

ASIAN INSTITUTE OF TECHNOLOGY
SCHOOL OF ENVIRONMENT, RESOURCES AND DEVELOPMENT
Urban Environmental Engineering and Management Program

Determination of Nitrogen Dioxide Content of the atmosphere
(Griess-Saltzman Reaction)

Because Nitrogen Dioxide is generally recognized to be considerably more toxic than nitric oxide, a chemical reagent, specific for NO_2 is desirable.

However, the determination of NO_2 had been generally hampered by difficulties in sample absorption and lack of specificity.

A formulation of sulfanilic acid and N-(1-naphthyl)-ethylene diamine dihydrochloride in dilute acetic acid has since proved one of the most popular methods for NO_2 analysis.

Principle:

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

Range and Sensitivity:

This method is intended for the manual determination of nitrogen dioxide in the atmosphere in the range of 0.005 to about 5 parts per million (ppm) by volume or 0.01 to 10 Ng/L, when sampling is conducted in fritted bubblers. The method is preferred when high sensitivity is needed.

Interferences:

1. A 10-fold ratio of SO_2 to NO_2 produces no effect. A 30-fold ratio slowly bleaches the color to a slight extent. The addition of 1 % acetone to the reagent before use retards the fading by forming another temporary product with SO_2 .
2. A 5-fold ratio of O_3 to NO_2 will cause a small interference, the maximal effect occurring in 3 h.
3. Peroxyacynitrate (PAN) can give a response of approximately 15 to 35 % of an equivalent molar concentration of NO_2 . In ordinary ambient air the concentration of PAN are too low to cause any significant error.
4. If strong oxidizing or reducing agents are present, the colors should be determined within 1 h, if possible, to minimize any loss.

Apparatus:

Spectrophotometer

Midget fritted Bubblers, capacity 60 mL with upward facing, 8 mm diameter fritted disks.

Grab-sample bottle, with calibrated volumes varying from 30 to 250 mL.

Sampling:

I: For levels of 1ppm and below

Place 10 mL of absorbing reagent in the midget fritted bubbler and draw a sample through it at the rate of 0.4 liter per min., for about 10 min, until sufficient color has developed.

II: For levels above 1 ppm

Sample in an evacuated bottle of approximate size (30 mL up to 100 ppm to 250 mL for down to 1 ppm). Containing 10 mL of absorbing reagent.

Allow 15 min with occasional shaking for complete absorption and color development.

Another more convenient but less accurate field method is use 50 mL glass syringes, 10 mL of absorbing reagent may be kept in the capped syringes and 40 mL of air may be drawn in at the time of sampling. If sufficient color is expected, the absorption may be completed by shaking vigorously for 1 to 2 min after which air may be expelled and additional air drawn in.

Analysis:

After collection or absorption of the sample, a direct red-violet color appears. At ordinary temperatures, color development is complete within 15 min.

Compare with standards visually or read in spectrometer at 550 nm, using unexposed reagent as a reference.

Calculations:

Correct V the volume in liters of the air sample to standard conditions.

Expressing quantities of microliters, defined a V time the ppm of NO₂.

It has been determined empirically that 0.72 moles of sodium nitrite produces the same color as 1 mole of NO₂, hence 2.03 V of NaNO₂ is equivalent to 1 μL of NO₂.

Plot the absorbencies of the standard colors, corrected for the blank, against the milliliters of standard solution. Beer's Law is followed.

Draw the straight line giving the best fit, and determine the value of milliliters of sodium nitrite intercepted at absorbency of exactly 1.

This value multiplied by 4 gives the standardization factor M, defined as the number of microliters of NO₂ required by 10 ml of absorbing reagent.

$$\text{NO}_2, \text{ PPM} = \frac{\mathbf{M}}{\mathbf{V}} \times \text{corrected absorbency}$$

Preparation of reagents:

All chemicals should meet ACS specifications for analytical reagents. All solutions are made in nitrite-free water. If available distilled or deionized water contains nitrite impurities (produces a pink color when added to absorbing reagent).

N-(1-naphthyl)-ethylenediamine dihydrochloride, 0.1

Dissolve 0.1 g in 100 mL water. Solution will be stable for several months if kept well-stopped in brown bottle in the refrigerator.

Absorbing reagent

Dissolve 5 g of anhydrous sulfanilic acid in about 1 L of water containing 140 mL of glacial acetic acid. Gentle heating is permissible to speed up the process. To the cooled mixture, add 20 mL of the 0.1% N-(1-naphthyl)-ethylenediamine dihydrochloride, and dilute to 1 L. The solution will be stable for several months if kept well-stopped in a brown bottle in the refrigerator. The reagent should be allowed to warm to room temperature before use.

