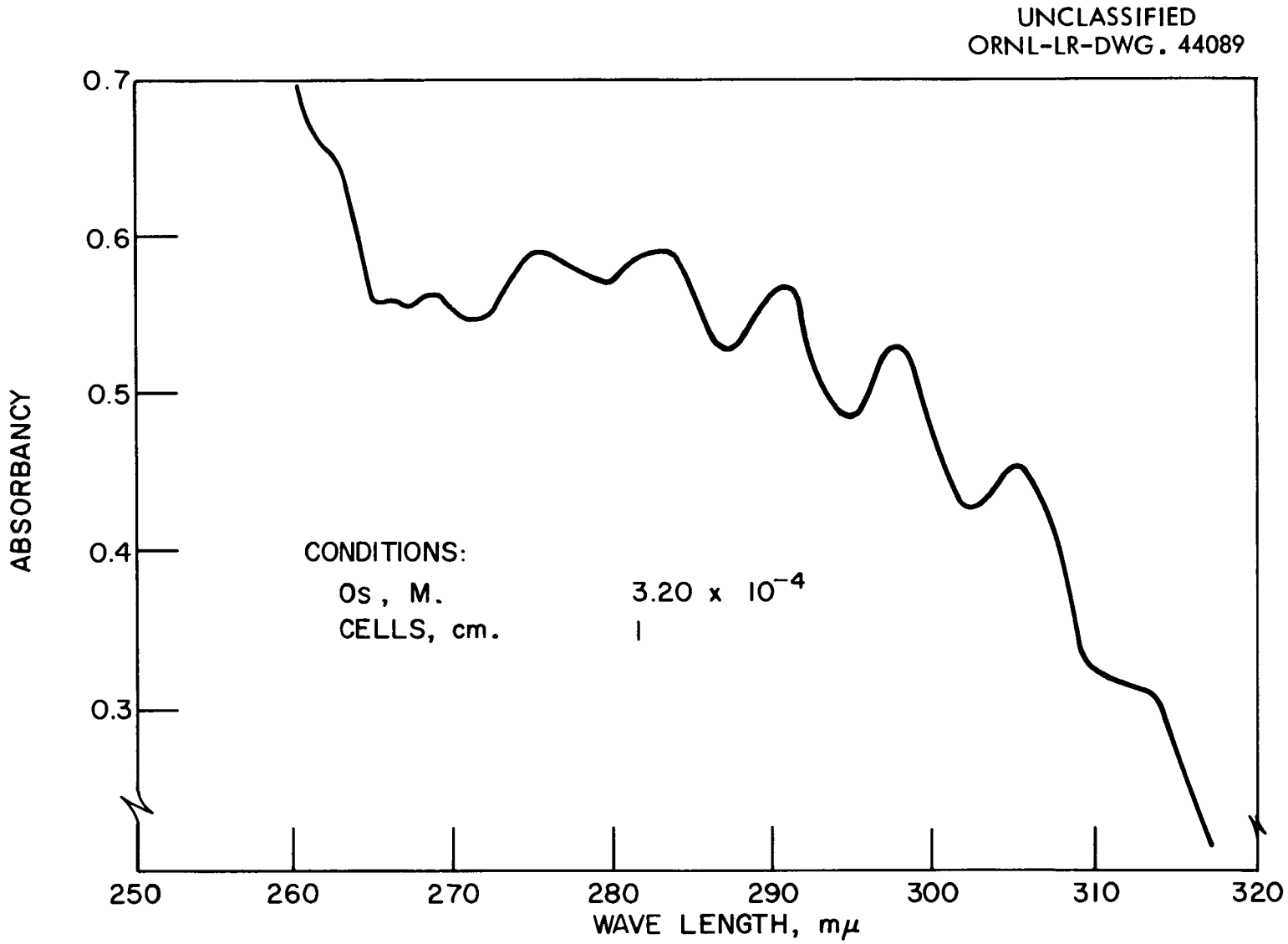

FIGURE 1. ULTRAVIOLET ABSORPTION SPECTRUM OF OSMIUM TETROXIDE IN CHLOROFORM

C. Calibration Curves for the Determination of Osmium

Aqueous Solutions were prepared containing from 0.4 to 2.7 mg. of osmium and were then extracted as previously described (Section A). The absorbancy of the extracts was measured versus a chloroform blank at the wave lengths of the five osmium tetroxide absorption peaks: 282, 289, 297, 304, and 312 mμ. These calibration data are presented in Table I, and, in the form of Ringbom plots,[26] in Figure 2. The optimum concentration ranges for the determination of osmium at each of the five wave lengths were determined from the Ringbom plots (Table II).

D. Effect of Foreign Substances

Solutions were prepared containing 1.14 mg. of osmium and the appropriate quantity of the foreign substance to be tested in 10 ml. of 30-per cent nitric acid, and the osmium was extracted as previously described (Section A). The absorbancy of the extracts was measured at 289 mμ versus a chloroform blank. These results are presented in Table III.

TABLE I

CALIBRATION DATA FOR THE ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

Conditions: Volume, ml. 25
Cells, cm. 1

Osmium		Wave Length, mμ				
		282	289	297	304	312
mg.	M. x 10^4	Absorbancy				
0.380	0.799	0.151	0.142	0.130	0.109	0.080
0.760	1.60	0.298	0.276	0.263	0.223	0.160
1.14	2.40	0.460	0.430	0.396	0.335	0.236
1.52	3.20	0.590	0.565	0.529	0.455	0.318
1.90	4.00	0.738	0.690	0.648	0.552	0.396
2.28	4.79	--	--	0.798	0.687	0.497
2.66	5.59	--	--	--	0.770	0.560
Molar Absorbancy Index		1870	1760	1640	1400	1000
Coefficient of Variation, per cent		2	2	1	2	2

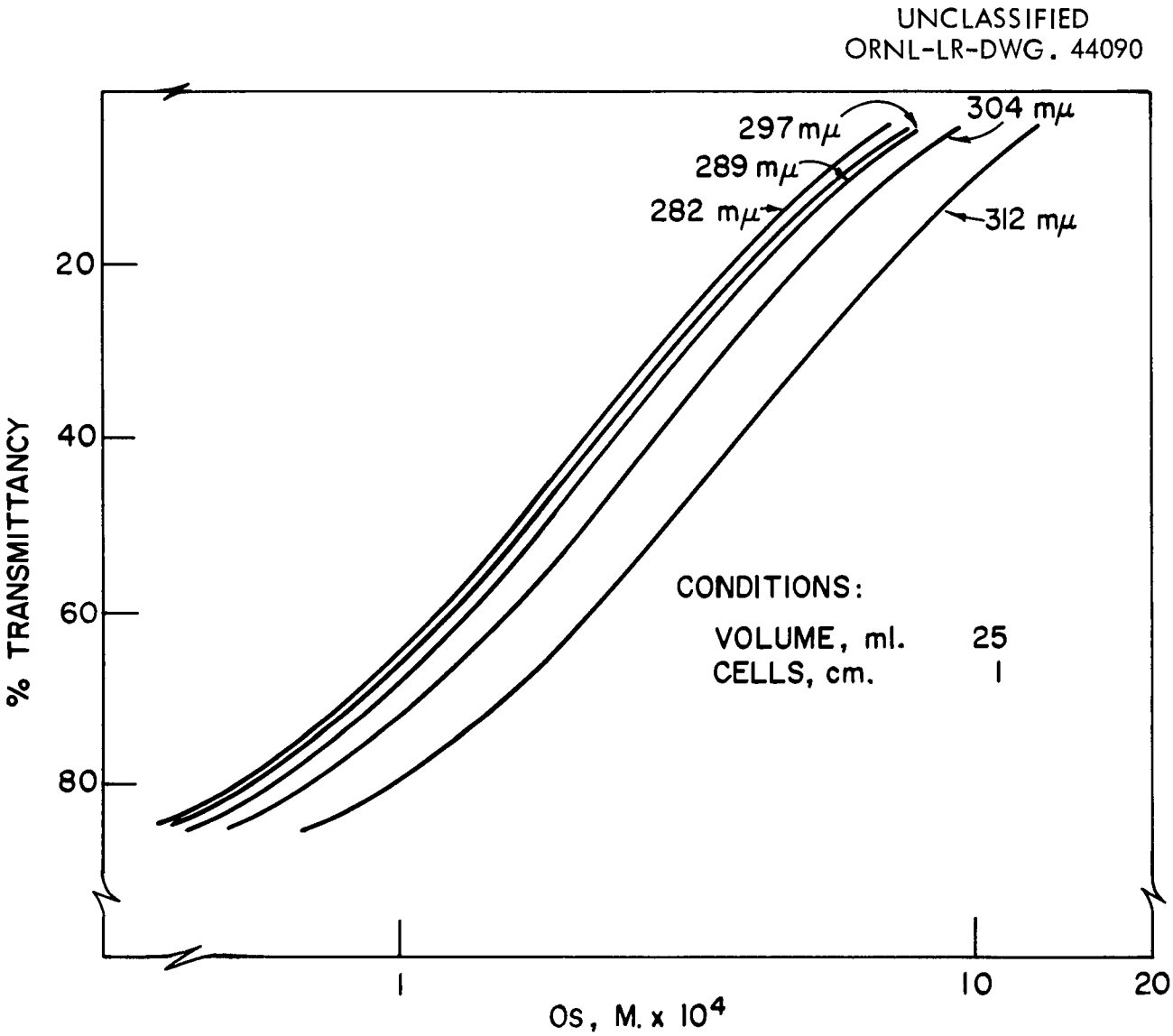

FIGURE 2. RINGBOM PLOTS FOR THE ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

TABLE II

OPTIMUM CONCENTRATION RANGES FOR THE ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM AT FIVE WAVE LENGTHS

Data from Ringbom plots in Figure 2.

Wave Length, mμ	Optimum Concentration Range	
	M. x 10^4	mg./25 ml.
282	0.8 - 3.7	0.4 - 1.8
289	0.9 - 4.0	0.4 - 1.9
297	0.9 - 4.3	0.5 - 2.0
304	1.1 - 5.0	0.5 - 2.4
312	1.5 - 7.0	0.7 - 3.3

TABLE III

EFFECT OF FOREIGN SUBSTANCES ON THE EXTRACTION AND ULTRAVIOLET SPECTROPHOTOMETRIC DETERMINATION OF OSMIUM

Conditions:		
	Volume, ml.	25
	Wave length, mμ	289
	Cells, cm.	1
	Osmium, mg.	1.14

Foreign Substance		Osmium, mg.	
Element	mg.	Found	Error
U(VI)	1000	1.19	0.05
Fe(III)	1000	1.22	0.08
Ni(II)	1000	1.18	0.04
Cu(II)	1000	1.19	0.05
Th(IV)	500	1.17	0.03
Cr(VI)	500	1.19	0.05
Cr(III)	500	1.16	0.02
Mo(VI)	500	1.14	0.00
Pd(II)	6	1.20	0.06
Au(III)	5	1.12	-0.02
Rh(III)	2	1.10	-0.04
Pt(II)	2	1.17	0.03
Ir(III)	1	1.16	0.02
Ru(III)	1	1.19	0.05

CHAPTER IV

EXPERIMENTAL: EXTRACTION OF OSMIUM TETROXIDE AND REACTION WITH DIPHENYLCARBAZIDE

In previous experimental work on the determination of osmium by extraction of osmium tetroxide with chloroform and measurement of its ultraviolet absorbancy, as described in Chapter III, molar absorbancy indexes ranging from 1000 to about 2000 were obtained. Preliminary experiments demonstrated that diphenylcarbazide reacts with the osmium tetroxide in chloroform to give a blue-violet reaction product, which can be used to provide a more sensitive method for determining osmium.

A. Absorption Spectrum of the Osmium-Diphenylcarbazide Complex

A solution was prepared containing 38 γ of osmium as osmium tetroxide in a volume of 10 ml. of 30-per cent nitric acid. The osmium was extracted with two 10-ml. portions of chloroform. The extracts were washed with 10 ml. of 0.1 M. sulfuric acid, drained into a 25-ml. volumetric flask containing 5 ml. of 0.2-per cent diphenylcarbazide and about 1 g. of anhydrous sodium sulfate, and then the solution was diluted to volume with chloroform. After an interval of twenty-four hours for color development, the absorption spectrum of the solution was determined versus a reagent blank (see Figure 3).

