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# Gas-Liquid Chromatographic Retention Data for Some *iso*Thiocyanates

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The gas-chromatographic behaviour of 32 *iso*thiocyanates on various stationary phases has been studied. The investigation comprises saturated and unsaturated, branched and unbranched aliphatic *iso*thiocyanates, aromatic *iso*thiocyanates, ω-methylthio-substituted compounds of the type $CH_3S(CH_2)_nNCS$ and *iso*thiocyanates containing ester- or sulfone-groupings. The results are mainly presented in retention time/reciprocal temperature diagrams.

As pointed out in a preliminary communication [1] the occurrence in higher plants of mixtures of mustard oil glucosides, enzymically hydrolyzed to mixtures of *iso*thiocyanates, renders the analytical separation of the latter a matter of considerable interest. But also from a gaschromatographic point of view considerable interest is associated with a study of this group of organic compounds.

It is the purpose of the present communication to present gas-liquid chromatographic retention data for a rather wide selection of *iso*thiocyanates, chromatographed on various stationary phases. Those employed include polar phases (dinonyl phthalate and tritolyl phosphate) as well as unpolar phases (squalane, Apiezon L, silicone grease and elastomer). The results are given as plots of logarithm of retention times *vs.* reciprocal values of the absolute temperature.

## APPARATUS

The apparatus used in the present investigation was a Griffin & George gas chromatograph (mark II), equipped with a katharometer detector of limited sensitivity. As many of the *iso*thiocyanates investigated are difficultly accessible, small quantities had to be used, requiring the highest obtainable sensitivity of the detector. The electrical current through the katharometer was fixed at 150 mA, which is near the upper limit of the detector. Furthermore, it was necessary to use a reduced outlet pressure on the column, though this arrangement results in lower efficiency. The outlet pressure was fixed at 40 mm by means of the manostat previously described [2].

*Table 1.* Summary of the columns used.

| Column | Stationary phase | character | Solid support | Column lenght |
|---|---|---|---|---|
| A | Apiezone L | unpolar | Celite | 1.8 m |
| B | Silicone elastomer | unpolar | Celite | 1.8 m |
| C | Silicone grease | unpolar | firebrick | 1.8 m |
| D | Squalane | unpolar | Celite | 1.8 m |
| E | Dincnyl phthalate | polar | firebrick | 0.9 m |
| F | Tritolyl phosphate | polar | Celite | 1.8 m |

Initially the samples were introduced by means of a micro syringe through a rubber cap. This system, however, was unsatisfactory and was exchanged with an ampoule breaker of stainless steel placed in a rubber stopper (Fig. 1). A sealed capillary tube provided with a little bulb (4—5 mm Ø) serves as the vessel and is placed at the bottom of the ampoule breaker. After temperature equilibrium has been attained the vessel is crushed by turning the piston. The heating element (30 Watt) is regulated by means of a variable transformer and compensates for the heat loss through the ampoule breaking system.

Some of the compounds investigated (*e.g.* many of the aliphatic *iso*thiocyanates) have so high vapour pressures that heating could be omitted. With the less volatile compounds it was impossible to get satisfactory chromatograms without heating. In all cases it was important to break the ampoule totally. If only the capillary was broken too long a time was required to force the sample completely into the column resulting in tailing.

For the present purpose the described procedure proved satisfactory. It was possible to work practically without any loss of material and a precise weighing of the samples thus was practicable. As an additional convenience, the air in the ampoule gives rise to a reliable zero point on the chromatograms (the air peak).

## STATIONARY PHASES ETC.

All columns were made of glass and had a diameter of 6 mm. They were available in U-shaped sections of 90 cm length. In most cases a total column length of 1.8 m was used. As stationary phases polar as well as unpolar systems were employed. In four of the columns, Celite 545, from which most of the finest material had been eliminated, served as the solid support, whereas two other columns were packed with firebrick, sieved to a definite particle size. The properties of the individual columns are listed in Table 1.

Helium was used throughout as a carrier gas at a rate of 1 litre per hour, measured at the column inlet. The standard sample size was 2—5 mg.