Standard Sodium Nitrite Solution

Stock solution: Dissolve 2.03 g sodium nitrite in a 1-L volumetric flask and dilute to mark with water. This solution is stable for a year if stored in a brown bottle and kept in the refrigerator.

Take 10.0 mL stock solution and dilute to 1 L with water. One mL of this working dilute solution produces a color equivalent to 10 µL of NO₂. This solution must be prepared fresh when used as a calibration standard.

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Determination of Atmospheric SO_2 : West & Gaeke Principle

The Waste and Gaeke pararosaniline method can be improved to give greater sensitivity for the spectrophotometric determination of sulphur dioxide in ambient air, and also closer adherence to Beer's law.

This can be achieved by optimizing important parameters such as temperature, pH, purity of the dye and water and standardization of the sulfite solution.

Principle:

Sulfur dioxide, in an air sample, is absorbed into a solution of potassium or sodium tetra chloromercurate, **TCM**, by aspirating a measured air sample through an absorber vessel. This procedure results in the formation of a monochlorosulfonatomercurate (II) complex, which resists oxidation by the oxygen in the air. Ethylenediamine-tetra acetic acid disodium salt (EDTA) is added to this solution to complex heavy metals that catalyze the oxidation of the collected sulfur dioxide. Once this monochlorosulfonatomercurate complex is formed, it is stable to strong oxidants (e.g. ozone, oxides of nitrogen and hydrogen peroxide). After sampling is completed, any ozone in the solution is allowed to decay. The liquid is treated first with a solution of sulfamic acid to destroy the nitrite anion formed from the absorption of oxides of nitrogen present in the atmosphere. It is then treated with solutions of formaldehyde and specially purified, acid-bleached pararosaniline containing phosphoric acid to control pH. Pararosaniline, formaldehyde, and the bisulfite anion react to form the intensely colored pararosanilinemethylsulfonic acid, which behaves as a two-color pH indicator. The pH of the final solution is adjusted to 1.6 ± 0.1 by the addition of a prescribed amount of 3M phosphoric acid to the pararosaniline reagent.

Range and Sensitivity:

The lower limit of detection of sulfur dioxide in 10 mL of TCM is 0.3 μL based on twice the standard deviation representing a concentration of 10 ppbv ($26 \mu\text{g}/\text{m}^3$) SO_2 in an air sample of 30 L.

Beer's Law is followed through the working range from 0.1 to 1.0 absorbance units (0 to 35 μg in 25 mL final solution).

Interferences:

The effects of the principal potential interferences [oxides of nitrogen, ozone and transition metals (e.g. iron, manganese, and chromium)] have been minimized or eliminated. The oxides of nitrogen are eliminated by sulfuric acid, the ozone by time delay, and the transition metals by EDTA and phosphoric.

Apparatus:

Spectrophotometer

Midget impinger

Calibrate rotameters or

Calibrated critical orifices (hypodermic needles)

Vacuum pump (capable of maintaining 1/2 atmosphere)

Sampling:

Draw air sample at the rate of 0.5 to 2.5 liter/min through the impinger containing 10 ml of the absorbing reagent. Flow rate is not critical as long as it is low enough to prevent entrapment of the liquid.

If sample must be stored for more than a day before analysis, keep it at 5° C in refrigerator.

Analysis:

After collection, transfer sample quantitatively to a 25 mL volumetric flask, filtering if necessary.

If ozone is present at concentrations greater than 0.01 ppm, delay analysis for 20 min to allow decomposition of ozone.

Add 1 mL of 0.6% sulfamic acid and allow to react for 10 min to destroy the nitrite from oxides of nitrogen.

Accurately pipette 2 mL of the 0.2% formaldehyde, then 5 mL of pararosaniline reagent.

Bring all flasks to 25 mL volume with distilled water.

After 30 min determine the absorbance in spectrophotometer at the wavelength of maximum absorbency, 548 nm, using distilled water as the reference cell.

Calculate Concentration of SO₂ as follow:

$$\text{SO}_2, \text{ ppm} = \frac{(A - A_0) \times 0.382 \times B}{V}$$

Where, A = sample absorbency

A₀ = blank absorbency (provided)

B = calibration factor x 25 mL (provided)

V = sample volume in liters corrected 25°C, 760 mmHg (by perfect gas law)

Preparation of Reagents:

All chemical except for the dye, are ACS (American Chemical Society) A R Grade.

