IS 5182-6 (2006): Methods for Measurement of Air Pollution, Part 6: Oxides of nitrogen [CHD 32: Environmental Protection and Waste Management]

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भारतीय मानक

वायु प्रदूषण मापने की पद्धति

भाग 6 नाइट्रोजन के ऑक्साइड

(पहला पुनरीक्षण)

Indian Standard

METHOD FOR MEASUREMENT OF AIR POLLUTION

PART 6 OXIDES OF NITROGEN

(First Revision)

ICS 13.040.20

BUREAU OF INDIAN STANDARDS
MANAK BHAVAN, 9 BAHADUR SHAH ZAFAR MARG
NEW DELHI 110002

November 2006

Price Group 3

Environment Protection and Waste Management Sectional Committee, CHD 32

FOREWORD

This Indian Standard (First Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Environment Protection and Waste Management Sectional Committee had been approved by the Chemical Division Council.

The standard was originally published in 1975. Based on the technological development in this area since last three decades, the committee decided to revise the standard. In this revision, details of the sampling apparatus and required glassware; precision and accuracy and also 4 h sampling have been incorporated.

The method is generally specific for nitrogen dioxide. In high temperature combustion processes, some other oxides of nitrogen and yielded which further oxidize to nitrogen dioxide in air at ordinary temperatures. So, the method is employed to determine the nitrogen oxide contents in the atmosphere as nitrogen dioxides.

There is no ISO Standard on this subject. In the preparation of this standard, considerable assistance has been derived from the following publications.

a) CHRISTIE (A A) *et, al.* Field method for the determination of nitrogen dioxide in air. Analyst, 95 : 510-524 (1970).

b) MAGESON, (J H) *et, al.* Evaluation of the sodium arsenite method for measurement of NO_2 in ambient air. J.A.P.C.A., 27 : 553-556 (1977).

c) JACOB, (M B) and HOCHHEISER (S). Continuous sampling and untra-micro determination of nitrogen dioxide in air. Anal. Chem. 30 : 426 (1958).

The composition of the Committee responsible for formulating this standard is given in Annex A.

In reporting the results of a test or analysis made in accordance with this standard, if the final value, observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard
METHOD FOR MEASUREMENT OF AIR POLLUTION
PART 6 OXIDES OF NITROGEN
(First Revision)

1 SCOPE

1.1 This standard prescribes a method for measurement of nitrogen oxides (as NO_2) in ambient air.

1.2 This method is applicable for 4 to 8 h integrated sampling of NO_2 in ambient air.

2 REFERENCES

The following standards contain provisions which through reference in this text constitute provisions of this standard. At the time of publication the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No.	*Title*
1070 : 1992	Reagent grade water (*third revision*)
2303 (Part 1/ Sec 1) : 1994	Grading glass for alkalinity: Part 1 Hydrolytic resistance, Section 1 Hydrolytic resistance of glass grains at 98°C — Method of test and classification (*first revision*)
4167 : 1980	Glossary of terms relating to air pollution (*first revision*)

3 TERMINOLOGY

The definitions given in IS 4167 shall apply.

4 PRINCIPLE

Ambient nitrogen dioxides are collected by bubbling air through a solution of sodium hydroxide and sodium arsenite. The concentration of nitrite ion (NO_2) produced during sampling is determined colorimetrically by reacting the nitrite ion with phosphoric acid, sulphanilamide and N-(1-naphthyl)-ethylenediamine di-hydrochloride (NEDA) and measuring the absorbance of the highly coloured azo-dye at 540 nm.

5 RANGE

The nominal range of the method is 6 to 750 µg NO_2 /m³ (0.003 to 0.4 ppm). The range of the analysis is 0.04 to 2.0 µg NO_2/ml following Beer's Law throughout this range (0 to 1.0 absorbance units). Under the specified conditions of 50 ml of absorbing reagent, a sampling rate of 200 cm³/min for 24 h and a sampling efficiency of 82 percent, the range of the method is, therefore, 6 to 420 µg NO_2/m³ (0.003 to 0.22 ppm). Nitrogen dioxide concentrations in the range of 420 to 750 µg/m³ (0.22 to 0.4 ppm) are accurately measured by 1 : 1 dilution of the collected sample.

