METHODS

GAS-CHROMATOGRAPHIC ANALYSIS OF EXPIRED AIR AND AN ACETYLENE MIXTURE

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The foundations of the method of chromatography were established in 1903 by M. S. Tsvet [1]. The possibility of using gases as a mobile phase was first mentioned by Martin and Synge in 1941 [6]. However, not until 10 years later could it be said that the method of gas-liquid chromatography truly existed.

Chromatography is based on the separation of a mixture of substances by distribution of the components between a stationary and a mobile phase. The stationary phase may be a solid substance (an adsorbent) or a liquid, and the mobile phase a liquid or gas.

For investigations in the field of respiratory physiology, distributive or gas-liquid (stationary phase – liquid, mobile – gas) and adsorption (stationary phase – solid, mobile – gas) chromatography may be used. The principle of separation of the components of the mixture is illustrated in Fig. 1. The mobile phase (the carrier gas – helium, for example) is passed through a column filled with the stationary phase at constant velocity. The test sample (the gas mixture A+B) is introduced into the column in the form of a plug (I). Because of the difference in the coefficients of absorption or solubility of the components, the speed at which they pass along the column varies (II), and after a short time the components are completely separated (III). Either the carrier gas or the binary mixture of carrier gas – components leaves the column.

The detector is located at the outlet of the column. During analysis of the atmospheric gases the most suitable detector is one with a thermoconductometric cell. The most important part of this detector is a thermistor or katharometer. The quantity of heat dissipated from a heated element depends on the thermal conductivity of the gas surrounding this element. The measuring and comparative elements are the arms of a Wheatstone bridge. When the binary mixture reaches the measuring cell, the temperature and resistance of the measuring element change and the bridge becomes unbalanced, and this is recorded by the pen as a peak, the amplitude of which is proportional to the concentration of the corresponding component.

In constant conditions of analysis, the time taken by the individual component to travel along the column is always the same. The time of elution is thus a qualitative index in chromatographic analysis.

For quantitative determination of the components of a mixture, the relationship between the amplitude of the deflection of the pen and the concentration of the component in the mixture must be known. This relationship is found by comparing the height of the peak of a component in known concentrations with the height of a peak obtained during the analysis of a mixture with known composition.

Where calibration mixtures with known composition are used, the concentration of the component is determined from the following formula:

$$K_x = K_a \frac{h_x}{h_a},$$

where K is the concentration (in vols.%), h the height of the peak (in mm), a the component in the calibration mixture (of known concentration), and x the component to be determined.

The object of this investigation was to develop a gas-chromatographic method of analysis of an acetylene mixture and of expired air which can be used to investigate the minute blood volume. A modified KhL-3 chromatograph was used in the experiments.

The scheme of the apparatus is illustrated in Fig. 2. The carrier gas (helium) enters the comparative cell (2) of the detector (3) through the drier (1). By means of a 6-way sampling cock (4), the dried sample (5) passes in a

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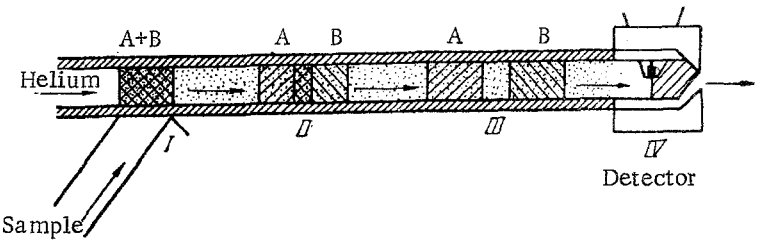

Fig. 1. Principle of separation of the components of a gas mixture in a chromatographic column. Explanation in text.

