Corresponding Member of the Academy of Sciences of the USSR A. P. Terent' ev, A. M. Turkel' taub,

E. A. Bondarevskaya, L. A. Domochkina

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Abstract

Full Text

CHEMISTRY

Corresponding Member of the Academy of Sciences of the USSR A. P. Terent' ev, A. M. Turkel' taub,
E. A. Bondarevskaya, L. A. Domochkina

GAS-CHROMATOGRAPHIC DETERMINATION OF NITROGEN AND OXYGEN IN ORGANIC COMPOUNDS

The determination of nitrogen by Dumas ([1]) and of oxygen by Unterzaucher-Korshun ([2,3]) leads to the formation, respectively, of nitrogen and carbon monoxide. Nitrogen is measured gasometrically, while CO is oxidized by various oxidizing agents to CO_2 and determined titrimetrically or gravimetrically.

Until now no ways had been proposed for combining both methods for the simultaneous determination of nitrogen and oxygen. The use of gas chromatography makes it possible to find such a solution. However, attempts had been made to use chromatography only for the separate determination of one or the other element. Thus, in 1961 a report was published ([4]) on the determination of nitrogen. The authors carried out oxidation of the substance and, in the mixture of gases obtained after pyrolysis, determined nitrogen chromatographically in the form of elemental nitrogen and its oxides. It is easy to calculate that such a method will hardly find application, since the determination of nitrogen from three factors (NO_2, NO, N_2) entails large errors.

Fig. 1. Chromatogram obtained in the analysis of acetanilide: **1** —peak for nitrogen; **2** —peak for methane; **3** —peak for carbon monoxide

Quite recently ([5]) a gas-chromatographic completion of the determination of oxygen from the carbon monoxide formed was proposed. The author carries out pyrolysis of the substance in the presence of carbon black in a stream of hydrogen. Replacing the titrimetric or gravimetric determination by a chromatographic one promises to create a number of advantages, including the possibility of automating the process, and will also make it possible in the future to develop ultramicro methods. However, the use of hydrogen as carrier gas is hardly

Fig. 2. Installation diagram

Figure 2: Fig. 2. Installation diagram

successful, since in this case the possibility increases of shifting the equilibrium

$$H_2 + CO \rightleftarrows H_2O + CO$$

toward the formation of water. This makes it necessary to heat to 1120°, which introduces many difficulties.

In the cases of determining nitrogen and oxygen, the authors ([4,5]) did not attempt to introduce any changes into the essence of the methods. Nor was any attempt made at the simultaneous determination of nitrogen and oxygen, apparently because the stage of nitrogen formation proceeds on an oxidizing agent, whereas the formation of carbon monoxide requires a reducing medium.

In the method of analysis proposed by us, the determination of nitrogen and oxygen from a single sample is carried out on a reducing agent. Substantial changes have been introduced into the stage of decomposition of the substance. The determination of the final reaction products (N_2 and CO) is carried out by means of gas-adsorption chromatography. To obtain the simplest gas mixture, we carried out pyrolysis in a rarefied, stationary helium atmosphere in a closed tube in the presence of carbon black. This makes it possible to conduct the process uniformly for substances of differing volatility, without fear of "breakthrough" and incomplete reduction of the oxides of nitrogen and carbon dioxide. In order to lower the temperature

pyrolysis to 900°, as the reducing agent we used "nickelized" carbon black, as had been done previously ([6]), with a slight modification. In contrast to previous authors, we prepared the "nickelized" carbon black by mixing a solution of nickel formate with carbon black (Ni : C = 1 : 1), followed by evaporating the solution to a paste, drying, and calcining the paste in a stream of nitrogen or helium at 900° for 3-4 h. The presence of nickel in the carbon black apparently sometimes leads to the formation, in small amounts, of methane as a result of intermediate hydrogenation of CO and CO_2

Fig. 2. Installation diagram: **1** –cylinder with helium; **2** –fine-control valve; **3** –drying column with ammonium perchlorate; **4** –rheometer; **5** –detector (C and P are the reference and working chambers); **6** –one-way valve for supplying helium free of oxygen; **7** –boat with the substance; **8** –electric furnace at 900°; **9** –quartz tube 6-7 mm in diameter, volume 10 ml, with "nickelized" carbon black; **10**, **11** –three-way stopcocks; **12** –gas burner; **13** –thermostat; **14**, **15** –three-way stopcocks; **16** –chromatographic column 600 mm long, 4 mm in diameter; **17** –electric furnace at 300°.

by hydrogen formed in the tube during the pyrolysis process. Thus, in the analysis of acetanilide, in addition to the peaks of nitrogen and carbon monoxide,

Fig. 3

Figure 3: Fig. 3

a peak for methane was obtained on the chromatogram (Fig. 1). The chromatogram showed that there was no carbon dioxide in the gas mixture after decomposition.

In the analysis of substances of composition C, H, O, N, two peaks are observed on the chromatogram, for CO and N_2. For substances of composition C, H, N, the chromatograph recorder traces a peak for N_2, and in place of the expected CO peak a straight line is obtained; in the case of analysis of compounds of composition C, H, O, a straight line is obtained in place of the N_2 peak.

Thus, the use of gas-adsorption analysis not only makes it possible to speed up the determination of pyrolysis products, but also permits complete monitoring of the decomposition process for various classes of organic substances.

