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SUBJECT: Ultraviolet Spectrophotometric Determination of Osmium Tetroxide in $CHCl_3$ by G. Goldstein

TO: See Distribution

GGs-27

FROM: Oscar Menis

ABSTRACT

A method was developed for the determination of osmium by measuring the absorbancy of osmium tetroxide in $CHCl_3$. The osmium is first oxidized to the octavalent state and the osmium tetroxide which is formed is extracted selectively with $CHCl_3$. The ultraviolet absorption spectrum of OsO_4 in $CHCl_3$ has a series of absorption bands with peak absorbancies at 282, 289, 297, 304 and 312 mμ, and molar absorbancy indices of 1870, 1760, 1640, 1400 and 1000, respectively. For each wavelength the optimum concentration range for the determination of osmium was evaluated by the method of Ringbom. Only chloride and octavalent ruthenium interfere in the determination. By this method, from 0.4 to 3 mg of osmium can be determined with a coefficient of variation of 3 per cent.

DISCLAIMER

DETERMINATION OF OSMIUM IN URANYL SULFATE SOLUTIONS

Ultraviolet Spectrophotometric Determination of Osmium Tetroxide in $CHCl_3$

Gerald Goldstein

INTRODUCTION

A method was desired for the determination of osmium in solutions of uranyl sulfate which contain numerous corrosion products such as iron, nickel and chromium. Since none of the existing methods[3] are sufficiently selective for the direct determination of osmium, a separation procedure was necessary. Moreover, osmium can exist in five different valence states and, therefore, a further problem was that of obtaining all the osmium in a single valence state. Accordingly, a procedure suggested by Sauerbrunn and Sandell[3] was tested whereby osmium is oxidized to the octavalent state and the OsO_4 which is formed is then extracted selectively with chloroform. The osmium is then determined by measuring the absorbancy of the extracted OsO_4 in the ultraviolet region of the spectrum. Although the ultraviolet absorption spectrum of osmium tetroxide in organic solvents has been previously reported,[1] the absorbancy of OsO_4 has not been utilized previously for analytical purposes.

Reagents

Osmium Tetroxide in 0.1 M H_2SO_4, 0.375 mg Os per ml. A vial containing 0.5 g of reagent-grade OsO_4 (available from Mallinckrodt Chemical Works, Reagent No. 2768) was weighed. The vial was then broken under 500 ml of 0.1 M H_2SO_4 and the OsO_4 was allowed to dissolve completely, after which the solution was filtered into a one-liter volumetric flask and diluted to volume with 0.1 M H_2SO_4. The broken glass collected on the filter was dried and weighed. The weight of OsO_4 in the vial was determined by difference and the concentration of Os in the standard solution was calculated. This solution was standardized by the gravimetric method of Wilson and Baye.[5] More dilute osmium solutions were prepared by appropriate dilution of the standard.

H_2SO_4, 0.1 M. Dilute 5.6 ml of conc. H_2SO_4 to one liter.

Apparatus

Beckman Model DU Spectrophotometer, equipped with ultraviolet accessories.

EXPERIMENTAL

A. Extraction of OsO_4. Solutions were prepared which contained known quantities of osmium as OsO_4 in 10 ml of 30% HNO_3. These solutions were transferred to 60-ml separatory funnels and extracted successively with 10-, 10-, and 5-ml portions of $CHCl_3$. The three extracts were drained into a second separatory funnel containing 10 ml of 0.1 M H_2SO_4 and washed with this solution in order to remove any traces of HNO_3 which may also have been extracted. The $CHCl_3$ phase was then drained into a 25-ml volumetric flask containing about 1 gm of anhydrous sodium sulfate and diluted to volume.

B. Ultraviolet Absorption Spectrum of OsO_4. An OsO_4 solution was prepared that contained 1.52 mg of osmium and the osmium tetroxide was extracted as previously described. The ultraviolet absorption spectrum of the extract was determined vs a $CHCl_3$ blank and is presented in Figure 1.

C. Calibration Curves for the Determination of Osmium. Solutions were prepared containing from 0.4 to 2.7 mg of osmium which was then extracted as previously described. The absorbancy of the extracts was measured versus a $CHCl_3$ blank at the wavelengths of the five OsO_4 absorption peaks: 282, 289, 297, 304, and 312 mμ. These calibration data are presented in Table I, and, in the form of Ringbom plots, in Figure 2.

