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CORRELATION BETWEEN REVERSED-PHASE RETENTION AND SOLUTE MOLECULAR SURFACE TYPE AND AREA

II. RETENTION OF LOW POLARITY NON-HYDROCARBONACEOUS SURFACES

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SUMMARY

On octadecylsilica (ODS) systems and pure methanol as eluent, the retention of homonuclear proton-free solutes like P_4, As_4, S_9, Se_8 and sulphur homocycles S_n with $n > 9$ appears to depend only on their respective total molecular surface area (TSA). When plotted *versus* TSA, their ln k' values lie on one straight line. The retention of these solutes is distinctly higher than that of *n*-alkanes having equal TSA. In terms of retention index, I_K, the difference is about + 500 units. It is proposed that the lower alkane retention is due to an additional interaction with the eluent methanol. The retention increments produced by chalcogen atoms in RS_nR, RSe_nR and RTe_nR chains are also proportional to their respective surface areas, and are influenced to a certain degree by the length of the terminal alkyl groups R. The retention of proton-free heteronuclear solutes like S_nSe_{8-n}, hexachlorobenzene, hexabromobenzene and carbon disulphide is lower than with homonuclear proton-free solutes, but higher than with alkanes if normalized to equal TSA. This is explained by the existence of stronger bond dipoles and an increased polarizability.

INTRODUCTION

In the first part of this series[1] we showed that in an octadecylsilica (ODS)–methanol system various hydrocarbonaceous solute molecular surfaces have in general different sorption free energies per unit area. Paraffinic areas produce more retention than aromatic areas, methyl more than methylene. The $-CH{=}CH_2$ group has a positive retention index contribution, I_K, which, however, is lower than that from $-CH_2CH_3$, and the $-C{\equiv}CH$ group even contributes a negative increment. The retention contributions from $-CH_2-$ groups are not constant but depend on the electron affinity of substituents within the solute molecule. All these effects can be rationalized in terms in changes of cavity free energies and interaction free energies. The latter appear to depend on the effective electron density in the respective C–H bonds.

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We now report on the retention contributions of proton-free solute molecular fragments having no or only low tendencies to act as electron donors. The elements S, Se, Te will collectively be referred to as chalcogens[2], their compounds as chalcogenides.

EXPERIMENTAL

The experimental conditions were as described before[1]. Yellow arsenic was made by rapid cooling of arsenic vapour. Dialkyl polytellurides were prepared according to the method of Grigsby *et al.*[3] using an excess of tellurium. Dialkyl polyselenides were obtained similarly, Te being replaced by Se. Dicycloalkyl polyselenides can be prepared by irradiation of Se_8 suspensions in the corresponding cycloalkane with light of wavelength 254 nm[4]. The preparation of dialkyl thiopolyselenides has been described elsewhere[5]. Sulphur rings were prepared in different ways: by liquid nitrogen quenching of sulphur melts[6], by illumination (254 nm) of S_8 in cyclohexane[7], by acid decomposition of sodium thiosulphate solution[8] or by thermal decomposition of methanolic polysulphane solutions[9].

RESULTS AND DISCUSSION

Vicinal thia substitution in *n*-alkanes leads to the formation of dialkyl polysulphides RS_nR. If S is replaced by Se or Te, we obtain the corresponding polyselenides RSe_nR or polytellurides RTe_nR, respectively. Fig. 1 shows chromatograms of EtS_mEt, $EtSe_nEt$ and $EtTe_nEt$ (where Et = ethyl). It is seen that for a given number of atoms in the chalcogen chain, n_X, the retention of the polyselenide is higher than that of the polysulphide and the polytelluride retention is higher still.

Within either of the chromatograms shown, ln k' depends linearly on n_X:

$$\ln k'(\mathrm{EtX}_n\mathrm{Et}) = a(\mathrm{X}) + b(\mathrm{X}) \cdot n_\mathrm{X} \qquad (1)$$

Also the retention index, I_K, which is analogous to the Kováts index in gas chromatography, and can be calculated[1] from

$$I_\mathrm{K}(\mathrm{Et_2X}_n) = \frac{100}{\bar{b}}\,[\ln k'(\mathrm{Et_2X}_n) - \bar{a}] \qquad (2)$$

is linear over n_X (bars indicate *n*-alkane data). This is shown in Fig. 2, which for comparison also contains the straight line $I_K = 100 \cdot n_C$ for *n*-alkanes. Several observations can be made:

(1) The index increase per chain element, δI, is 100 for $-CH_2-$, 139.2 for –S–, 161.8 for –Se– and 206.8 for –Te–. So a Te atom in a tellurium chain produces more than twice as much retention as a methylene group in an *n*-alkane.

