

CHROM. 11,659

## Note

### Liquid chromatography of metal complexes of N-disubstituted dithiocarbamic acids

#### IV. Separation of mixtures of Zn(II), Cu(II), Mn(II), Ni(II), Pb(II), Cr(III), Co(II), Cd(II) and Fe(II) diethyldithiocarbamate complexes by high-performance liquid chromatography

O. LIŠKA, J. LEHOTAY and E. BRANDŠTETEROVÁ

*Department of Analytical Chemistry, Slovak Technical University, 880 37 Bratislava (Czechoslovakia)*  
and

G. GUIOCHON and H. COLIN

*Laboratoire de Chimie Analytique Physique, École Polytechnique, Route de Saclay, 91128 Palaiseau Cédex (France)*

(Received December 11th, 1978)

The simultaneous detection and determination of several metal ions in mixtures at trace levels are possible by various instrumental methods. The choice is mainly a matter of convenience, depending on the specific problem and especially the matrix. High-performance liquid chromatography (HPLC) is one of the most recent methods, which permits the simultaneous separation and determination of many individual ions in mixtures.

The greatest interest has been devoted to the separation of metal mixtures by ion-exchange chromatography, but liquid-solid and even liquid-liquid chromatography have also been used.

Many workers have successfully used for these HPLC separations different acetylacetonate complexes<sup>1-4</sup>; others separated dithizonates<sup>5,6,20</sup>, Schiffbase chelates<sup>7</sup>,  $\beta$ -ketoamines<sup>8</sup>, neutral tetradentate chelates with fluorinated and non-fluorinated  $\beta$ -ketoamino and salicylaldehyde ligands<sup>9</sup>, 1-(pyridylazo)-2-naphthol chelates<sup>10</sup>, diacetylbis(thiobenzoyl)hydrazone chelates<sup>11,12</sup> and glyoxalbis(2,2,3,3-tetramethylbutyl)- and diacetylbis(cyclohexyl)thiosemicarbazones<sup>12</sup>.

In HPLC, only three papers have dealt with the separation of metal dithiocarbamate (DTC) complexes in spite of the fact that Hulanicki<sup>13</sup> pointed out in 1967 the general possibility of using DTC derivatives for the concentration of small amounts of many metals by extraction or precipitation followed by their determination using various conventional instrumental methods in trace analysis. Recently, Heizmann and Ballschmiter<sup>12</sup> published interesting results on the separation of diethyl-DTC, benzylmethyl-DTC and diethoxyethyl-DTC complexes of different metals and Moriyasu

\* This paper was presented at the *III. International Symposium on Column Liquid Chromatography, Salzburg, September 27-30, 1977*. The majority of the papers presented at this symposium has been published in *J. Chromatogr.*, Vol. 149 (1978).

and Hashimoto<sup>14</sup> reported the separation and determination of diethyl-DTC chelates of heavy metals by HPLC on a deactivated silica gel column using *n*-hexane or cyclohexane-ethyl acetate mixtures as the solvent. Quite recently O'Laughlin and O'Brien<sup>20</sup> reported the separation of seven metal diethyl-DTC chelates by HPLC on Corasil (30–50  $\mu\text{m}$ ) and  $\mu\text{Porasil}$  (10  $\mu\text{m}$ ) columns.

In the course of a general study of the HPLC analysis of metal DTC complexes, we have investigated the possibility of separating mixtures of different cations. We have studied the influence of the nature of the N-substituents on the chromatographic properties of the copper (II) DTC complexes in order to choose an appropriate ligand for the optimal separation of different metals. We have also investigated the influence of the mobile phase composition on the retention of DTC complexes.

## EXPERIMENTAL

All experiments were carried out on a Packard Model 8200 high-pressure liquid chromatograph with a UV detector at 254 nm. A stainless-steel column (200  $\times$  4.5 mm I.D.) filled with LiChrosorb SI 60 (particle diameter 10  $\mu\text{m}$ ) was used.

### Chemicals

The bisdiethyl-DTC complexes of Zn(II), Cu(II), Mn(II), Ni(II), Pb(II), Co(II), Cd(II) and Fe(II) and Cu(II) DTC complexes with different substituents on the nitrogen atom (dimethyl, methylpropyl, diisopropyl, methylphenyl and cyclopentamethylene) were prepared according to the usual procedure in the absence of oxygen<sup>15</sup>. The Cr(III)trisdiethyl-DTC complex was prepared according to the procedure of Tuljupa and Zeltobryuch<sup>16</sup>. The complexes were recrystallized from chloroform and characterized by elemental analysis, melting point determination and UV spectroscopy.

All chemicals were of analytical-reagent grade (Lachema, Brno, Czechoslovakia). The solvents were dried over magnesium perchlorate and redistilled before use.