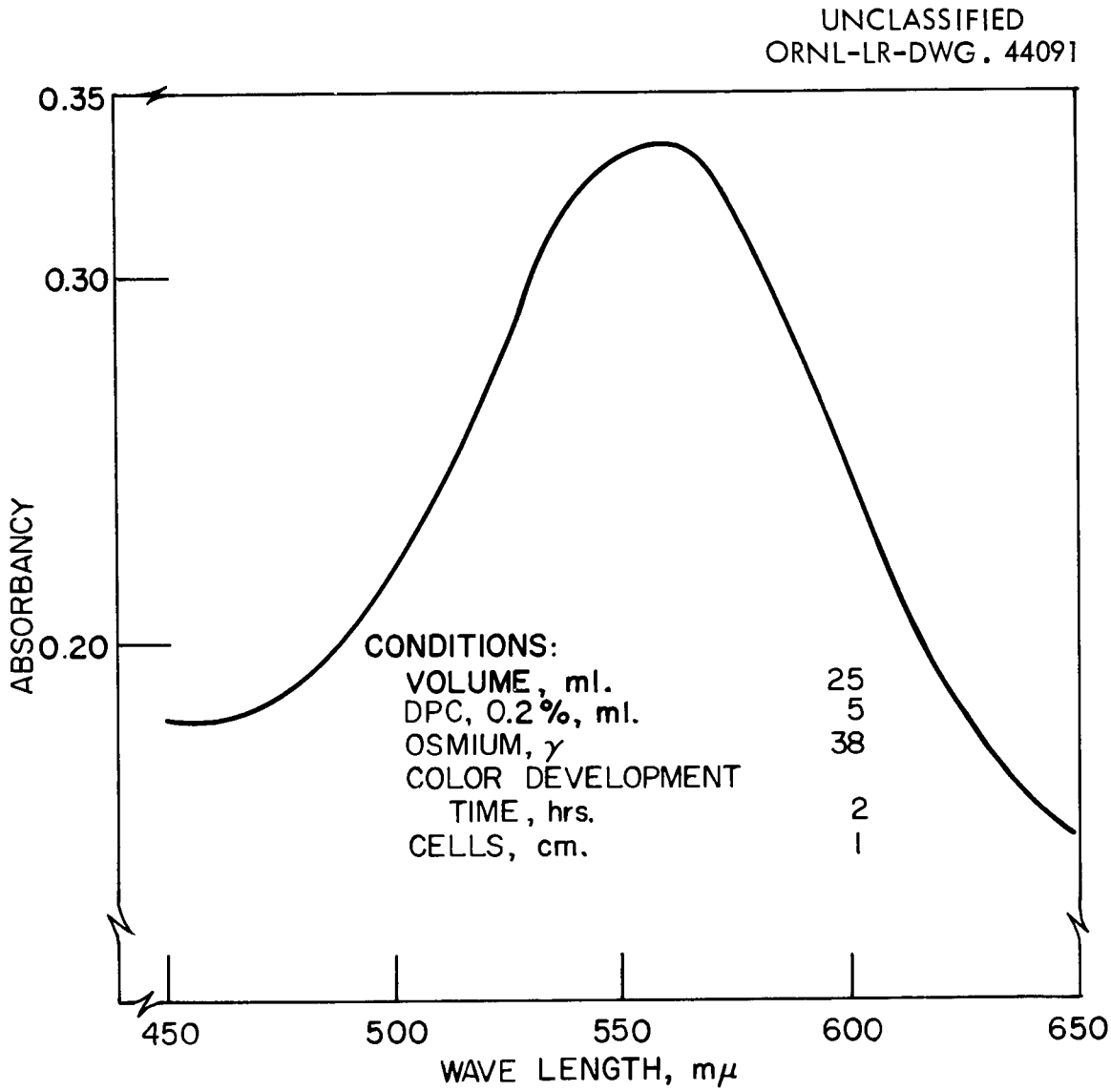

FIGURE 3. ABSORPTION SPECTRUM OF THE OSMIUM-DIPHENYLCARBAZIDE COMPLEX DEVELOPED IN A CHLOROFORM MEDIUM

B. Effect of Diphenylcarbazide Reagent Concentration

The reagent concentration necessary to produce maximum absorbancy was determined by extracting solutions containing 96 γ of osmium as in Section A, washing the extracts, and drawing them into flasks containing from 0.5 to 5 ml. of 0.2-per cent diphenylcarbazide. Sufficient ethanol was added to the extracts to bring the total volume of alcohol to 5 ml., the solutions were diluted to volume with chloroform, and their absorbancies were measured versus a reagent blank at 560 mμ. These data are presented in Table IV.

C. Effect of Time of Color Development

Solutions containing from 12 to 96 γ of osmium were treated as described in Section A. The absorbancy of each extract was measured as a function of time. These data are presented in Figure 4.

TABLE IV

EFFECT OF DIPHENYLCARBAZIDE CONCENTRATION ON THE ABSORBANCY OF THE OSMIUM-DIPHENYLCARBAZIDE COMPLEX

Conditions:	Volume, ml.	25
	Osmium, γ	96
	Ethanol, ml.	5
	Wave length, mμ	560
	Cells, cm.	1

Diphenylcarbazide, 0.2 Per Cent, ml.	Absorbancy
0.5	0.153
1	0.340
2	0.600
3	0.749
4	0.759
5	0.769

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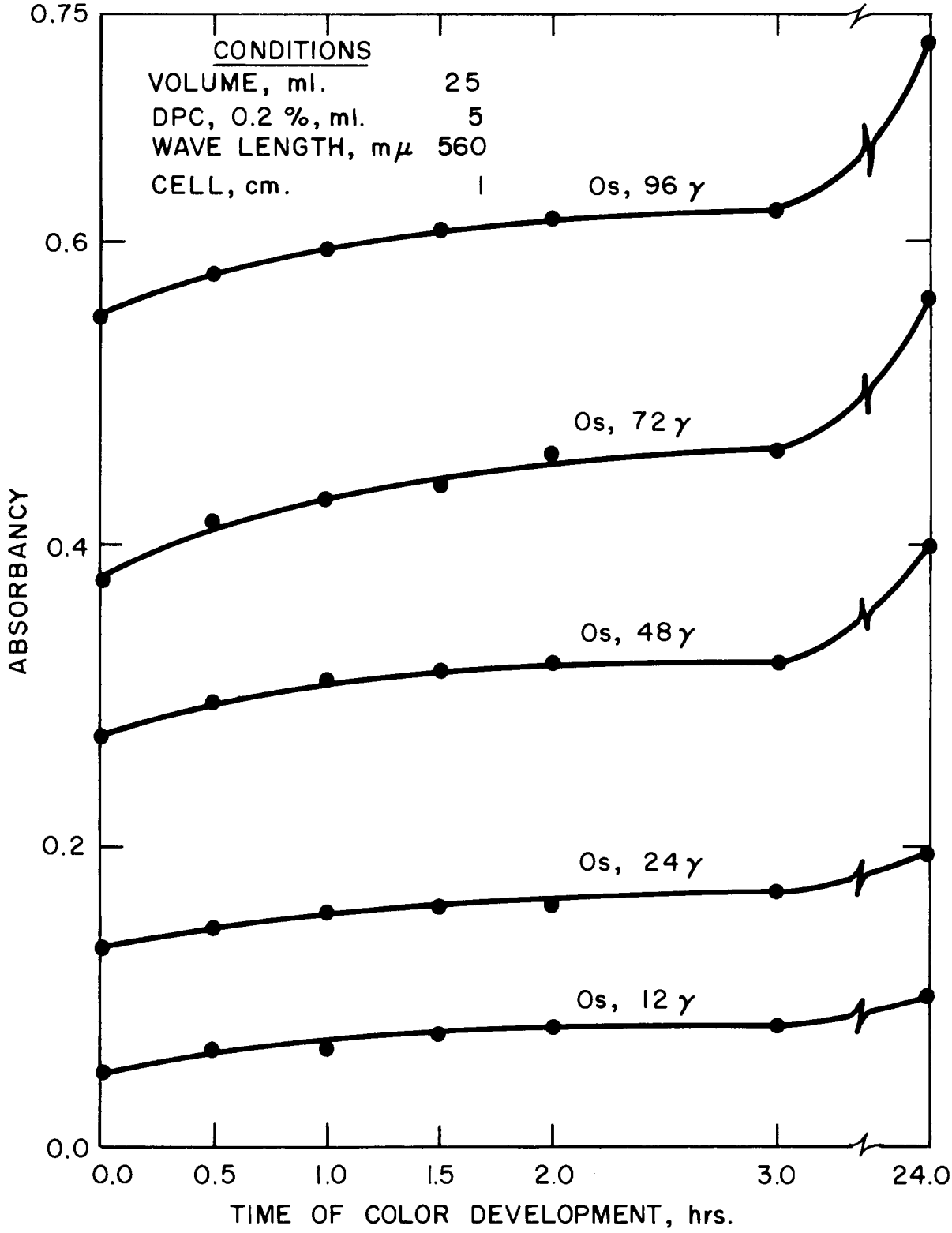

FIGURE 4. EFFECT OF TIME OF COLOR DEVELOPMENT ON THE ABSORBANCY OF THE OSMIUM-DIPHENYLCARBAZIDE COMPLEX

D. Adherence to Beer's Law

The adherence of the absorbancy of the osmium-diphenylcarbazide extracts to Beer's law, after a color development period of two hours, was tested by extracting 12 to 96 γ of osmium, processing the extracts as outlined in Section A, and measuring the absorbancy. Five series of solutions designated I to V were prepared over a period of two weeks. These results are shown in Table V.

E. Effects of Foreign Substances

Solutions containing 38 γ of osmium were prepared, and the appropriate quantity of the foreign substance to be tested was added. The solutions were processed and extracted as described in Section A, and the absorbancy of the extracts was measured after a color development period of two hours. The results are presented in Table VI.

TABLE V

ADHERENCE OF ABSORBANCY OF OSMIUM-DIPHENYLCARBAZIDE SOLUTIONS TO BEER'S LAW

Conditions:		
	Volume, ml.	25
	Diphenylcarbazide, 0.2 per cent, ml.	5
	Color development time, hr.	2
	Wave length, mμ	560
	Cells, cm.	1

Osmium, γ	Series I	II	III	IV	V	Average
	Absorbancy					
12	0.079	0.082	0.080	0.079	0.078	0.080
24	0.162	0.165	0.151	0.164	0.173	0.163
48	0.322	0.314	0.300	0.329	0.342	0.321
72	0.462	0.440	0.450	0.473	0.470	0.459
96	0.615	0.592	0.611	0.650	0.642	0.622
Molar Absorbancy Index	30,900	30,100	30,400	31,900	32,300	31,300
Coefficient of Variation, %	2	6	3	2	5	3

TABLE VI

EFFECT OF FOREIGN SUBSTANCES ON THE DETERMINATION OF OSMIUM

Conditions:	Volume, ml.	25
	Diphenylcarbazide, 0.2 per cent, ml.	5
	Color development time, hr.	2
	Wave length, mμ	560
	Cells, cm.	1
	Os, γ	38.0

Foreign Substance		Osmium, γ	
Element	mg.	Found	Error
U(VI)	500	38.7	0.7
Th(IV)	500	40.0	2.0
Fe(III)	1	39.9	1.9
Cr(VI)	1	38.5	0.5
Cr(III)	1	39.7	1.7
Ni(II)	1	40.3	2.3
Cu(II)	1	39.9	1.9
Co(II)	1	38.2	0.2
Mo(VI)	1	37.6	0.4
Zr(IV)	1	38.8	0.8
Au(III)	1	39.0	1.0
Pt(II)	1	39.3	1.3
Pd(II)	1	38.7	0.7
Ir(III)	1	37.1	0.9
Rh(III)	1	37.9	0.1
Ru(III)	1	38.8	0.8
Ru(VIII)	0.3	49.3	11.3

CHAPTER V

EXPERIMENTAL: REACTION OF OSMIUM WITH DIPHENYLCARBAZIDE IN AQUEOUS MEDIUM

In previous work on the determination of osmium with diphenylcarbazide, described in Chapter IV, osmium was extracted as the tetroxide with chloroform and the diphenylcarbazide reagent was added to the extracted osmium. Under these conditions a two-hour color development period was necessary and a molar absorbancy index of about 31,000 was obtained. Preliminary experiments showed that, when diphenylcarbazide was added to the aqueous solutions containing osmium tetroxide, a blue-violet compound was formed which could then be extracted with chloroform. Moreover, it appeared that the sensitivity of the method could be increased considerably, and the color development period decreased by adding the diphenylcarbazide reagent to the aqueous osmium solutions.

