

by comparing with a standard graph drawn under identical conditions; Sandell's sensitivity: $0.011 \mu\text{g}$ of Ru/cm^2 for 0.001 absorbance. Light yellow coloured DMP_m shows maximum absorption at 280 nm ($\epsilon = 1.5 \times 10^4$) and 390 nm ($\epsilon = 1.9 \times 10^3$). At λ_{max} of its osmium and ruthenium complexes, its absorbance is negligible. The complexes have 1:2 (metal-ligand) stoichiometry and are not extracted by organic solvents. The colour developed with ruthenium only on heating the solution on a steam-bath and it required 30 min for attaining the maximum absorbance. However, continued heating for 4 hr did not affect the colour. The tolerance limits of various ions were found (Table 1) in the determination of 3.8 ppm of osmium and 3.4 ppm of ruthenium.

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Spectrophotometric Determination of Os(VIII) with Thioglycollic Acid

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A rapid, spectrophotometric method for the determination of Os(VIII) in the concentration range $2.0\text{--}48.0 \mu\text{g}$ of Os(VIII)/ml is described using thioglycollic acid as chromogenic reagent in an acid medium of $0.1\text{--}1.0M$ perchloric acid. The reaction involves reduction of Os(VIII) to Os(VI) followed by complex formation as is evidenced by spectral data. The stoichiometry of the complex is found to be 1:2 [Os(VI)-thioglycollic acid]. At lower ligand concentration a 1:1 complex is also formed which rapidly changes to the 1:2 complex at higher [ligand]. The elimination of the interference of some of the cations is tried with a distillation method.

BEAMISH¹ and Boltz *et al.*² have recently reviewed the available optical methods for the determination of Os(VIII). A critical survey of literature reveals that no work has been done so far on the complexes of osmium with thioglycollic acid. The complexes of Os(VIII) with sulphur containing ligands is of interest in view of the fact that the reduction of metal ion precedes complexation^{3,4}. In this note the results of spectrophotometric investigation of osmium-thioglycollic acid complex in $0.1\text{--}1.0M$ perchloric acid medium and its analytical utility for the assay of microgram quantities of Os(VIII) are reported. The present method has several advantages as the colour development is instantaneous and quite stable for 48 hr at room temperature (25°C) over a wide range of acidity of $0.1\text{--}1.0M$ and tolerates interferences of many cations. The complex is stable even at boiling water-bath temperature.

A solution of Os(VIII) was prepared by dissolving OsO_4 (Johnson & Matthey) in $0.5M$ sodium hydroxide according to the procedure of Norkus and Stulgene⁵. The solution was standardized iodimetrically⁶. Os (VI) solution was prepared as per the method of Majumdar and Sengupta⁷. Roughly $0.05M$ solution of thioglycollic acid (GR, E. Merck) was prepared in oxygen-free doubly distilled water and was standardized iodimetrically⁸.

Standard sodium perchlorate solution ($5.0M$) was prepared by mixing equivalent amounts of perchloric acid and sodium carbonate. The resulting solution was boiled until it was free from carbon dioxide and the pH of the solution adjusted to 7.0.

All other reagents were of analytical grade and all dilutions were made with deionized water.

A Spectronic 20 spectrophotometer (Bausch and Lomb type) with matched glass tubes (internal diam. 1 cm) was used for spectral data. Quantitative absorption data were obtained using Hilger-Spekker absorptiometer model 760 with Kodak filter No. 1 (maximum absorption 429 nm). A Toshniwal type CL 44 pH meter was used for pH measurements.

In the presence of excess ligand in $1.0\text{--}0.1M$ perchloric acid both Os(VIII) and Os(VI) develop a brown colour instantaneously. A perusal of absorption spectra reveals that both Os(VIII) and Os(VI) yield the same product. Since the absorbance of the complex continuously decreases from $340\text{--}600 \text{ nm}$ quantitative absorption data were taken using filter No. 1 (maximum absorption 429 nm). The reagent and metal ions have no absorption in the wavelength range of the selected filter.

Recommended procedure — Perchloric acid ($0.5\text{--}5.0 \text{ ml}$, $5M$) was mixed with thioglycollic acid solution (5 ml , $0.05M$). The solution was made up to the mark (25 ml) with deionized water after the addition of an aliquot of osmium solution. The homogeneous solution gave a brown coloured complex instantaneously and its absorbance was measured against reagent blank. Ionic strength was kept constant ($1.0M$, sodium perchlorate). It was observed that no detectable change in absorbance occurs in perchloric acid concentration of $0.1\text{--}1.0M$, while the absorbance is low at lower acidities. The same coloured complex is developed instantaneously when equal acidity is maintained even with other mineral acids.

The absorbance of the complex was found to be constant at [ligand] in the range 20 to 200 times that of metal ion. Higher [ligand] was found to have little effect on the colour of the complex.

With excess ligand the absorbance of the complex was stable for 48 hr at room temperature (25°). The complex was stable even after heating in a boiling water-bath for 10 min.