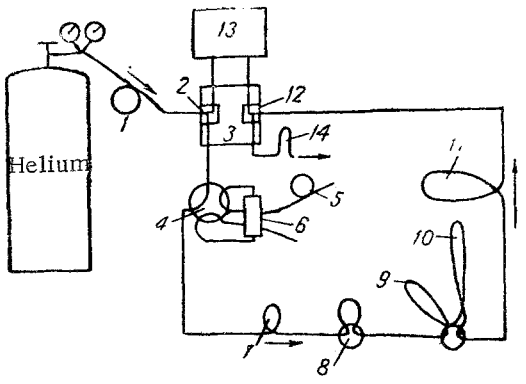

Fig. 2. Scheme of gas line of the modified KhL-3 laboratory chromatograph: 1) drier of carrier gas; 2) comparative cell of detector; 3) detector; 4) sampling cock; 5) drier of expired mixture; 6) measured volume; 7) drier; 8) forecolumn for absorption of CO_2; 9) forecolumn for absorption of C_2H_2; 10 and 11) distributive columns; 12) measuring cell of detector; 13) pen; 14) rheometer.

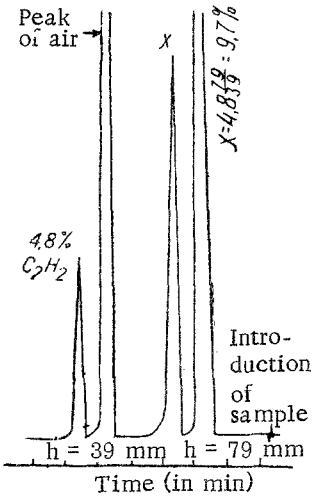

Fig. 3. Chromatogram of mixture consisting of 9.7% acetylene and air and example of calculation for calibration mixture. Temperature of column 20°, current of detector 5 mA, velocity of carrier gas 60 ml/min.

Results of Parallel Analysis of Acetylene (in vols.%) on Chromatographs and Grollman's Gas Analyzer

Mixture	Gas chromatograph	Grollman's gas analyzer
	M ± m	M ± m
Synthetic	8.95 ± 0.04	8.96 ± 0.07
Expired (sample I)	4.580 ± 0.006	4.59 ± 0.01
Expired (sample II)	5.53 ± 0.03	5.53 ± 0.08

measured volume (6) through the drier (7) to the forecolumn (8), where absorption of CO_2 takes place. Next, the gas flow is directed through the forecolumn (9) to the distributing columns (10 and 11), from which it passes through the measuring cell (12) and the rheometer (14) and escapes into the atmosphere. The signal from the detector is recorded by the pen (13). The column (8) and the system (9 and 10) are connected by 4-way cocks, so that they may be disconnected from the line of flow.

To separate oxygen and nitrogen, molecular screens of types 5A were used (column 10), after first absorbing the acetylene on the forecolumn (9). For separating acetylene (column 11), a modified TZK adsorbent proved most suitable. When it was necessary to determine the CO_2, the absorber (8) was disconnected from the gas line and a distributive column with hexamethylphosphoamide on chromosorb was used. The time of the complete analysis did not exceed 8 min.

By way of example, a chromatogram of separation of acetylene and a calculation for a calibration mixture are given in Fig. 3.

The accuracy of the chromatographic analysis of acetylene was demonstrated by the results of three parallel analyses of three gas mixtures in the chromatograph and Grollman's analyzer (see table).

Besides investigation in the field of respiratory physiology [3,5], gas chromatography may also be used for analysis of the blood gases [7], determination of traces of contamination in the air, the rapid analysis of gas mixtures for anesthesia, and so on.

By means of gas-chromatographic analysis, complex gas mixtures can be automatically or semi-automatically analyzed in a comparatively short time on one apparatus, with the result recorded on paper in the form of a chromatogram. A relatively small volume of the substance is needed for analysis (2-3 ml of the dry gas). The technique of analysis on the gas chromatograph may be learned in a few hours.

From the results thus obtained, the gas-chromatographic method can be recommended for work in physiological laboratories and in clinical practice, instead of the present volumetric analysis.

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