## ALIPHATIC *iso*THIOCYANATES

The chromatographic behaviour of aliphatic five-component mixtures was studied on six different columns, specified in Table 1. The mixtures had the following compositions:

| | |
|---|---|
| Methyl *iso*thiocyanate | ( 1— 3 %) |
| Ethyl *iso*thiocyanate | ( 16 %) |
| *Iso*propyl *iso*thiocyanate | (18—21 %) |
| Allyl *iso*thiocyanate | (31—32 %) |
| *Iso*butyl *iso*thiocyanate | (29—33 %) |

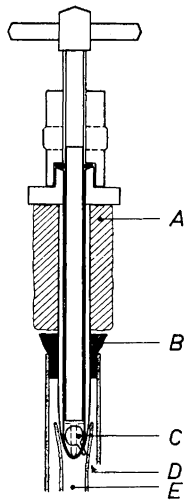


*Fig. 1.* Ampoule breaker. A, Heating element. B, Rubber stopper. C, Ampoule, D, Carrier gas inlet. E, To the column.

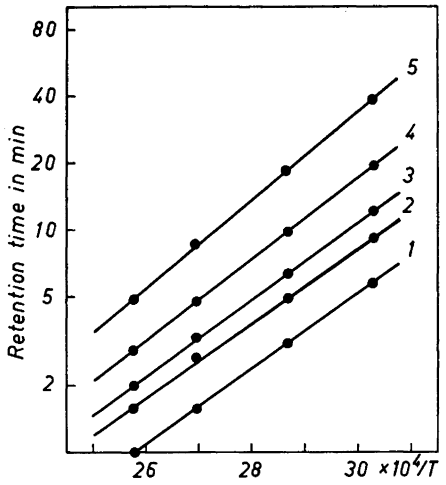


*Fig. 2.* Effect of temperature on retention of aliphatic *iso*thiocyanates. 1, Methyl. 2, Ethyl. 3, *Iso*propyl. 4, Allyl. 5, *Iso*butyl. Column: Apiezon grease L/Celite.

An expression of column efficiency in terms of theoretical plate number $n$ can be calculated by the equation: $n = 16 \cdot l^2/d^2$, in which $l$ represents the retention time and $d$ the peak width, the last quantity being determined as the segment of base line intercepted by tangents to the inflection points on either side of the peak.

Under the conditions used the squalane column proved to be the most efficient of the unpolar columns employed. But silicone grease on firebrick also appeared to be a good stationary phase for aliphatic *iso*thiocyanates. It should be mentioned that all the employed stationary phases produced well-shaped, symmetric peaks. The components of the above mentioned mixtures emerged from the columns in the same order as listed, *i.e.* according to increasing boiling points.

Although the columns used had only a rather limited number of theoretical plates (100—800), good separation of the components was achieved. The order of appearance of the individual components was not always the same, as apparent from Figs. 2—5. The ordinate is a logarithmic scale giving the retention time in minutes whereas the abscissa represents $10^4$ divided by the absolute temperature.

In addition to the above mustard oils, chromatographic runs of propyl, $\alpha$-methallyl, $\beta$-methallyl, *iso*pentyl and 4-pentenyl *iso*thiocyanate were made on the *silicone grease/firebrick column* (Fig. 4). It appears that allyl, propyl and $\alpha$-methallyl *iso*thiocyanate migrate at almost the same rate. Hence, this column is not suited for their separation. *Iso*butyl and $\beta$-methallyl *iso*thiocyanate also run closely together on the column.

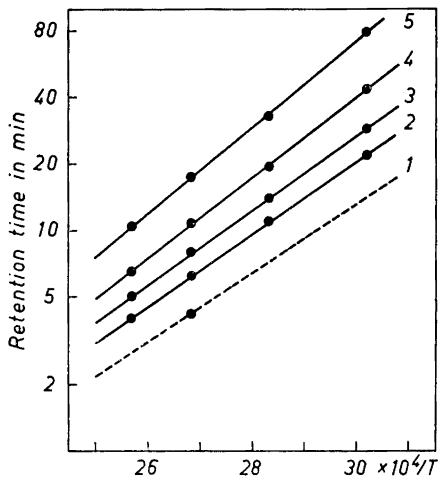


*Fig. 3.* Effect of temperature on retention of aliphatic *iso*thiocyanates. 1, Methyl (The curve has been estimated from only one point!). 2, Ethyl. 3, *Iso*propyl. 4, Allyl. 5, *Iso*butyl. Column: Silicone elastomer/Celite.

