

Spectrometric Determination of NO₂ in Ambient Air and its Control

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Abstract

Increasing concern over the air pollution has forced the man to develop the new technology for the better quality of life. In modern world, air pollution does not need any introduction. One of the major factors responsible for such degradation in the quality of life is air pollution. However, chief among them are carbon monoxide, sulphur dioxide, nitrogen oxides, ozone, etc. Nitrogen dioxide causes acute bronchitis at 0.1 ppm level and increased exposure for 30 minutes at 90 ppm results in pulmonary oedema. But the most significant aspect of nitrogen dioxide pollution is its role in the initiation of photochemical reactions in presence of hydrocarbons leading to the production of secondary pollutants. In this paper, determination and control of nitrogen dioxide has been discussed. In one method of low concentration determination less than 5 ppm, the air sample is drawn by sampling probe and is pumped through rotameter which force the air with high pressure into the impinger containing the absorbing reagent. In another method of high concentration determination more than 5 ppm, the reagent is kept in glass syringe which sucks the air sample into it and then shaken vigorously to allow the absorption of NO₂ completely resulting in change in color of absorbed sample. Several methods and technologies have been devised to control the emission of NO₂. These methods include two-stage combustion, flue gas recirculation, burner design modifications, effluent gas treatment, TYCO process, adsorption on solids, catalytic decomposition etc. by which NO₂ formation can be curbed.

Keywords: Nitrogen dioxide; ambient; air pollution; reagent.

1. Introduction

Several fuels containing nitrogen in the form functional group are source of nitrogen oxides. Even if the fuel does not contain any nitrogen, it mixes in form of air during combustion process and produces different oxides of nitrogen. Therefore, air acts as a source of nitrogen during combustion. Atmospheric nitrogen reacts with the oxygen present in the air forming nitrogen oxides. Hence, nitrogen oxides are always formed regardless of whether the fuel contains nitrogen or not. Bound non-reactive nitrogen present in the fuel also combines with the oxygen in the air to form various oxides of different combinations. Important among these are dinitrogen oxide (N_2O), nitrogen oxide (NO_2), nitrogen oxide (NO), dinitrogen dioxide (N_2O_4) and nitrogen pentoxide (N_2O_5).

2. Methodology

The methodology describes about the experimental details and determination of NO_2 concentration in ambient air.

2.1 Principle of the Method

The nitrogen dioxide is absorbed in an azo dye forming reagent. A stable red-violet colour is produced within 15 min which may be read visually at 550 nm.

2.2 Range and Sensitivity

This method is intended for the manual determination of NO_2 in the atmosphere in the range of 0.005 to about 5 parts per million (ppm) by volume or 0.01 to 10 $\mu\text{g/L}$, when sampling is conducted in fritted bubblers.

2.3 Interferences

A 30 fold ratio of sulphur dioxide to NO_2 produces colour to some extent. The addition of 1% acetone to the reagent before use retards the fading by forming another temporary product with SO_2 . A fivefold ratio of ozone to nitrogen dioxide will cause a small interference. The reagent gives a slightly orange tint. If strong oxidizing or reducing agents are present, the colours should be determined very fast.

2.4 Precisions

A precision of 1% of the mean can be achieved with careful work. The limiting factors are the measurements of the volume of the air sample and of the absorbance of the colour.

2.5 Apparatus

2.5.1 *Absorber*. The sample is absorbed in an all-glass bubbler with a 60 μm maximum pore diameter frit.

Calculate the maximum pore diameter as follows:

$$\text{Maxporediam}(\mu\text{m}) = \frac{4000s}{P}$$

where, s= surface tension of water at the test temperature in N/m (0.073 at 18°C, 0.072 at 25°C, and 0.071 at 31°C), and, P=measured vacuum, kPa.

2.5.2 *Air Metering Device*. A glass rotameter capable of accurately measuring a flow of 0.4 L/min is suitable. A wet test meter is convenient to check the calibration.

