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# Determination of Ni(II), Co(II) and Cu(II) as diethyldithiocarbamate complexes by high-performance liquid chromatography using hexadecyltrimethylammonium bromide in the mobile phase

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## Abstract

The enhancement of the selectivity and sensitivity in high-performance liquid chromatography due to the presence of the cationic surfactant hexadecyltrimethylammonium bromide (CTAB) in the mobile phase in the determination of three metal ions as complexes with sodium diethyldithiocarbamate was studied. The presence of an organic modifier such as 1-propanol in the mobile phase contributes to the decrease in the retention times of the complexes. The results show that under these conditions, the separation of the three metal ions is possible whereas in the absence of surfactant it is not possible. Also, the detection limits and selectivity are better in the presence of CTAB than in its absence. The method was applied to the determination of nickel and copper in real samples.

## 1. Introduction

High-performance liquid chromatography (HPLC) has been widely used for the separation and determination of metal ions as complexes [1]. Generally, ion-pair reversed-phase liquid chromatography in which a counter ion with opposite charge to the complex is introduced into the mobile phase has been employed. In this technique, two approaches are possible. In one, the metal ion complex is originated in the chromatographic system and in the other, the complex is formed prior to the chromatographic separation. The first possibility is called "on-column" complexation and implies that the mo-

bile phase employed contains the complexing ligand. The second mode is "precursor" complexation in which in most instances a solvent extraction step is necessary prior to the chromatographic separation. Optimum conditions for the solvent extraction of many metal ion complexes and their spectrophotometric characteristics have been reported [2]. Diethyldithiocarbamate (DDTC) has been used as a complexing agent to achieve the separation of metal ions by HPLC [3–12]. An organic solvent extraction step is usually used before introducing the complexes into the chromatographic system [3,4,8,10,11]. In some instances, the complexes are introduced into the chromatographic system directly formed in the mobile phase when it contains a high percentage of an organic modifier, e.g., metha-

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nol or acetonitrile [5–7,12], also adding carbon tetrachloride to the mobile phase in order to facilitate the solubilization of the hydrophobic complexes.

In most instances, the detection mode was UV–Vis spectrophotometry and in a few instances electrochemical [5–8].

The influence of surfactants in analytical methods [13–17] and, in particular, in separation methods has been described [18]. Surfactants have been used in chromatography to improve the separation and determination of organic and inorganic compounds owing to the increase in the solubility of hydrophobic solutes that the surfactant micelles produce. In fact, when a surfactant is introduced into the mobile phase, the retention of the solutes is modified owing to the interactions between the stationary phase, the mobile phase and the solute contained in the mobile phase. Some equations have been proposed to describe this process and the interactions mentioned above [18–25].

In some studies different stationary phases and a mobile phase containing a surfactant have been used for determining metal ions by HPLC [26–28]. Also, an aqueous–organic mobile phase in a gradient with another that contains the surfactant has been employed [29].

In this work, the separation and determination of Co(II), Ni(II) and Cu(II) as diethyldithiocarbamate complexes was achieved by HPLC using hexadecyltrimethylammonium bromide as a surfactant in the mobile phase. The need for solvent extraction for the formation of the complexes was avoided owing to the presence of the surfactant in the mobile phase. The proposed method was applied to the determination of Ni(II) and Cu(II) in real samples and the results were compared with those obtained for the same samples by flame atomic absorption spectrometry (FAAS).

## 2. Experimental

### 2.1. Reagents

All reagents were of analytical-reagent grade. Cu(II), Ni(II) and Co(II) solutions were pre-

pared from their nitrate salts. The ligand, sodium diethyldithiocarbamate (DDTC), the cationic surfactant, hexadecyltrimethylammonium bromide (CTAB), and 1-propanol (PrOH) were used as received. All these reagents and the  $\text{HNO}_3$  employed for the preparation of metallic samples, were obtained from Merck. Methanol (MeOH) for HPLC was supplied by Scharlau. Deionized water was obtained using a Milli-Q system (Millipore).

