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GAS CHROMATOGRAPHY IN VAPOURS AS MOBILE PHASES

A SHORT REVIEW

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SUMMARY

Chromatography in condensable gases and vapours, including the vapours of water and pure formic acid, has been investigated. Considerable advantages of this variant of chromatography in the separation of polar compounds and the analysis of aqueous solutions and dispersions have been found. Preparative-scale chromatography in ammonia, sulphur dioxide, freons and steam has been performed. Considerable reductions in separation time and improvements in peak shapes were demonstrated, even under overloading conditions. The complete condensation of all of the stream of effluent enabled the recovery of the separated substances to be increased to 95-100%.

For a long time, the possibility of utilizing the vapours of low-boiling substances as mobile phases under the usual conditions of gas chromatography (GC) at pressures of 1-10 atm has been known. The properties of a vapour mobile phase under such conditions are closer to those of an ideal gas than liquids or supercritical fluids. However, interaction of the mobile phase with the column packing takes place.

The use of vapours in GC was first reported in 1959. Schmauch and Dinerstein¹ studied in 1959 the response of a thermal conductivity detector in ethane. Dumazert and Chiglione², also in 1959, described the application of ethanol vapour in the separation of free organic acids. In 1960 they published the results of the use of water vapour in the separation of phenols, cresols and other compounds³. Masada and Hashimoto⁴ were granted a patent in 1960 for a chromatographic process with unsaturated steam as the mobile phase.

Later, a number of investigators studied the possibility of using condensable gases, vapours of organic solvents and other low-boiling compounds as mobile phases for GC. Revel'skii *et al.*⁵ utilised freon in measurements of the molecular weights of organic compounds. Wagaman and Smith⁶ used pentane to separate oil chemistry products. Ilkova and Mistryukov⁷ used ammonia to separate amines, amino alcohols and amino ketones in capillary columns. Tsuda *et al.*⁸ compared the results obtained in GC with permanent gases and organic vapours. Mixtures of *n*-alkanes and *n*-alkanols were separated by using heptane and ethanol vapours⁹. Nonaka¹⁰ studied

gas adsorption chromatography in water vapour and achieved an excellent separation of hydrocarbons, alcohols, aldehydes, ketones, esters, organic acids, phenols and amines. The substances to be analyzed were injected into the chromatograph as dilute aqueous emulsions or suspensions (10^{-1} – 10^{-4} %).

These papers indicate that the use of vapours, particularly those with high polarity and interacting with the sorbent, might be applicable in the GC of polar compounds. They facilitate the analysis, suppress adsorption in gas-liquid columns, improve the peak shape and increase the separation. Such features are especially pronounced in chromatography with the vapours of water and polar compounds such as alcohols.

All of the investigations carried out previously were performed with specially fabricated chromatographic equipment. The systems used for the generation of vapours and flow control were usually complicated and the sensitivity was not better than moderate. The use of simple but sensitive equipment with flame ionization and electron capture detectors for performing such chromatographic analyses was described in our recent papers^{11,12}. Some analytical applications of our investigations in chromatography with vapours of water, formic acid and methanol for the analysis of free fatty acids, amines, haloalkanes, sterols, alkaloids and other drugs were also published recently^{12,13}.

A number of chromatographic systems were studied in order to achieve the detection of components to be separated with adequate sensitivity. The utilization of selective detectors that are insensitive to the eluting vapour but with high sensitivity towards the components to be separated was demonstrated. One of the most useful systems of this type includes the combination of water vapour with a flame ionization detector. It was demonstrated that even very polar compounds are eluted as symmetrical peaks. A considerable increase in the speed of analysis and an improvement in peak shape occurred when water vapour was used and permitted the resolution of sterols, alkaloids and other drugs, injected as a dilute aqueous solution or dispersion^{12,13}. No baseline disturbance was observed when large volumes of aqueous samples were injected.

These results indicate the promising future for such a system for the determination of low concentrations of impurities in water. It could be of considerable importance in the analysis of industrial waste waters, environmental pollution control, prospecting, etc.

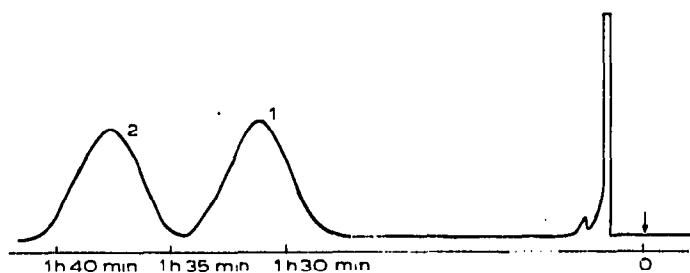


Fig. 1. Preparative-scale separation of stereoisomeric methyl esters of geranic acids. Carrier gas, sulphur dioxide at a flow-rate of 200 ml/min; column, 10% polydimethylsiloxane SCTV on Chromosorb, 10 m \times 12 mm I.D.; column temperature, 165°; recovery, 98%. 1 = *cis*-Isomer; 2 = *trans*-isomer.

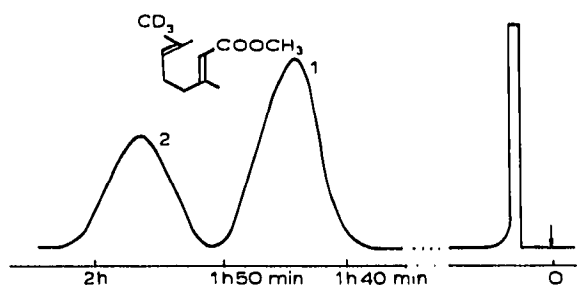


Fig. 2. Preparative-scale separation of trideuterogeranic esters in Freon 12 vapour at a flow-rate of 300 ml/min. Column, 10% PEG 6000 on Chromosorb A, 15 m \times 10 mm I.D.; column temperature, 175°; sample size, 0.5 ml; recovery, 100%. 1 = *cis*-Isomer, 2 = *trans*-isomer.