D. Effect of Foreign Substances. Solutions were prepared containing 1.14 mg of osmium, and the foreign substances in 10 ml of 30% HNO_3, and the osmium was extracted as previously described. The absorbancy of the extracts was measured at 289 mμ vs a $CHCl_3$ 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		Absorbancy, mμ				
mg	M x 10^4	282	289	297	304	312
0.380	0.799	0.151	0.142	0.130	0.109	0.080
.760	1.60	.298	.276	.263	.223	.160
1.14	2.40	.460	.430	.396	.335	.236
1.52	3.20	.590	.565	.529	.455	.318
1.90	4.00	.738	.690	.648	.552	.396
2.28	4.79	--	--	.798	.687	.497
2.66	5.59	--	--	--	.770	.560
Molar Absorbancy Index		1870	1760	1640	1400	1000
Coefficient of Variation, %,		2	2	1	2	2

Discussion

Although OsO_4 can be extracted from acid solutions by many organic solvents, $CHCl_3$ was chosen as the extractant for the following reasons. Since the extractions are made from a nitric acid solution, many elements besides osmium, including thorium and uranium, can be extracted if the solvent is polar and has a functional group which contains oxygen.(2) Therefore a non-polar solvent is 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 than water. Chloroform was chosen rather than CCl_4 since the distribution ratio of OsO_4 is 19.1 when $CHCl_3$ is used as the extractant compared to 13.0 when CCl_4 is used.(3) From the distribution ratio of 19.1 it was calculated that 99.6% of the osmium was extracted by the recommended procedure. Since the precision of ordinary spectrophotometric measurements is of the order of 3%,(4) a loss of 0.4% of the osmium is not significant.

The ultraviolet absorption spectrum of OsO_4 in $CHCl_3$, which is shown in Figure 1, exhibits the same features as the spectra previously reported in CCl_4 and in hexane.(1) Below 260 mμ the absorbancy of the OsO_4 solution increases rapidly. Since the absorbancy of the $CHCl_3$ blank is also appreciable below 260 mμ, this region is not suitable for spectrophotometric measurements. Above 320 mμ the absorbancy of the OsO_4 solution is very small.

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 indices is, in all cases, less than 2%. In order to determine the range of osmium concentrations which can be determined with the maximum accuracy for each wavelength, the calibration data were plotted as per cent transmission vs log of the osmium concentration according to the method of Ringbom.[4] From this plot, shown in Figure 2, the optimum concentration ranges were evaluated and are shown in Table II. From the results it is indicated that by proper choice of the wavelength, 0.4 to 3.3 mg of osmium can be determined with a coefficient of variation of about 3%. The absorbancy values of the OsO_4 extracts remained constant over a period of at least 5 hours.

Table II

Optimum Concentration Ranges for the Ultraviolet Spectrophotometric Determination of Osmium at Various Wavelengths

Wavelength, mμ	Optimum Concentration Range	
	M x 10^4	mg/25 ml
282	0.82 - 3.74	0.39 - 1.78
289	.88 - 3.98	.42 - 1.89
297	.94 - 4.26	.45 - 2.03
304	1.10 - 5.02	.52 - 2.39
312	1.54 - 7.00	.73 - 3.33

The effect of foreign substances on the determination of 1.14 mg of osmium is shown in Table III. 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 are obtained. The platinum group of metals in their lower valence states was also tested, and does not interfere. Ruthenium in the octavalent state is a known interference since RuO_4 extracts along with OsO_4, and also absorbs ultraviolet light.[1] However, RuO_4 and OsO_4 may be reduced with ferrous ion, and the osmium then selectively re-oxidized to the octavalent state with nitric acid and extracted.[3] Of the anions that were tested, ClO_4^-, $SO_4^=$, and $PO_4^{\equiv}$ do not interfere. In the presence of chloride, low results were obtained since chloride forms complex ions with tetra- and hexavalent osmium and inhibits the complete oxidation and subsequent extraction of osmium.[3] Since the chloride concentration in uranyl sulfate solutions is very low, the interference from such small amounts is insignificant.

