

CHROM. 9518

IDENTIFICATION OF ORGANIC COMPOUNDS BY AN ELUTION GAS CHROMATOGRAPHY-REACTOR-FRONTAL GAS CHROMATOGRAPHY SYSTEM

VLASTIMIL REZL and JIŘÍ BURSA

Institute of Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

SUMMARY

The on-line identification of gas chromatographic (GC) effluents is described using an automated elution GC-reactor-frontal GC instrumental system and exploiting a commercial gas chromatograph for this purpose. The identification is based on elemental analysis, *viz.*, the determination of the empirical formula without knowing the amount of the substances being analyzed. A detailed discussion is given of C,H,N,O determinations. With the system described, it is possible to analyze, with satisfactory precision, as little as 10 μg of a substance.

INTRODUCTION

During the rapid development of gas chromatography (GC) and its applications in organic chemistry, macromolecular chemistry, biochemistry and biology, a demand arose for the identification of components leaving the GC column after separation. A number of methods evolved gradually in this way, based essentially on the direct coupling of GC with mass spectrometry (MS), infrared spectrometry, Raman spectrometry, etc. In addition to the fact that these instrumental combinations are expensive, they usually require highly specialized operators, who are capable of interpreting the very complicated data that are produced.

Elemental analysis (EA), which is one of the most commonly employed identification methods in organic chemistry, has also been subjected to attempts to combine it with GC, particularly after the intensive development of automatic instrumentation¹⁻¹³. Nevertheless, only one such technique has found a commercial application^{14,15}, and there are a number of difficulties that have to be overcome in the realization of a practically utilizable instrumental arrangement. As the data that can be obtained from this coupling are as useful as those obtained from GC-MS, it deserves greater attention.

Some problems associated with the realization of the GC-EA coupling have been discussed earlier¹². They involve mainly the design of the elemental analyzer, the reaction section, arrangements for the isolation and/or conservation of the individually chromatographically separated components or fractions, and lastly the method of processing the data obtained. We shall restrict ourselves here to the description of

a relatively inexpensive automatic instrumental version that is suitable for use with most commercial gas chromatographs, on the reaction section, providing for the determination of C, H, N and O with the precision usually required in EA, and finally on the calculation of the percentage composition and the determination of empirical formulae without knowing the amount of substance being analyzed.

EXPERIMENTAL

The design of the instrument was based on experience obtained with an elemental analyzer based on the principle of frontal chromatography^{12,16-19}. Extensive alterations were made to the previously employed arrangement¹². The operation of the elemental analyzer was completely automated, and the analyzer utilizes the column oven, detectors and katharometer of a Shimadzu GC-4APTF gas chromatograph. A stream splitter was connected to the outlet of the chromatographic column, by means of which a small fraction of the effluent from the column is led to a flame-ionization detector (FID) while the larger fraction is led by means of a system of diaphragm valves into the atmosphere or into the reactor of the elemental analyzer. The diaphragm valves in the system and in the face of the dilution chamber of the elemental analyzer are operated by the pressure of the carrier gas by means of three-way solenoid valves situated outside of the analyzer. The operation of the valves is automated according to a programme. A flow diagram of the equipment is shown in Fig. 1.

The carrier gas (helium) is led into the gas chromatograph via a pressure controller (1) and, after splitting the stream by flow controllers (2 and 3), it flows through chromatographic columns (4 and 5) into a dual FID (6). The components separated by GC enter a resistance splitter with pneumatic resistors (7 and 8), where 7 is much larger than 8. The smaller amount flows through resistor 7 into the FID, and the

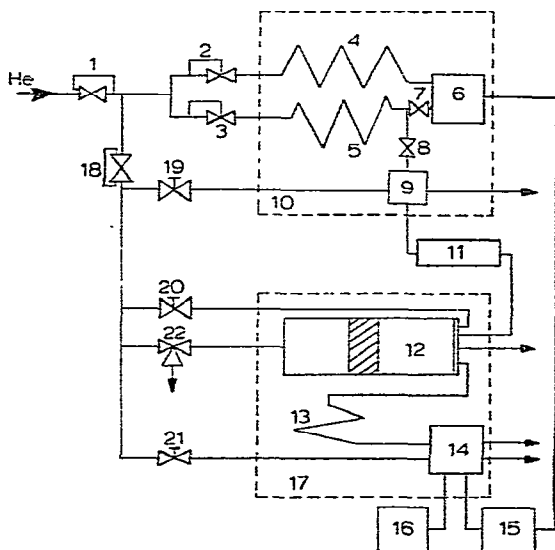


Fig. 1. Flow diagram of the equipment.

larger amount flows through resistor 8 into the system of diaphragm valves (9) and then either into the atmosphere or into a reactor (11) and a dilution chamber (12).

