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Spectrophotometric Determination of Palladium(II) by Extraction of Its 1-Pyrrolidinecarbodithioate into Molten Naphthalene

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A new spectrophotometric method for the determination of palladium after extraction of its 1-pyrrolidinecarbodithioate into molten naphthalene has been developed. Palladium forms a water-insoluble, thermally stable 1:2 complex with 1-pyrrolidinecarbodithioate which is easily extracted into molten naphthalene in the pH range of 3.0—6.0. At room temperature, solid naphthalene containing the metal-complex is dissolved in chloroform (10 ml). It has an absorption maximum in the range of 336—342 nm. Beer's law holds in the concentration range of 2.5—90.0 μg of palladium in 10 ml of chloroform solution. The molar absorptivity(1 mol^{-1} cm^{-1}) and sensitivity(μg/cm^2) are found to be 6.4×10^3 and 0.0166, respectively. Samples containing 30 μg of palladium gives a mean absorbance of 0.18 with a standard deviation of 0.0025. Other factors such as amount of reagent and naphthalene, pH, aqueous phase volume and diverse ions have been examined. The method has been applied to the analysis of some alloys.

Ammonium 1-pyrrolidinecarbodithioate has been used as an analytical reagent in the determination of various metal ions spectrophotometrically and atomic absorption spectrophotometrically after extracting their metal complexes into suitable solvents.[1-3] Recently it has been utilized in the spectrophotometric determination of copper, bismuth and cobalt after extracting their complexes into molten naphthalene.[4] The main advantages of this method are that the equilibrium distribution in the two phases is achieved in a few seconds and the metal chelates are dissolved merely by contact with the molten naphthalene. A very small amount (2 g) of the organic phase is required for the complete extraction which enhances the sensitivity as the whole of the organic phase may be taken for the analysis. This technique is especially useful for the extraction of those metal ions which form complexes with the complexing agent at high tempera ture.[5] The present communication describes conditions for the extraction of palladium with potassium 1-pyrrolidinecarbodithioate (PPDC) into molten naphthalene and its subsequent determination by spectrophotometric method after dissolution of naphthalene extract in chloroform. The interference of the various ions has been studied and the conditions have been developed for the determination of palladium in some alloys.

Experimental

Reagents. Palladium nitrate solution was prepared in redistilled water and standardized gravimetrically.[6]

PPDC solution, 0.2% was prepared by dissolving 0.2 g of PPDC in 100 ml of water.

Naphthalene and chloroform(analytical grade) were checked spectrophotometrically before use.

Alkali salt(1%) and metal salt(0.2%) solutions were prepared to study interference.

Dilute solution of perchloric acid, ammonia or acetate buffer prepared from 1 M(1 M=1 mol dm^{-3}) acetic acid and 1 M ammonium acetate were used to adjust pH.

Apparatus. An Elico pH meter and a SP-700 spectrophotometer were used.

General Procedure. An aliquot of palladium solution was taken in a beaker, to this was added 3.0 ml of reagent solution. The pH was adjusted to 4.2 with 2.0 ml of buffer solution. This solution was transferred to a 100-ml round bottomed flask and warmed on a water bath at about 60 °C and naphthalene (2 g) was added to it. The flask was stoppered and heating was continued till naphthalene melted and formed a separate liquid-layer. The flask was taken off from the water bath and stirred vigorously till the naphthalene separated out as a solid mass. Once more the naphthalene was melted, shaken vigorously and allowed to stand. The naphthalene was filtered off, dried on a filter paper and dissolved in chloroform in a 10 ml standard flask. This solution was dried by adding anhydrous sodium sulfate (2 g), and the absorbance was measured in a 1-cm cell at 340 nm against a reagent blank. A calibration curve was prepared under similar conditions.

