

**Some heterocyclic azo compounds as analytical reagents  
XXIV.\* 2-(2-Hydroxynaphthylazo)-7-oxo-5,5-dimethyl-4,5,6,7-  
-tetrahydrobenzothiazole as a chelate-forming extraction reagent  
for copper(II), zinc(II), nickel(II), and cadmium(II)**

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*Dedicated to Associate Professor RNDr. E. Kuchár, CSc., in memoriam on the occasion of the 30th anniversary of the foundation of the Department of Analytical Chemistry, Faculty of Natural Sciences, Komenský University, Bratislava*

The chelates of 2-(2-hydroxynaphthylazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole with Cu(II), Zn(II), Ni(II), and Cd(II) were studied spectrophotometrically. The molar absorption coefficients and stability constants of chelates were calculated. The applicability of this reagent to extraction was examined. The region of optimum extraction as well as the constants of extraction into chloroform, carbon tetrachloride, and methyl isobutyl ketone was determined for the chelates of the investigated reagent with the above metal cations. The synergistic influence of trioctylphosphine oxide on the extraction of cadmium into chloroform and methyl isobutyl ketone was confirmed.

С применением спектрофотометрического метода исследованы хелаты 2-(2-гидроксинафтилазо)-7-оксо-5,5-диметил-4,5,6,7-тетрагидробензотиазола (I) с Cu(II), Zn(II), Ni(II) и Cd(II). Вычислены молярные коэффициенты абсорбции и константы устойчивости хелатов. Исследована возможность использования данного реагента в целях экстракции. Для хелатов I с перечисленными катионами металлов установлена область оптимальной экстракции и константы экстракции хлороформом, тет-

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рахлорметаном и метилизобутилкетонем. Подтверждено синергическое влияние окиси триоктилфосфина на экстракцию кадмия хлороформом и метилизобутилкетонем.

Recently, the group of heterocyclic azo compounds was intensively studied. In spite of the fact that the pyridylazo compounds appear to be the most prospective among all hitherto available and known heterocyclic azo compounds, the series of heterocyclic azo compounds on the base of 2-amino-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole [1—6] and 2-amino-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole [7—12] has been investigated. The contrast in colour change accompanying the transformation of one form into another enables us to use these substances as acid-base indicators in analytical chemistry [13, 14]. The important characteristic of heterocyclic azo compounds is also the contrast in colour change in the course of chelate formation [11]. The neutral chelates can be easily extracted into organic solvents [15, 16] and thus the heterocyclic azo compounds are widely used in analytical practice, especially for concentration and separation of some metals.

The aim of this study has been to characterize the chelate-forming properties of 2-(2-hydroxynaphthylazo)-7-oxo-5,5-dimethyl-4,5,6,7-tetrahydrobenzothiazole (*I*) and on the basis of the obtained results to ascertain the possibility of its use as extraction reagent for determining the concentration of metals by the method of atomic absorption spectrometry.

## Experimental

The pH measurements were carried out with a pH-meter PHM 64 (Radiometer, Copenhagen) equipped with a glass electrode G 202 B and calomel electrode K 401. The instrument was adjusted to standard solutions with the pH values 1.68, 6.50, and 9.22. For spectrophotometric measurements a recording spectrophotometer Specord UV VIS (Zeiss, Jena) with quartz cells and spectral colorimeter Spekol were used. The concentration of metals was determined by means of an atomic absorption spectrometer, model 306 (Perkin—Elmer) with atomization in air—acetylene flame. One-element hollow cathode lamps were used as source of primary radiation.

The extractions were performed in 50 cm<sup>3</sup> tubes with polyethylene closures by the use of a mechanical shaking machine. For the separation of organic phase centrifuge WE-1 was used.

The solutions for analytical calibration curves and evaluation of metal concentration by the AAS method were prepared from spectrally pure metals according to instructions of the producer (Perkin—Elmer) [17].

The stock solutions of metals ( $c = 10^{-1}$  mol dm<sup>-3</sup>) were prepared from anal. grade metal nitrates and redistilled water. The concentration of solutions was checked chelatometrically [18]. The solutions of lower metal concentration were prepared by diluting the stock

solutions with redistilled water. The pH values were adjusted by means of Britton—Robinson acetate buffer solutions ( $c(\text{acetic acid}) = 0.2 \text{ mol dm}^{-3}$ ,  $c(\text{NaOH}) = 1 \text{ mol dm}^{-3}$  or  $0.2 \text{ mol dm}^{-3}$ ,  $c(\text{HClO}_4) = 1 \text{ mol dm}^{-3}$  or  $2 \text{ mol dm}^{-3}$ ). The ionic strength was adjusted with  $\text{NaClO}_4$  solutions ( $c(\text{NaClO}_4) = 1 \text{ mol dm}^{-3}$ ). The purity of the organic reagent prepared according to [19] was verified using ascending paper chromatography and elemental analysis.

