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SUBJECT: Spectrophotometric Determination of  
Microgram Quantities of Osmium With  
Diphenylcarbazide by G. Goldstein

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## ABSTRACT

A method was developed for the spectrophotometric determination of 30 to 100  $\mu\text{g}$  of osmium. The osmium as  $\text{OsO}_4$  is extracted with  $\text{CHCl}_3$  and diphenylcarbazide is then added to the organic extract. A blue-violet reaction product is formed, the absorbancy of which is measured at 560  $\text{m}\mu$ . A suitable reagent concentration is from 3 to 5 ml of 0.2% diphenylcarbazide in a volume of 25 ml and the preferred solvent for the reagent is ethanol. Beer's law is followed over a range of 8 to 130  $\mu\text{g}$  of osmium with a coefficient of variation of about 4%. After a 2-hour color-development period the molar absorbancy index is 31,300. Attempts to achieve reproducible measurements of absorbancy in less than 2 hours were unsuccessful. A study was made of the effects of foreign elements and only Ru(VIII) was found to interfere.

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## DETERMINATION OF OSMIUM IN URANYL SULFATE SOLUTIONS

### Spectrophotometric Determination of Microgram Quantities of Osmium With Diphenylcarbazide

Gerald Goldstein

## INTRODUCTION

Previous work on the determination of osmium by extraction of  $\text{OsO}_4$  with  $\text{CHCl}_3$  and measurement of its absorbancy<sup>(1)</sup> showed that from 0.4 to 3.3 mg of osmium can be determined by this method. Since it is also necessary to determine lesser quantities of osmium, a survey was made of various chromogenic reagents to determine if any would react with  $\text{OsO}_4$  in  $\text{CHCl}_3$  to form a colored solution and provide a more sensitive method for determining osmium. It was desirable for the chromogenic reagent to react with the  $\text{OsO}_4$  in the chloroform phase because of the selectivity of the extraction procedure. Diphenylcarbazide was found to react with  $\text{OsO}_4$  in  $\text{CHCl}_3$  to give a blue-violet color.

### Apparatus

Beckman Model DU Spectrophotometer.

### Reagents

Osmium Tetroxide Solutions in 0.1 M  $\text{H}_2\text{SO}_4$ . The preparation of this standard solution was described previously.<sup>(1)</sup>

Diphenylcarbazide (DPC), 0.2% in absolute ethanol. Dissolve 100 mg of diphenylcarbazide (available as reagent No. 618 from Eastman Organic Chemicals, Rochester 3, N. Y.) in 50 ml of ethanol. This reagent is not stable for more than one working day and should be prepared daily.

## EXPERIMENTAL

A. Absorption Spectrum of the Osmium-Diphenylcarbazide Complex. A solution was prepared containing 38  $\mu\text{g}$  of osmium as  $\text{OsO}_4$  in a volume of 10 ml of 30%  $\text{HNO}_3$ . The osmium was extracted with two, 10-ml portions of  $\text{CHCl}_3$ . The extracts were washed with 10 ml of 0.1 M  $\text{H}_2\text{SO}_4$ , drained into a 25-ml volumetric flask containing 5 ml of 0.2% diphenylcarbazide (DPC) and about 1 g of anhydrous sodium sulfate, and then the solution was diluted to volume with  $\text{CHCl}_3$ . After an interval of 24 hours for color development, the absorption spectrum of the solution was determined versus a reagent blank, (see Figure 1).

B. Effect of Diphenylcarbazide Reagent Concentration. The optimum reagent concentration was determined by extracting solutions containing 96  $\mu$ g of osmium, washing the extracts, and drawing them into flasks containing from 0.5 to 5 ml of 0.2% DPC. Sufficient ethanol was added to the extracts to bring the total volume of alcohol to 5 ml, the solutions were diluted to volume with  $\text{CHCl}_3$ , and their absorbancies were measured versus a reagent blank at 560  $\text{m}\mu$ . These data are presented in Table I.

