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CONTINUOUS ELEMENTAL ANALYSIS OF NITROGEN-CONTAINING SUBSTANCES BY THE USE OF GAS CHROMATOGRAPHY

JAROSLAV FRANČ and JAROSLAV POUR

Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví (Czechoslovakia)

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SUMMARY

A method has been developed for the continuous determination of the C:N ratio in organic substances by use of gas chromatography. The components leaving the gas chromatograph undergo combustion to carbon dioxide, nitrogen and water. After absorption of the water, the remaining $\text{CO}_2 + \text{N}_2$ mixture is determined by means of one detector and N_2 is determined by means of a second detector after absorption of the CO_2 . The ratio of the areas under the recorded peaks corresponds to the C:N ratio.

INTRODUCTION

The use of gas chromatography (GC) has been extended to the elemental analyses of organic substances, including the determination of nitrogen. However, the elemental analyses which have been described are mainly suitable for the determination of nitrogen in pure substances. If GC is employed for this purpose, the procedure involves combustion of the substance, passage of the combustion products through the chromatographic column where they are separated and detected by a sensor and determination of the individual elements present from the magnitudes of the detector signals. Various methods differ practically only in the method of combustion of the organic substances, or in their elution. Yevtushenko *et al.*¹ have reviewed the elemental analysis of nitrogen by use of GC. Two methods which are not included in this review are those of Walsh² and of Rezl *et al.*³. Few workers have described a method for the determination of nitrogen in substances after GC separation of the mixture. Coulson^{4,5} developed a special ammonia detector: the substance leaving the chromatographic column is hydrogenated in a stream of hydrogen gas in the presence of a nickel catalyst, and the ammonia formed from the nitrogen present in the molecule is detected by means of a special coulometric detector. The resulting chromatogram contains only peaks due to ammonia; substances which do not contain nitrogen are not recorded. Martin⁶ reported a similar method for which he designed a special automatic ammonia titrator. In none of these cases was the C:N ratio recorded for components leaving the chromatographic column. Only Liebman *et al.*⁷ separated the products of combustion on a second column.

We have already developed a method for the continuous determination of the C:H ratio for substances leaving a chromatographic column⁸, which is based on almost simultaneous monitoring of the signals from two detectors, through which passes the gaseous mixture formed on combustion of the separated components. The present paper describes an analogous method in which the same instrument can be employed under different conditions. The C:N ratio is determined and is used for the identification of unknown components in mixtures of organic substances. The principle of the method is as follows. The components are first separated on a conventional chromatographic column using helium as the carrier gas; they are then led to an oven where they are combusted, yielding a mixture of carbon dioxide, water and nitrogen. This mixture is first passed to an absorber in which water is removed and then to the first detector which records the sum of the carbon dioxide and nitrogen. The carbon dioxide is removed in a second absorber, so that the second detector records the amount of nitrogen. The signals from the two chromatographic detectors are recorded and compared, yielding the C:N ratio for each component of the mixture and determining whether a given substance contains nitrogen.

EXPERIMENTAL

The chromatographic separations were carried out on a chromatograph equipped with combustion detection⁹, and in combination with a thermal conductivity detector. The apparatus is depicted in Fig. 1. The carrier gas (helium) is led from cylinder 1 through gas-drying column 2, manostat 3 and manometer 4 into the reference chambers of the thermal conductivity detectors 7 and 8; it is then passed through chromatographic column 6 which is provided with injection device 5 and through oven 9 and flow-meter 13. The first absorber (10) is connected between oven 9 and detector 7, and the second absorber (11) is placed between detectors 7 and 8. Both detectors 7 and 8 are connected to recorder 12. Oven 9 consists of a quartz glass tube (*ca.* 34 cm \times 0.5 cm I.D.) packed with cupric oxide wires so that the dead volume is minimized. Heat can be applied to the tube by means of a resistor wire coil, the temperature of the combustion zone being *ca.* 800°. The first absorber (10) consists of a glass tube (10 cm \times 0.4 cm I.D.) filled with magnesium perchlorate. The second