### 2.2. Apparatus

A Waters liquid chromatograph was used with a Model 510 pump, a Model 481 UV–Vis detector, a Model 740 integrator and a Rheodyne injection valve with an injection volume of 20  $\mu\text{l}$ .

A LiChrosorb RP-18 column (150  $\times$  3.9 mm I.D.; particle size 10  $\mu\text{m}$ ), obtained from Sugelabor, was used in all HPLC runs.

The FAAS measurements were carried out in a Perkin-Elmer Model 2380 atomic absorption spectrometer.

### 2.3. Procedure

The mobile phases consisted of the cationic CTAB surfactant at an appropriate concentration, the ligand (DDTC) and an organic modifier (methanol or 1-propanol), which was needed to reduce the retention times. These mobile phases were prepared by weighing the necessary amounts of CTAB (at concentrations between 0.03 and 0.25  $M$ ) and  $10^{-4}$   $M$  DDTC and dissolving them in a mixture of 1-propanol or methanol and deionized water with the percentage of the alcohol varying from 20 to 50% (v/v). All mobile phases were filtered and placed in an ultrasonic bath for 20 min for degasification before introduction into the chromatographic system.

The complexes were prepared by dissolving the necessary amount of each salt directly in the mobile phase. These complexes were then injected into the chromatographic system. The variation of the retention times of the three complexes as a function of the concentration of CTAB in the mobile phase [with 45% (v/v) of 1-propanol as organic modifier and DDTC at a

concentration  $10^{-4}$  M] was determined. Next, the variations of retention times as a function of the concentration of DDTC in the mobile phase [with 0.03 M CTAB and 45% (v/v) 1-propanol] and finally as a function of percentage of organic modifier in the mobile phase using 1-propanol and methanol (with 0.03 M CTAB and  $10^{-4}$  M DDTC) were determined.

Detection was carried out by UV-Vis spectrophotometry using a wavelength of 326 nm for the Ni(II) and Co(II) complexes and 440 nm for the Cu(II) complex.

#### 2.4. Sensitivity and detection limits

The sensitivity and detection limits for the LC determination of the three complexes were determined using a mobile phase containing the surfactant with the composition 0.03 M CTAB– $10^{-4}$  M DDTC–45% (v/v) 1-propanol and, in order to compare the results obtained in the presence of CTAB with those in the absence of surfactant, a mobile phase with the same composition but without CTAB was employed. The amounts of the metal ions injected ranged from 0.23 to 26 ng for Ni(II) and Co(II) and from 0.25 to 210 ng for Cu(II).

#### 2.5. Determination of nickel and copper in real samples

The amounts of nickel and copper contained in metallic samples of a copper alloy which were anodized with nickel were determined. Six pieces of three different sizes (two of each) were used. For these determinations, the metal alloy pieces were dissolved completely in a minimum volume of concentrated nitric acid, transferred to a volumetric flask and diluted to 250 ml with deionized water. The samples were prepared by diluting appropriate volumes of these solutions with the mobile phase [0.03 M CTAB– $10^{-4}$  M DDTC–45% (v/v) 1-propanol] to 25 ml. Next, 20  $\mu$ l of sample were injected into the chromatograph. The amount of each metal contained in the samples was determined from appropriate calibration graphs.

In order to compare the HPLC results with those of another method of analysis, the con-

centrations of copper and nickel were also determined by FAAS. Each sample was measured six times and both the means and standard deviations were calculated.

### 3. Results and discussion

#### 3.1. Retention of the complexes in the chromatographic system

Diethyldithiocarbamate complexes of Co(II), Ni(II) and Cu(II) are insoluble in aqueous solution in the absence of CTAB and organic modifier, and only partially soluble when the 1-propanol content of the mobile phase is  $\leq 35\%$  (v/v) in the absence of CTAB. The presence of CTAB leads to solubilization of the metal ion complexes in aqueous medium and a decrease in their retention in the stationary phase, decreasing the analysis time and improving the selectivity.