A. Effect of Time of Color Development

The effect of the time of color development prior to extraction on the absorbancy of the extract was determined. The effect of the time of color development of the extracts was also studied. Solutions were prepared containing 48 γ of osmium in 20 ml. of an aqueous solution which was 1 M. in perchloric acid and 1.7 M. in acetic acid. Then 4 ml. of 0.2-per cent diphenylcarbazide in ethanol was added and, after

time intervals ranging from zero to thirty minutes the aqueous solutions were extracted with two 10-ml. portions of chloroform. The extracts were drained into individual 25-ml. volumetric flasks containing approximately 1 g. of anhydrous sodium sulfate and diluted to volume with chloroform. The absorbancy of the extracts was then measured as a function of time versus a reagent blank. These results are presented in Figure 5.

B. Effect of Temperature

Aqueous solutions containing 48 γ of osmium were prepared as described in Section A. These solutions were heated to temperatures between 35 and 65°, extracted as in Section A, and the absorbancy of the extracts was measured as a function of time. The data are shown in Table VII.

A series of solutions was prepared, containing 24 γ of osmium, as previously described in Section A. After heating to 65° the solutions were extracted at various time intervals ranging from zero to thirty minutes. The absorbancies of the extracts were measured as a function of time and are shown in Table VIII.

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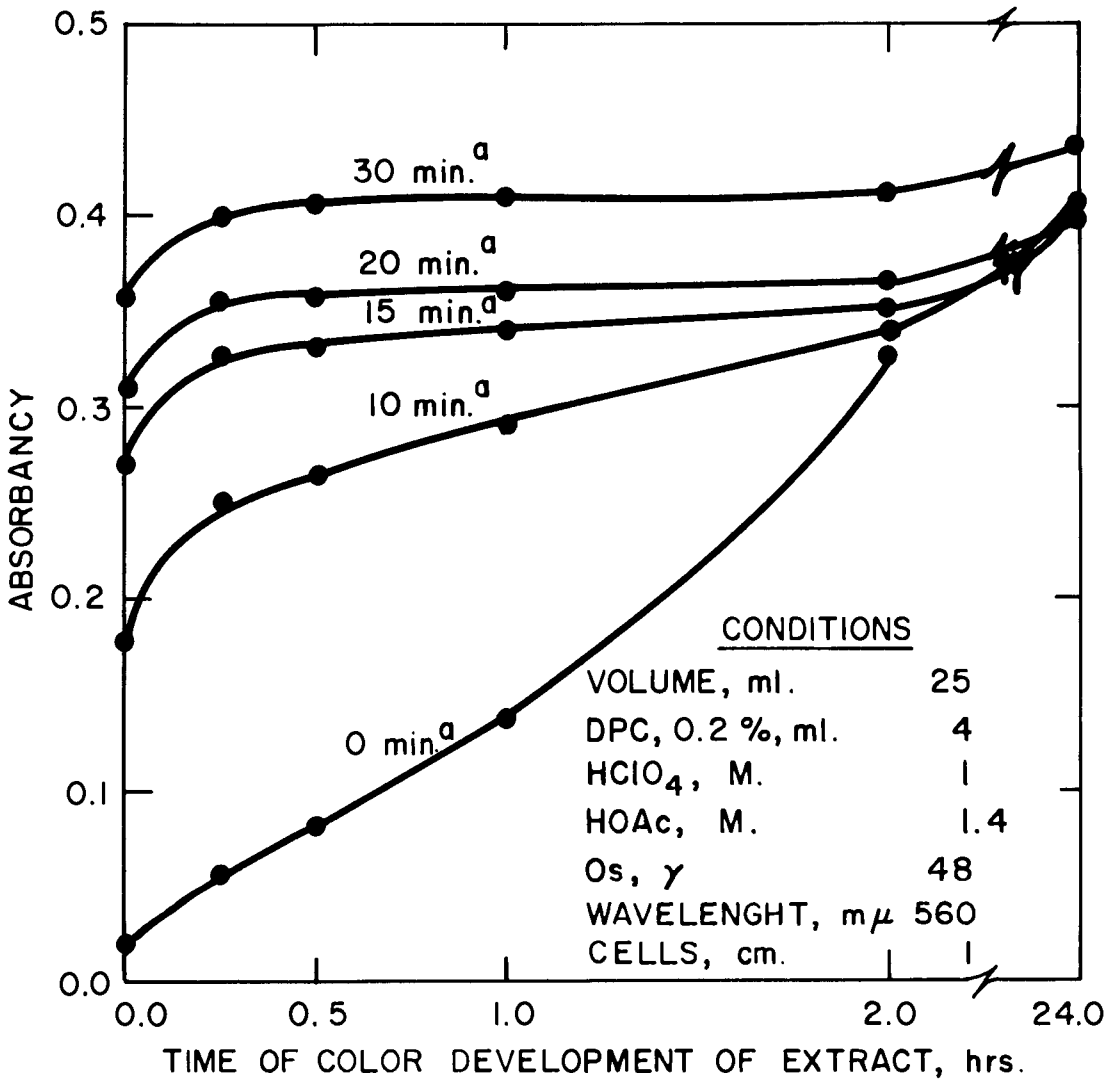

FIGURE 5. EFFECT OF TIME OF COLOR DEVELOPMENT ON THE ABSORBANCY OF THE OSMIUM-DIPHENYLCARBAZIDE EXTRACT

a - TIME OF COLOR DEVELOPMENT IN AQUEOUS PHASE

TABLE VII

EFFECT OF TEMPERATURE ON THE REACTION BETWEEN OSMIUM AND DIPHENYLCARBAZIDE

Conditions:	Volume, ml.	25
	DPC, 0.2%, ml.	4
	$HClO_4$, M.	1
	HOAc, M.	1.7
	Os, γ	48
	Wave length, mμ	560
	Cells, cm.	1

Time of Color Development of Extract, min.	Temperature of Aqueous Phase 35°	50°	65°
	Absorbancy		
0	0.375	0.530	0.840
15	0.375	0.550	0.850
30	0.385	0.560	0.850
60	0.410	0.570	0.861
120	0.452	0.582	0.862
24 hours	0.502	0.611	0.904

TABLE VIII

EFFECT OF TIME OF COLOR DEVELOPMENT ON THE ABSORBANCY OF OSMIUM-DIPHENYLCARBAZIDE EXTRACTS AFTER HEATING TO 65° C

Conditions:		
	Volume, ml.	25
	DPC, 0.2%, ml.	4
	$HClO_4$, M.	1
	HOAc, M.	1.7
	Os, γ	24
	Wave length, mμ	560
	Cells, cm.	1

Time of Color Development of Extract, min.	Time of Color Development of Aqueous, Min.				
	0	10	15	20	30
	Absorbancy				
0	0.460	0.488	0.498	0.500	0.500
15	0.480	0.506	0.501	0.508	0.503
30	0.480	0.500	0.501	0.510	0.510
60	0.485	0.501	0.507	0.510	0.510
120	0.487	0.506	0.509	0.511	0.510
24 hours	0.482	0.509	0.509	0.509	0.508

C. Effect of Perchloric Acid Concentration

Aqueous solutions were prepared containing 1 ml. of acetic acid, 5 ml. of diphenylcarbazide reagent, and 72 γ of osmium and were adjusted to pH values ranging from 0 to 7 by the addition of perchloric acid. These solutions were diluted to 25 ml. in a volumetric flask and their absorption spectra were measured by means of a Warren Spectracord versus an appropriate reagent blank. These spectra are presented in Figure 6.

The effect of the perchloric acid concentration on the absorbancy of the chloroform extracts was determined by preparing solutions containing 19 γ of osmium, 4 ml. of 0.2-per cent diphenylcarbazide and from 0.5 to 2.3 M. perchloric acid in a volume of 25 ml. These solutions were heated to 65°, allowed to cool to room temperature, and then extracted with two 10-ml. portions of chloroform. The extracts were transferred to 25-ml. volumetric flasks containing about 1 g. of anhydrous sodium sulfate, diluted to volume, and their absorbancy was measured at 560 mμ versus a reagent blank. These tests were repeated with similar solutions which contained in addition 0.70 and 1.4 M. acetic acid. The absorbancies of the extracts as a function of the perchloric acid concentration of the aqueous phase are shown in Figure 7. The spectra of two solutions were determined by means of the Warren Spectracord, and these spectra are shown in Figure 8.

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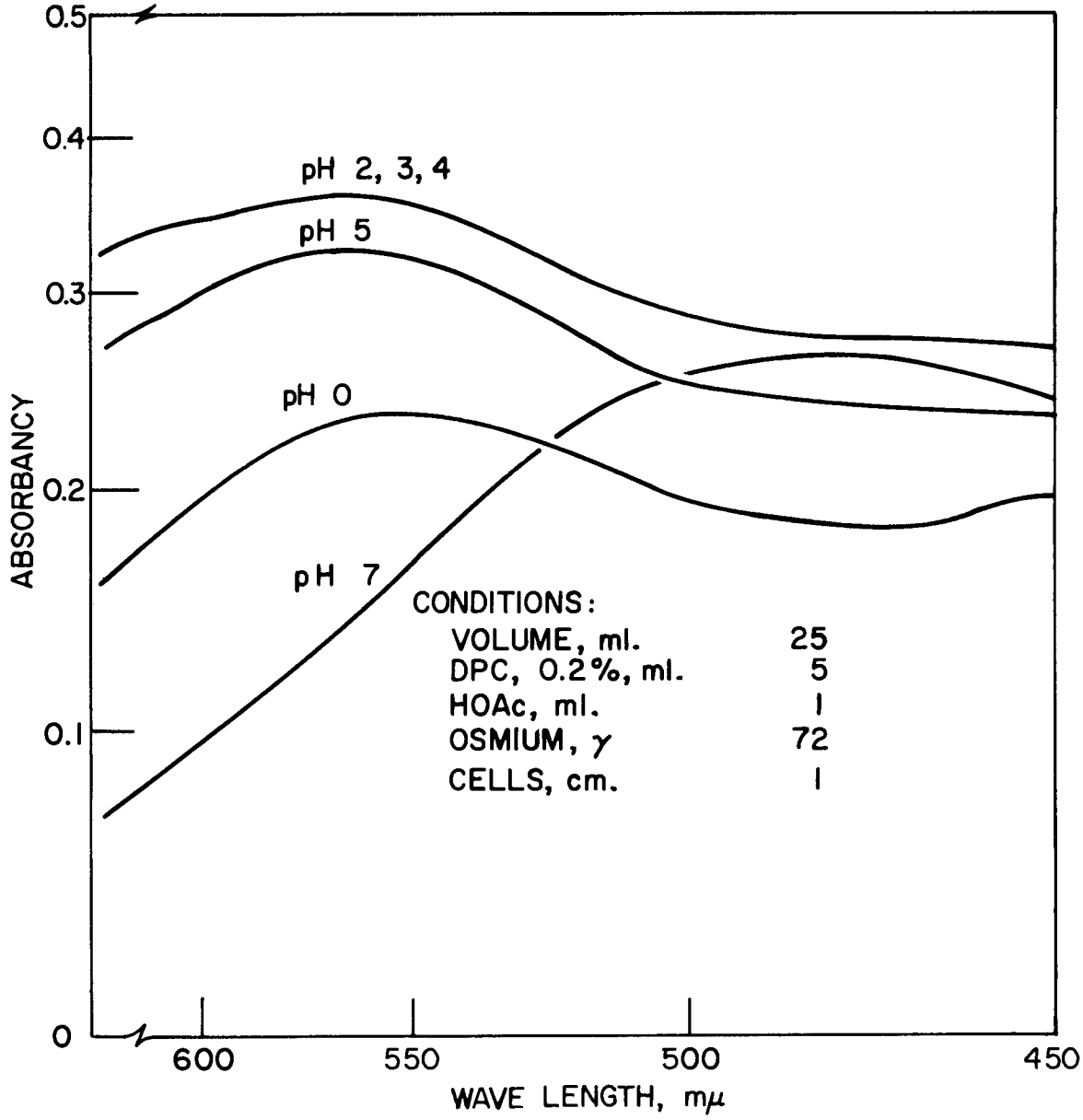