(2) For low chain atom numbers, the index I_K of diethyl polychalcogenides is lower than that of the *n*-alkane having the same number of skeletal atoms ($n_X + n_C$). The cross-over points where $I_K(Et_2X_n)$ becomes greater than $I_K(C_{n+4})$ occurs at $n = 10$ for the polysulphides. This means that $I_K(Et_2S_9) < 1300$ and $I_K(Et_2S_{10}) > 1400$. In the polyselenide series, equal retention is observed with shorter chains:

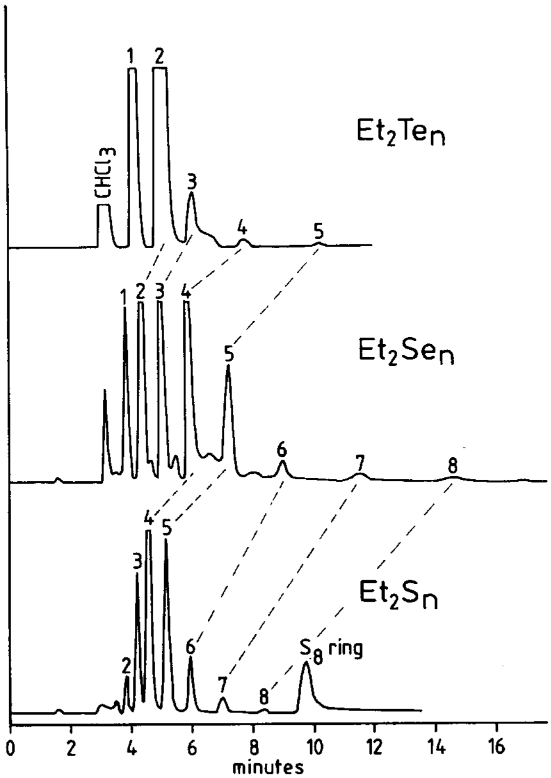


Fig. 1. Chromatograms of diethyl polychalcogenides, Et_2S_n, Et_2Se_n, Et_2Te_n. Numbers at peaks indicate the numbers of the respective chalcogen atoms in the solute molecules. Column: 10 cm × 8 mm I.D. RadPAK A. Eluent: 1 ml/min methanol (same conditions for all figures). (Figure taken from ref. 13, with permission.)

$I_K(Et_2Se_3) < 700$ and $I_K(Et_2Se_4) > 800$. With the polytellurides we find $I_K(Et_2Te) < 500$ and $I_K(Et_2Te_2) > 600$.

(3) The intercept for n(chain) = 0, which may be interpreted as the (entirely formal) index contribution of two ethyl groups, is 400 for alkanes, 16 for polysulphides, 192 for polyselenides and 216 for polytellurides.

Effects 2 and 3 are due to the build-up of local polar centres at the CH_2–X bond and to the mutual influence of chalcogen and carbon chains. They will be dealt with in part III of this series. The first effect has two causes, as is seen from Fig. 3. Here the respective ln k' per 100 Å^2 increase in total molecular surface area (TSA) is 0.874 for the methylene chain, 1.159 for the sulphur chain, 1.137 for the selenium chain and 1.111 for the tellurium chain. Since data are available only for Et_2Te to Et_2Te_5 and the mono- and dichalcogenides frequently show a somewhat irregular behaviour, the figure given for Et_2Te_n is less reliable. The ln k' increases of chalcogenide chains are very similar, possibly even indistinguishable.

The average is $\Delta \ln k' = 1.136$ per 100 Å^2 (±2%), whereas the methylene value is 26% lower. Obviously, in an ODS–methanol system, a CH_2 chain surface is distinctly less effective in producing retention than a chalcogen chain surface, both having the same area. The reason for the strong divergence of the lines in Fig. 2 is the

