

APPENDIX

List of Publications

1. Spectrophotometric Determination of Iron as Iron(II) Thiocyanate Cetyltrimethylammonium Bromide.
Paria, P.K., Thokdar, T.K., Majumdar, S.K., J.Indian Chem Soc. 1989, 66, 465.
2. Extraction Photometric Determination of Microgram Amounts of Cobalt with Thiocyanate and Cetyltrimethylammonium Bromide.
Paria, P.K., Thokdar, T.K., Majumdar, S.K., J.Indian Chem.Soc. 1990, 67, 787.
3. Extractive photometric Determination of Microgram Amounts of Palladium with Iodide and Cetyltrimethyl Ammonium Bromide.
Thokdar, T.K., Paria, P.K., Majumdar, S.K., Indian Journal of Chemistry, 1989, 28A, 443.
4. Extraction and Spectrophotometric Determination of Platinum with Cetyltrimethylammonium Bromide in Presence of Iodide.
Paria, P.K., Thokdar, T.K., Majumdar, S.K., Current Science, 1989, 58(2), 69.
5. Solvent Extraction and Spectrophotometric Determination of Molybdenum Using Cetyltrimethylammonium Bromide.
Thokdar, T.K., Paria, P.K., Majumdar, S.K., J.Indian Chem.Soc. (In press).

6. Extraction and Spectrophotometric Determination of Vanadium with Cetyltrimethylammonium Bromide in Presence of Thiocyanate.

Thokdar, T.K., Paria, P.K., Majumdar, S.K., J.Indian Chem Soc. (In press).

7. Spectrophotometric Determination of Micro Quantities of Gold with Cetyltrimethylammonium Bromide in Presence of Iodide.

Paria, P.K., Thokdar, T.K., Majumdar, S.K., Current Science, 1989, 58(17), 964.

8. Extractive Spectrophotometric Determination of Cobalt with 4-nitrosoresorcinol in Presence of Pyridine or Substituted Pyridines.

Sarkar, Miss Purabi, Thokdar, T.K., Sarkar, A., Paria, P.K., Majumdar, S.K., J.Indian Chem Soc. (Communicated for Publication).

9. Extractive Photometric Determination of Palladium(II) with 4-Nitrosoresorcinol in presence of Pyridine & Some of Its Methyl Substituted Derivatives.

Sarkar, A., Thokdar, T.K., Paria, P.K., Majumdar, S.K., Indian Journal of Chemistry, 1988, 27A, 650.

10. Extraction and Spectrophotometric Determination of Copper with 4-Nitrosoresorcinol in Presence of Pyridine and Substituted Pyridine.

Sarkar, A, Thokdar, T.K., Paria, P.K., Majumdar, S.K., J.Indian Chem.Soc., 1988, 65, 742.

11. Extractive Spectrophotometric Determination of Cobalt(II) with Ninhydrinoxime in Presence of Pyridine.

Paria, P.K., Thokdar, T.K., Majumdar, S.K., J.Indian Chem.Soc., 1990, 67, 532.

12. Diphenylthiocarbazide as Analytical Reagent for Spectrophotometric Determination of Copper.

Paria, P.K., Thokdar, T.K., Majumdar, S.K., J.Indian Chem.Soc., 1990, 67, 263.

Spectrophotometric Determination of Iron as Iron(II) Thiocyanate Cetyltrimethylammonium Bromide

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A spectrophotometric method of determination of iron is described. The red complex formed between iron(II), thiocyanate and cetyltrimethylammonium bromide is extractable into benzene. Addition of borate enhances the colour intensity. Absorbance, measured at 475 nm, shows a linear response upto 1.5 ppm of iron. Molar absorptivity of the complex and Sandell's sensitivity are determined and interferences studied. Iron has been determined in synthetic mixtures.

THIOCYANATE is extensively used for the colourimetric determination of iron, even though other reagents may give better results. The metal can be determined spectrophotometrically by using chrome azurol S and hexadecyltrimethylammonium chloride¹.

Nagahiro *et al.*² determined iron(II) by extraction of its ion-association complex with 5,6-diphenyl-3-(4-phenyl-2-pyridyl)-1,2,4-triazine and tetraphenyl borate into molten naphthalene. Another highly sensitive and selective method for spectrophotometric determination³ of iron(II) involves the use of bromopyrogallol red and pyrogallol red in presence of tetradecyltrimethylammonium bromide. Bayan⁴ developed a method to determine trace amounts of iron(III) using benzyltriethylammonium chloride and thiocyanate in presence of ethyl methyl ketone. The complex is extractable into 1,2-dichloroethane. Numerous other reagents are found reported for spectrophotometric determination of iron. Here we present a highly sensitive method involving application of ammonium thiocyanate and cetyltrimethylammonium bromide (CTA):

In our present investigation it has been found that the above reagents form red complex with iron(II) as well as iron(III). Addition of small amounts of sodium tetraborate enhances the colour of the solution initially containing iron as iron(II). To a solution containing iron as iron(III), addition of borate does not bring about any change in color intensity. Extraction into benzene of the ion-pair formed between the thiocyanate complex of iron(II) and the quaternary ammonium ion from cetyltrimethylammonium bromide (CTA) and measurement of absorbance of the organic extract, forms the basis of the method.

Experimental

Spectral measurements were made on a Shimadzu PR1 spectrophotometer, equipped with matched quartz cells of 10 mm optical path-length. An

ECL 5651 digital pH meter was used for pH measurements.

All chemicals and solvents used were of analytical grade. A stock solution of ferrous ammonium sulphate was prepared by dissolving it in distilled water and acidified with HCl (2-3 drops) and then standardised⁵.

Solutions of ammonium thiocyanate (0.2 M), cetyltrimethylammonium bromide (CTA) (0.1 M) and sodium tetraborate (0.025 M) were prepared in distilled water. KCl-HCl buffer was used to adjust pH of the aqueous solution.

Standard solutions of diverse ions were prepared from chlorides, nitrates or sulphates (in case of cations) and from sodium, potassium or ammonium salts (in case of anions) of the species concerned, to study interferences.

Procedure: To an aliquot of standard solution or sample containing upto 15 μg of iron(II), were added 0.2 M ammonium thiocyanate (0.5 ml), 0.1 M cetyltrimethylammonium bromide (0.1 ml) and 0.025 M sodium tetraborate solution (0.5 ml). KCl-HCl buffer (pH 1.0; 5 ml) and water as necessary were added to the above solution to give a total volume of 10 ml. The resulting mixture was equilibrated with benzene (10 ml) for 30 s. After phase separation, organic layer was poured over anhydrous sodium sulphate to remove any retained water. The absorbance of the organic extract was measured against a blank at 475 nm and the metal concentration computed from a calibration curve. To test the interference, the respective foreign ion was added to the aqueous solution before addition of the reagents.

Results and Discussion

Absorption spectra: The iron complex (in benzene) exhibits absorption maxima at 475 nm. The reagent blank itself, shows insignificant absorbance in this wavelength region. The pattern

of the absorption spectrum of the complex, extracted throughout the entire range, i.e. from 4 M HCl medium to pH 1.0, remains unchanged. This indicates the presence of a single variety of the complex species in the system.