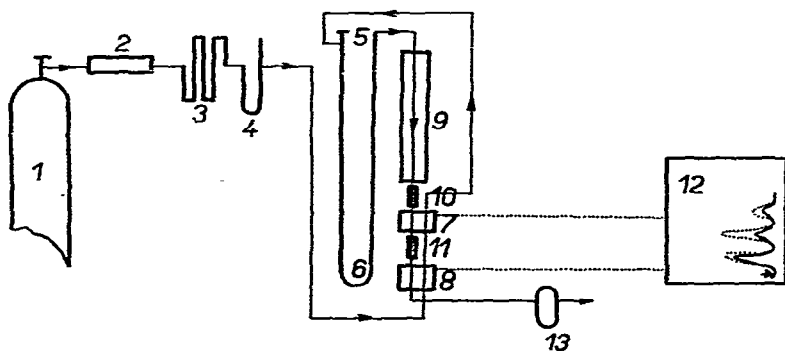


Fig. 1. Scheme of the equipment used. 1 = Carrier gas; 2 = gas-drying column; 3 = manostat; 4 = manometer; 5 = injection device; 6 = GC column; 7, 8 = thermal conductivity detectors; 9 = oven; 10, 11 = absorbers; 12 = recorder; 13 = flow-meter.

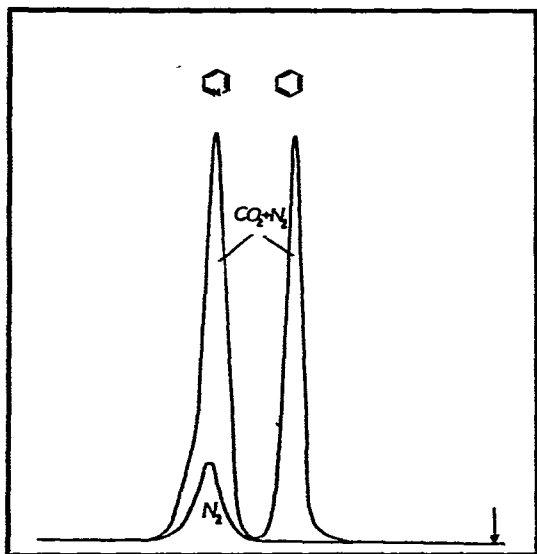


Fig. 2. Separation of benzene and pyridine.

absorber (11) is a glass tube (10 cm \times 0.4 cm I.D.) packed with caustic asbestos. Two-pen or single-pen recorders were used; the latter has a device which enables the signals from the two detectors to be switched on alternately at 5-sec intervals. The recorder range is 1 mV. Thermal conductivity sensors, supplied from a 6-V stabilizer, were employed as detectors, having identical baselines. The sample size was the same as in conventional chromatographic separations. The chromatographic column used (140 cm) was packed with a suitable material for separation of the analyzed mixture at the required temperature. The carrier gas (helium) flow-rate was *ca.* 2.0 l/h. A known substance, for which the ratio of the $\text{CO}_2 + \text{N}_2$ peak areas to the N_2 peak area was determined, was used for the calibration. Similarly, the $\text{CO}_2 + \text{N}_2$ to N_2 peak area ratio was determined for all of the substances separated by GC (Fig. 2).

RESULTS AND DISCUSSION

The results obtained are given in Table I. It can be seen that the precision attained does not reach the standard established by classical elemental analysis. However, the purpose of this study should be borne in mind, namely, the identification of substances through the determination of which chromatographic peaks correspond to nitrogen-containing substances and through the approximate C:N ratio. It follows from the table that this requirement has been attained. The error is somewhat high only with butylamines; this is caused by the high boiling points of these substances and the low temperature of the chromatographic column, so that the peaks are drawn out and the baseline is more difficult to determine.

