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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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