NOTES

Sodium-*p*-(mercaptoacetamido)benzenesulphonate as a Spectrophotometric Reagent for Palladium

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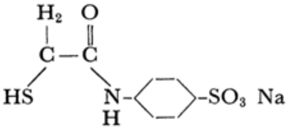
Berg and Roebling[1] introduced thionalide as an interesting analytical reagent. It possesses a marked precipitating action in relation to cations that are precipitated as sulphides in acid, neutral, and alkaline media. If the naphthyl radical in thionalide is replaced by phenyl, then the precipitating action of the resulting thioglycolic acid anilide is similar, but its sensitivity as a precipitant is less. The high selectivity of thionalide towards palladium in acid media suggests that the sodium salt of the sulphonic acid derivative of thioglycolic acid anilide, namely, sodium-*p*-(mercaptoacetamido)benzenesulphonate (I), should prove a useful spectrophotometric reagent for the metal.



(I)

The above compound is water-soluble and gives water-soluble coloured complexes with cobalt, nickel, palladium, platinum, rhodium, etc. In this communication its use as a spectrophotometric reagent for palladium will be described.

Experimental

Reagent Solution. Sodium-*p*-(mercaptoacetamido)-benzenesulphonate was prepared by employing the method given by Gupta and Sogani.[2] A 0.25% w/v solution of the reagent in distilled water was prepared a fresh each time.

Standard Palladium Chloride Solution. Approximately 1 g of reagent-grade palladium chloride was dissolved in a little water containing 6 ml of concentrated hydrochloric acid; the volume was then made up to 1 *l*. After standardisation, this solution was diluted to give a solution containing 25 ppm of palladium.

Buffer Solutions. Ten percent v/v hydrochloric acid and 10% w/v sodium acetate were used for adjusting the pH.

Instruments. The absorbance measurements were made with a Beckmann Quartz Spectrophotometer, Model DU, using 1.00 cm quartz cells for the ultraviolet region and Corex cells for the visible region. The pH measurements were made with a Cambridge bench-type pH Meter. The visual colour comparisons were made in 50 m*l* Nessler tubes of the standard type.

Absorbance Curves. Five millilitres of a standard palladium solution, containing 25 ppm of palladium, was pipetted into a 25 m*l* flask; then 5 m*l* of a 0.25% reagent (a large excess) solution and varying amounts of a 10% sodium acetate solution and a 10% hydrochloric acid solution were added so that the pH after final dilution was about 3.5. The volume was then made up to the mark, and the absorbance was measured after 10 min at different wavelengths, using the reagent solution as a blank.

A 4 ppm reagent solution was prepared and its absorbance was measured at different wavelengths using water as a blank. Similarly, the absorbance of a palladium chloride solution containing 12 ppm of palladium, with a pH of 3.5, was measured, using water as a blank.

Figure 1 gives the absorbance curve of the palladium complex with a "reagent blank solution," a reagent

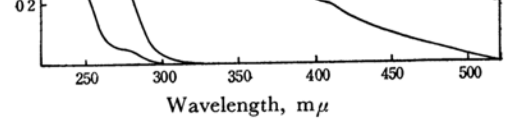


Fig. 1. Absorbance curves.
I: Palladium complex (5.0 ppm, Pd)
II: Reagent (4.0 ppm)
III: Palladium alone (12.0 ppm)

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1) R. Berg and W. Roebling, *Ber.*, **68**, 403 (1935); *Z. Angrew. Chem.*, **48**, 430, 597 (1935).

2) H. K. L. Gupta and N. C. Sogani, *Anal. Chem.*, **31**, 918 (1959).

solution and a palladium chloride solution using water as a blank. The absorbance of the reagent solution falls sharply at longer wavelengths than 250 mμ and is almost negligible at 310 mμ (Curve II). The absorbance peak of the palladium complex is at 310 mμ, where the reagent does not interfere. The absorbance of palladium complex then falls steadily and has a flat region from 400 to 410 mμ. Even in this region, however, the absorbance is fairly high—high enongh to be suitable for the estimation of palladium (Curve I). The absorbance curve of palladium chloride is given in curve III. This will not interfere with palladium estimations after 300 mμ. Hence, the palladium can be estimated spectrophotometrically at 310 mμ (the ultraviolet region) or at 400 mμ (the visible region), using water as a blank.

The Effect of the pH. The solutions used for studying the effect of the pH on the reaction were prepared as above, except that different amounts of 10% hydrochloric acid and 10% sodium acetate were added so that the final pH values ranged from 1.5 to 8.0. The absorbance was measured after 10 min. at both 310 mμ and 400 mμ.

Figure 2 shows the effect of pH on the absorbance. At both the wavelengths the absorbance is constant between pH 2.8 and 7.0. The increase in absorbance above pH 7.0 is due to the excess of the reagent, which has a light yellow colour in an alkaline medium. The increase in absorbance below pH 2.8, as is shown at 400 mμ (Curve II), presumably indicates the formation of a complex with a composition different than that formed between pH 2.8 and 7.0. The decrease in absorbance at 310 mμ below pH 2.8 indicates incomplete complex formation at a low pH value.