Results and Discussion

Absorption Spectra. The absorption spectra of potassium 1-pyrrolidinecarbodithioate and palladium(II) 1-pyrrolidinecarbodithioate in naphthalene and chloroform solution were measured against water and reagent blank, respectively and are shown in Fig. 1. The palladium complex absorbs strongly in the region 336—342 nm where the reagent absorbs very little. All absorbance measurements were made at 340 nm.

Effect of pH. Extraction was carried out at different pH, other conditions as described in the general procedure being kept constant. The characteristics of all spectral curves were the same, indicating the presence of only one complex. The results are shown in Fig. 2. Optimum pH corresponds to 3.0—6.0.

Effect of Reagent Concentration. Extractions were carried out at a fixed pH but at varying reagent concentrations and it was observed that the extractions were quantitative for 1.5—6.0 ml of 0.2% of potassium 1-pyrrolidinecarbodithioate (Fig. 3). Consequently, 2.0 ml of the reagent was used in each case.

Effect of Buffer Solution. Sample solutions containing 30 μg of palladium, 3.0 ml of 0.2% PPDC solution and various amounts of the acetate buffer solution (pH 4.2) were added and the extractions were carried out by the general procedure. The absorbance remained constant for 0.5—6.5 ml of the buffer used In all the cases, 2.0 ml of the buffer was used.

Effect of Amount of Naphthalene. At fixed pH and reagent concentration, the extractions were car-

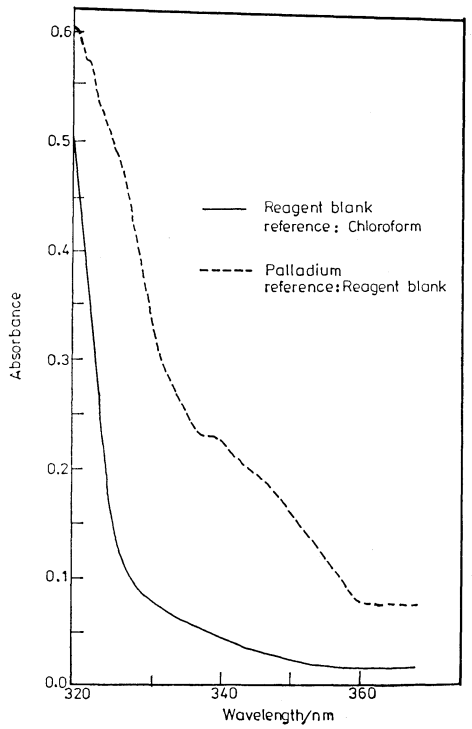

Fig. 1. Absorption spectra of 1-pyrrolidinecarbodithioate and palladium complex in naphthalene–chloroform solution.
Reagent blank: 1-pyrrolidinecarbodithioate: 3.0 ml (0.2%), naphthalene: 2.0 g, pH: 5.0, reference: water; palladium: 40 μg, rest of the conditions were the same as above, reference: reagent blank.

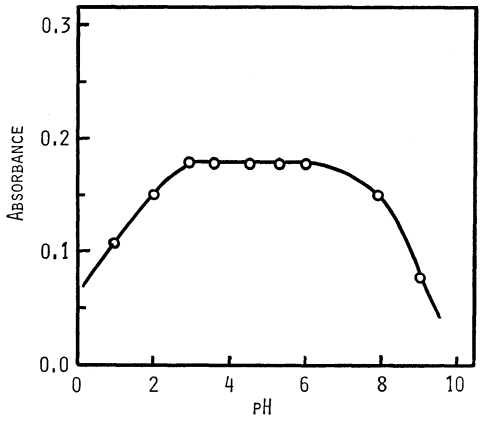

Fig. 2. Effect of pH on absorbance.
Palladium: 30 μg, wavelength: 340 nm, 1-pyrrolidinecarbodithioate: 3.0 ml (0.2%), naphthalene: 2 g, reference: reagent blank.

ried out by taking 0.5—3.5 g of naphthalene in different steps. It was observed that the absorbance remained constant for 1.0—3.0 g of naphthalene and thus 2.0 g of naphthalene was used throughout the experiment. Below 1.0 g, the extraction was incomplete while above 3.0 g of the naphthalene, it was difficult to dissolve it in a limited quantity of chloroform (10 ml).