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.[3]

Table III

Effect of Foreign Substances on the Extraction and Ultraviolet Spectrophotometric Determination of Osmium

Osmium, mg 1.14

Substances	Quantity, mg	Osmium, mg Found	Error
U^{+6}	1000	1.19	+ 0.05
Fe^{+3}		1.22	+ 0.08
Ni^{+2}		1.18	+ 0.04
Cu^{+2}		1.19	+ 0.05
Th^{+4}	500	1.17	+ 0.03
Cr^{+6}		1.19	+ 0.05
Cr^{+3}		1.16	+ 0.02
Mo^{+6}		1.14	--
Pd^{+2}	6	1.20	+ 0.06
Au^{+3}	5	1.12	- 0.02
Rh^{+3}	2	1.10	- 0.04
Pt^{+2}		1.17	+ 0.03
Ir^{+3}	1	1.16	+ 0.02
Ru^{+3}		1.19	+ 0.05

Conclusion

From 0.4 to 3.3 mg of osmium can be determined by oxidizing the osmium to the octavalent state, extracting the OsO_4 which is formed with $CHCl_3$, and measuring the absorbancy of the OsO_4 in $CHCl_3$ at a wavelength of 282, 289, 297, 304 or 312 mμ, depending on the concentration of osmium. The optimum concentration range was established for measurements at each wavelength. Only chloride and octavalent ruthenium interfere in the determination.

References

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3. E. B. Sandell, Colorimetric Determination of Traces of Metals, 3rd ed., Interscience Publishers, Inc., New York, 1959, Chap. XXXI.

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INDEX Os
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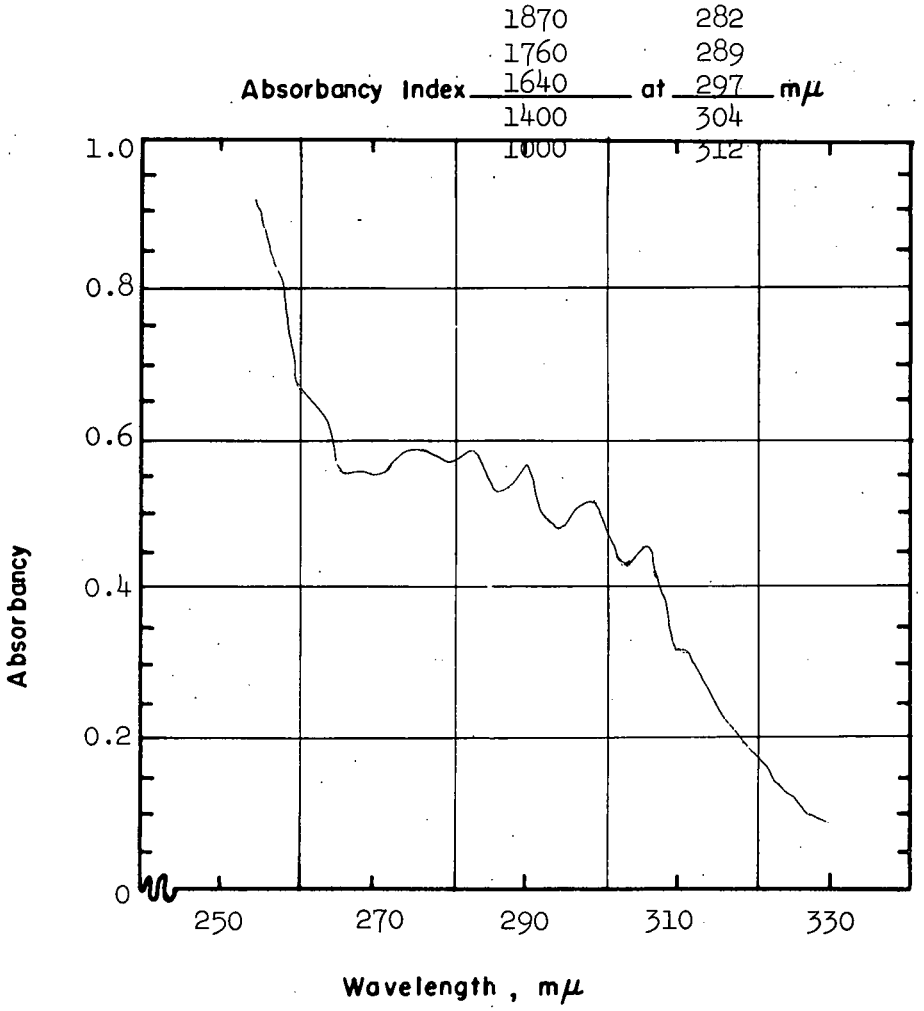
FIGURE 1

