THE ASSAY OF NITROGEN MONOXIDE.*

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INTRODUCTION.

The tenth revision of the United States Pharmacopœia gives neither purity rubric nor assay for nitrogen monoxide. In 1912 Smith and Leman (1) examined four commercial samples of nitrogen monoxide and found the percentage of purity to vary between 93.4 and 96.1 per cent. However, in a personal communication from one of the large manufacturers of the gas the authors learned that samples extant on the market contained sometimes as much as 20 per cent of nitrogen. Hackh (2) in 1924 urged the revision committee of the Pharmacopœia to increase the stringency of the purity tests for the compound and include an assay for it. This was neglected. Very recently Chaney and Lombard (3) devised an assay method based upon washing the nitrous oxide with water saturated with air. Hackh also urged the introduction of the Bureau of Mines (4) test for the higher oxides of nitrogen and a simple solution in water test as an assay. The former test depends upon the fixation of the higher oxides of nitrogen with sodium hydroxide and the subsequent oxidation to the pentavalent state by means of hydrogen peroxide. The nitrate is then quantitatively determined colorimetrically with phenoldisulphonic acid. In the assay recommended, running tap water was passed through a column of the gas for ten minutes and the undissolved gas measured, making the necessary corrections for the air dissolved in the water.

It is well known that the accepted method of analysis for nitrogen monoxide depends upon the explosion of a definite volume of the gas with hydrogen and measuring the residual nitrogen. This method requires considerable practice and skill to operate successfully. In an effort to obtain a method more readily adaptable to Pharmacopœial purposes, this work was conducted.

EXPERIMENTAL.

Nitrogen monoxide is soluble in water to the extent of 1.3 cc. in 1 cc. at S. T. P. (5). It is about four times more soluble in alcohol. An effort was made to devise an assay depending upon the differential solubility of nitrogen monoxide and its usual impurities (mixtures of O_2 and N_2) in alcohol (6) and in dehydrated alcohol. These methods were not successful on account of the solubility of the impurities in the solvent. More concordant results were obtained using water at 0° C. as the solvent.

The following analytical procedure was adopted.

ASSAY.

Place in a 100-cc. calibrated nitrometer, provided with a two-way stop-cock and two-way outlet, and properly connected with a balancing tube, a sufficient quantity of mercury. Connect one of the intake tubes of the nitrometer with a gas pipette of about 150 cc. capacity. Boil a sufficient quantity of distilled water to fill the gas pipette allowing a liberal supply for replenishing. Introduce the water into the pipette while still hot avoiding contact with air as far as possible. Place the pipette in a water-bath at 0° C. When the water in the pipette reaches 0° C., reduce the pressure in the nitrometer tube and open the stop-cock controlling the connection with the

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gas pipette. Draw the water (free from air bubbles) through the capillary opening, connection and stop-cock opening in the nitrometer. Close the stop-cock. Having filled completely the nitrometer, other stop-cock opening and intake tube with mercury, reduce the pressure in the bulb and introduce exactly 100 cc. of nitrogen monoxide measured at atmospheric pressure and 25° C. from the cylinder which must be in a horizontal position. Close the stop-cock. Increase the pressure of the nitrogen monoxide in the nitrometer tube and open the stop-cock controlling the connection with the gas pipette. Force the entire volume of gas into the pipette. Close the stop-cock, maintain the pipette at 0° C. and rock rapidly, shaking the water in contact with the gas as far as possible. Keep the pressure bulb of the gas pipette completely filled with boiled distilled water reduced to 0° C. After about thirty minutes most of the gas is dissolved by the water. At this point, to facilitate the solution of the last portion of the gas, draw some of the liquid into the nitrometer tube and force the residual gas back upon the surface of the liquid in the pipette. Continue agitation until the volume of gas which remains does not change in volume after three consecutive agitations of at least 2 minutes each. The residual gas, if any, is drawn into the nitrometer tube and the volume measured immediately at atmospheric pressure.

Not more than 3 cc. of gas remains, corresponding to not less than 97 per cent by volume of N_2O.

RESULTS.

1. Sample prepared through the courtesy of the Ohio Chemical Company, analyzed and found to contain 99.9 per cent N_2O.

Solution Method 99.5 per cent N_2O.