6 INTERFERENCES

6.1 Nitric oxide (NO) is a positive interferant and carbon dioxide (CO_2) is a negative interferant. The average error resulting from normal ambient concentrations on NO and CO_2 is small for most monitoring situations and does not necessitate applying a correction to measurements obtained with the method.

6.2 Potential interference from sulphur dioxide (SO_2) is eliminated by converting any SO_2 to sulphate using hydrogen peroxide during analysis.

7 SAMPLE PRESERVATION

Collected samples are stable for at least six weeks at room temperature 25 ± 2°C. Stored samples should be tightly sealed to prevent absorption of NO_2 from the atmosphere.

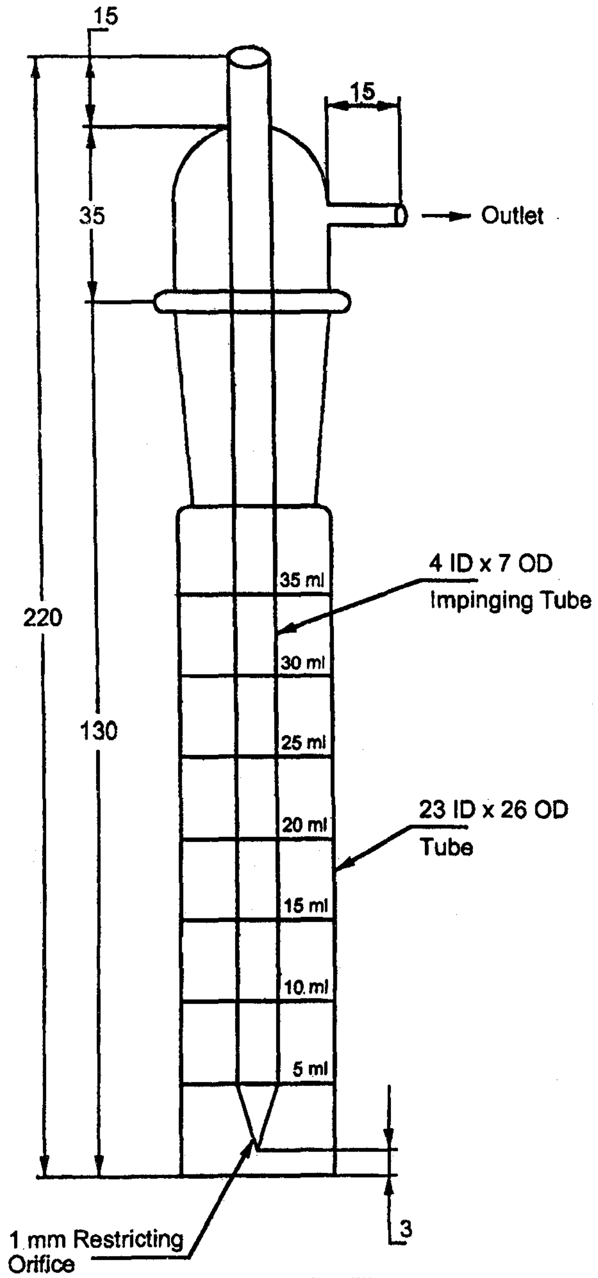
8 APPARATUS

8.1 Sampler — A sampler consists of the following components.

8.1.1 *Sample Inlet* — Teflon or glass tube with an inverted teflon or glass funnel at the sampling point to prevent entrance of precipitation.

8.1.2 *Absorber* — Standard glass midjet impinger shall be used for sampling purpose. The glass impingers shall be made from Class HGB 3 glass conforming to IS 2303 (Part 1/Sec 1). Dimensional details of midjet impinger shall be as given in Fig. 1.

