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Phenanthraquinone Monothiosemicarbazone as Sensitive Reagent for the Spectrophotometric Determination of Zinc(II)

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Phenanthraquinone monothiosemicarbazone has been found to be a sensitive and selective reagent for the spectrophotometric determination of zinc(II) in the pH range 7.0—8.6. The red complex formed shows maximal absorbance at 510 nm. Beer's law is obeyed up to 1.96 ppm and optimum range of concentration being 0.22—1.70 ppm. The sandell sensitivity is 0.0018 μg Zn^{II} cm^{-2}, with molar extinction coefficient being 3.52×10^4 mol^{-1} cm^{-1}. The method has been applied to the determination of zinc in 6% Zn–Al alloy.

Several organic reagents[1] have been used for the determination of micro amounts of zinc. Recently introduced reagents are 5,10,15,20-tetrakis(1-methylpridinium-4-yl)porphine,[2] 2-(3-sulfobenzoyl)pyridine thiosemicarbazone,[3] and 2-(5-nitro-2-pyridylazo)-1-naphthol.[4] But most of them suffer from various disadvantages.

Preliminary investigations have shown that phenanthraquinone monothiosemicarbazone (PTS) forms coloured complexes with several metal ions such as iron (II and III) (λ_{max}=510 nm), cobalt(II) (λ_{max}=500 nm), nickel (II) (λ_{max}=520 nm), copper (I and II) (λ_{max}=530 nm), cadmium(II) (λ_{max}=500 nm), ruthenium(III) (λ_{max}=660 nm), rhodium(III) (λ_{max}=510 nm), palladium(II) (λ_{max}=590 nm, when the final concentration of hydrochloric acid is in the range 0.28—1.14 M^+ and λ_{max}=540 nm at pH 8.0—9.5), osmium(VIII) (λ_{max}=530 nm), iridium(III) (λ_{max}=520 nm) and platinum(IV) (λ_{max}=510 nm). The present study deals with spectrophotometric determination of zinc with PTS. Zinc(II) reacts with PTS and forms red complex which is soluble in methanol and shows maximum absorbance at 510 nm.

Experimental

Apparatus. A Unichem SP 600 spectrophotometer with matched glass cells of 10 mm light path was used for absorbance measurements. An ECIL (PH 821 A) expanded scale pH-meter was used for pH measurements.

Reagents. *Synthesis of PTS*: Phenanthraquinone monothiosemicarbazone (PTS) was prepared by refluxing equimolar amounts of phenanthraquinone and thiosemicarbazide in methanol for 3 h on a boiling water bath. The hot solution was filtered under suction and cooled in refrigerator. Red crystals of PTS obtained, were recrystallized from methanol (yield, 80%). The purity was checked by thin-layer chromatography and elemental analysis. A 2.5×10^{-3} M PTS solution was prepared in *N,N*-dimethylformamide (DMF). Though the solution is stable for at least two days, a fresh solution was prepared each day to avoid possible decomposition.

Zinc(II) Solution. 0.1 M zinc (II) solution was prepared by dissolving zinc sulfate heptahydrate (AnalR BDH) in double distilled water, containing 0.5 ml of sulfuric acid in one liter of the solution. The solution was standardized volumetrically.

Sodium Tetraborate Solution. 0.01 M in double distilled water. All other solutions of cations and anions were prepared from A.R. grade chemicals in double distilled water.

Separation of Zinc. The separation of zinc from other cations by diethyldithiocarbamate has been suggested.[5] Zinc (II) solution was buffered with ammonium citrate and ammonium hydroxide at pH 8.5; the final solution containing approximately 1% citrate. The solution was then extracted with 5.0 ml portions of diethyldithiocarbamate in chloroform until the chloroform no longer changes colour. Zinc was again re-extracted from the combined chloroform extact with aqueous 0.16 M hydrochloric acid and determined spectrophotometrically with PTS.

Recommended Procedure for the Determination of Zinc. To an aliquot containing 2.24 to 17.0 μg of zinc(II), add 1 ml of 2.5×10^{-3} M PTS solution in DMF. Adjust the pH between 7.0—8.6 with 0.01 M sodium tetraborate. Add 5 ml of methanol and dilute the solution to 10 ml with distilled water. Measure absorbance at 510 nm against corresponding reagent blank prepared under identical conditions. Calculate the amount of zinc from the calibration curve.

