Chemistry

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1965

SovietRxiv

Abstract

Full Text

Chemistry

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A New Method for the Automatic Microdetermination of Carbon and Hydrogen in Organic Compounds

(Presented by Academician I. V. Knunyants, 29 July 1964)

In recent years, instrumental methods for completing the analysis in the microdetermination of carbon and hydrogen have been intensively developed as a necessary stage preceding automation of the method. Numerous investigators have shown that the gravimetric determination of the end products of oxidation of organic compounds—carbon dioxide and water—can be replaced by conductometric (1-9), chromatographic (10-19), coulometric (20-22), spectroscopic (23), and other instrumental methods (24, 25). All the proposed methods are characterized by the need for additional transformations of the final oxidation products. Thus, for example, in conductometric completion of the analysis, conversion of water into CO_2 is provided for; in chromatographic analysis—into H_2; the coulometric determination of carbon is based

[Figure 1 schematic]

Fig. 1. 1 –combustion tube, 2 –quartz container, 3 –movable furnace (900-1000°), 4 –oxidation furnace (800-900°), 5 –furnace for heating absorbers of halogens and sulfur oxides (400-800°); 6 –thermostated vacuum gasometer, 7 –capillary, 8 –optico-acoustic gas analyzer for water vapor, 9 –the same for carbon dioxide, 10 –fore-vacuum pump, 11 –manostat maintaining constant pressure in the combustion tube and in the gasometer. EK1-EK11 –electromagnetic valves switching gas lines during the course of the analysis

important in the conversion of CO_2 into water, etc. This is a drawback of the methods, since with each additional process new sources of error are introduced due to the apparatus, reagents, and the process itself. Other drawbacks include the determination of carbon and hydrogen from different samples (4-6, 9, 13), or the determination of these elements from a single sample but by fundamentally different methods, for example, spectroscopic (C) and with a thermal-conductivity detector (H) (23). By no means have all instrumental—

Table 1

Automatic combustion of organoelement compounds with gravimetric completion of the analysis

Substance	C, % found	C, % difference	H, % found	H, % difference
Polytrifluoroethylene $(C_2HF_3)_n$,C 29.28%; H 1.23%	29.3729.54	+0.09+0.26	1.211.14	−0.02−0.09
Triphenylphosphine $(C_6H_5)_3P$,C 82.43%; H 5.76%	82.5182.42	+0.08−0.01	5.945.80	+0.18+0.04
Phenylbarev[[unclear: structural formula in the table cell]]C 43.59%; H 7.32%	43.5743.77	−0.02+0.18	7.447.43	+0.12+0.11
Polyethyramidosiloxane; C 56.94%*; H 7.43%*	57.0857.2456.91	+0.14+0.30−0.04	7.577.477.46	+0.14+0.04+0.03
Bromobenzoic acid$C_6H_4BrCOOH$, C 41.82%;H 2.51%	41.7941.78	−0.03−0.04	2.582.70	+0.07+0.19
Sulfanilic acid$C_6H_4NH_2SO_3H$, C 41.61%;H 4.07%	41.8441.86	+0.23+0.25	4.154.16	+0.08+0.09

* Found by the manual method.

methods of completing the analysis been described in fully automatic form, although the possibility of automation is inherent in each of them.

For the automatic combustion of organic compounds we have developed a method for burning small samples in a large volume of oxygen, in a special quartz container placed in a combustion tube (Fig. 1). With this combustion method, burning of the substance takes place in a space bounded by the walls of container 2 and by the heated zone created by the movable electric furnace 3 at the open end of the container. Ignition of the sample is carried out by this same furnace. The sufficiently large volume of the container ensures quantitative combustion within it of milligram samples of the substance, while the absence of an oxygen current inside the container prevents the breakthrough of unburned particles or vapors of the substance beyond the heated zone. With this combustion method the main difficulty that hinders automation of the method of Korshun and Klimova (26) is eliminated—the need to decompose the substance within the limits of a small quartz test tube without ejecting the substance beyond the test tube. In addition, combustion in a large volume of oxygen makes it possible to sharply increase the rate of oxygen washing the container (from 50 to 200 ml/min), which substantially facilitates the design of an automatic apparatus. The reliability of the adopted automatic-combustion regime was preliminarily checked on a large number of organic compounds (more than 500). The applicability of this method was demonstrated for substances containing fluorine, chlorine, bromine, iodine, sulfur, silicon,

phosphorus, boron, nitrogen, metals, provided that interfering compounds are absorbed by appropriate reagents (magnesium oxide, silver, asbestos, etc.) (see Table 1).

