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The use of dihexyldithiocarbamate in reverse-phase HPLC of metal chelates

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Abstract. Dialkyldithiocarbamates have long been used as chelating agents in reverse-phase HPLC of transition metals. In the previous study, an alkyl homolog of this type of ligand, namely dihexyldithiocarbamate (DHDTC), was synthesized and characterized. The use of this particular ligand in the reverse-phase HPLC of some selected transition metal ions is now reported for the first time. The mobile phase comprising of the flow rate and of the detection, in the separation of the metal chelates of Cd(II), Fe(III), Cu(II), and Co(III), were investigated on a C-18 column. The results showed that dihexyldithiocarbamate could be used for separating Cd(II), Fe(III), Cu(II), and Co(III). Therefore, it could be used in simultaneous analysis.

1. Introduction

Major advances in the synthesis of derivative compounds from dihexyldithiocarbamate have been made, recently. These compounds are attractive because of their potential applications and use in a wide range of fields, such as in lubricating compositions as friction-modifier, antioxidant in vegetable oil [1,2], preparation thin films of bismuth sulfide [3], and for chelating agents [4,5].

As chelating agents, dithiocarbamate derivatives have been of a great interest. Many papers described that these derivative compounds reacted with many metal ions to form chelate complexes. Liquid chromatography of these chelate has reported with Nickel (II) to form complexes [6-8]. Dilli and Tong investigated the chromatographic behavior of a selected group of metal dialkyldithiocarbamates (R₂NCSSNa, where R is CH₃CH₂- (ethyl), CH₃CH₂CH₂-(propil), (CH₃)₂CH-(isopropil), CH₃CH₂CH₂CH₂-(butil), CH₃CH₂CH₂CH₂CH₂-(pentyl)) [9]. The chromatogram showed metal chelates of cadmium, copper, and cobalt. With dithiocarbamates having longer alkyl groups in their molecular structure, such as hexyl, it was expected that the ligand would have better properties to be used in the separation of metal complexes.

The purpose of this study was to use dihexyldithiocarbamate (DHDTC) for separating of a selected metal complexes in reverse phase HPLC. The selected metals used were cadmium (II), iron (III), copper (II), and cobalt (III).
2. Methods

2.1. Materials and instrumentation
Methanol and acetonitrile were obtained from J.T. Baker Inc. and all of the mobile phases were filtered through a Millipore filter (type FH, 0.45 µm) before used. Metal salts used for preparative work and reagents were also of analytical grade. The chromatographic system consisted of a Hitachi D-7000, oven column L-7300, UV Detector-L-7400, a Rheodyne 7125 valve injector fitted with a 20 µL loop, and a single C-18 reverse phase column (5 µm, 4.6 mm x 150 mm). Dihexyldithiocarbamate (0.0363 mole) in acetone was injected onto the column.

2.2. Preparation of the metal complexes
The dihexyldithiocarbamate of cadmium (II), iron (III), copper (II), and cobalt (III) were prepared by slow addition of an aqueous solution of metal ion (3.3 mole) to a slight excess of potassium dihexyldithiocarbamate (6.6 mole). After stirring (about for 2 hours at 300C), the precipitated was filtered off, and then washed with cold ethanol. All of these products were dried in a vacuum desiccator and their purity confirmed by elemental analysis.

2.3. Optimisation of mobile phase composition
A binary solvent system of methanol-acetonitrile was used under isocratic condition. When these condition applied to mixture of chelates, it is expected to not produce adequate separation. The optimal composition of mobile phase was richer in methanol with ligand for improving separation of the mixture.

3. Results and Discussion

3.1. Dihexyldithiocarbamate
Dihexyldithiocarbamate (DHDTC) 0.0363 mole in acetone was injected onto the column. The chromatogram resulted can be seen in figure 1.

![Chromatogram](image)

**Figure 1.** Chromatogram showing DHDTK 0.0363 M in acetone as solvent has retention time at 1.33 minute on C18, mobile phase methanol : acetonitrile (70:30 v/v), flow rate 2 mL/minute, detection at 282 nm
In that chromatogram, other peaks that rise at retention time of 3.8-6.0 minute was impurity of the ligand. A binary solvent system methanol-acetonitrile produced behavior chromatogram of dihexyldithiocarbamat after repeating this process.

3.2. Metal complexes
Individual injection of metal chelates of cadmium (II), iron (III), copper (II), and cobalt (III) were conducted in column, to achieve the chromatographic behavior. Retention time of these chelates showed at: 2.98; 3.77; 5.55; 10.50 minutes with mobile phase of methanol: acetonitrile-ligand (70:30 v/v, 3.6 x 10^{-4}M), respectively. A small amount of the appropriate ligand (3.6 x 10^{-4}M) was added in mobile phase to avoid dissociation of metal chelates in column. The mixture of metal chelates cadmium (II) and copper (II), also iron (III) and cobalt (III), resulted in chromatograms as illustrated in fig. 2 and 3.

![Figure 2](image2.png)

**Figure 2.** Chromatogram showing the mixture of metal chelates cadmium (II) and copper (II) with retention time respectively at 2.98 and 5.54 minute on C 18 column, mobile phase methanol: acetonitrile-ligand (70:30 v/v, 3.6 x 10^{-4}M), flow rate 2mL/minute, detection at 282 nm.

![Figure 3](image3.png)

**Figure 3.** Chromatogram showing the mixture of metal chelates iron (III) and cobalt (III) with retention time respectively at 3.77 and 10.05 minute on C 18 column, mobile phase methanol: acetonitrile-ligand (70:30 v/v, 3.6 x 10^{-4}M), flow rate 2mL/minute, detection at 282 nm.
From three organic solvents, including chloroform, acetone and toluene, tested on chelates, it was found that chloroform gave the best solubility (data not presented in this report). Thus, chloroform was used as the solvent throughout the rest of the chromatography study. Fig 4. shows a chromatogram obtained with the mixture of metal chelates cadmium(II), iron (III), copper (II), and cobalt (III) at the optimization condition of reverse-phase chromatography.

**Figure 4.** Chromatogram showing the mixture of metal chelates cadmium (II), iron (III), copper (II), and cobalt (III) with retention time respectively at 2.98; 3.77; 5.55 and 10.05 minutes on C-18 column, mobile phase methanol : acetonitrile - ligand (70:30 v/v, 3.6 x 10^-4M), flow rate 2mL/minute, detection at 282 nm.

It was generally accepted that the dihexyldithiocarbamate ligands are useful because of relative stability of complexes formed with selected metals, especially those of cadmium, iron, copper, and cobalt. Absorption spectra of all metal chelates recorded at 282 nm.

Disulphiden (DS) in the chromatograms were considered of importance because they are the normal oxidation product of ligand and may be decomposition product of the chelates also. Dihexyliditiocarbamate could be used for separating especially respectively for Cd (II), Fe (III), Cu (II), and Co (III), at 2.98; 3.77; 5.55; 10.50 minutes could be achieved, in the mobile phase of methanol-acetonitrile-ligand (70:30 v/v, 3.6 x 10^-4M), flow rate set a 1.5 ml/minute, and the detector was operated at 282 nm.

4. **Conclusion**
Dihexyliditiocarbamate could be used as chelating agent in reverse-phase HPLC and was applied for separating especially Cd(II), Fe(III), Cu(II), and Co(III) at the ternary system as metal chelates. Therefore, it could be used to simultaneous analysis.

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