Determination of Zinc in 6% Zn-Al Alloy (BCS No. 300). Dissolve 0.1 g alloy in about 5 ml of aqua regia and evaporate to almost dryness. Dissolve the residue in about 2 ml of hydrochloric acid and dilute to 100 ml. Take suitable aliquot and determine the amount of zinc following the recommended procedure after masking iron with fluoride.

The results obtained for three determinations are shown in Table 1.

Table 1. Determination of zinc in 6% Zn-Al alloy

Composition of 6% Zn-Al alloy (%)	Zinc found (ppm)	Zinc calculated (ppm)	Error (%)
C=1.28, Mn=0.41	0.594	0.598	−0.67
Si=0.16, Mg=2.76 Fe=0.30, Ti=0.15	0.890	0.897	−0.78
Zn=5.98, Cr=0.15 Pb=0.003 and Sn=0.006	1.122	1.196	−0.53

Results

Absorbance Spectra and Stability of the Complex. A study of the effect of pH on the complexation of zinc(II) with PTS showed that the red complex gives maximum absorbance at 510 nm (Fig. 1) which is constant in the pH range 7.0—8.6 (Fig. 2). Subsequent studies were carried out at pH 7.5±0.1. The complex is stable for 2 h.

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* 1M=mol dm^{-3}.

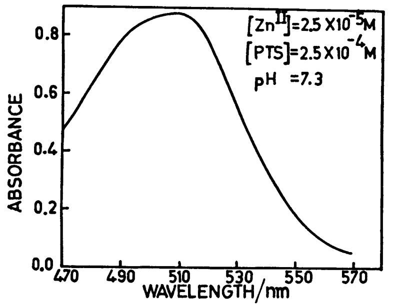

Fig. 1. Absorption spectra of Zn^{II}–PTS complex.

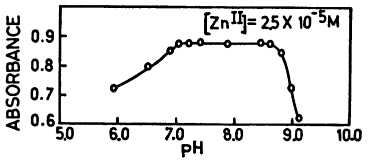

Fig. 2. Effect of pH on Zn^{II}–PTS compex.

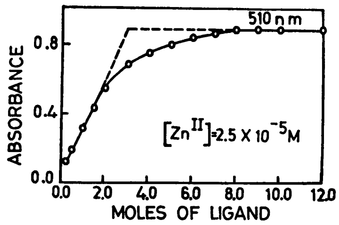

Fig. 3. Composition of Zn^{II}–PTS complex by mole ratio method.

Effect of Reagent Concentration. The ratio of reagent to metal ion necessary for maximum colour formation was ascertained. It was found that eight fold excess of reagent is required for the complete complexation (Fig. 3) but however 10 times PTS was used during all studies. Since the absorbance of the ligand at 510 nm is very small therefore the excess of the reagent is not critical.

Physical Constants of the Complex. Under the optimal conditions describred above, Beer's law obeyes up to 1.96 ppm of zinc(II). The potimum range of concentration of zinc(II) for accurate determination, as deduced from Ringbom plot[6] (Fig. 4) is 0.22—1.70 ppm. The molar absorptivity is 35200 $l\ mol^{-1}\ cm^{-1}$ at 510 nm with Sandell's sensitivity of 0.0018 μg Zn cm^{-2} for log $I_0/I=0.001$.

Precision of the Method. Measured under optimum conditions, eight samples containing 1.63 ppm of zinc, the average relative deviation was found to be 0.26% with maximum relative deviation of 0.41% and mean absorbance of 0.880. The standard deviation is 5.4×10^{-3}.

Stoichiometry of the Complex. The stoichiometry of the complex was determined by Job's method of continuous variations[7] (Fig. 5) and mole ratio method[8] (Fig. 3). Both showed the formation of 1:3 complex (metal:ligand).

Effect of Diverse Ions. Synthetic solutions containing 1.63 ppm of zinc(II) and different amounts of diverse ions were prepared and analyzed by the recommended procedure. An error of ±2% absorbance reading was neglected. The amounts (in ppm) of ions tolerated with masking ion if any, are given in parentheses:

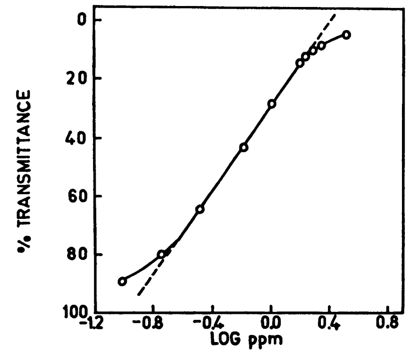

Fig. 4. Ringbom plot for Zn^{II}–PTS complex.