Table I

Effect of Diphenylcarbazide Concentration on the Absorbancy of the Osmium-Diphenylcarbazide Complex

Conditions:	Volume, ml	25
	Osmium, $\mu$ g	96
	Ethanol, ml	5
	Wavelength, $\text{m}\mu$	560
	Cells, cm	1

Diphenylcarbazide, 0.2% ml	Absorbancy
0.5	0.153
1	.340
2	.600
3	.749
4	.759
5	.769

C. Effect of Color Development Time. Solutions containing from 12 to 96  $\mu$ g of osmium were treated as in Section A. The absorbancy of each of the solutions was measured as a function of time. These data are presented in Table II.

Table II

Effect of Color Development Time on the Absorbancy of the Osmium-Diphenylcarbazide Solutions

Conditions: Volume, ml 25  
Diphenylcarbazide, 0.2%  
Methanol, ml 5  
Wavelength,  $\mu\mu$  560  
Cells, cm 1

Time, Minutes	Osmium, $\mu\text{g}$				
	12	24	48	72	96
	Absorbancy				
0	0.048	0.134	0.272	0.387	0.550
30	.064	.146	.295	.416	.579
60	.065	.155	.310	.430	.595
90	.074	.162	.316	.440	.608
120	.079	.162	.320	.460	.615
180	.079	.169	.322	.462	.620
24 hours	.100	.195	.398	.562	.730

D. Adherence to Beer's Law. The adherence of the absorbancy of the osmium-diphenylcarbazide solution to Beer's Law, after a color development period of 2 hours, was tested by extracting 12 to 96  $\mu\text{g}$  of osmium, treating the solutions as in Section A, and measuring their absorbancy after 2 hours. Five series of solutions designated as I to V were prepared over a period of two weeks. These results are shown in Table III.

Table III

Adherence of Absorbancy of Osmium-Diphenylcarbazide  
Solutions to Beer's Law

Conditions: Volume, ml 25  
Diphenylcarbazide, 0.2% in ethanol, ml 5  
Color development time, hours 2  
Wavelength,  $\mu$  560  
Cells, cm 1

Osmium, $\mu$ g	Absorbancy					Average
	I	II	III	IV	V	
12	0.079	0.082	0.080	0.079	0.078	0.080
24	.162	.165	.151	.164	.173	.163
48	.322	.314	.300	.329	.342	.321
72	.462	.440	.450	.473	.470	.459
96	.615	.592	.611	.650	.642	.622
Molar Absorb- ancy Index	30,900	30,100	30,400	31,900	32,300	31,300
Coefficient of Var., %	2	6	3	2	5	3

E. Effects of Foreign Ions. Solutions containing 38.  $\mu$ g of osmium were prepared, and the appropriate quantity of the foreign substance to be tested was added. The solutions were then adjusted and extracted as in Section A, and their absorbancies measured after a color development period of 2 hours. The results are presented in Table IV.

Table IV

Effect of Foreign Substances on the Determination of Osmium

Conditions:	Volume, ml	25
	Diphenylcarbazide, 0.2%, ml	5
	Color development time, hours	2
	Wavelength, $\mu$	560
	Cells, cm	1
	Os, $\mu$ g	38

Element	Foreign Substance	mg	Found	Osmium, $\mu$ g	Error
U <sup>+6</sup>		500	38.7	0.7	
Th <sup>+4</sup>			40.0	2.0	
Fe <sup>+3</sup>		1	39.9	1.9	
Cr <sup>+6</sup>			38.5	0.5	
Cr <sup>+3</sup>			39.7	1.7	
Ni <sup>+2</sup>			40.3	2.3	
Cu <sup>+2</sup>			39.9	1.9	
Co <sup>+2</sup>			38.2	0.2	
Mo <sup>+6</sup>			37.6	-0.4	
Zr <sup>+4</sup>			38.8	0.8	
Au <sup>+3</sup>		1	39.0	1.0	
Pt <sup>+2</sup>			39.3	1.3	
Pd <sup>+2</sup>			38.7	0.7	
Ir <sup>+3</sup>			37.1	-0.9	
Rh <sup>+3</sup>			37.9	-0.1	
Ru <sup>+3</sup>			38.8	0.8	
Ru <sup>+8</sup>		0.3	49.3	11.3	