The concentration of solutions of *I* in redistilled ethanol and in distilled organic solvents, *i.e.* chloroform, carbon tetrachloride, and methyl isobutyl ketone (MIBK) was  $c = 10^{-2} \text{ mol dm}^{-3}$  or  $10^{-3} \text{ mol dm}^{-3}$ . The reagent was also combined with trioctylphosphine oxide (TOPO) in chloroform and methyl isobutyl ketone ( $c(\text{reagent}) = 10^{-3} \text{ mol dm}^{-3}$ ,  $c(\text{TOPO}) = 10^{-3} \text{ mol dm}^{-3}$ ). All chemicals were anal. grade reagents.

The working conditions for determining the metal concentration with the atomic absorption spectrometer are given in Table 1.

Table 1  
Working conditions for AA spectrometer (Perkin—Elmer), model 306

| Metal | Wavelength<br>$\lambda/\text{nm}$ | Slit<br>$d/\text{nm}$ | Supply current of lamp<br>$I/\text{mA}$ |
|-------|-----------------------------------|-----------------------|---|
| Cu    | 324.7                             | 0.7                   | 25                                      |
| Cd    | 228.8                             | 0.7                   | 8                                       |
| Zn    | 213.9                             | 0.2                   | 15                                      |
| Ni    | 232.9                             | 0.2                   | 25                                      |

Flow-rate of acetylene  $6.2 \text{ dm}^3 \text{ min}^{-1}$ , flow-rate of air  $21.2 \text{ dm}^3 \text{ min}^{-1}$ .

## Results and discussion

The reagent *I* forms coloured chelates with several metals. We investigated the chelates with Cu(II), Cd(II), Zn(II), and Ni(II) in aqueous ethanolic solution. The ionization constant of *I* was also determined for this medium by calculation, graphical and logarithmic analysis [20]. The measured pH values were corrected with respect to  $\text{pH}^+$  by using the correction factor  $\delta(\text{pH}^+ = \text{pH} - \delta)$  [21]. The factor  $\delta$  relates to different solvation of ions in aqueous organic medium and aqueous solutions. The  $\text{p}K_{a2}$  values determined for aqueous ethanolic solution in paper [22],  $\varphi(\text{C}_2\text{H}_5\text{OH}) = 40\%$ , and in this study,  $\varphi(\text{C}_2\text{H}_5\text{OH}) = 57.5\%$ , are confronted in Table 2.

Table 2  
Ionization constants of *I*

| Ethanol<br>$\varphi/\%$ | Calculation     | Graphical<br>analysis | Logarithmic<br>analysis |
|-------------------------|-----------------|-----------------------|-------------------------|
| 40                      | $7.70 \pm 0.04$ | 7.78                  | 7.85                    |
| 57.5                    | $8.00 \pm 0.02$ | 8.05                  | 8.01                    |

### Study of chelate-forming equilibrium of the reagent

The chelates of azo compound *I* were investigated by the spectrophotometric method. The course of absorbance of solutions in the presence of excess cations and in equimolar solutions was recorded as a function of pH. The existence of a sharp isosbestic point of the absorption curves of solutions of the chelates reveals a simple equilibrium of absorbing chelate and reagent, which is evident from the record of the absorption curves of the solutions of reagent in the presence of 100-fold excess of the cation of cadmium (Fig. 1). The molar absorption coefficients, equilibrium constants, and stability constants of chelates were determined by calculation, graphical and logarithmic analysis of the curves  $A = f(\text{pH})$  in the presence of 100-fold excess of metal (Fig. 2). All the equilibrium constants

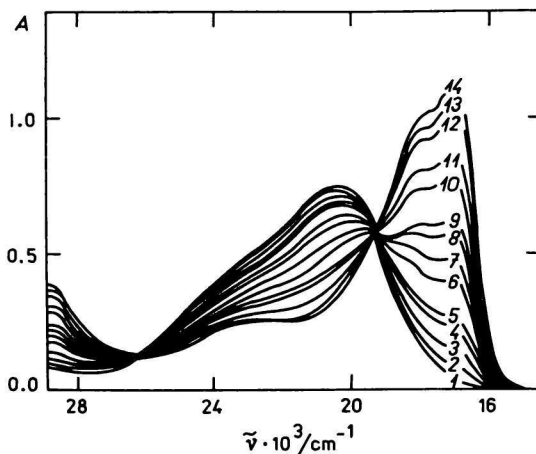


Fig. 1. Absorbance of solutions containing compound *I* with cadmium.