The influence of the concentration of CTAB in the mobile phase on the retention of the three metal complexes was examined. The CTAB concentration ranged from 0.02 to 0.08 M. 1-Propanol was added to the mobile phase at a concentration of 45% (v/v) in order to decrease the retention of the metal complexes. Fig. 1 shows that the variation of the inverse of the capacity factor ( $k'$ ) as a function of surfactant concentration is linear over the range of CTAB

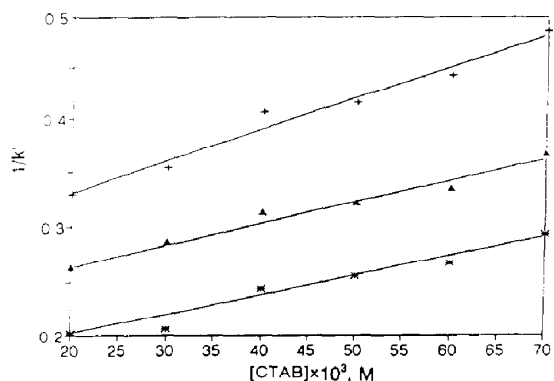


Fig. 1. Variation of the inverse of the capacity factor ( $k'$ ) with the concentration of CTAB in the mobile phase. ▲ = Ni(II); + = Co(II); \* = Cu(II). Mobile phase:  $10^{-4}$  M DDTC–45% (v/v) 1-PrOH–CTAB.

concentrations studied. This result is in agreement with the equations that have been proposed [17,18] to relate these parameters in the case of organic compounds with mobile phases in the absence (or with low percentages) of alcohols.

The retention of the DDTC complexes agrees with Armstrong's model [19,21] in which three equilibria are involved: the solute distribution between the mobile micellar pseudo-phase and the bulk mobile phase, the solute partitioning between the stationary phase and the mobile micellar pseudo-phase and the distribution of the solute between the bulk mobile phase and the stationary phase. According to this model, when the concentration of surfactant in the mobile phase increases, the solute affinity for this phase increases and the solute retention decreases. The experimental results are in agreement with this behaviour.

The concentration of DDTC was kept constant at  $10^{-4}$  M. Fig. 2 shows the variation of the sensitivity (in peak area) as a function of ligand concentration in the mobile phase. Maximum sensitivity is obtained at DDTC concentrations of  $10^{-4}$  M and above. The decrease in sensitivity at concentrations lower than  $10^{-4}$  M is due to the fact that at these low concentrations are insufficient to complex the metals completely.

A mobile phase  $10^{-4}$  M in DDTC and 0.03 M

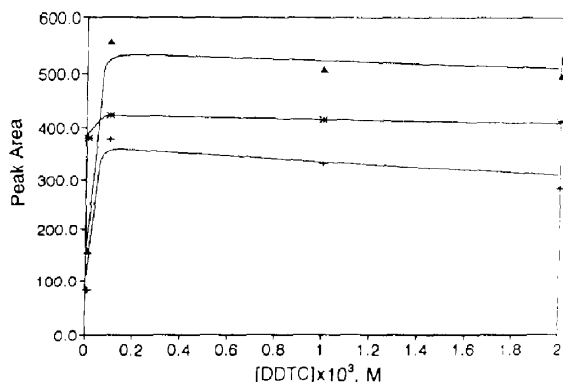


Fig. 2. Variation of the peak area with the concentration of DDTC in the mobile phase.  $\blacktriangle$  = Ni(II);  $+$  = Co(II);  $*$  = Cu(II). Mobile phase: 0.03 M CTAB–45% (v/v) 1-PrOH–DDTC.

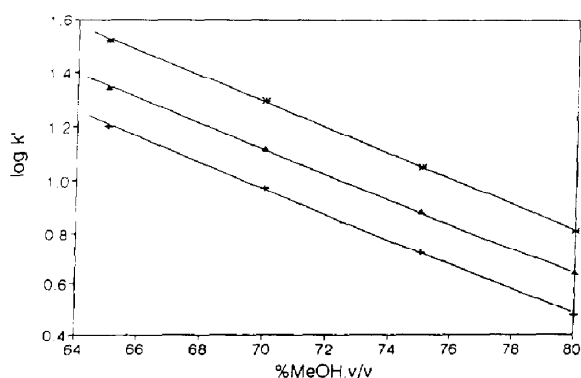


Fig. 3. Variation of the logarithm of the capacity factor ( $k'$ ) with the MeOH concentration in the mobile phase.  $\blacktriangle$  = Ni(II);  $+$  = Co(II);  $*$  = Cu(II). Mobile phase: 0.03 M CTAB– $10^{-4}$  M DDTC–MeOH.

