

Extractive spectrophotometric determination of microgram amounts of palladium with iodide and cetyltrimethylammonium bromide

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The coloured complex formed between palladium(II), iodide and cetyltrimethylammonium bromide, is extractable into chloroform. Absorbance, measured at 340 nm, shows a linear response upto 5 ppm of palladium. Molar absorptivity of the complex, based on palladium content, is $2.038 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity is $0.0052 \mu\text{g}/\text{cm}^2$. The influence of foreign ions has been studied.

Iodide complexes of palladium, which can be extracted by organic solvents have been reported¹⁻⁵. Presently it has been observed that tetraiodopalladate(II), obtained from the reaction between Pd(II) and KI in neutral or slightly acidic solution, forms with cetyltrimethylammonium bromide (CTAB) as ion-pair extractable into chloroform. This observation has led to the development of a sensitive method for the spectrophotometric microdetermination of palladium, which is being described in this note.

Absorbance measurements were made with a Shimadzu PR1 model spectrophotometer equipped with 10 mm matched quartz cells. An ECL digital pH meter was used to measure the acidity of the aqueous solution.

Experimental

Stock solution of palladium(II) was prepared from PdCl_2 (Johnson and Matthey) and standardised with dimethylglyoxime⁶. 0.1 M solution of cetyltrimethylammonium bromide (CTAB; SISCO) (0.1 M) and potassium iodide (BDH) solution (0.1 M) were prepared in conductivity water. Potassiumhydrogen phosphate - sodium hydroxide buffer was used to adjust the pH of the aqueous solution.

General procedure: An aliquot containing upto 50 μg of Pd(II) was treated with KI (0.5 ml), CTAB (0.1 ml) and adequate amount of buffer (pH 6) to make the aqueous volume to 10 ml. The mixture was equilibrated with chloroform (10 ml) and the separated organic layer was dried over anhydrous sodium sulphate. Fi-

nally the absorbance of the chloroform extract was measured at 340 nm against pure solvent. Palladium was computed from a calibration curve.

Results and discussion

With aqueous potassium iodide, palladium(II) gives a reddish-brown colouration due to the formation of $[\text{PdI}_4]^{2-}$. This complex anion, as such is not extractable into chloroform. On addition of CTAB to this coloured solution, an ion-association complex, probably of the type $[\text{CTA}^+]_2[\text{PdI}_4^{2-}]$ is formed, which is extractable into chloroform. The chloroform solution exhibits λ_{max} at 340 nm with a broad band of comparatively lower intensity around 440 nm. The reagent blank shows insignificant absorbance in this region. Palladium could be quantitatively extracted in the pH range of 2-10. The pattern of the absorption spectra of the complex in this pH range remained unchanged, indicating the formation of only one complex species in all cases.

Use of other extracting solvents like carbon tetrachloride, benzene or ethyl acetate offered no special advantages over chloroform. The system conforms to Beer's law over 5 ppm of palladium. The molar absorptivity of the complex, based on palladium content, was found to be $2.038 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and Sandell's sensitivity $0.0052 \mu\text{g Pd}/\text{cm}^2$ at 340 nm, which classifies the colour reaction as one of the most sensitive for palladium. CTAB (0.1 ml, 0.1 M) and KI (0.5 ml, 0.1 M) at the concentrations specified were sufficient to extract upto 50 μg of palladium in a single operation.

Interference: To test the effects of diverse ions on the extraction behaviour, palladium(II) was extracted and determined according to the recommended procedure in the presence of the desired foreign ions at pH 6.0. An ion was considered to interfere if the recovery of palladium differed by more than $\pm 3\%$ from the actual amount taken. Palladium(II) (41.75 μg) could be determined without interference in the presence of 200-fold excess of the following ions: Al(III), Ca(II), Ba(II), Sr(II), Be(II), Bi(III), Cd(II), Ce(III), Cr(III), Co(II), Cu(II), Fe(III), V(V), La(III), Pb(II), Mg(II), Mn(II), Ni(II), Rh(III), and Zn(II). Less than 50-fold excess of Th(IV), U(VI), Mo(VI) and Zr(IV) did not interfere in the determination of Pd(II). Mercury(II) and platinum(IV) interfered. In the presence of silver the organic extract becomes turbid due to some yellow precipitate.

Among the anions tested, 500-fold excess of the following are tolerable: EDTA, fluoride, ascorbate, citrate, tartrate, phosphate, borate and phthalate. Thiocyanate interfered. In the presence of thiosulphate, palladium could not be extracted.

The average of six determinations of 41.75 μg of Pd(II) was 41 μg with a relative mean deviation of 1.6%.

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