Investigation of Separation and Identification Possibilities of Some Metal–DEDTC Complexes by Sequential TLC–IR System

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Abstract

The separation and identification possibilities of some metal–diethyldithiocarbamate (DEDTC) complexes are investigated by thin-layer chromatography–IR sequential system. DEDTC complexes of metal cations are prepared in a predetermined optimum pH or pH range. Optimum separation conditions of these complexes and the reproducibilities of their retention factor (R_f) values are investigated on a series of precoated or laboratory-made TLC plates. R_f values are determined using the one-dimensional ascending technique. The precision of the procedures is determined for five replicates in terms of standard deviation. Detection limits are also determined for each of the metal complexes. The IR spectra are scanned and interpreted for their precise identifications after preconcentration with a wick-stick procedure for the complexes, giving the overlapped R_f values. The complexes could be identified by the aid of IR absorption bands. It has been determined that these IR absorption bands can also be used as reference spectral bands in possible quantitative studies. It is concluded that an efficient and successful qualitative analysis is possible for incompletely-separated complex compounds using an IR spectrophotometer as the TLC detector.

Introduction

In recent years an increasing amount of research has been devoted to the application of metal–ion complexes with carbamates in chemical and biochemical analysis. This study has been primarily focused on *N,N*-disubstituted carbamate chelates because they form stable complexes with many metals. Determinations of carbamates and related compounds (especially pesticides and herbicides) in environmental samples such as drinking water and sewage (1–3), biological materials (4), food (5,6), pharmaceutical agents (7), and steel (8) are also performed frequently.

The choice of metal ions was not accidental. Those studied include both heavy toxic metals (e.g., Cd, Hg, and Pb) and microelements essential for living organisms (e.g., Co, present in vitamin B12 and Fe, Cu, Zn, and Mn, components of many enzymes and metalloporphyrins). Sodium diethyldithiocarbamate (Na–DEDTC) is one reagent commonly used for chemical analysis of carbamates. This reagent reacts with many metals creating intrinsic chelates that are insoluble in water. Metal ions bind with DEDTC molecules through two atoms of sulfur, thus forming compounds with tetrasegmental rings. After extraction into an organic phase, metal–ion complexes with DEDTC can be separated by means of different chromatographic techniques.

TLC separations of metal chelates with DEDTC are most frequently performed on silica gel (9,10) or silica gel G (11,12). Depending on the stationary phase chosen, one- or two-component mobile phases have been used. Thus, for separation of metal–ion complexes with DEDTC on silica gel, benzene (9,10), xylene (8), toluene (9), 1,2-dichloroethane (9,10), and dichloromethane (9,10) have been used as mobile phases. On silica gel G, metal chelates have been separated by use of mixtures of benzene with dioxane or toluene (11), diethyl ether, or hexane (12). Additionally, on silica gel-60GF254 metal–DEDTC complexes of Cu^{2+}, Co^{2+} and Ni^{2+} cations have been successfully separated with the use of a toluene–cyclohexane mixture (3:1, v/v) as mobile phase (13).

The direct coupling of TLC [high-performance TLC (HPTLC), in fact] and Fourier transform IR (FTIR) was introduced in 1989. The in situ measurement of chromatograms and FTIR spectra was extensively studied by Kovar et al. (14). Afterwards, Stahlmann presented a detailed report on HPTLC–FTIR online coupling in 1999 (15). The in situ TLC–diffuse reflectance Fourier transform spectroscopy (DRIFT) system, which requires complete removal of solvent and subtraction of the IR spectrum of the layer measured on the same plate as the sample spectrum, allows both the qualitave and quantitative characterization of a TLC spot. Because in situ spectra may differ from those obtained in solution or from a KBr pellet, in situ standard and sample spectra must be compared to obtain zone identification. This approach is particularly useful when a TLC–DRIFT-interfaced system is used for monitoring unstable compounds such as diazonaptha-

quinones (16). In situ spot analysis requires blank experiments and correction except for situations having strong IR background absorption. The final IR spectra of a TLC spot are also obtained by overlapping sample and background measurements. Many approaches to FTIR measurement of IR spectra of TLC spots are made to reduce the problems involved in possible background interference on TLC plates (17–19).

