OPTIMIZATION OF CHROMATOGRAPHY WITH FLUORESCENT INDICATORS

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Previously [1] we reported studies on chromatography with fluorescent indicators. Upon introduction of the method in plant laboratories it was found that the column described is not quite good because it is very long (1364 mm) and brittle. For this reason a novel type of chromatographic column (Fig. 1), the so-called conical column with a capillary, was proposed. Nowadays, this column type is extensively used in the plant laboratory of the Novokuibyshev Petrochemical Combine.

The main shortcoming of elution chromatography is the diffuse character of the front of the separated components. The efficiency of elution chromatography in a column of the old type was improved by gradually reducing the diameters of the various parts. To achieve the highest possible sharpness of the front in the analysis section, the components of the tested mixture must pass through a capillary measuring more than 250 mm in length with a silica-gel filling.

In paper [2] it was established that a conical column has the highest efficiency in elution chromatography.

The separation section in the column of novel design has a conical shape. The smallest diameter of the cone equals the diameter of the capillary (1.6-1.65 mm). Consequently, the intermediate zone at the exit from the separation section attains a definite size which is minimum at the diameter considered (diameter of the analysis section).

For this reason the total length of the wetting zone and the length of the fluorescent zone are measured immediately after the red alcohol front has penetrated into the analysis zone.

Analyses of aromatic hydrocarbons obtained by sulfonation and by chromatography with fluorescent indicators are compared in Table 1.

As can be seen in Table 1, 0.2 ml product samples with 20-40% aromatic hydrocarbons are the main samples analyzed in the plant laboratory. A calibration factor is introduced to determine aromatic hydrocarbon contents below 5% [3]. The latter factor is determined for each column in which small amounts of aromatic hydrocarbons are analyzed.

To determine the calibration factor, the conical column with the capillary is filled with 5-6 g of silica-gel and placed in a VSP vibrator. Vibration is continued for 20 min.

An amount of 0.3 ml n-heptane is filled into the column; the needle-shaped tip of the pipette is kept in the upper part of the column and washed with a drop of the fluorescent indicator. The moment the n-heptane is completely sorbed, silica-gel (a 10 mm layer) is poured into the column and isopropyl alcohol colored with Sudan-3 is admixed. n-Heptane passes through the loading part under atmospheric pressure, and through the conical part (separation section) under an excess pressure of 250-400 mm Hg.

When the red alcohol zone enters the analysis section (capillary), the length of the n-heptane zone is measured (L, mm).

The calibration factor \( F \) is calculated from the formula:

\[
F = \frac{0.3 \cdot 100}{L} \text{ ml/mm.}
\]

If products with a low content of aromatic hydrocarbons are analyzed, 0.75 ml \((v)\) samples are poured into the column. The analysis is carried out as described above. The length of the fluorescent zone \( (L', \text{ mm}) \) is measured in ultraviolet light. The content of aromatic hydrocarbons \( A \) (in %) is calculated by means of the formula:

\[
A = F \frac{L'}{v}.
\]
The sorbent employed is not less important than the column shape.

The activity of silicagel is expressed in the amount of benzene (ml) adsorbed by 100 g silicagel from the standard mixture under standard conditions [4].

Previously we employed ACK silicagel; as can be seen in Table 2, this brand has a low activity during adsorption of benzene. Treatment of ACM silicagel (0.074-0.147 mm granules) with hydrochloric acid and hydrogen peroxide lowers the activity during adsorption of benzene, but, since organic contaminants have been removed by hydrogen peroxide, the accuracy of the analysis becomes higher than that achieved with silicagel treated with hot water. Admixture of the silicagel fraction in the size range below 0.074 mm yields also a good result.

The silicagel to be analyzed is prepared in the following way. ACM silicagel from the Voskresensk Combine is ground and sifted through a 40 sieve. The fraction passing through the sieve is washed with water until the reaction on chlorine ions is negative. Setting takes 10 min. The washed silicagel is continuously stirred and dried in a thermostat at 45-50°C. Subsequently it is heated at 150°C for 6 h, cooled in a desiccator and stored in a bottle closed with a cork.

The operation procedure in the column of novel construction does not differ from that described previously. The sharpness of the analysis makes it possible for one laboratory worker to carry out more than 20 determinations per shift (8 h). This is achieved, first, because four chromatographic columns can be shaken simultaneously on a single vibrator for 20 min and, second, because 10 columns can be operated simultaneously in a single ultrachromatograph (Fig. 2) and any of these columns can be disconnected at any moment from the common pressure system.