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GAS CHROMATOGRAPHIC DETERMINATION OF TRACE AMOUNTS OF ORGANIC COMPOUNDS IN SOLUTIONS WITH ADSORPTION OF THE MAJOR CONSTITUENT

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SUMMARY

A method is proposed for the direct gas chromatographic determination of the components of organic admixtures in aqueous and acetic acid solutions. Separation of the solvent from the admixtures is achieved by its selective adsorption in a pre-column.

The influence of the water content of the carrier gas on the sensitivity of the flame ionization detector is discussed.

INTRODUCTION

The determination of mixtures of organic compounds in water, acetic acid and their mixtures is a common analytical problem in many chemical production processes and in studies of environmental contamination. However, when the concentration of these substances is less than 100 ppm, direct gas chromatographic analysis of such systems is rather laborious. In order to carry it out successfully, the primary requirement is that the detector should be stable at maximum sensitivity and that the peaks of the solvent and those of the sample components should be completely separated.

Two different methods of separating sample components from the solvent are possible: in a chromatographic column or by conversion of the solvent in a single chromatographic system into a non-volatile compound or a compound whose retention time differs considerably from that of the sample components.

The first method necessitates a prolonged and not always successful search for selective stationary phases that are resistant to the effects of water or acetic acid, because with great amplification of the signal (electrometer scale $1-2.5 \cdot 10^{-12}$ A) the products of even slight decomposition of the liquid phase preclude the possibility of detecting micro-amounts of the sample components. The most serious disadvantage of this method lies in the fact that the chromatogram contains a peak of the solvent that either covers the peaks of the sample components with its tail or, owing to prolonged elution from the column, extends the time of analysis to several hours.

The second method, based on the use of reaction gas chromatographic tech-

niques¹, makes it possible to subtract completely the peaks that interfere in the analysis of the sample components. In our opinion, this is the most promising method for identifying micro-amounts of organic substances in solutions.

Usually, the chromatographic analysis of aqueous solutions is performed with the aid of a flame ionization detector (FID), which is assumed to be insensitive to water. It has been shown, however, in a number of investigations²⁻⁵ that if water vapour enters the FID burner, its sensitivity is decreased. When a thermal conductivity detector (TCD) is used, separation of water is achieved by converting it into acetylene or hydrogen in reactors with carbide⁶ or calcium hydride⁷. The disadvantages of these methods are the rapid deactivation of the reagents as a result of a heterogeneous reaction whereby a layer of hydroxide is formed on their surface, and also the reactivity of carbides and hydrides with respect to some oxygen-containing compounds. A method of temporary and selective retention of water by a protein in a beaded form placed in a pre-column has also been described⁸. However, protein does not retain organic acids nor does it adsorb water at a temperature above 100°.

In order to subtract admixtures of carboxylic acids, powdered zinc oxide mixed with a conventional chromatographic coating is used⁹. However, as our experiments have shown, the injection of even a few microlitres of pure acetic acid results in a sharp increase in the reactor resistance and its failure. Apart from this, the reactor is completely inadequate for the analysis of aqueous solutions because water passes through and deactivates it.

We have devised a method for the direct chromatographic analysis of micro-amounts of organic compounds in water, acetic acid and their mixtures without recording the solvent peak on the chromatogram. The solvent peak is subtracted by coating the solid support with Carbowax 600-20 000 (10-20% of the weight of the solid support) in combination with potassium hydroxide (20% of the weight of the solid support).

EXPERIMENTAL

We used a Tsvet-2 (U.S.S.R.) gas chromatograph with an FID and a Carlo Erba gas chromatograph with a TCD (Model Fractovap GV).

The columns were stainless-steel tubes of length 1-1.5 m and I.D. 0.2-0.6 cm; the solid supports Chromosorb W and Sferokhrom-1 (U.S.S.R.) and stationary liquid phases Carbowax 600-Carbowax 20M, Apiezon L and Tween 20 were used. Potassium hydroxide was applied on to the solid support together with the stationary liquid phase from solution in ethanol.