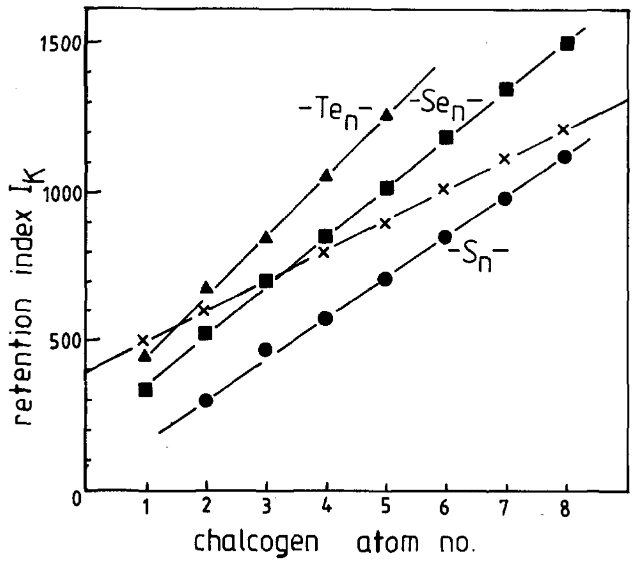
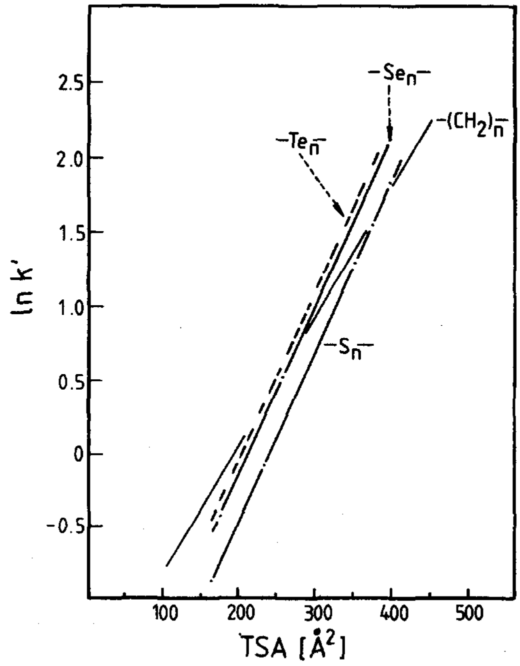


Fig. 2. Retention indices of Et_2S_n, Et_2Se_n and Et_2Te_n *versus* chalcogen chain length, based on retention data from Fig. 1. For comparison the retention indices of *n*-alkanes from pentane to dodecane are marked by crosses.



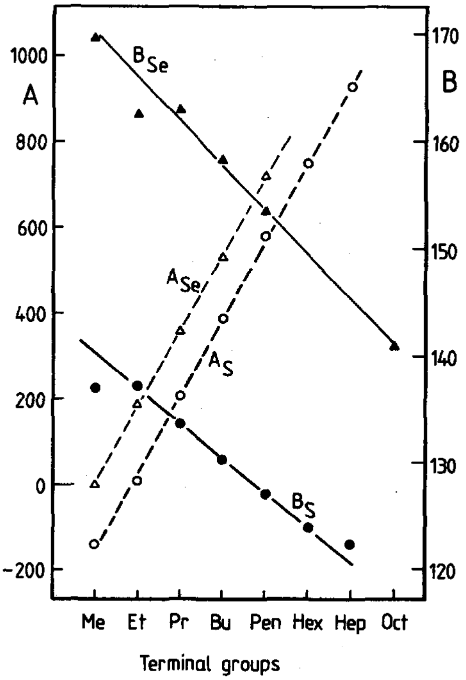


Fig. 3. The increase in ln k' with increasing total molecular surface area in diethyl polychalcogenides compared with *n*-alkanes.

Fig. 4. The coefficients of $I_K = A + Bn_X$ for X = S, Se as a function of increasing terminal alkyl chain length.

difference in surface area contribution of the respective chain elements. The formal TSA equations are:

$$\text{TSA}(n\text{-alkane}) = 25.372 + 22.668 \cdot n_\text{C}\ (\text{Å}^2),\ r = 1 \text{ for } n_\text{C} > 4 \tag{3}$$

$$\text{TSA}(\text{Et}_2\text{S}_n) = 116.06 + 23.44 \cdot n_\text{S}\ (\text{Å}^2),\ r = 0.99999 \text{ for } n_\text{S} > 3 \tag{4}$$

$$\text{TSA}(\text{Et}_2\text{Se}_n) = 117.20 + 28.09 \cdot n_\text{Se}(\text{Å}^2),\ r = 1 \text{ for } n_\text{Se} > 2 \tag{5}$$

$$\text{TSA}(\text{Et}_2\text{Te}_n) = 112.79 + 36.92 \cdot n_\text{Te}(\text{Å}^2),\ r = 0.99999 \text{ for } 1 \leqslant n_\text{Te} \leqslant 5 \tag{6}$$

Thus an area increase of 100 Å^2 is produced by 4.41 CH_2 groups, 4.27 S atoms, 3.56 Se atoms or 2.71 Te atoms, respectively.