There are interesting possibilities for the use of condensable gases and vapours in preparative-scale chromatography. The factors that prevent the wider introduction of preparative-scale GC in research laboratories and industry are well known and include distortion of the peak shape due to overloading, the slowness of the process and considerable losses of the separated substances upon condensation.

Our investigations showed that these factors could be almost completely eliminated by the utilisation of condensable gases and vapours. A high-performance all-glass preparative-scale chromatograph¹⁴ was used, equipped with a flame-ionization detector. Ammonia, sulphur dioxide, Freon 11, Freon 12 and water vapours were used as mobile phases. A remarkable improvement in peak shape was observed for hydrocarbons and terpenic acid esters (Fig. 1), even under overloading conditions, when the separation was carried out in ammonia and sulphur dioxide. Complete condensation of the whole of the eluent ensured a recovery of separated samples of 94–98%¹⁵. Very high recoveries were also achieved with freon vapour and permitted the preparative-scale chromatography of difficultly obtainable *cis*- and *trans*-isomers of trideuterogeranic esters to be carried out (Fig. 2). The use of steam in preparative-scale GC enabled the analysis time to be reduced considerably and symmetrical peaks of polar compounds such as aliphatic amines to be obtained, even when large samples were injected (Fig. 3).

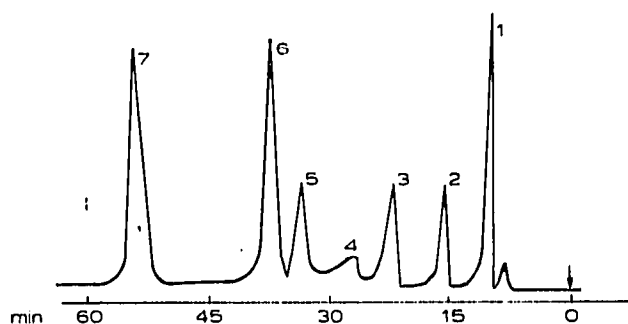


Fig. 3. Preparative-scale separation of amine mixtures in water vapour. Column, 12% polydimethylsiloxane SCTV on Chromatone, 15 m \times 10 mm I.D.; column temperature, 160°; steam pressure, 3.2 atm; sample size, 0.2 ml. 1 = $(\text{CH}_3)_2\text{CHNHCH}(\text{CH}_3)_2$; 2 = $(\text{CH}_3)_2\text{CHCH}_2\text{NHC}_2\text{H}_4\text{CH}(\text{CH}_3)_2$; 3 = $\text{C}_6\text{H}_5\text{NH}_2$; 4 = $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_2$; 5 = $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$; 6 = $\text{C}_6\text{H}_5\text{NH C}_2\text{H}_5$; 7 = $\text{C}_6\text{H}_5\text{N}(\text{C}_2\text{H}_5)_2$.

The quantitative recovery of the separated fractions was performed without the need for extensive cooling of traps, ambient temperature being adequate. Such a version of preparative-scale GC seems to be the most convenient for wide-scale industrial application.

The results described here indicate that GC with condensable gases and vapours as the mobile phase is an extremely promising branch of GC. It facilitates the separation of polar substances, the use of vapours makes the chromatographic separation more economic, and the way should be opened for the development of compact and light analyzers.

REFERENCES

- 1 L. I. Schmauch and R. A. Dinerstein, *Amer. Chem. Soc. Div. Petrol. Chem., Prepr.*, 4, No. 3 (1959) 119.
- 2 C. Dumazert and G. Chiglione, *Bull. Soc. Chim. Fr.*, (1959) 615.
- 3 C. Dumazert and G. Chiglione, *Bull. Soc. Chim. Fr.*, (1960) 1770.
- 4 I. Masada and I. Hashimoto, *Jap. Pat.*, No. 18097, 1960.
- 5 I. A. Revel'skii, R. I. Borodulina and T. M. Sovakova, *Neftekhimiya*, 6 (1966) 319.
- 6 K. L. Wagaman and T. G. Smith, *J. Chromatogr. Sci.*, 9, No. 4 (1970) 241.
- 7 E. L. Ilkova and E. A. Mistryukov, *J. Chromatogr.*, 54 (1971) 422.
- 8 T. Tsuda, N. Tokoro and D. Ishii, *J. Chromatogr.*, 46 (1970) 241.
- 9 V. G. Berezkin, E. A. Kyazimov and M. N. Aghaeva, *Azerb. Khim. Zh.*, No. 1 (1973) 69.
- 10 A. Nonaka, *Anal. Chem.*, 44 (1972) 271; 45 (1973) 483.
- 11 B. A. Rudenko, M. A. Baydarov'tzeva and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1972) 2634; (1973) 1773.
- 12 B. A. Rudenko, M. A. Baydarov'tzeva, V. A. Kuzovkin and V. F. Kucherov, *J. Chromatogr.*, 104 (1975) 271.
- 13 M. A. Baydarov'tzeva, B. A. Rudenko, V. F. Kucherov and M. I. Kuleshova, *J. Chromatogr.*, 104 (1975) 277.
- 14 B. A. Rudenko, V. A. Kuzovkin, V. N. Paukov and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1971) 1384.
- 15 V. A. Kuzovkin, B. A. Rudenko and V. F. Kucherov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, (1973) 1910 and 2634.