Effect of Aqueous Phase Volume. Since the organic phase is very small (2 g) as compared to the aqueous phase (40 ml), it was essential to study the

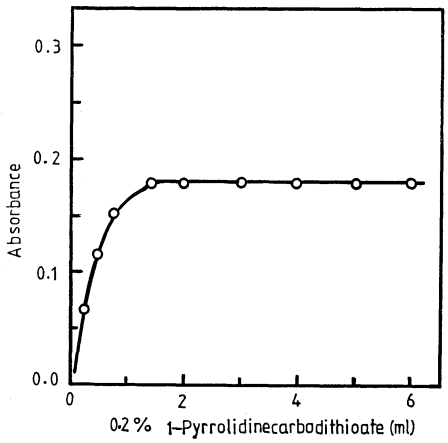

Fig. 3. Effect of reagent concentration on absorbance.
Palladium: 30 μg, rest of the conditions were the same as in Fig. 2.

TABLE 1. EFFECT OF DIVERSE SALTS

Alkali salt added	Anion added (mg)	Absorbance 340 nm
—	—	0.180
Potassium chloride	23.80	0.180
Potassium bromide	33.60	0.178
Potassium iodide	38.25	0.181
Potassium thiocyanate	29.85	0.182
Sodium acetate	40.00	0.180
Sodium sulfate	40.00	0.180
Sodium oxalate	33.60	0.177
Potassium sodium tartrate	39.40	0.178
Sodium citrate	31.45	0.177
Sodium orthophosphate	25.60	0.178
Sodium thiosulfate	21.00	0.182
Disodium EDTA	40.00	0.178
Sodium fluoride	22.60	0.178

Pd: 30.0 μg, pH: 4.2, 0.2% PPDC: 3.0 ml, buffer: 2.0 ml.

effect of the volume of the aqueous phase on the extraction. It was observed that the absorbance remained constant upto 50 ml of the aqueous phase. Above this volume of the aqueous phase, the extraction was not quantitative.

Effect of Digestion Time. The palladium(II) 1-pyrrolidinecarbodithioate in the solution was warmed on a water-bath at 60 °C and the effect of digestion time on the absorbance was investigated between 1—20 min. It was found that the absorbance remained constant during this period. Therefore, 10 min of digestion time was selected for all measurements.

Effect of Shaking Time. The sample solution containing palladium(II) 1-pyrrolidinecarbodithioate and 2.0 g of naphthalene was warmed on a water-bath for 10 min at the temperature 60 °C and the extraction was carried out by vigorous shaking of the contents upto 30 min. It was observed that the shaking time of 1 min was sufficient for the complete extraction.

Effect of Standing Time of Chloroform Solution. The absorbance of the complex in naphthalene–chloroform was noted at an interval of 20 min and it was noted that the absorbance remained constant for more than 24 h indicating that the complex is quite stable in the extract.

Effect of Electrolytes. Various electrolytes such as sodium perchlorate, sodium nitrate, sodium sulfate, and sodium acetate (0.01—1.0 M) caused no improvement in the extraction indicating that the extraction was complete.

Composition of the Complex. The composition of palladium(II) 1-pyrrolidinecarbodithioate was established by Job's method of continuous variation and the mole ratio method. A sharp peak at 0.33 mole fraction in Job's curve and a clear break at 1:2 metal: carbodithioate ratio in the mole ratio plot suggest the extraction of $Pd(C_4H_8NCS_2)_2$ under these conditions.