Spectral curves of benzene extracts obtained by applying the procedure to the solutions initially containing iron as iron(II) were identical in nature to those from iron(III) solutions.

Beer's law and reagent concentrations: The absorbance of the red complex in benzene shows a linear response upto 1.5 ppm of iron. The molar absorptivity of the complex, based on iron content, and the Sandell's sensitivity were calculated at 475 nm (Table 1).

With the variation of the reagent concentrations, it was found that 0.5 ml of 0.2 M ammonium thiocyanate along with 0.1 ml of 0.1 M cetyltrimethylammonium bromide and 0.5 ml of 0.025 M borate were sufficient to extract 9 µg of iron in a single operation. Increased concentration of the reagents, however, did not bring about any significant change in the λ_{max} value. Addition of borate raised the intensity of the colour when iron was present initially as iron(II). To a solution containing iron as iron(III), addition of borate had no effect.

Addition of reagents: Addition of reagents is important in the procedure. One must follow the sequence of adding the reagents as: thiocyanate, CTA, borate and buffer. No colour development was noted when borate was added before thiocyanate.

Effect of acidity: Effect of acidity on the system was examined in terms of absorbance of the complex in the organic phase. Maximum absorbance was obtained when the extractions were carried out from 4 M HCl medium to pH 1.0. In each case, the remaining aqueous phase, after a single operation, was clear and colourless. Furthermore, the aqueous phase, as tested by an independent method, was void of iron. Complete and quantitative extraction of iron occurred in the entire range. At higher acid concentrations, difficulty arises in separating the organic layer due to the formation of some emulsion. Beyond pH 1.0, iron showed no colour reaction with the reagents in the aqueous phase. The reagent blank absorbs minimum at pH 1.0, hence extractions were carried out at pH 1.0.

Effects of solvents and stability: Amongst the several solvents benzene, ethyl acetate, chloroform, carbon tetrachloride and butanol, and benzene were found to be suitable solvents for extraction of the iron complex (Table 1). The rapid development of the maximum absorbance and constancy of the absorbance with time indicate that time is not a critical factor in the determination. Spectral curves of the iron complex extracted into other water-immiscible liquids are identical in nature.

Interference: To test the effects of diverse ions on the extraction behaviour, iron(II) was extracted

TABLE 1—EFFECT OF SOLVENTS*

Solvent	λ_{max} nm	Molar absorptivity $\times 10^4 \text{ dm}^2 \text{ mol}^{-1} \text{ cm}^{-1}$	Sandell's sensitivity $\mu\text{g cm}^{-2}$
Benzene	475	3.59	0.001 5
Ethyl acetate	480	2.99	0.001 8
Chloroform	470	2.66	0.002 1
Carbon tetrachloride	NE	NE	NE
Butanol	NE	NE	NE

*NE = Complex not extractable.

and determined according to the recommended procedure in presence of the diverse ions. Extraction pH was set at 1.0, unless otherwise mentioned. An ion was considered to interfere if the recovery of iron differed by more than $\pm 3\%$ from the actual amount taken. Iron(II) (9 µg) could be determined without interference in presence of 500-fold excess of Al^{III} , Ba^{II} , Be^{II} , Ca^{II} , Sr^{II} , Ce^{III} , Cd^{II} , Cr^{III} , La^{III} , Pb^{II} , Mg^{II} , Ni^{II} , Rh^{III} , Bi^{III} , Tl^I , Th^{IV} , U^{VI} , Zr^{IV} and Ag^I ; 250-fold excess of Co^{II} , Mn^{II} and Mo^{VI} ; and 50-fold excess of Pt^{IV} . Upto 50-fold excess of V^V could be tolerated provided the extraction be carried out from 3 M HCl medium. In presence of Cu^{II} , the benzene extract became hazy and the absorbance of the organic layer could not be measured, and attempts to remove this interference failed. Zn^{II} , Hg^{II} and Sn^{II} must be absent, as iron(II) showed no colour reaction with the reagents in presence of them. Presence of Pd^{II} resulted low recovery of iron.

Among the anions tested, the presence of more than 500-fold excess of citrate, tartrate, acetate, phthalate, phosphate, nitrate had no effect. Extraction should be carried out from 3 M HCl medium to avoid the interference due to EDTA, fluoride and oxalate. The system, however, was found to be susceptible in presence of iodide, nitrite and ascorbate. In 3 M HCl medium 100-fold excess of thiourea could be tolerated.

Precision and accuracy: The proposed method was tested by analysing solutions containing a known amount of iron(II). The experimental results for the determination of 3–12 µg of iron(II) are shown in Table 2. The method is fairly precise and reproducible, requiring 10–15 min for each run.

TABLE 2—REPRODUCIBILITY OF IRON RECOVERY

Fe^{II} taken μg	Fe^{II} found μg			Mean μg	Std. Dev. %
3.0	3.1	3.0	2.9	2.96	0.10
	2.8	3.0	3.0		
6.0	6.2	6.0	5.9	5.95	0.15
	6.0	5.8	5.8		
9.0	9.0	9.2	8.9	9.05	0.12
	9.2	9.0	9.0		
12.0	11.8	12.0	12.2	12.00	0.17
	12.2	12.0	11.8		

TABLE 3—DETERMINATION OF IRON (9 µg) IN VARIOUS MIXTURES WITH 200 µg OF EACH ION ADDED

Sl. no.	Ions added	Fe found µg
1.	CoII, NiII, MnII	9.1, 9.1, 9.2
2.	NiII, MnII, CrIII	9.0, 9.2, 9.0
3.	MnII, CrIII, BiIII	9.3, 9.1, 9.0
4.	CrIII, BiIII, PbII	8.9, 9.1, 9.1
5.	AlIII, CdII, ThIV	9.0, 9.1, 9.1

The method has been tested on a number of synthetic mixtures and the results are shown in Table 3.

References

1. Y. NAKAMURA, H. NAGAI, D. KUBOTA and S. HIMENO, *Jpn. Analyst*, 1978, **22**, 1156.
2. T. NAGAIHIRO, M. SATAKE, B. K. PURI and J. L. LIN, *Mikrochim. Acta*, 1984, **1**, 85.
3. O. WAGANOWSKI, *Microchem. J.*, 1984, **29**, 143.
4. K. C. BAYAN, Ph.D. Dissertation, Gauhati University, 1987.
5. A. I. VOGEL, "Textbook of Quantitative Inorganic Analysis", Longmans, London, 1960.

Extraction Photo-metric Determination of Microgram Amounts of Cobalt with Thiocyanate and Cetyltrimethylammonium Bromide

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THE thiocyanate complex of cobalt, which is not extractable into chloroform, readily forms extractable ion-pair with the quaternary ammonium ion derived from cetyltrimethylammonium bromide. Measurement of absorbance of this extract forms the basis of the present method for the estimation of μg amounts of cobalt.

Experimental

Cobalt solution was prepared from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and standardised. Solutions of 0.2 M ammonium thiocyanate and 0.1 M cetyltrimethylammonium bromide (CTAB) was prepared in distilled water. Acetate buffer was used for adjustment of pH of the aqueous solution. Acidity was measured with an ECL 5651 digital pH meter.

A Shimazu PR-1 spectrophotometer was used for absorbance measurement.