8.1.3 *Moisture Trap* — The outlet impinger, a moisture trap made up of glass or polypropylene tube loosely packed



All dimensions in millimetres.

FIG. 1 STANDARD IMPINGER FOR AIR SAMPLING

with dry silica gel to trap moisture shall be available in sampler. This shall also protect the flow control device. The trap shall be packed with fresh dry glass silica gel before the start of each sampling period.

8.1.4 *Flow Control Device* — Any device capable of maintaining a constant flow through the sampling solution between 200-1 000 cm^3/min. A convenient flow control device is hypodermic needle of specific gauge 10 mm long used as a critical orifice or a needle valve.

8.1.5 *Air Pump* — Capable of maintaining a vacuum of at least 0.6 atmosphere across the flow control device. This value is based on the critical pressure differential 0.53 atmosphere plus a safety factor to allow for variations in atmospheric pressure and minor variations in pump performance.

8.1.6 *Flow Meter* — Properly calibrated flow meter for measuring air flow rates in the range of 200-2 000 cm^3/min. The use of a mass flow meter is particularly convenient since no corrections are required when used under temperature and pressure conditions that differ from the conditions under which it is calibrated *(See* **12.1**).

8.1.7 *Flow Measurement Standard* — Precision wet test meter (1 litre/revolution), bubble flow meter, or other reliable standard.

8.2 Spectrophotometer — Capable of measuring absorbance at wavelength 540 nm equipped with 1 cm optical path length cells.

8.3 Analytical Glassware

8.3.1 *Volumetric Flasks* — 50 ml, 100 ml, 250 ml, 500 ml and 1 000 ml.

8.3.2 *Pipettes* — 1 ml, 2 ml, 10 ml, 50 ml; volumetric pipettes of 2 ml and 1 ml shall be graduated in 1/10 ml.

9 REAGENTS

9.1 General

9.1.1 Unless specified otherwise, pure chemicals and reagent grade water (*see* IS 1070) shall be used in the tests.

NOTE — 'Pure Chemicals' shall mean chemicals that do not contain impurities which affect the results of analysis.

9.2 Absorbing Reagents — Dissolve 4.0 g of sodium hydroxide in distilled water, add 1.0 g of sodium arsenite and dilute to 1 000 ml with distilled water.

9.3 Hydrogen Peroxide, 30 percent.

9.4 Hydrogen Peroxide Solution — Dilute 0.2 ml of 30 percent hydrogen peroxide to 250 ml with distilled water. This solution may be used for one month, if refrigerated and protected from light.

9.5 N-(I-Naphthyl)-Ethylenediamine Di-Hydrochloride (NEDA) — 1 percent aqueous solution should have only one absorption peak at 320 nm over the range of 260-400 nm. NEDA showing more than one absorption peak of this range is impure and should not be used.

9.6 NEDA Solution — Dissolve 0.500 g of NEDA in 500 ml of distilled water. The solution is stable for one month if refrigerated and protected from light.

9.7 Phosphoric Acid, 85 percent.

9.8 Sodium Arsenite

> *CAUTION* — Arsenic compounds are highly toxic and should be handled with extreme care. Avoid contact with skin and especially with eyes. Avoid generating dust or breathing dust. Keep away from food. Wash hands after handling it. Do not take internally.

9.9 Sodium Hydroxide

9.10 Sodium Nitrite — Assay of 97 percent $NaNO_2$ or greater.

9.11 Sodium Nitrite Stock Solution (1 000 µg NO_2/ml) — Dissolve 1.500 g of desiccated sodium nitrite in distilled water and dilute to 1 000 ml such that a solution containing 1 000 µg NO_2/ml is obtained. The amount of $NaNO_2$ to be used if the assay percent is less than 100 percent, is calculated as follows:

$$G = 1.500/A$$

where

G = amount of $NaNO_2$ in g;.
1.500 = gravimetric conversion factor; and
A = assay, percent (should be 97 or greater).

