

## Spectroscopic Determination of Zinc with Dithizone in Anionic Micellar Media of Dodecyl Sulphate Salt

G. A. SHAR AND M. I. BHANGER  
*Center of Excellence in Analytical Chemistry,  
 University of Sindh, Jamshoro, Pakistan*

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**Summary:** A spectrophotometer study of zinc-dithizonate complex in aqueous phase in the presence of sodium dodecyl sulphate (SDS) anionic surfactant is reported here. The presence of micellar system avoids the previous steps of solvent extraction and reduces the cost, toxicity and enhance the molar absorptivity. The method obeys Beer's law in the concentration range of  $1.5 \times 10^{-5}$ – $1.5 \times 10^{-4}$  M. The detection limit of Zn(II) is  $3 \times 10^{-6}$  M. The molar absorption, sensitivity, critical micelle concentration, dithizone and metal ion concentration are studied and discussed. The method has been applied to the determination of Zn(II) in pharmaceutical preparation and vegetables. The present method was also compared with FAAS method and the results are comparable. There is no significant difference between the two methods at 95% confidence interval.

### Introduction

Dithizone (diphenyl thiocarbazon, H<sub>2</sub>Dz) is one of the most widely used photometric reagent and forms coloured water-insoluble complexes with a large number of metal ions [1-4]. Metal-dithizone complexes are water insoluble and thus the determination requires a prior solvent extraction step into chloroform or carbon tetrachloride [5-7] followed by photometric measurements. This problem has been overcome in recent years by introducing a hydrophobic micellar system generated by a surfactant similar to the one employed in phase-transfer reactions [8-14]. Nevertheless, the addition of surfactants in concentration above the CMC to the aqueous medium to form a micelle solution is the most commonly preferred procedure nowadays. Non-ionic surfactant like Triton X-100, have been used for the spectrophotometric determination of several metal ions e.g. Cu(II), Hg(II) and Ag(I) [15].

The present work describes a procedure to determine Zn(II) in the presence of an inexpensive anionic micelles the sodium dodecylsulphate. This method does not require a solvent extraction step, hence the use of carbon tetrachloride or chloroform is avoided. In place of the organic solvents less toxic agent [16] in the form of dodecyl sulphate salt is used.

### Results and Discussion

Complexation of dithizone, diphenyl thiocarbazon with several metal ions is well

established. Fig. (1) shows a reaction of zinc with dithizone to produce zinc-dithizone complex.

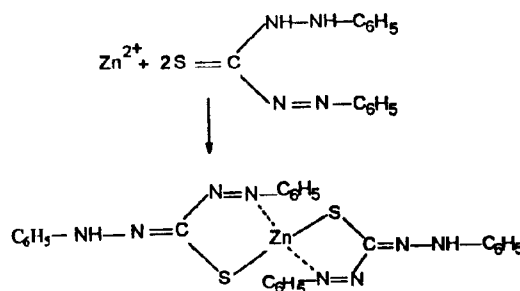


Fig. 1 Reaction of zinc with dithizone to form zinc-dithizone complex

### Spectrophotometric properties of zinc(II) dithizone complexes

In order to establish the experimental conditions for the spectrophotometric determination of zinc(II) dithizone was carried out. Fig. (2) is the spectra for a dithizone solution  $3.9 \times 10^{-5}$  M and shows absorbance maxima at 430 nm and 590 nm. The longer wavelength maximum corresponding to the thione form and the shorter to the thiol form [19]. Fig. (3) shows a spectra for a dithizone-zinc (II) complex with an absorbance maxima at 540 nm. Comparison of the analytical wavelengths with the