This study focuses on the scan and interpretation of the IR spectra after preconcentration of incompletely-separated spots at the end of the wick stick. Chromatographic behavior and identification possibilities of metal–DEDTC chelates were investigated using the IR characteristic absorption bands.

Experimental

Apparatus

A TLC applicator (Bibby Sterilin Ltd., Staffordshire, U.K.), UV lamp with two wavelengths (operating at 254 and 366 nm) for detection and pH meter having a measurement sensitivity of ± 0.02 (3010 Mark, Jenway Co., Essex, U.K.) were used. Additionally, a Unicam Mattson 1000 IR spectrometer (Unicam Ltd., Cambridge, U.K.) was used in the wavelength range of 400–4000 cm^{-1} with a resolution of 2 cm^{-1} for scanning and collecting the IR spectra of metal–DEDTC complexes.

Reagents

Four different adsorbents (Silica gel-60H, -60HF$_{254}$, -60GF$_{254}$, and -60PF$_{254}$) were used for the purpose of using one adsorbent type that is differentiated with or without the fluorescent indicator (F$_{254}$), (Merck, Darmstadt, Germany), acetic acid–sodium acetate buffer solution (pH 4–6), and Na-DEDTC for chelation of metal cations were used. All other reagents were also of analytical grade.

Test solutions

The stock test solutions (1%, w/v) were chloride or nitrate salts of Cu, Ni, Co, Cr, Mn, Zn, Pb, Cd, Hg, Bi, As, and Sb (Merck). Working solutions were prepared by diluting the stock solution with water. Doubly-distilled water was used to prepare and dilute the test solutions throughout the experimental studies. Solutions of 0.1% and 1.0% (w/v) chelating reagent in water were used on the TLC plates and preconcentration procedure, respectively.

Detection

The following detection systems were used to locate the analytes on chromatoplates: (*i*) dithizone (0.02%, w/v) in acetone for Zn^{2+}, Cd^{2+}, Pb^{2+}, and Hg^{2+} ions; and (*ii*) natural colors of their complexes for As^{3+}, Sb^{3+}, Bi^{3+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Cr^{3+} ions.

Mobile phase

Benzene, dichloromethane, dichloromethane–xylene (1:1, 1:4, and 4:1, v/v), dichloromethane–petroleum ether (1:1, 1:4, and 4:1, v/v), acetone–benzene (1:1, 1:4, and 4:1, v/v), benzene–isobutylmethylketone (1:1, 1:4, and 4:1, v/v) and ethylacetate–toluene (1:1, 1:4, and 4:1, v/v) mixtures were used.

Stationary phase

Laboratory-made TLC plates, which were coated with four different adsorbent (silica gel 60H, 60HF$_{254}$, 60GF$_{254}$, and 60PF$_{254}$), and commercial TLC plates, which were precoated with Silica gel-60F$_{254}$, were used for experimental studies.

Preparation of TLC plates

TLC plates were prepared by suspending silica gel with water in a 1:2.5 (w/v) ratio. The resulting slurry was mechanically shaken for several minutes, following the recommendations of a manufacturer. Afterward, the slurry was coated onto glass plates using a TLC applicator to give layers of 0.50- and 0.75-mm thicknesses for analytical and preparative purposes, respectively. The plates were air-dried at room temperature and then activated by heating at 100°C for 1 h. After activation, the plates were stored in an air-tight chamber until use.