FIGURE 6. ABSORPTION SPECTRA OF THE OSMIUM-DIPHENYL-CARBAZIDE COMPLEX IN AQUEOUS SOLUTIONS

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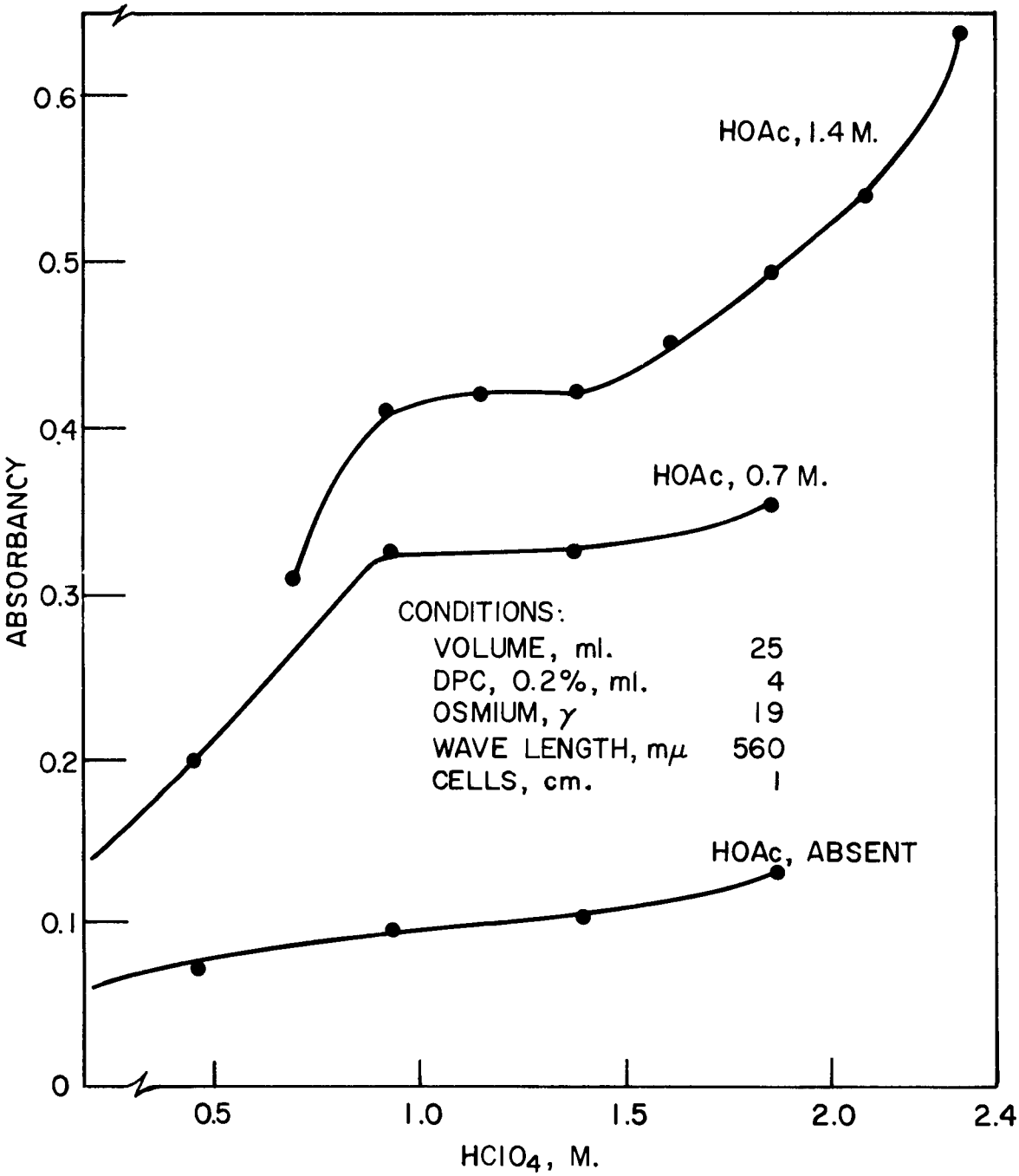

FIGURE 7. EFFECT OF PERCHLORIC ACID CONCENTRATION ON THE ABSORBANCY OF OSMIUM-DIPHENYLCARBAZIDE EXTRACTS

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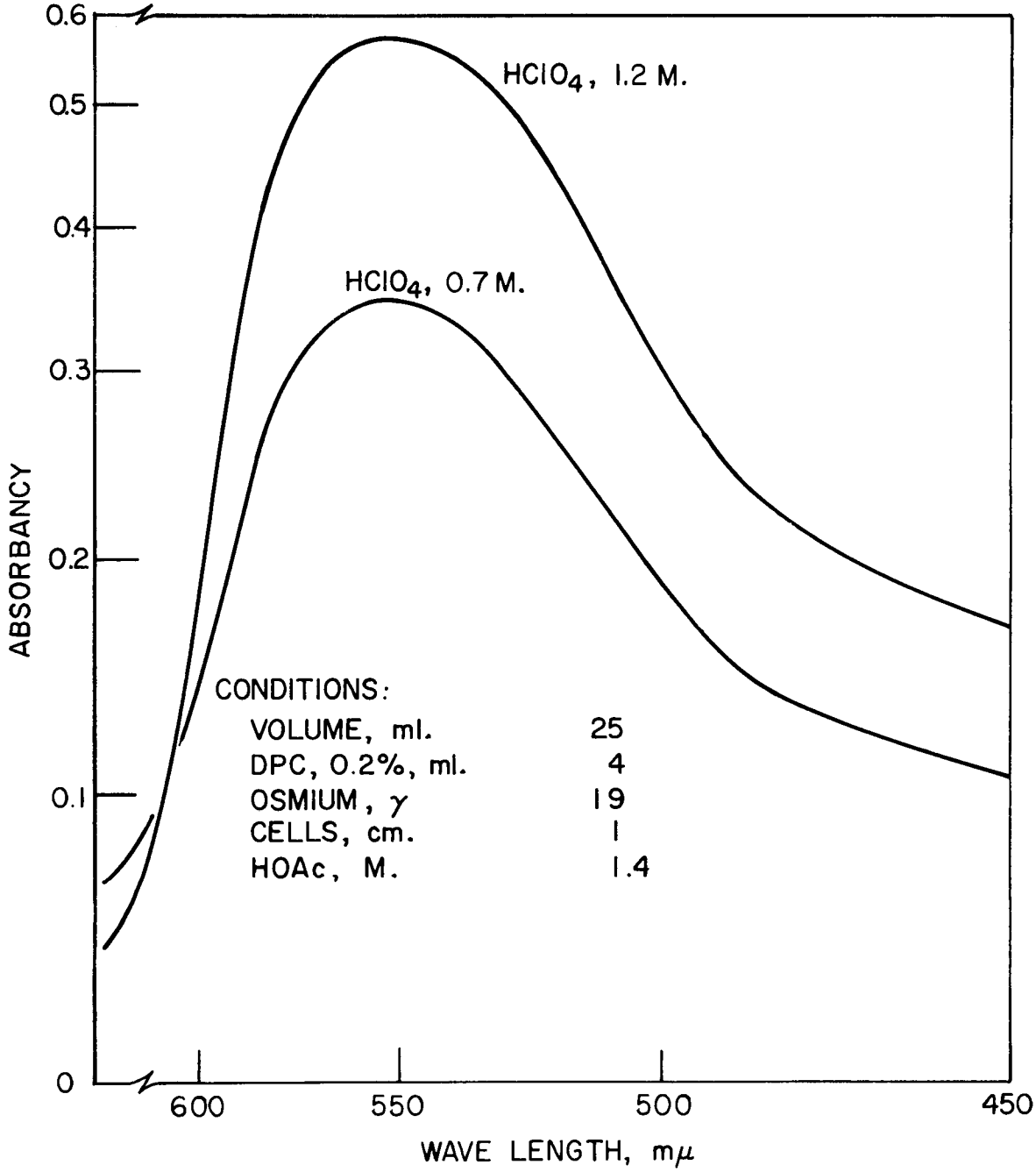

FIGURE 8. EFFECT OF PERCHLORIC ACID CONCENTRATION ON THE ABSORPTION SPECTRUM OF THE OSMIUM-DIPHENYLCARBAZIDE EXTRACTS

D. Effect of Acetic Acid Concentration

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Since the results of the previous experiments (Section C) indicated that the final absorbancy of the osmium-diphenylcarbazide extracts depended upon the acetic acid concentration of the aqueous solutions, a study was made of this effect. Solutions were prepared which contained 19 γ of osmium, 4 ml. of 0.2-per cent diphenylcarbazide, and 0 to 4 ml. of acetic acid in a total of 25 ml. of 0.46 M. perchloric acid. These solutions were heated, extracted, and their absorbancy measured versus a reagent blank as previously described in Section C. The experiments were repeated with solutions which were 0.93 and 1.4 M. in perchloric acid. The results of the experiments are presented in Figure 9. Absorption spectra of several of the extracts were also obtained and are shown in Figure 10.

E. Effect of Reagent and Ethanol Concentrations

Solutions were prepared which contained 0.16 M. perchloric acid, 1.4 M. acetic acid, and 19 γ of osmium. From 1 to 5 ml. of 0.2-per cent diphenylcarbazide in ethanol was added plus sufficient ethanol to make the volume of ethanol 5 ml. in a total volume of 25 ml. These solutions were treated as in Section C, and their absorbancy measured versus a reagent blank. This experiment was repeated, except that 0.5 to 2 ml. of 0.5-per cent diphenylcarbazide was added and the total volume of ethanol was adjusted to 2 ml. The results of these experiments are presented in Figure 11. The effect of ethanol concentration

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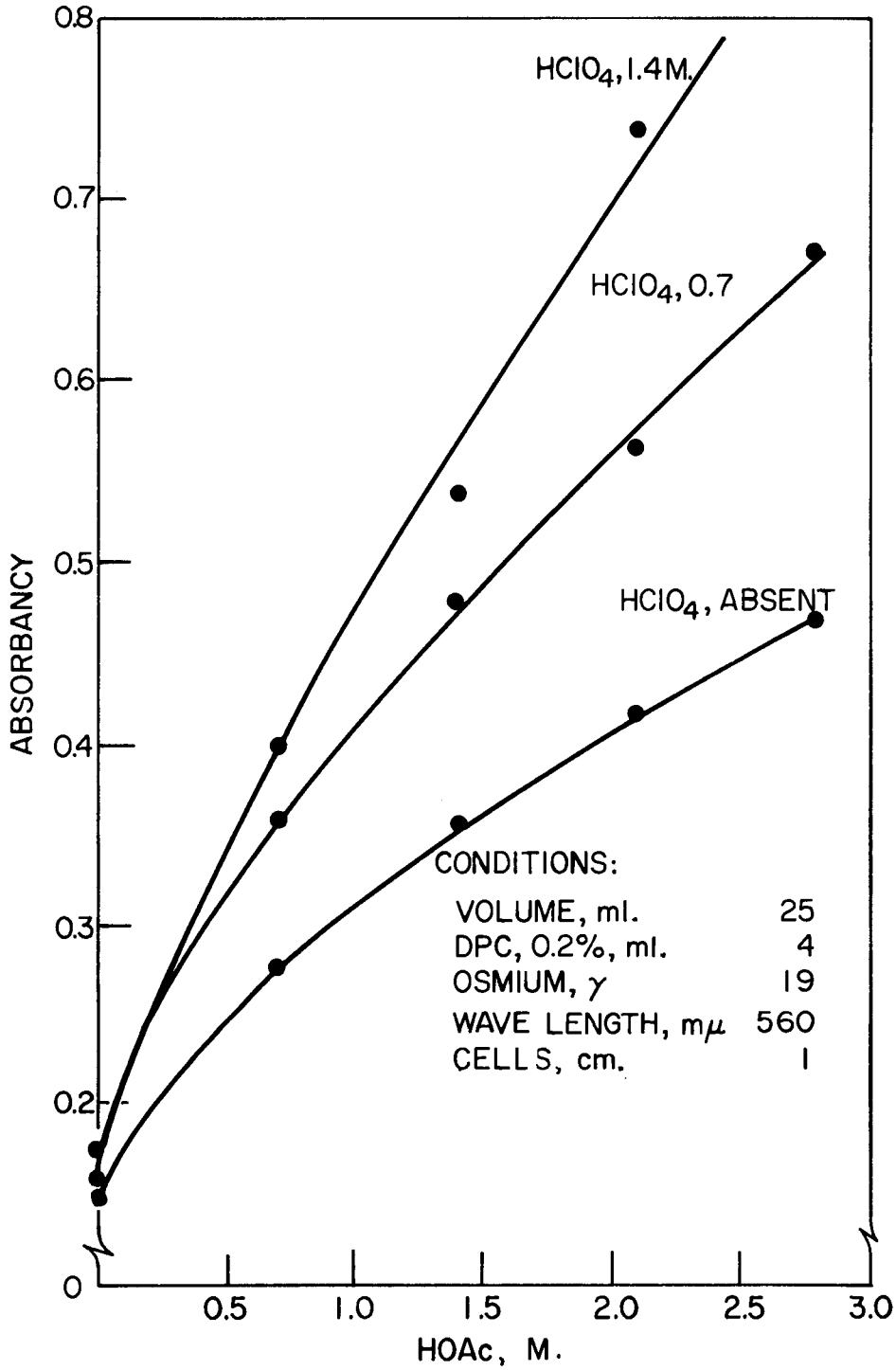