NOTE — This stock solution can be stored for six weeks, if refrigerated.

9.11.1 *Sodium Nitrite Solution* (10 µg NO_2/ml) — Pipette 5 ml of the stock solution (*see* **9.11**) in to a 500 ml volumetric flask and dilute to volume with distilled water.

9.11.2 *Sodium Nitrite Solution* (1 µg NO_2/ml) — Pipette 25 ml of the solution (*see* **9.11.1**) in to a 250 ml volumetric flask and dilute to volume with absorbing reagent solution (*see* **9.2**), prepare fresh daily.

9.12 Sulphanilamide — Melting point 165 to 167°C.

9.13 Sulphanilamide Solution — Dissolve 20.0 g of sulphanilamide in 700 ml of distilled water. Add with mixing 50 ml of 85 percent phosphoric acid and dilute to 1 000 ml.

NOTE — This solution is stable for one month, if refrigerated.

10 PROCEDURE

10.1 Sample Collection

10.1.1 *Four Hourly Sampling*

10.1.1.1 Assemble the sampling apparatus at the sampling site. Components upstream from the absorber may be connected where required with teflon/silicon tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with teflon or polypropylene. Add exactly 30 ml of absorbing reagent to the calibrated absorber. Disconnect the funnel. Connect the calibrated flow meter, measure the flowrate before sampling and record as F_1. Start sampling only after obtaining an initial flowrate of 1 litre per minute. Ensure packing of ice around bubbler for low temperature to improve absorption efficiency. For effective cooling thermoelectric cooling with thermostat to maintain temperature of absorbing reagent at 10-15°C should be used for better absorption efficiency.

10.1.1.2 *Sample for 4 hours*

Record the exact sampling time by recording initial time (t_i) and final time (t_f) of sampler. Measure and record the flowrate (f_i) before the sampling and flowrate (f_t) after the sampling. Seal the collected samples after making it up to 30 ml using distilled water and transport to the laboratory for analysis.

10.1.2 *24-Hourly Sampling*

10.1.2.1 Assemble the sampling apparatus at the sampling site. Components upstream from the absorber may be connected, where required, with teflon/silicon tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joint with tygon, teflon or polypropylene.

Add exactly 30 ml of absorbing reagent to the calibrated absorber. Disconnect the funnel, connect the calibrated flow meter, measure the flowrate before sampling and record as F_1. Start sampling only after obtaining an initial flowrate in this range. Sampling rate need to be chosen depending upon expected range of concentration.

10.1.2.2 *Sample for 24 hours*

Record the exact sampling time in minutes by recording initial (t_i) and final (t_f) time of sampling. Measure and record the flowrate before (f_i)and after (f_f) the sampling. Seal the collected samples after making it up to 30 ml using distilled water and transport to the laboratory for analysis.

10.2 Analysis

10.2.1 Pipette 10 ml of the collected sample into 50 ml volumetric flask. Now add 1 ml of hydrogen peroxide solution, 10 ml of sulfanilamide solution, and 1.4 ml of NEDA solution using pipette, with thorough mixing after the addition of each reagent and make up to 50 ml with distilled water.

10.2.2 Prepare a blank in the same manner using 10 ml of un-exposed absorbing reagent. After a 10 min colour development interval, measure and record the absorbance at 540 nm against the prepared reagent blank. Determine NO_2 from the calibration curve (*see* **12.3**). Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot of the collected samples with an equal quantity of un-exposed absorbing reagent.

NOTES

1 A randomly selected 5-10 percent of the samples should be reanalyzed as apart of an internal quality assurance program.

