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REVERSED-PHASE ION-INTERACTION CHROMATOGRAPHY OF SODIUM DIALKYLDITHIOCARBAMATES IN THE PRESENCE OF TETRAALKYLAMMONIUM SALTS

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SUMMARY

The elution behaviour of sodium dialkyldithiocarbamates (R_2NCS_2Na ; $R = CH_3$, C_2H_5 , $n-C_3H_7$ and $n-C_4H_9$) was examined by high-performance liquid chromatography on C_{18} -, C_8 - and C_{18} -bonded silica columns in the presence of tetraalkylammonium salts. The best separation of the carbamates was obtained from the C_8 -bonded column, with a mobile phase of methanol–1/15 *M* phosphate buffer (60:40) at pH 6.8 containing tetra-*n*-butylammonium bromide (0.025 *M*). This method was applied to the analyses of commercial R_2NCS_2Na . The results are in good agreement with those obtained by potentiometric titration.

INTRODUCTION

Dithiocarbamate salts are widely used as colouring or extracting agents or titrants for metal ions and also as pesticides or vulcanization accelerators. Many methods have been reported for the determination of R_2NCS_2Na ^{1–6}, but they are all specific only for the dithiocarbamate group and cannot simultaneously determine several R_2NCS_2Na salts with different alkyl substituents. The most suitable technique for their determination is high-performance liquid chromatography (HPLC).

In recent years, HPLC has been successfully applied to the separation of various dialkyldithiocarbamate–metal complexes in both normal-phase^{7–9} and reversed-phase^{10–12} modes for the simultaneous analysis of metals. On the other hand, Smith *et al.*¹³ reported the determination of R_2NCS_2Na by HPLC on a C_{18} -bonded silica column using transition-metal salts as ion-pairing reagents. The injection of more than two kinds of carbamate brought about the complicated interpretation of the results, because of the formation of mixed complexes. Kirkbright and Mullins¹⁴ used cetyltrimethylammonium bromide (CTAB) above its critical micelle concentration as

the surfactant in the mobile phase to achieve the micellar HPLC separation of five dithiocarbamates on a CN-bonded silica column. It is assumed in micellar chromatography that if a solute partitions to the micelle in the mobile phase, then its retention decreases with an increase of the micelle concentration. This is true for the above-mentioned separation: the retention of the carbamates decreased as the CTAB concentration increased.

We tried to determine R_2NCS_2Na directly or after esterification by HPLC with a column packed with hydrophobic styrene-divinylbenzene porous polymer beads, but could not achieve satisfactory precision. However, the application of a hydrophilic porous polymer column, together with tetraalkylammonium salts as ion-interaction reagents, gave satisfactory separation and quantification of four R_2NCS_2Na by HPLC¹⁵.

In this paper we describe the determination of R_2NCS_2Na by HPLC on a C_1 -, C_8 - or C_{18} -bonded silica column in the presence of tetraalkylammonium salts. This method was applied to the analysis of commercially available R_2NCS_2Na . The results indicate that the method is more precise than the previous one using the hydrophilic porous polymer column.

EXPERIMENTAL

Materials

The four kinds of R_2NCS_2Na ($R = CH_3$, C_2H_5 , $n-C_3H_7$ and $n-C_4H_9$) used in this study were obtained from Ohuchi Shinko (Tokyo, Japan) and are denoted by Me_2NCS_2Na , Et_2NCS_2Na , Pr_2NCS_2Na and Bu_2NCS_2Na , respectively. These were purified twice by recrystallization from ethanol. Methanol and deionized water were distilled, and all other chemicals from Wako (Osaka, Japan) were of analytical reagent grade.

Apparatus

A Shimadzu LC-4A system (Kyoto, Japan) was used for HPLC. The eluates were detected with a SPD-2AS UV detector at 254 nm. The C_1 -bonded silica column and the C_8 - and C_{18} -bonded ones (particle size 5 μm , 150 \times 4.6 mm I.D.) were obtained from Chemco (Osaka, Japan) and Gasukuro Kogyo (Tokyo, Japan), respectively. The column temperature was kept at 25°C, and the flow-rate of the eluents was 1.0 ml/min. All the eluents were filtered through a 0.45- μm membrane filter (Millipore) prior to use. A 10- μl portion of sample solutions was injected. The retention times and peak areas were measured with a Shimadzu C-R1A computer integrator.

A Kyoto Denshi AT-02 instrument (Kyoto, Japan) was used for potentiometric titration.