Procedure: To an aliquot of the cobalt(II) solution containing upto 300 μg of cobalt, ammonium thiocyanate (2 ml) and CTAB solutions (0.4 ml) were added. The total volume of the aqueous phase was made upto 10 ml with acetate buffer and distilled water so that pH of the solution was maintained at 3.5 ± 0.5 . The resulting mixture was then shaken (30 s) with chloroform (10 ml). The separated blue organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the chloroform extract was then measured at 625 nm against the reagent blank and the amount of cobalt estimated. To test the interference, foreign ions were added to the aqueous solution before addition of the reagents.

Results and Discussion

The reaction between cobalt(II), thiocyanate and CTAB was instantaneous. 1 ml of ammonium

thiocyanate along with 0.2 ml of CTAB was sufficient to extract 135 μg of cobalt in a single operation. Higher concentrations of the reagent, however, did not bring about any significant change in the maximum value of absorbance.

A steady and maximum absorbance was obtained when the extractions were carried out throughout the entire range, i.e. from 4 M HCl medium to pH 8.0. In each case the remaining aqueous phase, after a single extraction, was void of cobalt as tested by an independent method. At 0.1 M sodium hydroxide medium, cobalt(II) showed no colour reaction with the reagents.

The $\text{Co}^{\text{II}}\text{-SCN-CTAB}$ complex in chloroform exhibited absorption maxima at 625 nm with a shoulder around 585 nm. The reagent blank does not absorb in the aforesaid wavelength region. The pattern of the absorption spectrum of the complex, extracted throughout the entire range (4 M HCl medium to pH 8.0) remained unchanged. This indicates the existence of a single variety of the complex species in the system. The absorbance of the chloroform extract remained virtually constant for at least 96 h.

The absorbance of the blue complex in chloroform showed a linear response upto 30 ppm of cobalt. The molar absorptivity of the complex, based on cobalt content, was evaluated to be $1.92 \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ with the corresponding Sandell's sensitivity of 0.031 $\mu\text{g cm}^{-2}$ at 625 nm.

Interference: In order to study the effects of diverse ions on the extraction behaviour, cobalt was extracted and determined according to the recommended procedure in presence of the respective foreign ions. Extraction pH was set at 3.5 with acetate buffer, unless otherwise mentioned. An ion was considered to interfere if the recovery of cobalt differed by more than $\pm 3\%$ from the actual amount taken. Cobalt(II) (135 μg) could be determined without interference in presence of 50–60 fold excess of Be^{II} , Ti^{IV} , Al^{III} , Th^{IV} , U^{VI} , Pt^{IV} , Rh^{III} , La^{III} , Ca^{II} , Ba^{II} , Sr^{II} , Mn^{II} , Cr^{III} , Bi^{III} , Pb^{II} , V^{V} , Ni^{II} , Ag^{I} , Zr^{IV} , Mg^{II} , Ce^{III} , Sn^{II} . The system tolerated 20–25 fold excess of Mo^{IV} and Fe^{III} (more than 50-fold excess in presence of ammonium hydrogenfluoride), and 5–10 fold excess of Pd^{II} . A 30-fold excess of Cd^{II} did not interfere if the extraction be carried out from 3 M HCl medium. In presence of Cu^{II} , the chloroform extract became hazy and absorption of the organic layer could not be measured, and this interference could not be removed. Zn^{II} and Hg^{II} must be absent as Co^{II} showed no colour reaction in their presence.

Among the anions tested, a 100-fold excess of thiosulphate, iodide, fluoride, phosphate, acetate, phthalate, tartrate, ascorbate, sulphate, and a 30-fold excess of citrate and oxalate did not have any effect. Extraction should be carried out from 3 M HCl medium to avoid the interference due to EDTA.

The proposed method was tested by analysing

solutions containing a known amount of cobalt. The average of six determinations of 135 μg Co was found to be 133 μg with the relative mean deviation of $\pm 1.3\%$.

Reference

1. A. I. VOGEL, "Quantitative Inorganic Analysis", 3rd ed., Longmans, London, 1968.

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 $0.0052 \text{ } \mu\text{g}/\text{cm}^2$. 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 PR 1 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 $0.0052 \text{ } \mu\text{g Pd}/\text{cm}^2$ 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%.

References

- 1 Marcus Y, *Chem Rev*, 63 (1963) 139.
- 2 Khvatkova Z M, Shpet M A & Golovina V V, *Zh anal Khim*, 36 (1981) 2367.
- 3 Paria P K & Majumdar S K, *Indian J Chem*, 15A (1977) 158.
- 4 Bayan K C, *Ph D Dissertation*, Gauhati University, 1987.
- 5 Uesugi K & Shigematsu T, *Anal chim Acta*, 84 (1976) 377.
- 6 Vogel A I, *A textibook of quantitative inorganic analysis* (Longmans, London), 1978.

EXTRACTION AND SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM WITH CETYLTRIMETHYLAMMONIUM BROMIDE IN PRESENCE OF IODIDE

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LITERATURE reveals the extraction of platinum (IV)¹ into nitrobenzene as an ion-association complex with Fe(phenanthroline)₃²⁺. In presence of iodide or thiocyanate, platinum gets extracted into tributyl-phosphate². In the process the metal has been separated from rhodium and iridium. In our laboratory it has been noted that platinum forms an ion-association complex with cetyltrimethylammonium bromide (CTA) in presence of potassium iodide. The green complex is extractable into ethyl acetate. This property of the platinum complex suggested that further studies of the system might lead to the development of a simple spectrophotometric method for the determination of platinum.

Spectral curves and analytical measurements were made with a Shimadzu PR1 model spectrophotometer equipped with stoppered quartz cells of 10 mm optical path length.

Chloroplatinic acid (Johnson & Matthey) (1 g) was dissolved in 100 ml of distilled water followed by its standardization³. Solution of lower concentration of the metal was prepared by appropriate dilution. Ethyl acetate and other solvents were distilled before use. Cetyltrimethylammonium bromide (0.1 M solution) and 0.05 M potassium iodide (BDH) were prepared in distilled water. All other reagents used for the purpose were of analytical grade. Standard solutions of diverse ions were prepared from their corresponding salts.

To an aliquot containing up to 30 µg of Pt(IV) were added 0.1 ml of 0.05 M potassium iodide and 0.1 ml of CTA (0.1 M) followed by adequate amount of hydrochloric acid and water to make the aqueous volume up to 10 ml and 0.5 M with respect to HCl. The mixture was then equilibrated with 10 ml of ethyl acetate for 30 sec. The separated organic layer was poured over anhydrous sodium sulphate to remove any retained water droplets. Finally the

absorbance of the ethyl acetate extract was measured at 290 or 360 nm against a blank prepared under identical conditions. Amount of platinum was computed from a calibration curve. To test the effects of diverse ions, the respective foreign ions were added to the system before addition of the reagents.

When potassium iodide is added to a neutral or slightly acidic solution containing platinum (IV), a reddish-brown coloration due to the formation of [PtI₆]²⁻ is formed. This complex anion is not extractable into acetate. On addition of an aqueous solution of CTA to this coloured solution, an ion-association complex, probably of the type, [CTA⁺]₂ [PtI₆]²⁻ is formed. This is extractable into ethyl acetate.

