LIQUID CHROMATOGRAPHY OF DIETHYLDITHIOCARBAMATE COMPLEXES OF CADMIUM, LEAD, CHROMIUM, COBALT AND MERCURY

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Received November 14, 1991
Accepted February 16, 1992

The conditions of chromatographical analysis have been studied and the elution data have been determined of diethyldithiocarbamate complexes of cadmium, lead, chromium, cobalt, and mercury using an octadecylsilica gel column and mobile phases of water–methanol containing sodium diethyldithiocarbamate. The method is based on a direct injection of aqueous solution of the metal ions into the column and detection of the separated complexes by means of a UV detector in the wavelengths interval of 254 – 365 nm.

The high-performance liquid chromatography (HPLC) attracts increasing attention at present in connection with analyses of mixtures of inorganic ions. For these purposes it is possible to adopt beside the ion chromatography[1] also the chromatography in systems of reversed or normal phases, usually the technique of ion pairs or formation of neutral complex compounds[2]. The last method mentioned offers a broad spectrum of chromatographic analyses of solutions of metal ions, since there exist a large number of organic ligands forming stable complexes with these ions, which enables even the trace analyses[3]. Out of these reagents the following ones were successfully used: EDTA[4], 1,10-phenanthroline[5], tetramethylenedithiocarbamic acid[6], acetylacetone[7], dithizone[8,9], and some others[2]. Perhaps the most frequently used chelation reagents are N-substituted dithiocarbamates, particularly diethyldithiocarbamic acid[9 - 21], n-butyl-2-naphthylmethyldithiocarbamate[22], dibenzyldithiocarbamate[23], or bis(2-hydroxyethyl)-dithiocarbamate in the form of zinc(II) complex[24]. In most cases the samples for chromatography were metal complexes formed by addition of the chelation reagent to the original sample and subsequent extraction with a suitable solvent. The diethyldithiocarbamates (DEDTC) of Se(IV), Cr(III), Ni(II), Co(III), Pb(II), Cu(II), Hg(II), Cd(II), Te(IV) were thus analysed in systems of reversed phases[10 - 13], and some of them were also successfully separated on silica gel columns[15 - 16]. However, with regard to a good solubility and stability in aqueous solution, it is possible to form the DEDTC complexes of a number of metals and separate them directly in the chromatographic column in the system of reversed phases. In such cases the aqueous solution of ions is injected into alkylsilica gel column with an aqueous–organic mobile phase containing the diethyldithiocarbamate ligand. The analysis of aqueous samples is thus simplified and

accelerated in comparison with the extraction procedure[17 - 20]. In these cases the detection of DEDTC complexes is usually performed photometrically[19] at the wavelength of 320 – 440 nm; in this wavelength interval the interfering absorbance of the complex-forming reagent itself (whose absorption maximum lies at 240 – 300 nm like those of most DEDTC complexes[14,25]) is not very significant. If the complexes are prepared in advance and chromatographed in mobile phases without diethyldithiocarbamate, then the detection at the wavelength below 300 nm presents no problems[10 - 13]. The electrochemical detection is sensitive and selective[17,18].

The present paper evaluates the applicability of the glass chromatographical column Separon SGX to the analyses of DEDTC complexes of Cd(II), Pb(II), Cr(III), Co(III), and Hg(II) using the method of direct injection and in situ formation of the complexes in the column and deals with the optimization of chromatographical conditions in aqueous–methanolic mobile phases containing sodium diethyldithiocarbamate (NaDEDTC). For this purpose, we estimated the dependences of the retention of DEDTC complexes on the methanol content in mobile phases, since such data have not yet been published in available literature.

EXPERIMENTAL

Apparatus and Chemicals

The liquid chromatograph used consisted of a high-pressure linear doser HPP 5001, a UV-VIS detector LCD 2563 with interference filters for the wavelengths of 254, 290, 313, 365, 405, 436, nad 546 nm, an injection device LCI 20 (all the apparatus from Laboratorní přístroje, Prague), and a glass chromatographical column 150 × 3 mm, packed with an octadecylsilica gel sorbent Separon SGX C18, 5 μm, dead volume V_M = 0.72 ml (Tessek, Prague). The specific surface of the original silica gel was 500 $m^2 g^{-1}$, the carbon content after modification[26] was ca 18%. The output signal of the detector was recorded by means of an OH-814/1 recorder (Radelkis, Hungary); the pH meter OP-205/1 with a combined glass electrode OP 8083 was of the same provenience.