The dilution chamber serves to dilute and collect the reaction products. After homogenization, the products are pushed out by a piston into a chromatographic column (13) and the measuring part of the katharometer (14), which is connected to a recorder (15) and a digital voltmeter (16). The dual-channel recorder (15) is also connected to the FID. The second stream of carrier gas is led from the pressure controller (1) (*ca.* 5 kg/cm²) into another pressure controller (18) (*ca.* 1.2 kg/cm²), then via a needle valve (19) into the system of diaphragm valves (9), and, further, via another needle valve (20) into the diaphragm valve in the face of chamber 12, a three-way solenoid valve (22) and then into the space behind the piston of chamber 12 or into the atmosphere and, finally, via a needle valve (21) into the reference part of the katharometer (14). In the main thermostat (10) are situated chromatographic columns 4 and 5, the FID (6), resistors (7 and 8) and diaphragm valves (9). In the other thermostat (17), originally intended for thermostating detectors, *i.e.*, the katharometer and the FID, are situated the basic elements of the frontal gas chromatograph: the dilution chamber (12), chromatographic column (13) and katharometer (14), the last item being part of the original gas chromatograph. The thermostat maintains the temperature with a precision of $\pm 0.1^\circ$.

Columns 4 and 5 are 2 m \times 3 mm I.D., packed with Chromosorb W, 60–80 mesh, coated with 10% of Apiezon L, and maintained at 100°. Resistors 7 and 8 are made of metal capillaries. The interconnections of the diaphragm valves 9 are indicated in Fig. 2.

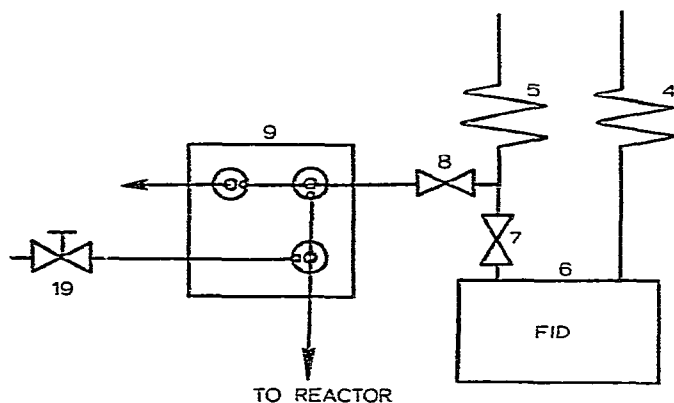


Fig. 2. Detailed scheme of the stream splitter and the valve system.

These valves, and also those in the face of the dilution chamber (12) are operated by three-way solenoid valves, which supply helium at a pressure of 2–3 kg/cm² to the membranes and/or release the helium into the atmosphere. Reactor 11 is a silica tube, 15 cm \times 10 mm I.D., which in the case of C,H,N analysis is filled with a layer of about 10 cm of copper(II) oxide wire and a 5-cm layer of copper and kept at 850°. In the analysis of C and O, where use is made of the reduction conversion of organic compounds into methane and water, the tube is filled with a nickel catalyst²⁰ and maintained at 450°. Before entering the reactor, the helium is mixed with hydrogen in the ratio of about 2:1 (30 and 60 ml/min, respectively). The mixture of gases leaving

the reactor enters a capillary made of a melt of palladium and silver (1 m × 1 mm I.D.), coiled into a spiral and maintained at 500°, in order to remove hydrogen from the reaction mixture by diffusion. The dilution chamber (12) consists of a glass cylinder of volume 100 ml with a silanized inner surface, inside which is a stainless-steel piston with sealing rings of silicone rubber; the faces are made of brass. The chromatographic column (13) is 80 cm × 3 mm I.D., packed with Porapak Q, 80–100 mesh.