The absorbance spectrum of the Pt(IV)-I⁻-CTA complex in ethyl acetate, taken against a blank, shows absorption maxima at 290 and 360 nm. The reagent blank exhibits absorption at 250 nm and the absorption becomes insignificant beyond 290 nm. Wavelength of 290 or 360 nm may be selected for all analytical measurements.

The effect of acidity on the extractibility of Pt (IV) into ethyl acetate was examined in terms of absorbance of the complex. The complex exhibits constant and maximum absorbance when the extractions were carried out from 0.1 to 1 M hydrochloric acid medium. In a second consecutive operation within this acidity range, the organic extract virtually showed no absorption. This indicated a quantitative extraction of platinum in a single extraction.

Apart from ethyl acetate, other solvents like benzene, chloroform and 1,2-dichloroethane were tested as the extracting solvents, but those offered no special advantages over ethyl acetate. The complex, however, is not extracted into carbon tetrachloride.

The absorbance of the platinum complex in ethyl acetate shows a linear response up to 3 ppm of platinum when measured at 290 or 360 nm. The molar absorptivities of the complex, based on platinum content, were found to be 5.36×10^4 and 3.08×10^4 l mol⁻¹ cm⁻¹ and sensitivities 0.0036 and 0.0063 µg/cm² at 290 and 360 nm, which classifies the colour reaction as one of the most sensitive for platinum. The colour is stable for at least 24 h.

With the variation of reagent concentrations, it

was noted that 0.1 ml of 0.05 M potassium iodide along with 0.1 ml of 0.1 M CTA was sufficient to extract up to 30 μg of platinum in a single extraction. Increased concentration of the reagents, however, did not bring about any significant change in the maximum value of absorbance. Order of adding the reagents had no effect on colour development.

To test the effects of diverse ions on the extraction behaviour, platinum (IV) was extracted and determined according to the recommended procedure in presence of the desired foreign ions. Extraction was carried out from 0.5 M hydrochloric acid medium. An ion was considered to interfere if the recovery of platinum differed by more than $\pm 3\%$ from the actual amount taken. Platinum (IV) (30 μg) could easily be determined without interference in presence of 100–200 fold excess of the following ions: Co (II), Ni (II), Cu (II), Pd (II), Fe (III), Cd (II), Zn (II), Mo (VI), V (V), Mn (II), U (VI), Zr (IV), Rh (III), Pb (II), Al (III), Ca (II), Ba (II), Sr (II), Be (II), Bi (III), Ce (III), Cr (III), La (III) and Mg (II). The system develops no colour in presence of mercury (II) and thorium (IV). In presence of silver, formation of some yellowish precipitate hampers the procedure.

Amongst the anions tested 200-fold excess of the followings do not interfere: borate, phosphate, tartrate, citrate, fluoride, phthalate, ascorbate, oxalate and EDTA. In presence of nitrate, high results are obtained. However, thiosulphate, thiocyanate and thiourea must be absent as these inhibit the colour development.

The precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of platinum following the recommended procedure. The average of six determinations of 30 μg of Pt (IV) was 29.25 μg with a relative mean deviation of 2.84%. The process is very simple and rapid requiring only 10–15 min for each run.

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1. Yamamoto, Y., Tsubouchi, M., Okimura, I. and Takaki, T., *Nippon Kagaku Zasshi*, 1967, **88**, 745.
2. Berg, E. W. and Lau, E. Y., *Anal. Chim. Acta*, 1962, **27**, 248.
3. Vogel, A. I., *A textbook of quantitative inorganic analysis*, ELBS, London, 1978.

It is noted that gold(III) forms a yellow ion-association complex with cetyltrimethylammonium bromide (CTAB) in presence of potassium iodide and is extractable into chloroform. Based on this a simple spectrophotometric method for the determination of gold is reported.

A stock solution of Au(III) was prepared by dissolving gold chloride (Johnson and Matthey) in distilled water and standardizing⁸. Solution of lower concentration of the metal was prepared by appropriate dilution of the stock. Aqueous solutions of CTAB (0.025 M SISCO) and potassium iodide (0.03 M BDH) were used. KH_2PO_4 -NaOH buffer was employed to adjust the pH of the aqueous solution. Standard solutions of diverse ions were prepared from their salts. Chloroform and other solvents were distilled before use. All other reagents used were of analytical grade.

Absorbance measurements were made with a Shimadzu PR1 model recording spectrophotometer. Stopped quartz cells of 10 mm optical path length were used for all measurements. An ECL 5651 digital pH meter was used to measure the acidity of the aqueous solution.

To an aliquot containing Au(III) (70 μg) were added potassium iodide (1 ml) and CTAB (0.1 ml). The mixture was adjusted to pH 7.0 with buffer. The volume of the aqueous phase was made up to 10 ml. The mixture was then equilibrated (30 sec) with chloroform (10 ml). The separated organic layer was dried over anhydrous sodium sulphate. Finally the absorbance of the chloroform extract was measured at 290 or 360 nm against a blank prepared in a similar manner. The amount of gold was computed from a calibration curve. To test for interference by other ions, the ions were added to the system before addition of the reagents.

When potassium iodide was added to a neutral or slightly acidic solution containing gold(III), a yellow coloration due to the formation of $[\text{AuI}_4]^-$ was formed. This complex anion was not extractable into chloroform. On addition of an aqueous solution of CTAB to the coloured solution, an ion-association complex, probably of the type $[\text{CTA}]^+ [\text{AuI}_4]^-$, was formed. This was extractable into chloroform. Other solvents like ethyl acetate, benzene and 1,2-dichloroethane were also tested as extracting solvents, but these offered no special advantages over chloroform (table 1). The complex was not extractable into carbon tetrachloride.

The reagent blank itself shows absorption maximum at 250 nm and the absorption becomes

SPECTROPHOTOMETRIC DETERMINATION OF MICRO QUANTITIES OF GOLD WITH CETYLTRIMETHYLAMMONIUM BROMIDE IN PRESENCE OF IODIDE

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THE reagents $[\text{Fe}(\text{phenanthroline})_3]^{2+}$ ¹, tetraphenylarsonium chloride², diethyl ether³, Rhodamine B⁴, mesityl oxide^{5,6} or primaquine phosphate⁷ have been used in spectrophotometric methods for determination of gold. In the present investigation

Table 1 Absorption maxima and molar absorptivities of Au(III)-I-CTAB complex extracted into different solvents

Solvent	Absorption maxima (nm)	Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$) ($\times 10^{-4}$)	Sensitivity ($\mu g/cm^2$)
Chloroform	290	2.14	0.009
	360	1.29	0.015
Benzene	298	1.97	0.010
	365	1.32	0.014
Ethyl acetate	290	2.08	0.009
	360	1.13	0.017
1,2-Dichloroethane	295	1.77	0.011
	365	1.07	0.018
Carbon tetrachloride*	—	—	—

*Complex not extractable.

insignificant beyond 290 nm. Hence all absorption measurements were made at 290 or 360 nm. The Au(III) complex showed constant and maximum absorbance when the extractions were carried out in the pH range 0-9, yielding quantitative recovery of gold in a single extraction.

