DETERMINATION OF OXYGEN, NITROGEN AND CARBON DIOXIDE IN AIR SAMPLES

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Studies connected with life systems in enclosed capsules and space suits require accurate measurements of the concentrations of atmospheric gases. Of these gases, nitrogen, oxygen, and carbon dioxide are of paramount importance. The determination of such gases, based on the gas chromatographic principle, shows great promise. Molecular sieves have been used with great success as column packing materials for the separation of oxygen and nitrogen[1]. Silica gel has been used for the gas chromatographic analysis of carbon dioxide[2]. However, neither of these solid stationary phases completely resolves all three gases. Molecular sieve 5 A, while resolving oxygen and nitrogen very efficiently, retains carbon dioxide permanently under the conditions of analysis; silica gel, on the other hand, while separating carbon dioxide, does not separate nitrogen from oxygen.

An attempt was made to resolve oxygen, nitrogen, and carbon dioxide from a single analytical sample, using a parallel dual column gas chromatograph[3]. Molecular sieve 5 A and silica gel-packed columns were used in the initial experiments. The parallel dual column arrangement permitted splitting of the injected sample into two columns, molecular sieve and silica gel, where the gases were separated simultaneously. A 5-ft., 1/4-in. diameter column packed with molecular sieve 5 A, 60–80 mesh, was used for the separation of oxygen and nitrogen. A 2-ft., 1/4-in. diameter column packed with silica gel, 20–200 mesh, was used for the separation of carbon dioxide from nitrogen and oxygen.

One injection of an air sample into this system was found to produce four peaks: an oxygen peak and a nitrogen peak, as they elute from the molecular sieve column, a peak for carbon dioxide, and a combined peak for oxygen and nitrogen as they elute from the silica gel column. The conditions of analysis may be adjusted in such a way that each peak appears at different retention times. With this arrangement, complete analysis of nitrogen, oxygen, and carbon dioxide is possible from one sample.

A slight modification permits determination of carbon dioxide at the p.p.m. level. Two valves were incorporated at the entry side of each column, permitting use of the columns in separate operations.

APPARATUS

The design of the instrument is shown in Fig. 1. A Gow-Mac pretzel-type thermoconductivity cell with four tungsten hot wires connected in a Wheatstone bridge arrange-

ment is used for detection. A Leeds and Northrup model G, o–1 mV recorder and a Perkin-Elmer integrator are used in the readout portion of the instrument. The sample injection system incorporates a modified Beckman two-way gas sampling valve, a
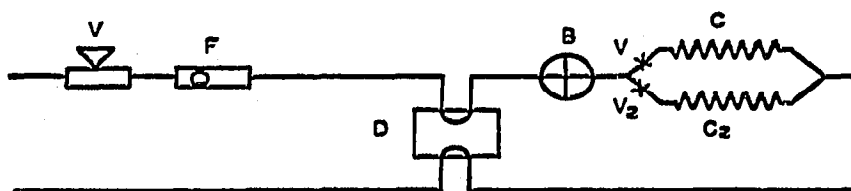

Fig. 1. Gas chromatograph. V = Needle valve; F = Flow meter; D = Detector; B = Beckman sampling valve; V_1, V_2 = Valves; C_1 = Molecular sieve column; C_2 = Silica gel column.

vacuum pump, and a manometer. The conventional spiral loops of the Beckman valve were replaced by 4-in., 1/4-in. diameter stainless steel U-tubes. This arrangement permits the application of a cold bath over the sampling loops.

EXPERIMENTAL

For the simultaneous determination of all three components, a sample of air is introduced into the loop of the Beckman valve and injected in the helium stream. The following operating conditions are used in the analysis.

Gas: He, inlet pressure $2^3/_4$ p.s.i.g.

Columns: (A) 5-ft., 1/4-in. diameter tube packed with molecular sieve 5 A 60–80 mesh,
(B) 2-ft., 1/4-in. diameter tube packed with silica gel 20–200 mesh, The columns are connected in parallel

Temperature: 26°

Bridge current: 150 mA,

Recorder: o–1 mV model G, L and N,

Speed: 1/2 in. per min.

