

CORRELATION BETWEEN GC RETENTION DATA AND RELATIVE MOLECULAR WEIGHT OF *N,N*-BIS(2,2,2-TRIFLUOROETHYL)-DITHIOCARBAMATES OF SOME DIVALENT METALSJan HROUZEK¹, Jan KRUPCIK^{2,*} and Ivan SKACANI³

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The correlation of gas-chromatographic retention data (retention times and linear retention indices) and relative molecular weight was examined for *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamate chelates of some divalent metals. Regression analysis of data obtained by capillary GC on a non-polar column heated by applying a dual-ramp temperature programme gave linear dependences possessing reasonable correlation coefficients.

Key words: Correlation of retention data and molecular weight; Gas chromatography; *N,N*-Bis(trifluoroethyl)dithiocarbamates of Ni(II), Cd(II), Sn(II), Pb(II).

Gas-chromatographic trace element analysis in aqueous solutions can be performed via quantitative reactions of element ions giving rise to volatile and thermally stable chelates^{1,2}. Sodium or lithium salts of bis(2,2,2-trifluoroethyl)dithiocarbamic acid (NaL or LiL, where L = C₅H₄F₆NS₂) are suitable reagents for the preparation of *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamate chelates [ML₂] with some biologically and environmentally important divalent metals M(II) (ref.²). Bis(2,2,2,-trifluoroethyl)dithiocarbamates can be analyzed by gas chromatography owing to their sufficient volatility, thermal stability, and inertness³. The linear dependence of the retention data on the relative molecular weight of the separated solutes in isothermal or linear temperature programmed conditions can be utilized for identification purposes. If the temperature programmed runs involve more than one variable parameter, this dependence can be rather complex.

The aim of this work was to study the relationships between the gas-chromatographic retention data of *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamates of Ni(II), Cd(II), Sn(II) and Pb(II) and their molecular weight, using a capillary column coated with a non-polar stationary phase and applying temperature programmes at two different gradients.

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EXPERIMENTAL

Instruments

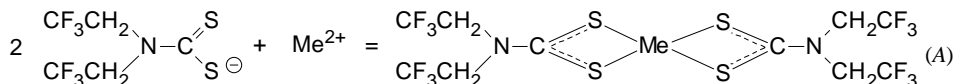
A HP 5890 series II gas chromatograph equipped with a cold on-column injector (both with a silicone septum and duck-bill), flame ionization detector (FID) and ^{63}Ni electron capture detector (ECD) were used applying a programmable inlet pressure and injector temperature. Hydrogen (99.996%) was employed as the carrier gas. Nitrogen (99.999%) at a flow rate of 60 ml/min served as the make-up gas for ECD. For FID, 30 ml/min of hydrogen (99.99%), 40 ml/min of nitrogen (99.99%) (make-up gas) and 400 ml/min of air were used. All gases were purchased from Linde, Bratislava, Slovak Republic. The chromatograms were recorded and evaluated by means of a 3396 Integrator Series II and ChemStation 3365 software (Hewlett-Packard, Avondale, U.S.A.).

The $[\text{ML}_2]$ chelates were separated on a fused silica capillary column (13.5 m long, 0.53 mm i.d.) coated with a 2.65 μm film of 5% phenyl-polydimethylsiloxane (HP-5, Hewlett-Packard, Avondale, U.S.A.).

The following working conditions were applied to the analysis of the $[\text{ML}_2]$ chelates by GC: A constant carrier gas inlet pressure (20 kPa). Column temperature was held at 50 $^\circ\text{C}$ for 1 min, then increased at a rate of 70 K/min to 200 $^\circ\text{C}$ at which it was held for 5 min, and finally increased to 230 $^\circ\text{C}$ at a rate of 5 K/min. After sample injection, the temperature of the on-column injection port was increased from 50 to 250 $^\circ\text{C}$ at a rate of 70 K/min. FID temperature 280 $^\circ\text{C}$.