The absorbance of the Au(III)-I-CTAB complex in chloroform showed a linear response up to 15 ppm of gold at 290 or 360 nm. The molar absorptivity of the complex on the basis of gold content worked out to be 2.14×10^4 and $1.29 \times 10^4\ l\ mol^{-1}\ cm^{-1}$, corresponding to Sandell's sensitivities 0.009 and $0.015\ \mu g/cm^2$, at 290 and 360 nm respectively. This classifies the colour reaction (stable for 24 h) as one of the most sensitive for gold. Further, with variation of reagent concentration, it was noted that 1 ml of 0.03 M of KI with 0.1 ml of 0.025 M of CTAB was sufficient to extract $70\ \mu g$ of gold(III) in a single extraction. Increasing the concentration of the reagent did not bring about any significant change in the maximum value of absorbance.

The average of six determinations of $70\ \mu g$ of Au(III) was $69.5\ \mu g$, with a relative mean deviation of 2.87%. The process is very simple and rapid, requiring only 10-15 min for each run.

In interference tests, an ion was considered to interfere if the recovery of gold differed by more than $\pm 3\%$ from the actual amount. In the present method, gold(III) ($70\ \mu g$) could be determined without interference in presence of 100-fold excess of Cr(III), V(V), Mo(VI), Hg(II), Rh(III), Al(III), Cu(II), Ni(II), Mg(II), Pt(IV), Pd(II), Zn(II), Cd(II), Pb(II), Zr(IV), Ca(II), Ba(II), Sr(II), Th(IV) and La(III). Fifty-fold excess of Fe(III), Co(II), Mn(II),

Table 2 Analysis of synthetic mixtures

Composition with amounts taken in μg	Recovery of gold (%)
Au(III) 70, Ag(I) 100, Cu(II) 100, Zn(II) 100	98
Au(III) 70, Fe(III) 100, Co(II) 100, Ni(II) 100	98
Au(III) 70, Pd(II) 100, Pt(IV) 100, Rh(III) 100	101

Ag(I) and Bi(III) could be tolerated. U(VI) interfered. Among the anions tested, 200-fold excess of borate, phosphate, tartrate, citrate, fluoride, bromide, phthalate, oxalate, acetate and nitrite, and lower concentrations of ascorbate and EDTA did not interfere in the estimation of gold. Thiocyanate, thiosulphate, thiourea and arsenate interfered.

In the absence of real samples, the applicability of the method was tested by analysing some synthetic mixtures containing Au(III), Ag(I), Cu(II), Zn(II), Fe(III), Co(II), Ni(II), Pd(II), Pt(IV) and Rh(III). The compositions of the mixtures and percentage recovery of gold are given in table 2. The results show that recovery of gold was highly satisfactory. Average of three determinations was taken in each case.

20 August 1988; Revised 13 December 1988

1. Yamamoto, Y., Tsubouchi, M. and Okimura, I., *Bunseki Kagaku*, 1967, **16**, 1176.
2. Murphy, J. W. and Affsprung, M. E., *Anal. Chem.*, 1961, **33**, 1658.

-
3. De, A. K., Khopkar, S. M. and Chalmers, R. A., *Solvent Extraction of Metals*, Van Nostrand, London, 1970.
 4. MacNulty, B. J. and Woollard, L. D., *Anal. Chim. Acta*, 1955, **13**, 354.
 5. Shinde, V. M. and Khopkar, S. M., *Anal. Chim. Acta*, 1968, **43**, 146.
 6. Shinde, V. M. and Khopkar, S. M., *Sci. Cult.*, 1967, **33**, 446.
 7. Ramappa, P. G., *Proceedings, Convention of Chemists (India)*, 1984, p. 19.
 8. Vogel, A. I., *A Textbook of Quantitative Inorganic Analysis*, ELBS, London, 1978.
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Extractive Photometric Determination of Palladium(II) with 4-Nitrosoresorcinol in Presence of Pyridine & Some of Its Methyl Substituted Derivatives

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An extractive photometric method is proposed for the determination of Pd(II) using 4-nitrosoresorcinol and pyridine/substituted pyridines. The mixed-ligand complexes of palladium(II) with 4-nitrosoresorcinol and pyridine/its methyl derivatives are extractable into chloroform and obey Beer's law. The molar absorptivities of the complexes are $(2.6-3.5) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at λ_{max} 395-400 nm and Sandell's sensitivities are 0.003-0.004 $\mu\text{g Pd(II)/cm}^2$. The influence of foreign ions is studied.

The use of pyridine-thiocyanate for extractive-photometric determination of various metals is well established¹⁻⁶. 4-Nitrosoresorcinol reacts with cobalt(II) and palladium(II) to form red complexes which are insoluble in chloroform. The reaction was used for detection and determination of the metals^{7,8} in aqueous solution by colour comparison. In the present note we report the extractive photometric determination of Pd(II) with 4-nitrosoresorcinol in presence of pyridine and some of its methyl substituted derivatives like α -picoline, β -picoline, γ -picoline and 2,4,6-collidine, extractable into chloroform under optimum conditions.

The absorbance measurements were made with a Shimadzu PR 1 spectrophotometer equipped with stoppered quartz cells of 10 mm path length. An ECL 5651 digital pH meter was used for pH measurements.

Palladium chloride (Johnson & Matthey) (1 g) was dissolved in hot conc. HCl (1 ml) and diluted to 250 ml with distilled water followed by standardisation with dimethylglyoxime⁹. A working solution (210.5 $\mu\text{g Pd/ml}$) was prepared by dilution. Chloroform (E Merck), pyridine (BDH), α -picoline (Riedel), β -picoline, γ -picoline (BDH), (Fluka) and 2,4,6-collidine (BDH) were distilled before use.

4-Nitrosoresorcinol was prepared according to γ -picoline the known procedure¹⁰. The light yellow crystalline solid, which was formed, was filtered off and recrystallized from dilute ethanol. The reagent in the solid state is very unstable, but its ethanolic solution is stable.

General procedure

An aliquot of sample solution was mixed with 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol followed by addition of (0.5 ml, 100%) pyridine/ α -picoline/ β -picoline/ γ -picoline/2,4,6-collidine. The pH of the solution was adjusted to 2 with KCl-HCl buffer. The volume of the aqueous phase was maintained at 10 ml. The solution was then equilibrated with 10 ml of chloroform in a separating funnel for 1 min. The two layers were allowed to settle. The separated organic layer was shaken with anhydrous sodium sulphate to remove any moisture. Finally the absorbance of the organic extract was measured at the corresponding absorption maxima (Table 1) against a palladium-free reagent blank. The amount of palladium(II) was determined from a previously prepared calibration curve.

The extraction of palladium complexes was investigated in the pH range 0-11. Chloroform extracts showed maximum and steady absorbance when the extractions were carried out in the pH range 1-8. When the extraction was repeated with the same aqueous phase, the organic extract virtually showed no absorbance. The aqueous phase, after extraction, was also tested for palladium by an independent method. This indicated a complete and quantitative extraction of palladium in this pH range.