### Procedure

Solutions (0.001 *M*) of metal DTC complexes in chloroform were freshly prepared for each series of experiments. For the determination of *k'* values, 10  $\mu\text{l}$  of solution were injected using a 10- $\mu\text{l}$  Hamilton syringe. A mixture of metal N,N-diethyl-DTC complexes was prepared as a standard solution by mixing equal volumes of 0.01 *M* solutions of each component. Samples of 5  $\mu\text{l}$  of this standard mixture were injected.

## RESULTS AND DISCUSSION

The results obtained in previous studies<sup>17,18</sup> facilitated the selection of an appropriate mobile phase. We chose chloroform-cyclohexane, which gives the optimal results.

We investigated the contribution of various N-substituents in the DTC ligand to the overall retention of Cu(II) complexes. These complexes were chosen in a search for the most suitable substituents, because they exhibit small retentions with the system we have used and the Cu(II) complexes with the six N-substituents studied are eluted in an acceptable range of *k'* values (0–10) (Fig. 1). The calculation of the eluotropic

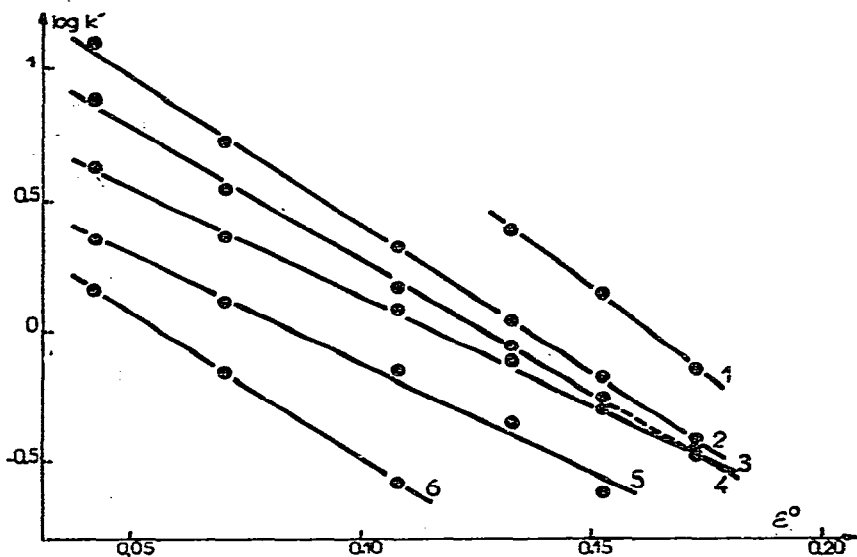


Fig. 1. Relationship between  $\log k'$  of Cu(II) bis(N,N-disubstituted)-DTC complexes and solvent eluotropic strength,  $\epsilon^\circ$ . Column: LiChrosorb SI-60, 200  $\times$  4.6 mm I.D.; particle size, 10  $\mu$ m. Mobile phase: chloroform-cyclohexane mixtures. 1 = N,N-Dimethyl; 2 = N,N-pentamethylene; 3 = N-methyl-N-isopropyl; 4 = N,N-diethyl; 5 = N-methyl-N-phenyl; 6 = N,N-diisopropyl.

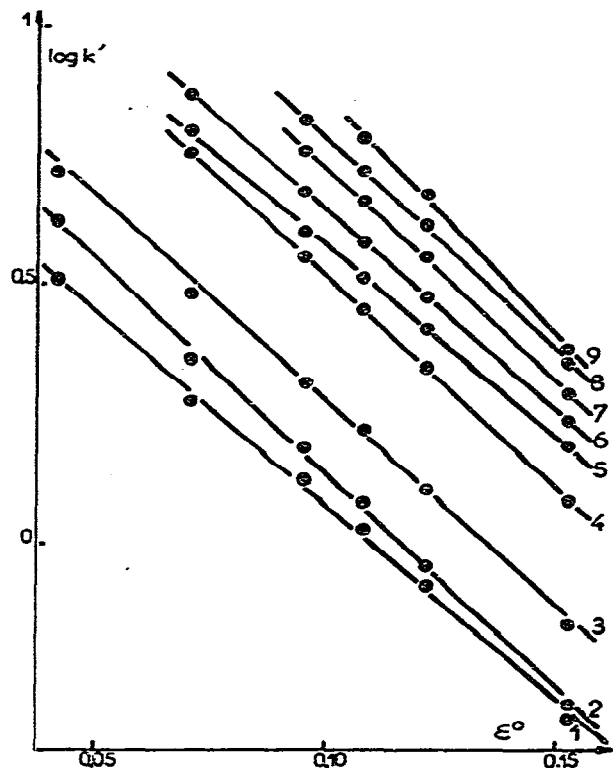


Fig. 2. Relationship between  $\log k'$  of N,N-diethyl-DTC metal complexes and solvent eluotropic strength,  $\epsilon^\circ$ . Column as in Fig. 1. Mobile phase: chloroform-cyclohexane mixtures. Metal complexes: 1 = Zn(II); 2 = Cu(II); 3 = Mn(II); 4 = Ni(II); 5 = Pb(II); 6 = Cr(III); 7 = Co(II); 8 = Cd(II); 9 = Fe(II).

strength of the binary solvent mixtures was made according to the theory of Snyder<sup>19</sup>. The elution sequence of these Cu(II) DTC complexes with the solvent systems studied was N,N-diisopropyl- < N-methyl-N-phenyl- < N,N-diethyl- < N-methyl-N-isopropyl- < N,N-pentamethylene- < N,N-dimethyl-DTC.