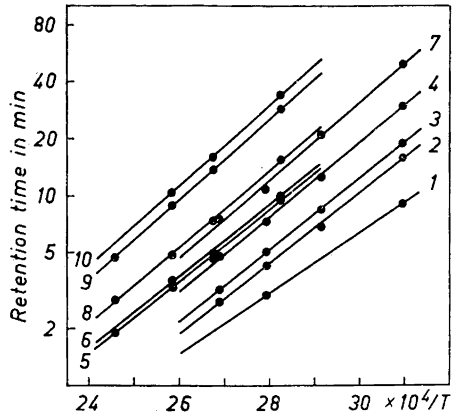


*Fig. 4.* Effect of temperature on retention of aliphatic *iso*thiocyanates. 1, Methyl. 2, Ethyl. 3, *Iso*propyl. 4, Allyl. 5, Propyl. 6, *α*-Methallyl. 7, *Iso*butyl. 8, *β*-Methallyl. 9, *Iso*pentyl. 10, 4-Pentenyl. Column: Silicone grease/firebrick.

All isothiocyanates mentioned were investigated on the *squalane column*. In this case the investigation was extended to include 3-butenyl, *n*-butyl and *trans*-crotyl *iso*thiocyanate as well as methyl 4-*iso*thiocyanatobutyrate (Fig. 5). It was not possible to distinguish between *iso*butyl and *β*-methallyl *iso*thiocyanate. The *n*-butyl isomeride and *trans*-crotyl *iso*thiocyanate also run at about the same rate with this filling, but between the three compounds: allyl, propyl and *α*-methallyl *iso*thiocyanate a better separation was achieved on the squalane column than on the silicone grease column. Under the conditions used the components emerged from the squalane column in the following order:

Methyl, Ethyl, *Iso*propyl, Allyl, Propyl,
*α*-Methallyl, *Iso*butyl and *β*-Methallyl,
3-Butenyl, *n*-Butyl, *trans*-Crotyl, *Iso*pentyl,
4-Pentenyl *iso*thiocyanate, and
Methyl 4-*iso*thiocyanatobutyrate.

The above five-component mixture was also investigated on the polar phases dinonyl phthalate (Fig. 6) and tritolyl phosphate (Fig. 7). It appears from the diagrams that the separation on the phthalate of ethyl and *iso*propyl *iso*thiocyanate is not as good as on the unpolar phases. On the tritolyl phosphate column the peaks of the two *iso*thiocyanates actually coincidide. The tritolyl column was used also in experiments with propyl, *α*-methallyl, *β*-methallyl, *n*-butyl, 3-butenyl, *trans*-crotyl, *iso*pentyl and 4-pentenyl *iso*thiocyanate. On a polar stationary phase there will be a tendency for a compound contain-

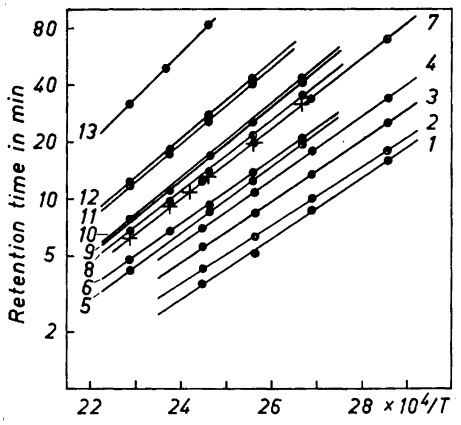


*Fig. 5.* Effect of temperature on retention of aliphatic *iso*thiocyanates. 1, Methyl. 2, Ethyl. 3, *Iso*propyl. 4, Allyl. 5, Propyl. 6, *a*-Methallyl. 7, *Iso*butyl and *β*-methallyl (+). 8, 3-Butenyl. 9, *n*-Butyl. 10, *trans*-Crotyl. 11, *Iso*pentyl. 12, 4-Pentenyl. 13, Methyl 4-*iso*thiocyanatobutyrate. Column: Squalane/Celite.