As mentioned previously, the detector signal corresponding to the mixture of carbon dioxide and nitrogen and that corresponding to nitrogen alone were recorded. Since the amount of nitrogen in a molecule is usually considerably smaller than that

TABLE I
DETERMINATION OF THE C:N RATIO

Compound	Number of determinations	C:N Ratio		ΔN^*
		Theory	Found	
Dimethylformamide	3	3.0:1.0	3.0:0.96	-0.04
Diethylformamide	1	5.0:1.0	5.0:1.08	+0.08
Monoethanolamine	3	2.0:1.0	2.0:0.95	-0.05
Aniline	5	6.0:1.0	6.0:1.00	± 0.00
Nitrobenzene	3	6.0:1.0	6.0:1.00	± 0.00
Pyridine	4	5.0:1.0	3.0:1.02	+0.02
Isopropylamine	2	3.0:1.0	3.0:1.05	+0.05
Isobutylamine	5	4.0:1.0	4.0:0.96	-0.04
<i>n</i> -Butylamine	4	4.0:1.0	4.0:0.98	-0.02
Diethylamine	4	4.0:1.0	4.0:0.98	-0.02
Di- <i>n</i> -propylamine	3	6.0:1.0	6.0:1.02	+0.02
Diisobutylamine	4	8.0:1.0	8.0:1.09	+0.09
Di- <i>n</i> -butylamine	5	8.0:1.0	8.0:1.10	+0.10
Tri- <i>n</i> -propylamine	3	9.0:1.0	9.0:1.01	+0.01
Tri- <i>n</i> -butylamine	1	12.0:1.0	12.0:0.91	-0.09
<i>n</i> -Propylamine	2	3.0:1.0	3.0:0.98	-0.02
α -Picoline	5	6.0:1.0	6.0:1.03	+0.03
2,6-Lutidine	5	7.0:1.0	7.0:0.97	-0.03
Acetamide	1	2.0:1.0	2.0:0.94	-0.06

* ΔN is the difference between theoretical and found nitrogen values.

of carbon, it is necessary to adjust the sensitivities of the detectors so as to obtain a favourable ratio of the two peak areas. The second detector, monitoring nitrogen, operates at the maximum sensitivity, while the sensitivity of the first detector is somewhat lower. The sensitivity should be adjusted so that the area of the carbon dioxide plus nitrogen peak is about twice that of the nitrogen peak at a C:N ratio of 1:1. A two-pen recorder is most suitable for this purpose; a single-pen recorder, with a switch alternating the detector signals at pre-set intervals, or two separate recorders can also be used.

The peak areas were determined by planimetry. The nitrogen peak was identified through its small shift in elution time compared with the carbon dioxide plus nitrogen peak.

The combustion tube contained a single packing, cupric oxide wires. If halogen-, sulphur- or phosphorus-containing substances were to be studied, a silver layer deposited on pumice would have to be placed at the end of the tube in order to absorb these elements. A certain amount of nitrogen oxides is always formed during combustion of nitrogen-containing substances. We found that the most accurate results were obtained when the combustion temperature was fairly high, *i.e.*, 800°. If nitrogen oxides are formed at this temperature, the results indicate that they are only formed in small amounts.

In order to attain accurate results, a standard substance, *i.e.*, a substance for which the C:N ratio is known, must be injected into the chromatograph. A standard having a boiling point corresponding to the distillation range of the separated mixture

should be selected. Although the results obtained differed somewhat from the theory, the precision was sufficient for safe estimation of the ratio of the number of carbon atoms in a molecule to the number of nitrogen atoms. The method cannot be used for substances that cannot be separated by GC.

When components which did not contain nitrogen occurred in large amounts in the mixture, the second detector sometimes recorded a low wave, thus apparently indicating the presence of nitrogen. However, this is only a pressure wave, and if the nitrogen content is calculated it is clear that the substance would had to have been so large that it certainly could not be chromatographed. In such cases the analysis was repeated with a smaller sample.

Finally, it should be emphasized that this method permits the determination of the C:N ratio not only for pure substances, but also for the individual components leaving the chromatographic column. If this method is combined with a determination of the C:H ratio, a complete picture of the individual components of an unknown mixture may be obtained.

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