It was first necessary to select conditions for separating a gas mixture containing hydrogen, oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide. Separation of such a mixture was carried out on a column 600 mm long and 4 mm in diameter, packed with sorbent–5A molecular sieves, previously ground to 0.5–1.0 mm and dried under vacuum at 300° for 2 h. Helium was used as the carrier gas (flow rate 50 ml/min). By this method it was possible to separate hydrogen, oxygen, methane, and carbon monoxide at room temperature. To displace carbon dioxide, which was absorbed by the sorbent–

therefore, at the beginning of the column, either back-flushing with helium or a side outlet (a) was used while heating the column with an electric furnace to 300° (Fig. 2).

From the chromatogram (Fig. 3) the completeness of separation of all the indicated components is evident. We transferred the conditions for separation of the artificial mixture to the analysis of vacuum-pyrolysis gases in the direct determination of oxygen and nitrogen in organic substances.

Fig. 3. Chromatogram obtained in the separation of an artificial mixture: 1 – peak for oxygen; 2 –peak for nitrogen; 3 –peak for methane; 4 –peak for carbon monoxide; 5 –peak for carbon dioxide

The analysis was carried out as follows (Fig. 2). A 5-10 mg sample of the substance to be analyzed, in a quartz or platinum boat, was introduced into a quartz tube 6-7 mm in diameter and of 10 ml capacity, containing a layer of "nickel-plated" carbon black at 900°. Stopcock (6) was closed, and stopcock (10) was turned toward the vacuum pump; a vacuum was created in the tube down to a residual pressure of 20 mm Hg, and it was kept under these conditions for 5 min. Then stopcock (10) was closed and stopcock (6) was opened for 3 min, admitting helium purified of oxygen. Next, vacuum was again produced in the tube for 5 min, as described above. During this time the air that had

entered the tube during introduction of the sample was removed from it. Then stopcock (10) was closed, and the sample was decomposed with a gas burner. Decomposition was complete in 5 min. After this, stopcock (10) was opened, stopcock (11) was turned toward the column, and the decomposition products were displaced onto the chromatographic column for 10 min by a stream of helium (flow rate 5 ml/min). Then stopcock (10) was closed, and through stopcock (11) the gas mixture under analysis was developed with a helium stream (flow rate 50 ml/min). The time required for displacement of the air, as well as of the decomposition products, from the reaction tube was determined by us experimentally in preliminary blank experiments. In this case a straight line was always obtained on the recorder chart.

Table 1

Substance	Sample, mg	O, % found	O, % calc.	Difference, %	N, % found	N, % calc.	Difference, %
Urea CH_4ON_2	5,535	26,7	26,64	+0,1	46,9	46,65	+0,25
Urea CH_4ON_2	5,259	26,6	26,64	0,0	47,0	46,65	+0,35
Anthranilic acid $C_7H_7O_2N$	5,102	23,6	23,33	+0,3	10,5	10,21	+0,3
Anthranilic acid $C_7H_7O_2N$	4,590	23,1	23,33	−0,2	10,3	10,21	+0,1
Acetanilide C_8H_9ON	6,950	12,0	11,8	+0,2	11,0	10,36	+0,6
Acetanilide C_8H_9ON	5,251	12,2	11,8	+0,4	10,8	10,36	+0,4
Hydrazine tartaric anhydride $C_5H_6O_5N_2$	4,999	45,9	45,9	0,0	16,5	16,1	+0,4
Hydrazine tartaric anhydride $C_5H_6O_5N_2$	6,005	45,8	45,9	−0,15	16,7	16,1	+0,6
Urotropine $C_6H_{12}N_4$	4,825	–	–	–	40,8	40,0	+0,8
Urotropine $C_6H_{12}N_4$	2,154	–	–	–	40,3	40,0	+0,3

Substance	Sample, mg	O, % found	O, % calc.	Difference, %	N, % found	N, % calc.	Difference, %
Benzoic acid $C_7H_6O_2$	7,518	25,9	26,2	−0,3	–	–	–
Benzoic acid $C_7H_6O_2$	6,638	26,5	26,2	+0,3	–	–	–
Salicylic acid $C_7H_6O_3$	5,127	34,4	34,8	−0,4	–	–	–
Salicylic acid $C_7H_6O_3$	3,830	35,0	34,8	+0,2	–	–	–
Oxalic acid $C_2H_2O_4$	4,002	71,1	71,1	0,0	–	–	–
Oxalic acid $C_2H_2O_4$	4,699	70,8	71,1	−0,3	–	–	–
Hydroquinone $C_6H_6O_2$	3,932	28,8	29,06	−0,2	–	–	–
Hydroquinone $C_6H_6O_2$	3,451	29,1	29,06	+0,1	–	–	–

The content of nitrogen and oxygen in the substance analyzed was calculated from the areas of the peaks on the chromatograms, comparing them with calibration curves. The calibration curves were constructed from the areas of peaks obtained upon decomposition of different weighed portions of urea. The area of the N_2 peak was determined by multiplying the peak height by the width at half-height. The area of the asymmetric CO peak was measured with a planimeter. A linear relationship was thereby obtained between the peak areas of carbon monoxide and nitrogen and the oxygen and nitrogen contents in the weighed portion of the substance.

By the method described, a number of organic substances containing carbon, hydrogen, oxygen, and nitrogen were analyzed (Table 1).

Moscow State University
named after M. V. Lomonosov

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