

Estimation of Nitrogen Dioxide and Nitric Oxide in Air

In addition to the method described below, a number of instruments have recently become available based on chemiluminescence: these are currently being evaluated and may be of considerable value.

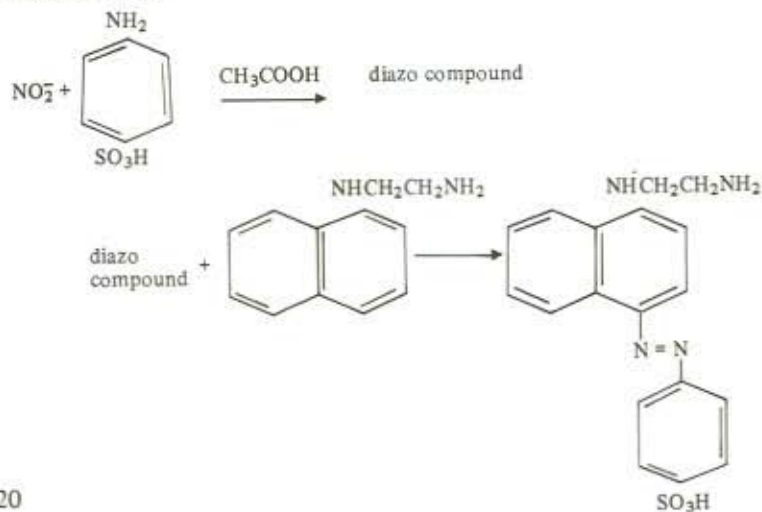
1. SCOPE

The method is applicable to nitrogen dioxide concentrations in the atmosphere from a few parts per thousand million to about 5 parts per million, with only slight interference from other gases.

2. PRINCIPLE OF METHOD

Nitrogen dioxide is absorbed in a solution of sulphanilic acid which is thereby diazotised; the diazonium salt is coupled with N-(1-naphthyl)-ethylenediamine and the azo-dye formed measured spectrophotometrically. The same process can be used for nitric oxide after oxidation to nitrogen dioxide by first passing the sample through an oxidising solution: this gives a measure of total nitrogen dioxide and nitric oxide, the latter being estimated by difference. The method is basically that of Saltzman (9.1) as recommended by the American Society for Testing Materials.

3. REACTIONS



4. REAGENTS

The reagents are made from analytical-grade chemicals in nitrite-free water prepared, if necessary, by redistilling distilled water in an all-glass still after adding a crystal of each of potassium permanganate and barium hydroxide. Unless otherwise stated, solutions are stable for several months if stored in well-stoppered, amber glass bottles at low temperature. The absorbing solution should be warmed to room temperature before use. Acetic acid, glacial; sodium nitrite; sulphanilic acid; N-(1-naphthyl)-ethylenediamine hydrochloride stock solution: dissolve 0.2 gram of the reagent in 100ml of water.

4.1 *Absorbing solution*

Dissolve 5 gram of sulphanilic acid in about 900ml of water containing 140ml of glacial acetic acid. Cool, add 20ml of the stock solution of N-(1-naphthyl)-ethylenediamine hydrochloride and dilute to 1 litre with water. Avoid lengthy exposure to air during preparation and use. Sodium nitrite stock solution: dissolve 2.03 gram of sodium nitrite in water and dilute to 1 litre. Solution stable for about 90 days.

4.2 *Sodium nitrite standard solution*

Dilute 10ml of the stock solution to 1 litre with water. Prepare fresh just before use. One ml of this solution produces a colour equivalent to that of 10 μ l of nitrogen dioxide (10ppm in 1 litre of air at 760mm Hg and 25°C). This is based on the empirical determination that 0.72 mole of sodium nitrite produces the same colour as 1 mole of nitrogen dioxide. There is some controversy concerning this stoichiometric factor which has ranged from 0.5 to 1.0 (9.2-9.5). For this reason for work of the highest accuracy the calibration graph should be prepared using standard atmospheres of nitrogen dioxide.

4.3 *Potassium permanganate (for determination of nitric oxide)*

Dissolve 2.5 gram of potassium permanganate in about 90ml of water, add 0.75ml of concentrated sulphuric acid (SG = 1.84), cool and dilute to 100ml with water. This solution has poor keeping properties and is preferably prepared fresh as required.

5. APPARATUS

5.1 *Bubblers*

These should be of the miniature fritted type. Alternatively all-glass midget impingers (which may be obtained commercially, eg from Mine Safety

Appliances Limited) may be used. It should be noted that if the latter are used, absorption efficiency may be lower than with the fritted type and it may be necessary to use more than two in series to ensure complete collection of sample.

6. SAMPLING AND PROCEDURE

6.1 *Nitrogen dioxide only*

Transfer, by means of a pipette, 10ml of the absorbing solution to two bubblers connected in series. By means of a suitable pump draw the atmosphere through the absorbing solution at the rate of 400ml/min until a reasonable red-violet colour has developed in the first bubbler. Note the volume of air sampled and the temperature and pressure. After a further 15min the optical density of each solution is measured in 20mm cells at 550nm using unexposed reagent as reference and the concentration of nitrogen dioxide determined from the prepared calibration graph. Correction for pressure and temperature may be made if necessary by means of the usual gas equation.

6.2 *Nitric oxide only*

Transfer 10ml of the absorbing solution to three suitable small bubblers and 10ml of the potassium permanganate solution to a fourth bubbler. Connect in series – bubblers 1 and 2 containing absorber, bubbler 3 containing oxidant and bubbler 4 absorber. Proceed as for nitrogen dioxide and measure optical density of the solution in bubbler 4 which will be a measure of the nitric oxide concentration in terms of nitrogen dioxide. Conversion of nitric oxide to nitrogen dioxide by acid permanganate is variable and can be as low as 70%, hence the method will give only an approximate value for nitric oxide concentration. Conversion efficiencies of 95 to 100% have been reported using other oxidants (9.6).

6.3 *Nitrogen dioxide and nitric oxide*

If a simultaneous estimation of these gases is required then the optical densities of solutions in bubblers 1 and 2, as described under nitric oxide, may also be measured.

7. SPECIAL CASES

Instruments for automatic continuous monitoring of oxides of nitrogen in the atmosphere utilising the Saltzman method are available commercially.

Their bulk, however, might preclude the use of such instruments in the upper atmosphere and no information is available regarding the availability of miniature models. Coulometric and non-dispersive infra-red spectroscopic methods which lend themselves to miniaturisation have been described. The former is however non-specific for nitrogen oxides being subject to interference from oxidants and water vapours. The latter in its present form is seriously affected by the presence of water vapour and is relatively insensitive below about 10ppm.

8. NOTES ON PROCEDURE

8.1 *Preparation of calibration graph*

Add known volumes, up to 1ml, of the standard nitrite solution to a series of 25ml volumetric flasks and dilute to volume with the absorbing solution. Mix well and after 15min measure the optical density of the solution in 20mm cells at 550nm using the reagent as reference and plot graph of optical density against concentration.

8.2 *Interferences*

The effect of interfering gases is relatively unimportant unless present in quantities much higher than that of nitrogen dioxide. Ozone in amounts greater than 5 times that of nitrogen dioxide cause a small interference imparting a slight orange tint to the reagent. A 10-fold ratio of sulphur dioxide produces no interference, but a 30-fold ratio slowly bleaches the colour to a slight extent. Interferences from other gases is negligible.

9. REFERENCES

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