The system obeys Beer's law in the concentration range of $2.0\text{--}48 \mu\text{g}$ of Os(VIII)/ml. From the Ringbom's plot⁹ (% transmission vs $\log [\text{Os(VIII)}]$) the optimum range for the determination was found to be $12.0\text{--}40.0 \mu\text{g}$ of Os(VIII)/ml. Sandell's sensitivity¹⁰ was calculated to be $0.0185 \mu\text{g}/\text{cm}^2$.

Nature of the complex — The complex may be a negatively charged species as it is strongly taken up by anionic resin, De-Acedite FF (polystyrene

quaternary ammonium resin)¹¹. The complex is not extractable into any of the following organic solvents, *n*-butanol, ethyl acetate, tri-*n*-butylphosphate, chloroform, benzene, methylisobutylketone, isopropyl alcohol, etc.

The composition of the complex Os(VI)-thioglycolic acid was established by mole-ratio method of Yoe and Jones¹² and Job's method of continuous variation¹³. As high metal to ligand concentration ratios resulted in a bluish black turbidity, Job's method in non-equimolar solutions was used. The results of the two methods indicate a ratio of 2 moles of the reagent to 1 mole of the metal ion. There is further evidence that with excess osmate a 1:1 complex is formed which rapidly changes to a 1:2 complex on the addition of more reagent.

Interference — Using the recommended procedure Os(VIII) can be determined precisely without interference from 0.4 mg/ml of Ba²⁺, Be²⁺, Ca²⁺, Mg²⁺, Mn²⁺, Sn²⁺, Sr²⁺, Zn²⁺, V⁴⁺, acetate, bromide, carbonate, chloride, nitrate, oxalate, periodate, phosphate sulphate, sulphite. Even trace amounts of Fe²⁺, Fe³⁺, As³⁺, Sb³⁺, Cr³⁺, Ru³⁺, Au³⁺, Ir⁴⁺, Pt⁴⁺, U⁴⁺, Zr⁴⁺, W⁶⁺, azide, nitrite and thiocyanate interfere strongly. The interference of the latter cations was obviated by separating the Os(VIII) (OsO₄) from the mixture by the distillation procedure as outlined by Steele and Yoe¹⁴.

Saturated solution of Os(VIII) was reported to be as good an oxidant as bromine water¹⁵. A thorough study of spectral data using excess ligand revealed that the coloured species formed with Os(VIII) and Os(VI) is one and the same. It is further evidenced, as both the valency states of the metal ion gave the full colour development under identical conditions. Os(VIII) is first reduced to Os(VI) before the complex formation with thioglycolic acid. The likelihood of further reduction of Os(VI) to lower valency state and subsequent complexation is ruled out as there is no complex formation with Os(IV) and other lower valency states of osmium. Since a very large excess of ligand was used in the assay of Os(VIII) it follows that it is the 1:2 complex that is being measured.

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Cerimetric Titration of As(III) in Acetic Acid Medium

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Arsenic(III) has been determined at room temperature by titration against cerium(IV) sulphate in AcOH-H₂SO₄ medium using ferroin as indicator and osmic acid, iodine monochloride or ferron as catalyst.

DURING a systematic study on the use of Nile Blue as a redox indicator in the titration of As(III) against cerium(IV) sulphate, Rao *et al.*¹ have observed that Osmic acid², iodine monochloride³ and ferron⁴, used earlier as catalysts in H₂SO₄ medium, can be employed in a largely acetic acid medium also. In view of this observation, we have reinvestigated the use of these three catalysts in the titration of As(III) against cerium(IV) sulphate using ferroin as indicator but employing an acetic acid medium for the titrand. The results are reported in this note.

The following standard solutions were prepared: ≈ 0.1N cerium(IV) sulphate in 1.0N H₂SO₄, 0.1N As(III) by dissolving As₂O₃ (E. Merck, pro analysi) in H₂O, 0.25% osmic acid, 0.017M iodine monochloride, 0.005M ferron and 0.025M ferroin. Acetic acid and other chemicals used were of reagent grade.

Procedure — A portion of (5-15 ml) of As(III) solution (0.1N or 0.01N) was treated with the requisite amount of 1:1 acetic acid, so as to give the required overall acidity when diluted to 50 ml, 3 drops of 0.25% osmic acid (or 1.0 ml of 0.017M ICl or 0.8 ml of 0.005M ferron) and one drop of 0.025M ferroin. The solution was titrated against 0.1N (or 0.01N) cerium(IV) sulphate solution till the colour changed from orange-red to pale blue. The acetic acid concentrations used with the three catalysts are: (a) osmic acid, 1.0-6.0N; (b) iodine monochloride, 3.0-5.0N; and (c) ferron, 3.0-5.0N acetic acid + 0.05-0.1N sulphuric acid (while using ferron as catalyst, 0.05-0.1N H₂SO₄ should be initially present in the titration mixture, otherwise the results obtained are not accurate). The results obtained are in excellent agreement with those obtained with these catalysts in other acid media.

The minimum amount of osmic acid required as catalyst is 3 drops of its 0.25% solution. At lower [osmic acid], the reaction between ferroin and As(III) becomes slow.