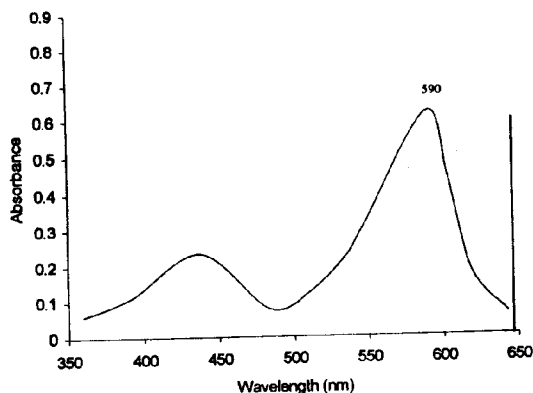


Fig. 2 Absorption spectra of dithizone at ( $\lambda_{\max}$  590 nm) in SDS at pH 5 (a) Dithizone  $3.9 \times 10^{-5}$  M (b) SDS  $1.8 \times 10^{-1}$  M

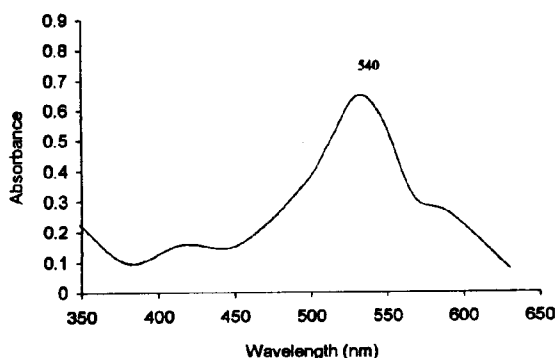


Fig. 3 Absorption spectra of zinc (II) dithizone complex at ( $\lambda_{\max}$  540 nm) in SDS at pH 5 (a) Zn  $3.5 \times 10^{-5}$  M (b) Dithizone  $3.9 \times 10^{-5}$  M (c) SDS  $1.8 \times 10^{-1}$  M

wavelength after solvent extraction see Table-1 reveals that the presence of sodium dodecyl sulphate (anionic micelle) causes a displacement of the maximum wavelength ( $\lambda_{\max}$ ) for the zinc(II)-dithizone in  $1.8 \times 10^{-1}$  M SDS. This behaviour is in accordance with that observed for DDTC metal complexes in similar media [20] as shown in Fig. (4) The pH of the solution also had a marked effect on the absorbance of the zinc(II)dithizone. On increasing pH to 6.5, the peak at 540 nm shifts hyperchromically and bathochromically to 560 nm. As the ligand absorbs significantly at the absorption maxima of the complex relative increase in absorbance of the complex was calculated and plotted

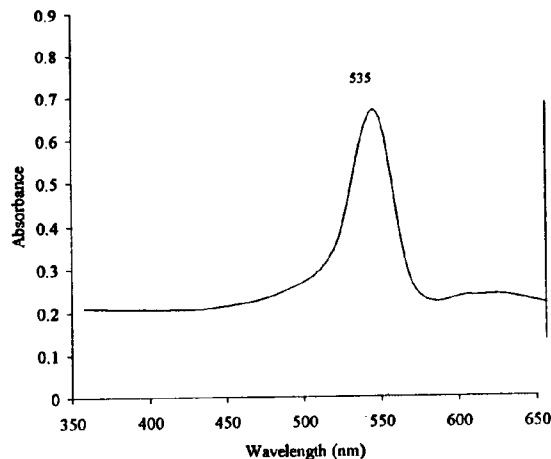


Fig. 4 Absorption spectra of zinc (II) dithizone complex at ( $\lambda_{\max}$  535 nm) in  $\text{CCl}_4$  at pH 5. (a) Zn (II)  $6 \times 10^{-5}$  M (b) Dithizone  $3.9 \times 10^{-5}$  M.

