Chemistry

I. A. Revel'skii, R. I. Borodulina, T. M. Sovakova, V. G. Klimova

1964

SovietRxiv

Abstract

Full Text

Chemistry

I. A. Revel' skii, R. I. Borodulina, T. M. Sovakova, V. G. Klimova

A Rapid Method for Determining the Number of Carbon and Hydrogen Atoms in Molecules of Gaseous Compounds

(Presented by Academician M. I. Kabachnik, April 15, 1964)

As is known, carrying out elemental analysis of gaseous compounds—especially fluorine-containing ones—presents considerable difficulties. Reliable results, as a rule, are obtained only for comparatively high-boiling compounds that can be condensed at the temperature of solid carbon dioxide ([1]). In the case of lower-boiling gases, the results are often incorrect because of inaccuracy in taking the sample of substance. The introduction of the sample into the combustion tube also causes considerable difficulties ([2]).

Gas chromatography, which has become widely used as one of the principal methods for analyzing mixtures of organic compounds, can be of great assistance in carrying out elemental analysis of gaseous compounds.

Recently, a number of works have appeared devoted to carrying out elemental analysis of pure organic compounds—liquid and solid—with the aid of gas chromatography. The use of gas chromatography has sharply reduced the time required for analysis, while in many cases the accuracy of the analysis is not inferior to that of the classical method.

In most of these works, the authors burn a sample of the substance in a stream of oxygen ([3]) or helium—in the presence of an oxidation catalyst ([4–6])—convert the water into acetylene, and trap it together with carbon dioxide in a liquid-air trap. The acetylene and CO_2 are then introduced into a chromatographic column and recorded by means of a thermal-conductivity detector. From calibration curves in coordinates "peak area—carbon and hydrogen content in milligrams," the elemental composition is determined.

A substantial drawback of the proposed methods, as in the case of the classical method, is the need to take an exact sample of the substance being analyzed, which is not always possible in the case of gaseous substances. In addition, the need to trap the conversion products and subsequently chromatograph them significantly increases the analysis time and complicates the procedure.

The aim of the present work was to develop a rapid method for determining the

Fig. 1. Diagram of the apparatus

Figure 1: Fig. 1. Diagram of the apparatus

number of carbon and hydrogen atoms in molecules of gaseous compounds.

Experimental Part

Procedure. The work was carried out on an apparatus consisting of two KhL-3 chromatographs and a combustion unit (Fig. 1).

On the first chromatograph (2), the purity of the compounds is checked and impurities are separated, while on the second (9), the carbon dioxide and hydrogen formed after combustion are determined. The thermostat temperature of the first chromatograph is set depending on the boiling point of the compound being analyzed. On the second chromatograph the thermostat temperature is maintained at 40°. The packing of the column of the first chromatograph

In the analysis of low-boiling compounds, as a rule, KSM-6S silica gel, pre-dried at 150°, is used.

The carrier-gas flow rate (nitrogen) is 25 ml/min. Samples with a volume of 0.2-2 cm^3 are introduced by means of a sampling valve. The compounds leaving the first chromatograph enter, in the carrier-gas stream, through valve (3), one of the combustion tubes. In the analysis of compounds containing no halogens, one of the tubes (4) is filled with copper oxide (in the form of wire), and the other —with copper oxide for two thirds (by volume) and with reduced iron (powder with grain size 0.5-1 mm) for one third (5). The tubes are quartz, $d_{\text{in}} = 6$ mm, length 75 cm. Combustion is carried out in a tubular electric furnace consisting of two sections: one 40 cm long (temperature 850–900°), the other 20 cm long ($720 \pm 10°$) (the lowering of the furnace temperature in the zone of reduced iron to 720° is due to the fact that at higher temperatures sintering of the iron granules occurs and the flow resistance increases greatly). The furnace temperature is regulated with the aid of a laboratory autotransformer. At the exit from the furnace, after the tube with copper oxide, an absorption tube with anhydrone (7) is placed; and after the tube with copper oxide and reduced iron, a tube with ascarite and hopcalite (8) is placed.

