GAS-SOLID CHROMATOGRAPHIC DETERMINATION OF NITROGEN DIOXIDE IN THE PRESENCE OF OXYGEN

RECENTLY, Greene and Pust described a method for determining nitrogen dioxide by gas-solid chromatography. Their method employs a Linde Molecular Sieve 5A column with the anterior portion wetted with water. Nitrogen dioxide will not pass through the column but reacts with the water:

\[ 2 \text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HNO}_2 + \text{HNO}_3 \]  

[1]

The nitrous acid, being unstable, decomposes:

\[ 3 \text{HNO}_2 \rightarrow \text{HNO}_3 + 2 \text{NO} + \text{H}_2\text{O} \]  

[2]

The nitric oxide, separated as a distinct peak by the column is measured.

In the course of studying nitrogen transformations in aerobic soils, it appeared desirable to determine nitrogen dioxide in soil atmospheres. The method of Greene and Pust was found to be unsuccessful in the presence of oxygen. Presumably the nitric oxide formed in reaction [2] combines with oxygen in the column and nitrogen dioxide is reformed. This leads, by reaction [1], to further formation of additional nitrogen as nitric acid, which introduces error into the determination. A procedure that was developed and is here described has been found to permit the uniform measurement of nitrogen dioxide in the presence of air. Briefly the method involves immersing the gas sample within aluminum tubing placed in an acetone-dry ice bath, sweeping the oxygen (and nitrogen dioxide) out of the column with helium, then vaporizing the frozen nitrogen dioxide (freezing point —10°C) in a warm water bath and sweeping it into the chromatographic column for determination by the method of Greene and Pust.

A Beckman GC-1 gas chromatograph was employed at room temperature using helium as the carrier gas at a flow rate of 70 ml per minute. Linde Molecular Sieve 5A was sized to 32-100 mesh and packed into ¾-inch OD aluminum tubing. A 12-inch wet section which contained 2 ml of water headed a 36-inch dry column section. A gas-sampling valve system found useful for separating traces of gases and diagrammed elsewhere was inserted into the gas chromatograph in front of the Molecular Sieve column. This valve system was fabricated from 24 inches of ¼-inch OD aluminum tubing and two 2-mm. three-way glass stopcocks. One side-arm of the stopcocks was equipped with two outlets which were capped with sleeve-type serum bottle stoppers. These were used for sample injection and for vacuum and manometer connections. The aluminum tubing section was crimped with pliers at about ½-inch intervals to increase the surface contact, and the tubing coiled to fit into a 400-ml beaker.

For a determination of nitrogen dioxide admixed with air or oxygen, the coiled tubing portion of the valve was immersed in an acetone-dry ice bath and...