The dead volume of the column was measured with the help of a refractometry detector RIDK 101 (Laboratorní přístroje, Prague), the mobile phase was degasified in an ultrasonic bath UC 002 BM 1 (Tesla Vráble, Czechoslovakia).

The mobile phases were prepared from methanol for UV and sodium diethyldithiocarbamate p.a. (both chemicals from Lachema, Brno) and from deionized water. The pH of the mobile phases was adjusted at the required value by addition of perchloric acid p.a. (Laborchemie, Apolda, Germany) diluted with water in the ratio of 1 : 4. The pH meter used was calibrated with the use of standard buffers pH 4, 7, and 9 (Ústav sér a očkovacích látek, Prague).

The Substances Chromatographed

All the salts used for preparation of ion solutions were of p.a. purity grade (Lachema, Brno). The stock standard solutions of Pb, Cd, Cr, and Hg (the concentration of 1 g l^{-1}) were prepared by dissolving the corresponding amounts of $Pb(NO_3)_2$, $CdSO_4$, $Hg(NO_3)_2$, and $Cr(NO_3)_3 . 9 H_2O$, respectively, in distilled water acidified with several drops of nitric acid. The solution of cobalt(II) salt was prepared by dissolving

$CoCO_3$ in diluted HNO_3. The solutions with lower metal ion concentrations were prepared by diluting the stock solutions with deionized water acidified with HNO_3; their final pH was ca 3 – 4.

Procedures

The mobile phases were prepared by mixing the corresponding volumes of methanol and water and adding the required amount of NaDEDTC. The pH of solution was adjusted precisely at the value chosen by addition of perchloric acid. Then the mobile phase was degasified in the ultrasonic bath. Before the measurements of retention characteristics, the column was washed with the mobile phase for ca 30 min. The samples of metal ion solutions with the concentration of the order of $10^1 - 10^3$ mg l^{-1} were injected into the column in the amounts of 1 – 10 μl; the flow rate of mobile phase was 0.6 ml min^{-1}; the eluate was detected at the wavelength chosen with the use of the UV-VIS detector using the difference method with the mobile phase in the reference cell. The retention volumes V_R of the complexes were measured and used for the calculation of values of capacity ratios $k = (V_R - V_M)/V_M$. The dead volume V_M was defined as the elution volume of heavy water D_2O in the given mobile phase (refractometric detection). The capacity ratios given in Tables are arithmetic mean values from results of two measurements each.

RESULTS AND DISCUSSION

Determination of the Optimum Wavelength of Detection

The optimum wavelength of detection of the DEDTC complexes with the differential photometric detector adopted was determined by measuring the peaks of individual complexes at discrete wavelengths choosable at the detector in the interval of 254 – 546 nm. The chromatographical analysis was carried out in the mobile phase in which the volume fraction φ of methanol was 70%, and the concentration ρ of NaDEDTC was 0.05% (w/v), i.e. 0.5 g l^{-1}. The pH of mobile phase was adjusted at the value of 8; the volume of injection 1 μl; the metal amount analyzed 1 μg; the flow rate of mobile phase 0.6 ml min^{-1}. The sensitivity of detector was adjusted at 0.08 A.U.F.S. The results of measurements corrected with respect to the noise level of the detector at the wavelength chosen are given in Table I. Therefrom it follows that the complexes of the metals studied are detected by the apparatus used with the highest sensitivity at the wavelength of 313 nm, the cobalt(III) complex also at 365 nm. All the chelates also absorb the radiation with the wavelengths of 254, 290, 365, and 405 nm (except for $Cr(DEDTC)_3$), $Co(DEDTC)_3$ also at 436 nm, which is in accordance with the published data[18 – 20]. In this context it must be noted that the response of detector did not depend on the absorbance of the eluate from the column, but depended on the difference of absorbances of the liquids in the sample and the reference cells of the apparatus, the detector sensitivity being obviously different for the individual wavelengths. Hence the obtained absorbance data of the DEDTC complexes which are presented in Table I as the peak heights need not fully agree with the dependence of the absorbance coefficients of complexes versus wavelength. However, they were sufficient for the optimization of the detection conditions on the apparatus used. The necessary information

