

TABLE 3—DETERMINATION OF IODIDE IN A MIXTURE OF CHLORIDE AND IODIDE USING *p*-AMINO-*o*'-DIMETHYLAZOBENZENE AS INDICATOR*

Concn. of solution <i>M</i>	Vol. of KI+KCl ml	Vol. of AgNO ₃ ml
0.1	10.00+10.00	10.05
0.2	10.00+10.00	10.00-10.02
0.01	10.00+10.00	10.02-10.04
0.05	10.00+10.00	10.00-10.02
0.1	5.00+10.00	4.98-5.02
0.2	5.00+10.00	5.00-5.02
0.01	7.00+10.00	6.98-7.03

* Titrations were performed at pH 4 where only I⁻ ions are titrated. The colour change yellow to pink was sharp and reversible and coagulation of AgX occurred near the end point

Results and Discussion

During the titration of halides thiocyanate by AgNO₃ using *p*-amino-*o*'-dimethylazobenzene as indicator, the colour change from yellow to pink at the end point is accompanied by a fall in pH from 4.05 to 3.60, which is more prominent in the case of iodide. The pH fall may be attributed to the deprotonation of the dye forming negatively charged dye ion. In the beginning AgX formed initially, is present in the medium containing abundance of halide ions. As the titration of X⁻ ions continues more and more AgX is formed and near the end point the amount of X⁻ ions is considerably reduced. These (X⁻) are, however, adsorbed on the surface of AgX at active points having adsorbed Ag⁺, forming weak mixed AgX-dye complex imparting a pink colour to the surface⁹. The colour changes in the reverse titration can similarly be explained.

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Dimethyldithiocarbamido-hydrazine as an Extractive Spectrophotometric Reagent for Determination of Palladium(II) and Nickel(II) Individually and also from Their Binary Mixture

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THE utility of organic thio-ligands having nitrogen atoms in their molecules has been widely investigated by several workers¹⁻⁹. Mention may be made of a few such reagents like thioamides, thioanilides, aminothiols, thiodiazoles, mercaptotriazoles, thio-carbamides and its various derivatives, aminothio-carboxylic acids, ruheanic acid, phenylhydrazine, sulfonic acid, etc. But their behaviour for the spectrophotometric determination of palladium and nickel, suffer from narrow pH range of extraction, variable composition of the complexes with variation of pH, interference from commonly associated metal ions, and difficulty of analytical separation of Pd^{II} and Ni^{II} from their binary mixture. All the above mentioned difficulties have been overcome in this present method of estimation of Pd^{II} and Ni^{II}. Moreover, the present reagent claims its superiority over the classical reagent, dimethylglyoxime for enabling the separation of Pd^{II} and Ni^{II}. The work involves the application of dimethyldithiocarbamido-hydrazine¹⁰ (METHALZIN), a newly introduced ligand, which can suitably be utilised for the spectrophotometric determination of Pd^{II} and Ni^{II} individually and also by separation from their binary mixture.

Methalzin forms a brown complex with Pd^{II} in aqueous solution within pH range 1.5-3.6, the complex being extractable in chloroform while the aqueous solution of Ni^{II} forms a brownish yellow complex with the reagent within pH range 7.5-9.6, the complex being equally soluble in chloroform. Thus by simply maintaining the proper pH of extraction, separation and determination of these two metal ions have been successfully achieved.

Experimental

Standard solutions of Ni^{II} and Pd^{II}: The metal ion solutions were prepared by dissolving known weights of AnalaR nickel chloride and palladium chloride in double-distilled water. The solutions were standardised by usual methods¹¹ using dimethylglyoxime.

Reagent solution: Dimethyldithiocarbamido-hydrazine (METHALZIN) was prepared by the method¹² described earlier. As the excess amount of reagent has no adverse effect on absorbance. A 0.025% (w/v) solution of the reagent in absolute alcohol was used throughout the experiment. All other reagents and chemicals used were of AnalaR

quality. Chloroform used for extraction was purified by the recommended method.

All the absorbance measurements were made with the help of Spectromom 204 spectrophotometer and pH values were determined with Elico Model L 1-10 pH-meter.

Procedure :

Palladium(II) : A measured quantity of Pd^{II} solution was taken in a 50 ml separatory funnel to which 1 ml of 0.025% (w/v) reagent solution was added followed by requisite amount of 1 N sodium hydroxide solution so as to maintain the pH of the resulting solution within 1.5-3.6 in a total volume of 25 ml made up with water. The solution was shaken gently for 5 min. Extraction of Pd^{II} complex was made twice by adding 3 ml portions of chloroform at a time. The mixture was shaken vigorously each time for 5 min. The solvent layer after separation was transferred into a small beaker containing 0.5 g anhydrous sodium sulphate. Extractions of the Pd^{II} complex with 2 ml portions of chloroform were again made twice and the extracted Pd^{II} complex was collected into the same beaker. The combined extract was transferred into a 10 ml volumetric flask and diluted to the mark with the solvent. The absorbance of each solution was measured at 345 nm, the wavelength of maximum absorption, against reagent blank.

Nickel(II) : A known quantity of Ni^{II} solution was taken in 50 ml separatory funnel to which was added 1 ml of 0.025% (w/v) reagent solution. The pH of the solution was maintained between 7.5-9.6 by addition of 1N sodium hydroxide solution in a total volume of 25 ml made up with water. The brownish yellow Ni^{II} complex was extracted in 10 ml chloroform by the same procedure as already described in case of Pd^{II} complex. The absorbance of this solution was then measured at 340 nm, the wavelength of maximum absorption, against reagent blank.