The chelating procedure

The stock cation solutions were adjusted to a pH range of 4–6 with a CH_3COOH–CH_3COONa buffer solution. The solutions were mixed with an excess of ligand for the preparation of metal–DEDTC complex solutions and then extracted into the chloroform phase. The extraction procedure provided some advantages such as preconcentration and selectivity. Additionally, to prevent the clustering of complexes, the organic phase has also eliminated some of the drawbacks such as chromatographic tailing and dispersion of R$_f$ values. The organic phase was separated from the aqueous phase and prepared for injection by drying with anhydrous Na_2SO_4 solid. Chloroform was selected as the organic phase because it provided additional stability to all of the metal complexes (19).

Chromatographic procedures

Approximately 10 µL of the complex solutions was spotted separately on the TLC plates by using adjustable Fisher pipettes. The spots were air-dried and the chromatograms were developed, allowing the solvent to ascend up to 10 cm from the point of application in all cases. After development, the chromatograms were air-dried at room temperature and the complex spots were visualized by either their natural colors on the plate or exposure to ammonia vapor after spraying the TLC plate with 0.02%(w/v) solution of dithizone in acetone for colorless complexes. When dithizone solution is sprayed onto the TLC plate, Cd^{2+}- and Hg^{2+}-containing zones turn yellowish orange in color, whereas Pb^{2+}- and Zn^{2+}-containing zones turn to a reddish/pink color. The R$_f$ values for the detected spots were established. Afterward, the standard deviation and relative standard deviation of the R$_f$ values were calculated.

To study the effect of concentration on the separation or R$_f$ values of metal complexes, 10 µL of the complex solutions prepared at the various concentrations (in a concentration range of 100–1000 mg/L) were spotted on the chromatograms. The plates were developed in dichloromethane and benzene separately, dried, and the spots were then detected as mentioned previously.

The limits of detection (LOD) of the metal complexes were determined by spotting 1–10 µL of the complex solutions of

decreasing concentrations on the TLC plates, which were developed with benzene. The spots were visualized using the appropriate detector. This was repeated until no detection was possible. The procedure was repeated three times for each metal complex. The amount of salt only detectable in solution was taken as the LOD.

Wick-stick procedure

Each of the complexes containing the spots were separated and concentrated from the coating matrix using the wick-stick procedure. The wick-stick procedure is described as follows:

Wick sticks are triangular wedges of compressed KBr powder that are porous. They are approximately 8 mm wide at the base, 25 mm in height, and 1.25 mm thick. The spot, which is separated by scraping from plate, is placed in a vial that is approximately 5 cm in height and 1.25 cm in diameter. Chloroform, which easily dissolves the relevant complex, is then added to a volume of $1/8$–$3/8$ of the vial. The wick stick is inserted in a metal holder and dropped into the vial. A cap with a hole in it is placed on top. The complex solution rises to the tip of the KBr wedge and evaporates from the tip. Soluble complex material rises to the tip along with the solvent and is concentrated there as the solvent evaporate. Insoluble material is left behind. The tip is broken off and a micro-KBr disk is prepared for the IR analysis. The effect of strong IR-absorbing matrices as silica gel on the IR spectra of spots is completely removed by solvent extraction with $CHCl_3$. Also, the complex contents of the spots are free of adsorbents that hinder the IR spectrum (19–21).

Results and Discussion

Plates prepared from silica gel were of almost the same quality as that of the ready-made plates prepared in a standardized manner by recognized manufacturing firms, providing well-formed and compact spots for the chromatographed metal complexes. Developments were made using solvents and solvent mixtures having medium polarity (such as dichloromethane, benzene, toluene, xylene, and petroleum ether) and high polarity (such as methanol, acetone, ethyl acetate, and methyl-isobutyl-methylketone). The development time for a 10-cm run was approximately 15 min. It was found that the most effective eluent systems were solvent and solvent mixtures, which have medium polarity in chromatographic separations. The identification in authentic TLC is based on the R_f value. After spot identification obtained with visual observation, the R_f values were established as the ratio of the distance of each spot to the front of the solvent or solvent system. The reported R_f values are the averages of five repeated observations for precision. The results of this study are summarized in Table I.