about absorption coefficients of all the complexes studied were not found in literature. The differential method of detection at the wavelength of 250 – 320 nm is particularly suitable in the cases of simultaneous analyses of the DEDTC complexes of cadmium, lead, or as the case may be, other metals, since the sensitivity of detection of $Cd(DEDTC)_2$ at 350 nm (where the mobile phase does not practically absorb) is approximately 100 times lower than that of $Pb(DEDTC)_2$ (ref.[20]). Our experiments have shown that increasing of detector sensitivity and injection volume enables reliable analyses of metals in the concentration order of 10^0 (Pb, Cd, Co) to 10^1 mg l^{-1} (Cr, Hg). At the above-given conditions of chromatography, i.e. sample injection of 10 μl, detection wavelength 313 nm, detector sensitivity 0.02 A.U.F.S., and the peak height to noise level ratio 2 : 1, the detection limits of determination of individual metals are: 0.6 ng Cd(II), 0.8 ng Pb(II), 2.3 ng Cr(III), 0.8 ng Co(II, III), and 2.8 ng Hg(II). The concentration interval in which the detector response is linearly proportional to the metal concentration in sample was not estimated.

Effect of pH of Mobile Phase on Retention of DEDTC Complexes

We estimated the retention of the DEDTC complexes on the Separon SGX C18 column in mobile phases with pH 5, 6, 7, 8, and 9 and with methanol volume fraction φ(MeOH) = 68% (in the case of Cd, φ(MeOH) = 60%), and NaDEDTC concentration ρ = 0.05% (w/v). The calculated values of capacity ratios are given in Table II. $Cd(DEDTC)_2$ and $Cr(DEDTC)_3$ were determined in the mobile phase of pH 8 and above, $Pb(DEDTC)_2$ was formed at pH ≥ 7, $Co(DEDTC)_3$ at pH ≥ 6, and $Hg(DEDTC)_2$ was stable over the whole pH interval measured, i.e. from as low as pH 5. In the transition pH region of mobile phase the chromatographic behaviour of the complexes was not studied in detail. The differences in retention of the complexes at various pH values can be ascribed to the worse reproducibility of elution data of the DEDTC complexes. Only in the

TABLE I
The heights of peaks (in mm) of complexes of Cd, Pb, Cr, Co, and Hg with DEDTC on a Separon SGX C18 column with mobile phase water–methanol–NaDEDTC[a] with UV detection at different wavelengths

Complex	λ, nm						
	254	290	313	365	405	436	546
Cd	120	29	225	39	5	0	0
Pb	65	31	165	35	5	0	0
Cr	25	12	55	8	0	0	0
Co	106	88	159	170	130	90	0
Hg	38	16	45	13	5	0	0

[a] φ(MeOH) = 70% (v/v), ρ(NaDEDTC) = 0.05% (w/v), pH 8.

case of cadmium, repeated experiments showed that $Cd(DEDTC)_2$ exhibits the strongest retention at pH 8, which agrees with the fact found by Smith and Yankey[19] that the retention of $Cd(DEDTC)_2$ in the mobile phase prepared from a buffer of pH 9.72 is lower than that in the eluent prepared from a practically neutral buffer. Hence, for analyses of mixtures of ions it is suitable to use a mobile phase of pH 8; more alkaline eluents decrease the lifetime of sorbent[26]. For this reason it is useful to decrease the pH value of the mobile phase water–methanol–NaDEDTC from the original value of 9.5 – 11 (depending on the content of methanol and NaDEDTC) to a lower value and/or to adopt a suitable buffer for the preparation of mobile phase.

Effect of NaDEDTC Concentration in Mobile Phase on Retention of Complexes

The extent to which the NaDEDTC concentration in mobile phase affects the chromatographical behaviour of the complexes studied was verified in a mobile phase with the methanol content φ = 60% (Cd, Pb) and φ = 68% (Cr, Co, Hg) in which the NaDEDTC concentration was ρ = 0.005 – 0.1% (w/v), and pH was adjusted at 8. The results are given in Table III. The NaDEDTC concentration in mobile phase significantly affects the behaviour of $Cd(DEDTC)_2$ only; if it decreases below ρ = 0.05% (w/v), then the retention of complex is markedly increased. The absence of dependence of retention of $Co(DEDTC)_3$ on concentration of NaDEDTC in mobile phase within the range of ρ = 0.01 – 0.1 was also proved in another paper[19]. The retention of the cadmium(II) complex is apparently markedly affected by the competition sorption equilibrium between the stationary phase and DEDTC ligand whose system peak lies between the peaks of $Cd(DEDTC)_2$ and $Pb(DEDTC)_2$. For practical purposes it can be recommended ρ = 0.05% (w/v); at lower NaDEDTC concentrations the peaks of the

