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GAS CHROMATOGRAPHY WITH VAPOURS OF LOW-BOILING SUBSTANCES AS MOBILE PHASES

B. A. RUDENKO, M. A. BAYDAROVTSEVA, V. A. KUZOVKIN and V. F. KUCHEROV
N. D. Zelinsky Institute of Organic Chemistry, Academy of Sciences of the U.S.S.R., Moscow (U.S.S.R.)

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SUMMARY

Chromatography with the vapours of water, pure formic acid and methanol as mobile phase has been investigated. The considerable advantages of this version of chromatography for the separation of polar compounds and in the analysis of aqueous solutions and dispersions are shown. Simple and robust equipment for vapour chromatography is proposed.

INTRODUCTION

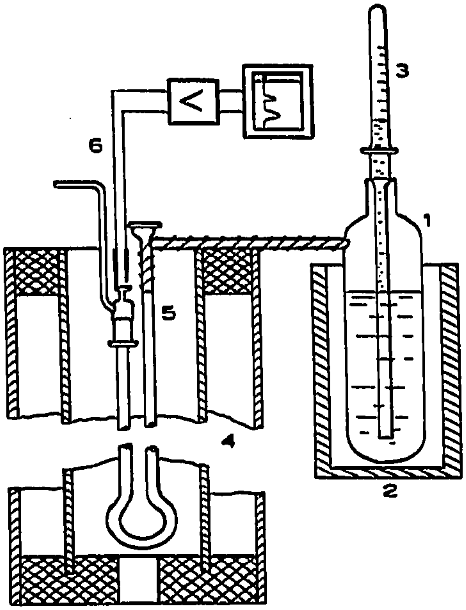
Recent developments in gas chromatography have been based on the utilisation of special properties acquired by gases and vapours near their critical point. Dumazert and Chiglione described the application of ethanol vapour for the separation of free organic acids[1], and the separation of phenol, cresols and other compounds with water vapour[2]. Masada and Hashimoto[3] have patented a chromatographic process with unsaturated steam as the mobile phase.

A number of investigators have studied the possibility of utilising the vapours of organic solvents and other low-boiling compounds as the mobile phase for gas chromatography. Revel'skii *et al.*[4] utilised Freon to measure the molecular weight of organic compounds. Wagaman and Smith[5] used pentane to separate oil chemistry products. A comparison of the results obtained in gas chromatography with the permanent gases and organic vapours was made by Tsuda *et al.*[6]. Mixtures of *n*-paraffins and normal alcohols were separated using heptane and ethanol vapours[7]. Nonaka[8] studied gas–solid chromatography using water vapour and obtained excellent separations of alcohols, aldehydes, ketones, esters, organic acids, phenols, amines and different hydrocarbons. The substances to be analyzed were injected into the chromatograph as dilute aqueous emulsions or suspensions. Recent work[9] has shown the considerable advantages of chromatography using vapours for preparative-scale separations. The purpose of this study was to develop simple but sensitive. robust and readily available equipment for such a mode of chromatography.

EXPERIMENTAL

The chromatographic apparatus used for separation in a vapour flow has an all-glass evaporator and column (Fig. 1). There are no long connections, regulators or valves along the vapour pathway, which enables condensation to be completely avoided.

The vapour-flow control is executed through alteration and precise control of the evaporator heater, fed by an appropriate electronic stabilizer and regulator. A P-71M precision electronic stabilizer was used. To detect the separated fraction, a flame ionization detector compatible with all-glass instrumentation (Fig. 2) and a Panchromatograph electron-capture detector were used. The amplifier of a commercially available LCM-8MD chromatograph provided adequate sensitivity of the system.



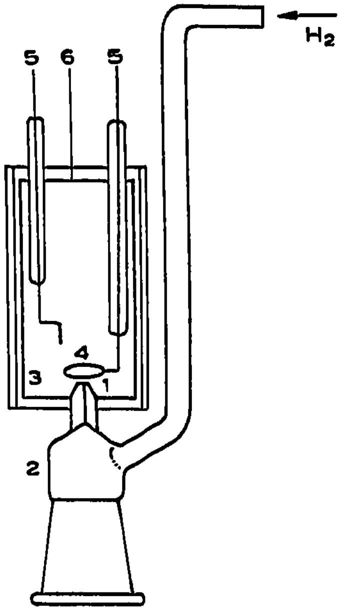


Fig. 1. Glass chromatograph for chromatography in a vapour flow. 1 = Vapour generator; 2 = vapour generator heater; 3 = gas manometer; 4 = column thermostat; 5 = chromatographic column; 6 = detector.

Fig. 2. Flame ionization detector compatible with glass instrumentation. 1 = Burner; 2 = body; 3 = screen; 4 = electrodes; 5 = electrode contacts; 6 = screen contact.

RESULTS AND DISCUSSION

The chromatograms of free fatty acids and amines in water vapour in Figs. 3 and 4 show that even very polar compounds are eluted as symmetrical peaks. The considerable acceleration of analysis and improvement of peak shape in water vapour allowed the resolution of sterols, alkaloids and other drugs, injected as a dilute aqueous solution or dispersion, to be achieved[10]. No baseline disturbance was observed when large-sized aqueous samples were injected.