The areas under the four peaks are integrated, and from the absolute values of the nitrogen-oxygen peak and of the carbon dioxide peak, concentration of carbon dioxide is calculated. The peak area for oxygen and nitrogen resolved on the molecular sieve columns provides a ratio of oxygen to nitrogen. The concentrations of nitrogen and oxygen are calculated after correction is made for the concentration of carbon dioxide in the sample.

For the analysis at the p.p.m. level of air samples containing carbon dioxide, the following procedure is used. An evacuated sample gas bulb of 10–250 ml volume is used for procuring the sample. With the valve to the molecular sieve column open, and the valve to the silica gel column closed, 1–2 ml of air are introduced into the helium stream and resolved on the molecular sieve column. A flowrate of 165 ml/min of helium is used with this column. The areas under the nitrogen and oxygen peaks are integrated, and the ratio is calculated in the conventional manner. The pressure of the remaining sample in the gas bulb is measured with a manometer. A Dewar Flask containing liquid nitrogen is placed over the collecting loop of the Beckman valve, and the sample is transferred into it by pumping. The carbon dioxide is con-

densed in the collecting tube of the Beckman valve while non-condensables are removed by vacuum pumping. The valve to the molecular sieve column is closed, the valve to the silica gel columns is opened, and the rate of helium flow is adjusted to 77 ml/min.

At this point, the collection tube containing carbon dioxide is pivoted into the helium stream; the liquid nitrogen trap is removed and a beaker containing hot water placed over the U-tube, to facilitate evaporation of the condensed gases. The area of the carbon dioxide peak is integrated as it is eluted from the silica gel column. For calibration purposes, a known volume of carbon dioxide is introduced in the gas chromatograph and analyzed under the conditions described above.

Calculation:

$$O_2 = \frac{c(O_2) \times (100 - \% \ CO_2)}{c(O_2 + N_2) \times 100} \%$$

$$N_2 = \frac{c(N_2) \times (100 - \% \ CO_2)}{c(O_2 + N_2) \times 100} \%$$

$$CO_2 = \frac{C_S \times P_R \times V_R}{C_R \times P_S \times V_S} \times 100 \%$$

where c = number of integral counts,
         C_S = number of integral counts for the peak of carbon dioxide (sample),
         C_R = number of integral counts of the peak of carbon dioxide (reference),
         P_R = pressure of the CO_2 reference,
         V_R = volume of the CO_2 reference,
         P_S = pressure of sample,
         V_S = volume of sample.

RESULTS

The retention times obtained under the described conditions of analysis are given in Table I.

The sensitivity of the method, with respect to carbon dioxide, was calculated by using the results of eight determinations of standard samples for carbon dioxide content. One cc volume of carbon dioxide at 1 mm mercury pressure, using the

TABLE I

RETENTION TIMES OF OXYGEN, NITROGEN AND CARBON DIOXIDE

Gas	Column	Retention time (min)	
		Simultaneous technique*	Separate technique**
Oxygen and nitrogen	Silica gel	1	0.7
Oxygen	Molecular sieve	2	1.2
Nitrogen	Molecular sieve	6	2.7
Carbon dioxide	Silica gel	26	8.4

* Inlet pressure, 2 3/4 p.s.i.g.
** Inlet pressure, 4 p.s.i.g.

maximum sensitivity of the instrument and the 0–1 mV range of the recorder produced an average of 29.5 integral counts. Under the conditions of analysis, quantities of carbon dioxide corresponding to 5 integral counts are detectable. Using sample sizes of 1 cc magnitude, 200 p.p.m. of carbon dioxide can be detected. With 10 cc samples, the lower level of detectability for carbon dioxide will be 20 p.p.m., and with 100 cc samples, 2 p.p.m. The sensitivity of the method can be increased replacing hot-wire detection with thermistor detection.

The argon and oxygen appears as one peak using this procedure; however, since the ratio of argon to oxygen in atmospheric air is known, necessary corrections for concentration of oxygen and argon can easily be made.

SUMMARY

A gas chromatographic system for analysis of nitrogen, oxygen, and carbon dioxide in air samples is described. The system utilizes a parallel dual column arrangement for simultaneous determination of all three components. The lower limit of detection for carbon dioxide is 2 p.p.m.

REFERENCES

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