SPECTROPHOTOMETRIC DETERMINATION OF ZINC WITH 5-METHYL-1,3,4-THIADIAZOLYL-(2-AZO-1)-2-NAPHTHOL*

Juan CACHO and Cristina NERIN
Department of Analytical Chemistry,
University of Zaragoza, Zaragoza, Spain

Received January 25th, 1982

The reaction of Zn(II) with 5-methyl-1,3,4-thiadiazolyl-(2-azo-1)-2-naphthol (MTDAN) and extraction of the complex formed in chloroform is studied. The optimum pH range for the extraction and formation of the complex is 10—11·2 and Beer's law is obeyed in the interval of 0—2 ppm of Zn(II) in the organic phase. The molar absorptivity is $5{\cdot}9 \cdot 10^4$ l mol^{-1} cm^{-1} at 568 nm. The stoichiometry of the complex corresponds to the type ML_2. Some interferences are studied and an easy way is given to eliminate them. The results are compared with those corresponding to TAN. The reaction is applied to the analysis of synthetic samples of bronzes with satisfactory results.

The azoderivatives of heterocyclic compounds have been widely used in the spectrophotometric determination of Zn(II), the most important being PAN (ref.[1]), PAR (ref.[2]), TAN (ref.[3]) and TAR (ref.[4]), due to their metallic complexes with high molar absorptivities. Ackerman and Koethe[5] have been made a comparative study of some reagents used in the spectrophotometric determination of Zn(II). The authors recommended PAR, PAN and TAR as more sensitive. However, their selectivity is rather low.

In the present work, the reaction of Zn(II) with a new azoderivative of thiadiazol, the 5-methyl-1,3,4-thiadiazolyl-(2-azo-1)-2-naphthol (MTDAN) is studied, and the reagent proposed as an alternative for the determination of Zn(II), for its higher selectivity as compared with the other reagents mentioned, and for a similar accuracy and precision of the zinc determination with this reagent. The results obtained are favourably compared with those corresponding to TAN.

EXPERIMENTAL

Apparatus and Reagents

A Pye Unicam SP8-100 spectrophotometer with 1 cm silica cells was used for measuring absorbance, and a Radiometer 51 pH meter for pH measurements. Standard Zn(II) solution con-

---

* Part II in the series Contribution to the Study of Azo Derivatives of Thiadiazol as Analytical Reagents; Part I: Afinidad *38*, 345 (1981).

taining 1 g l^{-1} of the metal was prepared; other work solutions were obtained by appropriate dilution. Buffers solutions were prepared as described by Clark and Lubbs. The synthesis MTDAN was described previously[6]. The concentration of ethanolic reagent solution was $2 . 10^{-3}$ mol l^{-1}. All reagents used were of AR grade.

Procedures

Absorbance versus pH *graphs.* Absorption spectra of free MTDAN in ethanolic solution and of the extract of its Zn(II) complex in chloroform were obtained as follows: Zn(II) solution, containing 10 μg of metal, was diluted to 25 ml with distilled water and 2 ml MTDAN solution were added. After mixing, the needed pH was adjusted by adding 10 ml of buffer solutions. To prevent the formation of emulsion, 10 ml of a saturated K_2SO_4 solution were added and the aqueous solution was extracted with 10 ml of chloroform.

Stoichiometry of the Complex by Job's Method

The concentrations of Zn(II) aqueous solution and of reagent solution in chloroform were $2{\cdot}5 . 10^{-4}$ mol l^{-1}. A constant volume of 20 ml and pH 10 in the aqueous phase were used[7-9].

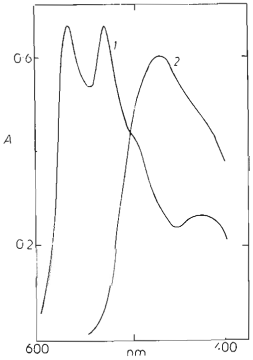

FIG. 1

Absorption spectra of MTDAN-Zn(II) complex (curve 1) and of free MTDAN (curve 2) extracted at pH 10 against chloroform as reference

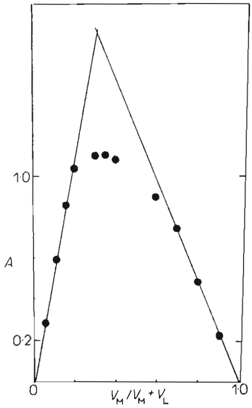

FIG. 2

Job's method of continuous variations modified applied to MTDAN-Zn(II) complex in chloroform V_M, V_L volumes of metal and ligand solutions, resp.