FIGURE 9. EFFECT OF ACETIC ACID CONCENTRATION ON THE ABSORBANCY OF OSMIUM-DIPHENYLCARBAZIDE EXTRACTS

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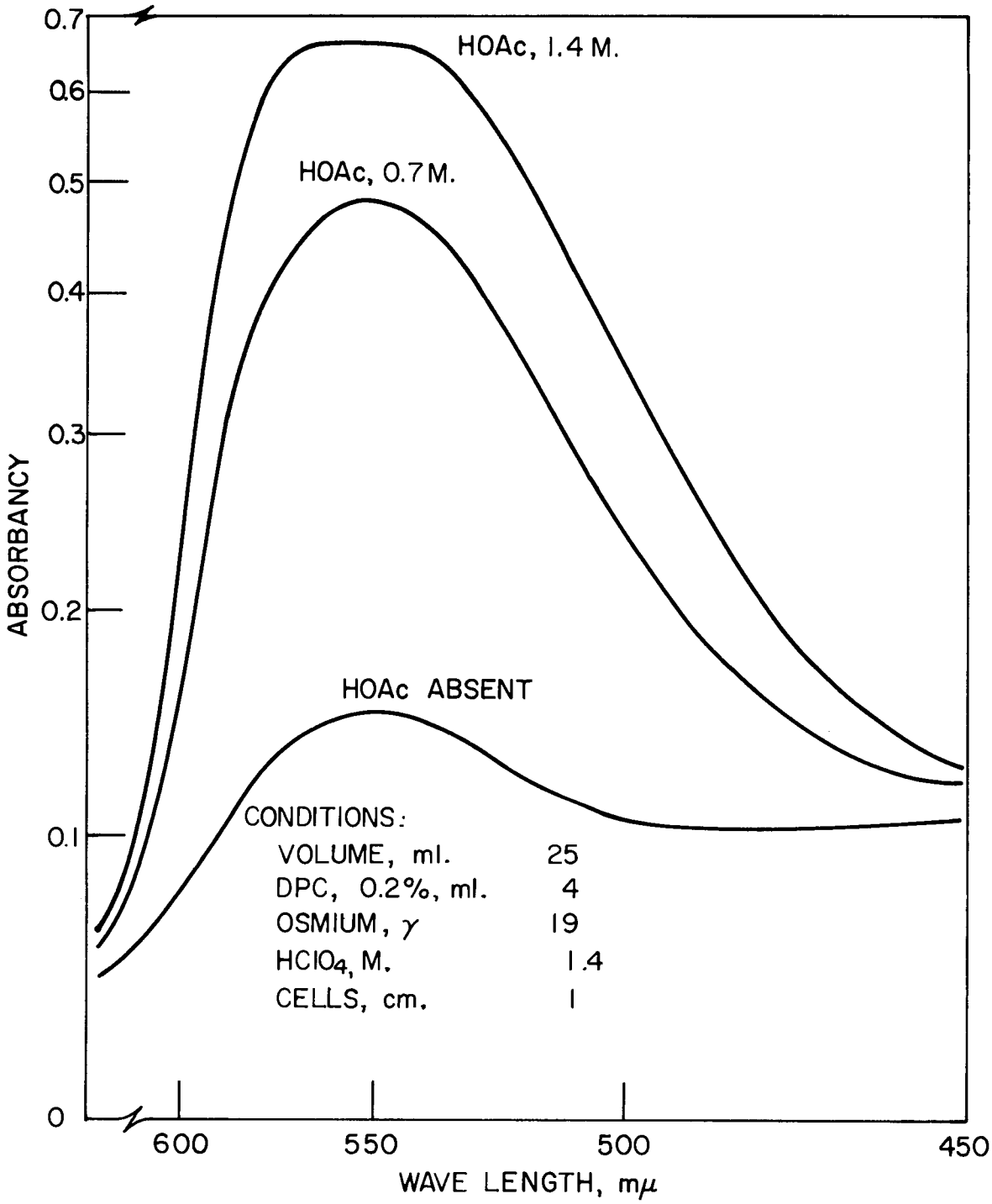

FIGURE 10. EFFECT OF ACETIC ACID CONCENTRATION ON THE ABSORPTION SPECTRUM OF THE OSMIUM-DIPHENYL-CARBAZIDE EXTRACTS

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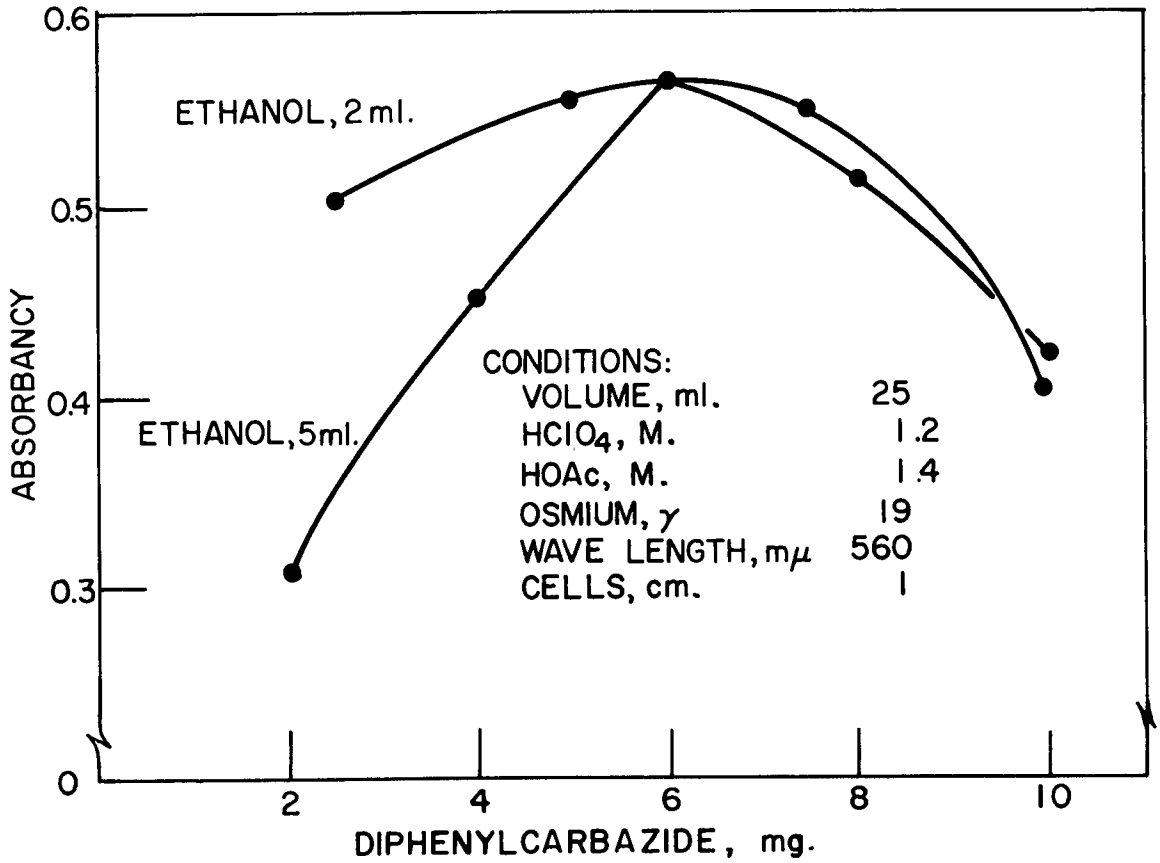

FIGURE 11. EFFECT OF REAGENT CONCENTRATION ON THE ABSORBANCY OF THE OSMIUM-DIPHENYLCARBAZIDE EXTRACTS

on the absorbancies was determined by preparing solutions containing the same concentration of perchloric acid, acetic acid and osmium concentration as previously plus 2 mg. of diphenylcarbazide. Then from 1 to 5 ml. of ethanol was added and the solutions were extracted as usual. This was repeated with aqueous solutions containing 6 mg. of diphenylcarbazide. The results of both experiments are presented in Figure 12.

F. Effect of Order of Addition of Reagents

Solutions were prepared which were 1.2 M. in perchloric acid, 1.4 M. in acetic acid, and contained 3 ml. of 0.2-per cent diphenylcarbazide in ethanol and from 7.6 to 22.8 γ of osmium in a total volume of 25 ml. In series A the order of addition of the reagents was osmium, acid, diphenylcarbazide; in series B, acid, osmium, diphenylcarbazide; and in series C, acid, diphenylcarbazide, osmium. These solutions were heated, and extracted as previously described (Section C) and their absorbancies measured at 560 mμ versus a reagent blank. The data are presented in Table IX. The absorption spectrum of a solution containing 19 γ of osmium which was treated as in series C is shown in Figure 13.

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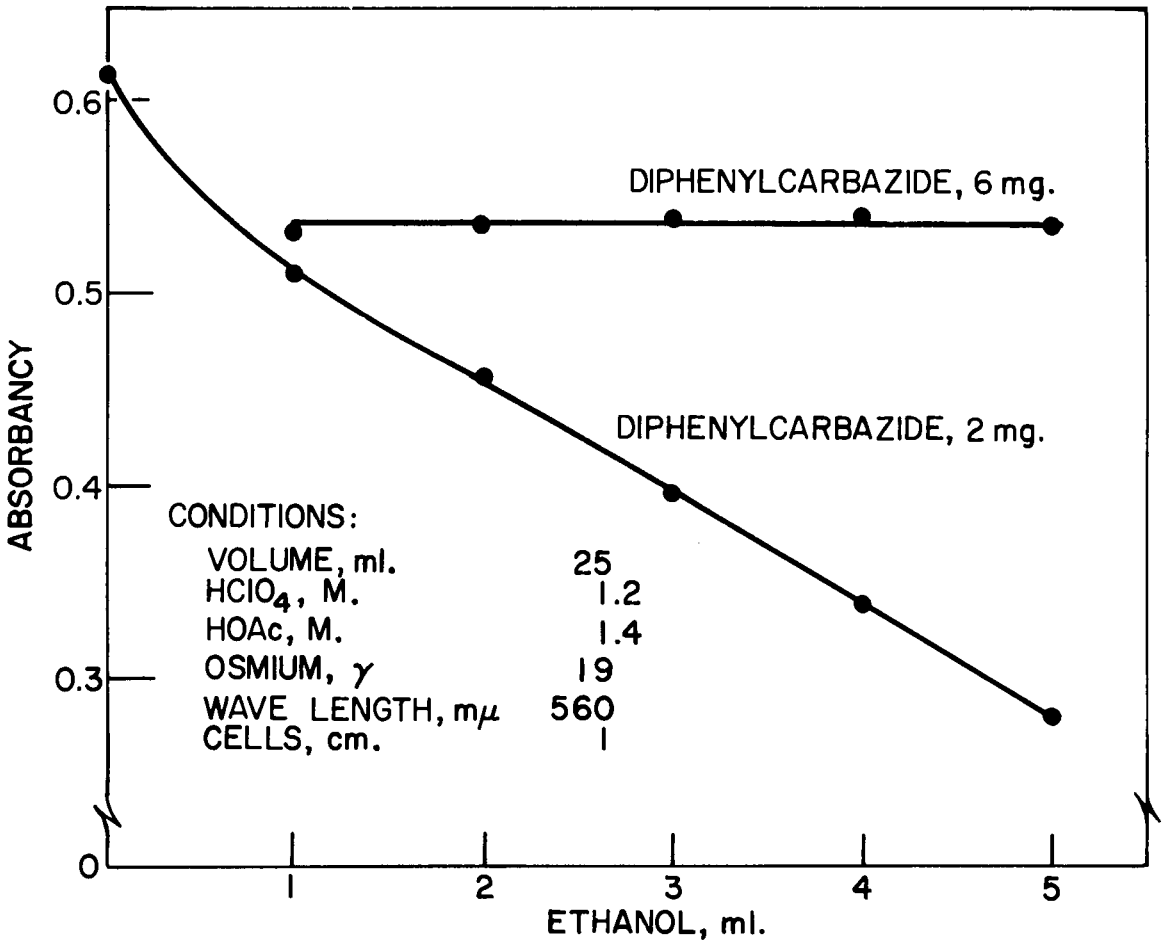

FIGURE 12. EFFECT OF ETHANOL CONCENTRATION ON THE ABSORBANCY OF THE OSMIUM-DIPHENYLCARBAZIDE EXTRACTS

TABLE IX

EFFECT OF ORDER OF ADDITION OF REAGENTS

Conditions:	
Volume, ml.	25
$HClO_4$, M.	1.2
HOAc, M.	1.4
DPC, 0.2%, ml.	3
Wave length, mμ	560
Cells, cm.	1

Osmium		A[a]	B[a]	C[a]
γ	M. x 10^6	Absorbancy		
7.6	1.60	0.137	0.195	0.225
11.4	2.40	0.230	0.293	0.335
15.2	3.20	0.288	0.452	0.483
19.2	4.00	0.387	0.531	0.617
22.8	4.80	0.479	0.632	0.771
Molar absorbancy index		93,600	129,000	148,000
Coefficient of variation, per cent		6	6	6

(a) Refers to order of addition of reagents described on page 36.

