Notes

CHROM. 6021

Simultaneous carbon and oxygen determination by fluorine combustion gas chromatography[*]

A fluorine combustion gas chromatographic method has been proposed[1] in organic elemental analysis that offered the possibility of determining carbon and hydrogen[2]. Various conditions were used in the present work to determine organic carbon and oxygen. The techniques for determining corrosive gases using gas chromatography have been reported[3,4] and these techniques were adopted in the present work. Further, new techniques for separating carbon tetrafluoride and oxygen from corrosive gases such as fluorine and hydrogen fluoride were found. It has been shown that corrosive gases could be eliminated completely from these gases by using sodium hydroxide and activated charcoal absorption columns.

The combustion gases could be separated on a molecular sieve type 13X gas chromatographic column.

Experimental

Apparatus. A Mark II type of combustion vessel, newly designed with a magnetic stirrer so as to give as small an error as possible, was used, because of incomplete combustion of the sample.

A commercial gas chromatograph had to be modified so as to analyze the corrosive products successfully. Nickel and Teflon were used for all the tubing that carried gases. The apparatus is shown in Fig. 1. Operating conditions are given in Table I.

A fluorine generator described in a previous paper[1] was used.

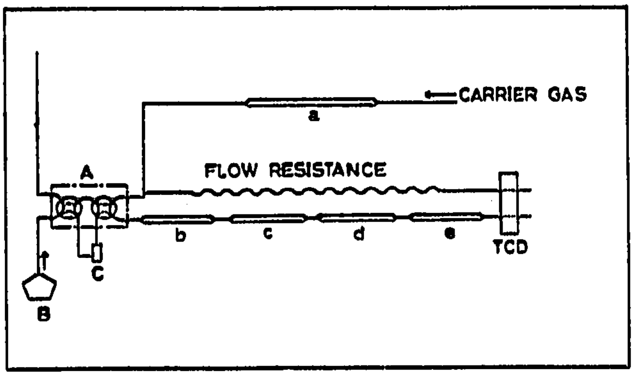

Fig. 1. Schematic diagram of complete system. A = Introduction system; B = fluorine generator; C = fluorine combustion vessel; a = refiner for carrier gas; b = potassium chloride reaction column; c = sodium hydroxide absorption column; d = activated charcoal absorption column; e = molecular sieve gas chromatographic column.

Procedure. Organic liquid samples of 0.1–0.3 µl volume were injected with a microsyringe into the combustion vessel (C) filled with fluorine, and then the vessel

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[*] Part III of the study of elemental analysis with fluorine combustion gas chromatography.

TABLE I

COLUMN AND OPERATING CONDITIONS

	Packing material (mesh)	*Tube (length; diameter)*	*Temperature (°C)*
a	Molecular sieve 5A (30–60)	Ni (1 m; 4 mm)	Room temp.
b	Potassium chloride (28–40)	Ni (1.2 m; 4 mm)	115
c	Sodium hydroxide (30)	Daiflon (60 cm; 4 mm)	25
d	Activated charcoal (30–60)	Ni (1 m; 4 mm)	80
e	Molecular sieve 13X (30–60)	Ni (1 m; 4 mm)	50

Operating conditions
Carrier gas, helium
Flow-rate of gas, 35 ml/min
Fluorine combustion vessel:
Volume, 2.5 ml
Temperature, 80°

was heated while the contents were stirred with the magnetic stirrer. Combustion gases and excess of fluorine were introduced via A into the gas chromatograph.

Excess of fluorine was converted into chlorine in the reaction column containing potassium chloride (b), and the chlorine produced was removed in the absorption columns containing sodium hydroxide (c) and activated charcoal (d). Other combustion gases were separated by the molecular sieve type 13X and detected by the thermal conductivity cell detector.

Helium gas, refined in the column (a) with molecular sieve type 5A, was used as the carrier gas.

Removal of corrosive gases. Combustion gases, such as carbon tetrafluoride, oxygen, hydrogen fluoride and the excess of fluorine, were used as gas chromatographic samples. However, there is no appropriate gas chromatographic column for separating these gases owing to the presence of the last two corrosive gases. Therefore, a method for eliminating the corrosive gases from the other gases was developed. In the first procedure, excess of fluorine was converted into chlorine in the potassium chloride reaction column.