in CTAB were chosen with the aim of determining the variation of the capacity factor as a function of organic modifier concentration in the mobile phase. Two short-chain alcohols, methanol and 1-propanol, were used as organic modifiers. Figs. 3 and 4 show the variation of the logarithm of the capacity factor of the three DDTC complexes as a function of the percentage of methanol and 1-propanol, respectively, in the mobile phase. Fig. 3 shows that the logarithm of the capacity factor varies linearly with methanol percentage as in reversed-phase

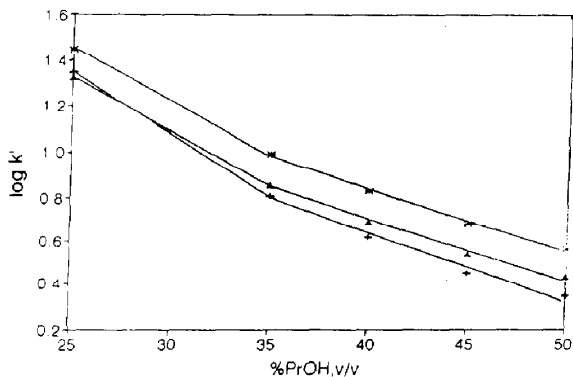


Fig. 4. Variation of the logarithm of the capacity factor ( $k'$ ) with 1-PrOH concentration in the mobile phase.  $\blacktriangle$  = Ni(II);  $+$  = Co(II);  $*$  = Cu(II). Mobile phase: 0.03 M CTAB– $10^{-4}$  M DDTC–1-PrOH.

HPLC with conventional aqueous–organic mobile phases [30]. However, with 1-propanol, a linear variation is obtained only for concentrations >35% (v/v). For both alcohols, the solute retention decreases when the percentage of organic modifier in the mobile phase increases. However, according to eluent strength, the percentage of alcohol necessary to obtain short retention times is much lower when using 1-propanol than methanol.

With respect to the selectivity, Fig. 3 shows that separation selectivity does not vary as a function of the methanol percentage in the mobile phase. However, with 1-propanol, the selectivity increases as its concentration increases. In fact, although Cu(II) can be separated from Ni(II) or Co(II) with any 1-propanol percentage, the separation of Ni(II) from Co(II) is possible only with >40% (v/v) 1-propanol. For these reasons, a mobile phase containing 45% (v/v) 1-propanol was utilized to achieve the separation of DDTC complexes.

The observed increase in selectivity with increases in the 1-propanol percentage in the mobile phase (Fig. 4) is the opposite of that seen in reversed-phase HPLC with conventional aqueous–organic mobile phases. However, our results are in good agreement with those obtained by others who added surfactants to the mobile phase [31] and reported an increase in selectivity with eluent strength.

As can be observed in Fig. 4, a change in the elution order of the Ni(II) and Co(II) complexes occurs. This change is obtained when the concentration of 1-propanol ranges from 25% to 35%. The behaviour of these complexes at these 1-propanol percentages cannot be studied in the absence of CTAB because in these media the DDTC complexes are not soluble and the retention times are very long.