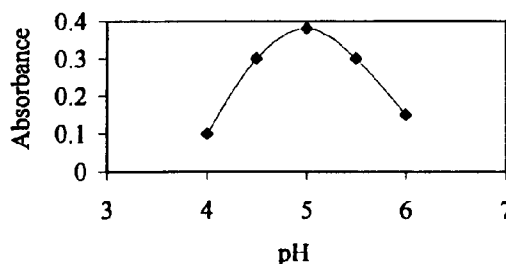


Fig. 5 Effect of pH on the absorbance of zinc(II) dithizone complex at ( $\lambda_{\max}$  540 nm). (a) dithizone  $3.9 \times 10^{-5}$  M (b) SDS  $1.8 \times 10^{-1}$  M (c) Zn  $4.5 \times 10^{-5}$  M.

against pH as shown in Fig.(5) This plot shows a maximum at pH 5, which has been taken as the pH of maximum complex formation throughout this work.

Table-1 Experimental conditions for zinc metal ion determination by complexation with dithizone in (a) aqueous anionic micellar medium and (b) by solvent extraction in  $\text{CCl}_4$

Solvent	Method	pH	$\lambda_{\max}$ (nm)	Conc. of SDS (M)	Conc. of $\text{H}_2\text{Dz}$ (M)
Aqueous	Micellar	5	540	$1.8 \times 10^{-1}$	$3.9 \times 10^{-5}$
$\text{CCl}_4$	Solvent Extraction	5 - 5.5	535	—	0.005 %

The absorbance spectra of the solutions containing increasing amounts of sodium

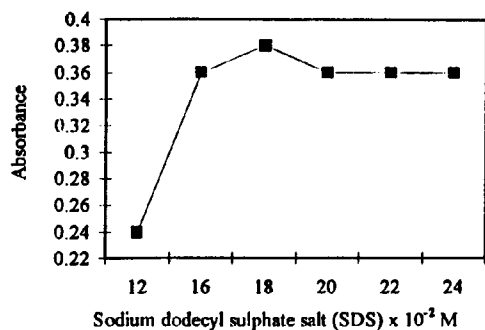


Fig. 6 Effect of SDS conc. on the absorbance of zinc-dithizone complex at ( $\lambda_{\max}$  540 nm). (a) dithizone  $3.9 \times 10^{-5}$  M (b) SDS  $1.8 \times 10^{-2}$  M (c) Zn  $3.5 \times 10^{-5}$  M.

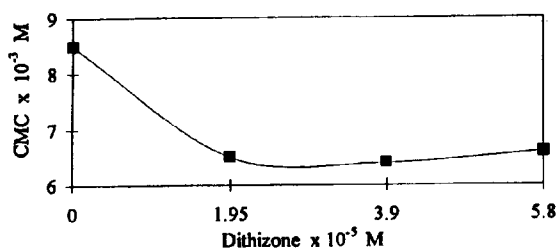


Fig. 7 Variation of critical micelle concentration (CMC) of dodecyl sulphate salt (SDS) with dithizone concentration.

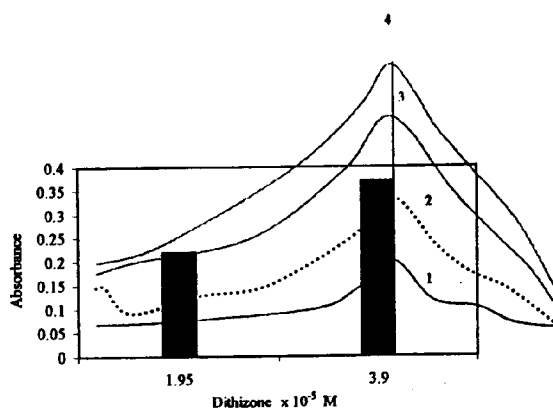


Fig. 8 Effect of dithizone conc. on the absorbance of zinc-dithizone complex at ( $\lambda_{\max}$  540). (a) dithizone  $3.9 \times 10^{-5}$  M (b) SDS  $1.8 \times 10^{-1}$  M (c) Zn  $4.5 \times 10^{-5}$  M.

dodecylsulphate showed an increase in optical density with an increase in SDS concentration up to  $1.8 \times 10^{-1}$  M of the complex and the ligand as shown