Optimum conditions for the chromatographic analysis of aqueous and acetic acid solutions are given in the captions to Figs. 1 and 2.

The TCD was calibrated with volumes of water of 0.1-10 μ l and diethyl ether saturated with water at 25°. The following conditions were used: glass column 30 \times 0.6 cm with 20% Tween 20 on Chromosorb W (0.1-0.2 mm); temperatures, column 100°, evaporator 150°, detector 160°; carrier gas, helium (flow-rate 60 ml/min); current, 170 mA.

RESULTS AND DISCUSSION

Of a large number of polar and non-polar liquid phases tested, Carbowaxes were found to be the most suitable because they readily dissolve the alkali and are not degraded during aqueous and acetic acid chromatography. The use of small amounts of alkali and non-polar liquid phases¹⁰ sharply decreases the ability of the coating to adsorb carboxylic acids and completely deprives it of the ability to retain water.

Acetic acid and the C₃-C₅ organic acids investigated are completely entrapped in the column filled with the proposed coating. The adsorption capacity of the coating with respect to acids can be assessed from stoichiometric relationships.

Fig. 1 shows the chromatograms of the same solution of aromatic hydrocarbons in acetic acid (concentration of components analysed = 10⁻⁴%) with (Fig. 1a) and without (Fig. 1b) subtraction of the solvent peak. The time, needed to analyze benzene, toluene and *m*-xylene in trace amounts with complete entrapment of the acid by the alkali is less than 5 min, whereas the time required to elute 1 μl of this solvent, under the conditions specified in Fig. 1, is about 2 h.

The separation of water from the admixtures analyzed when using the proposed coating is based on another principle. Injection of alkali into the column coating results in considerable selective retention of water and its elution for several hours in the form of a very diffuse peak (Fig. 2). The time of elution of water from the column and its concentration in the carrier gas flow were established with the aid of a TCD. It was observed that successive injections of water in 1-μl doses at 10-15-min intervals into a 100 × 0.6 cm column filled with 20% potassium hydroxide and 15% Carbowax 600 on Sferokrom-1 (0.2-0.25 mm) at 100° and with a carrier gas (helium) flow-rate of 60 ml/min results in the concentration of the water vapour

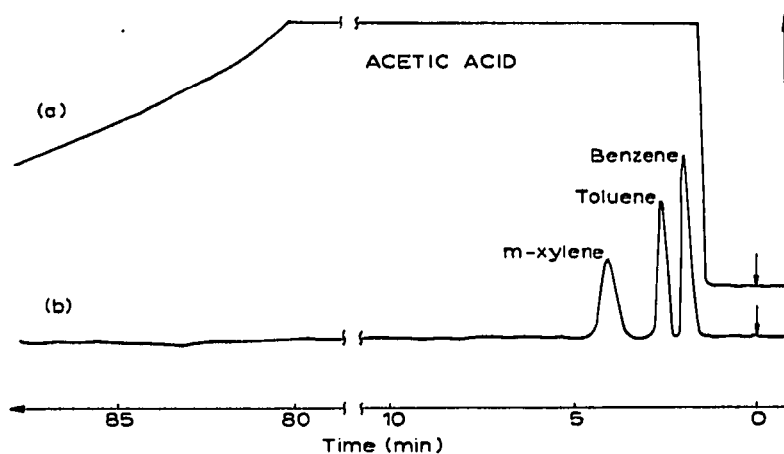


Fig. 1. Chromatograms of the solution of aromatic hydrocarbons in acetic acid (concentration 10⁻⁴%) (a) without and (b) with solvent adsorption. Conditions: temperature, 100°; flow-rate of carrier gas (argon), 60 ml/min; detector, FID; electrometer scale, 2 · 10⁻¹² A; dose, 1 μl. (a) Pre-column, 50 × 0.4 cm with 10% Carbowax 600 on Sferokrom-1 (0.1-0.2 mm); column, 100 × 0.4 cm with 20% Apiezon L on Chromosorb W (0.1-0.2 mm). (b) KOH (20% of solid support weight) added to pre-column coating.

