

Determination of Nitrogen Dioxide by Gas-Solid Chromatography

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기 · 고 크로마토그래피법에 의한 이산화질소 측정

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Nitrogen dioxide is rapidly converted to nitric oxide by the water absorbed on a Linde Molecular Sieve column. The resultant wave form is indistinguishable from that of pure nitric oxide introduced to the column. Thus, by conversion to the low boiling nitric oxide, the complication of oxidation of organic partitioning liquids is obviated.

이산화질소는 Linde Molecular Sieve 칼럼에 흡수된 물에 의해 일산화질소로 급속히 전환된다. 합성된 파형은 칼럼에 도입된 순수 일산화질소의 것과 구별할 수 없는 것이다. 따라서 저비점 일산화질소로 전환함으로써 유기분배액의 산화의 복잡성은 미연에 방지된다.

Key words : Nitrogen Dioxide, Molecular Sieve, Adsorption Column, Gas-Solid Chromatography, Conversion.

I. Introduction

The various techniques of gas chromatography have resulted in very useful methods for the separation and quantitative analysis of gaseous mixtures¹⁻³⁾. In particular, Patton and co-workers⁴⁾ have shown good separations of some gases ; the mixtures were separated on thermostated columns packed with charcoal, alumina, or silica gel, by elution with an inert carrier gas. They state that continually increasing column temperature during elution permits a more efficient separation of materials

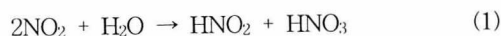
with widely different affinities for adsorbents, but were unable to take advantage of this technique because of the experimental difficulties attending reproduction of heating and carrier gas flow rate.

On the other hand, because nitrogen dioxide boils at approximately room temperature, attempts were made to separate it on gas-liquid hydrocarbon columns. Sharp peaks followed by a long tailing peak seemed to indicate complications involving oxidation of the column liquid.

Use of column liquids such as fluorinated

hydrocarbons and silicone oils gave essentially the same phenomena; long tailing peaks were observed, and the retention time of the leading edge was not predictable. The wave forms did not yield data amenable for quantitative analysis.

If nitrogen dioxide reacted at room temperature with water, the following reactions would take place :



Nitrous acid, being unstable, would decompose :



liberating nitric oxide. The theoretical yield—i.e., nitric oxide to nitrogen dioxide—is 1 to 3. It would also be convenient if the water was adsorbed in an adsorption column and the reaction and separation of mixtures took place on a single adsorption column. Nitric acid from the reaction would be strongly adsorbed on the column and would not be eluted.

Because the reaction product would be nitric oxide (a low boiling liquid), an adsorption column, such as Molecular Sieve, alumina, or silica gel, would be needed. The separation of nitric oxide by gas chromatography has been described in the literature⁵⁾.

A Molecular Sieve column was chosen for evaluation because methane, another low boiling gas, and nitric oxide could be conveniently separated at room temperature.

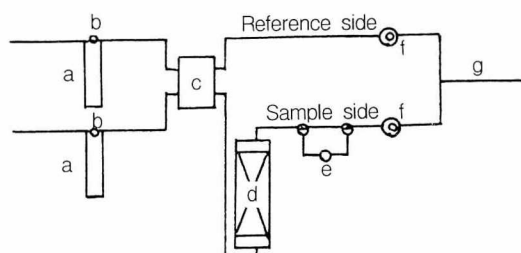


Fig. 1. Schematic diagram of flow apparatus.
a : Manometer, b : Orifice, c : T/C cell,
d : Column, e : Sample volume,
f : Pressure regulator, g : Tank helium.

II. Experimental

A schematic diagram⁶⁾ of the flow adsorption apparatus is shown in Fig. 1.

Linde Molecular Sieve, 5A, was crushed to 16 to 42 mesh and packed into a ten-foot length of aluminum tubing, 1/4 inch in outside diameter. The column was not activated, and 2 millilitre of water was pipetted onto the anterior end of the adsorbent. Helium carrier gas—flow rate was 60 millilitre per minute, and column temperature was 22°C.

III. Results and Discussion

The retention volumes of some gases of the column were : 180 cc. for oxygen, 325cc. for nitrogen, and 475cc. for nitric oxide.

The curve A of Figure 2 shows the calibration obtained with pure nitric oxide. When equal pressures of nitrogen dioxide are admitted to the column, a wave form of the same shape (but of diminished size) is found

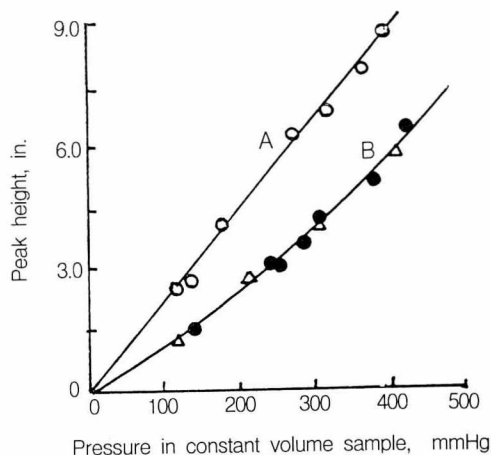


Fig. 2. Calibrations obtained with nitric oxide and nitrogen dioxide.

Nitric oxide (open circle), Nitric oxide yield from nitrogen dioxide-water reaction (closed circle), and theoretical yield of nitric oxide from nitrogen dioxide-water reaction (triangle).

at the same position as the nitric oxide.

If the gas eluted after adding nitrogen dioxide is trapped in liquid nitrogen, it is colorless after warming but becomes brown after being mixed with oxygen. This gas is unquestionably nitric oxide because nitrogen dioxide, with its high boiling point, would not be eluted at room temperature from the Molecular sieve.

The curve B of Figure 2 shows the calibration obtained with nitrogen dioxide in the sample bulb-i.e., the peak height of the resultant nitric oxide yield. A constant-volume sample bulb was used, and the pressure in the bulb is plotted vs. peak height.

The calibration of nitrogen dioxide is complicated by association.



The position of the equilibrium is a function of the total pressure in the sample tube. By utilizing data on the equilibrium constants⁷⁾ and taking into account to degree of association as a function of pressure, the points represented as crosses were plotted as the peak heights which would have been observed had the stoichiometry of the reaction of nitrogen dioxide and water been that predicted by Equations 1 and 2.

The degree of association was determined at the given pressure, and the theoretical equivalence of the mixture was calculated in terms of nitric oxide.

From this procedure, the peak height which should have been observed was taken from the original nitric oxide calibration. The agreement of the data is good and calibrations for nitrogen dioxide are accomplished conveniently with nitric oxide.

It was qualitatively established that the same process takes place on wet alumina and silica gel columns.

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