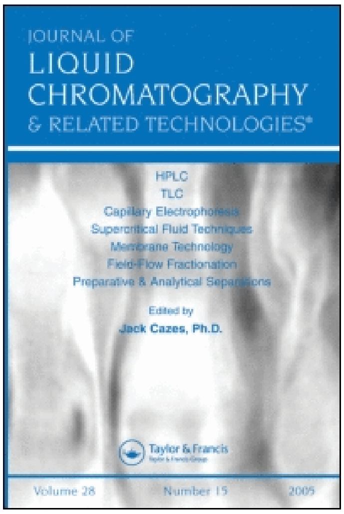

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Use of Complexation TLC to Investigate Monosulfides. II. Silica Impregnated with the Cd(II), Sr(II), Eu(III), and V(IV) Cations as Stationary Phase

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ABSTRACT

In this paper we present the results from recent investigations of the use of complexation thin-layer chromatography to separate 10 monosulfides. In our study, we made use of the fact that monosulfides contain in their molecules easily polarizable sulfur atoms, which enables complex formation. In an attempt to establish the most convenient working conditions for separation of the monosulfides, the silica layer was impregnated with the salts of four metals. This procedure modified the chemical nature of active sites present on the stationary phase surface, thus enabling more

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efficient separation of the analytes, although, in this introductory study the monosulfides investigated were chromatographed singly in order to examine their retention behavior unperturbed by intermolecular interactions with the other components of a mixed sample.

Key Words: Monosulfides; Complexation chromatography; Complex compounds; Impregnation with metal cations.

INTRODUCTION

This is the second study of a program devoted to the thin-layer chromatography of selected organic monosulfides. In Part I,[1] we focused our attention on the retention of the compounds on silica layers impregnated with the metal cations Cu(II), Co(II), Ni(II), Mn(II), Al(III), Cr(III), and Fe(III). In this paper, we present results from recent analyses conducted on silica layers impregnated with different cations—Cd(II), Sr(II), Eu(III), and V(IV).

It seems worth explaining that monosulfides, rather than any other group of organic compounds, became the target of our investigations because of the considerable practical importance of these compounds, which can be used as, e.g., polymer stabilizers, accelerators in the vulcanization of Indian rubber, or as supplementary compounds added to oils and greases. Monosulfides also play an important role as biomimetics in biochemical processes. Because they form complexes, monosulfides can also be used for selective detection and efficient removal of toxic metals from the human environment.[2–6]

To devise a proper system for complexation chromatography, common adsorbents (e.g., silica layers) are often impregnated with the salts of transition metals, which changes the nature of the active sites on the adsorbent surface. Metals deposited on the surface of the adsorbent affect the characteristics of the silanol groups according to the equation:

$$m\mathrm{Si{-}OH} + \mathrm{Me}^{m+} \leftrightarrow (\mathrm{Si{-}O})_m\mathrm{Me} + m\mathrm{H}^+$$

Formation of complexes on the adsorbent surface is apparent from changes of retention times compared with those measured on the unmodified stationary phase.[7]

In our study, monosulfides were analyzed (individually, rather than as mixtures) by use of a variety of experimentally selected mobile phases. The specific chemical structure of the monosulfides—a sulfur atom bonded to two hydrocarbon (alkyl or aryl) groups—was particularly well suited for complexation chromatography, because the readily polarizable sulfur atom has a tendency to form coordination (most frequently charge-transfer) bonds with a metal cation. The strength of these bonds can differ from weak with alkali metal cations to strong with the cations of heavy metals.

The stationary phases used could be divided into two general groups, unmodified silica and silica impregnated with metal salts. Impregnated silica was spiked with the cations at the 2+, 3+, and 4+ oxidation levels [i.e., with Cd(II), Sr(II), Eu(III), and V(IV)]. After development, the respective R_F values were calculated; this enabled evaluation of the chromatographic behavior of the monosulfides by study of the dependence of their R_F values on mobile-phase composition.