Discussion

The absorption spectrum of the product of the reaction between osmium tetroxide and diphenylcarbazide, which is shown in Figure 1, has a broad absorption band between 500 and 600  $\mu$  with peak absorbancy between 550 and 560  $\mu$ ; consequently, absorbancy measurements were made at 560  $\mu$ . Since the diphenylcarbazide reagent itself does not absorb appreciably between 400 and 700  $\mu$ , its spectrum is not shown.

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

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.

During these experiments it was observed that the absorbancy of the osmium-DPC solutions increases with time; therefore, a time-study was carried out whereby the absorbancy of the solutions was measured as a function of time. These results are presented in Table II. The color increases over a period of at least 24 hours; however, the rate of increase is small after the first hour. For instance, between 60 and 120 minutes, the absorbancies increase by about 5%; between 120 and 180 minutes the increase is about 1%; and over the next 21 hours the increase is about 17%. After a color development period of 2 hours, the rate of increase of the absorbancies is therefore only about 1% per hour and, within reasonable limits, the time of color development is not a critical factor after the first 2 hours.

The data in Table III showing the adherence of the absorbancies of the osmium-DPC solutions to Beer's law after a color development period of 2 hours also demonstrates the reproducibility of the absorbancy measurements. Statistical analysis of the five sets of data showed that there is no significant difference in the molar absorbancy index and 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%; the average was 3%. Using the average molar absorbancy index of 31,300, this method is suitable for the determination of 8 to 130  $\mu$ g of osmium, with an optimum range of 30 to 100  $\mu$ g, and a coefficient of variation of about 4%.

Attempts were made to increase the rate of color development so that maximum color 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 final solutions 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 final solutions resulted in higher absorbancy measurements; however, the rate of increase of the absorbancy was appreciable even after 2 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 final solutions. 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.

Tests of the elements which are commonly found in uranyl sulfate solutions revealed that none of them interfere in the determination of osmium. The maximum error which was found, even in the presence of 500-mg quantities of uranium or thorium, was 5%. 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 in the platinum group which revealed that Ru(VIII) alone of this group of elements interferes with the determination of osmium. Ruthenium tetroxide is co-extracted with  $OsO_4$  and reacts with diphenylcarbazide to give a violet colored reaction product. However, it is possible to oxidize osmium to  $OsO_4$  without oxidizing ruthenium to  $RuO_4$ <sup>(2)</sup>, 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.

#### Conclusion

Optimum conditions were established for the determination of osmium by the extraction of  $OsO_4$  with  $CHCl_3$  and the addition of diphenylcarbazide to the  $CHCl_3$  extract. The procedure involves the extraction of osmium from a 30%  $HNO_3$  medium with two, 10-ml portions of  $CHCl_3$ . The combined  $CHCl_3$  extracts are washed with 10 ml of 0.1 M  $H_2SO_4$  and then drained into a 25-ml flask containing 5 ml of 0.2% diphenylcarbazide in ethanol and about 1 g of anhydrous  $Na_2SO_4$ . The absorbancy is measured, after a color-dévelopement period of 2 hours, at 560  $m\mu$  vs a reagent blank, using 1-cm cells. From 8 to 130  $\mu g$  of osmium can be determined with a coefficient of variation of about 4%. Attempts to eliminate the 2-hour period for color development by heating, or by the addition of other compounds to the final solution, were unsuccessful.