Calibration Curve. With the optimum conditions described above a calibration curve was constructed for palladium complex at 340 nm. It was observed that Beer's law was obeyed over the concentration

Table 2. Effect of diverse cations

Metal ion	Metal ion added(mg)	Absorbance	Remarks
—	—	0.180	
Ag^{+}	1.500	0.150	
Ag^{+}	1.125	0.178	
Al^{3+}	0.900	0.184	
Al^{3+}	0.625	0.182	
As^{3+}	0.740	0.182	
As^{3+}	0.555	0.180	
Be^{2+}	0.404	0.176	
Be^{2+}	0.303	0.178	
Bi^{3+}	0.860	0.192	
Bi^{3+}	0.645	0.182	
Cd^{2+}	1.200	0.184	
Cd^{2+}	0.900	0.181	
Co^{2+}	0.666	0.340	
Co^{2+}		0.186	* After masking with 5 ml of 1% EDTA solution
Co^{2+}	0.500	0.330	
Co^{2+}		0.184	* After masking with 5 ml of 1% EDTA solution
Cr^{3+}	0.520	0.183	
Cr^{3+}	0.390	0.181	
Cu^{2+}	0.431	0.334	
Cu^{2+}		0.183	* After masking with 5 ml of 1% EDTA solution
Cu^{2+}	0.323	0.295	
Cu^{2+}		0.180	* After masking with 5 ml of 1% EDTA solution
Fe^{3+}	0.332	0.280	
Fe^{3+}		0.184	* After masking with 10 ml of 1% EDTA solution
Fe^{3+}	0.240	0.220	
Fe^{3+}		0.182	* After masking with 10 ml of 1% EDTA solution
Hg^{2+}	0.294	0.242	
Hg^{2+}		0.188	* After masking with 10 ml of 1% EDTA solution
Hg^{2+}	0.220	0.210	
Hg^{2+}		0.184	* After masking with 10 ml of 1% EDTA solution
Ir^{3+}	0.520	0.186	
Ir^{3+}	0.390	0.180	
Mn^{2+}	0.960	0.182	
Mn^{2+}	0.720	0.180	
Mo^{6+}	1.088	0.183	
Mo^{6+}	0.816	0.180	
Ni^{2+}	0.500	0.780	
Ni^{2+}		0.210	* After masking with 5 ml of 1% EDTA solution
Ni^{2+}	0.375	0.480	
Ni^{2+}		0.183	* After masking with 5 ml of 1% EDTA solution
Os^{8+}	1.080	0.185	
Os^{8+}	0.810	0.182	
Pb^{2+}	0.616	0.180	
Pb^{2+}	0.462	0.180	
Pt^{4+}	0.240	0.188	
Pt^{4+}	0.180	0.182	
Rh^{3+}	0.202	0.188	
Rh^{3+}	0.156	0.183	
Ru^{3+}	0.387	0.184	
Ru^{3+}	0.289	0.182	
Sb^{3+}	0.640	0.182	
Sb^{3+}	0.480	0.180	
Te^{4+}	0.200	0.178	
Te^{4+}	0.150	0.178	
Th^{4+}	0.320	0.184	
Th^{4+}	0.240	0.182	
Tl^{+}	0.204	0.184	
Tl^{+}	0.152	0.182	
U^{6+}	0.560	0.184	
U^{6+}	0.420	0.181	
V^{5+}	0.870	0.182	
V^{5+}	0.652	0.180	
W^{6+}	1.114	0.182	
W^{6+}	0.834	0.180	
Zn^{2+}	0.596	0.178	
Zn^{2+}	0.427	0.180	
Zr^{4+}	0.916	0.182	
Zr^{4+}	0.687	0.181	

Pd: 30.0 μg, pH: 4.2, 0.2% PPDC: 3.0 ml, buffer: 2.0 ml.