Fig. 1. Diagram of the apparatus: 1—nitrogen source; 2, 9—chromatographs of type KhL-3; 3—three-way valve; 4—tubular electric furnace; 5—combustion tube with copper oxide; 6—combustion tube with copper oxide and reduced iron; 7—absorption tube with ascarite and hopcalite; 8—absorption tube with anhydrone

In the analysis of fluorine-containing and other halogen-containing compounds, the packing of the combustion tubes and the furnace temperature are changed somewhat: tube (4)—I layer copper oxide—15 cm at 800–900°; II layer magnesium oxide—10 cm at 900°; III layer copper oxide—15 cm at 900–800°; IV layer silver

–5 cm at 400–500°; and V layer copper oxide–20 cm at 720°. Tube (5)–layers I-IV the same as in tube (4); V layer–reduced iron–20 cm at 720°.

When the substance passes through tube (4) during combustion, carbon dioxide and water are formed.

In this case the water is absorbed by anhydrone, and only carbon dioxide enters the measuring cell of the detector of the second chromatograph; i.e., the peak of the chromatogram of the first chromatograph in this case will correspond to the CO_2 peak on the chromatogram of the second instrument.

When the stream passes through the other tube (5), the water formed during combustion of the compound is reduced to hydrogen, the carbon dioxide is absorbed by ascarite, and the second chromatograph records only the hydrogen peaks (hopcalite serves to convert small amounts of CO, formed from CO_2 on iron, into CO_2).

Thus, upon combustion of the substance we obtain separate peaks of CO_2 and H_2.

In the case where the substance contains no impurities (as shown by the first chromatograph), simultaneous recording of the CO_2 and H_2 peaks obtained upon combustion of the compound is possible in order to accelerate the analysis. For this purpose, a column for separating H_2 and CO_2 (KSM-6S silica gel, 1 m) is connected to the second chromatograph, and the stream after combustion tube (5) enters the second chromatograph, bypassing the tube with ascarite and hopcalite.

Calculation of the number of carbon and hydrogen atoms in the molecule of the compound is carried out from the peak areas of CO_2 and H_2 (S_{CO_2} and S_{H_2}) after preliminary calibration of the detector, for which volumes of carbon dioxide and hydrogen equal to the volume of the compound being analyzed are introduced into the first chromatograph.

The time for one determination is 5 min.

Results of the experiments and their discussion

When any substance is burned, CO_2 and H_2 are formed according to the equation:

$$\mathrm{C}_n\mathrm{H}_m \xrightarrow{\mathrm{O}} n\mathrm{CO}_2 + \frac{m}{2}\mathrm{H}_2,$$

Obviously, the peak areas of CO_2 and H_2 will be proportional to the number of moles of CO_2 and H_2.

The number of carbon atoms (n) and hydrogen atoms (m) in a molecule can be determined if the peak areas of CO_2 and H_2–the conversion products of a given volume of the compound being analyzed–and the peak areas obtained when equal volumes of carbon dioxide and hydrogen, respectively, are introduced into the apparatus are known.

Then: $n = S'_{CO2}/S_{CO2}$ and $m = S'_{H2}/S_{H2}$, where S'_{CO2} and S'_{H2} are the peak areas of CO_2 and H_2—the conversion products of the compound being analyzed; S_{CO2} and S_{H2} are the peak areas obtained when equal volumes of CO_2 and H_2 are introduced; n and m are the numbers of carbon and hydrogen atoms in the molecule of the compound, respectively.

The experiments showed that, under the combustion conditions given above, complete conversion into carbon dioxide and hydrogen is achieved for the most difficult-to-oxidize substances, such as methane and fluorine-containing gaseous compounds.

Data on determining the number of carbon and hydrogen atoms in the molecules of a number of fluorine-containing compounds and hydrocarbons are given in Table 1 (the degree of purity of the compounds listed was 97–99%).

