

The reverse titrations, i.e. titrations of sodium thiosulphate, arsenic(III), ascorbic acid and hydrazine with iodine, can be carried out using 0.1N and 0.01N solutions under the same conditions as in the direct titrations and the colour changes at the end points are just the reverse of those observed in the direct titrations. In the reverse titrations no blank correction is necessary in titrations of 0.1N solutions, but while titrating with 0.01N solutions, a blank correction of 0.04-0.06 ml 0.01N iodine has to be applied for 0.2 ml of 0.01% indicator solution added.

While titrating with 0.01N solutions, the amount of the indicator added should be 0.1-0.3 ml; when higher amounts of indicator solution are employed, the colour changes at the end points are not quite satisfactory.

With a view to applying the method now developed for the titrimetric determination of ascorbic acid in commercial vitamin C tablets, we have studied the interferences of some substances. The results indicate that citric, tartaric, oxalic, succinic, malic, maleic and mandelic acids, dextrose, lactose, mannitol, Ca^{2+} , Mn^{2+} , and Mg^{2+} do not interfere, whereas Fe^{2+} , Ba^{2+} , Li^+ , and Pb^{2+} interfere.

The ascorbic acid content in the commercial vitamin C tablets was determined as follows: The tablet was dissolved in deionized water, and the solution filtered through a G4 sintered glass crucible. The filtrate was made up to 100 ml and an aliquot of this solution titrated against 0.1N iodine solution, using any one of the five dyes as indicator. A similar aliquot was titrated following the literature method. The results presented in Table 2 show that they are in excellent agreement with those obtained by the official method.

In their studies on the use of neutral red as indicator in the argentometric titration of bromide and iodide, Sierra and Asensi¹² stated that the colour change at the end point is due to the formation of a compound between iodine and neutral red. Since the dyes of the present investigation have almost similar structures as neutral red, we believe that a compound is formed between iodine and the dye, and at the end point, thiosulphate, arsenic (III), hydrazine and ascorbic acid react with the compound and regenerate the dye.

TABLE 2—DETERMINATION OF ASCORBIC ACID IN COMMERCIAL VITAMIN C TABLETS

Trade name	Manufacturer	Amount of ascorbic acid found (mg)	
		BP method*	Present method
Redoxon	Roche	461.9 ± 0.3	461.5 ± 0.4
Celin	Glaxo	498.6 ± 0.5	497.6 ± 0.4
Sukcee	IDPL	502.3 ± 0.4	501.9 ± 0.3
Chewcee	Lederle	480.3 ± 0.4	480.7 ± 0.3

*British Pharmacopoeia, 1973, 36.

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Spectrophotometric Investigation of Os(VI)-Thiocyanate Complex

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A simple and rapid method for the spectrophotometric determination of 2.5-38.0 $\mu\text{g/ml}$ of Os(VIII) using thiocyanate as the chromogenic reagent in 0.5-3.0M H_3PO_4 is described. The reaction involves reduction of Os(VIII) to Os(VI) which forms a 1:1 (metal-ligand) complex with thiocyanate as is evidenced from the spectral data. The interference of various cations has also been investigated.

APART from the importance of thiocyanate in thyroid and brain metabolism^{1,2,3}, it gained wide popularity as a chromogenic reagent for the spectrophotometric determination of transition metal ions^{4,5}. Qureshi *et al.*⁶ and Shlenskaya *et al.*⁷ proposed spectrophotometric assay of Os(VIII) as osmium-thiocyanate complex without mentioning either the valency state of the metal ion or the stoichiometric composition of the product formed. Thus in view of the above and in continuation of our interest in the redox behaviour of thocyanate⁸⁻¹⁰, we have now reinvestigated the nature of the species in aq. medium and successfully explored optimum conditions for the rapid spectrophotometric determination of Os(VIII) as Os(VI)-thiocyanate complex in aq. H_3PO_4 medium at room temperature (25°).

A solution of Os(VIII) was prepared by dissolving OsO_4 (Johnson Matthey Co., London) in 0.5M Na-OH (ref. 11) and standardized iodometrically¹². Os(VI) solution was prepared by the addition of 0.1 ml of aq. ethanol (1:2) to 10 ml of 10^{-3}M alkaline

Os(VIII) solution¹³. About 1.0M aq. solution of sodium thiocyanate (GR; E. Merck) was prepared in doubly distilled water and standardized argentometrically using sodium fluoresceinate as adsorption indicator¹⁴. NaClO₄ solution (5M) was prepared by mixing the equivalent amounts of HClO₄ and Na₂CO₃. All other reagents used were of AR grade and all dilutions were made with deionized water.