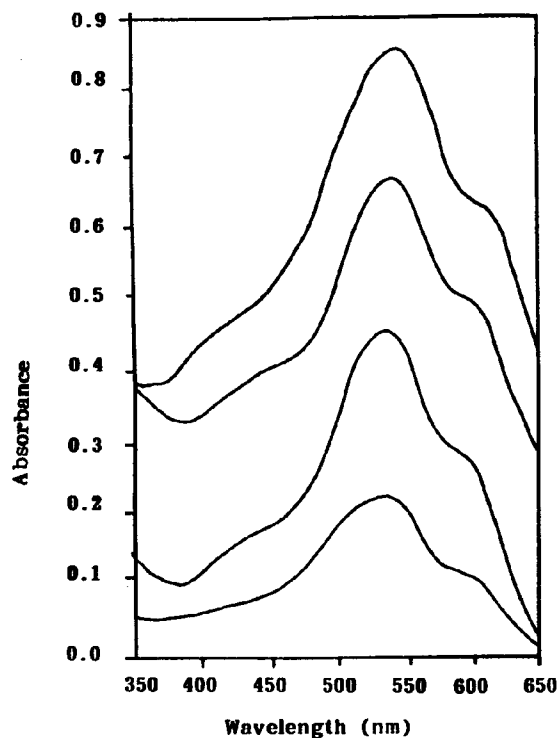


Fig. 9 Spectra (1 to 4) of the solution containing increasing ( $3 \times 10^{-5}$  –  $1.2 \times 10^{-4}$ ) amount of  $Zn^{+2}$  at pH 5 (a) dithizone  $3.9 \times 10^{-5}$  M (b) SDS  $1.8 \times 10^{-1}$  M.

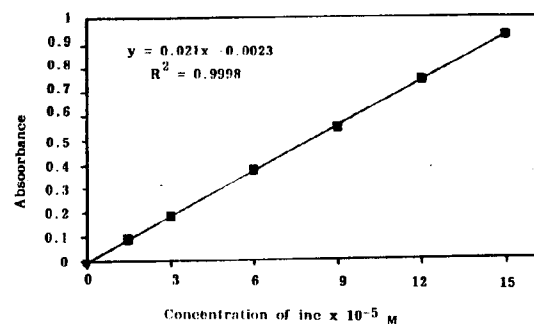


Fig. 10 Calibration graph of zinc determination for zinc-dithizone complex at ( $\lambda_{\max}$  540) in SDS. (a) dithizone  $3.9 \times 10^{-5}$  M (b) SDS  $1.8 \times 10^{-1}$  M.

in Fig.(6). A slight decrease, however, was observed above this concentration. The surfactant concentration was maintained at  $1.8 \times 10^{-1}$  M during subsequent studies. The critical micellar

concentration was determined from conductivity measurements. A CMC of  $8.5 \times 10^{-3}$  M was obtained in pure aqueous solution. This value is in agreement with the literature value [21] Fig. (7) shows variation in CMC with the addition of dithizone concentration. The absorption maximum at ( $\lambda_{\text{max}}$  540 nm) of the solution containing varying amounts of dithizone in presence of constant zinc(II) concentration ( $6 \times 10^{-5}$  M) increased with increase in dithizone concentration. Fig. (8) shows an increase up to  $3.9 \times 10^{-5}$  M.

Higher ligand concentration posed dissolution problem besides introducing error in the absorbance correction due to higher ratio of ligand to complex absorptivity. Metal to ligand ratio in the complex is 1 : 2 (M : L), and the complex remained constant for at least 2h. Absorption spectra of solution containing increasing amounts of zinc(II) from  $1.5 \times 10^{-3}$ – $1.5 \times 10^{-4}$  M and fixed amount of dithizone was found to show a linear increase in absorbance at 540 nm as shown in Fig. (9). Fig. (10) shows a calibration graph of zinc concentration against the absorbance at 540 nm. Linear regression was carried out from which the regression coefficient was calculated as 0.999. The relative standard deviation for a  $1.5 \times 10^{-4}$  M standard (n=8) was 1.2%. In the present study the effect of the presence of foreign ions, on the determination of micro quantities of zinc by this method has been investigated by studying the absorption spectra. Sodium thiosulphate (0.04 M) was added to mask interference from cobalt, nickel, mercury, bismuth, lead and cadmium.