It was suggested that dichloromethane–petroleum ether mixture (9:1, v/v) be used as the most effective eluent system for the separations of metal–DEDTC complexes (20). In this study, benzene and dichloromethane were found as the most effective eluent systems, separately. However, the reproducibilities of the R_f values were poor because of tailing or band-broadening caused by high application loading into the plate for some complex species such as MnL_2, CrL_3, AsL_3, and CdL_2 with both of the solvents.

The effect of the concentration on the R_f values was examined in a concentration range of 100–1000 mg/L. It was observed that the R_f values of the Fe(III), Sn(II), Sn(IV), and Ag(I) complexes decreased at a considerable ratio in low concentrations; namely; this was dependent upon the concentration. Additionally, these metal complexes, except for Fe(III), gave approximately the same R_f values with both dichloromethane and benzene in Tables II and III. However, the other

Table I. R_f, Standard Deviation in R_f Values, and LOD of Metal–DEDTC Complexes Developed with Dichloromethane and Benzene* on TLC Plate†

Metal complex	R_f (ave.)	SD (R_f)	RSD (R_f)	Confidence interval (95% confidence level)	LOD (μg)
AsL_3	0.64–0.38*	0.05–0.04*	6.25–10.52*	0.05–0.05*	2.50*
SbL_3	0.73–0.37	0.07–0.03	9.58–8.11	0.09–0.04	2.60
PbL_2	0.75–0.48	0.04–0.03	5.33–6.25	0.05–0.04	0.50
ZnL_2	0.84–0.69	0.03–0.03	3.57–3.35	0.04–0.04	0.40
BiL_3	0.63–0.35	0.03–0.03	4.76–8.57	0.04–0.04	0.75
CuL_2	0.86–0.68	0.03–0.03	3.49–4.41	0.04–0.04	0.25
MnL_2	0.62–0.34	0.08–0.02	12.90–5.88	0.1–0.03	0.65
CdL_2	0.71–0.49	0.07–0.05	9.86–10.20	0.09–0.09	2.00
HgL_2	0.79–0.60	0.07–0.03	8.86–5.00	0.09–0.04	1.75
CrL_3	0.58–0.33	0.08–0.02	13.79–6.06	0.1–0.03	3.5
CoL_2	0.71–0.51	0.07–0.02	9.86–3.92	0.09–0.03	0.30
NiL_2	0.78–0.42	0.07–0.03	8.97–7.14	0.09–0.04	0.28

* L = DEDTC.
† Precoated with commercial silica gel 60F254 adsorbent with 10- × 10-cm, 0.20-mm thickness for five repeated runs.
  SD = standard deviation and RSD = relative standard deviation.

Table II. Metal–DEDTC Complexes with Behaviors Dependent on Concentration when Developments Made with Dichloromethane and Benzene on TLC Plates

Concentration (mg/L)	Retention factors (R_f)			
	Fe $(DEDTC)_3$	Sn $(DEDTC)_2$	Sn$(DEDTC)_4$	Ag–DEDTC
100	0.56–0.24*	0.54–0.23	0.52–0.25	0.48–0.21
250	0.61–0.28*	0.60–0.27	0.55–0.28	0.51–0.25
500	0.62–0.29*	0.61–0.29	0.56–0.29	0.52–0.26
750	0.62–0.29*	0.62–0.29	0.56–0.29	0.52–0.26
1000	0.63–0.29*	0.63–0.29	0.57–0.29	0.53–0.27

* Developments made with benzene.

remaining metal complexes expressed an unchanged chromatographic behavior with decreasing concentration. Because this dependence was more pronounced in terms of a chromatographic result, the previously-mentioned metal complexes were eliminated for subsequent studies.

