

Qualitative Analysis of Cu^{2+} , Co^{2+} , and Ni^{2+} Cations Using Thin-Layer Chromatography

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Abstract

The $M(\text{DEDTC})_2$ ($M = \text{Cu}$, Co , or Ni) and $M(\text{PyDTC})_2$ ($M = \text{Cu}$ or Co) complexes prepared by reactions of sodium diethyldithiocarbamate and ammonium pyrrolidinedithiocarbamate with metal (II) nitrates are examined for qualitative analysis and separation using thin-layer chromatography systems. These complexes and their mixtures are spotted to the activated thin layers of silica gel 60GF₂₅₄ (Si-60GF₂₅₄) with a 250- μm thickness. Pure toluene and a toluene–cyclohexane mixture (3:1, v/v) are used as mobile phases for running of the complexes. These chromatographic systems are successfully used for qualitative analysis of corresponding metal cations and separation of components in both $M(\text{DEDTC})_2$ and $M(\text{PyDTC})_2$ complex mixtures.

Introduction

The qualitative and quantitative analysis of Cu^{2+} , Co^{2+} , and Ni^{2+} cations in environmental media and various samples is challenging for analytical chemists because of the similarities in their properties. Thin-layer chromatography (TLC) is a rapid, easy, and simple separation technique extensively used for organic species but rarely used for inorganic cations. However, TLC has some advantages compared with alternative methods. For instance, components of mixture samples can be easily separated without interference. In addition, several samples can be separated simultaneously using TLC, and the positions of spots that appear can be determined with a number of different methods (1–3).

Ligands that contain N,S or O,S donor atoms are mostly used for the separation of metals because these ligands form the coordinatively saturated complexes with metals at high formation rates. In addition, when the ligands of complexes are the same, the chromatographic parameters of these complexes are affected by electronic properties of metals. Dithiocarbamate ligands, such as diethyldithiocarbamate (DEDTC) and pyrrolidinedithiocarbamate (PyDTC), contain N,S donor atoms, and they form coordinatively saturated complexes with metals (3).

The structures and abbreviations of the complexes of $M(\text{DEDTC})_2$ ($M = \text{Cu}$, Co , and Ni) and $M(\text{PyDTC})_2$ ($M = \text{Cu}$ and Co) with DEDTC and PyDTC ligands are given in Figures 1 and 2 (3). There are relatively less applications of TLC in the literature about qualitative analysis of metallic cation mixtures (4–7).

In this study, $M(\text{DEDTC})_2$ and $M(\text{PyDTC})_2$ complexes are investigated on activated thin layers of silica gel 60GF₂₅₄ (Si-60GF₂₅₄) using two different mobile phases with respect to qualitative analysis of Cu^{2+} , Co^{2+} , and Ni^{2+} cations.

Experimental

Chemicals, reagents, and materials

Si-60GF₂₅₄, NaDEDTC, NH_4PyDTC , $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Co}(\text{NO}_3)_2$ chemicals were purchased from Merck (Darmstadt, Germany).

$\text{Cu}(\text{DEDTC})_2$, $\text{Co}(\text{DEDTC})_2$, $\text{Ni}(\text{DEDTC})_2$, $\text{Cu}(\text{PyDTC})_2$, and $\text{Co}(\text{PyDTC})_2$ complexes were prepared by the reactions of NaDEDTC and NH_4PyDTC with $\text{Ni}(\text{NO}_3)_2$, $\text{Cu}(\text{NO}_3)_2$, and $\text{Co}(\text{NO}_3)_2$. The toluene–cyclohexane mixture (3:1, v/v) and pure toluene were used as the mobile phase. The layers of Si-60GF₂₅₄

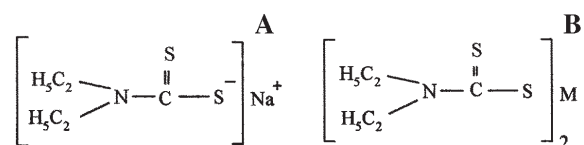


Figure 1. Molecular structures for (A) NaDEDTC complexing agent and (B)

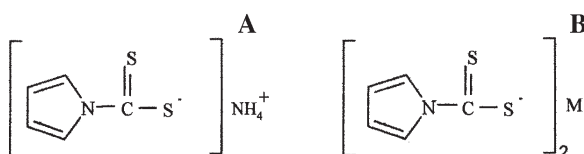


Figure 2. Molecular structures for (A) NH_4PyDTC complexing agent and (B) $M(\text{PyDTC})_2$ complexes.

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were prepared using a Loughborough-Griffin & George TLC Unikit (Leicestershire, England). All the chemicals were of analytical grade.