TITLE: Ultraviolet Absorption Spectrum of Osmium Tetraoxide in Chloroform



TEST CONDITIONS

Concentration Os, M, 3.2×10^{-4}
Medium $CHCl_3$
Chromophore
pH
Temperature, °C, 25
Reference
Remarks Silica cells
Hydrogen lamp

Instrument Beckman Model DU
Slit Width, mm. variable
Cell Thickness, Cm 1
Blank $CHCl_3$

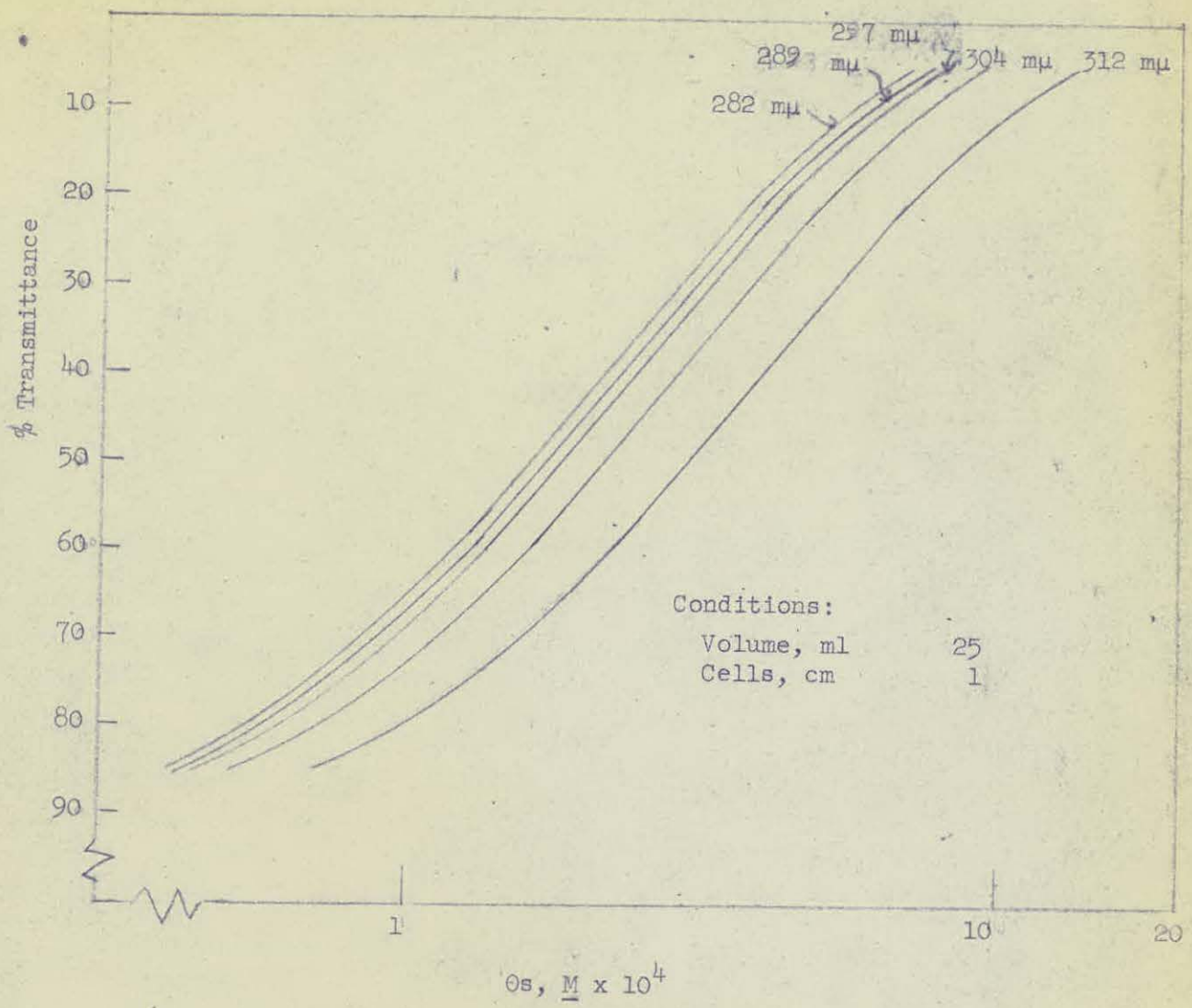


Figure 2. Ringbom Plots of Calibration Data for the Ultraviolet Spectrophotometric Determination of Osmium

Distribution

1. M. T. Kelley
2. R. B. Briggs
3. C. D. Susano
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