2.5.3 *Sampling Probe*. A glass or stainless steel tube 6 to 10 mm in diameter provided with a downward facing intake is suitable. Plug of glass wool may be inserted to exclude water droplets and particulate matter.

2.5.4 *Glass Syringes*. 50 or 100 mL syringes are convenient for sampling.

2.5.5 *Air Pump*. A vacuum pump capable of drawing the required sample flow for intervals of up to 30 min is suitable.

2.5.6 *Spectrophotometer or Colorimeter*. A laboratory instrument suitable for measuring the pink color at 550 nm, with stoppered tubes or cuvettes.

2.6 Reagents

2.6.1 *N-(1-Naphthyl)-EthylenediamineDihydrochloride, Stock Solution (0.1%)*. Dissolve 0.1 g of the reagent in 100 mL of water. Solution will be stable for several months if kept well-stoppered in a brown bottle in the refrigerator.

2.6.2 *Absorbing Reagent*. Dissolve 5 g of anhydrous sulphanic acid (or 5.5 g of p-NH₂.C₆H₄SO₃H.H₂O) in almost a litre of water containing 140 mL of glacial acetic acid, add 20 mL of the 0.1% stock solution of N-(1-naphthyl)-ethylenediaminedihydrochloride, and dilute to 1 L.

2.7 Procedure

Two methods are described below. Concentrations below 5ppm are sampled by the 'bubbler method' and higher concentrations may be sampled by the 'glass syringe method'. After collection or absorption of the sample, a red-violet colour appears. Colour development is complete within 15 min at room temperature.

2.7.1 *Bubbler Method*. Assemble in order, a sampling probe, a glass rotameter, fritted absorber, trap, and pump. Use ground-glass connections upstream from the absorber. The sampling rotameter may be used upstream from the bubbler provided occasional checks are made to show that no NO₂ is lost. The rotameter must be kept free from spray or dust. Pipet 10 mL of absorbing reagent into a dry fritted bubbler. Draw an air sample through it at the rate of 0.4 L/min (or less) long enough to develop sufficient final colour (about 10 to 30 min). Note the total air volume sampled. Measure and record the sample air temperature and pressure.

2.7.2 *Glass Syringe Method*. 10 mL of absorbing reagent is kept in a capped 50 (or 100) mL glass syringe and 40 (or 90) mL of air is drawn in at the time of sampling.

The absorption of NO₂ is completed by capping and shaking vigorously for 1 min, after which the air is expelled. Additional air may be drawn in and the process repeat several times, if necessary, to develop sufficient final colour.

2.8 Calibration and Standardization

Standardization is performed using the diluted sodium nitrite solution prepared, which contains 10 µL of NO₂ per mL. Add to a series of 25 mL volumetric flasks 0, 0.2, 0.4, 0.6, and 1.0 mL of the diluted sodium nitrite solution. These standards will contain respectively 1, 2, 4, 6 and 10 µL equivalents of NO₂. Dilute the volumetric flasks to the mark with absorbing reagent. Mix, allow 15 min for complete colour development and read the formed colours. The standards contain progressively, 0, 0.08, 0.16, 0.24 and 0.40 µL NO₂ per mL of absorbing solution. Plot the respective absorbances versus the µL NO₂ per mL of absorbing reagent.

2.9 Calculations

Determine the µL of NO₂ per mL of absorbing reagent from the measurement made and the calibration curve prepared. Compute the concentration of NO₂ in the sample as follows:

$$ppmNO_2 = \left(\frac{\mu L NO_2}{mL} \right) * \frac{mL \text{ of absorbing reagent}}{\text{sample volume in L}}$$

where, sample volume is corrected to 25°C and 101.3 kPa.

3. Control of Emission of Nitrogen Dioxide (NO₂)

3.1 Two stage combustion

Lowering the excess air temperature is another method of NO_x control. Generally, waste heat is used to preheat the air entering the combustion process to effect considerable energy savings. Unfortunately, as the temperature of preheated air increases from 25-300°C causes a three-fold increase in NO_x emissions. For controlling NO_x, cooling the flaming zone by heat transfer to surrounding surfaces water or steam injection to the extent of 10-15% is one of the preferred techniques. This reduces the NO_x emissions to some extent without compromising the combustion efficiency.

