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p-Chloroisonitroso Acetophenone Thiosemicarbazone as an Extractive Reagent for the Spectrophotometric Determination of Zn(II)

R.S. LOKHANDE*, S.V. POMAN† and U.R. KAPADI‡
Department of Chemistry, University of Mumbai, Vidyanagari, Santacruz (E), Mumbai-400 098
E-mail: lokhanders@yahoo.com

A new method is developed for the extractive spectrophotometric determination of Zn(II) at microgram level by using 4-chloroisonitroso-acetophenone thiosemicarbazone as an analytical reagent. Zinc(II) forms coloured complex with 4-chloroisonitrosoacetophenone thiosemicarbazone which can be extracted into chloroform in the pH range under optimum conditions. Chloroform extract shows maximum absorbance at 397 nm. Beer's law is obeyed over the range 0.8 to 12 μg/mL of Zn. The molar absorptivity calculated is 3.96×10^3 L mol^{-1} cm^{-1} at 397 nm and Sandell's sensitivity is observed to be 0.0016 μg cm^{-1}. The composition of the extracted species is obtained from mole ratio method, Job's continuous variation method and slope into ratio method are found to be 1 : 2 (M : L) stoichiometry. Interference due to various cations and anions has also been invested. The stability of the complex is observed to be up to 48 h. The developed method has been successfully applied for the determination of Zn(II) in alloys, pharmaceuticals and synthetic mixtures. The method is comparable with the known method.

INTRODUCTION

Zinc[1] occurs in nature as a sulfide, silicate and as an oxide. Zinc is used extensively in industry[2] to make alloys such as bronze, brass, german silver and galvanized iron, steel. It is also used as a protective coating for other metals, dry battery cells, jar caps and water pipes. Brass contains 20 to 45% of Zn, together with copper and sometimes, with other metals. Zinc poisoning[3] is mostly accidental from the intake of pesticides, inadvertent therapeutic use of heavy doses of zinc salts or drinking of acidic juices or brews made in galvanized iron utensils. In plants, zinc is a constituent of the enzyme[4] carbonic anhydrase, a catalyst involved in the conversion of CO_2 into carbonic acid. Zinc finds its use in pharmaceutical samples[5] because of its inherent property to protect any affected skin and also to dry a wound or ulcer, *e.g.*, ZnO.

Several isonitroso compounds are known to react with metal ions to give coloured complexes and have been employed for the extraction and spectrophotometric determination of metals at trace level[6–9]

†Bayer India Limited, Kolshet Road, Thane-400 607, India.
‡Department of Chemical Sciences, North Maharashtra University, P.B. 80, Jalgaon-425 001, India.

EXPERIMENTAL

For pH measurements Li-120 model of digital pH meter supplied by Elico Pvt. Ltd. was used. All the measurements of absorption spectra were made on Shimadzu UV-Visible spectrophotometer (model 1601). All chemicals used were of AR grade. Zinc solution was analyzed for zinc content by standard method[10].

Synthesis of *p*-chloroisonitrosoacetophenone thiosemicarbazone (ClNAPT) was carried out as described in the literature[11, 12].

Procedure for the extraction and separation of zinc: 1 mL of 1% solution containing zinc (1 mg), 2 mL of sodium acetate (1 M) and 1 mL of 4-chloroisonitrosoacetophenone thiosemicarbazone (ClNAPT) in ethanol (1%) were mixed in a 10 mL beaker. The pH of the solution was adjusted to required value with dilute solutions of NH_4OH and/or HNO_3 keeping the total volume to 10 mL. The solution was then transferred into a 60 mL separating funnel and equilibrated for 1 minute with 10 mL of organic solvent and the two phases were allowed to separate. The organic phase was collected in a 10 mL volumetric flask and made up to the mark with organic solvent, if required. After separation of two phases, pH of the aqueous phase was measured and zinc in each phase was determined by atomic absorption spectroscopy to determine the extraction coefficient of zinc. The extraction was carried out with different solvents to find out the most satisfactory solvent for the extraction of zinc.

Absorption spectra: To determine the absorption maxima of Zn(II) : ClNAPT complex, 100 μg of Zn(II) in 10 mL of aqueous solution containing 1 mL of sodium acetate (1 M) and 1 mL of ClNAPT (1%) was extracted quantitatively at pH 8.0 into chloroform and the absorption spectrum was recorded against chloroform blank in the range 280 to 600 nm.