Double distilled water

Free from oxidants, must be used.

1-Butanol

Certain batches of 1-Butanol should be checked for oxidants that can consume SO_2 , by shaking 20 mL of 1-Butanol with 5 mL of 20% aqueous KI. A yellow color in the alcohol phase indicates the present of oxidants, redistill the Butanol from silver oxide, and collect middle fraction.

Sulfamic Acid 0.6%

Dissolve 0.6 g of sulfuric acid in 100 mL of distilled water. This reagent can be kept for 10 days if it is stored in a stopped bottle.

Formaldehyde 0.2%

Dilute 5 mL of 37% formaldehyde to 1 L with water. Prepare daily.

Buffer stock solution (pH 4.7)

In a 100-mL volumetric flask, dissolved 13.61 g sodium acetate trihydrate in water, add 5.7 mL glacial acetic acid, and dilute to mark with water.

Purified pararosaniline 0.2% (Nominal)

Stock solution: Weigh 0.200 g and completely dissolve by shaking with 100 mL of 1 N HCl in a 100-mL glass-stopped graduated cylinder (Purified dye, 0.2% in 1 N HCl solution is available from Eastman Kodak, J.T.Baker or Harleco)

Parasoniline Reagent

To a 250-mL volumetric flask, add 20 mL stock purified pararosaniline. Add 25 mL of 3M H_3PO_4 and dilute to mark with water. This reagent is stable for at least 9 months.

Absorbing Reagent (0.04M Potassium Tetrachloromercurate (TCM), K_2HgCl_4)

Dissolve 10.86 g mercuric chloride and 5.96 g of potassium chloride and 0.066 g EDTA in water and bring to mark in a 1-L volumetric flask. The pH of this reagent should be 4 ± 1 . The reagent is normally stable for six months, but if a precipitate forms, discard the solution.

***Caution! Highly poisonous and corrosive.** If spilled on skin, flush off with water immediately.

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**Suspended Particulate Matter in the atmosphere
(High-Volume Method)**

Principle:

Air is drawn through a size-selective inlet and through a 20.3 x 25.4 cm (8 x 10 in) filter at a flow rate which is typically 1132 L/min (40 ft³/min). Particles with aerodynamic diameters less than the cut-point of the inlet are collected by the filter. The mass of these particles is determined by the difference in filter weights prior to and after sampling. The concentration of suspended particulate matter in the designated size range is calculated by dividing the weight gain of the filter by the volume of air sampled.

Range and Sensitivity:

Lower Quantifiable Limit. For a 24-h sample duration at 1132 L/min, the detection limit is determined by the reproducibility of the filter weight difference which shows a standard deviation (sigma) of approximately ± 2 mg. The three-sigma detection limit is then approximately 3.5 $\mu\text{g}/\text{M}^3$. The three-sigma lower quantifiable limit depends on the filter used and may be as high as 5 $\mu\text{g}/\text{m}^3$.

Upper Quantifiable Limit. For a 24-h sample duration at 1132 L/min, this limit is in the range of 400 to 1000 $\mu\text{g}/\text{m}^3$. The exact value depends on the nature of the aerosol being sampled: very small particles will clog the filter at a relatively low mass loading while larger particles will fall off during sample transport at high concentrations.

Interferences:

Passive deposition

Inlet loading and re-entrainment

Recirculation

Filter artifact formation

Filter conditioning

Filter integrity

Shipping losses

Electrostatic charge

Calculations:

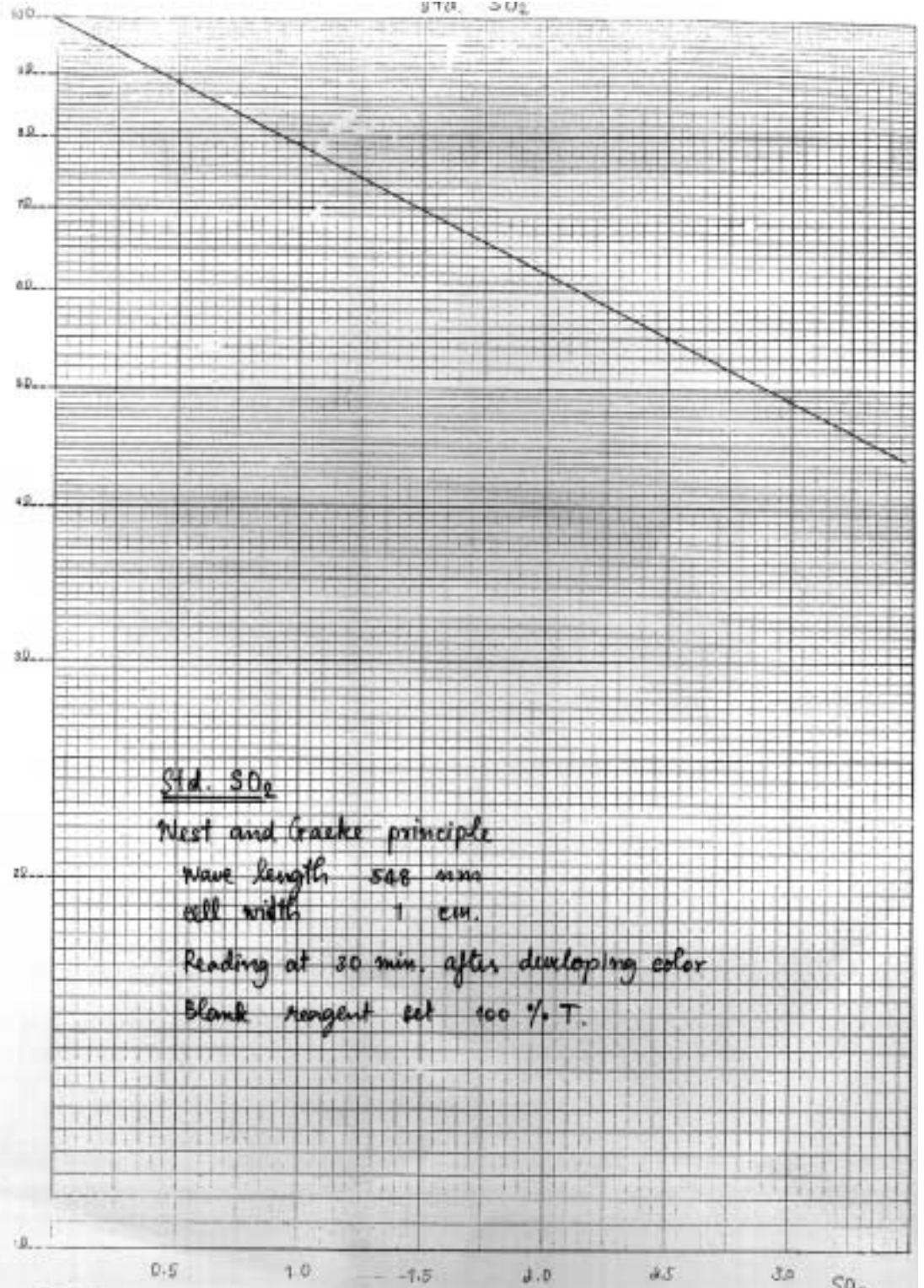
Data collected from High Volume Method

Time	(hr)	Temp (°C)	Flow rate (ft ³ /min)
15.15	0	35.5	65.5
16.15	1	34.5	66
17.15	2	33	66.5
18.15	3	31	67
19.15	4	29.5	67
20.15	5	29	66
21.15	6	29	65
22.15	7	28	66
23.15	8	27.8	65
24.15	9	27	65.5
01.15	10	27	66
02.15	11	26.5	66
03.15	12	26	66
04.15	13	26	65
05.15	14	26	65
06.15	15	26	65
07.15	16	26	65
08.15	17	28.5	62
09.15	18	30	61
10.15	19	-	-
11.15	20	34	60
12.15	21	35	60
13.15	22	35	59
14.15	23	35	59
15.15	24	33.2	59
Average		29.97	64.06

Average flow rate = 64.06 (ft³ / min)
 = 64.06 ft³ x (0.02832 m³ / ft) / min
 = 1.8141 m³ /min
 Total flow for 24 hr = 1.8141 x 60 x 24 = 2612.418 m³
 Vol of air (76 mm Hg) = 2612.418 m³
 Vol of air (76 mm Hg) at 29.97 °C = (2612.418 / (273 + 29.97)) x 273 m³
 = 2353.996 m³
 Wt of (filter paper + SPM) = 3.9352 g
 Wt of filter paper = 3.4160 g
 Wt of SPM = 0.5192 g
 Concentration of SPM = 0.5192 x 10⁶ / 2353.996 µg / m³
 = 220.56 µg / m³
 = 0.22 mg / m³