An attempt was also made to establish the LOD of the method with the analysis of standard water samples containing only one cation or its complex with benzene on TLC plates for the cations in question. The results are shown in Table I. Because the purpose was to identify and detect the metal complexes that have overlapping R_f values, no attempt was made to establish the applicability of the proposed TLC–IR system to the analysis of real samples containing the relevant metal cations.

The complexes that have overlapping R_f values in development with dichloromethane could successfully be distinguished by interpretation of their characteristic IR bands. The Co(II)– and Pb(II)–DEDTC complexes having the fully-overlapped $\nu_{C=N}$ vibration frequencies can also be differentiated by giving different $\nu_{C=S}$ vibration frequencies (Table IV). It can be observed that Bi(III)–, As(III)–, and Mn(II)–DEDTC complexes having the overlapped R_f values are identified by help of both $\nu_{C=N}$ and $\nu_{C=S}$ vibration frequencies. Again, it was observed that Ni(II)– and Hg(II)–DEDTC complexes having the same R_f values will be differentiated by fully exhibiting the different vibration frequencies of $\nu_{C=N}$ double-bond because of the interaction of the C–N bond with active –OH groups of silica gel. It was concluded that these metal complexes, having the same R_f values, had at least one or more ($\nu_{C=N}$ and $\nu_{C=S}$) vibration frequencies, and they will be be identifiable from real samples by a TLC–IR sequential system, although no chromatographic separation has occurred.

Also, the Zn(II)–/Cu(II)–DEDTC, Pb(II)–/ Cd(II)–/Ni(II)–DEDTC, and As(III)–/Sb(III)–/Mn(II)–/Cr(III)–DEDTC complex groups give the overlapping R_f values with benzene. Nevertheless, these complexes can be differentiated by the help of both the $\nu_{C=N}$ and $\nu_{C=S}$ vibration frequencies. It can easily be seen that the characteristic $\nu_{C=N}$ and $\nu_{C=S}$ vibration frequencies for these complexes are partly or fully different from each other (Table V).

Finally, a conclusion was drawn that any metal–DEDTC complex, except the Cr(III) cation in the high concentrations (1000 mg/L; because of gel formation in the organic phase during extraction and a low extractability), will be useful in the identification of metal cations present in real samples.

Conclusion

Identification of an unknown compound in a complex matrix is always difficult. With each passing year and complicated

Table III. R_f Values of Concentration-Depended Complexes Developed with Dichloromethane and Benzene on TLC Plates*

Complexes	Retention factors (R_f)	
	Dichloromethane	Benzene
Na–DEDTC	$0.84 \pm 0.028^\dagger$	$0.66 \pm 0.022^\dagger$
Fe (DEDTC)$_3$	0.64 ± 0.033	0.31 ± 0.012
Sn (DEDTC)$_2$	0.63 ± 0.031	0.30 ± 0.016
Sn (DEDTC)$_4$	0.63 ± 0.028	0.30 ± 0.015
Ag–DEDTC	0.61 ± 0.024	0.27 ± 0.017

* Initially coated with silica gel HF$_{254}$ adsorbent with 20- × 20-cm dimension at 0.50-mm thickness for six repeated runs.
$\dagger$ The average R_f and its standard deviation for six replicate measurements.

Table IV. Separation and Identification of Metal–DEDTC Complexes with Overlapping R_f Values in Size of SD by Characteristic IR-Absorbing Bands* after Preconcentration with Wick-Stick Procedure