Fig. 5 shows a chromatogram for the separation of the three DDTC complexes using the mobile phase 0.03 M CTAB– $10^{-4}$  M DDTC–45% (v/v) 1-propanol. The separation selectivity is fairly good although it is better for the Co(II)–Cu(II) and Ni(II)–Cu(II) separations than for the Co(II)–Ni(II) separation. The Ni(II)–Co(II)–Cu(II) separation can be achieved with

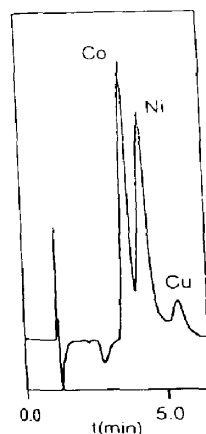


Fig. 5. Chromatogram of a mixture of Ni(II), Co(II) and Cu(II) in the presence of CTAB in the mobile phase. Mobile phase: 0.03 M CTAB– $10^{-4}$  M DDTC–45% (v/v) 1-PrOH.

an analysis time of less than 5 min. Fig. 6 shows a chromatogram for the separation of the same complexes using a mobile phase with the same DDTC and 1-propanol concentrations but in the absence of CTAB. In this instance it is not possible to separate Ni(II) and Co(II), even

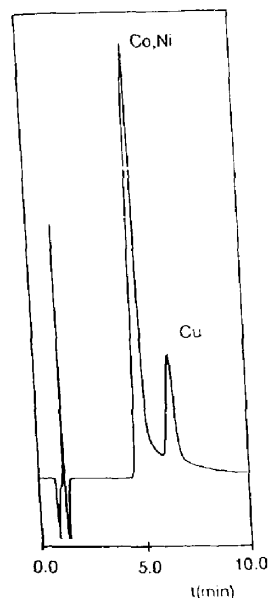


Fig. 6. Chromatogram of a mixture of Ni(II), Co(II) and Cu(II) in the absence of CTAB in the mobile phase. Mobile phase:  $10^{-4}$  M DDTC–45% (v/v) 1-PrOH.

Table 1  
Detection limits and sensitivity for the three metal ion complexes by HPLC with the mobile phases (1)  $10^{-4}$  M DDTC–45% (v/v) 1-PrOH and (2)  $10^{-4}$  M DDTC–0.03 M CTAB–45% (v/v) 1-PrOH

Mobile phase	Metal ion	Detection limit (pg)	Sensitivity	Linear range (ng)	Wavelength (nm)
1	Ni(II)	134.4	2.5671	0.23–16	326
	Co(II)	77.9	1.9236	0.23–16	326
	Cu(II)	314.8	0.8820	0.25–140	440
2	Ni(II)	68.1	3.1547	0.23–14	326
	Co(II)	67.2	2.3676	0.23–17	326
	Cu(II)	35.4	0.8123	0.25–180	440

Table 2  
Results obtained for the determination of Ni(II) and Cu(II) in metal samples by HPLC with the mobile phase 0.03 M CTAB– $10^{-4}$  M DDTC–45% (v/v) 1-PrOH and by FAAS

Analysis No.	Cu(II) (mg)		Ni(II) (mg)		Sample mass (g) <sup>a</sup>		Cu(II) (%)		Ni(II) (%)	
	FAAS ( $\lambda = 325$ nm)	HPLC ( $\lambda = 440$ nm)	FAAS ( $\lambda = 232$ nm)	HPLC ( $\lambda = 326$ nm)	FAAS	HPLC	FAAS	HPLC	FAAS	HPLC
1	224.3 ± 2.0	223.9 ± 2.8	15.6 ± 0.3	14.9 ± 0.9	–	–	–	–	–	–
2	927.9 ± 8.6	923.1 ± 11.5	18.5 ± 0.2	17.9 ± 0.7	–	–	–	–	–	–
3	804.2 ± 9.4	803.5 ± 13.6	10.3 ± 0.2	10.1 ± 0.2	1.5253 ± 0.0040	52.7	52.7	52.7	0.7	0.7
4	831.4 ± 7.8	841.0 ± 10.8	11.9 ± 0.2	11.9 ± 0.3	1.5253 ± 0.0040	54.5	55.1	55.1	0.8	0.8
5	419.4 ± 2.9	417.4 ± 9.0	6.6 ± 0.1	6.4 ± 0.2	0.7054 ± 0.0019	59.4	59.2	59.2	0.9	0.9
6	400.4 ± 5.8	410.0 ± 9.1	6.1 ± 0.1	6.2 ± 0.2	0.7054 ± 0.0019	56.8	58.1	58.1	0.9	0.9

<sup>a</sup> Mass of samples corresponding to the mean of eight pieces of size 3 and 4, or to the mean of eleven pieces of size 5 and 6. Samples in analyses Nos. 1 and 2, 3 and 4, and 5 and 6 were of the same size.

partially, showing that the presence of the surfactant is necessary for this separation.