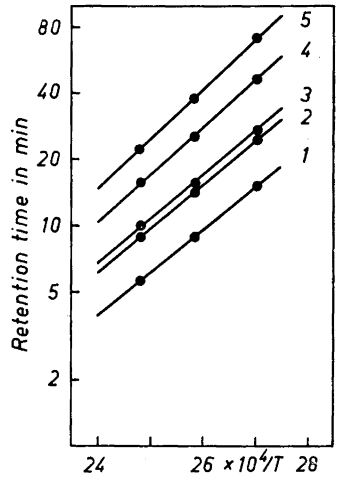


*Fig. 6.* Effect of temperature on retention of aliphatic *iso*thiocyanates. 1, Methyl. 2, Ethyl. 3, *Iso*propyl. 4, Allyl. 5, *Iso*butyl. Column: Dinonyl phthalate/firebrick.

ing double bonds to be retarded. This also applies to the tritolyl phosphate column where different retention times are observed for *n*-butyl and 3-butenyl *iso*thiocyanate (Fig. 7). In the case of the allyl-propyl system, however, the result is not comparable. According to boiling points, the allyl compound should be expected to emerge before the propyl compound, and this is in fact the case with an unpolar phase. With a polar system, however, the two tendencies will be opposite, and under the present conditions no separation of the two *iso*thiocyanates occurred. The compounds investigated on the tritolyl phosphate column emerged in the following order:

Methyl, Ethyl and *iso*propyl,
Allyl and propyl, *a*-Methallyl, *Iso*butyl,
*β*-Methallyl, *n*-Butyl, 3-Butenyl,
*trans*-Crotyl, *Iso*pentyl, and 4-Pentenyl *iso*thiocyanate.

## AROMATIC *iso*THIOCYANATES

Some aromatic *iso*thiocyanates were chromatographed on the silicone elastomer column under the conditions already described. The compounds were phenyl, benzyl, 1-phenylethyl, 2-phenylethyl, *o*-methoxybenzyl, *m*-methoxybenzyl, *p*-methoxybenzyl and 3-benzoyloxypropyl *iso*thiocyanate, and they emerged from the column in the above order (Fig. 8). The benzyl and the 1-phenylethyl compounds run closely together, and the

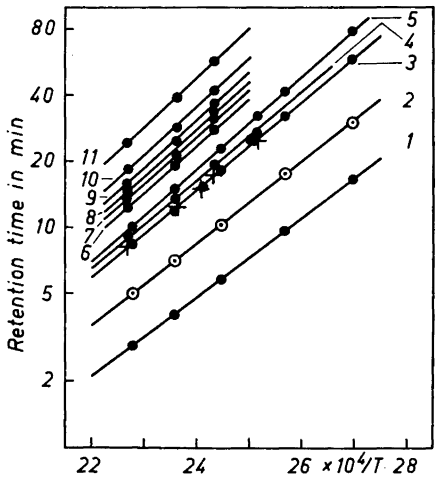


*Fig. 7.* Effect of temperature on retention of aliphatic *iso*thiocyanates. 1, Methyl. 2, Ethyl and *iso*propyl (o). 3, Allyl and propyl (+). 4, *α*-Methallyl. 5, *Iso*butyl. 6, *β*-Methallyl. 7, *n*-Butyl. 8, 3-Butenyl. 9, *trans*-Crotyl. 10, *Iso*pentyl. 11, 4-Pentenyl. Column: Tritolyl phosphate/Celite.