RESULTS AND DISCUSSION

Effects of eluent composition and tetraalkylammonium salts

First, the retention of the four R_2NCS_2Na salts was examined by changing the ratio of methanol to 1/15 *M* phosphate buffer (pH 6.8) in the eluent in the absence of tetraalkylammonium salts. Each R_2NCS_2Na was retained strongly on the C_1 , C_8

and C_{18} stationary phases and could not be eluted, so the retention was reduced by the addition of tetramethyl- or tetrabutylammonium bromide (TMAB or TBAB, respectively) or CTAB to the eluents. At a constant concentration of the tetraalkylammonium salt, the retention and separation of all four R_2NCS_2Na salts increased as the methanol content in the eluent was decreased: a large decrease led to considerable peak tailing. The retention of each R_2NCS_2Na also varied with both the stationary phase and the tetraalkylammonium salt.

Optimum separation conditions

In order to obtain the optimum separation of the four R_2NCS_2Na salts, the effect of the methanol content in the eluent on the retention and on the peak shape was investigated for each of the nine combinations stationary phase and tetraalkylammonium salt. The concentration of the latter was kept constant at 0.025 *M*.

Fig. 1 shows the results for the C_{18} stationary phase, which is used widely in the reversed-phase mode. The optimum eluent compositions, chosen with regard to both the separation and the retention times of R_2NCS_2Na , are marked with arrows. The liquid chromatograms obtained in such optimum eluents are depicted in Fig. 2. It is apparent that the four peaks are well separated in the presence of TMAB, TBAB or CTAB. However, the considerable peak tailing is observed with both TMAB and TBAB.

The equivalent results for the C_1 stationary phase are shown in Figs. 3 and 4. The peak tailing is much less marked than with the C_{18} phase, but the separation of Me_2NCS_2Na and Et_2NCS_2Na is poor. The four solutes cannot be separated at all in the presence of TMAB.

As shown in Figs. 5 and 6, the C_8 stationary phase gives sharp, well separated peaks of the four R_2NCS_2Na . In particular, the addition of TBAB to the eluent of containing 60% methanol results in a complete separation within 10 min (Fig. 6b).

The effect of TBAB concentration on the retention was examined over a range

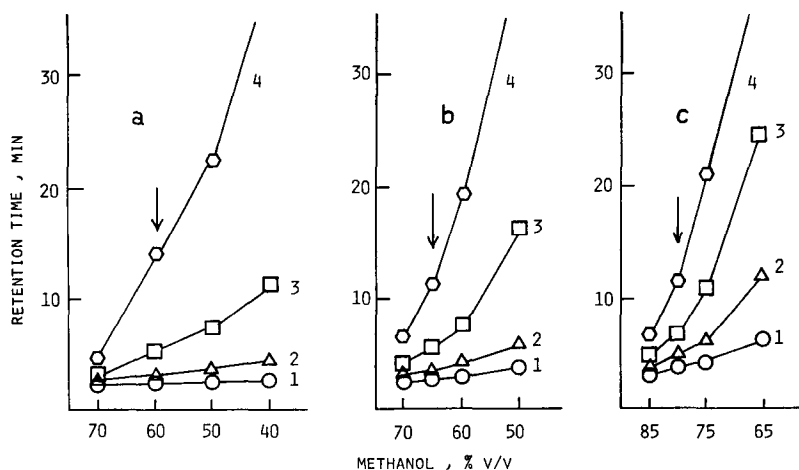


Fig. 1. Effect of methanol content in the eluent methanol-1/15 *M* phosphate buffer (pH 6.8) on the retention of R_2NCS_2Na on C_{18} -bonded silica in the presence of (a) TMAB, (b) TBAB and (c) CTAB. Carbamates: 1 = Me_2NCS_2Na ; 2 = Et_2NCS_2Na ; 3 = Pr_2NCS_2Na ; 4 = Bu_2NCS_2Na .

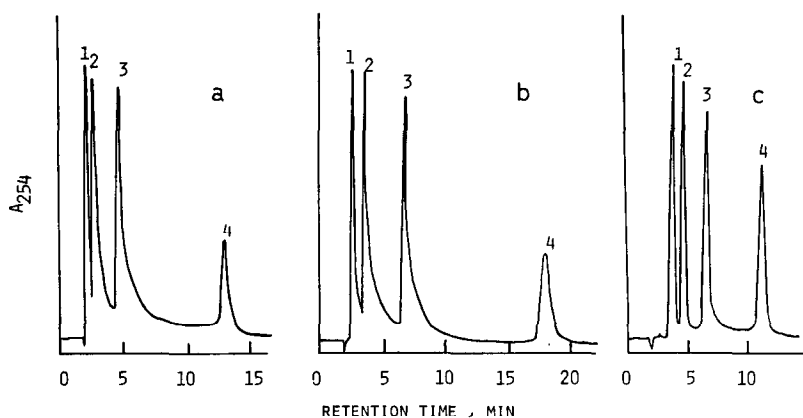


Fig. 2. Separation of R_2NCS_2Na in the eluents marked with arrows in Fig. 1. Other details as in Fig. 1.

