

SVENDSEN², on the other hand, reported no difficulty in separating propylhexedrine and methamphetamine on a column containing QF-1 on silanized Chromosorb W.

The results described above indicate that conversion of tertiary amines to olefins by Hofmann exhaustive methylation prior to gas chromatography is a useful technique in cases where separation is incomplete or excessive tailing occurs. Quantitative application of the technique is illustrated, and has an inherent advantage in that the products have shorter retention times, thereby shortening analysis time. A further important application is in qualitative identification of an unknown amine by comparison of the retention time before and after exhaustive methylation with an authentic reference compound.

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Solid support as subtractor in gas chromatographic trace analysis*

Subtractive analytical techniques, in which certain classes of compounds are selectively removed from complex samples, have often been described in GLC¹⁻³. To this end precolumns with a selective reagent have been used. In a previous communication it was stated that the selective adsorption of traces of polar compounds by the solid support of a nonpolar GLC column may be used in the analysis of air contamination⁴. Following up this work, a more generally applicable procedure for this kind of selective retention has been investigated for trace analysis. For this purpose a precolumn packed with an active solid support and positioned in front of a GLC partition column has been tested.

Experimental

The experiments were carried out with an Aerograph 1520 gas chromatograph equipped with a flame ionisation detector (F.I.D.). Precolumns of 20 cm × 1/8 in. O.D. packed with 80-100 mesh Chromosorb P were used for the selective retention of polar substances as well as those coated with 0.1% of Apiezon L. The precolumn used was placed in the oven between the injector and the partition column.

Nitrogen was used as carrier gas and with a 75 lb/sq. in. pressure a flow of 15 ml/min was maintained. For separation a 3 m × 1/8 in. O.D. column was used

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packed with 10% Carbowax 1500 on silanised 80-100 mesh Chromosorb W. The oven was kept at 56°, the injector and detector, respectively, at 200° and 230°.

Different polar and nonpolar compounds were dissolved in concentrations of 0.1% (v/v) in various solvents (Table I). The resulting test solutions were analysed with the partition column as well as with the combination of precolumn and partition column. To get an impression of the maximal quantities of polar substances which show selective retention, some 1% (v/v) solutions of polar compounds (Table I) were tested in the same way. In all cases samples of 2 μ l were injected.

TABLE I

COMPOSITION OF TEST SOLUTIONS

<i>Solvent</i>	<i>Dissolved compounds</i>	<i>Concentration of each compound (vol. %)</i>
Water	Acetone, isopropyl alcohol, isobutyl acetate	0.1
Nitrobenzene	Pentane, acetone, isopropyl alcohol, isobutyl acetate, <i>o</i> -xylene	0.1
Pentane	Acetone, isopropyl alcohol, isobutyl acetate, <i>o</i> -xylene	0.1
Carbon disulfide	Pentane, isopropyl alcohol, isobutyl acetate, <i>o</i> -xylene	0.1
Carbon disulfide	Benzene, toluene, <i>m</i> -diethyl benzene	0.1
Carbon disulfide	Methyl ethyl ketone, methyl propyl ketone	0.1
Carbon disulfide	Hexane, octane, decane	0.1
Carbon disulfide	Methyl acetate, ethyl acetate	0.1
Carbon disulfide	Methanol, ethanol, isopropyl alcohol, <i>sec.</i> -butyl alcohol	0.1
Carbon disulfide	Acetone	1
Carbon disulfide	Ethanol	1
Carbon disulfide	Isobutyl acetate	1

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In other experiments 1 μ l of a mixture of equal volumes of benzene, toluene, isopropyl alcohol, isobutyl acetate and methyl propyl ketone was injected into an intravenous bottle of 75 ml (provided with a serum cap) and then vaporized. By means of a Hamilton gas tight syringe 1 ml samples of the resulting artificial atmosphere were taken and analysed both with and without precolumn.

Results and discussion

It became clear from the results of the first four test solutions (Table I) that there is no selective retention when a polar solvent is used. This in contrast to a non-polar solvent (Fig. 1). The excess of polar solvent obviously prevents the adsorption of polar solutes. In case of an aromatic hydrocarbon such as *o*-xylene better elution (less tailing and retardation) was obtained with a precolumn packed with 0.1% Apiezon L coated Chromosorb P, than with a precolumn with a non-coated packing. With a 5% Apiezon L coating this elution was even better, but the adsorption of more polar compounds was not complete any more.

In analysing solutions of representatives of various groups of compounds carbon disulfide has been used as the solvent, because it has no significant response when using a F.I.D. It became evident however that substances which enter the detector con-