Table 3. Determination of palladium in alloys

Alloy	Composition of alloy (%)	Amount of palladium taken/μg	Amount of palladium found/μg	Average μg	Other method[a]
Oakay	Ni:60, Pt:20, V:9.5, Pd:10.5	31.5	31.4 31.6 31.6 31.8 31.6	31.6	31.1
Platinum-Iridium	Pt:55, Ir:28, Rh:7, Cu:3, Fe:3.5, Pd:3.5	39.2	39.3 39.5 39.3 39.0 39.4	39.3	39.5

a) Average of the five determinations.

range of 2.5—90.0 μg in 10 ml of the final solution. Ten samples containing 30 μg of palladium were prepared by the general procedure gave a mean absorbance of 0.18 when measured in a 1-cm cell with a relative standard deviation of 0.0025. The molar absorptivity was calculated to be 6.4×10^3 l mol^{-1} cm^{-1} at 340 nm, and the sensitivity 0.0166 μg of palladium per cm^2 for the absorbance of 0.001.

Interference. The interference of various ions was studied in detail. Generally, 50 mg of alkali salt and 2 mg of metal ion were added individually to the aliquots containing 30 μg of palladium. Among the anions examined (Table 1) none interfered. This non-interference of the various anions may be attributed to their low stability constants as compared to palladium 1-pyrrolidinecarbodithioate.[7] Among the metal ions studied (Table 2) only Fe(III), Ni(II), Co(II), Hg(II), and Cu(II) interfered but their interference was eliminated by using suitable masking agents (Table 2). Obviously, the method is quite selective for the extraction of palladium.

Analysis of Alloy. 25—50 mg of the alloy of known composition, and 20—40 ml of aqua regia were added and the solution evaporated to about 5 ml. Concentrated hydrochloric acid (10 ml) was added, the solution was warmed, transferred to a 500 ml standard flask and made upto the mark with distilled water.[8] An aliquot was taken, 5 ml of 1% EDTA, and 3.0 ml of the reagent solutions were added. The pH of this solution was adjusted to 4.2 with 2 ml of the buffer solution and the palladium complex was extracted into molten naphthalene according to the general procedure. The results are given in Table 3 and are compared with a recent method.[9]

In conclusion, this simple and inexpensive procedure for palladium can be successfully applied to the alloy sample analysis.

The extraction with molten naphthalene is useful for the strongly hydrated oxinates of zinc,[10] magnesium[11] and cadmium,[12] and for the nioxime complexes[13] of nickel and palladium and bismuth 2-mercaptobenzothiazole complex[14] that offer a low solubility in nonaqueous solvents.

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References

1) C. H. McMaster, *Anal. Chem.*, **41**, 1489 (1969).
2) K. A. Uvarova and Yu. I. Usatenko, *Zavod. Lab.*, **38**, 1431 (1972).
3) W. Crump, J. Hans, and W. C. Purdy, *Talanta*, **16**, 124 (1969).
4) M. Shimizu, K. Taniguchi, and M. Satake, *Fukui Daigaku Kogakubu Kenkyu Hokoku Jpn.*, **24**, 337 (1976).
5) B. K. Puri and M. Gautam, *Talanta*, **25**, 484 (1978).
6) F. E. Beamish, J. J. Russel, and J. Seath, *Ind. Eng. Chem., Anal. Ed.*, 174 (1937).
7) D. D. Perrin, "Masking and Demasking of Chemical Reactions," Wiley-Interscience, New York (1970).
8) N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th ed, D. Van Nostrand Company, Inc., New York (1959), Vol. 1, p. 722.
9) B. K. Deshmukh and R. B. Kharat, *J. Indian Chem. Soc.*, **58**, 131 (1981).
10) T. Fujinaga, M. Satake, and T. Yonekubo, *Jpn. Analyst*, **19**, 216 (1969).
11) M. Satake, *Memoirs Fac. Eng., Fukui Univ.*, **18**, 225 (1970).
12) T. Fujinaga, M. Satake, and T. Yonekubo, *Bull. Chem. Soc. Jpn.*, **46**, 2090 (1973).
13) M. Satake, *Anal. Chim. Acta*, **92**, 423 (1977).
14) M. Satake and T. Yamauchi, *Memoirs Fac. Eng., Fukui Univ.*, **25**, 107 (1977).