Effect of salting out agents: Various salting out agents such as Na, Mg, Ca, K and Ba nitrates were used in the extraction of 1 mg of Zn(II) in 10 mL of aqueous solution. This was extracted at pH 8 using chloroform and the effect of these salts on the extraction was found at 397 nm.

Preparation of calibration curve: To an aqueous solution containing 0.1 to 120 μg of zinc in a 10 mL beaker, 2 mL of sodium acetate (1 M) and 1 mL of ClNAPT (1%) were added and the pH of the solution was adjusted to 8.0 with dilute solutions of NH_4OH and/or HNO_3 keeping the total volume to 10 mL; the mixture was then transferred to a 60 mL separating funnel and then equilibrated with $CHCl_3$ (2×5 mL) for 1 min. The organic layer was separated and shaken with anhydrous Na_2SO_4 to remove any traces of water and made up to 10 mL using $CHCl_3$, if necessary. The absorbance of the $CHCl_3$ extract was measured at 397 nm against a free reagent blank. The amount of zinc can be determined from the calibrated curve obtained by plotting absorbance readings against the corresponding concentration of zinc. Various experimental conditions for the extraction and spectrophotometric determination of zinc(II) were optimized as under by varying one parameter and keeping all other parameters constant.

Effect of equilibration time: To determine the minimum equilibration time for the extraction of Zn(II) : ClNAPT complex, various solutions containing 100 μg of Zn(II) 1 mL of sodium acetate (1M) and 1 mL of ClNAPT (1%) were

equilibrated for different time intervals from 0.5 to 10 min, keeping other parameters constant and the absorbance was recorded at 397 nm.

Effect of reagent concentration: The minimum amount of reagent for the complete colour development for 100 μg of Zn(II) in 10 mL of aqueous solution at pH 8.0 containing 2 mL of sodium acetate (1 M) was found by varying the reagent concentration from 0.1 to 3.5% of ClNAPT, keeping other factors constant. The extraction and absorbance measurements were carried out as described earlier.

Stability of the complex with time: The stability of the complex with time for 100 μg of Zn(II) solution was determined by measuring the absorbance of the chloroform extract of Zn(II) : ClNAPT complex at 397 nm at different intervals of time.

Interference study: The effect of the presence of diverse ions on the extraction and absorbance of 50 μg of zinc was studied by adding the ion of interest to the zinc solution prior to the adjustment of pH in the procedure for extraction and spectrophotometric determination of zinc described above.

Precision and accuracy: The precision and accuracy of the present method were tested by multiple analysis of the solution containing a known amount of Zn(II). Average of seven determinations with 10 μg/mL of Zn(II) was calculated along with standard deviation, variance and variation from mean at 95% confidence limit.

Job's continuous variation method: To a series of aqueous solutions containing 0 to 1.5292×10^{-3} M Zn(II), 1 mL of sodium acetate (1 M) was added to 2 to 0 mL of 1.5292×10^{-3} M ethanolic solution of ClNAPT and each solution was treated as mentioned earlier. The absorbance of the chloroform extract was measured at 397 nm using reagent blank and was plotted against mole fraction of zinc taken.

Mole ratio method: To a series of solutions containing 1 mL of 0.15292×10^{-3} M Zn(II) and 1 mL of sodium acetate were added increasing amounts of ethanolic ClNAPT solution of the same strength (0.15292×10^{-3} M) such that the molar proportion of ClNAPT : Zn varied from 0.5 to 5.0 mL. Each solution was then extracted with chloroform and the absorbance of the organic phase was measured at 397 nm against the reagent blank. The absorbance values were plotted against the mole ratio of concentration of ClNAPT to Zn(II).

Slope ratio method: In slope ratio method, the distribution ratio (D) was calculated while varying the reagent concentration, to ascertain the nature of the complex in solution. A graph of log D *vs.* log R at constant hydrogen ion concentration gives a straight line with the slope n. From the value of the slope n, the empirical formula of the complex was calculated.

Application

(1) Determination of Zn(II) in pharmaceutical samples

(a) Nycil powder: 0.200 g of nycil powder was dissolved in 2 to 3 mL of conc. HCl. The solution was boiled and evaporated to dryness. The residue was

leached with water and filtered to remove insoluble matter. It was then diluted to 25 mL and 1 mL of this solution was taken for extraction and estimation of Zn(II) by the proposed method.

(b) Boroline antiseptic cream: 1.1 g of Boroline cream was taken and digested with 3 mL of conc. H_2SO_4 and 2 drops of conc. HNO_3 and the solution was boiled for 20–25 min. Excess acid was neutralized with alkali solution. The neutralized solution was filtered and diluted to 25 mL and an aliquot of this solution was used for estimation of Zn(II).