$c_L = 4 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $c_M = 4 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $d = 1.0 \text{ cm}$ .

pH: 1. 3.36; 2. 3.52; 3. 3.74; 4. 4.03; 5. 4.24; 6. 4.33; 7. 4.61; 8. 4.76; 9. 4.98; 10. 5.10; 11. 5.37; 12. 5.47; 13. 5.80; 14. 6.97.

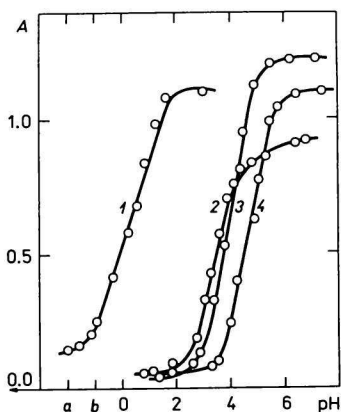


Fig. 2. Relationship  $A = f(\text{pH})$  for solutions of compound I with copper, nickel, zinc, and cadmium.

$$c_L = 4 \times 10^{-5} \text{ mol dm}^{-3},$$

$$c_M = 4 \times 10^{-3} \text{ mol dm}^{-3}.$$

1. Cu,  $\tilde{\nu} = 16\,378 \text{ cm}^{-1}$ ;

2. Ni,  $\tilde{\nu} = 17\,208 \text{ cm}^{-1}$ ;

3. Zn,  $\tilde{\nu} = 16\,542 \text{ cm}^{-1}$ ;

4. Cd,  $\tilde{\nu} = 16\,822 \text{ cm}^{-1}$ .

a) pH for  $c(\text{HClO}_4) = 2 \text{ mol dm}^{-3}$ ;

b) pH for  $c(\text{HClO}_4) = 1 \text{ mol dm}^{-3}$ .

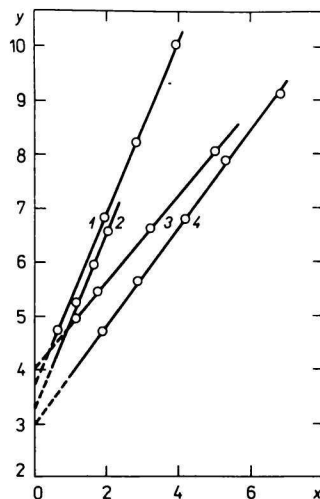


Fig. 3. Graphical analysis of the relationship  $A = f(\text{pH})$  for solutions of compound I with excess metal cations.

$$c_L = 4 \times 10^{-5} \text{ mol dm}^{-3},$$

$$c_M = 4 \times 10^{-3} \text{ mol dm}^{-3}.$$

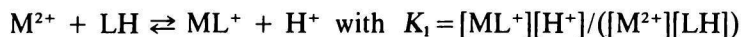
1. Cu,  $x = ([\text{H}^+]/c_M) \times 10^{-1}$ ,  $y = (c_L/A) \times 10^5$ ;

2. Zn,  $x = ([\text{H}^+]\sqrt{A}/A) \times 10^4$ ,  
 $y = (c_L/A) \times 10^5$ ;

3. Cd,  $x = ([\text{H}^+]\sqrt{A}/A) \times 10^5$ ,  $y = (c_L/A) \times 10^5$ ;

4. Ni,  $x = ([\text{H}^+]\sqrt{A}/A) \times 10^2$ ,  $y = (c_L/A) \times 10^5$ .

(stability, ionization) were calculated using relative equilibrium concentrations and, therefore, they are dimensionless. The graphical analysis of the relation  $A = f(\text{pH})$  was carried out, as described in [3] (Fig. 3), on the assumption of existence of the equilibria



The assumed equilibria were confirmed by logarithmic analysis of the relation  $A = f(\text{pH})$  for  $c_M \gg c_L$  (Fig. 4).

The values of molar absorption coefficients, equilibrium constants, and stability constants of chelates  $\beta_1$  and  $\beta_2$  are given in Table 3.

The slopes resulting from logarithmic analysis have confirmed the composition of chelates, i.e.  $n(\text{M}) : n(\text{L}) = 1 : 1$  for Cu and  $n(\text{M}) : n(\text{L}) = 1 : 2$  for Ni, Cd, and Zn.

