

Gas Chromatographic Analysis of Oxygen and Argon at Room Temperature

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Abstract

A simple and accurate method for the analysis of oxygen and argon at room temperature with a dual-column gas chromatographic system is described. The system consists of a 5A molecular sieve (MS 5A) column and a combination column (MS 5A and palladium alumina catalyst). The MS 5A column is used to separate the air sample into two main peaks at room temperature: an argon and oxygen combined peak and a nitrogen peak. The combination column is used to separate the argon and oxygen peaks; the oxygen is eliminated due to the catalytic reaction with hydrogen (hydrogen is used as the carrier gas), so only the argon peak is eluted. The concentrations of oxygen and argon can be calculated by comparing the output of both columns.

Introduction

The gas chromatographic (GC) separation of oxygen and argon with commercially available columns is difficult at room temperature. In the process of developing a technique for the separation of argon from air that involved adsorption at low temperature, it was necessary for us to analyze samples of air for oxygen, argon, and nitrogen content with a GC method to find the efficiency and breakthrough capacity for argon. A method for combining O₂ with H₂ had already been developed in our laboratory and was suitably adopted for the GC analysis (1). CO₂ and H₂O did not interfere in this method of analysis, as they were not detected along with O₂ or Ar. Instead, they were retained in the column under the operating conditions used. The response of air in the working range of 0.2–1 mL was linear. This technique can also be used to determine the purity of O₂–Ar cylinders.

Separation methods

The following columns and conditions are generally used for the separation of air samples:

- A molecular sieve 5A column at –80°C (2)

- A MS 5A column for the elution of argon and oxygen as a composite peak at 100°C. O₂ is subsequently removed with the use of a reducing agent to obtain the argon peak only (2)
- A column of fire bricks loaded with 8 wt% of blood at 20°C (for the separation of oxygen and argon) (2)
- A molecular sieve column at temperatures higher than 300°C under a helium flow (3)
- A molecular sieve column heated in an argon purge at a humidity of 100 ppm at 450°C–500°C for 30 h followed by slow cooling for 8 h. A 2.2-m column packed with MS 5A (70–80 mesh) treated as above is used to separate argon and oxygen at 23°C. Helium is used as the carrier gas at a flow rate of 90 mL/min (4).
- Porous polymer column custom made from high-purity divinylbenzene (11 m × 1.04-mm i.d.) (for the separation of N₂, O₂, Ar, and CO). Helium is used as the carrier gas at a flow rate of 15 mL/min and a temperature of 22°C (5).

Procedure

As all the aforementioned techniques are either tedious or require extreme conditions, we developed a technique that uses a dual-column system (GC 9A with a thermal conductivity detector from Shimadzu [Duisburg, Germany]).

The dual-column system consisted of a molecular sieve 5A (MS 5A) column and a combination column of MS 5A and palladium alumina (Pd/alumina) catalyst. Specifications are given in Table I (1). The MS 5A column was used to separate the air

Table I. Specifications for the Palladium Alumina Column

Alumina source	M/S Associated Cement Co., Thane, Bombay
Size supplied	3–5-mm spheres
Size made in our lab	50–60 BSS
Palladium loading	2 wt%
Surface area	150 m ² /g
Crushing strength	15 kg/cm ²
pH	Alkaline
Porosity	40%
Range of oxygen in outlet of catalyst bed	6–10 ppm

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sample at room temperature into two main peaks (an argon and oxygen combined peak and a nitrogen peak). Only argon was eluted from the combination column because O₂ was eliminated by a catalytic reaction with H₂, which was used as the car-

rier gas. By comparing the area of peaks of both the columns, the concentrations of O₂ and Ar can be calculated. The GC parameters under which the analysis was carried out are given in Table II. The arrangement of columns in the gas chromatograph is shown in Figure 1, and sample chromatograms from both columns are shown in Figure 2.

The analysis can be carried out without the use of subambient temperatures and with a maximum column length of only 3 m. These columns do not require long hours of pre-treatment before analysis.

Experimental

The combination column in the dual-column system was prepared in our laboratory. It was a 3-m stainless steel column (3-mm o.d.) of which 1 m was packed with palladium alumina catalyst (50–60 BSS) and the remaining length of 2 m was packed with MS-5A (60–80 BSS; M/S Chromatopak, Bombay, India). Palladium acted as a catalytic site for hydrogen–oxygen reaction. Room air was taken as a standard homogeneous mixture of oxygen and argon for all the experiments that were performed. Calibration was performed with the use of pure gases, and the linearity in the working range of the experiments was observed.

Figure 2 shows a sample chromatogram from which the areas under various peaks were computed with the Chromatopak CR 3A. Typical values for the peak areas of the pure gases that were used for calibration are given in Table III.

Analyses were carried out at three different temperatures (30°C, 50°C, and 80°C) to determine the effect of temperature on the analytical results. Sample volumes of 0.2, 0.5, and 1.0 mL were injected to determine the effect of sample volume on analytical results.

To prepare calibration standards with different concentrations of Ar–O₂ in air, a sampling tube of calibrated volume was filled with air and known amounts of argon, nitrogen, or helium. Analyses were carried out at three different temperatures to determine the range of temperature for which this technique could be used for various types of applications.