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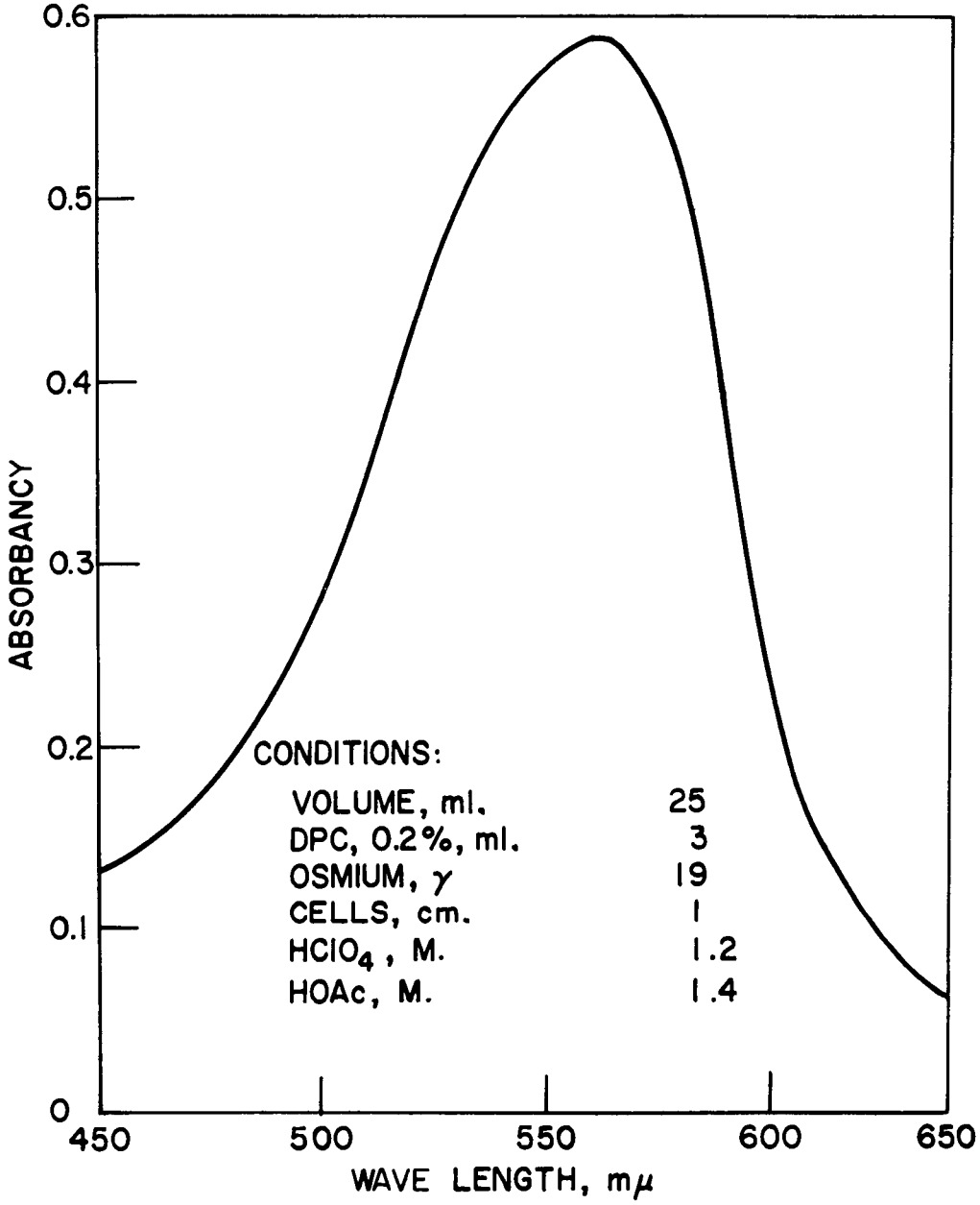

FIGURE 13. ABSORPTION SPECTRUM OF THE OSMIUM-DIPHENYLCARBAZIDE COMPLEX EXTRACTED WITH CHLOROFORM FROM AN AQUEOUS MEDIUM

G. Effect of Foreign Substances

Solutions were prepared which were 1.2 M. in perchloric acid, 1.4 M. in acetic acid, and which contained 3 ml. of 0.2-per cent diphenylcarbazide and 1 mg. of the substance to be tested, in a volume of 25 ml. Each substance was tested separately. These solutions were heated, extracted, and the absorbancy of the extracts measured as previously described (Section E). The results of these experiments are presented in Table X.

The effects of various anions were determined by preparing osmium tetroxide solutions containing 19 γ of osmium per ml. in 0.1 M. hydrochloric acid, nitric acid, hydrofluoric acid or phosphoric acid individually and then treating 1-ml. aliquots of these solutions as previously described in Section C.

TABLE X

EFFECT OF FOREIGN SUBSTANCES

Conditions:		
	Volume, ml.	25
	$HClO_4$, M.	1.2
	HOAc, M.	1.4
	DPC, 0.2%, ml.	3
	Wave length, mμ	560
	Cells, cm.	1

Foreign Substance	mg.	Osmium, γ Present	Osmium, γ Found	γ of Substance Equivalent to 1 γ Os
U(VI), Th(IV), Cr(III), Co(II), Ti(IV), Mn(II), Cd(II), Zr(IV), La(III), Pt(II), Pd(II), Rh(III)	1	0	0	-
Fe(III)	1	0	54	17
Cr(VI)	1	0	6.6	150
Ni(II)	1	0	3	330
Cu(II)	1	0	14	70
Mo(VI)	1	0	2.5	420
Ru(III)	1	0	18	55
Ir(III)	1	0	4	250
Au(III)	1	0	25	40
Cl^-	(a)	19.0	12.8	-
NO_3^-	(a)	19.0	20.1	-
$PO_4^{\equiv}$	(a)	19.0	19.2	-
F^-	(a)	19.0	19.8	-

(a) 0.1 M.

CHAPTER VI

RESULTS AND DISCUSSION

The experimental work described in Chapters III, IV, and V on the development of three methods for the determination of osmium consisted of a study of several variables. The results of these experiments, together with observations which were made, were evaluated in order to establish the optimum conditions for analytical procedures. Conditions which were considered were: the composition and temperature of the aqueous solutions, the organic solvent, wave length of maximum absorbancy, the effect of time on color development, and the effects of foreign substances. The precision of each method was also evaluated.

A. Extraction of Osmium Tetroxide and Measurements Of Its Ultraviolet Absorbancy

1. Extraction of Osmium Tetroxide

Although osmium tetroxide can be extracted from acid solutions by many organic solvents, chloroform was chosen as the extractant for several reasons. Since the extractions are made from a nitric acid solution, many elements besides osmium, including thorium and uranium, would be extracted if the solvent is polar and has a functional group which contains oxygen.[27] A non-polar solvent is, therefore, preferred for the selective extraction of osmium. In addition, it is more convenient to use a solvent heavier than water than one which is lighter.

Chloroform was chosen rather than carbon tetrachloride since the distribution ratio of osmium tetroxide between the organic and aqueous phases is 19.1 when chloroform is used as the extractant compared to 13.0 when carbon tetrachloride is used.[21] From the distribution ratio of 19.1 it was calculated that 99.6 per cent of the osmium was extracted by the recommended procedure. Since the precision of ordinary spectrophotometric measurements is of the order of 3 per cent,[8] a loss of 0.4 per cent of the osmium is not significant.

The absorption spectrum of osmium tetroxide also depends on the solvent. Well defined absorption bands are observed in non-polar solvents, while the spectrum in polar solvents, such as water or ethanol, is a smooth, featureless curve.

Although, in these experiments, the osmium originally present was in the octavalent state, the method has general applicability since osmium can be oxidized readily from any of its lower valence states to the octavalent state by nitric acid or potassium permanganate.[13]

2. Ultraviolet Absorption Spectrum of Osmium Tetroxide

Although the ultraviolet absorption spectra of osmium tetroxide in organic solvents have been previously reported,[28] the absorbancy of osmium tetroxide has not been utilized previously for analytical purposes.

The ultraviolet absorption spectrum of osmium tetroxide in chloroform, which is shown in Figure 1, exhibits the same features as the spectra previously reported in chloroform and hexane.[28] A series of absorption bands is present which have absorption peaks at 282, 289,

297, 304 and 312 mμ. Below 260 mμ the absorbancy of the osmium tetroxide solution increases rapidly. Since the absorbancy of the chloroform blank is also appreciable below 260 mμ, this region is not suitable for spectrophotometric measurements. Above 320 mμ the absorbancy of the osmium tetroxide solution is very small.

3. Calibration Curves for the Determination of Osmium

The calibration data for the determination of osmium which were obtained for the five band systems which center at 282, 289, 297, 304 and 312 mμ adhere to Beer's law. The coefficient of variation of the calculated molar absorbancy indexes is, in all cases, less than 2 per cent. In order to evaluate the range of osmium concentrations which can be determined with minimum error for each wave length, the calibration data were plotted as per cent transmittancy versus log of the osmium concentration according to the method of Ringbom.[26] From this plot, shown in Figure 2, the optimum concentration ranges were evaluated and are shown in Table I. From the results it is indicated that by proper choice of the wave length, 0.4 to 3.3 mg. of osmium can be determined with a coefficient of variation of about 3 per cent. The absorbancy values of the osmium tetroxide extracts remained constant over a period of at least five hours.

4. Effect of Foreign Substances

The effect of foreign substances on the determination of milligram quantities of osmium is shown in Table II. From the results it can be seen that the cations which are normally found as minor components in

uranyl sulfate solutions do not interfere. In the presence of more than 500 mg. of Cr(VI), however, high results were obtained. Metals of the platinum group in their lower valence states were also tested, and it was found that they do not interfere. Ruthenium in the octavalent state is known to interfere since ruthenium tetroxide extracts along with osmium tetroxide,[29] and also absorbs ultraviolet light. Ruthenium tetroxide and osmium tetroxide, however, may be reduced with iron(II) and the osmium then selectively reoxidized to the octavalent state with nitric acid and extracted.[21] Of the anions that were tested, perchlorate, sulfate, and phosphate do not interfere. In the presence of chloride, low results were obtained since chloride forms complex ions with quadrivalent and sexavalent osmium and inhibits the complete oxidation and subsequent extraction of osmium.[21] Since the chloride concentration in uranyl sulfate solutions is very low, the interference from such small amounts is insignificant.

B. Extraction of Osmium Tetroxide and Reaction with Diphenylcarbazide

1. Absorption Spectrum of the Osmium-Diphenylcarbazide Complex

The absorption spectrum of the product of the reaction between osmium tetroxide and diphenylcarbazide, which is shown in Figure 3, has a broad absorption band between 500 and 600 mμ with peak absorbancy between 550 and 560 mμ. Consequently, absorbancy measurements were made at 560 mμ. Since freshly prepared diphenylcarbazide reagent itself does not absorb appreciably between 400 and 700 mμ, its spectrum is not shown.

2. Effect of the Diphenylcarbazide Reagent Concentration

Tests were made of the reagent concentration necessary to produce maximum absorbancy. From the results, which are shown in Table IV, it is indicated that 3 ml. of 0.2-per cent diphenylcarbazide in a volume of 25 ml. is sufficient for complete color development. No significant increase in absorbancy was observed when up to 5 ml. of reagent solution was utilized. To assure an adequate excess of reagent, however, a 5-ml. volume was utilized in subsequent experiments. This represents an 80:1 molar ratio of reagent to osmium.

3. Effect of Ethanol Concentration

The effect of the total ethanol concentration was investigated and it was established that the absorbancy was constant when between 1 and 5 ml. of ethanol was present in the 25-ml. volume.

4. Effect of Time of Color Development

It was observed that the absorbancy of the osmium-diphenylcarbazide solutions increased with time. Therefore, a study was carried out whereby the absorbancy of the solutions was measured as a function of time. The results are presented in Figure 4. The color increased over a period of at least twenty-four hours. However, the rate of increase was small after the first hour. For instance, between one and two hours the absorbancies increased by about 5 per cent; between two and three hours the increase was about 1 per cent; and over the next twenty-one hours the increase was only about 17 per cent. After a color development period of two hours, the rate of increase of the absorbancies was

therefore, only about 1 per cent per hour and, within reasonable limits, the time of color development was not a critical factor after the first two hours.