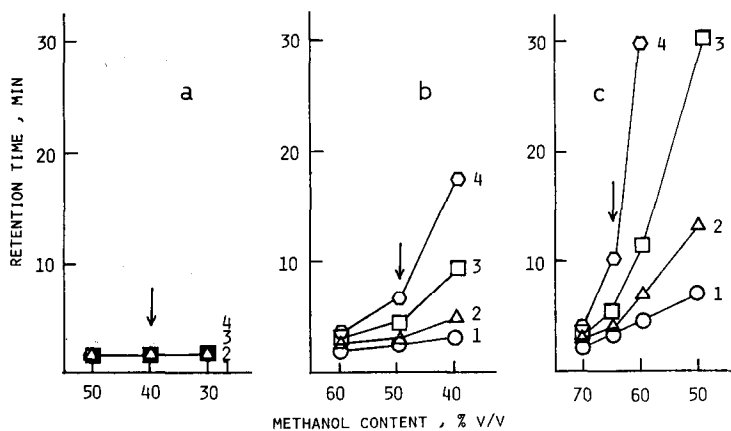


Fig. 3. Effect of methanol content in the eluent on the retention of R_2NCS_2Na on C_1 -bonded silica. Other details as in Fig. 1.

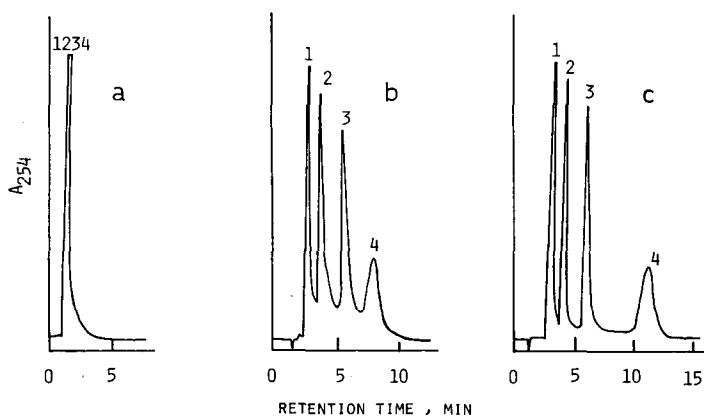


Fig. 4. Separation of R_2NCS_2Na in the eluents marked with arrows in Fig. 3. Other details as in Fig. 3.

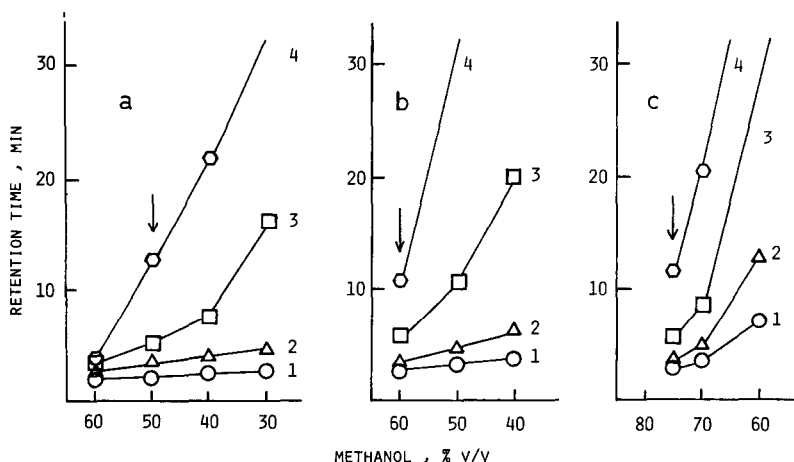


Fig. 5. Effect of methanol content in the eluent on the retention of R_2NCS_2Na on C_8 -bonded silica. Other details as in Fig. 1.

of 0.001–0.1 M . A linear relationship was obtained between \log (capacity factor) and \log (TBAB concentration), as shown in Fig. 7. A decrease in the retention of R_2NCS_2Na is observed as the concentration of TBAB increases. This suggests an important role for micelles in this system, as previously reported for CTAB¹⁴. The optimum separation was obtained by eluting with 60:40 methanol–1/15 M phosphate buffer (pH 6.8) containing 0.025 M TBAB. Under these conditions, the retention times of the solutes are: Me_2NCS_2Na , 2.42 min; Et_2NCS_2Na , 3.00 min; Pr_2NCS_2Na 4.70 min and Bu_2NCS_2Na 9.84 min (see Fig. 6b).