If the ln k' equation analogous to eqn. 1 are combined with the above TSA equations, we get:

$$\ln k'(n\text{-alkane}) = -1.4488 + 0.1981 \cdot n_\text{C} = 0.00874 \cdot \text{TSA} - 1.6705 \tag{7}$$

$$\ln k'(\text{Et}_2\text{S}_n) = -1.4272 + 0.2718 \cdot n_\text{S} = 0.01159 \cdot \text{TSA} - 2.7730 \tag{8}$$

$$\ln k'(\text{Et}_2\text{Se}_n) = -1.0618 + 0.3195 \cdot n_\text{Se} = 0.01137 \cdot \text{TSA} - 2.3948 \tag{9}$$

$$\ln k'(\text{Et}_2\text{Te}_n) = -0.9886 + 0.4097 \cdot n_\text{Te} = 0.01110 \cdot \text{TSA} - 2.2402 \tag{10}$$

If the surface quality factors, f_i, which are the coefficients of TSA in eqns. 7–10, are multiplied by $RT = 2477.69$ J/K · mol we get δG, which can be regarded as the chromatographic free energy of sorption for the type of area under consideration. It has the dimensions of J/mol · Å^2. We find $\delta G = 21.65$ for alkanes, 28.7 for Et_2S_n, 28.2 for Et_2Se_n and 27.5 for Et_2Te_n. We assume that the differences for diethyl polychalcogenides are artifacts, caused by some data scatter as well as by some uncertainty in the Van der Waals radii.

The values found for $\delta G(\text{X})$ are valid for ethyl terminal groups. In general, the chalcogen retention increment depends on the terminal alkyl chain length. The dependence of ln k' on the surface area (SA) of a dialkylpolychalcogenide $\text{C}_m\text{X}_n\text{C}_{\bar{m}}$ with $m = n_\text{C}/2$ is:

$$\ln k' = 2\,\text{SA}_{\text{CH}_3} \cdot f_{\text{CH}_3} + (n_\text{C} - 2) \cdot \text{SA}_{\text{CH}_2} \cdot f_{\text{CH}_2} + \text{RA}_{\text{CH}_2} \cdot f_{\text{CH}_2} + $$

$$+ \text{SA}_\text{X} \cdot f_\text{X} \cdot n_\text{X} + \text{RA}_\text{X} \cdot f_\text{X} + \ln \varphi \tag{11}$$

where RA is the residual area. When both n_C and n_X are varied, we can regard this system either as C homologues or as X homologues. For C homology

$$\ln k' = a_\text{C} + b_\text{C} n_\text{C} \text{ with } b_\text{C} = \text{SA}_{\text{CH}_2} \cdot f_{\text{CH}_2} \tag{12}$$

and in terms of retention index:

$$I_\text{K} = A_\text{C} + B_\text{C} n_\text{C} \text{ with } B_\text{C} = 100 \cdot \frac{b_\text{C}}{\bar{b}} \text{ and } A_\text{C} = \frac{100}{\bar{b}}(a_\text{C} - \bar{a}) \tag{13}$$

X homology gives:

$$\ln k' = a_X + b_X n_X \quad \text{with} \quad b_X = \mathrm{SA}_X \cdot f_X \tag{14}$$

$$I_K = A_X + B_X n_X \quad \text{with} \quad B_X = 100 \cdot \frac{b_X}{\bar{b}} \quad \text{and} \quad A_X = \frac{100}{\bar{b}}(a_X - \bar{a}) \tag{15}$$

Previously, we have shown that B_C is a non-linear function of n_X in polysulphides. A very similar function is found for polyselenides.