TABLE II
Effect of pH of mobile phase water–methanol–NaDEDTC[a] on the value of capacity ratio (k) of complexes of Cd, Pb, Cr, Co, and Hg with DEDTC on a Separon SGX C18 column

Complex	pH				
	5.0	6.0	7.0	8.0	9.0
Cd[c]	[b]	[b]	[b]	2.50	1.58
Pb	[b]	[b]	7.12	7.16	7.10
Cr	[b]	[b]	[b]	6.80	6.90
Co	[b]	9.80	9.62	9.66	9.00
Hg	22.91	22.34	22.33	22.34	22.00

[a] φ(MeOH) = 68% (v/v), ρ(NaDEDTC) = 0.05% (w/v); [b] no complex was formed; [c] φ(MeOH) = 60% (v/v).

complexes become more or less asymmetrical, the reproducibility of their shape, height, and retention volumes being worsened.

Dependence of Retention of DEDTC Complexes on Methanol Content in Mobile Phase

According to the presumption that the retention of complexes is decreased with increasing methanol content in mobile phase, the dependences of $\log k$ vs φ(MeOH) are practicaly linear (Fig. 1), the values of correlation coefficients of the regression straight lines being greater than 0.998. For practical separations and determinations of Pb(II),

TABLE III
The effect of concentration ρ(NaDEDTC) in mobile phase water–methanol[a] on the value of capacity ratio (k) of complexes of Cd, Pb, Cr, Co, and Hg with DEDTC on a Separon SGX C18 column

Complex	ρ(NaDEDTC), % (w/v)			
	0.1	0.05	0.01	0.005
Cd[b]	1.64	2.50	7.05	9.55
Pb[b]	22.40	19.83	21.63	21.50
Cr	6.55	6.80	6.95	8.00
Co	9.50	9.66	9.83	9.83
Hg	21.00	22.34	22.66	22.33

[a] φ(MeOH) = 68% (v/v), pH 8; [b] φ(MeOH) = 60% (v/v).

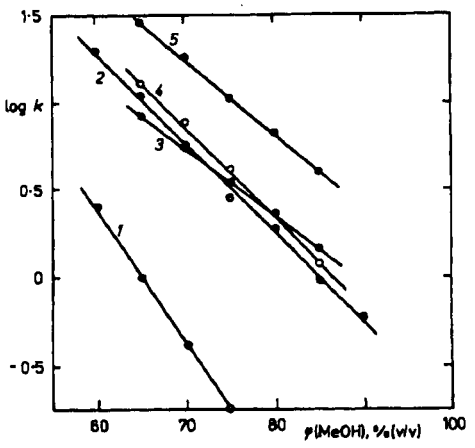

FIG. 1
The dependence of logarithm of capacity ratios (k) of DEDTC complexes of Cd, Pb, Cr, Co, and Hg on the volume fraction (φ) of methanol in mobile phase water–methanol–NaDEDTC on a Separon SGX C18 column. ρ(NaDEDTC) = 0.05% (w/v), pH 8. The straight lines: *1* $Cd(DEDTC)_2$, *2* $Pb(DEDTC)_2$, *3* $Cr(DEDTC)_3$, *4* $Co(DEDTC)_3$, *5* $Hg(DEDTC)_2$

Cr(III), Co(II), and/or Co(III) ions ($Co(DEDTC)_3$ is formed in the last two cases[18,19]) the mobile phase with φ(MeOH) = 70 – 75% can be recommended, for determination of Hg(II) it is possible to recommend 80% aqueous methanol, ρ(NaDEDTC) = 0.05% (w/v). If the methanol content decreases below the value of φ = 70%, then the peak of $Pb(DEDTC)_2$ shows a tail due probably to lower stability or solubility of the complex in the medium of higher content of water[20]. Some authors[13,20] try to treat this unfavourable phenomenon by adding some of less polar solvents (chloroform, ethyl acetate) to the mobile phase. Orientational experiments carried out within the present work, however, did not lead to a demonstrable improvement. At the given conditions no tails were observed with the peaks of the other complexes. The diethyldithiocarbamate complex of cadmium is retained substantially less than the other complexes; for practi-