#### Application

The proposed spectroscopic method was applied to the determination of Zn(II) in industrial

waste-water, vegetable and pharmaceutical samples. The lowest detection limit for this metal was found to be  $3 \times 10^{-6}$  M. Table-2 shows the results obtained with the above samples. These results correlate well with those obtained by atomic absorption spectrophotometry at 95% confidence level.

#### Experimental

All chemicals used were analytical grade reagents (Merck and Fluka) unless otherwise stated. Stock solution of Zn ( $1 \text{g L}^{-1}$ ) in 0.085 M hydrochloric acid. As dithizone (diphenyl thiocarbazon)  $500 \text{mg L}^{-1}$  is sparingly soluble in SDS, it was dissolved in the minimum volume of 1 M NaOH solution followed by 4 percent SDS. Finally the solution was acidified with dilute  $\text{H}_2\text{SO}_4$ . In order to prevent the dithizone from oxidation 0.5ml of 0.72 molar hydroxylamine hydrochloride was added and solution kept at  $10^\circ \text{C}$ . Fresh solution was prepared daily [17]. Sodium dodecyl sulphate (SDS) 0.6 M was prepared in hot water (below  $20^\circ \text{C}$  the solution was hazy), sodium acetate (0.2 M) buffer solution adjusted to pH 5 with acetic acid (0.2 M). Sodium thiosulphate (0.04 M) was added to mask interference. A UV / VIS Spectrometer Perkin Elmer model Lambda 2 was used throughout this study. Atomic absorption spectrometer, model Spectra AA. 20 Varian was used for comparative metal ion study. The following analytical parameters were used: photomultiplier voltage 349.9, wavelength 213.9 (nm), slit width 1.0 nm, flame air –acetylene, acetylene flow rate 1.5 L/min. Conductivity meter (WTW), LF 330 model was used for determining CMC of the solution.

#### Determination of surfactant CMC

The CMC value of SDS was determined using a conductivity measurements. The surfactant

Table- 2: Determination of Zn(II) in real samples

Sr. No.	Sample	Amount of Zn(II) determined (mg)		
		Present method	FAAS	C.V %
1.	Industrial waste (mg/L)*	32.10	32.50 ± 0.36	1.12
2.	Vegetable sample (mg/kg) (field vetch) <i>caymopsis psoralides</i>	15.50	15.71 ± 0.40	2.58
3.	** Pharmaceutical sample <i>Surbex z</i> ( ug/tablet) Abbot lab. Karachi Pakistan	21.70	22.1 ± 0.63	2.81

At 95% t-test, n=6

\*Kotri Site Area, \*\*per tablet

concentration ranged from  $1 \times 10^{-3}$  –  $2.8 \times 10^{-1}$  M. The occurrence of a sharp inflection point in the plots of specific conductivity versus surfactant concentration indicated the CMC.

*Determination of surfactant CMC. in the presence of dithizone*

The CMC values in the presence of different concentrations ( $1.95 \times 10^{-5}$  –  $3.9 \times 10^{-5}$  M) of dithizone was obtained from conductivity measurements. The surfactant concentration was determined over the same concentration range as in the absence of dithizone and the CMC was obtained from the sharp inflection point occurring in the plots of specific conductivity versus surfactant concentration.

*Spectrophotometric metal ion determination in micellar solution.*

Appropriate volumes of stock solutions of Zn(II) ion, dithizone and SDS were added to a series of 25 ml calibrated flasks and made up to volume with distilled water. The following concentration was used Zn(II)  $3 \times 10^{-6}$  –  $1.5 \times 10^{-4}$  M, dithizone  $3.9 \times 10^{-5}$  M and SDS  $1.8 \times 10^{-1}$  M. The surfactant concentration, pH values and analytical wavelength used are listed in Table 1.