3.2 Flue gas recirculation

Flue gas recirculation into the combustion chamber is another practical way of reducing NO_x formation. Normal practice is to mix 10-20% of the flue gas along with the primary air prior to combustion. Since oxygen content is quite low in the flue gas, the peak operating temperature automatically reduces. Due to the deficiency in oxygen, nitrogen to oxygen ratio (N/O) is also reduced automatically. A 10% recirculation of the flue gas while maintaining 15% excess air reduces NO_x emissions by almost 50% in oil fired furnaces. At 20% recirculation, NO_x emissions can come down by 20-25%.

3.3 Burner Design Modification

There are two basic designs of combustion chambers in vogue: Tangential firing and horizontal firing. In tangential firing, the furnace itself is used as the burner. The combustion gases spiral upwards around the walls of the furnace. The combustion gas environment in the furnace reduces the peak operating temperature resulting in the reduction of NO_x emissions. In horizontal firing units, the flame is positioned at right angles to the walls of the chamber. This tends to concentrate the hot gases thereby leading to higher temperatures and higher NO_x emissions. Boilers where combustion area is wider will have lower peak operating temperatures and lower NO_x emissions.

3.4 The TYCO Process

Polluted air containing NO_x and SO₂ is led into a reactor containing NO oxidizer. Air and water vapour are introduced into the reactor. The gases containing sulphuric acid mist, nitric oxide and nitrogen dioxide enter a sulphuric acid scrubber. NO_x is absorbed to produce nitrosylsulphuric acid (NOHSO₄). The collected liquid containing NOHSO₄ and unreacted sulphuric acid is led into a stripper where hot stripping gas is introduced from the bottom. Nitric oxide and nitrogen dioxide are separated in the gaseous form which is absorbed in dilute nitric acid. Unreacted nitric oxide and nitrogen dioxide are recirculated after passing through a mist eliminator. Diluted sulphuric acid leaving the stripper is again led into an evaporator to remove the water vapour and concentrate the acid. Part of the acid is withdrawn for marketing purpose and the rest is recycled back into the reactor. The scrubber must be designed for an efficiency of 99% absorption of NO.

3.5 Adsorption on solids

Ferrous sulphate is promising adsorbent for NO. Here water vapour and carbon dioxide present in the tail gases are not adsorbed. The process is suitable for the adsorption of 50-100 ppm of nitric oxide. The adsorption is an exothermic process and typically associated with 2-4% conversion of ferrous salt to ferric. However, oxidation of some ferrous to ferric is not a practical hindrance in the process since the main aim is to remove nitric oxide which is not adversely affected. This technique is yet to be applied for the large-scale removal of NO_x.

3.6 Catalytic decomposition

The homogenous decomposition of NO is extremely slow. Heterogeneous decomposition using a variety of catalysts such as alumina (Al₂O₃), chromium trioxide (Cr₂O₃), zirconium oxide (ZrO₂), etc., also does not proceed rapidly. None of these reactions are capable of reducing NO at low temperatures. However, at higher temperatures the reaction is reasonably fast. There are two types of NO_x reduction processes: selective and non-selective. In selective reduction the reactant preferentially reduces NO_x whereas non-selective reduction involves the consumption of oxygen first followed by reduction of NO_x. Therefore, in non-selective reduction the

consumption of the reagent will also be much higher. Hence, selective reduction is preferred as it is economical.

4. Conclusion

Though there have been considerable advances in dealing with problems of air pollution, with developed and sophisticated technologies adopted in some countries, excessive and often unnecessary pollution is prevalent in many industrial areas. In the present state of knowledge, complete elimination of pollution is not practicable, but there could be much scope for greater improvement than has so far been achieved. Such improvement will only be achieved by adopting the technology that has been discussed above.

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