The absorbances of the organic layers were measured at 568 nm against pure chloroform as reference.

Spectrophotometric Determination of Zn(II) with MTDAN

To a sample solution containing not more than 12 μg Zn(II) add 300 mg sodium tartrate, 10 mg dimethylglyoxime and dilute with distilled water up to 25 ml. Then, add 2ml of ethanolic MTDAN solution (0·06%), 10 ml of buffer solution pH 10, 10 ml of saturated aqueous solution of K_2SO_4 and extract 1—2 min with 10 ml of chloroform. Measure the absorbance of the organic layer at 568 nm against a blank reagent solution, prepared simultaneously at the same conditions.

RESULTS AND DISCUSSION

Absorption Spectra

The absorption spectra of the extract of the reagent and its Zn(II) complex in chloroform are in Fig. 1. Two absorption maxima at 568 and 530 nm of the Zn(II)-MTDAN complex correspond to ligand-metal charge transfer transitions or *vice-versa*. At these wavelengths the absorbance of free reagent is negligible. The A–pH study indicated that the complex formation occurs in basic medium. The absorbance of the zinc complex remains almost constant in the pH range 10 – 11·2.

Beer's Law

Beer's law is followed at 568 nm in the range 0·2 to 2 ppm Zn. Greater values of Zn(II) content were not studied as the high absorbances obtained show a great photometric error. The equation of the straight line obtained is $y = 5{\cdot}9 \,.\, 10^4\ x - 0{\cdot}0263$ (x in mol l^{-1}), with a correlation coefficient of 0·9997 and a standard deviation of $\pm 0{\cdot}0137$. The molar absorptivity of the complex found is $5{\cdot}9 \cdot 10^4$ l mol^{-1} cm^{-1} and the Sandell sensitivity index 0·0011 μg cm^{-2}. A Ringbom plot of the system was obtained, showing that the optimum interval of Zn(II) concentrations is 0·2 – 1·2 ppm for which, the photometric error is about 1·0%.

Stoichiometry of the Complex

Results obtained are plotted in Fig. 2. Obviously, the stoichiometry of the complex corresponds to ML_2 type.

Interferences

A study of the interferences in the determination of Zn(II) with MTDAN was made. The results are shown in Table I. It is seen that Mn(II), Cu(II), Cd(II), Ni(II), Co(II), interfere even in proportion 0·5 : 1 with respect to Zn(II). A great majority of the elements studied, however, do not disturb the determination of Zn(II), although present in quantities up to 10–100 times that of Zn(II). In order to eliminate the mentioned interfering ions, some complexing agents were studied and a test of tolerance limit for each was made under conditions given in the procedure. The results are shown in Table II and it may be observed that a large quantity of tartrate does not interfere. It is, therefore, possible to mask high concentrations of Fe(III) and Pb(II), when present. Also dimethyl glyoxime is well tolerated, at least up to

TABLE I

Cation interference in the determination of 10 μg of Zn(II)

Ion	μg	Zn found, μg	Ion	μg	Zn found, μg
Ni(II)	5	13·2	Al(III)	1 000	10·0
Co(II)	5	12·8	Zr(IV)	100	10·0
Fe(III)	20	10·0	UO_2(II)	100	10·0
Hg(II)	100	11·0	Mo(VI)	1 000	10·0
Pb(II)	100	10·9	W(VI)	1 000	10·0
Mn(II)	5	13·8	Bi(III)	1 000	10 0
Cd(II)	5	13·5	Cr(III)	100	10·0
Cu(II)	5	11·7	V(IV)	100	10·0
Ca(II)	100	10·0	Pd(II)	12·5	10·9
Mg(II)	100	10·0	Ag(I)	50	12·0

TABLE II

Interference of some complexing substance in the determination of 10 μg of Zn

Substance	mg	Zn found μg
Sodium thiosulfate	60	10·0
	100	10·6
Sodium citrate	20	10·0
	30	10·3
Sodium oxalate	30	10 0
Dimethyl glyoxime	5	10·0
	10	10 0
Sodium tartrate	300	10 0
o-Phenantroline	2	10·0
	3	11·5

TABLE III

Interference of some ions in presence of tartrate and dimethyl glyoxime, in the determination of 10 μg of Zn with MTDAN

Ion	μg	Zn found, μg
10 mg dimethyl glyoxime added		
Ni(II)	100	10·0
Co(II)	100	10·0
Cu(II)	10	10·0
	50	10·0
300 mg tartrate added		
Fe(III)	1 000	10·0
Pb(II)	1 000	10·0