(c) Zincula (eye drops): 1 mL of zincula was taken and to this 1 mL of 1% CINAPT was added and the pH was adjusted to 8. The resulting solution was extracted in chloroform and the absorbance of chloroform extract was measured at 397 nm and the amount of Zn(II) was estimated from the calibration plot.

(2) Determination of Zn(II) in synthetic mixtures

Synthetic mixture containing Zn(II) and other ions of interest was taken in a beaker and to it was added 1 mL of 1% ClNAPT. The pH of the solution was adjusted to 8.0. The mixture was then equilibrated for 1 min wth 10 mL of chloroform. Two layers were separated and dried over sodium sulphate and collected in a 10 mL standard volumetric flask and diluted with chloroform. The absorbance of the solution was measured against reagent blank at 397 nm. The amount of Zn(II) was determined from the calibration plot.

RESULTS AND DISCUSSION

4-chloroisonitrosoacetophenone thiosemicarbazone (ClNAPT) forms a yellow complex with Zn(II), which can be extracted into an organic phase. The extraction of Zn(II) from the aqueous phase by ClNAPT in chloroform is studied.

Effect of pH on the extraction of zinc: The extraction of zinc with ClNAPT has been studied over the pH range of 1–12. Extraction coefficient of zinc increases with rise in the pH of the aqueous solution up to 8.0 and is maximum in the pH range 8.0–9.0. Above this pH range it again decreases.

Effect of salting out agents: Presence of 0.5 m nitrate salts of alkali and alkaline earth metals such as K, Na, Mg, Ca and Ba does not show any improvement in the extraction coefficient of zinc between chloroform and aqueous phase. Hence, these salts have not been added in the aqueous phase before extraction for subsequent studies.

Effect of solvent: The values of the extraction coefficient of zinc (Table-1) give the following order of the organic solvent used:

Chloroform > diethyl ether > toluene > benzene > n-butanol > isobutanol > ethyl methyl ketone > carbon tetrachloride > ethyl acetate > nitrobenzene

Chloroform, being the most satisfactory solvent, has been selected for the subsequent experimental work.

TABLE-1
PRECISION AND ACCURACY OF THE METHOD

Concentration of Zn(II) metal : 10 μg/mL
Aqueous phase : 10 μg/mL of Zn(II), 2 mL of 1% ClNAPT and 1 mL of 1 M sodium acetate
Organic phase : 10 mL chloroform
Wavelength : 397 nm
pH : 8.0

Sr. No.	Absorbance	Amount of Zn(II) found in μg/mL	Deviation from mean	δ^2
1	0.151	9.92	–0.06	0.0036
2	0.153	10.02	0.04	0.0016
3	0.153	10.03	0.05	0.0025
4	0.152	9.98	0.00	0.0000
5	0.151	9.90	–0.08	0.0064
6	0.154	10.10	0.12	0.0144
7	0.152	9.96	–0.02	0.0004

Mean : 9.98 μg/mL
Standard deviation : 0.069 μg/mL
95% confidence interval : 9.98 ± 0.061
Variance : 0.0047

Absorption spectrum: The absorption spectrum of Zn : ClNAPT in chloroform shows an intense absorption peak at 397 nm and absorbance due to reagent is negligible at this wavelength. Hence, the absorption measurements were taken at this wavelength using a reagent blank.

Calibration curve: The calibration plot of absorbance against concentration of Zn(II) gives a linear and reproducible graph in the concentration range 0.8 to 12 μg per mL of zinc (Fig. 1) indicating that Beer's law is obeyed in this range. The molar absorptivity of the coloured species calculated on the basis of the total amount of zinc taken is 3.96×10^3 L mol^{-1} cm^{-1} at 397 nm. Sandell's sensitivity is found to be 0.0016 μg cm^{-2}.

Effect of equilibrium time: The study of change in the absorbance with variation in equilibrium time for the extraction of lead shows that the equilibrium time of 1 min is sufficient for the quantitative extraction of Zn(II).

Reagent concentration: The effect of variation in the concentration of ClNAPT shows that 1 mL of 1% alcoholic solution of ClNAPT is sufficient for colour development and extraction of 100 μg of zinc.