Procedure — Phosphoric acid (1.5 ml; 8.5%, BDH) was mixed with sodium thiocyanate solution (5.16 ml, 0.5M) in a 25 ml volumetric flask. The solution was made up to the mark after the addition of an aliquot of Os(VIII) solution containing not more than 950 µg of the metal ion. The homogeneous solution was left for 10 min for full colour development. The absorbance of the resulting orange-yellow-coloured complex was measured on a Hilger Spekker absorptiometer using filter No. 1 against the reagent blank.

In the presence of excess [thiocyanate], superimposable spectra (Spectronic 20, Bausch & Lomb) were obtained for the osmium-thiocyanate complex in H₃PO₄ (0.5M) or HClO₄ (0.5M) media, the metal ion being added in octavalent or hexavalent state suggesting the formation of the complex with Os(VI)¹⁵. Spectra with various metal ligand molar ratios (1:1, 1:2, 1:3, 1:10) in 0.5M HClO₄ and at an ionic strength of 0.70 suggest the presence of a single absorbing species, having the absorption band in the region 440-470 nm.

The empirical formula of Os(VI)-thiocyanate complex was determined by the methods of Bent and French¹⁶, Yoe and Jones¹⁷ (Fig. 1) and Manning and Harvey¹⁸. All these methods unequivocally suggested the formation of a complex with a metal to ligand ratio of 1:1.

It was observed that no detectable change in the absorbance occurs at [H₃PO₄] = 0.5-3.0M. The colour development was found to be slow when equal concentrations of other mineral acids were employed. The absorbance of the complex was found to be constant when 300 molar excess of the ligand was present in the solution. Higher [ligand] had little effect on the colour of the complex.

It was found that the system obeys Beer's law in the concentration ion range of 2.5-38 µg/ml of Os(VIII). From Ringbom's plot¹⁹ the optimum range for the determination of Os(VIII) was found to be 9.0-27.0 µg/ml. Sandell's sensitivity²⁰ was calculated to be 0.0048 µg/cm².

The ions Cd(II), Mn(II), Ni(II), Zn(II), Mo(VI), Cr(III), W(VI), As(III), Sb(III), Cl⁻, NO₃⁻ and ClO₄⁻ (10 mg each), Sn(II) (5 mg) and Pd(II) and CN (2 mg each) did not vitiate the determination of Os(VIII) by the present procedure while even trace amounts of Au(III), Ru(III), Rh(III), Ir(IV), Pt(IV), Zr(IV), Fe(III), Co(II) and Cu(II) interfered seriously. The interference of these cations was obviated by distilling Os(VIII) by the procedure of Steele and Yoe²¹.

The saturated solution of OsO₄ was reported to be as good an oxidant as bromine water²². In view of the good reducing properties of thiocyanate a reduction-cum-complexation reaction²³⁻²⁵ was anti-

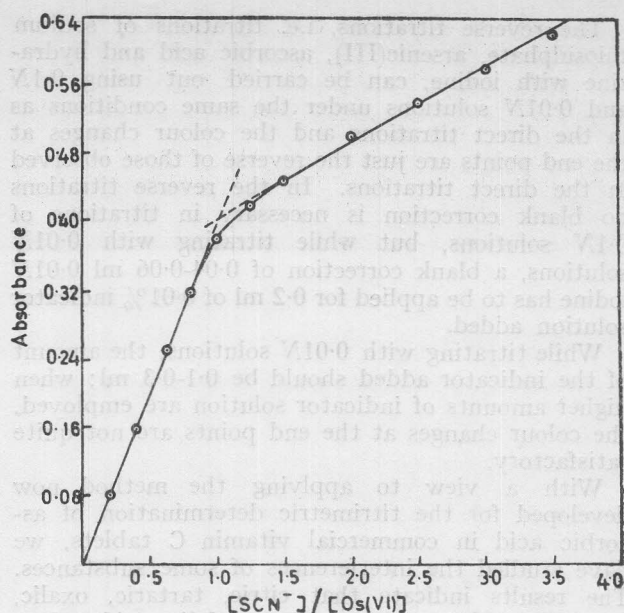


Fig. 1 — Mole ratio plot {[Os(VI)] = $1.6 \times 10^{-4}M$; [H⁺] = 0.50M; $\mu = 0.70M$; cell length = 4 cm}

icipated. A thorough study of the spectral data using an excess of [ligand] revealed that the coloured species formed with Os(VIII) and Os(VI) were one and the same. The absorbance of orange-yellow Os(VI)-thiocyanate complex was stable for about 48 hr at room temperature (25°). The likelihood of further reduction to Os(IV) and complexation is eliminated by the fact that the spectrum of Os(IV) remains unaltered in the presence and in the absence of thiocyanate.