Chlorine and hydrogen fluoride were trapped by two kinds of absorption columns, one of which contained sodium hydroxide particles as the packing material and the other activated charcoal particles (30–60 mesh). The length of the latter column was 1 m, and the column temperature was about 80°. Under these conditions, corrosive gases could be trapped completely, whereas under the same conditions carbon tetrafluoride and oxygen passed completely through this column.

Separation of carbon tetrafluoride and oxygen. For the separation of carbon tetrafluoride and oxygen, suitable conditions were obtained using molecular sieve type 13X as the column packing material. In the case of the molecular sieve, the retention volume of carbon tetrafluoride depends greatly on the column temperature. At a column temperature of 50°, carbon tetrafluoride and oxygen could be separated satisfactorily on the molecular sieve type 13X column.

Results and discussion

Analysis of organic compounds. A series of runs was made using ethyl alcohol, methyl alcohol and dioxan as samples. A typical chromatogram is shown in Fig. 2.

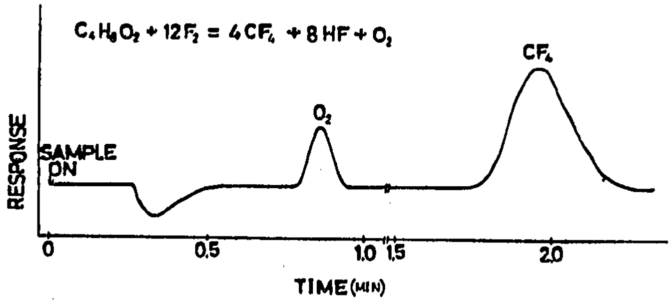

Fig. 2. Typical chromatogram for carbon and oxygen determination.

Dioxan was used as a standard to calculate the composition ratio of the oxygen to carbon for the other compounds. This composition ratio was calculated from the relation between the peak areas of the combustion gases (CF_4, O_2) obtained from dioxan and those from the other samples. The oxygen number was calculated by the following equation:

$$n_{(O)} = \frac{S_{(\text{sample})O_2}}{S_{(\text{sample})CF_4}} \times \frac{\frac{1}{2} \times S_{(C_4H_8O_2)CF_4}}{S_{(C_4H_8O_2)O_2}}$$

where S = peak area of the chromatograms and $n_{(O)}$ = oxygen number (carbon number = 1).

Relative standard deviation of the dioxan sample was 0.9%. The analytical results for ethyl alcohol and methyl alcohol are given in Table II.

TABLE II

RESULTS OF CARBON AND OXYGEN DETERMINATIONS OBTAINED BY THE FLUORINE COMBUSTION OF ORGANIC SAMPLES

Standard sample, dioxan.

Sample	*C:O ratio*	
	Theory	*Found*
Ethyl alcohol[a]	1.00 : 0.500	$1.00_0 : 0.50_8$ $1.00_0 : 0.49_0$ $1.00_0 : 0.49_7$ Mean = 0.49_0
Methyl alcohol[b]	1.000 : 1.000	$1.00_0 : 0.99_0$ $1.00_0 : 0.99_8$ $1.00_0 : 0.99_4$ Mean = 0.99_0

[a] $C_2H_5OH + 7\,F_2 = 2\,CF_4 + 6\,HF + \frac{1}{2}O_2$.
[b] $CH_3OH + 4\,F_2 = CF_4 + 4\,HF + \frac{1}{2}O_2$.

Hence, we have been able to show the possibility of determining carbon and oxygen by this method.

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1 K. ASAI AND D. ISHII, *Kogyo Kagaku Zasshi*, 74 (1971) 167.
2 K. ASAI AND D. ISHII, *Kogyo Kagaku Zasshi*, 74 (1971) 1950.
3 K. ASSAI AND D. ISHII, Y. MIZUTANI, *Kogyo Kagaku Zasshi*, 74 (1971) 368.
4 K. ASAI AND D. ISHII, *Kogyo Kagaku Zasshi*, 74 (1971) 1107.

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