TABLE IV

Comparison of MTDAN and TAN reagents for the spectrophotometric determination of Zn(II)

Parameters	MTDAN	TAN
Optimum pH	10	8
Optimum range of Zn content, ppm	0·1—1·2	0·1—0·8
ε, l mol^{-1} cm^{-1}	$5{\cdot}9 \,.\, 10^4$	$5{\cdot}0 \,.\, 10^4$
Sensitivity μg cm^{-2}	0·0011	0·0013
λ_{max}, nm	568	581
Interferences (μg of cation showing the same absorbance as 1μg of Zn)		
Co(II)	2·0	1·3
Mn(II)	8·6	1·3
Cd(II)	1·4	2·8
Hg(II)	286·6	15
Cu(II)	2·6	1·6
Ni(II)	2·5	1·2

10 mg Ni(II), Co(II) and Cu(II) may be masked with this reagent. This is shown in Table III.

Comparison of MTDAN *and* TAN *in the Determination of* Zn(II)

In the Table IV some results are presented as obtained in the study of reagent MTDAN for the determination of Zn(II) compared with those obtained with thiazolyl(2-azo-1)-2-naphthol[10] (TAN). With both reagents, the most appropriate solvent for extraction of the complex is chloroform. Absorption spectra for both Zn complexes are similar although the bathochromic shift between the reagent and the complex is a little higher with MTDAN (100 nm) than with TAN (95 nm).

Although, the optimum pH is different (pH 8 withTAN and pH 10 with MTDAN), it may be observed for both reagents that for pH higher than 7, the change of absorbance with pH is very small. Beer's law with TAN is obeyed in the interval 0·1 – 8·0 μg of Zn(II). With MTDAN this interval is extended up to 20 μg, although the optimum range of work, in which the minimum error is found, is 0·1 – 12 μg of Zn(II) in 10 ml of chloroform. Both TAN and MTDAN chelates have a ML_2 composition. Due to the higher selectivity of MTDAN, more interferences are found by using TAN as reagent in this determination.

Applications

The method described may be applied to the analysis of different types of samples in which Zn is a minor component, in presence of large quantities of Fe, Ni, Al and Cu (*e.g.* in light alloys, rocks, *etc.*). To apply the method to the analysis of bronze, some synthetic samples were prepared containing those elements present in the alloy and in quantities commonly found. For an aluminium bronze, a synthetic sample was made of the following composition: 0·60% Zn, 4·75% Ni, 4·71% Fe, 9·50% Al. This composition corresponds to a bronze sample from which, Cu has been removed by electrolysis as it is done in regular analysis[11].

A solution was prepared equivalent to 0·5 g of solid sample. From this, 3 ml were pipetted in a separation funnel and the recommended procedure was followed. The results of five determinations of Zn are: $\bar{x} = 0{\cdot}609\%$, $s = 0{\cdot}011$, rel. error = 1·5%. Another synthetic sample was prepared, equivalent to phosphor bronze after removing Cu by electrolysis[11]. Its composition was: 0·75% Zn, 8·92% Sn, 1·01% P, 0·80% Pb, 0·76% Ni, 0·20% Fe, 0·052% Al. After following the same procedure, the results obtained for five determinations of Zn are: $\bar{x} = 0{\cdot}749\%$, $s = 0{\cdot}010$, rel. error = 1·2%. These results may be considered satisfactory in accuracy and precision.

The authors express their thanks to Dr J. L. Aznárez, chief of Analytical Department for the experimental facilities granted to carry out this research, and Dr A. Calvo Calvo for the interest shown in this work.

REFERENCES

1. Berger W., Elvers H.: Anal. Chem. *171*, 185 (1959).
2. Kitano M., Ueda J.: Nippon Kagaku Zasshi *91*, 983 (1970).
3. Boni E., Hemmeler A.: Chim. Milano *34*, 445 (1958).
4. Evans W. H., Sayers G. S.: Analyst (London) *97*, 453 (1972).
5. Ackerman G., Koethe J.: Talanta *26*, 693 (1979).
6. Cacho J., Nerin C.: Afinidad *38*, 345 (1981).
7. Job P.: Ann. Chim. (Rome) *9*, 114 (1927).
8. Komar N. P.: Tr. Khim. Fak. Nauch. Issled. Inst. Khim. Khar'kovskogo Univ. *14*, 119 (1956).
9. Irving H., Pierce T. B.: J. Chem. Soc. *195 9*, 2565.
10. Kawase A.: Talanta *12*, 195 (1965).
11. ASTM *Standards*, Part. 32. American Society for Testing and Materials, 1965.