### 3.2. Sensitivity and detection limits

The sensitivity and detection limit for the determination of the three complexes using a mobile phase of  $10^{-4} M$  DDTC–45% (v/v) 1-propanol, first containing and then without CTAB, were determined. The sensitivity is defined as the gradient of the calibration graph of peak area versus the amount in nanograms of metal cation injected. The detection limit is defined as the amount of metal cation necessary to obtain a peak height double that of the background noise. Peak heights were measured rather than peak areas because they are more reproducible and also because it is not possible to measure the peak area of the background noise.

The results are summarized in Table 1. The sensitivity obtained in the presence of CTAB is greater than that in its absence for Ni(II) and Co(II). For the determination of Cu(II) no difference in the sensitivity was observed in the presence and absence of CTAB. The increase produced in the sensitivity means that in the presence of CTAB peaks are obtained with a greater height for the same concentration of metal cation, so either a larger amount of complex was formed, or the peaks obtained had a greater efficiency than in the absence of CTAB, in addition to as modifying the retention of the complexes.

The detection limits are greater, in all instances, when CTAB is presence in the mobile phase, as shown in Table 1. The detection limits obtained in the presence of CTAB decrease in all instances, the difference being greatest for Cu(II), with a decrease of 279 pg.

### 3.3. Determination of the nickel and copper in metallic samples

Using the proposed method, nickel and copper were determined in metallic samples. These samples were components used in electronics, composed of a copper alloy anodized with a

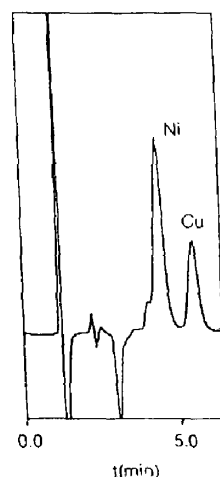


Fig. 7. Chromatogram of a real sample containing Ni(II) and Cu(II) in the presence of CTAB in the mobile phase. Mobile phase:  $0.03 M$  CTAB– $10^{-4} M$  DDTC–45% (v/v) 1-PrOH.

nickel alloy to give a covering of depth between 3 and 15  $\mu m$ . A chromatogram of one of these samples is shown in Fig. 7. To investigate the validity of the proposed method, nickel and copper were also determined by FAAS and the results obtained with the two methods were compared.

Three different sizes of metallic sample were available, and two of each size were chosen. Table 2 gives the results, as the average of six analyses each sample with the corresponding standard deviation for the proposed HPLC method in presence of CTAB and FAAS.

The results obtained by HPLC show good agreement with those obtained by FAAS. Hence the HPLC method in the presence of CTAB is valid for the proposed purpose.

## 4. Conclusions

The complexes of Co(II), Ni(II) and Cu(II) with DDTC, which are insoluble in aqueous solution, dissolved in the cationic micellar medium CTAB, making it possible to introduced them into a chromatographic system without first having conduct a solvent extraction. A sensitive and valid HPLC method for determination of these metals has been developed.

This work shows the possibility of separating metal ions as complexes formed on-column in RP-HPLC using a surfactant in the mobile phase, which increases the solubility of the complexes, the sensitivity and the selectivity of the detection. When the complexes are formed precolumn, the ligand and complex decomposition prevent a good separation and detection of the peaks of the complexes.

One of the main advantages of RP-HPLC with UV-Visible detection over ion chromatography is that in RP-HPLC only the metal ions that form complexes with the ligand in the mobile phase are detected, avoiding interferences from other species, and in addition RP-HPLC allows the separation and determination of non-ionic complexes.

This method allows the separation and determination of metal complexes using a mobile phase that contains a surfactant, 1-propanol and a complexing ligand at the pH value of the mobile phase in the absence of other additives in a short analysis time and with better sensitivity and detection limits than in the absence of the surfactant.

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