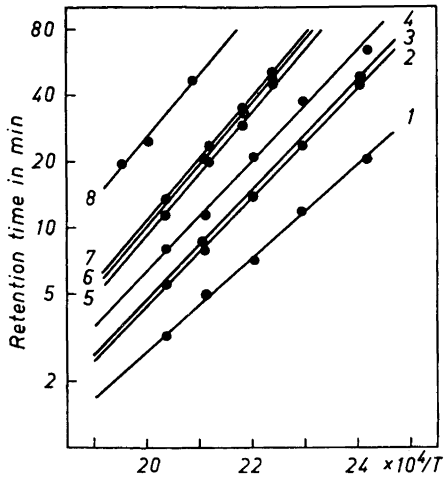


*Fig. 8.* Effect of temperature on retention of aromatic *iso*thiocyanates. 1, Phenyl. 2, Benzyl. 3, 1-Phenylethyl. 4, 2-Phenylethyl. 5, *o*-Methoxybenzyl. 6, *m*-Methoxybenzyl. 7, *p*-Methoxybenzyl. 8, 3-Benzoyloxypropyl. Column: Silicone elastomer/Celite.

same applies to the three methoxybenzyl *iso*thiocyanates. Difficulties may arise in connection with 3-phenylpropyl *iso*thiocyanate (which is not included in this investigation) as it probably runs closely to *o*-methoxybenzyl *iso*thiocyanate. The next number in this series (4-phenylbutyl *iso*thiocyanate) would be expected to emerge later than all the methoxybenzyl compounds.

## METHYLTHIOALKYL *iso*THIOCYANATES

This type of isothiocyanates, characterized by containing a terminal methylthio-grouping in a straight alkyl chain, have the general formula $CH_3S(CH_2)_nNCS$. The eight homologues from 2-methylthioethyl *iso*thiocyanate (n = 2) to 9-methylthiononyl *iso*thiocyanate (n = 9) were chromatographed on the silicone elastomer column (Fig. 9). This column allowed good separations of all the *iso*thiocyanates in eight-component mixtures.

In Fig. 10 the retention times (on a logarithmic scale) of some eight-component mixtures at different temperatures are given as functions of n in the above general formula. As in similar cases (*e.g.* fatty acid methyl esters [2]) straight lines are obtained. This can be of diagnostic value in connection with the identification of *ω*-methylthioalkyl *iso*thiocyanates.

## SULFONE *iso*THIOCYANATES

Chromatographic runs in the range 200—240° of the two sulfone *iso*thiocyanates *cheirolin*, $CH_3SO_2(CH_2)_3NCS$, and *erysolin*, $CH_3SO_2(CH_2)_4NCS$, were performed on the silicone elastomer column. It appeared that under these

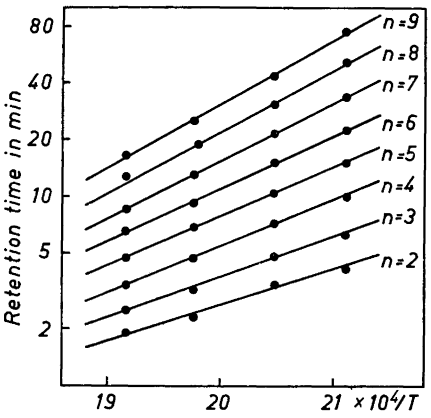


*Fig. 9.* Effect of temperature on retention of ω-methylthio-substituted *iso*thiocyanates. 2-Methylthioethyl (n = 2). 3-Methylthiopropyl (n = 3). 4-Methylthiobutyl (n = 4). 5-Methylthiopentyl (n = 5). 6-Methylthiohexyl (n = 6). 7-Methylthioheptyl (n = 7). 8-Methylthioöctyl (n = 8). 9-Methylthiononyl (n = 9). Column: Silicone elastomer/Celite.

