

Spectrophotometric Determination of Os(VIII) & Ru(III) with 4,5-Diamino-2-mercaptopyrimidin-6-ol

A. K. SINGH, MOHAN KATYAL* & R. P. SINGH

Chemistry Department, Delhi University, Delhi 110007

Received 5 June 1975; accepted 11 August 1975

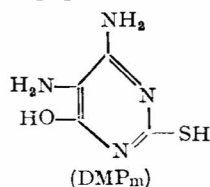
4,5-Diamino-2-mercaptopyrimidin-6-ol is proposed for detection and spectrophotometric determination of Os(VIII) in alkaline medium. The red coloured complex containing osmium and the ligand in 1:2 molar ratio shows a maximum absorption at 520 nm ($\epsilon=2.7 \times 10^4$) and obeys Beer's law up to 8.0 ppm. The reagent also forms a 1:2 complex with Ru(III) in the pH range 2.2-3.3. Ru(III) has also been successfully estimated.

FASCINATED by the analytical potentialities of pyridinol¹, it was thought worthwhile to investigate the similar aspects of biologically important pyrimidinols. In the course of study, it is found that 4,5-diamino-2-mercaptopyrimidin-6-ol (DMP_m) reacts selectively with Os(VIII). It also forms a red coloured complex with Ru(III) on heating the solution. This property has been utilized to develop a spectrophotometric method for the determination of Os(VIII) and Ru(III) in the presence of many-fold concentrations of many ions including the rest of platinum group metals².

Standard solutions of DMP_m, Os(VIII) and Ru(III) were prepared by dissolving appropriate amounts of the ligand (K & K Laboratories, USA) in either 10% acetic acid or 0.1N sodium hydroxide, OsO₄ (Johnson Matthey, UK) in 0.2N sodium hydroxide and RuCl₃·3H₂O (Koch-Light Laboratories, UK) in 1.0N hydrochloric acid. They were standardized by standard methods. Ru(III) solution was preserved under nitrogen atmosphere. Sodium acetate-acetic acid and ammonium chloride-ammonium hydroxide buffers were used for pH adjustments. All the solutions were prepared from analytical grade chemicals and deionized water.

Absorbance readings were taken on a Unicam SP-600 spectrophotometer and a Metrohm E 350 pH meter was used for checking pH of the solutions.

Detection of Os(VIII) — A drop of the test solution was placed on a spot plate or filter paper (Whatman No. 1) and to this was added a drop each of 5.0N NaOH and DMP_m (0.01M in 0.1N NaOH) solution. The development of red colour shows the presence of Os(VIII); limits of identification: 0.05 µg on spot plate; and 0.10 µg on filter paper; limits of dilution: 1:1,000,000 on spot plate; 1: 500,000 on filter paper.



Determination of Os(VIII) — To an aliquot solution of Os(VIII), in the concentration range of 14.0-56.0 µg, was added 2.0 ml of 0.01M DMP_m solution (in 0.1N NaOH) followed by conc. NaOH solution so that the final solution (total volume 10.0 ml) was roughly 2N with respect to alkali. The absorbance of the complex was measured at 520 nm ($\epsilon_{\max} = 2.7 \times 10^4$ litre mole⁻¹ cm⁻¹) against a reagent blank. The amount of Os(VIII) was calculated from a standard curve; Sandells sensitivity: 0.007 µg of Os/cm² for 0.001 absorbance.

Detection of Ru(III) — A drop of the test solution was taken in a microtube or on a filter paper (Whatman No. 1) and to this was added a drop each of 0.1N NaOH and 0.01M DMP_m (in 10% acetic acid) solution. The tube was kept in a boiling water-bath (or filter paper in an oven at 100°) for 10 min when a red colour appeared showing the presence of ruthenium(III); limits of identification: 0.08 µg in micro tube; 0.20 µg on filter paper; limits of dilution: 1:625,000 in microtube; 1:250,000 on filter paper.

Determination of Ru(III) — To ruthenium solution (concentration between 23 and 57 µg), was added 3.0 ml of 0.01M DMP_m (in 10% acetic acid). The solution was neutralized with 0.1N NaOH and the buffer added to bring the pH between 2.2 and 3.3. It was heated on a steam-bath for 45 min, cooled and diluted to 10.0 ml. The absorbance of the red complex produced, at 540 nm ($\epsilon_{\max} = 9.6 \times 10^3$ litre mole⁻¹ cm⁻¹), was measured against a reagent blank. The strength of ruthenium solution was calculated

TABLE 1 — EFFECT OF FOREIGN IONS

Foreign ion	Tolerance (ppm)	
	Os(VIII) (3.8 ppm)	Ru(III) (3.4 ppm)
F ⁻ ; Cl ⁻	200; 1000	1000; 2000
Br ⁻ or I ⁻	2000	2000
CN ⁻ ; NO ⁻	20; 2000	10; 10
NO ₃ ⁻ or ClO ₄ ⁻	2000	2000
CNS ⁻ ; S ₂ O ₃ ²⁻	1200; 1000	Interferes; 5
CH ₃ COO ⁻ or SO ₄ ²⁻	2000	2000
C ₂ O ₄ ²⁻ ; tartrate	150; 1200	500; 1000
Thiourea; EDTA	5; 2000	Interferes; 2000
PO ₄ ³⁻ ; BO ₃ ³⁻	200; 1000	2000; 1000
Citrate	1500	500
Cu ²⁺ ; Ag ⁺	20; 20*	3; 20*
Ca ²⁺ or Sr ²⁺	100	100
Ba ²⁺ ; Zn ²⁺	100; 25	100; 10
Cd ²⁺ ; Hg ²⁺	20; 20	10; 30†
Al ³⁺ ; Sn ⁴⁺	50; 10	50; 5
Pb ²⁺ ; V ⁵⁺	20; 5	25; 5
Mn ²⁺ ; Fe ³⁺	30; 50	20; 10
Co ²⁺ ; Ni ²⁺	15; 15	5; 2
Ru ³⁺ ; Rh ³⁺	45; 100	—; 10
Pd ²⁺ ; Os ⁸⁺	20; —	Interferes; 5
Ir ⁴⁺ ; Pt ⁴⁺	40; 150	5; 15

*Masked with chloride.

†Masked with iodide.

In case when the foreign ion was precipitated as hydrated oxide, it was centrifuged off, washed and the solution brought up to the volume.

*Present address: St Stephen's College, Delhi 110007.

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.

One of us (A.K.S.) thanks the CSIR, New Delhi, for the award of a junior research fellowship.

References

1. KUSHWAHA, V., KATYAL, M. & SINGH, R. P., *Talanta*, **21** (1974), 763.
2. BOLTZ, D. F. & MELLON, M. G., *Analyt. Chem.*, **46** (1974), 233R.

Spectrophotometric Determination of Os(VIII) with Thioglycollic Acid

U. MURALIKRISHNA, P. KANNA RAO & K. V. BAPANAIHA
Chemistry Department, Andhra University, Waltair

Received 16 June 1975; accepted 18 July 1976

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