Synthesis of M(DEDTC)₂ complexes

Prepared were 0.10 mol/L solutions of metal nitrates [Cu(NO₃)₂, Co(NO₃)₂, Ni(NO₃)₂] at pH 5.5–6.0 (adjusted by acetic acid–sodium acetate buffer). From these solutions, a 1.0-mL aliquot was poured into a beaker and 1.0 mL of 0.1 mol/L NaDEDTC solution was added to it and then was shaken. Four milliliters of pure chloroform was added to the beaker and was shaken for 1 min. This mixture was transferred into a separatory funnel and shaken. The phases were allowed to separate for 5 min. The aqueous phase was separated from the chloroform phase and discarded. Subsequently, the chloroform phase containing the complex was dried by treating with anhydrous Na₂SO₄. The dried phase was used as sample for TLC applications.

Synthesis of M(PyDTC)₂ complexes

Prepared were 0.10 mol/L solutions of metal nitrates [Cu(NO₃)₂ and Co(NO₃)₂] at pH 5.5–6.0 (adjusted by acetic acid–sodium acetate buffer). From these solutions, a 1.0-mL aliquot was poured into a beaker, and 1.0 mL of 0.1 mol/L NH₄PyDTC solution was added to it and then was shaken. Four milliliters of pure chloroform was added to the beaker and shaken for 1 min. This mixture was transferred into a separatory funnel and shaken. The phases were allowed to separate for 5 min. The aqueous phase was separated from the chloroform phase and discarded. Subsequently, the chloroform phase that contained the complex was dried by treatment with anhydrous Na₂SO₄. The dried phase was used as sample for TLC applications.

Preparation of thin-layer plates

Slurries of Si-60GF₂₅₄ in water (1:2, w/v) were spread onto cleaned glass plates (7.5 × 15 cm) with a thickness of 250 μm using a spreader kit. Nonactive plates were obtained by keeping the plates at room temperature for 12 h. They were activated by heating in an oven at 110°C for 2 h. For TLC applications, activated plates were used.

TLC applications

Two-microliter aliquots from each of the complex solutions and their mixtures were spotted onto a straight line 2.0 cm up to the bottom of the plate with micropipettes. The original spots on the layers were dried at room temperature for 3 min. Two developing chambers with 10- × 50- × 20-cm dimensions were used for running. Sixty milliliters of the toluene–cyclohexane mixture (3:1, v/v) was poured into one chamber and 60 mL of toluene into the other. The chambers were closed with the lids and allowed to stand for 15 min to ensure the saturation of air in each chamber with solvent vapors. The activated plates that contained spotted samples were then carefully immersed into the developing chambers. The plates were taken out of the chambers when the solvent fronts reached 5.5 cm. The solvent fronts on the plates were marked with a pencil, and the plates were dried. After all of these steps, the migration distance of the solvent (Z_f), the migration distance of each spot (Z_x), and the width (W) were measured. The retention factor (R_f , from $R_f = Z_x/Z_f$) and theoretical plate number [N , from $N = 16(Z_x/W_x)^2$] were calculated (1,9).

Results and Discussion

The challenger Cu²⁺, Co²⁺, and Ni²⁺ cations in the qualitative and quantitative analysis require to be separated satisfactorily. TLC is extensively used for organic species but has potential usage for inorganic cations. In this context, TLC has been examined for qualitative analysis of Cu²⁺, Co²⁺, and Ni²⁺ cations via forming fast and stable complexes. For this purpose, in choosing DEDTC and PyDTC ligands, neutral M(DEDTC)₂ and M(PyDTC)₂ complexes were prepared.

DEDTC and PyDTC ligands with N,S donor atoms formed the coordinatively saturated stable complexes with the cations cited. Because of these properties, they cannot interact chemically with the stationary and mobile phases in TLC systems. The formation rates of complexes are very high, which also means saving time. Furthermore, these complexes are colored and can be easily visualized in the chromatograms.

In this work, to prepare M(DEDTC)₂ and M(PyDTC)₂ complexes, aqueous solutions of Cu²⁺, Co²⁺, and Ni²⁺ at pH 5.5–6.0 (adjusted by acetic acid–sodium acetate buffer), were treated with DEDTC and PyDTC solutions. The reason for working at pH < 7 was to keep the cations in solution as stable complexes. The complexes were extracted to the chloroform phase at pH < 7 to ensure preconcentration and cation selectivity via complexation. Moreover, as the result of organic phase extraction, the chromatographic tailing and, hence, scattering of R_f values were prevented. The chloroform was used as the organic phase because of its complex solubility and solvent volatility advantages.