The course of the chromatographic analysis is as usual; after their separation, the components leave the column (5) and are detected with the FID (6) and recorded with a recorder (15). A large proportion of the components is vented via the diaphragm valves (9). At the moment when EA of some components leaving the GC column is to be carried out, upon pushing a button and holding it during the recording of the corresponding peak the component passes through system 9 and enters the reactor 11 and then the frontal chromatograph. Upon releasing the button, an automatic cycle of EA is started; the purging of the contents of the reaction space into the dilution chamber is carried out with helium directed by a valve (19) to flow through system 9. The other components leaving the column are vented through system 9. It is possible to include in this circuit a separator for the isolation of virtually all of the components of the chromatogram and gradually to provide their EA.

RESULTS AND DISCUSSION

The most frequent group of substances that come into consideration in GC are those which contain C, H, N and O. EA of these elements places specific requirements on the reaction section. Thus, C,H,N analysis is carried out after the complete oxidation of the sample, usually with the aid of a catalyst. The determination of O can be performed either after the conversion of the sample into carbon monoxide on a carbon catalyst or after its hydrogenation to water. We chose the second alternative, *i.e.*, hydrogenation on nickel, in which simultaneously all of the oxygen and carbon in the sample are converted into water and methane, respectively. As shown below, the simultaneous determination of O and C is very important in the determination of empirical formulae without knowledge of the amount of the sample.

A prerequisite in EA without knowledge of the amount of the sample is knowledge of the proportions of all of the elements in the sample being analyzed. The calculation proper is based on the determination of the relative proportions of the individual atoms²¹. If the empirical formula $C_aH_bN_cO_d$ is to be obtained, the percentage contents of the individual atoms are divided by the appropriate atomic weights. The results so obtained are then divided by the smallest of them and, if necessary, multiplied by a small integer (usually 2 or 3) so as to obtain the empirical formula in the form of integers. Further, the ratio of the atoms is related to a particular one of them, usually N (or C with substances that do not contain nitrogen).

Thus, in the case of C,H,N analysis, we obtain for the individual subscripts

$$a = \frac{\%C \cdot 14.0067}{12.01115 \cdot \%N}$$

$$b = \frac{\%H \cdot 14.0067}{1.00797 \cdot \%N}$$

$$c = 1$$

If we substitute for $\%X$, where X represents the individual atoms, from the relationship

$$\%X = \frac{K_X (H_X - h_X)}{w}$$

K_X is the response factor of the given element, which is obtained by means of a standard compound of known percentage composition, employing the relationship

$$K_X = \frac{\%X_{st} \cdot w_{st}}{(H_X - h_X)_{st}}$$

where H represents the height of the integral record and/or the area or height of the peak corresponding to the analysis of the unknown, h represents the same quantities corresponding to the blank experiment and w is the sample weight. In this way, we obtain for the individual subscripts

$$a = 1.1661 \cdot \frac{(H_C - h_C) K_C}{(H_N - h_N) K_N}$$

$$b = 13.896 \cdot \frac{(H_H - h_H) K_H}{(H_N - h_N) K_N}$$

$$c = 1$$

It follows from the previous relationships that

$$\frac{K_C}{K_N} = \frac{\%C_{st} (H_N - h_N)_{st}}{\%N_{st} (H_C - h_C)_{st}}$$

and

$$\frac{K_H}{K_N} = \frac{\%H_{st} (H_N - h_N)_{st}}{\%N_{st} (H_H - h_H)_{st}}$$

so that

$$a = 1.1661 \cdot \frac{(H_C - h_C) \cdot \%C_{st} (H_N - h_N)_{st}}{(H_N - h_N) \cdot \%N_{st} (H_C - h_C)_{st}}$$

$$b = 13.896 \cdot \frac{(H_H - h_H) \cdot \%H_{st} (H_N - h_N)_{st}}{(H_N - h_N) \cdot \%N_{st} (H_H - h_H)_{st}}$$

$$c = 1$$

We have obtained in this way the atomic ratios in the empirical formula for C,H,N without the necessity of knowing the weights of the charges of sample and standard.