In Fig. 4, A_S and B_S as well as A_{Se} and B_{Se} are shown as functions of the carbon atom number, n_C. The intercept, A, of the retention index equation (eqn. 13) increases with increasing n_C. This is exactly as expected since the second term on the right-hand side of eqn. 11 increases linearly with increasing n_C. The slope term, B, however, decreases with increasing terminal alkyl chains. To a first approximation, the dependence is assumed to be linear. The index increment of chalcogen atoms in an hypothetical chain without any terminal groups, B_X^0, is found by extrapolating to $n_C = 0$. The corresponding chromatographic free sorption energy is:

$$\delta G_X^0 = B_X^0 \bar{b} RT/100 \cdot \mathrm{SA}_X \tag{16}$$

The δG_X^0 values for S, Se and Te are 29.78, 30.12 and 31.7 J/mol · Å^2, respectively. The value for Te is not very reliable since only a few data points are available, and the effective radius is not precisely known. Most probably the δG_X^0 values are identical. They are clearly higher than with hydrocarbonaceous solute surfaces, which is attributed to the existence of the solute–eluent interactions exceeding the purely dispersive ones in hydrocarbons. While the proton-free chalcogenide chains are subject only to dispersion forces, the hydrocarbon solutes experience additional forces due to the heteronuclear C–H bonds. The dependence of B_X on the length of the alkyl groups may be explained by an increase in electron density in the chalcogen chain which enhances its electron pair–donor ability.

In Fig. 5 the retention index of various proton-free solutes is displayed as a function of the TSA. Several homonuclear solutes with very low or zero dipole moment like P_4, As_4, S_9, Se_8, S_{10} to S_{15} lie on a single straight line, which lies about 500 index units above the n-alkane line. The fact that chemically quite different species show practically the same dependence of retention on their surface area indicates that their respective interactions are qualitatively the same. Then, $\Delta G_{\mathrm{inter}}^{\mathrm{mob}}$ and $\Delta G_{\mathrm{inter}}^{\mathrm{stat}}$ are governed only by dispersion forces and entropy effects. As far as data are available, the ionization potentials of compounds of As, P, S and Se are fairly constant, in the range 9–10 eV. Also the dielectric constant does not seem to vary much. So the determining factor for dispersion forces is the molecular volume which, for these molecules, is practically proportional to TSA. From earlier investigations[10] we know that the area-normalized sorption entropy of sulphur rings is less negative than that of n-alkanes. Obviously the paraffinic chain allows for the greatest entropy loss when the sorbed solute state is formed. At the same time, the heat of sorption, $\Delta H^{\mathrm{sorption}}$, is more negative for the S rings, which indicates that the alkanes have a stronger solute–eluent interaction, due to the presence of C–H bonds.

The P_4 to S_{15} line runs almost parallel to the alkane line. If the absolute

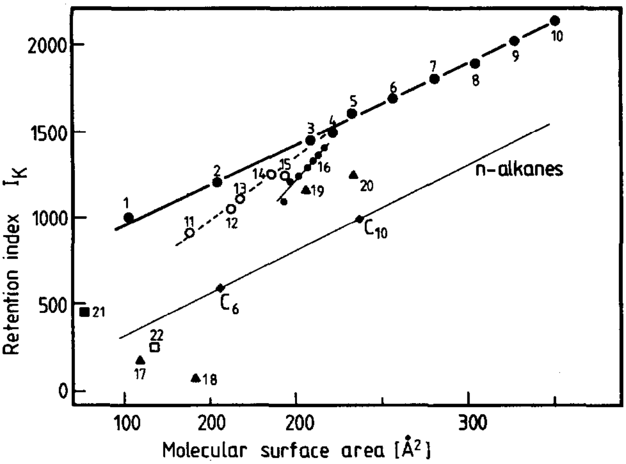


Fig. 5. Retention indices of proton-free solutes as a function of the molecular surface area. 1 = P_4; 2 = As_4; 3 = S_9; 4 = Se_8; 5–10 = S_{10}–S_{15}; 11 = S_6; 12 = S_7; 13 = Se_6; 14 = S_8; 15 = Se_7; 16 = sulphur–selenium rings Se_nS_{8-n}; 17 = benzene; 18 = hexafluorobenzene; 19 = hexachlorobenzene; 20 = hexabromobenzene; 21 = carbon disulphide; 22 = carbon tetrachloride. Reference line: *n*-alkanes, *i.e.*, *n*-hexane and *n*-decane.

number of hydrogen atoms present in the solute were the deciding factor, we would expect strong divergence of these lines. Since that is not observed, we propose that, as far as $\Delta G^{\mathrm{mob}}_{\mathrm{inter}}$ is concerned, the hydrogen atom density per unit area yields the difference between proton-free solutes and alkanes. In terms of chromatographic sorption free energy change, the retention difference of 500 index units in the ODS–methanol system amounts to 8.9 J/mol · Å².