Tests of the effects of foreign substances showed that the elements commonly found in uranyl sulfate samples do not interfere in the determination of osmium. Of the platinum group elements, only octavalent ruthenium interfered. However, this interference can be eliminated by reduction of ruthenium and osmium to the trivalent state followed by selective oxidation of osmium to  $OsO_4$ , after which the  $OsO_4$  is extracted with  $CHCl_3$ .

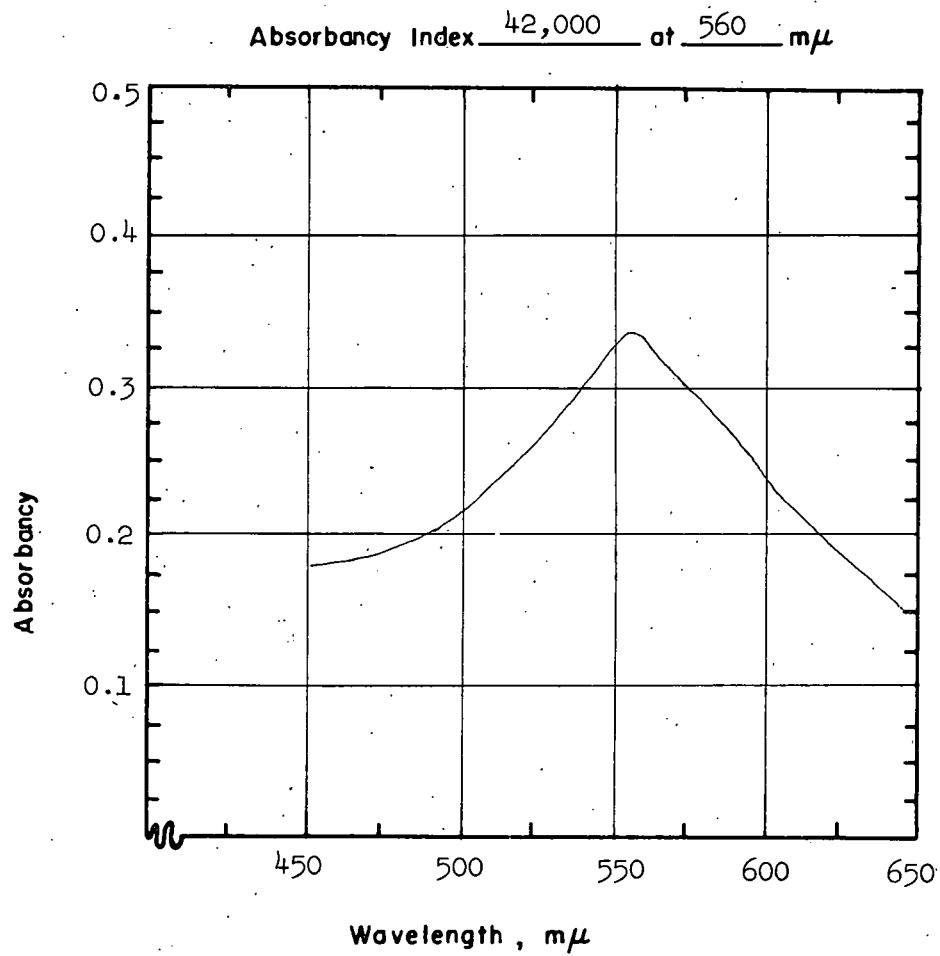
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1. G. Goldstein, ORNL CF-59-6-43, June 9, 1959.
2. E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd Ed., Interscience Publishers, Inc., New York, 1959, Chapter XXXI.

*Gerald Goldstein*  
Gerald Goldstein

FIGURE 1

TITLE: Absorption Spectrum of the Osmium-Diphenylcarbazide Complex



TEST CONDITIONS

Concentration Os, M,  $7.99 \times 10^{-6}$   
Medium CHCl<sub>3</sub>  
Chromophore Diphenylcarbazide  
pH   
Temperature, °C, 25  
Reference   
Remarks Color development time, hours, 24  
Diphenylcarbazide, 0.2 per cent in ethanol, ml 5

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