Complex	R_f	$R_f \pm$ SD	Vibration frequency (cm^{-1})	
			$\nu_{C=N}$ stretching	$\nu_{C=S}$ stretching
CoL$_2$	0.71	0.71 ± 0.07	1489, 1455, 1274	1217, 1149, 1138, 1081
CdL$_2$	0.71	0.71 ± 0.07	1501, 1455, 1274	1206, 1149, 1092, 1081
SbL$_3$	0.73	0.73 ± 0.07	1501, 1467, 1274	1194, 1149, 1092, 1080
PbL$_2$	0.75	0.75 ± 0.04	1489, 1455, 1274	1206, 1138, 1092, 1069
BiL$_3$	0.63	0.63 ± 0.03	1501, 1467, 1274	1240, 1194, 1115, 1092
AsL$_3$	0.64	0.64 ± 0.04	1501, 1455, 1274	1194, 1149, 1115, 1092, 1001
MnL$_2$	0.62	0.62 ± 0.08	1489, 1455, 1262	1206, 1149, 1092, 1035
HgL$_2$	0.79	0.79 ± 0.07	1489, 1455, 1262	1206, 1138, 1092, 1069
NiL$_2$	0.78	0.78 ± 0.07	1523, 1444, 1274	1206, 1149, 1092, 1069

* In development with dichloromethane on plates.

Table V. Separation and Identification of Metal–DEDTC Complexes with Overlapping R_f Values in Size of SD by Their Characteristic IR-Absorbing Bands* after Preconcentration with Wick-Stick Procedure

Complex	R_f	$R_f \pm$ SD	Vibration frequency (cm^{-1})	
			$\nu_{C=N}$ stretching	$\nu_{C=S}$ stretching
AsL$_3$	0.38	0.38 ± 0.04	1501, 1455, 1274	1194, 1149, 1115, 1092, 1069, 1001
SbL$_3$	0.37	0.37 ± 0.03	1501, 1467, 1274	1194, 1149, 1115, 1092
BiL$_3$	0.35	0.35 ± 0.03	1501, 1467, 1274	1240, 1194, 1115, 1092
MnL$_2$	0.34	0.34 ± 0.02	1489, 1455, 1262	1206, 1149, 1092, 1035
CrL$_3$	0.33	0.33 ± 0.02	1501, 1455, 1274	1194, 1126, 1103, 1001
PbL$_2$	0.48	0.48 ± 0.03	1489, 1455, 1262	1194, 1149, 1092, 1069
CdL$_2$	0.49	0.49 ± 0.05	1501, 1455, 1274	1206, 1149, 1092, 1035
NiL$_2$	0.51	0.51 ± 0.03	1523, 1444, 1274	1266, 1149, 1092, 1069
ZnL$_2$	0.69	0.69 ± 0.03	1501, 1433, 1274	1206, 1149, 1092, 1069
CuLv	0.68	0.68 ± 0.03	1512, 1467, 1274	1206, 1149, 1092, 1081

* In development with benzene on plates.

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sample requiring analysis, demands for accuracy and speed of analysis have also increased. In order to overcome these problems, chemical methods have been replaced by more complex hyphenated instrumental approaches. A sequential technique that has great analytical potential is the chromatographic FTIR system. One of the important aspects of improving these systems is the investigation of "analytical windows" in IR spectra according to components separated. The analytical window can be defined as the spectral interval that is useful to the analytical evaluation of a species regardless of the complexity of the matrix containing the analyte. In samples with complex matrices, a theoretical suggestion of these analytical windows is not a very applicable technique. On the other hand, when analytical species with the same behaviors are in question, the availability of such suitable windows is also rare. The fact that chromatography and IR spectrophotometer are complementary has also been demonstrated here. The qualitative vibration bands (those of C–N and C=S bonds) concerning metal complexes is sufficient for more quantitative study of their degree shifts because of different central cations. After the analytical species having different R_f values are separated by TLC, these peaks will be a good measure for quantitative determination of each cation. In this case, such analysis will be performed with success in the TLC–IR sequential system, and suitable data to quantitate these complexes from a mixture containing metal complexes is directly acquired by FTIR.

In this study, instead of identifying the pairs of cations by the FTIR method directly from a solution without chromatography, the TLC–IR sequential system was preferred as an instrumental remedy to a poor TLC separation for the relevant complex pairs. In this context, the TLC–IR sequential system can be seen as an alternative, selective, and semiquantitative analysis method for small-budget laboratories.

Acknowledgments

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