Attempts were made to increase the rate of color development so that maximum absorbancy was reached rapidly by heating the final solution, by the addition of various compounds to the final solution, and by the introduction of the diphenylcarbazide reagent in solvents other than ethanol. When the organic extracts were heated, erratic results were obtained. In some cases the diphenylcarbazide reagent was apparently oxidized, giving the solutions a deep red color, and in other cases the solutions were completely decolorized. No advantage was realized through the use of acetone or methanol as the solvent for the diphenylcarbazide instead of ethanol. Although higher absorbancy values were obtained after a period of two hours for development of color when methanol was used as the solvent, the measurements were not reproducible. The addition of about 2 g. of formic acid, acetic acid, or phenol to the organic extracts resulted in higher absorbancy measurements. However, the rate of increase of the absorbancy was appreciable, even after two hours, so that the time of color development was a critical factor in obtaining reproducible measurements. The color was bleached when 2 g. of triethylamine was added to the extracts. In general, the methods tested for decreasing the period required for color development adversely affected the sensitivity or reproducibility of the osmium determination and none of them, therefore, was completely successful.

5. Adherence to Beer's Law

The data in Table V showing the adherence of the absorbancies of the osmium-diphenylcarbazide solutions to Beer's law after a color development period of two hours also demonstrates the reproducibility of the absorbancy measurements. Statistical analysis of the five sets of data showed that there was no significant difference in the molar absorbancy index or coefficient of variation obtained for each individual set. In no case was the coefficient of variation for any of the five series of absorbancy measurements more than 6 per cent; the average was 3 per cent. Using the average molar absorbancy index of 31,000, this method is suitable for the determination of 8 to 130 γ of osmium, with an optimum range of 30 to 100 γ, with a coefficient of variation of about 4 per cent.

6. Effect of Foreign Substances

Tests of the elements which are commonly found in uranyl sulfate solutions (Table VI) demonstrated that none of them interfere in the determination of osmium. The error which was found, even in the presence of 500-mg. quantities of uranium or thorium, was 5 per cent. Although it is possible that some of the elements tested will react with diphenylcarbazide, the extraction procedure selectively separates the osmium. Interference tests were carried out on metals of the platinum group which revealed that Ru(VIII) alone of this group of elements interfered with the determination of osmium. Ruthenium tetroxide is co-extracted with osmium tetroxide and reacts with diphenylcarbazide to

give a violet-colored reaction product. However, it is possible to oxidize osmium to osmium tetroxide without oxidizing ruthenium to ruthenium tetroxide, and, therefore, osmium can be separated from ruthenium if both are initially present in a reduced state. Ruthenium(III) does not interfere in the determination of osmium.

C. Reaction of Osmium with Diphenylcarbazide in Aqueous Media

1. Effect of Time of Color Development

From the results given in Figure 5 it was established that when the osmium-diphenylcarbazide compound is formed in an aqueous solution and is then extracted with chloroform, two variable time factors must be considered; the period of time during which the color develops in the aqueous phase after addition of the chromogenic reagent, and the period of time which elapses after the extraction and prior to the measurement of the absorbancy. Of these two factors the former seems to be more critical. A period of thirty minutes for color development in the aqueous phase followed by a short color development period in the extract resulted in a much higher absorbancy than the reverse situation. After a fifteen-minute period for color development in both the aqueous and the organic phases, the rate of increase of the absorbancies of the extracts was very small. However, the final absorbancy obtained depended on the time allowed for color development in the aqueous phase.

2. Effect of Temperature

Since it was apparent that the final absorbancy of the extracts depended on the extent to which the osmium had reacted with diphenylcarbazide prior to the extraction, the aqueous solutions were heated in order to increase the reaction rate. From these data which are shown in Table VII, it is indicated that the reaction is accelerated by heating the aqueous solution because, as the aqueous phase is heated to higher temperatures, the absorbancy is increased. When the aqueous solutions were heated to 65° prior to extraction the rate of increase of the absorbancy of the extracts was very small; an increase of about 8 per cent was observed over a period of twenty-four hours. When the aqueous solutions were heated to 35° or 50° the absorbancy of the extracts was not constant but depended on the time allowed for color development in the organic phase. In general, it appeared that the reaction between osmium and diphenylcarbazide was forced almost to completion by heating the solutions to 65°, and therefore when the reaction product was extracted no further period for color development in the organic phase was necessary. This conclusion was confirmed by heating a series of solutions to 65°, allowing the solutions to cool for periods of time from zero to thirty minutes and then extracting with chloroform. The data, which are presented in Table VIII, demonstrated that by heating the aqueous solutions to 65°, allowing them to cool for about fifteen minutes, and then extracting with chloroform, the absorbancy of the extracts reached

its maximum value immediately and did not further increase with time. It is probable that maximum absorbancy can also be obtained by heating the solutions at a lower temperature for a longer period of time. At temperatures higher than 65° there is a tendency for the reagent to oxidize.

3. Effect of Perchloric Acid Concentration

Results of studies of the absorbancy of the aqueous osmium-diphenylcarbazide solutions as a function of pH (Figure 6), indicated that maximum absorbancy was obtained over a pH range of 2 to 4. At higher and lower pH values the absorbancy decreased sharply. In alkaline solutions the diphenylcarbazide reagent was apparently oxidized by atomspheric oxygen since the solutions turned a deep red color.

When the aqueous solutions were extracted with chloroform and the organic extracts diluted with chloroform to the same volume as the original aqueous solutions, the absorbancy of the extracts was much higher than that of the original aqueous solutions. Greater sensitivity was therefore obtained by means of the extraction. In Figure 7 the absorbancy of the extracts is plotted as a function of the perchloric acid concentration of the aqueous phase, at various acetic acid concentrations. In contrast to the absorbancy of the aqueous solutions, which reached a maximum when the pH of the solutions was between 2 and 4, the absorbancies of the extracts increased as the perchloric acid concentration was increased up to about one molar. The absorbancy of the extracts was constant when the perchloric acid concentration was between

about 1 and 1.5 M. Further increasing the acidity up to 2.3 M. resulted in a further increase in the absorbancies. The absorption spectrum of the extracts also depended on the acidity of the aqueous phase as shown in Figure 8. As the perchloric acid concentration of the aqueous phase increased, not only did the absorbancy of the extracts at the absorption peak increase but the absorbancy at all wave lengths below 600 mμ also increased. This change in the absorption spectrum of the extracts resulted in a change in their color from blue-violet to red-violet. It is possible that the shift in the absorption spectrum of the extracts is due to a change in the composition of the osmium-diphenylcarbazide compound which is extracted. In subsequent work the perchloric acid concentration was adjusted to 1.2 M. since small variations in the acidity at this concentration level had no effect on the final absorbancy of the extracts.

4. Effect of Acetic Acid Concentration

As the acetic acid concentration of the aqueous phase was increased the absorbancy of the chloroform extracts also increased (Figure 9). This increase in absorbancy was almost linear with respect to the acetic acid concentration, and apparently occurred at all perchloric acid concentrations. Since small variations in the acetic acid concentration of the aqueous phase will seriously affect the absorbancy of the extracts, the acetic acid concentration must be carefully controlled. Consequently, all the components of the aqueous solutions, including the water, were added by means of a pipet or a buret. The

absorption spectra of the extracts from solutions containing various concentrations of acetic acid (Figure 10), showed that as the acetic acid concentration increased, the absorption of the extracts in the region between 500 and 600 mμ increased. In contrast to the effect of the perchloric acid concentration on the absorption spectrum, in which case there was an apparent change in the spectrum, an increase in the acetic acid concentration resulted in an increase in the intensity of the absorption band without any shift of the absorption spectrum.

5. Effect of Concentration of Chromogenic Reagent and Ethanol on Absorbancy

Both the concentration of the chromogenic reagent (diphenylcarbazide) and ethanol affect the absorbancy and the two effects are interdependent. With either 2 or 5 ml. of ethanol in a total volume of 25 ml., the absorbancy increases as the amount of diphenylcarbazide added is increased up to 6 mg., after which it decreases somewhat (see Figure 11). The absorbancy of solutions containing less than 6 mg. of diphenylcarbazide is greater when 2 ml. of ethanol is added than when 5 ml. is used. When 6 mg. of diphenylcarbazide is added, the absorbancy is constant for different proportions of ethanol ranging from 1 to 5 ml. in 25 ml. of total volume (see Figure 12). If, however, only 2 mg. of diphenylcarbazide is added, the absorbancy decreases with an increase in ethanol content, the decrease being practically linear over the concentration range from 1 to 5 ml. of ethanol.

Although the highest absorbancy was obtained when no ethanol was present, it was concluded that it was not desirable to eliminate ethanol from the aqueous solutions. When the diphenylcarbazide reagent was prepared in an acetic acid solution rather than ethanol the reagent solution was much less stable than the ethanolic reagent solution of the same concentration, and decomposed significantly in a period of one hour. In addition, the reagent-grade chloroform which was used to extract the osmium-diphenylcarbazide complex contained about 0.5 per cent ethanol as a preservative, and, therefore, it would be necessary to purify the chloroform if ethanol were to be excluded completely. Moreover, when 6 mg. of diphenylcarbazide was present the ethanol concentration was not a critical factor, and the decrease in the absorbancy as a result of the introduction of ethanol was only about 10 per cent. This loss of sensitivity can be compensated for by increasing the perchloric or acetic acid concentration.

6. Effect of Order of Addition of Reagents

The order of the addition of the reagents to the aqueous solutions had a substantial effect on the final absorbancy of the extracts (Table IX). Highest absorbancies were obtained when the osmium was added to acidic aqueous solutions containing the diphenylcarbazide reagent; somewhat lower absorbancies were observed when the osmium was added to the acidic solutions prior to the diphenylcarbazide reagent; and the lowest absorbancies were found when the acids and then the diphenylcarbazide

were added to aqueous osmium solutions. In all three cases the absorbancies adhered to Beer's law with a coefficient of variation of about 6 per cent, as shown in Table IX. Therefore, in the recommended procedure for maximum sensitivity, the sample containing the osmium should be added to the aqueous solutions of the proper acid concentrations, containing the diphenylcarbazide reagent.

The optimum concentration range for the determination of osmium by this procedure was evaluated by the method of Ringbom and was found to be from 7.5 to 26 γ of osmium in the sample taken for analysis. A total range of from 1.5 to 30 γ can be determined.

The absorbancy of the extracts was constant over a period of twenty-four hours.

7. Absorption Spectrum of the Osmium-Diphenylcarbazide Complex

The absorption spectrum of the osmium-diphenylcarbazide complex formed in an aqueous medium in the presence of perchloric and acetic acids and then extracted (Figure 13), was compared with the absorption spectrum of the osmium-diphenylcarbazide complex formed in a chloroform medium (Figure 3). The two spectra showed the same general features, a broad absorption band between 500 and 600 mμ. However, the absorbancy at 560 mμ, the absorption peak, is much higher when the complex is extracted with chloroform rather than formed in the chloroform solution, and the absorbancies at wave lengths below 500 mμ and above 600 mμ are lower. When acetic acid was added to osmium-diphenylcarbazide-chloroform solutions (see p. 47) the absorbancy of the solutions

at 560 mμ was increased indicating that the presence of acetic acid does have an effect on the absorption spectrum of the osmium-diphenylcarbazide species. Since the extracted osmium-diphenylcarbazide species is probably associated with perchlorate ion or acetic acid molecules, the difference in absorption spectra can probably be attributed to this difference in the composition of the absorbing species.

8. Effect of Organic Extractant

In conjunction with these tests, several solvents besides chloroform were utilized for the extraction of the osmium-diphenylcarbazide complex. The absorbancy of the extracts at 560 mμ was essentially the same when chloroform, carbon tetrachloride, or xylene was utilized as the extractant. Lower absorbancies were obtained with bromobenzene, isoamyl alcohol, and isoamyl acetate, and only a very small absorbancy was observed with methyl isobutyl ketone.

Since the extractions were performed with two successive portions of the solvent, the efficiency with which each solvent extracted the osmium-diphenylcarbazide complex could be compared by noting the intensity of the blue-violet color in the second extract. In this respect, chloroform was clearly a more efficient extractant than either carbon tetrachloride or xylene since the second chloroform extract was almost colorless while the second carbon tetrachloride and xylene extracts were substantially colored. The absorbancies of the reagent blank extracts were about the same in all cases.