Stability of the complex with time: The study of the stability of the colour

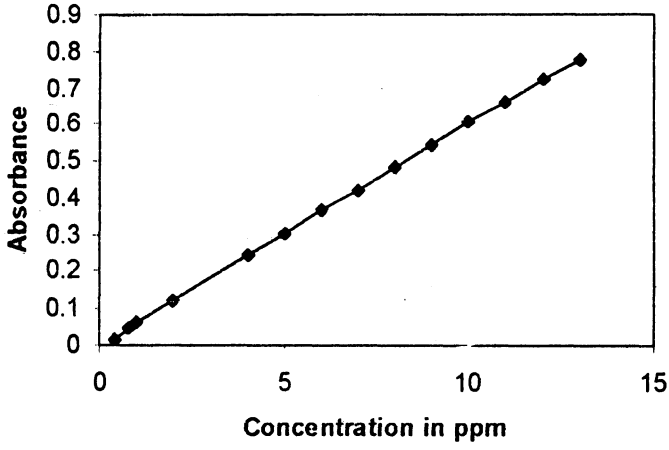

Fig. 1. Calibration plot for Zn: CINAPT complex

of the extracted species with time shows that the absorbance due to extracted species is stable up to 48 h after which a slight decrease in absorbance is observed.

Throughout the experimental work, for the purpose of practical convenience, the absorbance measurements have been carried out within 1 h of the extraction of zinc.

Effect of other ions: The following ions when present in amounts indicated below do not interfere in the spectrophotometric determination of 100 μg of zinc:

10 mg each of K(I), Na(I), Li(I), Sr(II), Mn(II); 5 mg each of Ba(II), Ca(II), Mg(II), Hg(II), Al(III), Bi(III), As(III), Mo(IV), V(V), W(VI); 10 mg each of chloride, bromide, iodide, fluoride, chlorate, bromate, iodate, sulphate, nitrate, cyanate, acetate, pyrophosphate, perchlorate, thiourea, thiocyanate.

The interference by the ions Ag(I), Co(II), Ni(II), Cu(II), Cd(II), Pb(II), cyanide, citrate, tartrate, oxalate, EDTA can be overcome by using appropriate masking agents.

Precision and accuracy: The precision and accuracy of the spectrophotometric method have been tested by analyzing seven solutions each containing 10 μg per mL of Zn(II) aqueous solution. Average of seven determinations is 9.98 μg per mL of zinc which varies between 9.92 and 10.04 μg per mL at 95% confidence limit. The standard deviation observed from the analysis of seven solutions is 0.069 and the coefficient of variance obtained is 0.0047 at 397 nm.

Nature of the extracted species: The composition of the extracted species has been determined by Job's continuous variation method, mole ratio method and slope ratio method.

Job's continuous variation method shows a sharp maximum at 0.35 mole

fraction of zinc indicating that the coloured complex species extracted into chloroform is formed by the reaction of Zn(II) and ClNAPT in the ratio 1 : 2.

The plot of absorbance against mole ratio of Zn(II) : ClNAPT shows a sharp break corresponding to the mole ratio 1 : 2, which supports the composition of the extracted species.

A graph of log D *vs.* log R plot at pH = 9.0 gives a straight line with slope equal to 2, which indicates that the probable composition of the complex is equal to 1 : 2.

Applications

(1) Determination of Zn(II) in synthetic mixture: The present method has been employed for the determination of zinc in synthetic mixture. The results of the analysis (Table-2) are comparable with the values obtained by atomic absorption spectroscopy.

(2) Determination of Zn(II) in pharmaceutical samples: Pharmaceutical samples were analyzed by the present method and it was found that the results obtained are in close agreement with the results obtained by atomic absorption spectroscopy. Table-2 shows that the present method can be applied to pharmaceutical samples for its zinc content with fairly good accuracy.

TABLE-2
DETERMINATION OF ZINC(II) IN SYNTHETIC MIXTURES, PHARMACEUTICAL AND ALLOY SAMPLES

Sr. No.	Sample	Zinc found	
		By AAS	Present method
1	**Synthetic mixtures**		
	(a) Zn (100), Cu (50), Zr (100)	100 ppm	99.30 ppm
	(b) Zn (100), Pb (100), Sn (50)	100 ppm	99.20 ppm
2	**Pharmaceutical samples**		
	(a) Nycil prickly heat power	12.85 mg per 100 mg	12.80 mg per 100 mgm
	(b) Boroline antiseptic cream (G.D. Pharma)	2.41 mg per 100 mgm	2.38 mg per 100 mgm
	(c) Zinculla eye drops	0.39 mgm per 100 mL of liquid	0.32 mg per 100 mL of liquid
3	**Alloy samples**		
	(a) Brass	40.00%	39.8%

Thus, the proposed method is simpler, faster and accurate and hence can be extended for the analysis of zinc in various analytical samples.

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