Results and Discussion

The absorption spectrum of Pd^{II} complex has the maximum absorption at 345 nm whereas that of the Ni^{II} complex at 340 nm. But it is a matter of interest to note that the reagent has practically no absorption within the range of wavelength 340-345 nm. The absorption spectrum of the ligand in both the pH ranges of estimations of Ni^{II} and Pd^{II} at 7.5-9.6 and 1.5-3.6, respectively do not change.

A 0.025% (w/v) solution of the reagent in absolute alcohol was used for all measurements. Excess reagent has no adverse effect on the optical density of the solution.

The brown Pd^{II} complex was found stable in aqueous medium for 3 h even upto 60° and after extraction in chloroform the colour remains stable for more than 12 h at room temperature.

The brownish yellow Ni^{II} complex was found stable for more than 2 h in aqueous medium even

above 40° whereas the chloroform extract was found stable for more than 8 h at room temperature.

Effect of pH : The optimum pH range for maximum development of colour of Pd^{II} complex was found to be between 1.5-3.6 and in case of Ni^{II} complex it was 7.5-9.6. This marked difference in the optimum ranges of pH helps to the separation and determination of these two metal ions from their binary mixtures.

Optimum range and photometric sensitivity and molar-extinction co-efficients : In the case of Pd^{II} complex Beer's law is obeyed within 1-7 ppm of Pd^{II}. The optimum concentration range as determined by Ringbom's ¹⁸ curve lies within 2.0-6.4 ppm of Pd^{II}, and the photometric sensitivity as per Sandell's definition was 0.0139 µg/cm³. Beer's law was found to obey for Ni^{II} complex within the range 2.0-8.8 ppm of Ni^{II} whereas the optimum concentration range according to Ringbom's curve was 1.8-7.0 ppm of Ni^{II} and the photometric sensitivity according to Sandell's definition comes out to be 0.01205 µg/cm³.

The molar extinction coefficient of Pd^{II} complex calculated from Beer's law was found to be 7650 mol⁻¹cm⁻¹, and that of Ni^{II} complex 4870 mol⁻¹cm⁻¹.

Precision and accuracy : The independent determinations containing 2.0 ppm of both Pd^{II} and Ni^{II} per 10 ml gave mean absorbance values 0.155 and 0.161, the standard deviations being 0.002 and 0.005 absorbance units, respectively.

Composition of the complexes : Ten stoichiometric composition of the complexes was determined by Job's method of continuous variation¹⁴ and molar ratio method¹⁵. The result showed that Pd^{II} and Ni^{II} combined with the reagent in the ratio 1 : 1.

Effect of diverse ions : Fe^{III} is masked by NH₄HF₂ in case of Pd^{II} and Ni^{II}. Be^{II} does not interfere in the determinations in case of both the metal ions. La^{III} does not interfere in the determination of Pd^{II} but it does in case of Ni^{II}. Various common ions, e.g. Na^I, Ba^{II}, Sr^{II}, Ca^{II}, Mn^{II}, Cu^{II}, Mo^{VI}, Pt^{IV}, U^{VI}, Ga^{III}, Th^{IV}, Ru^{III}, Rh^{III}, Au^{III}, Os^{VI}, Re^{VII}, Ag^I, Cd^{II}, Zn^{II}, Hg^{II}, NO₃⁻, Cl⁻, SO₄²⁻, oxalate, acetate, citrate and tartrate were tolerated in more than 100 times excess in case of Pd^{II}. Only cyanide ion interfere in determination of Pd^{II}. In case of nickel ions Ag^I, Bi^{III}, Hg^{II}, Co^{II}, Tl^I, citrate, cyanide and tartrate interfere seriously with the determination.

Determination of Pd^{II} and Ni^{II} by separation from their binary mixture : First to an aliquot of the mixture of acidic solutions of both the metal ions taken in a separatory funnel was added 2 ml of 0.1% (w/v) reagent solution and the pH of the solution was maintained between 2-3 by adding requisite amount of 1N sodium hydroxide solution in a total volume of 10 ml made up with water. The Pd^{II} complex was then extracted in 10 ml chloroform in the usual way already described and the absorbances were

measured at 345 nm against the reagent blank. The aqueous layer remaining after the extraction of Pd^{II} complex was treated with 2 ml of 0.1% (w/v) reagent solution and the pH of the mixture maintained between 8-9 with the help of 1N sodium hydroxide solution in a total volume of 25 ml made up with water. The Ni^{II} complex was then extracted in 10 ml chloroform according to the procedure already described and the absorbances of the nonaqueous layers were measured at 340 nm against the reagent blank. The results are shown in Table 1.

TABLE 1—DETERMINATION OF Pd^{II} AND Ni^{II} FROM THEIR BINARY MIXTURE

Amount of metal ions taken' ppm	Pd^{II} found ppm	Ni^{II} found ppm
2.5 Pd^{II}	2.497	2.507
2.5 Ni^{II}		
8.0 Pd^{II}	3.011	3.510
8.5 Ni^{II}		
4.0 Pd^{II}	4.018	4.008
4.0 Ni^{II}		

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