For TLC applications, pure toluene and a toluene–cyclohexane mixture (3:1, v/v) were used as the mobile phases because of their low polarities. In addition, these solvents were chemically inert for the complexes and surface of the thin layer. Silica gel was used most frequently as the adsorbent for the separation of coordinatively saturated complexes (3). Thus, Si-60GF₂₅₄ was chosen as the stationary phase.

The samples used were solutions of M(DEDTC)₂ and M(PyDTC)₂ complexes in chloroform. As an exception, peculiar to this study, Ni(PyDTC)₂ was not used for TLC applications. Ni(PyDTC)₂ does not reach the required concentration in the chloroform phase by virtue of its low solubility, hence it was impossible to observe its spot on the chromatograms with the naked eye. The solubilities of M(PyDTC)₂ and M(DEDTC)₂ in chlo-

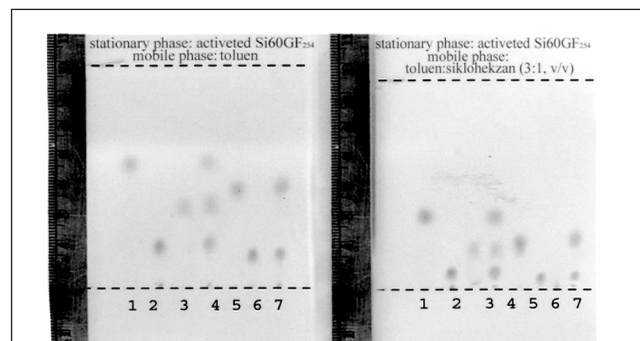


Figure 3. Chromatograms of the complexes and their mixtures: (1) Cu(DEDTC)₂; (2) Co(DEDTC)₂; (3) Ni(DEDTC)₂; (4) the mixture of 1, 2, and 3; (5) Cu(PyDTC)₂; (6) Co(PyDTC)₂; and (7) the mixture of 5 and 6.

reiform were higher compared with the solubility of Ni(PyDTC)₂ in chloroform. As seen from Figure 3, M(DEDTC)₂ and M(PyDTC)₂ could be easily identified because of their distinctive colors.

Chromatograms of M(DEDTC)₂ and M(PyDTC)₂ complexes on activated Si-60GF₂₅₄ layers with pure toluene and a toluene–cyclohexane mixture (3:1, v/v) are shown in Figure 3. As appear in these, the spots of complexes and their mixtures were developed without any tailing or decomposition and were separated into their components. This chromatographic property is peculiar to coordinatively saturated dithiocarbamate complexes. *R_f* and *N* values for these complexes are given in Table I.

As seen from Table I, for the TLC application using pure toluene as the mobile phase, the *R_f* values of Cu(PyDTC)₂ and Co(PyDTC)₂ were 0.44 ± 0.02 and 0.15 ± 0.01; the *N* values belonging to these complexes were 1024 and 114, respectively. For the TLC application using the toluene–cyclohexane mixture (3:1, v/v) as the mobile phase, *R_f* values of Cu(PyDTC)₂ and Co(PyDTC)₂ were 0.18 ± 0.01 and 0.04 ± 0.01; the *N* values of the complexes were 400 and 16, respectively. Based on these results, TLC applications using two different mobile phases, Cu(PyDTC)₂ and Co(PyDTC)₂, were developed with different *R_f* values and separated chromatographically. Furthermore, the positions of their spots were determined from the chromatograms in Figure 3 by the naked eye. As a result, a mixture containing Cu²⁺ and Co²⁺ ions could be analyzed qualitatively using TLC following the complexation of the cations in sample with NH₄PyDTC. On the other hand, TLC application using pure toluene as the mobile phase is more successful than a toluene–cyclohexane mixture (3:1, v/v) because of the higher *N* values belonging to complexes.

According to Table I, for the TLC application using pure toluene as the mobile phase, the *R_f* values of Cu(DEDTC)₂, Co(DEDTC)₂, and Ni(DEDTC)₂ were 0.55 ± 0.03, 0.18 ± 0.01, and 0.36 ± 0.02; the *N* values belonging to these were 1600, 178, and 711, respectively. For the TLC application using a toluene–cyclohexane mixture (3:1, v/v) as the mobile phase, the *R_f* values of these were 0.33 ± 0.02, 0.07 ± 0.01, and 0.18 ± 0.01; the *N* values of these were 1296, 64, and 400, respectively.

Based on these results, for TLC applications using two different mobile phases, the *R_f* values of M(DEDTC)₂ complexes were sufficiently different from each other and were separated chromatographically. In addition, the positions of their spots were determined on the chromatograms given in Figure 3 with the naked eye. Thus, a mixture that contains Cu²⁺, Ni²⁺, and Co²⁺ can be analyzed qualitatively using TLC following the complexation of

the cations in sample with NaDEDTC. Although TLC application using pure toluene as the mobile phase is more successful than a toluene–cyclohexane mixture (3:1, v/v) because of the higher *N* values belonging to complexes, either of the mobile phases can be used successfully for qualitative analysis of cations and separation of M(DEDTC)₂ complexes as to the relative *N* values.

