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B. M. Luskina, S. V. Syavshillo,

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Abstract

Full Text

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B. M. Luskina, S. V. Syavshillo,
Corresponding Member of the Academy of Sciences of the USSR A. P. Terent' ev, and N. M. Turkel' taub

Microdetermination of Carbon and Hydrogen in Organic Compounds by Gas Chromatography

Existing methods for the analysis of carbon and hydrogen in organic compounds by combustion in a stream of oxygen in a tube filled with appropriate catalysts, or in an empty tube, followed by gravimetric or volumetric determination of carbon dioxide and water, are time-consuming and require continuous observation. A further development of elemental analysis is the combustion and determination of the oxidation products by gas chromatography; this simplifies and accelerates the analysis. The chromatographic methods described in the literature for determining carbon and hydrogen are based on the combustion of organic compounds in a stream of oxygen ([1]) or helium ([2]) in the presence of copper oxide. In this case the reaction products are greatly diluted by the gas in whose stream the combustion is carried out; therefore they are frozen out, the resulting condensate is separated on a column packed with silica gel, and analyzed chromatographically.

Fig. 1. Schematic diagram of the apparatus: 1—gas source; 2—needle valve; 3—pressure regulator (PDV); 4—drying column packed with perchlorate; 5—rheometer; 6—gas-flow regulator; 7—detector (C and P—reference and working chambers); 8—four-way valve; 9, $9'$—clamps; 10—quartz cup with sample; 11—electric furnaces; 12—quartz tube 35-40 cm long, 3-5 mm in diameter; 13—gas burner; 14—chromatographic column 60 cm long, 3 mm in diameter; 15—valve; 16—thermostat.

Since water is practically irreversibly absorbed by silica gel, the water formed is first converted into acetylene by reaction with calcium carbide. This complicates the determination and may lead to partial absorption of CO_2 by the calcium hydroxide released during interaction with CaC_2. Fogel and Quattrone ([3]) burned

organic substances in a specially constructed bomb in an oxygen atmosphere under pressure. The carbon dioxide and water formed were separated on a

Fig. 2

Figure 2: Fig. 2

column with dodecyl phthalate deposited on diatomaceous earth at 104°.

In contrast to the methods described, we carried out oxidation of the substance with copper oxide in a closed tube at a residual pressure of 10 mm Hg. Combustion in vacuum had previously been used for the determination of carbon, hydrogen, and nitrogen (4). In the method we propose, after combustion the reaction products were displaced by a stream of helium directly into a chromatographic column containing Inza brick impregnated with tricresyl phosphate in an amount of 20% of the weight of the support (5). A katharometer served as the detector. With this procedure, the disadvantages inherent in ordinary combustion methods were eliminated: breakthrough of the unburned portion of the substance, occurrence of flashes and explosions. In addition, it proved possible to avoid a number of difficulties of the previously proposed chromatographic methods of elemental analysis. The oxidation products were displaced directly by a stream of helium from the combustion tube and fed into the chromatographic column, and thus the need to use a dosing device was eliminated. The use of tricresyl phosphate as the stationary phase made it possible to separate CO_2 and H_2O at a temperature of 30°. The analysis was carried out under strictly defined conditions of temperature, pressure, and time and did not require continuous observation. Thus, the method can subsequently be fully automated.

The determination was carried out as follows (Fig. 1). Into tube *12* was placed a quartz cup *10*, 3 cm long and 2 mm in diameter, containing 2–5 mg of substance sprinkled with powdered copper oxide. Helium was passed through the entire system at a rate of 60 ml/min until the air was completely displaced, which was recorded on the chart of the EPP-09 recorder. Stopcock *15* was then closed in sequence, clamp *9′* was closed, and by means of stopcock *8* tube *12* was connected to a vacuum or water-jet pump; it was evacuated to a residual pressure of 10 mm Hg in furnaces *11* heated to 700°, after which clamp *9* was closed. Next the sample was heated for 8–10 min with the flame of gas burner *13*, clamp *9* was opened, and helium immediately entered the tube. Then clamp *9′* and stopcock *15* were opened in succession, and the combustion products formed were transferred by the helium stream into chromatographic column *14*, 60 cm long and 3 mm in diameter. Since carbon dioxide was rapidly removed from the column and the resulting peak did not fit on the chromatogram, the helium feed rate was reduced to 20 ml/min, and the scale was made five times less sensitive. After the CO_2 had emerged, the helium flow rate was increased to 60 ml/min, and the recorder was switched to a more sensitive scale (10 mV). These latter conditions were necessary for obtaining water peaks on the chromatogram. Fig. 2 shows a chromatogram obtained upon combustion of salicylic acid.

Fig. 2

The carbon and hydrogen contents were calculated by comparing the areas obtained for the CO_2 and H_2O peaks with a previously constructed absolute calibration curve based on peak areas obtained upon combustion of salicylic acid. The area of the CO_2 peak was measured by multiplying the peak height by the band width. The area of the asymmetric water peak was measured planimetrically. The completeness of combustion of the salicylic acid, from which the calibration curve was constructed, was checked as follows. After combustion of the sample under the conditions described above and

Table 1

Substance	C, % found	C, % calculated	Difference	H, % found	H, % calculated	Difference
Benzoic acid, $C_7H_6O_2$	69.23	68.84	+0.39	4.66	4.95	−0.29
Benzoic acid, $C_7H_6O_2$	69.18	68.84	+0.34		4.95	−0.20
Acenaphthene, $C_{12}H_{10}$	93.50	93.46	+0.04	4.75	6.54	−0.17
Acenaphthene, $C_{12}H_{10}$	93.62	93.46	+0.16	6.37	6.54	−0.11
2-Ethylanthraquinone, $C_{16}H_{12}O_2$	81.26	81.34	−0.08	6.43	5.12	−0.12
2-Ethylanthraquinone, $C_{16}H_{12}O_2$	81.14	81.34	−0.20	5.00	5.12	−0.11
2-Phenyl-3-carbethoxy-5-methoxy-6-methylbenzofuran, $C_{13}H_{18}O_4$	73.20	73.53	−0.33	5.01	5.84	0.0

Substance	C, % found	C, % calculated	Difference	H, % found	H, % calculated	Difference
2-Phenyl-3-carbethoxy-5-methoxy-6-methylbenzofuran, $C_{13}H_{18}O_4$	73.68	73.53	+0.15	5.84	5.84	+0.07
Ascorbic acid, $C_6H_8O_6$	40.64	40.92	−0.28	5.91	4.58	+0.21
Ascorbic acid, $C_6H_8O_6$	41.24	40.92	+0.32	4.79	4.58	−0.26
Ascorbic acid, $C_6H_8O_6$		40.92		4.32	4.58	

After obtaining the chromatogram, the tube was heated a second time; in this case a straight line was obtained on the recorder tape, which indicated the absence of additional combustion products.

By the described method, organic compounds containing C, H, and O were analyzed (see Table 1).

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References Cited

1. A. A. Duswalt, W. W. Brandt, *Anal. Chem.*, **32**, No. 2, 210 (1960).
2. O. E. Sundberg, C. Maresh, *Anal. Chem.*, **32**, 274 (1960).
3. A. M. Vogel, J. J. Quattrone, *Anal. Chem.*, **32**, 1754 (1960).
4. P. N. Fedoseev, L. S. Ignatenko, *Izv. AN TurkmSSR*, No. 1, 45 (1959).
5. N. M. Turkeltaub, *ZhFKh*, **31**, 2102 (1957).

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