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Promethazine Hydrochloride as a New Reagent for Spectrophotometric Determination of Pd(II)

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Promethazine hydrochloride (PH) forms a red-coloured 1:1 (metal: ligand) complex instantaneously with Pd(II) at a pH 1.3-4.0. The sensitivity of the reaction is $0.027 \mu\text{g}/\text{cm}^2$ and the molar absorptivity is 3.86×10^3 litre mole⁻¹ cm⁻¹ at 470 nm. Beer's law is valid over the concentration range 0.4-20.0 ppm. However, the optimum range for the effective colorimetric determination is 2.0-19.0 ppm. The stability constant of the complex at 27° and pH 3.0 ± 0.1 is found to be 5.1.

CAVATORTA¹ studied the reaction of PdCl₂ with promethazine hydrochloride (PH) and used it for the colorimetric determination of the latter. Sanke Gowda and Ramappa² studied the complex formation of Pd(II) with diethazine hydrochloride. The present paper describes PH as a sensitive reagent for the spectrophotometric determination of Pd(II).

The stock solution of Pd(II) was prepared by dissolving PdCl₂ (0.9886 g) of Johnson Matthey grade in dil. HCl (Analar) and diluted to 1 litre to give 0.1M with respect to HCl. The solution was standardized gravimetrically using dimethyl glyoxime. It was further diluted to give a standard solution containing 30 μg Pd(II)/ml. The stock solution of PH (May & Baker grade) was prepared by dissolving a known amount in doubly distilled water and stored in an amber-coloured bottle in a refrigerator.

Walpole buffers³ in the pH range 0.65-5.20 were prepared using sodium acetate (1M) and HCl (1M) solutions. Solutions of diverse ions of suitable concentrations were prepared using AR grade reagents.

Procedure—To an aliquot of Pd(II) solution (10 to 500 μg) in a 25 ml volumetric flask were added 5 ml of Walpole buffer (pH 2.6) and 3 ml of PH solution (0.2%) and the volume made up to the mark with doubly distilled water. The solution

was mixed well and the absorbance measured at 470 nm against a solution containing all the reagents except Pd. The amount of Pd was read from a standard calibration curve.

PH forms a red-coloured complex with Pd at pH 1.3-4.0. If the pH of the medium is >4, the absorbance readings are not constant and above 7 a white precipitate is formed. A maximum colour is produced when the mixture contains a thirteen-fold [reagent] with respect to (metal ion). The red complex exhibits λ_{max} at 466-476 nm. The reagent under similar conditions does not absorb at this wavelength. The absorbance values remain constant for 24 hr and at 5-97°C. Beer's law is valid over the (Pd) range 0.4-20.0 ppm. However, the optimum concentration range evaluated by Ringbom's method^{4,5} is 2.0-19.0 ppm. The Sandell's sensitivity, as calculated from Beer's law data, is $0.027 \mu\text{g}/\text{cm}^2$ and the molar absorptivity is 3.86×10^3 litre mole⁻¹ cm⁻¹. There is no appreciable change in the absorbance or in colour intensity of the complex if the order of addition of reactants are changed.

Job's method of continuous variation^{6,7} ($\mu = 0.1M$ NaNO₃; pH 3.0 ± 0.1; temperature 27° ± 1°C; λ_{max} 470 nm) and the mole ratio method indicate the formation of 1:1 complex between the metal and reagent. The observations recorded at 450 and 500 nm also confirm the existence of only one complex.

The apparent stability constants of the complex calculated from the absorbance data by (a) method of Foley and Anderson⁹ modified by Mukherji and Dey¹⁰ and (b) mole ratio method⁸ are 5.05 ± 0.1 and 5.15 ± 0.1 respectively.

The following amounts ($\mu\text{g}/\text{ml}$) of foreign ions are found to cause error <2% in the determination of 10 μg of Pd(II) per ml: Os(VIII), 40; Pt(IV), 12; Ir(III), 12; Rh(III), 9; Ru(III), 0.6; Ni(II), 575; Cu(II), 500; Co(II), 96; Fe(III), 4; Cl⁻, 7500; NO₃⁻, 2850; F⁻, 1500; SO₄²⁻, 1000; acetate, 600; PO₄³⁻, 550; Br⁻, 180 and I⁻, 0.8. The present spectrophotometric method for the determination of Pd(II) using PH has the following advantages over that using diethazine hydrochloride²: (a) Pd(II) may be determined in a wider range of concentration, (b) longer stability of colour (24 hr in contrast to 4 hr with diethazine hydrochloride), (c) insensitivity towards temperature (5-97°C), and (d) lower amount of reagent used.

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