Table 3

Spectrophotometric characteristics of the chelates of reagent *I* with Cu(II), Cd(II), Zn(II), and Ni(II)

| Metal | $\tilde{\nu}$<br>cm <sup>-1</sup> | $\epsilon_{\max}$ (ML)<br>dm <sup>3</sup> cm <sup>-1</sup> mol <sup>-1</sup>               | $K_1^a$               |                       |
|-------|-----------------------------------|--|-----------------------|-----------------------|
|       |                                   |  | Calculation           | Graphical analysis    |
| Cu    | 16 378                            | $(2.60 \pm 0.12) \times 10^4$  | $2.27 \times 10^2$    | $2.15 \times 10^2$    |
| Metal | $\tilde{\nu}$<br>cm <sup>-1</sup> | $\epsilon_{\max}$ (ML <sub>2</sub> )<br>dm <sup>3</sup> cm <sup>-1</sup> mol <sup>-1</sup> | $K_{1,2}^d$           |                       |
|       |                                   |  | Calculation           | Graphical analysis    |
| Cd    | 16 822                            | $(4.90 \pm 0.05) \times 10^{-4}$   | $7.20 \times 10^{-3}$ | $7.10 \times 10^{-3}$ |
| Zn    | 16 542                            | $(5.99 \pm 0.06) \times 10^{-4}$   | $1.60 \times 10^{-1}$ | $1.26 \times 10^{-1}$ |
| Ni    | 17 208                            | $(6.70 \pm 0.05) \times 10^{-4}$   | $4.26 \times 10^3$    | $4.70 \times 10^3$    |

a)  $K_1 = [\text{ML}][\text{H}]/c_M[\text{LH}]$ ; b)  $\beta_1$  (ML) =  $K_1/K_a$ ; c)  $k_L$  = slope of linear section obtained from logarithmic analysis; d)  $K_2 = [\text{ML}_2][\text{H}]^2/c_M[\text{LH}]^2$ ; e)  $\beta_2$  (ML<sub>2</sub>) =  $K_2/K_a^2$ ;  $K_a$  = ionization constant of *I*.

### Extraction of chelates of reagent *I*

The chelates of reagent *I* containing some metal cations are soluble in organic solvents, such as chloroform, carbon tetrachloride, and methyl isobutyl ketone. Reagent *I* was studied as extraction agent. The extractions were performed with  $V_{\text{org}} = V_{\text{aq}} = 10 \text{ cm}^3$  by means of a mechanical shaking machine for 2 h at  $(20 \pm 0.2)^\circ\text{C}$ . The concentration of metal was determined by the method of atomic absorption spectrometry after reextraction of metal from the chelate into dilute nitric acid. The calibration graphs were modelled ( $\text{HNO}_3$ ) and saturated by the used organic solvents ( $\text{CHCl}_3$ ,  $\text{CCl}_4$ ). The working procedure is described in paper [5]. Provided methyl isobutyl ketone was used as a solvent, the organic phase was directly sucked into the flame after the aqueous phase was separated by centrifugation. The analytical calibration graph was constructed by the use of the standard of the corresponding chelate of metal in methyl isobutyl ketone.

The extraction is characterized by the extraction constant and  $\text{pH}_{1/2}$  value which is characteristic of the extraction of a given metal with reagent and depends on its concentration. The dependence on the pH value of the metal quantity extracted into organic solvent in the aqueous phase  $E = f(\text{pH})$  enabled us to determine the  $\text{pH}_{1/2}$  value of extraction. The values of the conditioned constants of extraction were calculated according to the equation  $1/2 \text{ p}K_{\text{ext}} = \text{pH}_{1/2} + \log \{[\text{HL}]_{\text{org}}\}$  (Table 4) for 50 % extraction and distribution ratio  $D = 1$  on the assumption that the metal was present in the organic phase as a neutral chelate and in the aqueous phase only as

Table 3 (Continued)

| $K_1^a$               | $\log \beta_1 (\text{ML})^b$   |                  |                    | $k_L^a$ |      |
|-----------------------|--------------------------------|------------------|--------------------|---------|------|
|                       | Logarithmic analysis           | Calculation      | Graphical analysis |         |      |
| $2.26 \times 10^2$    |                                | $10.04 \pm 0.08$ | 10.34              | 10.37   | 1.10 |
| $K_{1,2}^d$           | $\log \beta_2 (\text{ML}_2)^e$ |                  |                    | $k_L$   |      |
|                       | Logarithmic analysis           | Calculation      | Graphical analysis |         |      |
| $5.90 \times 10^{-3}$ |                                | $9.87 \pm 0.27$  | 9.87               | 9.73    | 2.05 |
| $1.47 \times 10^{-1}$ |                                | $7.21 \pm 0.26$  | 7.07               | 7.15    | 2.14 |
| $3.95 \times 10^3$    |                                | $11.64 \pm 0.17$ | 11.51              | 11.51   | 2.07 |