Results and Discussion

An amount of sample in the range of 0.2–1 mL did not affect the performance of the column (Table IV). Table V shows the tem-

Table II. GC Operating Conditions

Gas chromatograph	Shimadzu GC 9A
Column oven temperature	30°C–80°C
Injection port	30°C–50°C
Detector oven temperature	70°C–100°C
Detector current	100 mA
Carrier gas inlet pressure	5 kg/cm ²
Column 1 inlet pressure	3.25 kg/cm ²
Column 2 inlet pressure	2 kg/cm ²
Carrier flow	60 cc/min

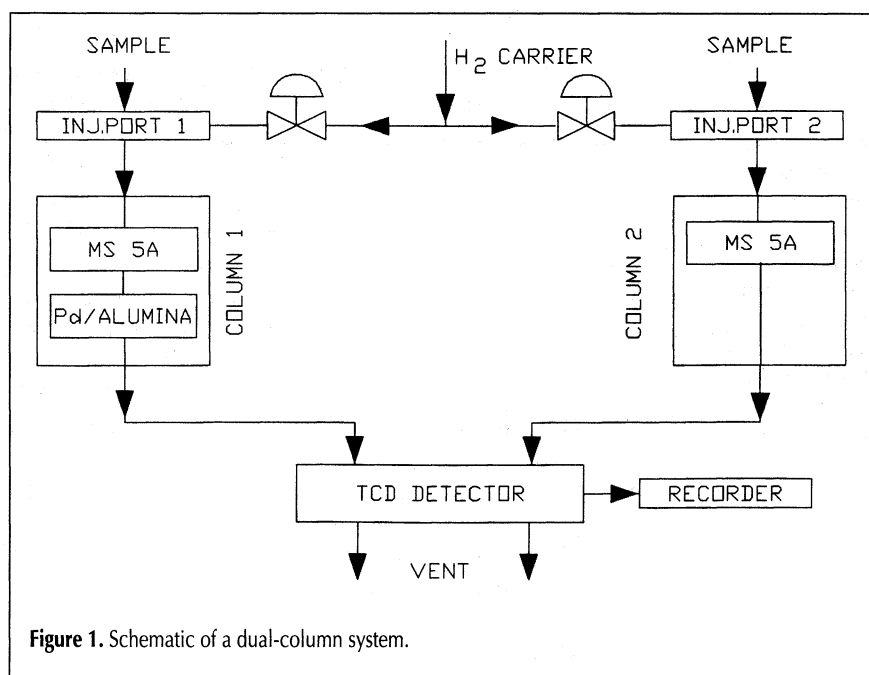


Figure 1. Schematic of a dual-column system.

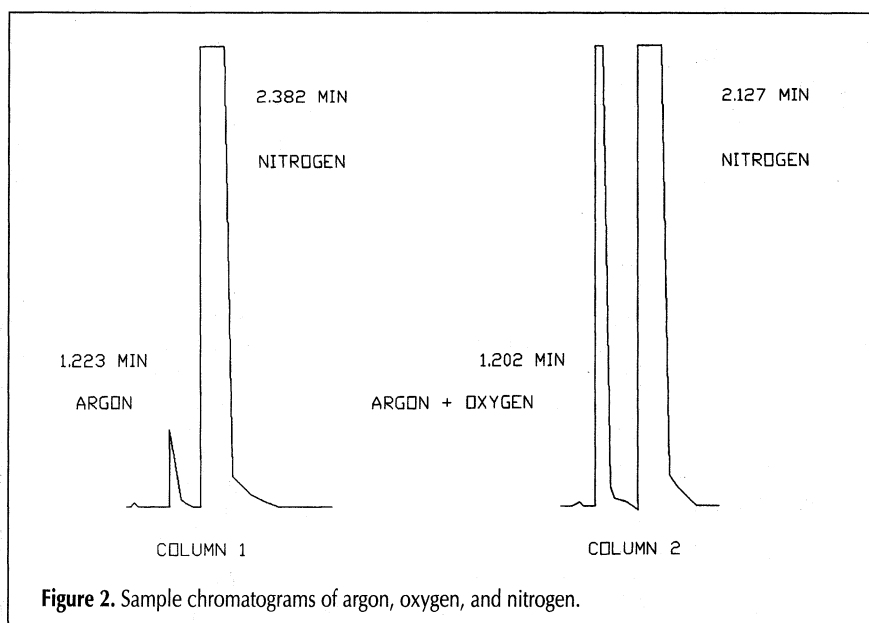


Figure 2. Sample chromatograms of argon, oxygen, and nitrogen.

Table III. Typical Peak Areas of Pure Gases Used for Calibration

Calibration Sample	Area Under the Peak (counts)	Deviation (%)
0.2 mL N ₂	174,984	0.05
0.2 mL Ar	178,027	0.05
0.2 mL O ₂	163,036	0.06

Table IV. Variation in Measured Concentration with Sample Volume

Composition (%)		Amount of Sample (mL)
Ar	O ₂	
0.9536	20.946	0.2
0.9537	20.946	0.5
0.9537	20.946	1.0

Table V. Variation in Measured Concentration at Different Column Oven Temperatures

Oven Temperature	Composition (%)	
	Ar	O ₂
30°C	0.954	20.946
50°C	0.945	20.99
80°C	0.921	20.99

perature at which O₂, which is present in the sample, combined completely with the H₂, which was the carrier gas. Once this reaction was complete, the concentration of argon in air was close to the actual concentration. Our results suggest that a temperature close to 60°C is suitable for an accurate analysis.

At a signal-to-noise ratio of 5:1, the detection limits of oxygen and argon were 0.41 µg and 0.51 µg, respectively. The noise level peak area corresponded to 50 units. Hence, 5 times the noise level will be 250 units, which is equal to 0.284 µL argon and 0.51 µg argon. This was the limit of detection. If it is assumed that the same quantity is present in 0.2 mL of a sample, the concentration can be calculated to be 15 ppm.

The same procedure was used in the calculation of the detection limits for oxygen (0.41 µg).

Conclusion

The method is simple, and the technique has been used for the analysis of more than 500 samples of air at 60°C. The results were found to be reproducible within ± 2%.

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