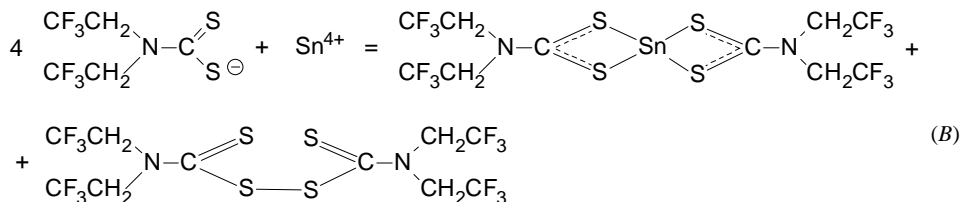
Preparation

The $[\text{ML}_2]$ chelates were prepared from equal volumes of an 0.02 mol/l aqueous solution of MCl_2 and an 0.04 mol/l aqueous solution of NaL by following the procedure described by Neeb et al.⁴. The synthesis of the $[\text{ML}_2]$ chelates is based on the reaction:



The chelates are planar and well soluble in organic solvents^{2,3}.

SnL_2 was prepared from Sn^{4+} by the following reaction:



The disulfide $(\text{CF}_3\text{CH}_2)_2\text{NCSS}-\text{SSCN}(\text{CH}_2\text{CF}_3)_2$ was identified by the retention data vs relative molecular weight correlation of the solutes separated (see below) as well as by the GC/MS (ref.⁵) combination.

The results of elemental analysis listed in Table I show that the synthesized tin complex is $[\text{SnL}_2]$ with a relative molecular weight $M_r = 631.10$, which is in agreement with the relative molecular weight found by gas chromatography ($M_r = 620$ in Table II). For SnL_4 the data in Table I display a substantial difference between the theoretical elemental composition and the observed values.

The GC separation of 1 μl of a fresh toluene solution of $[\text{SnL}_2]$ is shown in Fig. 1. The purity of all the $[\text{MeL}_2]$ chelates synthesized was checked by elemental analysis, using an EA-1108 Elemental Analyser (Carlo Erba, Milan, Italy) (Table I).

Chemicals

All chemicals were of reagent grade (Lachema Brno, Czech Republic). n-Hexane pure (Slovnaft Bratislava, Slovak Republic), purified by the procedure published by Perrin et al.⁶. Benzene p.a. (Lachema Brno, Czech Republic), toluene for chromatography (Riedel de Haen AG, Germany).

RESULTS AND DISCUSSION

Since the HP-5 column is regarded as non-polar, a semilogarithmic linear dependence of the retention data on the relative molecular weight of the separated solutes could be expected in isothermal conditions*. A linear dependence of the retention of solutes on the relative molecular weight can be expected in linear temperature programmed gas chromatography^{8,9}. The retention data obtained on the HP-5 column in our temperature programmed runs and the relative molecular weights of the $[\text{ML}_2]$ chelates are given in Table II. The dependence of the retention time (t_R) on the relative molecular weight of $[\text{ML}_2]$ could be fitted by the linear equation:

$$t_R = -16.73 + 0.0421M_r \quad (I)$$

with a reasonable correlation coefficient $r = 0.9592$.

The relative molecular weights ($M_{r,\text{calc}}$) calculated from the retention times by this equation are given in the last column of Table II. The reliability of this correlation can be assessed based on a comparison of the M_r and $M_{r,\text{calc}}$ values. This correlation confirms that peak A in Fig. 1 is due to $(\text{CF}_3\text{CH}_2)_2\text{NCSS}-\text{SSCN}(\text{CH}_2\text{CF}_3)_2$, because the calculated and true relative molecular weights of this disulfide are in agreement ($M_{r,\text{calc}} = 510.5$ corresponding to $t_R = 4.27$, vs $M_r = 512.4$). This agreement is quite surprising as the retention times t_R rather than the adjusted retention times $t'_R = t_R - t_M$ were correlated with the relative molecular weights. Since the gas hold-up time (t_M) in temperature programmed runs with more than one variable parameter is very difficult to measure or calculate, it may be useful instead of the retention times to correlate the linear indices (I_i) from which the gas hold-up time is eliminated**:

* Several semilogarithmic linear dependences between the retention volumes of solutes separated by GC under isothermal conditions and some of their physical parameters were found for homologous series⁷.

**Linear retention indices can also be calculated for isothermal gas chromatography.

$$I_i = 100z + \frac{t_{R,i} - t_{R,z}}{t_{R,z+1} - t_{R,z}}, \quad (2)$$

where z is the carbon atom number in the n -alkyl chain⁸.

Since some peaks of n -alkanes overlapped with those of $[\text{ML}_2]$, the chelates and n -alkanes were chromatographed separately (Fig. 2). The linear dependence of I_i on M_r was fitted by the linear equation:

$$I_i = 657.2 + 2.267M_r \quad (3)$$

with nearly the same correlation coefficient ($r = 0.9598$) as in the previous case.