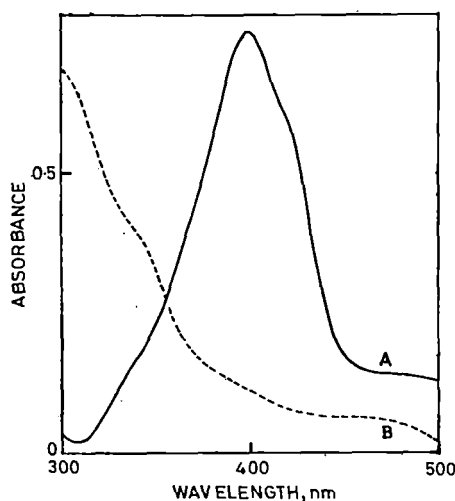
The spectra of the mixed-ligand complexes were scanned in the wave-length region 300-600 nm against the corresponding reagent blanks. The Pd(II)-complexes showed absorption maxima at 395-400 nm. As the reagent blanks showed some absorbances in the aforesaid wave-length region, all the analytical measurements were carried out against the respective reagent blanks. Figure 1 shows the spectrum of Pd(II)-4-nitrosoresorcinol- γ -picoline system and the corresponding reagent blank. The optimum concentration of the reagents for the purpose of quantitative extraction of the complexes was ascertained by extracting palladium(II) at various concentrations of 4-nitrosoresorcinol and pyridine bases. Extraction was found to be quantitative when 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol and 0.5 ml of pyridine/ α -picoline/ β -picoline/ γ -picoline/2,4,6-collidine were used. Under these optimum conditions 84.2 μg of Pd(II) was found to be quantitatively extracted. The higher concentrations of the reagents had no adverse effects on the extraction.

The quantitative extraction of palladium occurred in a single operation when the layers were shaken

Table 1—Details of Extractive Methods

Parameter	Base employed				
	Pyridine	α -picoline	β -picoline	γ -picoline	2,4,6-collidine
λ_{\max} (nm)	395	400	395	395	400,410*
Molar absorptivity ($l\ mol^{-1}\ cm^{-1}$)	3.28×10^4	2.68×10^4	3.44×10^4	3.52×10^4	3.47×10^4
Sandell's sensitivity ($\mu g/cm^2$)	0.0032	0.0039	0.0030	0.0029	0.0031

*shoulder

Fig. 1—Absorbance spectra of (A) Pd(II)-4-nitrosoresorcinol- γ -picoline complex (4.2 ppm Pd) and (B) reagent blank

for 1 min. Chloroform extracts, obtained after the recommended procedure, showed a steady absorbance for at least 12 hr.

In all the cases Beer's law was found to be valid over the concentration range 1-20 ppm of palladium. The corresponding molar absorptivities of the complexes (on the basis of palladium content) and respective Sandell's sensitivities were calculated and are presented in Table 1.

Effect of diverse ions

In order to study the effects of diverse ions on the extraction behaviour, palladium was extracted and determined according to the general procedure in presence of the respective foreign ions. Deviation of not more than $\pm 3\%$ from the expected absorbance was taken as the standard tolerance limit. In practice all the pyridine bases i.e., pyridine/ α -picoline/ β -picoline/ γ -picoline/2,4,6-collidine showed similar behaviour regarding interferences.

Palladium(II) (84.2 μg) can be determined without interference in presence of 50-60 fold excess of Ni(II), Cd(II), Hg(II), Zn(II), V(V), Pt(IV), Rh(III), Mn(II) and Be(II). The system tolerated 20-25-fold excess of Mo(VI), Zr(IV), U(VI), La(III), Al(III), Tl(I), Pb(II) and Cr(III). 10-fold excess of Fe(III) and Cu(II) could be tolerated in presence of ammonium bifluoride and citrate respectively. High results were obtained in presence of Co(III).

Among the anions tested, 100-fold excess of borate, phosphate, bromide, iodide, phthalate, acetate, tartrate, citrate, fluoride, ascorbate, oxalate did not interfere. 30-Fold excess of EDTA did not have any effect. Thiocyanate and thiosulphate interfere seriously. More than 100-fold excess of chloride, nitrate and sulphate was found to be harmless.

With γ -picoline the precision and accuracy of the proposed method was tested by analyzing solutions containing a known amount of Pd(II) following the recommended procedure. The average of six determinations of 84.2 μg Pd was found to be 83.4 μg with the relative mean deviation of $\pm 1\%$.

References

- 1 Chattopadhyay P & Majumdar S K, *Indian J Chem*, **22A** (1983) 91.
- 2 Forsythe J H W, Magee R J & Wilson C L, *Talanta*, **1** (1958) 249.
- 3 Moeller T & Zogg R E, *Analyt Chem*, **22** (1950) 612.
- 4 Yatirajan V & Arya S P, *Talanta*, **22** (1975) 861.
- 5 Ayres G H & Scroggie I E, *Analyt chim Acta*, **26** (1962) 470.
- 6 Deshmukh G S & Tatwawadi S Y, *J scient ind Res*, **20B** (1961) 506.
- 7 Overholser L G & Yoe J H, *Ind Engng Chem Anal Ed*, **15** (1943) 310; *Chem Abstr*, **37** (1943) 3691.
- 8 Takaki S & Nagase Y, *J Phar Soc Japan*, **58** (1938) 324.
- 9 Vogel A I, *A textbook of quantitative inorganic analysis* (ELBS, London) 1962.
- 10 Welcher F J, *Organic analytical reagents*, Vol 3 (Van Nostrand, Princeton) 1962.

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Extraction and Spectrophotometric Determination of Copper with 4-Nitrosoresorcinol in Presence of Pyridine and Substituted Pyridines

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EXTRACTIVE-PHOTOMETRIC determination of various metals with pyridine bases-thiocyanate has been reported¹⁻⁷. We have undertaken a systematic programme to study the extraction behaviour of copper(II) with 4-nitrosoresorcinol in presence of pyridine and some of its methyl-substituted derivatives. Based on these studies, a few rapid and sensitive methods for the extraction and spectrophotometric determination of copper(II) have been developed. The substituted-pyridines used are α -picoline, β -picoline, γ -picoline and 2,4,6-collidine.

Experimental

A Shimadzu PR1 spectrophotometer was used for absorbance measurements. A ECL 5651 digital pH meter was used to measure the acidities of the aqueous solutions.

A stock solution of copper(II) was prepared from $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and standardised⁸ and solution of lower concentration made by appropriate dilution. Chloroform (E. Merck), pyridine (B.D.H.), α -picoline (Riedel), β -picoline (B.D.H.), γ -picoline (Fluka) and 2,4,6-collidine (B.D.H.) were distilled before use. 4-Nitrosoresorcinol was prepared as reported⁹ and its ethanolic solution (1%) was used. KCl-HCl buffer was used for pH adjustment.

General procedure: An aliquot containing upto 100 μg of Cu^{2+} was mixed with 1% ethanolic

solution (0.2 ml) of 4-nitrosoresorcinol followed by addition of pyridine/ α -picoline/ β -picoline/ γ -picoline/2,4,6-collidine (0.5 ml). Buffer solution (pH 2; 5 ml) was then added and volume of the aqueous phase was made upto 10 ml with distilled water. The solution was then equilibrated with chloroform (10 ml) in a separating funnel for 1 min. The separated organic layer was poured over anhydrous sodium sulphate to remove retained water droplets. Finally, the absorbance of the organic extract was measured at the corresponding absorption maxima against a copper-free reagent blank, and the amount of copper(II) determined. To test the effect of diverse ions, the respective foreign ions were added to the system before addition of the reagents.