102 SEMIQUANTITATIVE 48-4887
1 CYCLE 2 TO 200000 48 IN 11.1.
KODAK SAFETY FILM

STANDARD SO₂



Std. SO₂

Nest and Craeke principle

wave length 548 nm

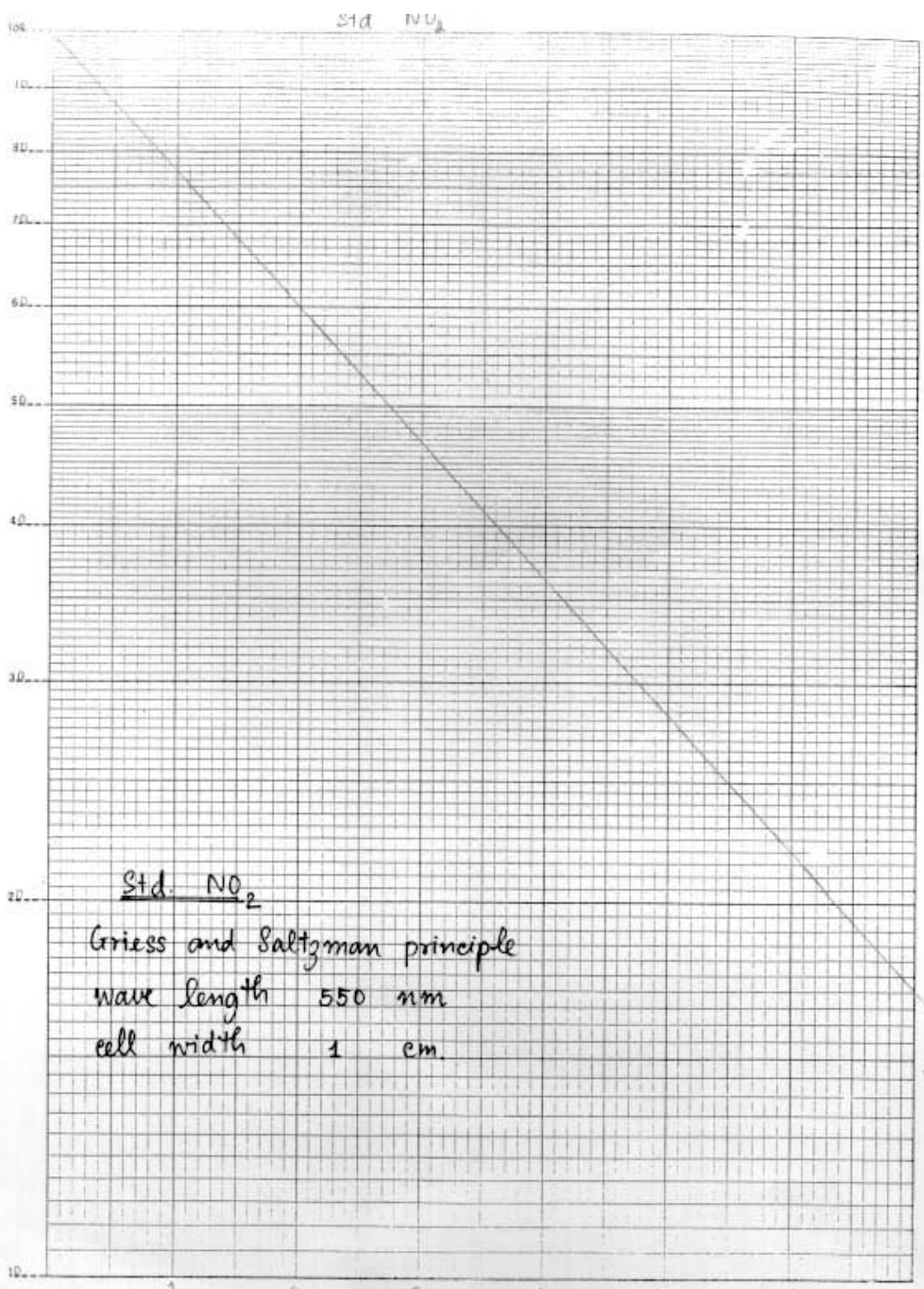
cell width 1 cm.

Reading at 30 min. after developing color

Blank reagent set 100 % T.

SO₂
ml/25 ml

NO₂ SEMI-LOGARITHMIC 46-4052
EYELA TO DIVISION
KUPPER, 4-2884-1-00



Std NO₂
Griess and Saltzman principle
wave length 550 nm
cell width 1 cm.

NO₂
μl/10 ml