Rapid Gas Chromatographic Analysis of a Mixture of Oxygen, Nitrogen, Methane, Carbon Monoxide, and Carbon Dioxide

By Yûichi Murakami

(Received February 10, 1959)

Gas chromatography has been widely used as method for separation or analysis of many complex mixtures of gases or liquids. However, a mixture of oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide has not been separated successfully. "Molecular Sieves 5-A" is effective in separating hydrogen, carbon monoxide, oxygen, nitrogen, and methane but it adsorbs irreversibly carbon dioxide[1].

Activated charcoal can separate hydrogen, carbon monoxide, oxygen, methane, and other hydrocarbons, but for practical use carbon dioxide shows too long a retention time as well as too widely a diffuse band and nitrogen can not be separated from oxygen[2,3]. Silica gel is very poor in separating hydrogen, oxygen, and methane[2] but for some rather complex procedure[4], and gives longer retention time for carbon dioxide than that for the above gases. Alumina is also very poor in separating the above gases[2] and adsorbs irreversibly carbon dioxide.

The present author will propose a new method of gas chromatography, with which the above mixture can be completely analyzed within a few minutes. The principle and the procedure of the method are rather simple as follows.

---

1) G. Kyryacos, and C. E. Boord, *Anal. Chem.*, **29**, 787 (1957).
2) H. W. Patton, J. S. Lewis, and W. I. Kaye, ibid., **27**, 170 (1955).
3) N. H. Ray, *J. Appl. Chem.*, **4**, 82 (1954).
4) D. H. Szulczewski, and T. Higuchi, *Anal Chem.*, **29**, 1541 (1957).

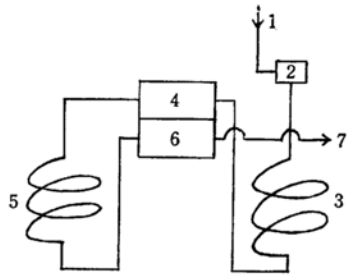

Fig. 1. Flow diagram of the present method.

1. Carrier gas inlet
2. Sample inlet
3. Column I
4. Cell I
5. Column II
6. Cell II
7. Outlet

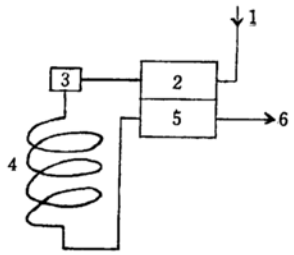

Fig. 2. Flow diagram of the usual method.

1. Carrier gas inlet
2. Reference cell
3. Sample inlet
4. Column
5. Sensitivity cell
6. Outlet

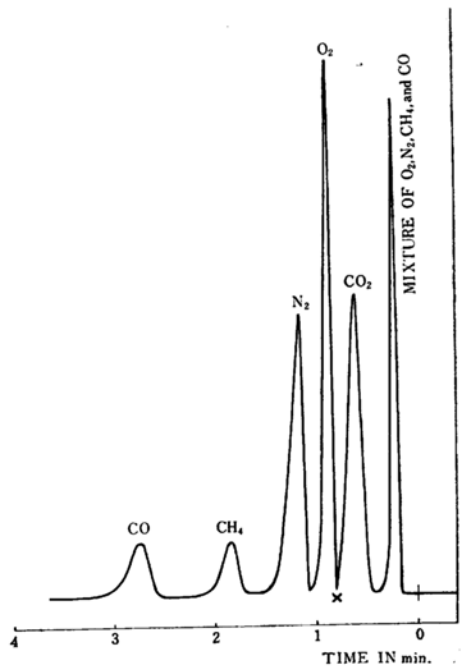

Fig. 3. Gas chromatogram.
× Switching the poles of recorder.

Apparatus.—The flow diagrams of the present new method and the usual one are illustrated in Figs. 1 and 2 respectively. In the usual method the carrier gas passes through successively a thermal-conductivity cell, a sample inlet, a column, and the other cell. The former cell works as a reference cell while the latter as a sensitivity cell. On the other hand, in the present method the carrier gas passes through successively a sample inlet, column I, thermal-conductivity cell I, column II, and cell II. The two cells are the same in construction. The electrical circuit comprises a Wheatstone bridge, the two arms of which are the platinium wires of the thermal-conductivity cells. In order to measure both positive and negative deflections, it is necessary either to adjust the base line to the middle of the chart or to be able to switch the poles of the recorder.

Columns.—*Column I*: A spiral copper column used was 40 cm. long and 4 mm. in inner diameter. Silica gel supplied by Chiyoda & Co. was used as the adsorbent. It was comminuted into 50~80 mesh and heated for one hour at 350°C. *Column II*: A spiral copper column used was 200 cm. long and 4 mm. in inner diameter, and "Molecular Sieves 5-A", comminuted into 50~80 mesh and heated for one hour at 400°C was used.

Procedure and Principle of the present method.—The test gas is separated firstly into carbon dioxide and a mixture of remaining gases by means of column I: they pass through thermal-conductivity cell I. During this period, in cell II the carrier gas alone is flowing, and then cell I is working as a sensitivity cell while cell II as a reference cell. Successively the mixture of remaining gases is separated further into oxygen, nitrogen, methane and carbon monoxide through column II and they pass through cell II. The situation in the second period is entirely changed, so that the role of each cell is interchanged and the direction of deflection is reversed.

The columns were operated at 80°C. The inlet pressure was 0.63 kg./cm^2 gage, the outlet atmospheric. The flow rate of hydrogen as carrier gas was 70 cc./min. Fig. 3. is an example of the gas chromatogram thus obtained and it shows that a mixture of oxygen, nitrogen, methane, carbon monoxide, and carbon dioxide has been completely separated. The time required for analysis is not more than four minutes.

The author wishes to express his sincere thanks to Dr. T. Keii and Mr. S. Terasawa for their kind encouragement.

Tokyo Institute of Technology
Meguro-ku, Tokyo