As a final evaluation of data in Table I regarding qualitative analysis and separation of Cu(II), Ni (II), and Co(II) complexes, it can be said that the best TLC application is performed on an activated Si-60GF₂₅₄ layer with pure toluene as the mobile phase. Additionally, the DEDTC ligand is more successful than the PyDTC ligand.

In view of the contributions to chromatographic separation of the cations and their complexes, in addition to effects of mobile phases and ligands considered previously, the effect of metals must be taken into account.

According to Table I, the *R_f* values of Cu(DEDTC)₂, Co(DEDTC)₂, and Ni(DEDTC)₂ complexes in pure toluene as the mobile phase were 0.55 ± 0.03, 0.18 ± 0.01, and 0.36 ± 0.02, respectively. *R_f* values of Cu(PyDTC)₂ and Co(PyDTC)₂ complexes in pure toluene as the mobile phase were 0.44 ± 0.02 and 0.15 ± 0.01, respectively. Although the ligands and the mobile and stationary phases are the same, the great and significant difference in the *R_f* values of either group complexes results from the difference in the electronic structures of the metal atoms. For example, for pure toluene as the mobile phase, *R_f* values of Cu(DEDTC)₂, Cu(PyDTC)₂, and Co(DEDTC)₂ were 0.55 ± 0.03, 0.44 ± 0.02, and 0.18 ± 0.01, respectively. The *R_f* difference of Cu (II) complexes is 0.11, whereas the *R_f* difference of Cu(DEDTC)₂ and Co(DEDTC)₂ is 0.37. The difference stems from that the metal of complexes is higher than those from ligand. Although the charges, radii, and charge densities of Cu²⁺ and Co²⁺ in aqueous solutions were close to each other, their d⁹ and d⁷ electronic configurations, respectively, lead to different physical and chemical properties of the complexes. This relation is valid for the other metals and their complexes in a toluene–cyclohexane mixture (3:1, v/v) mobile phase, as well.

Conclusion

This study shows that it is possible to analyze qualitatively and to separate satisfactorily a mixture of Cu²⁺, Ni²⁺, and Co²⁺ cations using TLC following the complexation of the cations with DEDTC ligand.

Cu(DEDTC)₂, Co(DEDTC)₂, and Ni(DEDTC)₂ complexes do not interact chemically with the stationary and mobile phases in TLC systems. Because the formation rates of complexes are very high, the application was carried out in a short time. These complexes were colored and are easily visualized in the chromatograms.

For TLC applications using two different mobile phases, Cu(PyDTC)₂ and Co(PyDTC)₂ were developed with different *R_f* values and were separated chromatographically. A mixture that contains Cu²⁺ and Co²⁺ ions was analyzed qualitatively using TLC following the complexation of the cations in sample with NH₄PyDTC. TLC application using pure toluene as the mobile phase was more successful than with a toluene–cyclohexane mix-

Table I. *R_f* and *N* values of M(DEDTC)₂ and M(PyDTC)₂ Spots on Activated Si-60GF₂₅₄ Layers Using Pure Toluene and a Toluene–Cyclohexane Mixture

Complex	Running time	I* <i>R_f</i> (± SD)	II† <i>R_f</i> (± SD)	I‡ <i>N</i>	II <i>N</i>	Color
Cu(DEDTC) ₂	12	0.55 ± 0.03	0.33 ± 0.02	1600	1296	Brown
Co(DEDTC) ₂	12	0.18 ± 0.01	0.07 ± 0.01	178	64	Green
Ni(DEDTC) ₂	12	0.36 ± 0.02	0.18 ± 0.01	711	400	Green
Cu(PyDTC) ₂	12	0.44 ± 0.02	0.18 ± 0.01	1024	400	Brown
Co(PyDTC) ₂	12	0.15 ± 0.01	0.04 ± 0.01	114	16	Green

ture (3:1, v/v) because of the higher N values belonging to the complexes.

Although the ligand and mobile and stationary phases are the same, the great and significant difference in the R_f values of two group complexes results from the difference in the electronic structures of the metal atoms. The difference stemmed from that metal of complexes is higher than those from ligand. Although the charges, radii, and charge densities of Cu^{2+} , Ni^{2+} , and Co^{2+} in aqueous solutions were close to each other, their d^9 , d^8 , and d^7 electronic configurations, respectively, lead to different physical and chemical properties of the complexes. This relation is valid for the metals and their complexes in a toluene–cyclohexane mixture (3:1, v/v) mobile phase, as well.

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