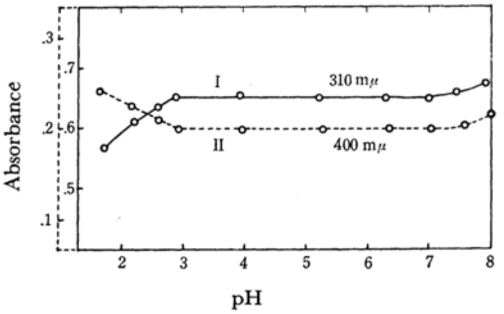

Fig. 2. Effect of pH. Pd: 5.0 ppm

The Ratio of the Amount of Reagent to That of the Metal Ion Needed for Full Absorbance. A series of solutions were prepared as above, and varying amounts of equimolecular solutions of the reagnet were added so that the mole ratio of Palladium to reagent was from 1 : 1 to 1 : 20. The pH of the solutions was then adjusted between 3.0 to 3.5 The absorbance was measured after 10 minutes at 310 mμ. The absorbance increases with the ratio until it becomes constant at and after a 1 : 10 ratio of palladium to reagent.

The Rate of Reaction and the Stability of the Complex. The colour of the palladium complex is initially reddish-yellow, but it slowly changes to an intense yellow. There was a gradual increase in the absorbance with time, until it became steady after about 8 min at 25°C. It was then stable for more than 48 hr.

The Effect of the Temperature. It was found that there is no change in colour intensity over the temperature range from 25 to 85°C.

Beer's Law. Beer's law is obeyed in both cases. At 310 mμ the concentration range is from 0.5 to 7.0 ppm and the molecular extinction coefficient of the palladium complex is 1.38×10^4. At 400 mμ the concentration range is from 3 to 24 ppm and the molecular extinction coefficient is 4.25×10^3.

The Sensitivity of the Colour Reaction. The sensitivity of the colour reaction as determined in a 50-m*l* Nessler tube is 1 part in 4000 parts of the solution. The spectrophotometric sensitivity is determined to be 0.0077/cm² at 310 mμ and 0.025/cm² at 400 mμ for $I_0/I=0.001$.

Recommended Procedure. A palladium solution, containing 1.5 to 600 γ of the metal ion, is taken into a 25-ml. volumetric flask; then a 10% v/v hydrochloric acid solution and a 10% w/v sodium acetate solution are added to bring the pH of the final solution to between 3.0 and 3.5. Five millilitres of a 0.25% reagent solution is then added, and the volume is made up to the mark. The absorbance is measured after 10 min. at 310 mμ when the palladium content is from 0.5 to 7 ppm, and at 400 mμ when the palladium content is from 3 to 24 ppm At both these wavelengths, water is used as a blank.

The Tolerance of Diverse Ions. Below pH 4.0, zinc(II), manganese(II), iron(II), iron(III), aluminium(III), chromium(III), mercury(II), cadmium(II), antimony(III), aresenic(III), tin(II), titanium(IV), cerium(III), uranium(IV), thorium(III), zirconyl(II), uranyl(II), tungstate, alkali and alkaline earth metals and common anions do not give any colour reaction with the reagent; thus, they are not likely to interfere with direct spectrophotometric determination of palladium. Molybdate in acid media gives a yellow colour, which changes to green, and finally to blue, on standing. The reagent appears to reduce molybdate to molybdenum blue. Silver(I), lead(II) and gold(III) interfere. Copper(II) gives a bluish-black colour which disappears when an excess of the reagent is added. Nickel(II) and cobalt(II) do not interfere at a low pH.

For studying the interference of diverse ions in the

Table 1. The tolerance of diverse ions (3 ppm Pd)

Ion	Added as	Concn., ppm
Zn(II)	sulphate	740
Mn(II)	sulphate	740
Ni(II)	sulphate	40
Co(II)	sulphate	12
Cu(II)	sulphate	10
Fe(II)	sulphate	20
Fe(III)	sulphate	10
Al(III)	sulphate	8
Pt(IV)	chloride	3
Rh(III)	chloride	3
Ir(IV)	Na_2IrCl_6	10_{16} (with 32 ppm EDTA)
Ru(III)	chloride	4
		12 (with 32 p.p.m. EDTA)

determination of palladium, the recommended procedure was followed. Table 1 summarises the tolerance of diverse ions.

Precision. The precision of the method was determined for a set of ten samples of solutions containing 3 ppm of palladium and 1 ppm each of ruthenium, rhodium, iridium and platinum. The standard deviation was 0.045 ppm of palladium.

Discussion

Several spectrophotometric methods have been described for the determination of palladium. *p*-Nitrosodiphenylamine,3) 3-hydroxyl-1-*p*-sulphonatophenyl-3-phenyltriazene,4) and 5-amino-2-benzimidazolethiol5) are the reagents commonly recommended. Didodecyldithio-oxamide,6) diallyldithiocarbamido hydrazine,7) *N*, *N*'-bis(2-sulphoethylditio-oxamide),8) xylenol orange,9) 1-thioglycerol,10) 2-mercaptobenzoxazole,11) 8-aminoquinoline12) and quinoxaline-2, 3-dithiol13) have also been reported during the last four years. The majority of these compounds do not, however, possess the properties required for a good spectrophotometric reagent. In certain cases, the pH adjustment is very rigid; in others, the coloured complex has to be extracted with a solvent before the absorbance is measured. The advantage of using sodium-*p*-(mercaptoacetamido)benzenesulphonate is that it does not react with common metals at a low pH; it also compares favourably with other reagents in sensitivity.

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