HOKKAIDO UNIVERSITY

Title	DETERMINATION OF ARGON PRESENT IN THE AIR BY GAS ADSORPTION CHROMATOGRAPHY
Author(s)	KWAN, Takao
Citation	JOURNAL OF THE RESEARCH INSTITUTE FOR CATALYSIS HOKKAIDO UNIVERSITY, 8(1), 14-17
Issue Date	1960-07
Doc URL	http://hdl.handle.net/2115/24713
Type	bulletin (article)
File Information	8(1)_P14-17.pdf

Instructions for use

Hokkaido University Collection of Scholarly and Academic Papers : HUSCAP

DETERMINATION OF ARGON PRESENT IN THE AIR BY GAS ADSORPTION CHROMATOGRAPHY

By

Takao KWAN*)

(Received February 10, 1960)

Gas adsorption chromatography has been adequately used for the separation of permanent gases, including those even such as hydrogen isotopes[1] and hydrogen isomers[2]. Usually, silica gel, alumina, charcoal and synthetic zeolite have been used as column packings for the purpose, their efficiencies being the subject of many investigations[3-9]. To resolve air into its components, activated Linde molecular-sieve column has proved useful in these investigations. Yet, oxygen and nitrogen were the apparent components just similarly as on silica gel[1] or on charcoal[5], *i.e.* argon in the air used to elute with oxygen presenting a single peak. Thus, to determine argon content *e.g.* in air or in ammonia synthesis gas, KREJČI and JANÁK[12] had to remove oxygen, beforehand, by passing the sample gas over palladium catalyst in hydrogen stream.

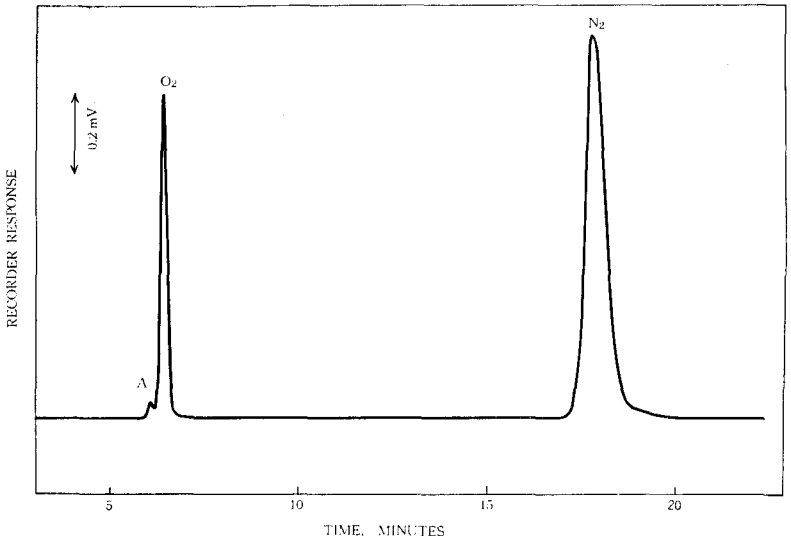
During the work carried out on the very long molecular-sieve column, we found unintentionally that argon present in the air was able to be separated from oxygen in the chromatogram. We were informed later that such separation is already known to occur, according to the technical informations[10-11], when Linde molecular sieve 5A is used as column packing and kept at or below the room temperature. However, to obtain nitrogen peak according to the information, one has to wait several hours particularly at reduced temperatures, and furthermore there are still some investigations which do not reproduce the argon-oxygen separation around room temperature. The present paper, in this connection, would involve an affirmative result that is readily obtainable at room temperature or at 0°C.

Shimadzu Gas Chromatograph GC-1A No. 58035 was used in this work, the detection system of which was the thermal conductivity gauge. The column that was prepared originally for the separation of ortho-para deuterium isomers[2] was used; copper spiral column of 10 meter long and 0.4 cm inside diameter was filled with 30 to 60 meshes Linde Molecular Sieve Type 13 X

*) Research Institute for Catalysis and Chemistry Department, Hokkaido University, Sapporo, Japan.

(Tonawanda Research Laboratory) activated beforehand at 350°C in vacuum. Commercial cylinder hydrogen, used as the carrier gas, was purified by passage through a cooled trap containing molecular sieves. The sampling procedure was described elsewhere[1)9)].

In Figure 1 (a) is shown the elution chromatogram of the air at the temperature of the column 21–22°C. As shown there, a certain small *extra* peak was found to emerge in front of the oxygen peak. The separation of this peak became more pronounced when the column was cooled down to 0°C (Figure 1 (b)). A mixture of the air and pure argon (Nippon Electric Co. Tokyo) in a ratio of 2 : 1 was then sampled and subjected to chromatographic separation under the same condition as that of Figure 1 (b). The resultant chromatogram is shown in Figure 1 (c). By comparing Figure 1 (b) and (c), it was ascertained



