Notes

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A simple device for the selection of fractions in gas chromatography

The sampling of separate components after their separation in a chromatographic column for the purpose of identification by chemical and physical methods is of great importance in gas chromatography. Studies of IR spectra of separated components have a particular application.

At present the selection of fractions of separated components is principally used in preparative chromatography. The selection of fractions in analytical chromatography by formerly suggested methods is difficult because of small volumes of the samples analysed.

Many different types of traps for fraction selection are described in the literature. It was suggested that sealed glass tubes with a narrow end[1], U-tubes[2], thin hollow steel needles[3], polyethylene capillaries[4], and other devices be used as traps. The condensation of fractions can also be carried out in a tube filled with potassium bromide[5] or directly on a tablet of this material[6] prepared for taking IR spectra.

Various types of connecting systems including distribution combs with a number of taps, glass or metal ground joints, etc., are used for joining the traps. Such systems cause losses and impurity in the components. Furthermore, the complete condensation of samples in traps is not always achieved; the number of selected components is generally limited.

In this paper a new simple and reliable device is proposed[7]. It allows practically any number of components in a mixture to be collected quantitatively. The apparatus may be applied to both preparative and analytical chromatography.

Apparatus and procedure

The main feature of the proposed device is that the samples of components

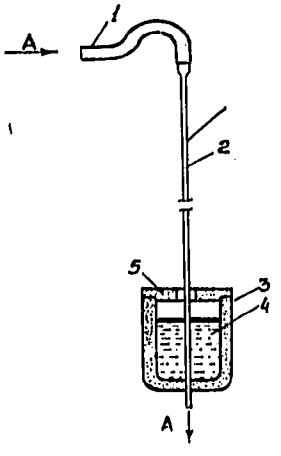

Fig. 1. Schematic layout of the device for fraction selection. 1 = flexible hose; 2 = capillary; 3 = vessel of heat-insulating material; 4 = cooling agent; 5 = lid; A = input and output of carrier gas.

separated in a chromatographic column are in a series condensed in a capillary tube passed through a cooling cell, rather than selected into separate samplers. The selected samples remain on the walls of the capillary in a liquid or solid state, depending on the physical properties of the components and on the temperature of the cooling agent. After condensing one of the samples, the tube is moved over a certain distance, and then the condensation of the following fraction occurs. One of the modifications of the proposed apparatus is shown in Fig. 1.

The total flow of carrier gas passed through the heat conductivity detector or its portion selected before the flame-ionization detector is involved in fractionation. The carrier gas from the detector passes through a flexible hose of silicone rubber (1) and enters a thin-walled capillary tube (2). The length of the tube is directly proportional to the number of components in the mixture; the choice of its diameter depends upon the quantity of the mixture introduced for the separation: the less the sample, the smaller the diameter. The condensed fraction is distributed in a thin layer on the inner walls of the capillary. Filling the total cross section of the capillary with the separated substance is impermissible here, otherwise the flow of the carrier gas will be disturbed. The cooling agent (4) (liquid N_2, solid CO_2 and its various mixtures, etc.) is placed into a plastic foam condenser (3). The capillary is passed through the bottom of the condenser (3). The thin plastic foam bottom or the walls of the vessel are easily pierced by the capillary tube. In this case no leakage of liquefied gas is observed. The condensation of the components occurs in the cooled capillary part. Completeness of their condensation depends upon the temperature of the cooling agent in the vessel.

The condensation of the first component being completed (control on the potentiometer of the chromatograph), the capillary tube (2) is passed through the condenser (3) over the length exceeding the layer thickness of the cooling agent (4). The piece of the capillary with liquid or solid fraction is broken off and sealed at both ends. In doing so, it is a good practice to hold the capillary tube with special pincers of heat-insulating material to prevent evaporation of the fraction due to heating. A small notch can be made on the capillary before breaking it off. Fractions of the second and subsequent components are selected in the similar way.

For the purpose of decreasing the evaporation velocity of the liquefied gases, the vessel (3) is closed with a lid (5). While sampling high-boiling substances, it is advisable to heat the capillary above the condenser approximately to the chromatographic column temperature in order to prevent their condensation on the walls of the capillary. This heating can be ensured by means of a ventilator with air heating ("Fan" type). The temperature in the capillary zone is controlled by a thermometer. When operating on sufficiently volatile components, no condensation on the walls of the capillary is observed before the cooling zone.