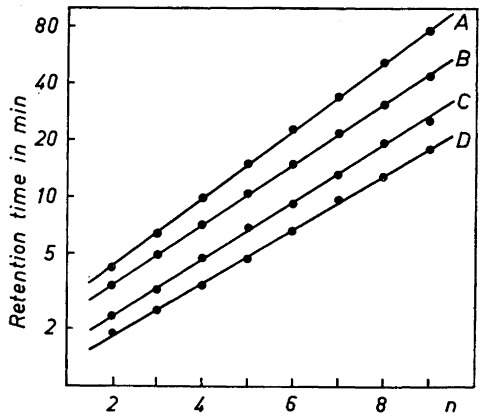


*Fig. 10.* Retention for methylthioalkyl *iso*thiocyanates as function of n in the general formula: $CH_3S(CH_2)_nNCS$ at different temperatures. A, 201°. B, 215.5°. C, 233°. D, 249°. Column: Silicone elastomer/Celite.

conditions the two sulfones almost coincided with the curves, n = 6 and n = 7, respectively, of Fig. 9. Further work on the gaschromatographic behaviour of the sulfones is planned.

## APPLICATION

The present investigation has demonstrated that gas chromatography is a very useful method for separation, quantitative determination and identification of *iso*thiocyanates. Even with columns of a rather low efficiency — as in the present work — it is possible to solve many analytical problems. Under such conditions it is important to employ a stationary phase, which is well suited for the problem in question; perhaps the use of more than one column would be advantageous.

## EXPERIMENTAL

Iso*thiocyanates*. The purity of the *iso*thiocyanates used in the present investigation ranged from 90 % to above 99 %. They were all supplied by professor A. Kjær, and references to their syntheses and properties may be found in a recent comprehensive survey [3].

*Column A*. The stationary phase consisted of 20 % Apiezon grease L on Kieselguhr, prepared as follows: 300 g of Celite 545 (Johns Manville Co., Ltd.) was size-graded by repeated suspension in water in a 5 l beaker and all the material that did not settle out in less than 2 min was discarded. The procedure was repeated twice, and the product was oven-dried for 3—4 h at 150°. The powder was treated in vacuum with sufficient amounts of a solution of Apiezon grease L in chloroform to produce a slurry. The solvent was then slowly

evaporated and the last traces were removed by oven-drying at 110° for 30 min. The material was carefully packed into U-shaped column sections. The pressure drop over the column with a rate of carrier gas of 1.0 l He per hour was 405 mm at 24° and 490 mm at 124°.

*Column B.* The stationary phase consisted of 25 % silicone elastomer (E 301) on Celite. In this case the suspension procedure was performed only once, and the material was heated in a muffle oven for 3 h at 300° and then washed with conc. hydrochloric acid and with water. After drying for 1 h at 145° the material was treated with the stationary phase as described for column A. The pressure drop over the column with a rate of carrier gas of 1.0 l He per hour was 755 mm at 24°, 935 mm at 124° and 1 130 mm at 224°.

*Column C.* The stationary phase consisted of 25 % silicone grease on firebrick. The silicone grease was "Dow Corning" from wich a great part of the low-molecular constituents had been removed by precipitation from a 15 % solution in ethyl acetate by adding the same volume of 96 % ethanol. The firebrick was prepared by crushing a brick and sieving the material; the 40 – 50 mesh fraction was used for the preparation of this column. The pressure drop over the column with a rate of carrier gas of 1.0 l He per hour was 405 mm at 24° and 525 mm at 124°.

*Column D.* The stationary phase consisted of 25 % squalane on Celite, pretreated as described for column B. The squalane was a commercial product (B.D.H.), the purity of which was first controlled by gas chromatography on column C at 270°. The pressure drop over the column with a rate of carrier gas of 1.0 l He per hour was 565 mm at 24° and 690 mm at 124°.

*Column E.* The stationary phase consisted of 30 % dinonyl phthalate on firebrick. In this case the 60 – 80 mesh fraction was selected for preparation of the column. The pressure drop over the column with a rate of carrier gas of 1.0 l He per hour was 890 mm at 24° and 1 070 mm at 124°.

*Column F.* The stationary phase consisted of 25 % tritolyl phosphate on Celite. The solid support was pretreated as described for column B, and the stationary phase was prepared by distillation of a technical grade tri-*o*-tolyl phosphate, the fraction boiling over the range 190 – 230° at 0.2 mm being used. The pressure drop over the column with a rate of carrier gas of 1.0 l He per hour was 685 mm at 24° and 850 mm at 124°.

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