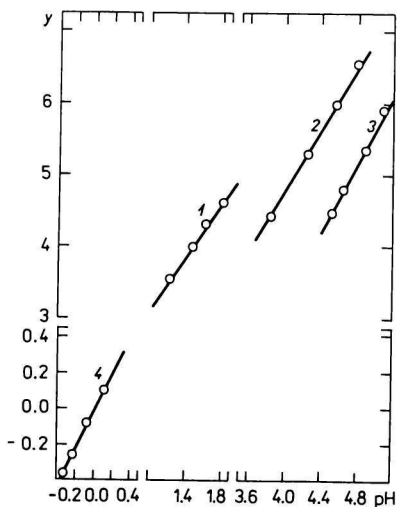


Fig. 4. Logarithmic analysis of the relationship  $A = f(\text{pH})$  for solutions of compound *I* with excess metal cations.

1. Ni; 2. Zn; 3. Cd; 4. Cu.

$$y(\text{for } 1, 2, 3) = \log \left( \frac{\{\epsilon_2\} A}{\{\epsilon_2 c_L\} - 2A} \right)^2.$$

$$y(\text{for } 4) = \log (A / \{\epsilon_1 c_L\} - A).$$

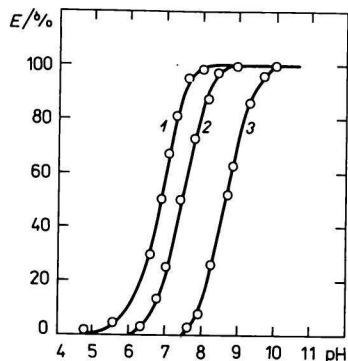


Fig. 5. Extraction (%) into  $\text{CHCl}_3$  of the chelate of cadmium and compound *I* as a pH function of the aqueous phase.

$c_{\text{Cd}} = 5 \times 10^{-5} \text{ mol dm}^{-3}$ ,  $I = 0.10 \text{ mol dm}^{-3}$ .

1.  $c_L = 10^{-3} \text{ mol dm}^{-3}$  +  $c_{\text{TOPO}} = 10^{-3} \text{ mol dm}^{-3}$ ;

2.  $c_L = 10^{-3} \text{ mol dm}^{-3}$ ; 3.  $c_L = 10^{-4} \text{ mol dm}^{-3}$ .

Table 4

Values of  $\text{pH}_{1/2}$  ( $c_L = 10^{-3} \text{ mol dm}^{-3}$ ) and  $\log K_{\text{ext}}$  for the extraction of copper, zinc, cadmium, and nickel with reagent *I* into organic solvent

| Metal | $\text{CHCl}_3$   |                       | $\text{CCl}_4$    |                       | MIBK              |                       |
|-------|-------------------|-----------------------|-------------------|-----------------------|-------------------|-----------------------|
|       | $\text{pH}_{1/2}$ | $\log K_{\text{ext}}$ | $\text{pH}_{1/2}$ | $\log K_{\text{ext}}$ | $\text{pH}_{1/2}$ | $\log K_{\text{ext}}$ |
| Cu    | 5.0               | -4.0                  | 3.1               | -0.2                  | 3.2               | -0.4                  |
| Zn    | 6.5               | -7.0                  | 6.7               | -7.4                  | 5.7               | -5.4                  |
| Cd    | 7.5               | -9.0                  | 6.4               | -6.8                  | 6.8               | -7.6                  |
| Ni    | 8.5               | -11.0                 | 7.0               | -8.0                  | 3.9               | -1.8                  |

$\text{Me}^{2+}$ . The total initial concentration of the reagent in the organic phase was  $c(\text{HA})_{\text{org}} = 1 \times 10^{-3} \text{ mol dm}^{-3}$ .

The study of the extraction of the chelate of cadmium with reagent *I* into chloroform and methyl isobutyl ketone confirmed the synergistic influence of trioctylphosphine oxide on this extraction as well as the influence of the change in concentration of ligand on the  $\text{pH}_{1/2}$  value of extraction. As obvious from Fig. 5, an increase in concentration of the reagent by one decimal order reduces the  $\text{pH}_{1/2}$  value of extraction by one pH unit (from 8.5 to 7.5). Furthermore, an addition of TOPO cuts down the pH value approximately by half a pH unit, which makes possible to use some heterocyclic azo compounds for extraction. A real application of the investigated reagent was employed for determining cadmium in samples of biological origin in connection with contamination of the environment by this element, as described in paper [23].

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