To measure the amount of carbon dioxide and water, optico-acoustic gas analyzers (27) were selected; they have high sensitivity and selectivity, which made it possible to analyze small concentrations of components in gas mixtures both in a continuous and in a periodic process. Since combustion of the substance and, accordingly, the entry of CO_2 and H_2O into the measuring instruments are nonuniform, it is necessary either to have a device for integrating the instantaneous readings of the instrument or to accumulate the combustion products in a constant volume (gasometer) and measure the average concentration of CO_2 and H_2O. The latter approach was chosen, since it eliminates errors associated with the inertia of the system. The volumetric concentration of CO_2 and H_2O in the gas mixture obtained in a 1.5-liter gasometer after combustion of 3-8 mg samples does not exceed 1%. For these concentrations, gas analyzers were developed with the following main parameters: a) for CO_2—the length of the working chamber is 2 mm, the volumetric concentration of CO_2 in the optico-acoustic chamber filled with argon is 2-3% at a ray-receiver depth of 5 mm; and b) for H_2O—the length of the working chamber is 70 mm, the volumetric concentration of H_2O in the thermostated optico-acoustic chamber filled with argon is 0.7% at a ray-receiver depth of 40 mm. The filter chambers, 20 mm long, are filled with CO_2. The instrument scales are graduated in milligrams of carbon and hydrogen. The operating mode of the apparatus is set by means of a multicontact time relay. The entire analysis cycle, from introduction of the sample to recording of the readings, lasts 17 min. Calibration curves (Fig. 2) were constructed from analyzer readings during combus-

Fig. 2

Table 2

Analyses performed on a fully automated apparatus

Substance	C, % found	C, % difference	H, % found	H, % difference
Benzoin $C_{14}H_{12}O_2$,C 79.22%;H 5.70%	79.76	+0.54	5.78	+0.08
Benzoin $C_{14}H_{12}O_2$,C 79.22%;H 5.70%	78.68	−0.60	5.84	−0.14
Dibenzoylethylene $C_{16}H_{12}O_2$,C 81.33%; H 5.12%	81.70	+0.37	4.75	−0.37
Dibenzoylethylene $C_{16}H_{12}O_2$,C 81.33%; H 5.12%	81.60	+0.27	4.77	−0.35
Polymer B-7086,C 92.02%;H 7.76%	91.79	−0.23	7.46	−0.30
Polymer B-7086,C 92.02%;H 7.76%	91.56	−0.46	7.48	−0.28
Dichloropropionic acid $C_3H_4O_2Cl_2$,C 45.41%; H 2.84%	25.52	+0.11	2.92	+0.08
Dichloropropionic acid $C_3H_4O_2Cl_2$,C 45.41%; H 2.84%	25.46	+0.05	2.88	+0.04
Dichlorocrotonic acid $C_4H_4O_2Cl_2$,C 31.00%; H 2.60%	31.44	+0.44	2.59	−0.01

Substance	C, % found	C, % difference	H, % found	H, % difference
Dichlorocrotonic acid $C_4H_4O_2Cl_2$,C 31.00%; H 2.60%	31.29	+0.29	2.64	+0.04
Bromobenzoic acid $C_7H_5O_2Br$,C 41.82%; H 2.51%	41.34	−0.48	2.31	−0.20
Bromobenzoic acid $C_7H_5O_2Br$,C 41.82%; H 2.51%	41.35	−0.47	2.31	−0.20

of standard substances—sucrose, salicylic and palmitic acids, and anthracene. Examples of analyses performed with automatic combustion and measurement of the amounts of CO_2 and H_2O are given in Table 2. The root-mean-square error of the method is 0.37 abs.% for carbon and 0.17 abs.% for hydrogen.

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Received
21 VII 1964

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