9. Effect of Foreign Substances

To determine whether other elements also produced colored extracts, 1-mg. quantities of various elements were treated by the recommended procedure. As shown in Table X, Fe(III), Cr(VI), Ni(II), Cu(II), Mo(VI), Ru(III), Ir(III), and Au(III) formed extractible complexes with diphenylcarbazide which would interfere in the determination of osmium. In the case of Cr(VI), the aqueous solution was an intense red-violet in color, however, the colored complex was only partially extractible under these conditions. The other interfering elements produced a brown color in the aqueous solutions, and red-violet extracts. Palladium(II) produced yellow colored aqueous solutions and extracts which showed no absorbancy at 560 mμ. In order to indicate clearly the amount of each interfering element which can be present without interfering in the determination of osmium, the quantity of the element which produces the same absorbancy measurement as 1 γ of osmium was calculated. It was assumed that the absorbancy of the interfering elements adhered to Beer's law. Therefore, if the approximate amount of osmium present in a sample and the permissible error in the determination are known, the quantity of the interfering ions which may also be present can be readily calculated from the data in Table X.

The effect of some common anions was determined by preparing solutions containing 19 γ of osmium per ml. in 0.1 M. solutions of the appropriate acid, allowing these solutions to stand for twenty-four hours, and then treating a 1-ml. aliquot by the recommended procedure. Identical

results were obtained when the acid anion was perchlorate, sulfate, phosphate, fluoride, or nitrate. In the presence of chloride the absorbancies were significantly lower, probably due to the formation of osmium chloro-complexes which prevented the complete reaction of osmium with the diphenylcarbazide.

D. Nature of the Complex

No actual experimental work was performed to elucidate the nature of the reaction between osmium and diphenylcarbazide, the valence state of osmium in the reaction product, and the structure of the reaction product. It is possible, however, to postulate the nature of the osmium-diphenylcarbazide complex by comparing the results obtained here with previously reported work on diphenylcarbazide reactions and on organo-metallic osmium compounds. It has been shown[30] that osmium tetroxide reacts with 1:2:3-benzotriazole to yield an insoluble product with the formula $Os(OH)_3(C_6H_4NHN_3)_3$. Osmium tetroxide also reacts with thiourea[31] to yield $Os(NH_2CSNH_2)_6^{+3}$. Yoe and Steele[16] have reported on the reaction of osmium tetroxide with various naphthylaminesulfonic acids to give products which contained two moles of reagent for each mole of osmium. They suggest that the reaction involves the amine group since compounds in which substitutions had been made on the amine nitrogen failed to react with osmium, and in every case where sulfonic acid groups were adjacent to the amine group the reaction was very slow. The valence state of the osmium in the final product was not determined.

The colored compounds were not soluble in organic solvents, indicating that they are charged species. In the method suggested by Geilman and Neeb[14] for the determination of osmium with o,o'-ditolylthiourea and 1,4-diphenylthiosemicarbazide, the osmium was originally present in their samples as $OsCl_6^{=}$. It was necessary, however, to add stannous chloride for the formation of the colored product, which indicates that the osmium must first be reduced from the quadrivalent to the trivalent state. Moreover, compounds such as Os(1,10-phenanthroline)$_3$(ClO_4)$_3$.H_2O and Os(2,2'-bipyridine)$_3$(ClO_4)$_3$.H_2O[32,33] have been prepared. All these reactions strongly suggest that osmium, in the trivalent state, is capable of forming up to six coordinate linkages with primary, secondary, or tertiary amino-nitrogen atoms. The resulting compounds have a net positive charge and are not normally extractible by organic solvents unless a sufficiently high concentration of anions is present which lead to the formation of ion-association compounds.

Diphenylcarbazide reacts with numerous metal ions to form inner complex compounds.[34] Its reaction with Cr(VI), however, is apparently of a different nature. On the basis of their studies, Pflaum and Howick[35] concluded that the colored species was a Cr(III)-diphenylcarbazone complex but not an inner complex salt; that the complex is a cationic species; and that the complex is extracted, together with an anion, into non-aqueous media as a neutral molecule. Other workers have confirmed the fact that the complex is a cation which contains chromium and is extractible from solutions which contain a high concentration of

salts.[36] The reaction of diphenylcarbazide with Os(VIII) is similar in many respects to the Cr(VI) reaction. The reactions in both cases depend on the acid concentration of the aqueous solutions, and the optimum acid concentration for maximum color development is fairly high; about 0.1 M. for the Cr(VI) reaction and about 1.2 M. for the Os(VIII) reaction.

It was also shown that the extractibility of the osmium-diphenylcarbazide complex increased as the concentration of anions in the solution increased. Since the reaction of diphenylcarbazide with metal ions to form inner complex salts generally occurs in weakly acid or basic solutions to form a neutral molecule which is completely extractible from aqueous solutions of very low ionic concentration,[34] it is probable that the osmium-diphenylcarbazide complex is a cation, and that it is not an inner complex salt. From the previous discussion of known organometallic osmium compounds, it is also probable that the osmium in the reaction product is in the trivalent state, and that coordinate linkages are formed between the osmium and the amino-nitrogen groups of the diphenylcarbazide, or its oxidation product, diphenylcarbazone.

CHAPTER VII

CONCLUSION

Three methods were developed for the determination of osmium. From 0.4 to 3.3 mg. of osmium can be determined by Method A which involves first oxidizing the osmium to the octavalent state. The osmium tetroxide in 10 ml. of 30-per cent nitric acid is then extracted three times with 10-, 10-, and 5-ml. portions of chloroform. After washing with 10 ml. of 0.1 M. sulfuric acid, the extracts are drained into 25-ml. volumetric flasks containing about 1 g. of anhydrous sodium sulfate, and diluted to volume with chloroform. The absorbancy of the osmium tetroxide in chloroform is then measured at a wave length of 282, 289, 297, 304 or 312 mμ, depending on the concentration of osmium. The optimum concentration range and the coefficient of variation of determinations in that range were established for measurements at each wave length (Tables I and II). Of the foreign substances which were tested only chloride and octavalent ruthenium interfered in the determination. The primary advantages of this method are its rapidity and simplicity, its selectivity for osmium, and the fact that the initial valence state of the osmium does not have to be considered since the osmium can easily be oxidized to osmium tetroxide. The chief limitation of the method is the interference of chloride. If osmium is separated by the distillation of osmium tetroxide, the distillate is generally collected in 6 N. hydrochloric acid saturated with sulfur dioxide. Therefore, the method for

the determination of osmium as described is not applicable to solid samples or to other types of samples from which osmium must be separated by distillation. A procedure has been proposed, however, for eliminating chloride from aqueous osmium solutions;[9] or it may also be possible to utilize chloride-free solutions as absorbing solutions for osmium tetroxide distillates.[16] The interference of ruthenium can be eliminated by first reducing both ruthenium and osmium. Osmium can then be selectively oxidized to the octavalent state with nitric acid. Under these conditions, ruthenium remains in the trivalent state and is not extracted with chloroform. Although this method is not a very sensitive means of determining osmium and is best suited to the estimation of milligram quantities, its sensitivity is about three fourths that of the commonly utilized thiourea method. In the latter method a molar absorbancy index of about 2900 has been obtained compared to a value of 1870 found for Method A at 282 mμ.

For the determination of from 30 to 100 γ of osmium (Method B), osmium tetroxide in 10 ml. of 30-per cent nitric acid is extracted with two 10-ml. portions of chloroform, the extracts are washed with 10 ml. of 0.1 M. sulfuric acid, and then drained into 25-ml. volumetric flasks containing 5 ml. of 0.2-per cent diphenylcarbazide in ethanol and about 1 g. of anhydrous sodium sulfate. The absorbancy of the extracts is measured, after a color development of two hours, at 560 mμ versus a reagent blank. The molar absorbancy index is about 31,000 and a coefficient of variation of about 4 per cent was found in determinations

by this procedure. Attempts to eliminate the two-hour period for color development were unsuccessful. Octavalent ruthenium and chloride interfere in the determination of osmium. This method is also highly selective for osmium since the extraction of osmium as the tetroxide is employed. In addition Method B is about 20 times more sensitive than Method A and ten times more sensitive than the thiourea method. In general, a simple, selective, and precise method is provided for the determination of microgram quantities of osmium. A disadvantage of the method is the fact that a period of two hours for color development is required. The discussion of interfering substances and their elimination in Method A also applies here.

Method C involves the formation of the osmium-diphenylcarbazide complex in an aqueous medium, rather than in an organic extract. The complex is extracted with chloroform and the absorbancy of the extract is measured. Maximum sensitivity is obtained when the sample solution containing from 7.5 to 26 γ of osmium as the tetroxide is added to aqueous acid solutions containing 3 ml. of a 0.2-per cent diphenylcarbazide solution in ethanol. Suitable acid concentrations in the final solution are 1.2 M. for perchloric acid, and 1.4 M. for acetic acid. These solutions are then heated to 65°, allowed to cool to room temperature over a period of about fifteen minutes, and then extracted with two 10-ml. portions of chloroform. The extracts are drained into 25-ml. volumetric flasks containing about 1 g. of anhydrous sodium sulfate, diluted to volume with chloroform, and the absorbancy is measured at 560 mμ versus a reagent blank. Under these conditions, a molar

absorbancy index of about 150,000 was obtained with a coefficient of variation of 6 per cent. Of the foreign substances which were tested, Fe(III), Cu(II), Ru(III), and Au(III) interfere seriously in the determination of osmium, while Cr(VI), Ni(II), Mo(VI) and Ir(III) interfere only when the weight ratio of these elements to osmium is greater than 100:1. High concentrations of chloride (about 0.1 M.) prevent the complete formation of the complex. With the possible exception of the catalytic method,[22] the proposed method is by far the most sensitive means of determining osmium. A molar absorbancy index 50 times greater than that of the thiourea complex, and at least 5 times greater than in most other methods was obtained. It is necessary to sacrifice some of the selectivity for osmium which can be achieved through the extraction of osmium tetroxide, in order to obtain greater sensitivity. The substances interfering in this determination are no more numerous than in most other methods, and are fewer than the substances which interfere with the catalytic method.

In general, the three methods which were developed for the determination of osmium cover a concentration range of from 7 γ to 3.3 mg. of osmium in the sample taken for analysis. Very few sample types will contain osmium in concentrations outside of this range. The separation of osmium by extraction of the tetroxide can be utilized in preference to the tedious and time-consuming osmium tetroxide distillation. Measuring the absorbancy of osmium tetroxide in the chloroform extracts is a rapid means of determining osmium and developing the

osmium-diphenylcarbazide complex in the extracts provides a more sensitive method of determination. The formation of the osmium-diphenylcarbazide complex in the aqueous phase, followed by its extraction with chloroform, provides an extremely sensitive means of determining osmium. All three methods which have been proposed are applicable primarily to liquid samples and involve the oxidation of osmium to the octavalent state.

CHAPTER VIII

SUMMARY

Methods are described for the spectrophotometric determination of osmium over a concentration range from 7 γ to 3 mg. of osmium in the sample portion taken for analysis.

In Method A osmium is first oxidized to the octavalent state and the osmium tetroxide which is formed is selectively extracted with chloroform. The ultraviolet absorption spectrum of osmium tetroxide in chloroform has a series of absorption bands with peak absorbancies at 282, 289, 297, 304, and 312 mμ, and molar absorbancy indexes of 1870, 1760, 1640, 1400, and 1000, respectively. For each wave length, the optimum concentration range for the determination of osmium was evaluated by the method of Ringbom. By this method, from 0.4 to 3.3 mg. of osmium can be determined with a coefficient of variation of 3 per cent. Only chloride and octavalent ruthenium interfere in the determination.

In Method B the osmium is oxidized to osmium-tetroxide and then extracted with chloroform. Diphenylcarbazide is then added to the organic extract. A blue-violet colored reaction product is formed, which exhibits maximum absorbancy at 560 mμ. Beer's law is adhered to over a range of 30 to 100 γ of osmium with a coefficient of variation of about 4 per cent. After a period of two hours for color development the molar absorbancy index is about 31,000. A study was made of the

effects of foreign substances and only Ru(VIII) and chloride were found to interfere.

In Method C the osmium-diphenylcarbazide complex is formed in an aqueous acid solution at 65° and the complex is then extracted with chloroform. The absorbancy of the extract is measured at 560 mμ. From 7 to 26 γ of osmium can be determined with a coefficient of variation of about 6 per cent. A molar absorbancy index of about 150,000 is obtained. It was established that Fe(III), Cu(II), Ru(III), and Au(III) seriously interfere in the determination of osmium by this method, while Cr(VI), Ni(II), Mo(VI), Ir(III) and chloride interfere only when present in high concentrations.

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