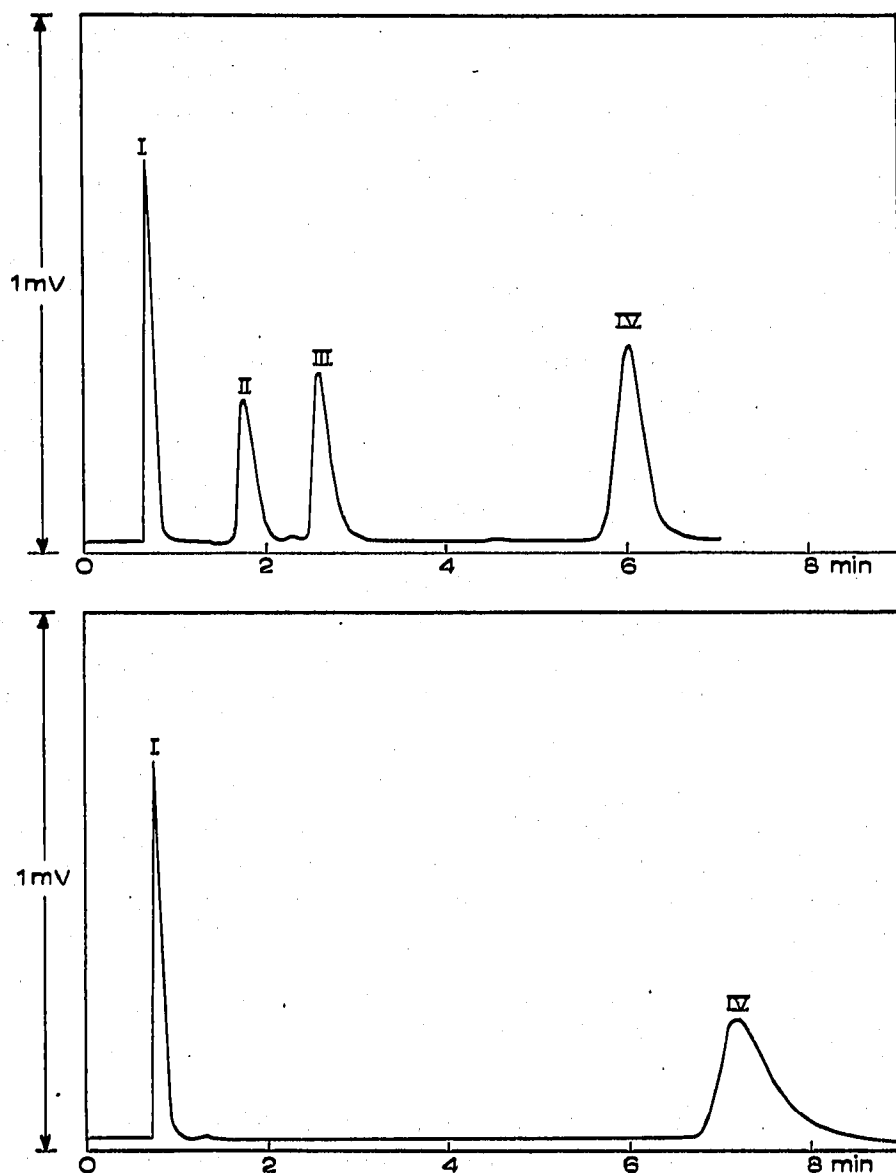


Fig. 1. Subtraction of polar substances by Chromosorb P. Top: partition column; bottom: partition column plus subtractive precolumn. Sample: 2 μ l of a carbon disulfide solution with 0.1% of respectively pentane (I), isopropyl alcohol (II), isobutyl acetate (III) and *o*-xylene (IV). Partition column: 3 m \times 1/8 in. O.D., 10% Carbowax 1500 on 80-100 mesh silanised Chromosorb W. Precolumn: 20 cm \times 1/8 in. O.D., 80-100 mesh Chromosorb P coated with 0.1% Apiezon L. Column and precolumn temperature: 56°. Electrometer: R.1, Att. 16.

currently with carbon disulfide will show an attenuated response, just as in the case of water¹⁰.

Alkanes show only little retardation and tailing when a precolumn is used. Aromatic hydrocarbons elute with somewhat more retardation and tailing. Esters, ketones and alcohols are no longer observed.

However, if the chromatograms are produced at a much less important attenuation, "peaks" of polar compounds are found. They have much longer retention times than without the precolumn and have very big peak widths so that they hardly rise above the base line. When water is injected during such a very much retarded elution a normal peak is observed, with an area dependent on the time between the

water injection and the preceding injection and with an expulsion time (the time between injection of water and the elution of the peak) about equal to the retention time of the polar compound without precolumn. Evidently the retarding influence of the precolumn is eliminated by water.

The disappearance of polar substances when precolumns packed with an active solid support are used, is not caused by permanent adsorption. It is attributed to an important retardation by weak, reversible adsorption resulting in such an increase of peak width that polar compounds are virtually no longer observed with respect to nonpolar ones. The weakly polar aromatic hydrocarbons only show this property to a smaller extent. The appearance of this phenomenon is not only dependent on the polarity of a substance but also on the temperature of the precolumn. At higher temperatures there is less retardation. In a homologous series the lower members are less retarded than the higher ones at a certain temperature.

With the more concentrated solutions the influence of the precolumn is much smaller. For polar compounds tailing peaks are observed with little retardation. From these results and from those from the more dilute solutions we gather that selective retardation may be useful in gas chromatographic analysis when the samples do not contain more than 2 μg per polar compound.

Selective retardation of polar compounds was also observed for the artificial atmosphere.

Conclusions

Traces of polar compounds may be retarded considerably by weak, reversible adsorption on a solid support in a precolumn, so that after GLC analysis they are no longer observed with respect to nonpolar ones. This property may be useful in trace analysis of solutions (with nonpolar solvents) and in that of air and gas samples. Furthermore it may be used for the removal of one component whose elution band overlaps that of a nonpolar peak of interest.

The advantages of the above mentioned procedure over the one published previously⁹ are:

(1) The precolumns used retard a bigger quantity of a polar compound than a normal nonpolar coated column. This is evident from the fact that precolumns loaded with 5 % Apiezon L coated Chromosorb P are less useful for selective retardation.

(2) Precolumns as described may be used in combination with any kind of GLC partition column.

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