2 A known concentration of NO_2 solution may analyze with sample as an internal quality assurance program.

11 CALCULATIONS

11.1 Air Volume

Calculate the volume of air drawn for sample as follows:

$$V_a = \frac{f_i + f_f}{2} \times (t_f - t_i) \times 60 \times 10^{-3}$$

where

V_a = volume of air sample, m^3;
f_i = air flowrate before sampling, litre per minute;
f_f = air flowrate after sampling, litre per minute;
t_i = initial time in hours;
t_f = final time in hours;
10^{-3} = conversion of litre to m^3; and
60 = conversion of hours to min.

If the temperature and pressure conditions at the time of the initial and final air flowrate measurements are substantially different from the condition under which the flow meter was calibrated. appropriate corrections to the flowrate measurements may be made to improve the accuracy of the resultant NO_2 concentration measurement. The mathematical form of these correction depends on the type of flow meter used; consult an appropriate reference for guidance.

11.2 NO_2 Concentration in Analyzed Sample

Determine μg NO_2/ml graphically from the calibration curve or compute from the slope and intercept values.

11.3 NO_2 Concentration in Air Sample

Calculate NO_2 as μg per cubic metre of air as follows:

$$NO_2 \mu g/m^3 = \frac{NO_2 \times D \times V_s}{V_a \times 0.82 \times V_t}$$

where

NO_2 = NO_2 concentration in analyzed sample, μg; [Graph Factor × (Sample Abs.-Blank Abs)]
D = dilution factor ($D = 1$ for no dilution : $D = 2$ for 1 : 1 dilution);
V_s = final volume of sampling solution, ml;
V_a = volume of air sample, ml;
0.82= sampling efficiency; and
V_t = aliquot taken for analysis.

11.4 The NO_2 concentration as ppm shall be calculated as follows:

$$NO_2\text{, ppm} = (NO_2 \mu g/m^3) \times 5.32 \times 10^{-4}$$

12 CALIBRATION

12.1 Flow Meter

Calibrate the flow meter against a calibrated standard flow measurement device such as a wet test meter, bubble flow meter, or other reliable volume measurement standard. Calibrate in units of standard cm^3/min, that is, correct to 25°C and 760 torr.

12.2 Absorber

Calibrate midjet glass impinger as follows:

a) Pipette 35 ml distilled water absorbing reagent using 5 ml calibrated pipette and check correctness of marking on impinger.
b) Use 3 mm thickness metal disk and check gap between bottom and tip of the impinger. 3 mm disk must not be loose after fitting head of impinger.
c) Use three drill bits of 0.9 mm 1.0 mm and 1.1 mm and check bore size of nozzle. Bore size has to be 1.0 mm with tolerance of 0.1mm. Impingers must be cleaned thoroughly fortnightly and also before attempting calibration. Grease must be put on mouth of impinger while using.

12.3 Spectrophotometer

12.3.1 Prepare calibration curve using 1 μg/ml working standards (*see* **9.11.2**) in accordance with the analytical procedure given in **12.3.2**. Measure and record the absorbance for each calibration standard (0, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, 15, 20 μg NO_2).

12.3.2 Plot absorbance (y-axis) *versus* the corresponding concentration in μg NO_2/50 ml solution (x-axis). Draw or compute the straight line best fitting the data to obtain the calibration curve.

13 PRECISION AND ACCURACY

Based on results from a collaborative study the within laboratory standard deviation is 8 μg/m^3 (0.004 ppm) and the between laboratory standard deviation is 11 μg/m^3 (0.006 ppm) over the range of 50 to 300 μg NO_2/m^3 (0.027 to 1.16 ppm). Based on results from a collaborative study the method has an average bias of 3 percent over the range of 50 to 300 μg NO_2/m^3 (0.027 to 0.16 ppm).

ANNEX A

(Foreword)

COMMITTEE COMPOSITION

Environment Protection and Waste Management Sectional Committee, CHD 32

Organization	*Representative(s)*
In personal capacity (*40/14, C.R. Park, New Delhi 110019*)	Prof Dilip Biswas (***Chairman***)
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Amendments Issued Since Publication

Amend No.	Date of Issue	Text Affected

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