2. Sample prepared through the courtesy of the Ohio Chemical Company, mixed with nitrogen, analyzed and found to contain 90.9 per cent N_2O.

Solution Method 89.8 per cent N_2O
88.0 per cent N_2O
88.6 per cent N_2O.

3. Sample prepared through the courtesy of the Ohio Chemical Company, mixed with nitrogen, analyzed and found to contain 94.3 per cent N_2O.

Solution Method 93.0 per cent N_2O
92.7 per cent N_2O.

4. Sample prepared through the courtesy of the Ohio Chemical Company, mixed with nitrogen, analyzed and found to contain 86.1 per cent N_2O.

Solution Method 83.2 per cent N_2O.

5. Sample was a mixture of 90 volumes of 99.9 per cent N_2O and 10 volumes of air.

Solution Method 89.0 per cent N_2O
90.0 per cent N_2O.

6. Sample was a mixture of 95 volumes of 99.9 per cent N_2O and 5 volumes of air.

Solution Method 95.2 per cent N_2O.

7. The following samples of commercial nitrogen monoxide were assayed by the solution method.

A. 97.4, 97.2, 99.2 per cent N_2O
B. 98.2 per cent N_2O
C. 98.0 per cent N_2O
D. 95.6, 93.8 per cent N_2O.

8. A series of determinations was conducted on one commercial sample.

1. 98.0 per cent N_2O
2. 98.0 per cent N_2O
3. 98.6 per cent N_2O
4. 98.2 per cent N_2O
5. 98.6 per cent N_2O
6. 98.2 per cent N_2O
7. 98.2 per cent N_2O
8. 98.4 per cent N_2O
9. 98.2 per cent N_2O
10. 99.1 per cent N_2O

Mean 98.35 per cent N_2O.

The P. E. of a single determination of this series calculated by the simplified formula P. E. $= 0.8453 \frac{\Sigma\eta}{N} = 0.23$ per cent.

CONCLUSION.

1. A method of estimating the approximate purity of commercial samples of nitrogen monoxide has been devised.

2. Several commercial samples have been tested.

BIBLIOGRAPHY.

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BUREAU OF CHEMISTRY, STATE OF MARYLAND,
DEPARTMENT OF HEALTH.

PHARMACISTS IN THE AUSTRALIAN ARMY.

Correspondence in the Australasian Pharmaceutical Journal.

"In the *Journal* (Australasian Pharmaceutical) for November 12, 1932, page 430, I notice a letter from Mr. H. Long, in which he mentions the position of pharmacist in the British Army. It may be of interest to your readers to know that the pharmacist is recognized in the Australian Forces. I myself hold a commission of O. C., Base Medical Depot, 5th Military District, and the following will show the position of pharmacists in other departments of the Australian Army:

"No dispensing of any description is permitted except by a qualified pharmacist. The rank of staff-sergeant is granted to the dispenser in a field ambulance. In hospitals a pharmacist holds the rank of lieutenant with a staff-sergeant as assistant. The O. C., Base Medical Depot ranks as a lieutenant or captain, and the staff officer of pharmaceutical service is a major. The position generally is very satisfactory, as the whole of the work of supervising equipment, drugs, etc., and all the dispensing, are in the hands of qualified pharmacists. The conditions of service include passing the necessary military examination and holding the qualification."—W. BRENDON GARNER.

Dec. 14, 1932, Perth, Western Australia.

ANTI-OPIUM MESSAGE ISSUED BY MANCHUKUO MINISTER.

On November 30th, a message was issued by the Manchukuo Government in connection with the Anti-Opium Act, to the following effect:

"The habit of opium smoking appears to have taken a deep root among our people. It goes without saying that the habit will cause much wasteful expenditure among the people. It will invite the contempt of foreign nations. It is against the fundamental principle on which our State is founded. Whether we can deal with the problem of opium smoking successfully or not, largely will decide the fate of our national policy. We are now laying the foundation of our State by undertaking various important reforms and by establishing various new systems. It is necessary, therefore, to adopt a fundamental policy regarding opium smoking. It would be a futile attempt to eradicate the habit of opium smoking by disregarding the confirmed addicts Only by a wise and efficient method of controlling this habit among such people can we hope to deal with this big problem with a measure of success."