EXPERIMENTAL

Chromatography was performed on plastic-backed sheets precoated with silica gel as stationary phase (#1.05735, Merck KGaA, Darmstadt, Germany). The general characteristics of the monosulfides investigated are given in Table 1. The analytes were chromatographed both on plain silica and on silica impregnated with 5% aqueous solutions of salts of Cd(II), Sr(II), or V(IV), or with a 1% aqueous solution of europium oxide containing the Eu(III) cation.

After impregnation, the chromatographic plates were dried for 24 h at ambient temperature, and immediately before use they were activated for 15 min at 110–120°C. On the pre-conditioned adsorbent layers, we spotted 1% solutions of the monosulfides in dichloromethane; the volume applied was ca. 3 μL. Chromatograms were developed to a distance of 8 cm in classical, Stahl-type chromatographic chambers (Camag, Muttenz, Switzerland) with the mobile phases listed in Table 2. After development and drying, the plates were visualized in UV light at 254 nm, and numerical values of R_F were calculated.

RESULTS AND DISCUSSION

It was observed that solute retention was affected by impregnation of the silica surface with the cations used in our experiment. For most of the monosulfides investigated (i.e., irrespective of the impregnating cation and mobile phase employed), the range of R_F values obtained on the impregnated layers was wider than on plain silica, i.e., for most of the monosulfides investigated impregnation of the stationary phase layer with a metal cation resulted in either an increase or a decrease in R_F compared with the value obtained on the unmodified layer. Increases in R_F were most probably because adsorption of the monosulfide by the impregnated layer was less than on the unmodified layer. Reductions in R_F most probably resulted from

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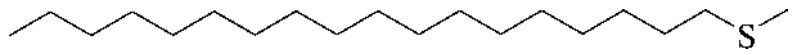
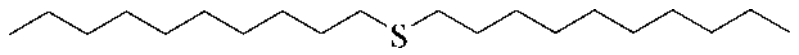
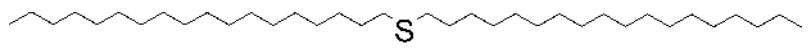
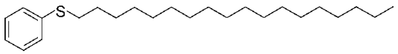
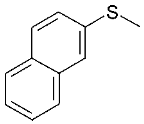
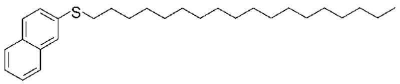
Table 1. Characteristics of the monosulfides investigated.

No.	Symbol	Structural formula	Compound	Molecular weight
1	JSB-53		1-(Methylthio)octadecane	300.6
2	JSB-25		Didecylsulfide	314.6
3	JSB-47		Dioctadecylsulfide	539.0
4	DKJ-2		Octadecylthiobenzene	362.7
5	DOD-6		2-(Methylthio)naphthalene	74.3
6	DKJ-3		2-(Octadecylthio)naphthalene	412.7

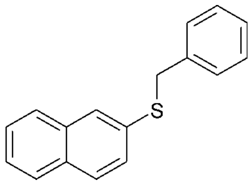
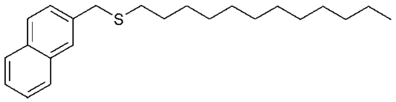
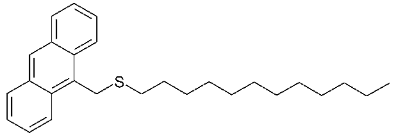
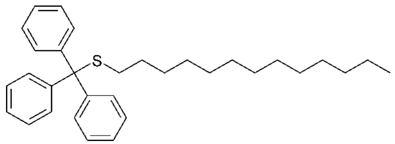
7	DOD-9		2-(Benzylthio)naphthalene	250.4
8	DKJ-6		2-(Dodecylthiomethyl)naphthalene	342.6
9	JSB-51		9-(Dodecylthiomethyl)anthracene	392.6
10	DKJ-1		1-(Triphenylmethylthio)dodecane	444.7

Table 2. Qualitative and quantitative composition of the mobile phases used, and the respective symbols used as their descriptors.