On the basis of the results obtained we selected the N,N-diethyl-DTC ligand for further studies. The influence of the composition of the mobile phase on the capacity ratios of the metal N,N-diethyl-DTC complexes is illustrated in Fig. 2. According to this figure we chose, as the optimal mobile phase composition, cyclohexane-10% chloroform ( $\epsilon^\circ = 0.108$ ). An example of the separation of a synthetic mixture of nine metal DTC complexes is shown in Fig. 3, which demonstrates the usefulness of HPLC for the rapid separation of the metal complexes studied.

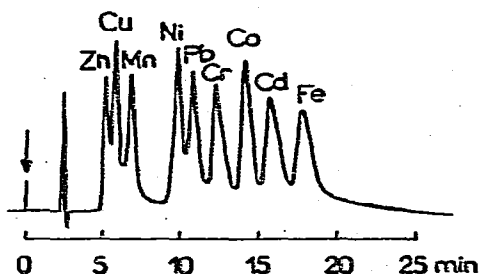


Fig. 3. Separation of a synthetic mixture of N,N-diethyl-DTC complexes of Zn(II), Cu(II), Mn(II), Ni(II), Pb(II), Cr(III), Co(II), Cd(II) and Fe(II). Column as in Fig. 1. Mobile phase: 10% chloroform in cyclohexane. Inlet pressure: 2.5 MPa. Solvent velocity:  $0.13 \text{ cm} \cdot \text{sec}^{-1}$ . Detector: UV (254 nm). Sample size:  $5 \mu\text{l}$  of a synthetic mixture of complexes in chloroform ( $5.6 \cdot 10^{-7} \text{ M}$  of each compound).

The conditions for the extraction of the metals as the DTC complexes from different aqueous solutions and the quantitative analysis of trace amounts of metals will be published later.

## REFERENCES

- 1 J. F. K. Huber, J. C. Kraak and H. Veening, *Anal. Chem.*, 44 (1972) 1554.
- 2 I. Jonas and B. Norden, *Nature (London)*, 258 (1975) 597.
- 3 K. Saitoh and N. Suzuki, *J. Chromatogr.*, 109 (1975) 333.
- 4 D. R. Jones and S. E. Manahan, *Anal. Lett.*, 8 (1975) 569.
- 5 K. Lorben, K. Mueller and H. Spitzzy, *Mikrochim. Acta*, (1975) 602.
- 6 M. Lohmüller, P. Heizmann and K. Ballschmiter, *J. Chromatogr.*, 138 (1977) 156.
- 7 P. C. Uden and F. H. Walters, *Anal. Chim. Acta*, 79 (1975) 175.
- 8 E. Gaetani, C. F. Laureri, A. Mangia and G. Parolari, *Anal. Chem.*, 48 (1976) 1725.
- 9 P. C. Uden, E. M. Pares and F. H. Walters, *Anal. Lett.*, 8 (1975) 795.
- 10 A. Galik, *Anal. Chim. Acta*, 57 (1971) 399.
- 11 P. Heizmann and K. Ballschmiter, *Z. Anal. Chem.*, 266 (1973) 206.
- 12 P. Heizmann and K. Ballschmiter, *J. Chromatogr.*, 137 (1977) 153.
- 13 A. Hulanicki, *Talanta*, 14 (1967) 1371.
- 14 M. Moriyasu and Y. Hashimoto, *Anal. Lett.*, A11 (1978) 593.
- 15 G. D. Thorn and R. A. Ludwig, *The Dithiocarbamates and Related Compounds*, Elsevier, Amsterdam, 1962.
- 16 F. M. Tuljupa and L. P. Zeltobryuch, *Ukr. Khim. Zh.*, 1 (1976) 72.
- 17 O. Liška, G. Guiochon and H. Colin, *J. Chromatogr.*, 171 (1979) 145.
- 18 O. Liška, J. Lehotay, E. Brandšteterová and G. Guiochon, *J. Chromatogr.*, 171 (1979) 153.
- 19 L. R. Snyder, *Principles of Adsorption Chromatography*, Marcel Dekker, New York, 1968.
- 20 J. W. O'Laughlin and T. P. O'Brien, *Anal. Lett.*, (1978) 829.