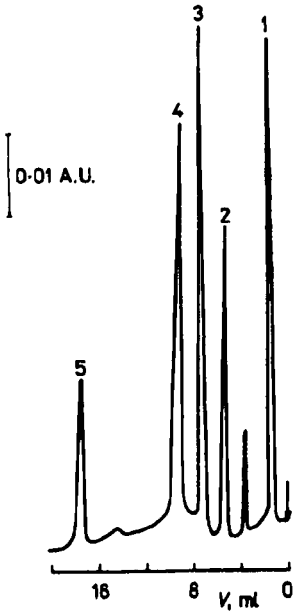

FIG. 2

A chromatogram of a mixture of DEDTC complexes of Cd, Pb, Cr, Co, and Hg on a Separon SGX C18 column. Mobile phase: water–methanol–NaDEDTC, φ(MeOH) = 67% (v/v), ρ(NaDEDTC) = 0.05% (w/v), pH 8, F_m = 0.6 ml min^{-1}. Feed: 10 μl, 0.8 μg Cd, 2.1 μg Cr, 1.1 μg Pb, 0.9 μg Co, 1.4 μg Hg. Detection: UV, 313 nm, 0.08 A.U.F.S. Peaks: 1 $Cd(DEDTC)_2$, 2 $Cr(DEDTC)_3$, 3 $Pb(DEDTC)_2$, 4 $Co(DEDTC)_3$, 5 $Hg(DEDTC)_2$

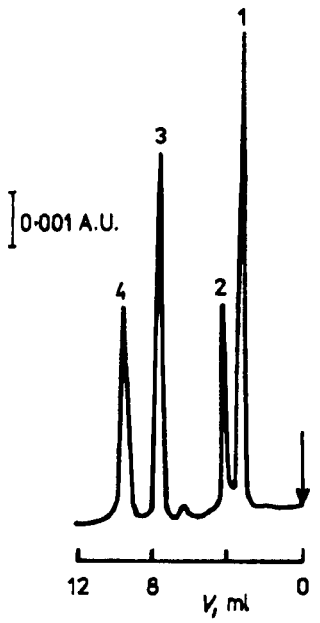

FIG. 3

A chromatogram of a mineralizate of volatilizing dust from the town of Chrudim. Separon SGX C18 column. Mobile phase: water–methanol–NaDEDTC, φ(MeOH) = 67% (v/v), ρ(NaDEDTC) = 0.05% (w/v), pH 8, F_m = 0.6 ml min^{-1}. Feed: 10 μl. Detection: UV, 313 nm, 0.02 A.U.F.S. Peaks: 1 $Mn(DEDTC)_2$, 2 unidentified substance, 3 $Pb(DEDTC)_2$, 4 $Zn(DEDTC)_2$

cal purposes it is conceivable to adopt the mobile phase with φ(MeOH) ≤ 70%, ρ(NaDEDTC) = 0.05% (w/v), and pH 8, when the retention of $Cd(DEDTC)_2$ is stronger. The elution order of the complexes studied is in accordance with the data published in papers dealing with HPLC of DEDTC complexes in systems of reversed phases, both for the cases of formation of the complexes directly in the column[18 - 20] and for analyses of the carbamates prepared in advance[11 - 13]. The flow rate of mobile phases in the range of 0.1 – 0.7 ml min^{-1} has no demonstrable effect on the retention of complexes.

An example of separation of DEDTC complexes of Cd, Pb, Cr, Co, and Hg is presented in Fig. 2. Figure 3 shows that the method described can also be adopted for determination of other metals, in this particular case manganese and zinc which were found along with lead in a mineralizate of volatilizing dust from the town of Chrudim.

It must not be forgotten, however, that a long-term application of mobile phases with pH ≥ 8 leads to a stepwise worsening of quality of octadecylsilica gel sorbent, a decrease in the efficiency of column and in the retention of complexes. In spite of that, it can be stated that the described method of HPLC of diethyldithiocarbamate complexes of heavy metals in a system of reverse phases extends the applicability of this separation technique to the region of inorganic analysis and thus suitably complements the spectral or electrochemical methods with which it has practically comparable detection limits.

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Translated by J. Panchartek.