Qualitative composition	Volume ratio (v/v)	Symbol
CCl_4		M1
$C_6H_{14} + CHCl_3$	9 : 1	M2
$C_6H_{14} + CCl_4$	9 : 1	M3
$C_6H_{14} + C_6H_5CH_3$	9.5 : 0.5	M4
$CCl_4 + C_6H_{14} + CHCl_3$	7 : 2 : 1	M5

complexation interactions between the monosulfide, acting as a ligand, and the cation deposited on the adsorbent surface, acting as the central atom.

To illustrate these general statements, representations of one set of R_F values, obtained for the 10 monosulfides chromatographed on unmodified silica and on silica impregnated with the vanadium(IV) cation, are illustrated graphically in Figs. 1 and 2, respectively. The experimental R_F values obtained for the 10 monosulfides chromatographed on unmodified silica by use of mobile phases M1–M5 (Table 2) are given in Table 3.

The numerical R_F values measured for the monosulfides on silica impregnated with the Cd(II), Sr(II), Eu(III), and V(IV) cations, using the same mobile phases, are listed in Tables 4 and 5. These tables also contain

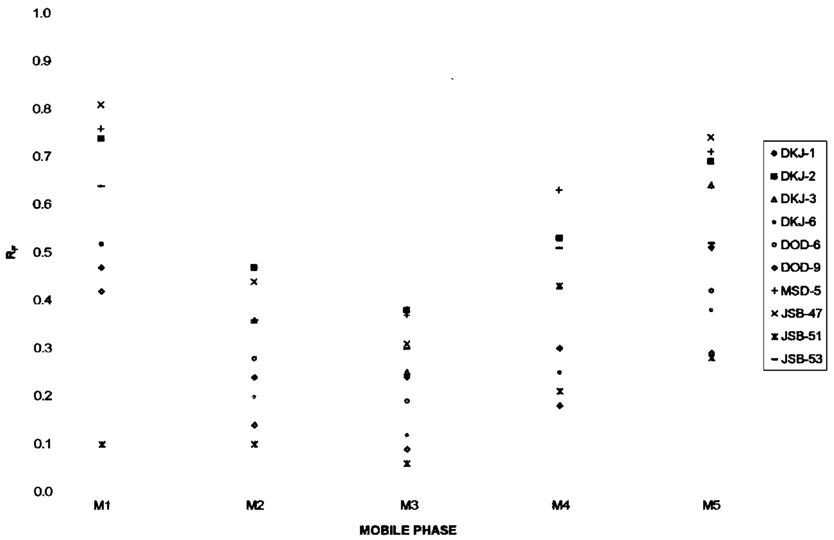


Figure 1. R_F coefficients of the monosulfides chromatographed on unmodified silica with mobile phases M1, M2, M3, M4, and M5.