Results and Discussion

The optimum pH for extraction for copper was ascertained by extracting the mixed-ligand complexes in the pH range 1.0-11.0. In all the cases maximum absorbance was attained at pH 1.5-2.5. In a second consecutive operation within this pH range, the organic extract virtually showed no absorbance. This indicated that copper(II) was quantitatively extracted in this condition.

The spectra of the mixed-ligand complexes were recorded in the wavelength region 300-600 nm against the corresponding reagent blank. The copper complexes showed λ_{max} at 365-375 nm.

Different amounts of copper(II) were extracted as described in the general procedure. In all the cases, Beer's law was found to be valid over the concentration range 1-10 ppm of copper. The Ringbom's optimum concentration range for measurement was found to be 3-10 ppm of copper(II). The corresponding molar absorptivity of the complexes (on the basis of copper content) and the respective Sandell's sensitivity values are shown in Table 1.

The optimum concentration of the reagents for extraction of copper(II) has been ascertained. It has been found that 0.2 ml of 1% ethanolic solution of 4-nitrosoresorcinol along with pyridine/ α -picoline/

TABLE 1 - DETAILS OF EXTRACTIVE METHODS

Parameter	Base employed				
	Pyridine	α -Picoline	β -Picoline	γ -Picoline	2,4,6-Collidine
pH	1.5-2.5	1.5-2.5	1.5-2.5	1.5-2.5	1.5-2.5
λ_{max} (nm)	365	375	370	370	365
Molar absorptivity ($\text{dm}^2 \text{mol}^{-1} \text{cm}^{-1}$)	0.71×10^4	0.45×10^4	0.89×10^4	1.06×10^4	0.21×10^4
Sandell's sensitivity ($\mu\text{g cm}^{-2}$)	0.009	0.014	0.007	0.006	0.03

NOTES

β -picoline/ γ -picoline/2,4,6-collidine (0.5 ml) was sufficient to extract 100 μg of copper(II) quantitatively. Higher concentration of the reagents had no adverse effect on the extraction but was avoided due to reagent economy. Moreover, in presence of higher concentration of the reagents, the absorbances of the reagent blanks become higher. Chloroform extracts showed a steady absorbance for at least 24 h.

Copper (II) was determined in presence of other diverse ions. Deviation of not more than $\pm 3\%$ from the expected absorbance was taken as the standard tolerance limit. In practice, all the pyridine bases showed similar behaviour while studying interferences. Copper(II) (48 μg) could be determined without interference in presence of 50–60-fold excess of Ni^{2+} , V^{5+} , Pt^{4+} , Rh^{3+} , Ca^{2+} , Ba^{2+} and Sr^{2+} . The systems tolerated 20–25-fold excess of Cd^{2+} , Zn^{2+} , Mo^{6+} , U^{6+} , La^{3+} , Al^{3+} , Th^{4+} , Be^{2+} and Mn^{2+} . High results were obtained in presence of Co^{2+} and Pd^{2+} . Hg interfered seriously. Presence of Fe^{3+} and Zr^{4+} showed low recovery of copper. Among the anions tested, 100-fold excess of borate, phosphate, bromide, phthalate, iodide, acetate did not interfere. Thiocyanate, thiosulphate, EDTA, oxalate, tartrate, citrate, fluoride and ascorbate interfered.

γ -Picoline was found to be comparatively more sensitive among the pyridine bases used. With this reagent the precision and accuracy of the proposed method were tested by analysing solutions containing a known amount of copper(II) following the recommended procedure. The average of six determinations containing 48 μg of Cu^{2+} gave a value of 48.25 μg , which varies between 46.81 to 49.68 at 95% confidence limit. The standard deviation is 1.37 μg and relative mean deviation 1.8%.

References

1. P. CHATTOPADHYAY and S. K. MAJUMDAR, *Indian J. Chem., Sect. A*, 1983, 22, 91.
2. J. H. W. FORSYTHE, R. J. MAJEE and C. L. WILSON, *Talanta*, 1958, 1, 249.
3. T. MOELLER and R. E. ZOGG, *Anal. Chem.*, 1950, 22, 612.
4. V. YATIRAJAN and S. P. ARYA, *Talanta*, 1975, 22, 861.
5. G. H. AYRES and I. E. SCROGGIE, *Anal. Chim. Acta*, 1962, 26, 470.
6. G. S. DESHMUKH and S. Y. TATWADI, *J. Sci. Ind. Res., Sect. B*, 1961, 20, 506.
7. P. CHATTOPADHYAY and S. K. MAJUMDAR, *J. Indian Chem. Soc.*, 1984, 61, 621.
8. A. I. VOGEL, "A Textbook of Quantitative Inorganic Analysis", ELBS, London, 1962.
9. F. J. WELCHER, "Organic Analytical Reagents", Von Nostrand, Princeton, 1962, Vol. 3.

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Extractive Spectrophotometric Determination of Cobalt(II) with Ninhydrin Oxime in Presence of Pyridine

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THE most sensitive colourimetric methods for determination of cobalt are based on its reaction with compounds containing the grouping $=C(OH)-C(OH)=$. Various oximes have been reported¹ to determine cobalt spectrophotometrically. In pH 3–6 ninhydrin oxime forms a yellowish brown complex with cobalt, which by itself is not extracted into organic solvents. In presence of pyridine, the complex is extractable into chloroform. Measurement of absorbance of this extract shows a linear response with cobalt concentration. Taking advantage of this, a method has been devised to determine cobalt in micro quantities.

Experimental

Absorbance measurements were made with a Shimadzu PR1 spectrophotometer. A ECL 5651 pH-meter was used to measure the pH. A stock solution of cobalt(II) was prepared by dissolving $CoCl_2 \cdot 6H_2O$ (AnalaR) in distilled water. This was standardised by complexometrically using xylenol orange as indicator². Pyridine, chloroform and other organic solvents were distilled before use. Potassium hydrogen phthalate–hydrochloric acid buffer was used to adjust the pH.

Synthesis of ninhydrin oxime: To a solution of ninhydrin (2 g) dissolved in pyridine (2 ml), was added ethanolic solution (100 ml) of hydroxylaminehydrochloride (2 g) and the mixture was refluxed for 2 h. The resulting solid was recrystallised from ethanol (80%) (Found: C, 57; H, 4.2; N, 6.8. $C_9H_7O_4N$ calcd. for: C, 56; H, 3.6; N, 7.25%).

General procedure: To an aliquot containing upto 40 μg of cobalt(II) was added 0.6% ethanolic solution (1 ml) of ninhydrin oxime followed by pyridine (0.2 ml). Buffer solution was then added to adjust the pH to 4. The mixture was left for 1 min and the volume of the aqueous phase was made upto 10 ml. This was then equilibrated with chloroform (10 ml) for 30 s. After phase separation, the organic extract was poured over anhydrous sodium sulphate to remove water droplets. Finally the absorbance of the chloroform extract was

measured at 330 nm. Amount of cobalt was computed from a previously prepared calibration curve. To test the interferences, the respective diverse ions were added to the system prior to the addition of the reagents.

