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Fig. 1 and Fig. 2

Figure 1: Fig. 1 and Fig. 2

Abstract

Full Text

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The Use of Sodium Chloride as a Solid Support in Gas-Liquid Chromatography

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The solid supports currently used in gas-liquid chromatography (diatomaceous brick, crushed faience, “Risorb,” “Sterchamol,” etc.) are porous materials whose basis consists of silicates. Despite their great versatility,

Fig. 1. A —Chromatogram of a mixture of ethyl alcohol (peak *1*), β-ethoxyacrolein (peak *2*), β,β-diethoxypropionaldehyde (peak *3*), β,β-diethoxy-α-methylpropionaldehyde (peak *4*), diethyl diacetals of malonic (peak *5*) and methylmalonic (peak *6*) dialdehydes. Column: 1% polysiloxane on NaCl, length 5 m, temperature 100°, He flow 50 ml/min.
B —Chromatogram of a mixture of substances obtained in the dimerization of the acetal of crotonaldehyde. Column: 1% polysiloxane on NaCl, length 1 m, temperature 150°, He flow 65 ml/min.

Fig. 2. Sensor of an ionization microflame detector. *1* —capillary with ground joint, *2* —protective tube, *3* —platinum electrodes.

these solid supports have a number of shortcomings that limit the possibilities of their use in gas-liquid chromatography of certain classes of organic compounds. The content in them of aluminosilicates and slight impurities of elements of the third group, iron oxides and

chromium may promote decomposition and isomerization of the substances being separated under the conditions of chromatographic analysis, which is completely inadmissible for comparatively unstable compounds (^{1}). On the other hand, the rather high surface area of such supports leads to the retained volumes of high-boiling compounds, even at a low content of the liquid phase, being very substantial (^{2}). This makes it necessary to maintain a rather high temperature in the chromatographic column, which in a number of cases is entirely undesirable.

These circumstances prompted us to search for a solid support that contains no

Fig. 3. Chromatogram of mixtures of isomeric enol ethers.

Figure 2: Fig. 3. Chromatogram of mixtures of isomeric enol ethers.

catalytically active impurities, has low adsorption activity, and has a relatively small surface area. With such a solid support it was possible to hope, after selecting the appropriate liquid stationary phase, to carry out gas-liquid chromatography of high-boiling and unstable compounds, which is often necessary in the practice of scientific research.

Fig. 3. Chromatogram of mixtures of isomeric enol ethers. **A** –Δ^5-4-phenyl-indanedione-1,3. Column: 1% polysiloxane on NaCl, length 2 m, temperature 175°, 50 ml H_2 per 1 min. **B** –column temperature 130°. All other conditions the same.

It turned out that a sufficiently satisfactory solution to this problem can be achieved by using a column packed with sodium chloride (chemically pure) with a particle size of 0.5–0.25 mm, containing 1% of the silicone elastomer "Gomotsai 410" (Siss company, France). Such a column contains absolutely no metal impurities capable of causing secondary chemical transformations of the substances analyzed. In addition, it has definite advantages over the previously proposed method of gas-liquid chromatography on a column with glass beads ([3]), since it practically excludes the catalytic and adsorption action of the glass surface.

The weak adsorption capacity of sodium chloride determines a linear sorption isotherm of the support, which gives strictly symmetrical peaks on the chromatogram. The small surface area of this solid phase ($S = 100$ cm^2/g at $d = 0.03$ cm), in combination with the low content of the liquid stationary phase, makes it possible to obtain a comparatively small retained volume even for very high-boiling substances. The efficiency of such a column, calculated from chromatograms of test compounds, proved to be approximately 70 theoretical plates per 1 meter (HETP 1.5 cm), which is in good agreement with data for columns with sodium chloride previously proposed for chromatography in vacuum ([4]). The use of such a column 5 m long (total efficiency on the order of 350–400 theoretical plates), with a sample size of about 1 mg (temperature 100°, carrier-gas He flow rate 50 ml/min) in a chromatograph with a thermal-conductivity detector ([5]), made it possible successfully to carry out gas-liquid analysis of mixtures of a number of acetals, ortho esters, and certain polyalkoxy compounds that previously could not be separ-

···were separated by means of this method. Some of the results obtained are shown in Fig. 1.

We have established that, for a column with 1% silicone elastomer on sodium chloride, reducing the size of the injected sample by a factor of 10 increases its efficiency to 250–300 theoretical plates per 1 m; this is quite sufficient for the successful analysis of many high-boiling compounds with a column length of 2 m. However, for recording such small concentrations it becomes impossible to

Fig. 4. Chromatogram of a mixture of phenols: 2-methyl-6-norbornylphenol (peak 1), 2-methyl-4-norbornylphenol (peak 2), isomeric 2-bornylphenols (peaks 3 and 4), and isomeric 4-bornylphenols (peaks 5 and 6). Conditions as in Fig. 3 A

Figure 3: Fig. 4. Chromatogram of a mixture of phenols: 2-methyl-6-norbornylphenol (peak 1), 2-methyl-4-norbornylphenol (peak 2), isomeric 2-bornylphenols (peaks 3 and 4), and isomeric 4-bornylphenols (peaks 5 and 6). Conditions as in Fig. 3 A

use a thermal-conductivity detector, even with preliminary conversion of the substances leaving the column to carbon dioxide (in a helium stream). To overcome this difficulty we used the simplest ionization microflame detector. The sensor of this detector, whose design is shown in Fig. 2, is connected in series with a 200 V anode battery and an EPV-51 recording potentiometer.

The relatively low sensitivity of this detector (10^5 mV·ml/mg) is compensated by the simplicity of its design and its reliability in operation. Even with a detector sensitivity of $3—5 \cdot 10^4$ mV · ml/mg, it proves possible to chromatograph, on a 2-meter column with sodium chloride containing 1% silicone elastomer, at a comparatively low temperature, a whole series of substances with low vapor pressure. Thus, at a temperature of 130–150° it was possible to separate isomeric enol ethers of certain polycyclic β-diketones (Fig. 3), whose chromatography on ordinary columns is unsuccessful.

Fig. 4. Chromatogram of a mixture of phenols: 2-methyl-6-norbornylphenol (peak 1), 2-methyl-4-norbornylphenol (peak 2), isomeric 2-bornylphenols (peaks 3 and 4), and isomeric 4-bornylphenols (peaks 5 and 6). Conditions as in Fig. 3 A.

Also at a comparatively low temperature (175°), separation of isomeric bornylphenols was carried out (Fig. 4); their chromatography on a 3 m column with 20% silicone elastomer on diatomaceous brick requires a temperature not below 250°.

In addition to these cases, use of a NaCl column in combination with an ionization microflame detector made it possible to carry out, with sufficient reliability, gas-liquid chromatographic analysis of mixtures of α- and β-ionones, α-, β-, and γ-dihydroionones (column temperature 80°), and products of the selective ketalization of certain bicyclic diketones.

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Note: Figure translations are in progress. See original paper for figures.