At this point it appears appropriate to compare the solute solubility in the eluent with retention. S_8 has TSA = 190 Å and k' = 2.662 in the ODS–methanol system. Its saturation mole fraction is $3.5 \cdot 10^{-5}$ in methanol[11]. An hypothetical *n*-alkane with TSA = 190 Å would have 7.26 carbon atoms. For C_9 to C_{16}, $\ln c_{\mathrm{sat}} = 2.852 - 0.342 \cdot n_C$ was determined[12]. For $n_C = 7.26$ an extrapolation yields $x_{\mathrm{sat}} = 6.7 \cdot 10^{-2}$ in methanol and, from the n_C dependence of retention, a capacity factor, $k' = 0.934$. So, for equal TSA, x(alkane)/x(sulphur) ≈ 1900, but k'(sulphur)/k'(alkane) ≈ 3. This indicates that large solubility differences result in only small retention changes which, in turn, gives support to the idea that in water-free reversed-phase liquid chromatography (RPLC) the mobile and stationary phases are very similar.

The smaller homonuclear rings S_6, S_7, S_8, Se_6 and Se_7 do not lie on the above mentioned straight line; their retention is lower than expected. The reason for this behaviour is not known. We have proposed that it is due to a strongly disturbed cavity structure. An eluent cavity "lives" on the counteraction of cavity formation and solute–eluent interaction. Since a substantial fraction of the surface of these small rings is not accessible to the eluent, the degree of order of the eluent molecules around such solutes may be lower than usual, leading to an increased solubility in the eluent. The deviation of S_6 to S_9 is exactly the same when an C_8 instead of an C_{18} column is used. This indicates that it is indeed a solution phenomenon.

Still lower retention than that of the small homonuclear rings is exhibited by heteronuclear proton-free solutes like sulphur–selenium rings Se_nS_{8-n}, carbon disulphide, hexachlorobenzene and hexabromobenzene. However, their retention is still higher than that of equal size *n*-alkanes. This can be rationalized on the basis of high cavity energy and the lack of C–H interactions on the one hand and the occurrence of permanent dipole moments and strong bond dipoles on the other.

In hexachlorobenzene 82.2% of the exposed surface is chlorine, in hexabromobenzene 85.4% is bromine. It is worth comparing this with carbon tetrachloride where 99.5% of the area is chlorine. The area-normalized I_K of the latter is lower than that of *n*-alkanes. This means that aliphatic chlorine clearly produces less retention than aromatic chlorine. Hexafluorobenzene has an extremely low retention which cannot be attributed to ordinary dipole moments, but must be explained by strong hydrogen bonds to the eluent methanol. In that sense, the surface of hexafluorobenzene is polar and not solvophobic in methanol.

REFERENCES

1 H. J. Möckel, G. Welter and H. Melzer, *J. Chromatogr.*, 388 (1987) 255.
2 K. W. Bagnall, in A. F. Trotman-Dickenson (Editor), *Comprehensive Inorganic Chemistry*, Vol. 2, Pergamon, Oxford, 1973, p. 935.
3 R. A. Grigsby, K. J. Irgolic and F. F. Knapp, Jr., *J. Organomet. Chem.*, 253 (1983) 31.
4 T. Fojtik, H. J. Möckel and H. Melzer, in preparation.
5 H. J. Möckel, F. Höfler and H. Melzer, *Chromatographia*, 20 (1985) 471.
6 R. Steudel, H.-J. Mäusle, D. Rosenbauer, H. J. Möckel and T. Freyholdt, *Angew. Chem.*, 93 (1981) 402.
7 H. J. Möckel and H. Melzer, unpublished results.
8 H. J. Möckel and H. Melzer, in H. Aigner (Editor), *Königsteiner Chromatographietage 1984*, Waters, Königstein, 1984, pp. 76–86.
9 H. J. Möckel, *Fresenius' Z. Anal. Chem.*, 318 (1984) 116.
10 H. J. Möckel, *J. Chromatogr.*, 317 (1984) 589.
11 B. Meyer, *Sulphur, Energy, and Environment*, Elsevier, Amsterdam, 1977, p. 48.
12 H. J. Möckel and T. Freyholdt, *Fresenius' Z. Anal. Chem.*, 308 (1981) 401.
13 H. J. Möckel, in H. Engelhardt (Editor), *Practice of High Performance Liquid Chromatography*, Springer, Berlin, 1986.