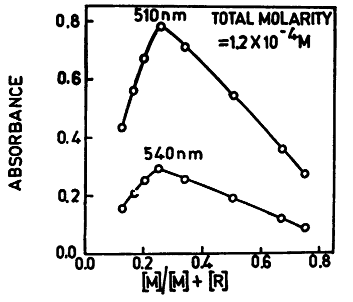

Fig. 5. Composition of Zn^{II}–PTS complex by Job's method.

Chloride, bromide, and nitrate (1000 each); fluoride and thiourea (700 each); nitrite (350); thiocyanate (250); tartrate (100): iodide (100); thiosulfate (300); oxalate (30); sulfite (500); magnesium(II), calcium (II), barium(II), and strontium(II) (150 each); aluminium(III) (75); uranyl(VI) (100); molybdenum (VI) and tungsten(VI) (50 each); manganese(II) (F^-, 15); vanadium(V) (F^-, 20); thorium(IV) and titanium(IV) (50 each); silver(I) (Cl^-, 10); rhodium (III) (thiourea, 5); iridium(III) (SCN^-, 1); osmium (VIII) (SCN^-, 5); platinum(IV) (I^-, 5); nickel(II) (SCN^-, 10); lead(II) (15); tin(II) (10); copper(II) (thiourea, 2); iron(II) (F^-, 5); mercury(II) (I^-, 10); cadmium(II) ($C_2O_4^{2-}$, 5) and chromium(III) (5).

EDTA, phosphate, citrate, and cyanide interfere seriously.

Discussion

Among various reagents reported for the determination of zinc, dithizone[9–11] is notable. The reagent is highly sensitive but excess of dithizone has to be removed by shaking with very dilute ammonia solution which can often contain traces of zinc. It is important in the determination of traces of zinc and the procedure is tedious. Zincon[12,13] is another important reagent but the sensitivity is low, and a large number of metals interfere, making it necessary to separate the zinc first. PAN[14,15] and Chrome Azurol S[16] are sensitive reagents but highly unselective. The disadvantage of 5, 10, 15, 20-tetrakis-(1-methyl-

TABLE 2. SENSITIVITIES OF REAGENTS FOR THE SPECTROPHOTOMETRIC DETERMINATION OF ZINC(II)

Reagent	Sensitivity (μg Zn cm^{-2})
Dithizone	0.0007/538 nm
Zincon	0.0032/625 nm
1-(2-Pyridylazo)-2-naphthol	0.0012/550 nm
Chrome Azurol S	0.0015/510 nm
Methylthymol Blue	0.0047/584 nm
2-(2-Pyridylazo)-*p*-cresol	0.0022/580 nm
Arsenazo III	0.0023/570 nm
Thiodibenzoylmethane	0.0019/410 nm
Biacetyl bis[4-phenyl-(thiosemicarbazone)]	0.003/440 nm
2-(3-Sulfobenzoyl)pyridine thiosemicarbazone	0.0022/390 nm
5,10,15,20-tetrakis-(1-methyl-pyridinium-4-yl)porphine	0.0028/437 nm
Phenanthraquinone monothiosemicarbazone (PTS)	0.0018/510 nm

pyridinium-4-yl) porphine[2] is that free reagent which absorbs at 423 nm has to be removed by forming the lead complex (λ_{max}=476 nm) before measuring the absorbance of the zinc complex. Among thiosemicarbazones, 2-(3-sulfobenzoyl) pyridine thiosemicarbazone[3] is fairly sensitive but effect of diverse of ions, in the determination of zinc, has not been investigated.

In the present investigation, PTS compares favourably with other well-known reagents. The procedure is simple and large amounts of ligand do not interfere, which is an advantage over dithizone. The reagent is more selective than PAN and Chrome Azurol S. There is no extraction *etc.* which is an advantage over other methods. Although small amounts of the metals such as copper, iron, nickel *etc.* can be masked, they should be separated if present in large amounts before the determination of zinc. The sensitivity of the different methods for the determination of zinc are compared in Table 2.

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