Results and Discussion

The complex exhibits λ_{max} at 330 nm. The reagent itself shows high absorbance below 300 nm. However, the absorbance becomes insignificant beyond 320 nm. The complex exhibits constant and maximum absorbance when the extractions were carried out at pH 3–6. In each case, the aqueous phase after extraction was free from cobalt. The pattern of the absorption spectra of the complex extracted at pH 0–10 remains unchanged, indicating the formation of the single complex species in all cases. Apart from chloroform, other solvents like ethyl acetate, 1,2-dichloroethane, benzene and carbon tetrachloride were tested as extracting solvents. The use of ethyl acetate and 1,2-dichloroethane offered no special advantages over chloroform. Lower absorbance resulted in case of benzene. Carbon tetrachloride did not extract the complex. Apart from pyridine, some other bases were tested as auxiliary ligands. The use of β -picoline or γ -picoline did not bring about any significant change in the maximum value of absorption. In presence of α -picoline or 2,4,6-collidine, the complex is not extractable into chloroform. The nature of the extracted species is 1 : 3 (M : L) (mole ratio method).

The system conforms to Beer's law. The absorbance of the cobalt complex in chloroform shows a linear response upto 4 ppm of cobalt at 330 nm and the molar absorptivity of the complex is $1.97 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ with Sandell's sensitivity $0.003 \mu g \text{ cm}^{-2}$.

Cobalt (24 μg) could be determined without interference in presence of 200-fold excess of the following ions: Fe^{III} , Ni^{II} , Pd^{II} , Pt^{IV} , Th^{IV} , Zn^{II} , Cd^{II} , Ca^{II} , Ba^{II} , Sr^{II} , U^{VI} , Sn^{II} , Cr^{III} , Hg^{II} , V^{V} , Mo^{VI} and Mn^{II} . The system tolerated less than 25-fold excess of Be^{II} , Bi^{III} , Cu^{II} and La^{III} . Rh^{III} interfered. The following anions did not interfere when present in 400-fold excess: ascorbate, oxalate, arsenate, bromide, iodide, fluoride, phosphate, citrate, tartrate and thiocyanate. Less than 50-fold excess of EDTA, thiosulphate and thiourea were permissible. Nitrite interfered.

References

1. R. B. SINGH, B. S. GARG and R. P. SINGH, *Talanta*, 1979, 26, 425.
2. A. I. VOGEL, "A Textbook of Quantitative Inorganic Analysis", Longmans, London, 1978.

**Diphenylthiocarbazide as Analytical
Reagent for Spectrophotometric
Determination of Copper**

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DIPHENYLTHIOCARBAZIDE can be used for the detection of a number of metals¹ since it forms characteristic coloured complexes. A method is presented for the extractive spectrophotometric determination of copper. The metal has been estimated in synthetic mixtures and standard samples.

Experimental

A Shimadzu PR-1 model spectrophotometer with optically matched quartz cells of 10 mm path length was used for absorbance measurements. Acidity of the aqueous solution was measured with a ECI 5651 pH meter.

Diphenylthiocarbazide was prepared¹ and a 0.4% acetic solution of the reagent was used. Stock solution of copper(II) was prepared by dissolving $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (B.D.H.) in distilled water followed by its standardisation as bezoin- α -oximate². A working solution of copper was prepared by appropriate dilution. Ethyl acetate was distilled before use. KH_2PO_4 - NaOH buffer was employed to adjust pH of the aqueous solution. All other chemicals used were of analytical grade.

Determination of copper(II): To a suitable volume of sample solution containing 5–30 μg of copper(II) was added 0.4% acetic solution (0.5 ml) of diphenylthiocarbazide followed by phosphate buffer (pH 6; 5 ml). The aqueous phase was then diluted to 10 ml with distilled water and left for 1 min to ensure complete complexation. The solution was then equilibrated with ethyl acetate (10 ml) for 1 min. The separated organic layer was shaken with anhydrous sodium sulphate to remove any retained water droplets. The absorbance of the organic extract was read at 540 nm against the reagent blank and the amount of copper deduced from a calibration curve. To study the effects of diverse ions, the respective foreign ions along with the masking agents, if needed, were added to the aqueous sample solution before addition of the reagent.

Results and Discussion

The optimum conditions for extraction of copper have been established from critical evaluation of the pertinent factors.

The brown coloured complex of Cu-diphenylthiocarbazide shows a maximum absorption at 540 nm. Beer's law obeyed over 0.2–4 ppm of copper. The molar absorptivity was $5.04 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ with Sandell's sensitivity 0.0013 μg Cu/cm^2 at 540 nm. Quantitative extraction of copper was achieved in the pH range 4–8.

Interference: Copper (20 μg) was determined in presence of known quantity of diverse ions. Interference due to Fe^{III} and Sn^{II} is eliminated by masking with ammoniumhydrogen fluoride. To avoid the interference due to Pd^{2+} , copper was extracted in presence of ammonium thiocyanate. Potassium iodide masks Hg^{II} , Pb^{II} and Bi^{III} . The tolerance limits for other ions (mg, in parenthesis) are as follows: Ni^{II} , Mo^{VI} , Ca^{II} , Mn^{II} , Cr^{III} , La^{III} , Al^{III} , Ba^{II} , Sr^{II} and Mg^{II} (all 4); Co^{II} , and U^{VI} (3.5); Be^{II} and As^{III} (3); Pt^{IV} , Rh^{III} and Th^{IV} (2.5); V^V and Cd^{II} (0.1); Zn^{II} (90.1). Among the anions tested, 500-fold excess of tartrate, citrate, oxalate, bromide, iodide, phosphate, acetate, thiocyanate, fluoride, phthalate and thiourea do not interfere. The system tolerated 200-fold excess of ascorbate, EDTA and thiosulphate. However in presence of borate and nitrite high results are obtained.

Determination of copper in cupronickel alloys: The alloy sample (100 mg) was dissolved in a mixture of HCl and HNO_3 (2:1). The solution was evaporated to dryness after adding a few drops of concentrated H_2SO_4 . The residue was dissolved in water and the resulting solution was diluted to 250 ml with distilled water. The solution was further diluted as needed. A 2 ml aliquot was taken and copper determined by following the procedure outlined earlier. Copper was found to be 69.2% (average of four determinations; certified: 68.12% Cu in cupronickel alloy).

Determination of copper in white metal in presence of Pb, Sb, Sn, Bi, Ni, As: The sample (1 g) was dissolved in 6 M HCl (10 ml) and digested on a hot-plate. The clear solution was evaporated, cooled and diluted with distilled water. The solution was filtered to remove a major portion of lead, precipitated as lead chloride. The filtrate was diluted to a known volume. A 2 ml portion was taken followed by addition of KI (10 mg) and NH_4HF_6 (5 mg) along with acetic solution (0.5 ml, 0.4%) of diphenylthiocarbazide. Copper in white metal was estimated by the recommended procedure and was found to be 0.13% (average of four determinations; certified: 0.12% Cu in lead base white metal).

References

1. F. J. WELCHER, "Organic Analytical Reagents", Van Nostrand, Princeton, 1962, Vol. 3.
2. A. I. VOGEL, "A Textbook of Quantitative Inorganic Analysis", Longmans, London, 1978.