TABLE I
Elemental analysis of $[\text{ML}_2]$ chelates, where $\text{L} = \text{C}_5\text{H}_4\text{F}_6\text{NS}_2$

Compound	Calculated/Found		
	% C	% H	% N
[NiL ₂]	21.20	1.41	4.90
	21.18	1.32	4.78
[PbL ₂]	16.69	1.12	3.89
	16.80	1.12	3.93
[CdL ₂]	19.22	1.29	4.48
	19.42	1.59	4.53
[SnL ₂]	21.18	1.42	4.94
	20.99	1.32	4.70
[SnL ₄]	23.66	1.59	5.52
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TABLE II
Retention times (t_R) and molecular weights (M_r) of $[\text{ML}_2]$ chelates

M	t_R , min	I_i	M_r	$M_{r,\text{calc}}$, from Eq. (1)	$M_{r,\text{calc}}$, from Eq. (3)
Ni	8.12	1 995	571.1	594.0	589.9
Cd	8.81	2 033	624.8	609.0	606.7
Sn	9.32	2 060	631.1	620.0	618.6
Pb	14.06	2 315	719.6	722.8	731.1

In conclusion the results obtained give evidence that the linear dependence of the retention indices on the relative molecular weight can serve as a useful tool for identification purposes in gas-chromatographic analysis of elements in the form of their bis(2,2,2-trifluoroethyl)dithiocarbamate chelates.

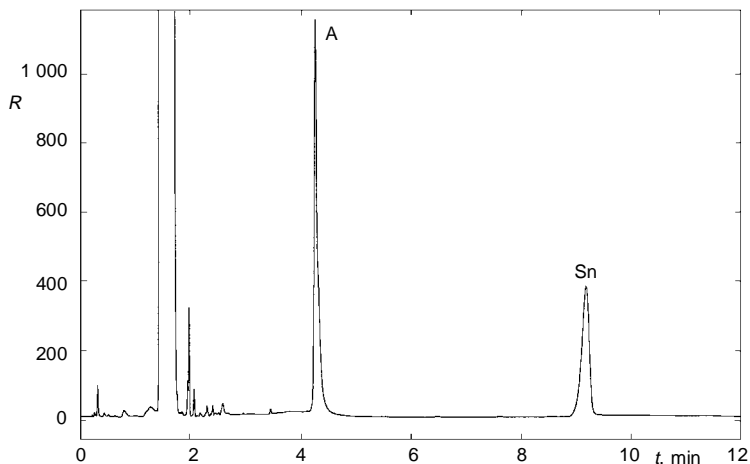


FIG. 1

Gas chromatographic separation of 1 μ l (220 ng) of a fresh toluene solution of $[\text{SnL}_2]$. A disulfide $(\text{CF}_3\text{CH}_2)_2\text{NCSS}-\text{SSCN}(\text{CH}_2\text{CF}_3)_2$, Sn $[\text{SnL}_2]$, R response. For working conditions see Experimental

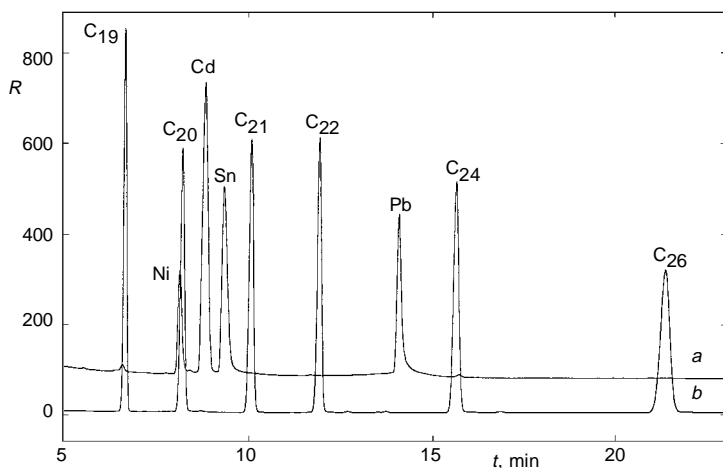


FIG. 2

Gas chromatographic separation of fresh toluene solution of $[\text{NiL}_2]$ (90 ng), $[\text{CdL}_2]$ (330 ng), $[\text{SnL}_2]$ (540 ng), and $[\text{PbL}_2]$ (250 ng) (a) and hexane solution of C_{19} - C_{26} n-alkanes (b). R response. For working conditions see Experimental

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