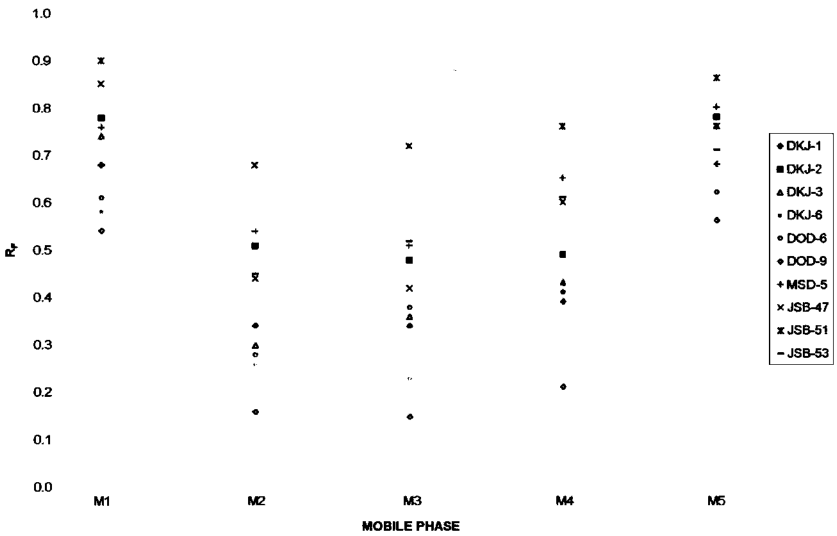


Figure 2. R_F coefficients of the monosulfides chromatographed on silica impregnated with a 5% aqueous solution of the V(IV) salt with mobile phases M1, M2, M3, M4, and M5.

measures of ΔR_F values averaged for neighboring pairs of monosulfides, calculated as $\sum \Delta R_F / n$ (where $\sum \Delta R_F$ is the sum of the differences of the R_F values for all pairs of neighboring analytes and n is the number of such pairs).

Table 3. Experimental R_F values obtained by use of mobile phases M1, M2, M3, M4, and M5 on unmodified silica, and averaged estimates of the separations obtained ($\sum \Delta R_F / n$).

	R_F				
Monosulfide	M1	M2	M3	M4	M5
DKJ-1	0.47	0.24	0.24	0.30	0.51
DKJ-2	0.74	0.47	0.38	0.53	0.69
DKJ-3	0.74	0.36	0.25	0.43	0.64
DKJ-6	0.52	0.20	0.12	0.25	0.38
MSD-5	0.76	0.47	0.37	0.63	0.71
JSB-47	0.81	0.44	0.31	0.43	0.74
JSB-51	0.10	0.10	0.06	0.21	0.28
JSB-53	0.64	0.36	0.30	0.51	0.52
DOD-6	0.52	0.28	0.19	0.53	0.42
DOD-9	0.42	0.14	0.09	0.18	0.29
$\sum \Delta R_F / n$	0.0789	0.0411	0.0356	0.0500	0.0511

Table 4. Effect of the metal cation used for impregnation on the experimental R_F values obtained by use of binary mobile phases M4, M3, and M2, respectively, and averaged estimates of the separations obtained ($\sum \Delta R_F/n$).

	R_F											
	M4				M3				M2			
Monosulfide	Cd(II)	Sr(II)	Eu(III)	V(IV)	Cd(II)	Sr(II)	Eu(III)	V(IV)	Cd(II)	Sr(II)	Eu(III)	V(IV)
DKJ-1	0.33	0.36	0.41	0.39	0.23	0.26	0.39	0.34	0.33	0.38	0.48	0.31
DKJ-2	0.53	0.61	0.60	0.49	0.44	0.42	0.59	0.48	0.54	0.51	0.60	0.51
DKJ-3	0.38	0.28	0.34	0.43	0.28	0.18	0.38	0.36	0.34	0.28	0.28	0.30
DKJ-6	0.29	0.36	0.40	0.41	0.15	0.16	0.33	0.23	0.24	0.36	0.41	0.26
MSD-5	0.63	0.71	0.65	0.65	0.37	0.54	0.61	0.51	0.53	0.18	0.64	0.54
JSB-47	0.46	0.64	0.33	0.60	0.43	0.28	0.46	0.42	0.48	0.45	0.68	0.44
JSB-51	0.74	0.78	0.74	0.76	0.13	0.10	0.75	0.72	0.18	0.24	0.78	0.68
JSB-53	0.53	0.58	0.56	0.61	0.38	0.41	0.59	0.52	0.50	0.56	0.60	0.45
DOD-6	0.35	0.38	0.38	0.41	0.30	0.25	0.36	0.38	0.35	0.38	0.44	0.28
DOD-9	0.31	0.34	0.24	0.21	0.16	0.08	0.20	0.15	0.24	0.23	0.20	0.16
$\sum \Delta R_F/n$	0.0500	0.0556	0.0556	0.0611	0.0344	0.0511	0.0611	0.0633	0.0400	0.0422	0.0644	0.0578

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Table 5. Effect of the metal cation used for impregnation on the experimental R_F values obtained by use of the monocomponent and ternary mobile phases M1 and M5, respectively, and averaged estimates of the separations obtained ($\sum \Delta R_F/n$).