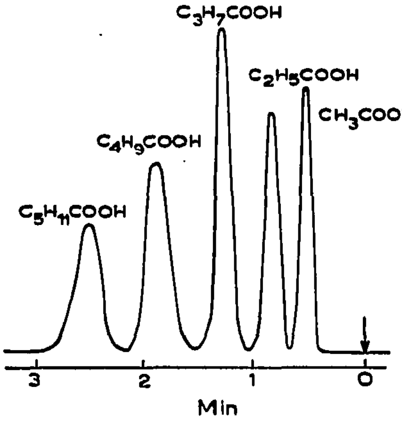


Fig. 3. Chromatogram of free fatty acids in water vapour. Column: 10% polyethylene glycol 20M on Chromaton, 4 mm I.D., 1.0 m long. Temperature, 150°; vapour pressure, 0.5 kg/cm².

It seems that this technique may be of considerable importance for the determination of low concentrations of impurities in water, such as in the analysis of industrial waste water, environmental pollution control and prospecting. Some results on this aspect have been published recently[11].

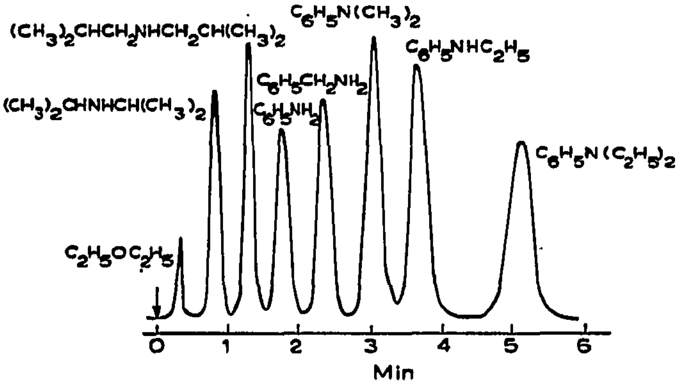


Fig. 4. Chromatogram of amines in water vapour. Column: 10% polydimethylpolysiloxane SCTV on Chromaton, 4 mm I.D., 2 m long. Temperature, 150°; vapour pressure, 0.5 kg/cm².

The use of water vapour in chromatography decreases the analysis time, lowers the column temperature and facilitates considerably the separation of highly polar components. The analysis of aqueous solutions and dispersions is also considerably simplified.

The second vapour chromatography system studied was the combination of pure formic acid vapour with a flame ionization detector. Considerable improvement in the peak shape of polar substances in the presence of small amounts of formic acid

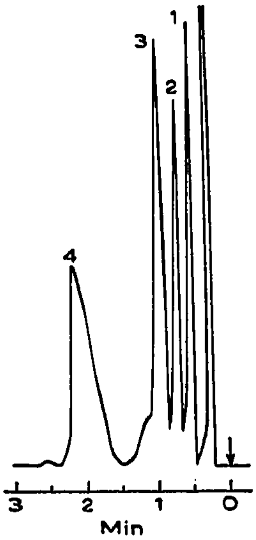


Fig. 5. Chromatogram of amines in pure vapour of formic acid. Column as in Fig. 4. Temperature, 150°; formic acid vapour pressure, 0.3 atm. 1 = Diisobutylamine; 2 = aniline; 3 = benzylamine; 4 = dimethylaniline.

in the carrier gas is well known[12]. The absence of a marked response of the flame ionization detector to formic acid permits the use of the pure vapor as the mobile phase in the same manner as water vapour.

The use as a carrier gas of a substance more polar than water and its simple replacement with any other sorbate lead to new possibilities for gas chromatographic analysis. In such a system, symmetrical peaks of free fatty acids up to palmitic acid were obtained. Amines (Fig. 5) and alcohols also gave very good chromatograms with a considerable reduction in analysis time. The proposed system also involves a combination of an organic vapour with an electron capture detector. The choice of mobile phase in this case is almost unlimited, because a great number of substances have no response to the electron capture detector. In such a system using methanol vapour, the haloalkanes were detected with a sensitivity of 10^{-6}–10^{-8} mole (Fig. 6).

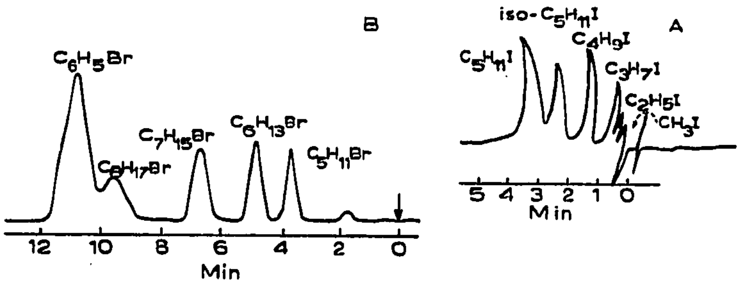


Fig. 6. Chromatograms of haloalkane mixtures in methanol vapour with electron capture detector. Column: 10% polydimethylsiloxane SCTV on Chromosorb, 4 mm I.D., 2 m long; methanol vapour pressure, 0.3 atm. A: Temperature, 120°; B: temperature, 130°.

The results obtained show that chromatography using vapours, especially water vapour, is a very promising branch of gas chromatography. This method facilitates the separation of polar substances and creates new possibilities for separation processes. The use of vapours makes the chromatographic separation more economical and enables one to avoid the use of compressed gases in flasks, and so opens the way for the development of compact and light analyzers.

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