The fractions of substances under study selected into sealed capillaries by the above method can be kept without any changes for a long period of time. For the identification of these components it is possible to use the IR spectroscopy, elementary analysis, chemical reactions as well as repeated chromatography by various methods.

In order to obtain a sufficient number of components for identification, one may consecutively accumulate the samples while performing several chromatographic analyses of the mixture.

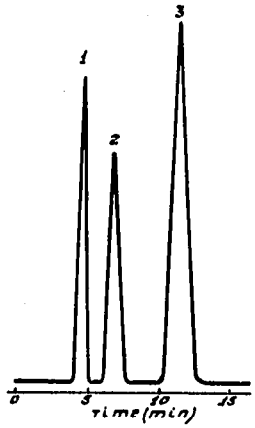

Fig. 2. Example of chromatographic separation of a model mixture with a simultaneous selection of fractions. 1 = acetone; 2 = methyl ethyl ketone; 3 = chloroform.

Experimental

The experimental investigation was carried out on HL-4 analytical laboratory chromatographs with a heat conductivity detector and on LHM-7a chromatographs containing heat conductivity and flame-ionization detectors. As an example, we provide the results of the separation of a model mixture of three components: acetone, methyl ethyl ketone, and chloroform.

The chromatographic separation was performed in a column (180 × 0.6 cm) containing 10% of polyethyleneglycol 15 000 on Celite-545 (30–60 mesh) at the column and detector temperature 110°; the carrier gas (N_2) flow was 50 ml/min. The chromatogram of the model mixture separation obtained at the simultaneous selection of fractions of the separated components is shown in Fig. 2.

Glass capillaries of different inner diameters (0.5–2.0 mm) connected through a flexible hose with the heated yield of carrier gas were used for the preparative selection of the components under investigation. Such a capillary was passed through a vessel of plastic foam (I.D. 85 mm, height 55 mm, wall thickness 20 mm) containing liquid N_2 (boiling point = −195.8°).

The model mixture to be investigated was introduced into the evaporation cell of the chromatograph with the help of a microsyringe which was weighed before and after introducing the sample. The yield of the components was controlled by a poten-

TABLE I

FRACTIONATION OF THE MODEL MIXTURE

Component	*Composition of the model mixture (%)*	*Introduced into the chromatograph (g)*	*Weight of the filled capillary (g)*	*Weight of the empty capillary (g)*	*Weight of the component in the capillary (g)*	*Losses of the component (g)*
Acetone	26.17	0.0025	0.1275	0.1255	0.0020	0.0005
Methyl ethyl ketone	24.63	0.0024	0.3339	0.3318	0.0021	0.0003
Chloroform	49.20	0.0046	0.2839	0.2800	0.0039	0.0007

tiometer. At the moment the yield of chromatographic peak ended, the capillary with the solid sample was moved out of the cooling cell, broken off, sealed and weighed on an analytical balance with an accuracy of 0.0001 g. The absolute weight contents of the capillary was estimated by the difference in weights of the filled and empty capillary.

The data on the fractionation balance of the model mixture are illustrated in Table I. The data obtained show a high efficiency of sampling separated components by the method described.

The selected components were identified in IR spectra with a Zeiss (Jena) UR-20 spectrometer. The substances were removed from sections of the capillary with an indifferent solvent (CCl_4). To obtain a quantity of substance sufficient to take spectra, five parallel analyses of the model mixture with the selection of the separated components were performed.

The techniques described have been used for solving a number of analytical problems[8], in particular when identifying the components formed in pyrolytic gas–liquid chromatography of polysaccharide mixtures and their technical products.

Simplicity and reliability of the proposed method allow it to be recommended for a wide application to analytical and preparative gas chromatography. It is advisable that chromatographs produced by industry be provided with arrangements for sampling based on the described method.

Department of Chemical Technology of Wood, YU. I. KHOL'KIN
The Kirov Byelorussian Institute of Technology, G. S. GRIDYUSHKO
Minsk (U.S.S.R.)
Institute of Physics, The Byelorussian Academy of Sciences, A. K. POTAPOVICH
Minsk (U.S.S.R.)

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