An analogous procedure is followed if the substance does not contain nitrogen, *i.e.*, in C,H analysis. In this instance, the number of hydrogen atoms is usually related to the number of carbon atoms, so that

$$a = 1$$

$$b = 11.9162 \cdot \frac{(H_H - h_H) K_H}{(H_C - h_C) K_C}$$

As

$$\frac{K_H}{K_C} = \frac{\%H_{st} (H_C - h_C)_{st}}{\%C_{st} (H_H - h_H)_{st}}$$

we have

$$a = 1$$

$$b = 11.9162 \cdot \frac{(H_H - h_H) \cdot \%H_{st} (H_C - h_C)_{st}}{(H_C - h_C) \cdot \%C_{st} (H_H - h_H)_{st}}$$

As for the analysis of oxygen, this is based on an entirely different reaction principle compared with C,H,N analysis. If the ratio of O to C,H,N is to be determined, it is necessary to determine simultaneously with oxygen some of the other three elements. As carbon is virtually universal in this respect, we chose hydrogenolysis on nickel for the simultaneous determination of carbon and oxygen.

When proceeding in an analogous manner to the procedures considered above and relating the number of carbon atoms to those of oxygen, we obtain

$$a = 1.3320 \cdot \frac{(H_C - h_C) K_C}{(H_O - h_O) K_O}$$

$$d = 1$$

As

$$\frac{K_C}{K_O} = \frac{\%C_{st} (H_O - h_O)_{st}}{\%O_{st} (H_C - h_C)_{st}}$$

we have

$$a = 1.3320 \cdot \frac{(H_C - h_C) \cdot \%C_{st} (H_O - h_O)_{st}}{(H_O - h_O) \cdot \%O_{st} (H_C - h_C)_{st}}$$

$$d = 1$$

The determination of the empirical formula can suffer from an uncertainty in the value found, especially for hydrogen in C,H,N analysis. In this instance, the determination of the empirical formula is usually related to nitrogen, the atomic ratio of which to hydrogen is small. Therefore, in questionable cases it is expedient to complement the determination by another one referred to carbon, which is usually represented by a larger number of atoms in the molecule. Obviously, the corrected result for carbon from the first determination is used, rounded off to an integral value. At the same time, the rule is observed according to which a substance containing an even number of odd-valent atoms in the molecule cannot contain an odd number of hydrogen atoms.

Tables I and II give examples of C,H,N and C,H,O analyses for various types of compounds using the above procedures. Fig. 3 shows a record of EA of oxygen and carbon. This record differs from an exclusively frontal one, such as that in C,H,N analysis^{18,19}, for instance, in that it is a mixed frontal-elution record, obtained as a result of a shorter charging time (2 min).

TABLE I
EXAMPLE OF C₅H₇N ANALYSIS
Standard: pyridine (average of four determinations)

Compound	Response (μV)			Number of atoms referred to N			Number of atoms referred to C	
	N	C	H	N	C	H	C	H
Aniline (C ₆ H ₇ N)	90	1188	259	1	5.98	7.15	1	1.19
	99	1304	264	1	5.97	6.63	1	1.11
	83	1095	218	1	5.97	6.53	1	1.09
	99	1312	277	1	6.00	6.96	1	1.16
3-Picoline (C ₈ H ₇ N)	127	1658	346	1	5.91	6.77	1	1.14
	105	1382	302	1	5.96	7.15	1	1.20
	121	1593	361	1	5.98	7.41	1	1.23
	121	1607	367	1	6.02	7.53	1	1.25

TABLE II
EXAMPLE OF C₅H₁₀O ANALYSIS
Standard: acetone (average of two determinations)

Compound	Response (μV)		Number of atoms referred to O		Response (μV)		Number of atoms referred to C	
	C	O	O	C	C	H	C	H
Diethyl ketone (C ₆ H ₁₀ O)	865	106	1	5.16	2933	1324	1	1.99
	905	112	1	5.11	3002	1370	1	2.02
	1105	139	1	5.03	3034	1374	1	2.00
	1026	130	1	4.99	3025	1373	1	2.00
Methyl isobutyl ketone (C ₈ H ₁₂ O)	2259	353	1	5.89	3181	1450	1	2.01
	2379	368	1	5.95	3250	1493	1	2.03
	2136	335	1	5.87	3230	1480	1	2.02
	2230	350	1	5.87	2977	1358	1	2.01

The method described for EA of GC effluents without knowing their amounts offers a number of possibilities. The possibility of rounding off the results to integral values in the determination of empirical formulae makes it possible, to a certain extent, to carry out the determination with a lower precision. The size of the sample is limited only by the detector sensitivity, stability of the conditions and/or the sorption properties of the analytical system with respect to some of the compounds being analyzed (water for instance). In our work, it was possible to analyze, with an acceptable precision, as little as 10 μg of a substance.