	R_F							
	M1				M5			
Monosulfide	Cd(II)	Sr(II)	Eu(III)	V(IV)	Cd(II)	Sr(II)	Eu(III)	V(IV)
DKJ-1	0.63	0.75	0.70	0.68	0.74	0.70	0.70	0.68
DKJ-2	0.74	0.85	0.78	0.78	0.82	0.80	0.76	0.78
DKJ-3	0.68	0.80	0.66	0.74	0.75	0.70	0.74	0.76
DKJ-6	0.40	0.65	0.69	0.58	0.64	0.66	0.71	0.68
MSD-5	0.65	0.54	0.75	0.76	0.80	0.80	0.80	0.80
JSB-47	0.86	0.86	0.88	0.85	0.75	0.80	0.80	0.76
JSB-51	0.53	0.64	0.89	0.90	0.56	0.58	0.88	0.86
JSB-53	0.66	0.78	0.74	0.68	0.73	0.74	0.69	0.71
DOD-6	0.56	0.68	0.71	0.61	0.63	0.64	0.66	0.62
DOD-9	0.48	0.58	0.65	0.54	0.61	0.58	0.64	0.56
$\Sigma\sigma\Delta R_F/n$	0.0511	0.0356	0.0267	0.0400	0.0289	0.0244	0.0267	0.0333

Thorough analysis of the experimental data presented in these tables reveals that the best results (i.e., the greatest differentiation of the R_F values of the monosulfides) are obtained by use of the binary mobile phases M2, M3, and M4. Unfortunately, application of the ternary mobile phase M5 did not result in enhanced differentiation of the R_F values.

Of the four different metal cations used for impregnation of the silica layers, V(IV) proved the most advantageous for differentiation of the R_F values of the monosulfides. Thorough analysis of the data contained in Tables 4 and 5 also reveals that satisfactory results are obtained when the silica is impregnated with Eu^{3+} cations.

In this study, the monosulfides investigated were analyzed as individual chemical species only, in order to enable examination of their retention behavior unperturbed by the other components of a sample mixture. Despite this, the results obtained are valuable because they enable recommendation of mobile phase compositions suitable for successful TLC separation of binary, ternary, quaternary, and even more complex mixtures of the monosulfides. These suggestions will be checked in a forthcoming and thorough experimental study.

CONCLUSIONS

The work described in this paper has revealed the possibility of using complexation TLC to investigate the retention of 10 randomly chosen monosulfides. The working procedure elaborated, resulted in enhanced differentiation of the experimental R_F values of these organic analytes. The experiment was conducted on silica impregnated with metal cations having 2+, 3+, and 4+ oxidation states [specifically, Cd(II), Sr(II), Eu(III), and V(IV)], and also on the plain silica as reference material. Our investigations were performed with five qualitatively and quantitatively different mobile phases. The results obtained can be summarized as follows:

1. Comparison of data obtained for the monosulfides chromatographed on plain and impregnated silica reveals that impregnation of the silica with metal cations results in somewhat greater differentiation of R_F values.
2. Differentiation of the R_F values of the monosulfides is indisputably better when mobile phases of relatively low-polarity are used.
3. Experimental results collected in this study, which illustrate the retention behavior of individual monosulfides when chromatographed with a variety of mixed mobile phases, will be used for further selection and testing of mobile phases most suitable for efficient separation of binary, ternary, quaternary, and even more complex mixtures of monosulfides.

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