A METHOD FOR THE MICRODETERMINATION OF CARBON AND HYDROGEN WITH CHROMATOGRAPHIC COMPLETION

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The development of the chemistry of natural compounds requires the creation of express methods in elementary analysis with the minimum consumption of the material being analyzed. However, work with small samples is possible only with the aid of a more accurate instrumental method of identifying the final decomposition products than the existing gravimetric method. The most promising method is gas chromatography, the use of which in organic elementary microanalysis permits working with very small amounts of substance with an objective evaluation not only of the end-products but also of the actual process of the decomposition of the initial sample.

The triggering device for chromatographs is calculated for the introduction of samples of a gas by a metering device located in the path of the gas flow. The nonhomogeneity of the mixture of gases during the time of the decomposition and complete oxidation of the substance excludes the possibility of taking an aliquot sample. From this the necessity arose of feeding the whole amount of gases into the chromatograph column, and this in the shortest possible time and without the dilution of the desired components in the mixture of gases. These problems can be solved by using the methods of decomposing the sample in a closed vessel by means of solid oxidizing agents [1, 2]. However, the existence of additional materials in the reaction tube is undesirable; the most convenient oxidizing agent and one which is very vigorous at high temperatures is oxygen [3]. Our method is based on the principle of the oxidation of the substance solely with gaseous oxygen [4]. The decomposition of the sample takes place by the method of "flash combustion" [5] in an excess of oxygen but in a closed system.

EXPERIMENTAL

We used a chromatograph of the KhL-4 type made in 1964. The reaction tube (volume 10 ml), attached directly to the inlet of the chromatograph, was simultaneously the metering vessel. To prevent the condensation of water vapor, the cock of the metering device and of the gas conduit up to its entry into the column was heated. The direct chromatography of the water and the selective separation of the components obtained by the given method of combustion (CO_2, O_2, H_2O) was achieved by the use of a two-section column. The alternate use of the first and second sections was based on the difference in the times of retention of water and the light gases by the corresponding filler [6]. The sections of the column were connected with one another and with the inlet by a three-way cock.

The substance (1-2 mg) in a micro platinum boat was placed in the reaction tube which was then purged with purified oxygen (2 min). The sample was burnt in the closed volume of the tube by means of an electric heater at 1100°C (1.5-2 min). The contents of the reaction tube were subsequently washed by the carrier gas into the chromatograph column.

The mixture of gases entered the first section, where the separation of the water from the CO_2 and O_2 took place, and then the second section, from which the separated gases passed through the outlet of the column into the katharometer and recorder.

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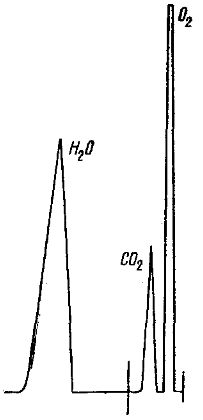

Fig. 1. Chromatogram of the products of the combustion of a standard substance.

TABLE 1

Substance	Sample h • a, mm²			Calculated %**	
	mg	CO_2 peak	H_2O peak	C	H
Sucrose $C_{12}H_{22}O_{11}$, C* 42.12, H 6.48	1,064	366,2	1175,7	42,19	6,65
Hederagenin [7] $C_{30}H_{48}O_4$, C 76.20, H 10.23	1,076	443,9	1227,0	76,26	10,37
	1,064	439,2	1169,0	76,30	10,00
Anthrone $C_{14}H_{10}O$, C 86.59, H 5.15	1,179	553,4	686,8	86,74	5,29
	1,227	574,1	696,6	86,46	5,15
Palmitic acid $C_{16}H_{32}O_2$, C 75.00, H 12.50	1,253	507,3	1734,2	74,82	12,56
	1,215	493,0	1671,6	74,98	12,48

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*C and H given in %.

**Titer established with respect to sucrose: for C 0.001848 mg/mm², for H 0.00009074 mg/mm².

The retention times of oxygen and carbon dioxide were 82 and 290 sec, respectively. At the moment when the water issued (430 sec), the second section was cut off from the flow of gas by turning the cock. Because the water passed into the detector without passing through the activated carbon, the recorder strip of the apparatus showed a narrow symmetrical peak (Fig. 1).

Working Conditions. Carrier gas helium at the rate of 35 ml/min; column temperature 110° C, diameter 0.4 cm. First section, *l* 250 cm, polyethyleneglycol 1540 (15%) on Teflon, 60-80 mesh (the outlet column, *l* 50 cm, was filled with the same material); second section: *l* 50 cm, SKT activated carbon, 100-120 mesh.

Calculation of the Results. The quantitative calculation was performed by formulas taking into account titers determined for each element by the combustion of a standard substance under analogous conditions.

$$E = \frac{T \cdot h \cdot a \cdot 100}{n},$$

where E is the content of the element in the substance being analyzed, %;

E_s is the content of the element in the standard, %;

h is the height of the peak, mm;

a is the width of the peak measured at $1/2$ h, mm;

n is the weight of the sample in mg; and

$$T = \frac{E_s}{h^c \cdot a^c},$$

Here, all the magnitudes are referred to the standard, mg/mm².

The results of analyses of several organic compounds are given in Table 1.

SUMMARY

A method for the microdetermination of carbon and hydrogen with the chromatographic determination of the products of the oxidation of the substance has been developed.

The accuracy of the method is within 0.2%.

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