The extension of the method to other elements (sulphur for example) is a question of the choice of a suitable reaction system. However, the procedure would remain analogous to that described for the analysis of C₅H₇N and O₂C.

The determination of the molecular formulae from empirical formulae (if they are not identical) is a matter of the use of the elution chromatographic data of the substances being analyzed.

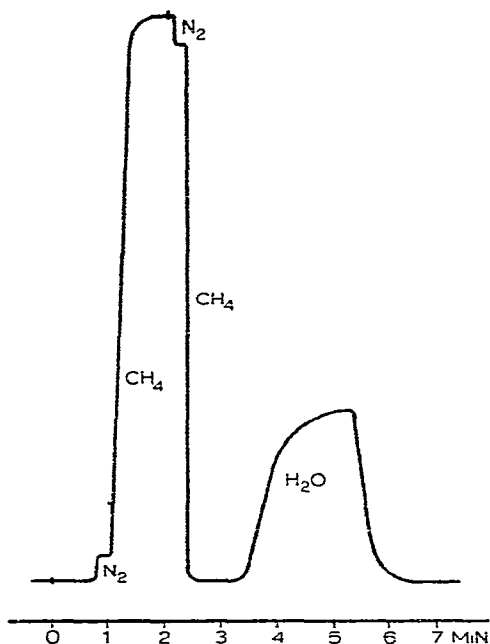


Fig. 3. Frontal elution record of an analysis of oxygen and carbon.

The practical utilization of the possibilities outlined above requires coupling of the analytical system described with a small computer and/or a programmable calculator with a digital output and record.

REFERENCES

- 1 F. Cacace, R. Cipollini and G. Perez, *Science*, 182 (1960) 1253.
- 2 F. Cacace, R. Cipollini, G. Perez and E. Possagno, *Gazz. Chim. Ital.*, 91 (1961) 804.
- 3 F. Cacace, R. Cipollini and G. Perez, *Anal. Chem.*, 35 (1963) 1348.
- 4 E. P. Skorniyakov, *Aut. Cert. SSSR*, 155,026 (1962); *Byull. Izobr.*, No 11 (1963).
- 5 I. A. Revel'skii, R. I. Borodulina and T. D. Khokhlova, *Neftekhimiya*, 4 (1964) 624.
- 6 I. A. Revel'skii, R. I. Borodulina, T. M. Sovakova and V. G. Klimanova, *Dokl. Akad. Nauk SSSR*, 159 (1964) 861.
- 7 I. Klesment, *Izv. Akad. Nauk Est. SSR*, 15 (1966) 436.
- 8 R. F. Reitsema and N. L. Allphin, *Anal. Chem.*, 33 (1961) 355.
- 9 F. H. Huyten and G. W. A. Rijnders, *Z. Anal. Chem.*, 205 (1964) 244.
- 10 J. Franc and J. Pour, *J. Chromatogr.*, 32 (1968) 2.
- 11 S. A. Liebman, D. H. Ahlstrom, T. C. Creighton, G. D. Pruder, R. Averitt and E. J. Levy, *Anal. Chem.*, 44 (1972) 1411.
- 12 V. Rezl, B. Kaplanová and J. Janák, *J. Chromatogr.*, 65 (1972) 47.
- 13 V. G. Berezkin and V. S. Tatarinskii, *Zh. Anal. Khim.*, 25 (1971) 398.
- 14 S. A. Liebman, D. H. Ahlstrom, C. D. Nauman, G. D. Pruder, R. Averitt and E. J. Levy, *Res. Develop.*, 23 (1972) 24.
- 15 S. A. Liebman, D. H. Ahlstrom, T. C. Creighton, G. D. Pruder and E. J. Levy, *Thermochim. Acta*, 5 (1973) 403.
- 16 V. Rezl, *Microchem. J.*, 15 (1970) 381.
- 17 V. Rezl, *J. Chromatogr. Sci.*, 10 (1972) 419.
- 18 V. Rezl and B. Kaplanová, *Mikrochim. Acta*, i (1975) 493.
- 19 V. Rezl and J. Uhdeová, *Int. Lab.*, (1976) 11.
- 20 B. N. Dolgov, *Kataliz v Organicheskoi Khimii*, Goskhimizdat, Leningrad, 1959, p. 288.
- 21 E. Häberli, *Mikrochim. Acta*, (1973) 597.