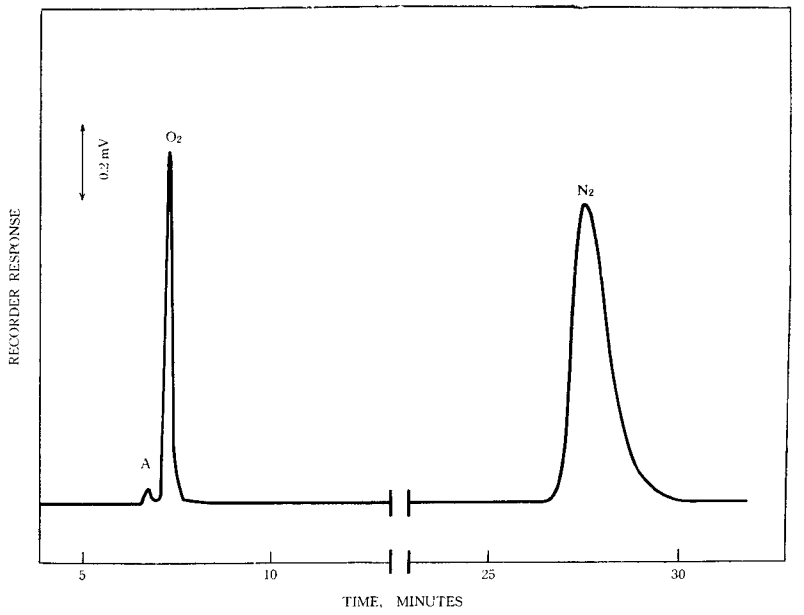
(a)

Fig. 1. Gas chromatographic separation of air into argon, oxygen and nitrogen on Linde molecular sieve Type 13 X column.

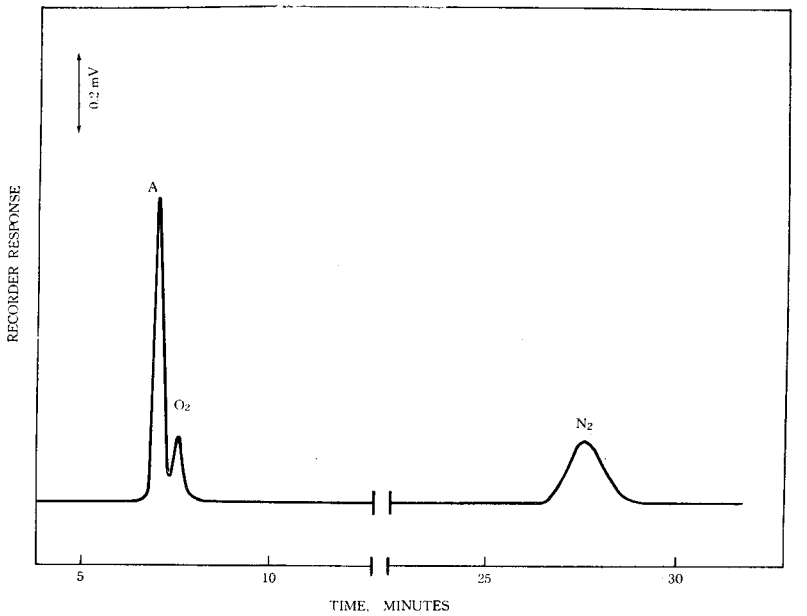
(a) Sample, air 0.25 cc STP. Span, 2 mV.
Carrier gas, hydrogen. Bridge current, 210 mA.
Flow rate, 66 mℓ/min. Inlet pressure, 0.85 kg/cm².
Column length, 10 meters. Chart speed, 10 mm/min.
Column temperature, 21–22°C.

(b). Sample, air 0.25 cc STP. Experimental variables are the same with (a) except the temperature of the column kept at 0°C.

(c). Sample, a mixture of air and pure argon (2 : 1) 0.097 cc STP. All other conditions are the same with (b).


0.2 mV
O_2
N_2
A
RECORDER RESPONSE
5
10
25
30
TIME, MINUTES

(b)


0.2 mV
A
O_2
N_2
RECORDER RESPONSE
5
10
25
30
TIME, MINUTES

(c)

that the first small peak obtained in Figure 1 (a) or (b) was due to the argon present in the air.

The area under the argon peak was about one-twentieth of that of oxygen, *i.e.* about one volume per cent of the total sample. The content of argon is agreed with the natural abundance known to be 0.93 per cent.

Acknowledgments

The author is much indebted to Mr. S. OHKOSHI for his assistance throughout this work and to Mr. T. HARUKI of SHIMADZU Manufacturing Co. Kyoto for the information concerning the argon-oxygen separation. He also wishes to extend his thanks to Dr. J. JANÁK who kindly informed him works done in Czechoslovakia on the gas chromatographic analyses of rare gases.

References

1) S. OHKOSHI, Y. FUJITA and T. KWAN, Bull. Chem. Soc. Japan, **31**, 771 (1958).
2) W. R. MOORE and H. R. WARD, J. Am. Chem. Soc. **80**, 2909 (1958).
T. KWAN, this Journal, p. 18.
3) S. A. GREENE, M. L. MOBERG and E. M. WILSON, Anal. Chem. **28**, 1369 (1956).
4) S. A. GREENE and H. PUST, Anal. Chem. **29**, 1055 (1957).
5) S. A. GREENE and H. PUST, J. Phys. Chem. **63**, 55 (1958).
6) D. H. SZULCYEWSKI and T. HIGUCHI, Anal. Chem. **29**, 1541 (1957).
7) H. W. PATTON, J. S. LEWIS and M. I. KAYE, Anal. Chem. **27**, 170 (1955).
8) J. JANÁK, *Vapor Phase Chromatography*, edited by Desty, London 1956, p. 247.
9) S. OHKOSHI, Y. FUJITL and T. KWAN, Catalyst (Hokkaido Univ.), **15**, 1 (1958).
10) SHIMADZU *Sci. Instrument News*, Vol. 1, No. 3 (1959).
11) S. TOMINAGA, *Kagaku-no-Ryoiki* (J. Japan Chem.), **12**, 16 (1958).—Technical explanation and examples on Perkin-Elmer Model 154-C Vapor Fractometer.
12) M. KREJČI and J. JANÁK, Collection Czechoslov. Chem. Commun. **24**, 3887 (1959).