Analytical calibration and application

To evaluate the quantitative applicability of the method, standard reference samples containing each R_2NCS_2Na over the concentration range 0.1–1.0 mg/ml were determined, and each calibration curve was constructed by plotting the peak

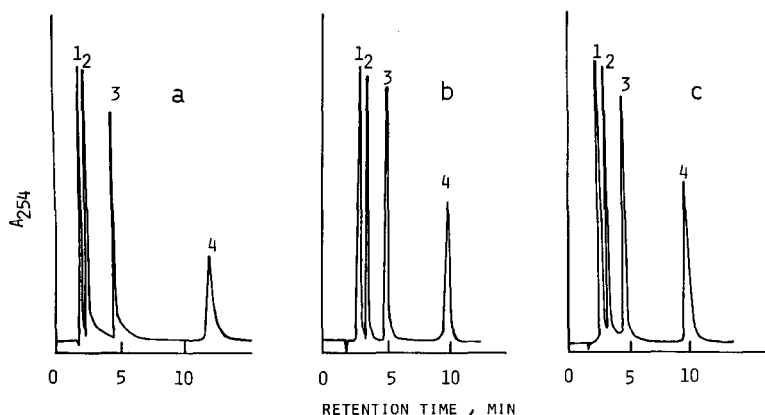


Fig. 6. Separation of R_2NCS_2Na in the eluents marked with arrows in Fig. 5. Other details as in Fig. 5.

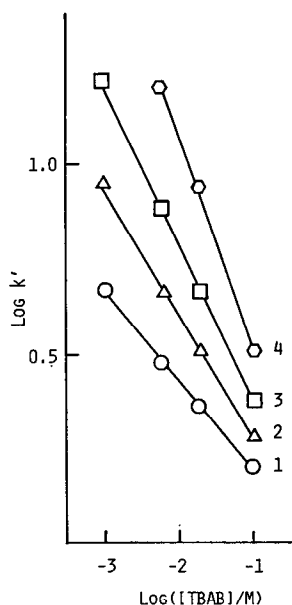


Fig. 7. Variation of log capacity factor (k') with log concentration of TBAB. Numbers as in Fig. 1.

TABLE I

REGRESSION ANALYSIS

Y = concentration of R_2NCS_2Na (10^{-6} M); X = peak area.

Sample	Regression equation	Correlation coefficient
Me_2NCS_2Na	$Y = 1.6489X + 0.0034$	0.999
Et_2NCS_2Na	$Y = 1.9061X - 0.0021$	1.000
Pr_2NCS_2Na	$Y = 2.3502X + 0.0069$	0.998
Bu_2NCS_2Na	$Y = 2.9426X - 0.0072$	0.998

area against the concentration of R_2NCS_2Na . Table I gives the results for these regression analyses and indicates good applicability of the method to the determination of R_2NCS_2Na .

The proposed HPLC method was applied to the analysis of commercial

TABLE II

COMPARISON STUDY OF THE ANALYSIS OF COMMERCIAL R_2NCS_2Na

Sample	This method		Potentiometric method		G-320 method	
	Purity (%)	c.v.	Purity (%)	c.v.	Purity (%)	c.v.
Me_2NCS_2Na	78.72	0.32	78.71	0.27	78.69	1.34
Et_2NCS_2Na	75.88	0.15	75.89	0.24	75.94	1.15
Bu_2NCS_2Na	51.20	0.87	51.22	0.95	51.43	1.87

R_2NCS_2Na , and the results obtained were compared with those determined by both the potentiometric method¹⁶ and the G-320 method¹⁵ using hydrophilic porous polymer beads (cross-linked poly(vinyl alcohol); Asahipack G-320 from Asahi Kasei, Tokyo, Japan) as column packing with methanol-water (30:70) containing TMAB (0.10 M) as eluent. As shown in Table II, the purities for each sample determined by the three methods are in good agreement. The coefficients of variation (C.V.) for this method are comparable with those for the potentiometric method and smaller than those for the G-320 method.

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