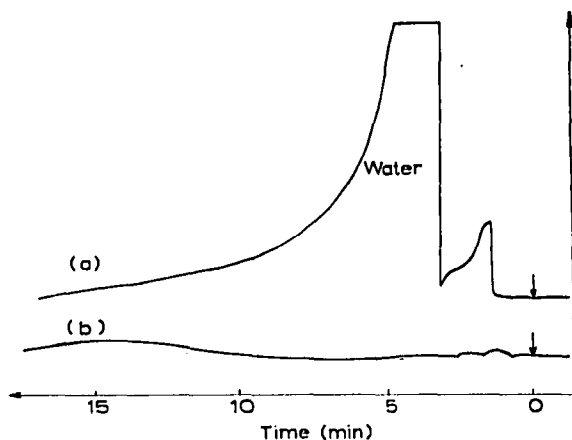


Fig. 2. Chromatograms of distilled water on a column (a) without adding alkali to the stationary phase and (b) with alkali included in the coating. First peak on chromatogram (a) is unidentified. Conditions: temperature, 100°; flow-rate of carrier gas (argon), 40 ml/min; detector, FID; electrometer scale, 10^{-11} A; dose, 1 μ l. (a) Pre-column, 50 \times 0.4 cm with 15% Carbowax 600 on Sferokhrom-1 (0.1–0.2 mm); column, 100 \times 0.4 cm with 20% Tween 20 on Chromosorb W (0.1–0.2 mm). (b) KOH (20% of solid support weight) added to pre-column coating.

at the column outlet changing smoothly within the range $2.8\text{--}3.0 \cdot 10^{-4}\%$. Increasing the doses injected up to 10 μ l increases the water vapour concentration in the carrier gas up to $1\text{--}2.2 \cdot 10^{-3}\%$.

It is thought² that the decrease in FID sensitivity caused by penetration of water vapour into the burner flame is mainly associated with a sharp disturbance of the ionization processes of the compounds analyzed, leading to the formation of hydrated H_3O^+ , $\text{H}_3\text{O}^+ \cdot \text{H}_2\text{O}$ and $\text{H}_3\text{O}^+ \cdot 2\text{H}_2\text{O}$ ions, the efficiency of collection of which by the electrodes is extremely small. To a lesser extent, the decrease in detector sensitivity is caused by changes in the shape, temperature and thermal capacity of the flame under the influence of water molecules.

As FID characteristics depend on the presence of water in the burner flame, one should take into account the possibility of the results being distorted owing to the change in detector sensitivity. According to the results of Hill and Newell³, however, variations in the concentration of water vapour in the range $(1.6 \pm 0.6) \cdot 10^{-3}\%$ cause the FID sensitivity to change by not more than $\pm 1\%$. The FID sensitivity, when water is injected into the above-mentioned column in 1–2- μ l doses, changes by only a few tenths of a sensitivity.

Strong diffusion of the water peak makes it possible to detect admixtures against the background of the solvent (when the dose does not exceed 2 μ l) even with a thermal conductivity detector operating at maximum sensitivity.

Preparing a coating with the alkali for operation consists in successive injections of pure solvent in 1–2- μ l portions until extraneous peaks disappear. For the chromatography of water vapour, it is better to use Carbowax 600 as the stationary liquid phase as it is more resistant to the action of water and ensures its good retention.

The method of analysis described above was checked on examples of practical

importance in order to identify admixtures of alcohols, carbonyl compounds, hydrocarbons, amines and ethers over the concentration range 0.1–10⁻⁶%. It should be noted that when analyzing mixtures containing ethers (or substances unstable in alkaline media), in order to exclude the possibility of their hydrolysis before entering the column with the alkali, it is necessary to separate the zone of water vapour from that of ether vapour. This is easily achieved if the coating with the alkali is placed at the outlet from the chromatographic column.

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