Table 1

Results of experiments on determining the number of carbon and hydrogen atoms in gaseous compounds

Substance	Number of C atoms in the molecule, calculated	Number of C atoms in the molecule, true	Relative error, %	Number of H atoms in the molecule, calculated	Number of H atoms in the molecule, true	Relative error, %
C_2F_4	2,11	2,00	5,5	–	–	–
C_2F_4	2,10	2,00	5,0	–	–	–
C_2F_4	2,09	2,00	4,5	–	–	–
$C_2F_2H_2$	2,04	2,00	2,0	1,96	2,00	2,0
$C_2F_2H_2$	2,09	2,00	4,5	1,95	2,00	2,5
$C_2F_2H_2$	2,10	2,00	5,0	1,92	2,00	4,0
C_2F_3H	2,00	2,00	0,0	0,97	1,00	3,0
C_2F_3H	1,95	2,00	2,5	0,97	1,00	3,0
C_2F_3H	1,94	2,00	3,0	0,96	1,00	4,0
CF_2ClH	0,99	1,00	1,0	1,05	1,00	5,0
CF_2ClH	0,98	1,00	2,0	1,04	1,00	4,0
CF_2ClH	0,99	1,00	1,0	1,02	1,00	2,0
CF_2Cl_2	1,04	1,00	4,0	–	–	–
CF_2Cl_2	1,06	1,00	6,0	–	–	–
CF_2Cl_2	1,05	1,00	5,0	–	–	–
CH_4	0,99	1,00	1,0	3,87	4,00	3,3
CH_4	0,98	1,00	2,0	3,73	4,00	6,7
CH_4	1,00	1,00	0,0	3,72	4,00	7,0

Substance	Number of C atoms in the molecule, calculated	Number of C atoms in the molecule, true	Relative error, %	Number of H atoms in the molecule, calculated	Number of H atoms in the molecule, true	Relative error, %
C_2H_4	1,98	2,00	1,0	3,94	4,00	1,5
C_2H_4	2,07	2,00	3,5	3,91	4,00	2,3
C_2H_4	2,10	2,00	5,0	3,93	4,00	1,8
C_3H_6	3,04	3,00	1,1	6,39	6,00	6,5
C_3H_6	3,02	3,00	1,0	6,34	6,00	5,7
C_3H_6	3,12	3,00	4,0	6,42	6,00	7,0
C_4H_8	4,14	4,00	3,5	7,84	8,00	2,00
C_4H_8	4,12	4,00	3,0	7,80	8,00	2,5
C_4H_8	4,13	4,00	3,2	7,98	8,00	0,25

From the data presented it follows that direct and rapid determination of the number of carbon and hydrogen atoms in molecules of individual gaseous compounds is possible. This eliminates the need to determine the weighed amount of the substance being analyzed, which substantially simplifies and speeds up the analysis; moreover, the error of determination in most cases does not exceed 5% relative.

If impurities are present in the substance being analyzed, the use of two chromatographs makes it possible to introduce the appropriate correction for the impurity volume and to carry out the analysis with greater accuracy than is possible by the classical method of elemental analysis.

A rapid method has been proposed for determining the number of carbon and hydrogen atoms in molecules of gaseous compounds, without preliminary weighing of samples. The method is based on thermoconductometric determination of the ratio of the amounts of carbon dioxide and hydrogen in equal volumes of the gases being analyzed and of a standard substance.

Received
3 IV 1964

CITED LITERATURE

1. N. E. Gel' man, M. O. Korshun, K. I. Novozhilova, *ZhAKh*, **15**, No. 5, 628 (1960).

2. M. O. Korshun, N. E. Gel' man, *New Methods of Elemental Microanalysis*, Moscow–Leningrad, 1949, p. 45.

3. A. M. Vogel, J. J. Quattrone, *Anal. Chem.*, **32**, 1754 (1960).

4. A. A. Duswalt, W. W. Brandt, *Anal. Chem.*, **32**, 272 (1960).

5. O. E. Sundberg, C. Maresh, *Ibid.*, **32**, 274 (1960).

6. W. Walisch, *Chem. Ber.*, **94**, 2314 (1961).

Note: Figure translations are in progress. See original paper for figures.