Extractive Photometric Determination of Palladium & Platinum with o-Mercaptoacetoacetanilide

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o-Mercaptoacetoacetanilide forms 1:2 complexes with palladium ($\lambda_{max}$, 518 nm) and platinum ($\lambda_{max}$, 593 nm) at lower pH in hydrochloric acid medium and these are extractable in chloroform. The molar absorbivities of the complexes are $7.57 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ for palladium and $9.56 \times 10^3$ dm$^3$ mol$^{-1}$ cm$^{-1}$ for platinum. Sandell's sensitivities for the two metals are respectively 0.014 and 0.019 $\mu$g cm$^{-2}$. The applicable range of concentrations are 0.1-11.0 ppm and 0.2-16.0 ppm for palladium and platinum respectively. The methods are free from interferences from associated noble and base metals. The solid complexes have been isolated and characterised.

Beamish$^1$ critically reviewed a variety of organic reagents including a number of thiol ligands which have been employed for the spectrophotometric determinations of palladium and platinum. Only a few thio ligands have been reported thereafter for the determinations of palladium and platinum. Only a few thio ligands have been employed for the spectrophotometric reagents including a number of thiol ligands which have been reviewed critically by Beamish$^1$.

A Beckman double beam UV-visible spectrophotometer (model 26), a Beckman Zeromatic pH-meter and a Beckman IR spectrophotometer (Acculab-10) were used. Palladium(II) and platinum(II) chlorides (J. Mathey, London) were dissolved separately in dil. hydrochloric acid and the solutions diluted suitably with doubly distilled water. The metal contents were determined by conventional methods$^7-8$. o-MAA solution was prepared by condensation of o-aminothiophenol and ethyl acetoacetate$^6$. A $1.0 \times 10^{-3}$ M reagent in 50% (v/v) ethanol was used. All other reagents used were of A R or G R grade.

Procedure for palladium—An aliquot (1 ml) of palladium(II) solution containing 10-120 $\mu$g was taken and to this was added the reagent solution (10 ml, 1.0 $\times 10^{-3}$ M). The pH of the solution was kept between 0.3 and 1.0 by adding hydrochloric acid and extracted with chloroform (2 x 5 ml). The volume of the organic layer was brought up to the mark in a calibrated 10 ml volumetric flask after it had been dried over anhydrous sodium sulphate. The absorbance was measured at 518 nm against solvent blank.

Procedure for platinum—To the platinum(II) (10-200 $\mu$g) solution was added the reagent solution (8 ml, 1.0 $\times 10^{-3}$ M). The acid strength of the resulting solution was adjusted between 2 and 4 M in hydrochloric acid and extracted with chloroform (2 x 5 ml). The volume of the organic layer was brought up to the mark in a calibrated 10 ml volumetric flask after it had been dried over anhydrous sodium sulphate. The absorbance was measured within 1 hr at 593 nm against solvent blank.

The absorbances of several extracts containing different amounts of palladium were measured against solvent blank and the plots showed maximum absorption at 518 nm. Similarly, for platinum maximum absorption was at 593 nm. The corresponding Sandell sensitivities were 0.014 and 0.019 $\mu$g cm$^{-2}$.

Beer's law was obeyed over the ranges 0.1-11.0 ppm and 0.2-16.0 ppm for palladium and platinum respectively. According to Sandell$^9$ the optimum concentration ranges were respectively 2.9-9.9 ppm and 4.5-14.2 ppm. The corresponding Sandell sensitivities were 0.014 $\mu$g palladium cm$^{-2}$ and 0.019 $\mu$g platinum cm$^{-2}$. The relative standard deviations were found to be $\pm 0.65\%$ and $\pm 1.06\%$ respectively. The confidence limits (95%) were 10.01 $\pm$ 0.07 ppm palladium and 7.99 $\pm$ 0.09 ppm platinum for 7 determinations in each case.

For efficient extraction of the complexes it was found that 0.3-1.0 pH was suitable for palladium and 2-4 M hydrochloric acid medium was required for platinum to produce a maximum colour intensity. For 1 $\mu$g of palladium 1 ml of the reagent solution (1.0 $\times 10^{-3}$ M) was found to be sufficient and addition of an excess amount (upto 6 ml) had no effect on the absorbance. Similarly, experiments using 2 $\mu$g of platinum showed that 1 ml of the reagent was required and addition of 3 to 4 fold excess did not interfere.

Chloroform was found to be most suitable extractant for both palladium and platinum complexes. The two complexes were recovered to the extent of about 95% in the first step. The extract for the
palladium complex was stable for 12 hr whereas that for platinum complex was stable for 4 hr.