To study the effect of varying dithizone concentration, solutions with increasing ligand concentrations were prepared under the conditions of maximum complex formation keeping all other variables constant.

*Spectrophotometric metal ion determination after extraction with CCl<sub>4</sub>.*

Appropriate volumes of stock metal and dithizone aqueous solutions were placed into a separating funnel and 10 ml of CCl<sub>4</sub> were added. The organic layer was transferred to a 25 ml volumetric flask. In order to obtain complete extraction, the process was repeated twice, the first time with 10 ml and the second time with 5 ml of CCl<sub>4</sub>. For the 25ml total volume of the organic layer, absorbance was measured at the appropriate wavelength for metal ion [18].

*Sensitivity and detection limit*

The sensitivity of the spectrophotometric method was determined from the slope of the

analytical calibration curve and expressed as the molar absorptivity. The detection limit was defined as the sample solution concentration giving a signal equal to the blank signal plus three times the standard deviation of the blank. A least-square method was used to calculate the linear relationship between the analytical signal (absorbance) and the concentration. The regression curve thus calculated was used to estimate sensitivity and the detection limit.

*Determination of Zn(II) in real samples*

*a. Industrial waste water*

Industrial waste water sample, 1L obtained from an industrial effluent collected from Kotri site area was filtered using Whatman filter paper. Concentrated nitric acid 4 ml and 30 % hydrogen peroxide 2 ml were added to the filtrate. The resulting solution was preconcentrated in an oven at 110 ° C to a final volume of 25 ml. Appropriate amounts of SDS and dithizone was added to a 25 ml calibrated flask to obtain final concentration of  $1.8 \times 10^{-1}$  M in SDS and  $3.9 \times 10^{-5}$  M in dithizone. Then 5 ml of the sample was added and the absorbance was measured against water. The same sample, 5 ml was diluted to 25 ml with double distilled water for FAAS analysis.

*b. Vegetable sample*

Vegetable sample, fruit lomentum of *caymopsis psoralides*, (field vetch), locally called (guwar), was collected from Jamshoro locality, washed with triple distilled water and dried in an oven at 110° C. The sample was ground in a mortar from which 5 g was digested in 10 ml concentrated nitric acid, 2 ml 30% hydrogen peroxide, by heating on a hot plate continued for two hours until the volume was reduced to 2-3 ml, then it was filtered. The volume was then made up to 25ml with deionized water and the pH was adjusted as required. Appropriate amounts of SDS and dithizone was added to a 25 ml calibrated flask to obtain final concentration of  $1.8 \times 10^{-1}$  M in SDS and  $3.9 \times 10^{-5}$  M in dithizone. Then 5 ml of the sample was added and the absorbance was measured against water. The same sample, 25 ml was then analyzed for FAAS analysis.

*a. Pharmaceutical sample*

Tablet Surbex-z (Abbot Ltd. Pakistan), 1g was dissolved in 10 ml concentrated nitric acid and 2 ml

30% H<sub>2</sub>O<sub>2</sub>, then solution was evaporated for 2 hours until volume was reduced to 2-3ml. The solution was filtered and made up the final volume of 100 ml. The pH was adjusted to 5. Appropriate amounts of SDS and dithizone was added to a 25 ml calibrated flask to obtain final concentration of  $1.8 \times 10^{-1}$  M in SDS and  $3.9 \times 10^{-5}$  M in dithizone. Then appropriate volume of sample (0.2-1.1 ml) was added and the absorbance was measured against water. Same sample, 1 ml diluted to 25 ml with double distilled water for FAAS analysis.

#### Conclusion

Determination of trace amount of Zn(II) is carried out directly using dithizone in anionic micellar media of sodium dodecyl sulphate in aqueous solutions. The method is simple and rapid with greater sensitivity, better selectivity, improved precision and replaces difficult step of extraction with toxic organic solvents. Zn(II) content in various matrixes can be determined by the present method.

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