For the study of the tolerance limits (within relative error \( \pm 2\% \)) for diverse ions, 100 \( \mu g \) palladium(II) and 80 \( \mu g \) platinum(II) were taken separately with varying concentrations of other ions and the analyses were carried out by the recommended procedures. The tolerance limits in the determination of palladium were as follows: 10 mg for Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Al(II), Ga(III), In(III), Zn(II), Ti(IV), Cd(II), Th(IV); 7 mg for Te(IV), Zr(IV); 5 mg for Cr(III), Mn(II), Co(II), Ni(II), Cu(II), As(III), Sb(III), Bi(III), Se(IV), Au(III), V(IV), Mo(VI), W(VI), Ce(IV); 100 \( \mu g \) for Os(VIII), Ir(III), Rh(III); 50 \( \mu g \) for Fe(III) in presence of PO$_4^-$, Ru(III); 700 mg for Cl$^-$; 500 mg for NO$_3^-$, BO$_3^{3-}$; 400 mg for SO$_4^{2-}$; and 300 mg for PO$_4^{3-}$, tartrate. On the other hand, the tolerance limits in the determination of platinum were: 10 mg for Mg(II), Ca(II), Sr(II), Ba(II), Al(III), Ga(III), In(III), Co(II), Ni(II), Cu(II), Zn(II), As(III), Sb(III), Bi(III), Se(IV), Au(III), V(IV), Mo(VI), W(VI), Ce(IV); 5 mg for Cr(III), Mn(II), Sb(III), Mo(II), W(VI), Ce(IV); 2 mg for Se(IV), Au(III), V(IV); 100 \( \mu g \) for Ru(III), Rh(III); 50 \( \mu g \) for Fe(III) in presence of PO$_4^{3-}$, Os(VIII), Ir(III); 600 mg Cl$^-$; 500 mg BO$_3^{3-}$; 400 mg NO$_3^-$, SO$_4^{2-}$; and 200 mg PO$_4^{3-}$, tartrate. Estimations were not possible in the presence of U(VI), Sn(II), Hg(I), citrate, cyanide and EDTA in either case.

**Determination of palladium and platinum in a mixture**—A mixture containing 100 \( \mu g \) of palladium and 80 \( \mu g \) of platinum was used. The pH of the solution was adjusted to 1.0 and 10 ml of 1.00 \times 10^{-3} \( M \) o-MAA were added. Palladium was extracted with chloroform and the absorbance measured. The acidity of the aqueous layer was then adjusted to 4.0 \( M \) in hydrochloric acid and to this was added 1.00 \times 10^{-3} \( M \) reagent solution (10 ml) and platinum determined in the chloroform layer. Errors in the determination of both metals were less than \( \pm 2\% \).

The method was checked by analysing the synthetic samples of the following compositions: (i) Pd (100 \( \mu g \)), Pt (50 \( \mu g \)), Ru (50 \( \mu g \)), Rh (50 \( \mu g \)), Au (50 \( \mu g \)), Os (50 \( \mu g \)), Ir (50 \( \mu g \)), (ii) Pd (100 \( \mu g \)), Pt (100 \( \mu g \)), Cu (5 \( mg \)), Co (5 \( mg \)), Ni (5 \( mg \)), As (5 \( mg \)), Te (5 \( mg \)), (iii) Pd (60 \( \mu g \)), Pt (50 \( \mu g \)), Rh (50 \( \mu g \)), Cu (5 \( mg \)), Co (5 \( mg \)), Te (5 mg); and (iv) Pd (60 \( \mu g \)), Pt (100 \( \mu g \)), Ru (50 \( \mu g \)), Rh (50 \( \mu g \)), Os (50 \( \mu g \)), Au (50 \( \mu g \)). In all the cases errors in the determination of the two metals were within \( \pm 1.5\% \).

**Nature of complexes**—A small amount of either of the complexes was precipitated in the same condition used for extraction. The results of elemental analyses of these complexes indicated metal to ligand ratio as 1:2. The composition of the complexes were also determined by conventional molar ratio method and in both cases sharp breaks were also observed at the molar ratio of 1:2 (metal to reagent). The TG analysis showed that the thermal stability of the Pd complex was more than that of the Pt complex. The decomposition of these complexes was completed at 810 and 665°C respectively and the loss in mass corresponded to the formation of PdO and Pt respectively. The IR spectra of the complexes were compared with that of the ligand showing the presence of free SH grouping as was found in the ligand$^9$. The present ligand (o-MAA) thus behaves as a bidentate chelating agent. The probable composition of the complexes is M(C$_4$H$_4$O$_{10}$NO$_3$S)$_2$, where M = Pd(II), Pt(II). Furthermore, the diamagnetic nature of the complexes indicated square-planar arrangement.

**References**