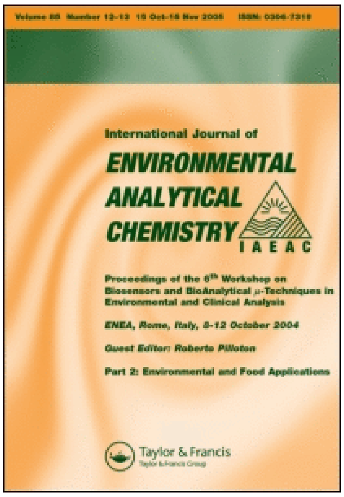

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Development and Optimization of Twenty-Four Hour Manual Methods for the Collection and Colorimetric Analysis of Atmospheric NO_2

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Manual twenty-four hour colorimetric procedures for the determination of atmospheric NO_2 are described. The methods are based on collecting NO_2 by bubbling ambient air for twenty-four hours through reagents that form stable nitrite solutions. The reagents described have a 93% collection efficiency over the range of 20 to 750 $\mu g/m^3$ NO_2 with no apparent interferences. The inadequacies[1] of the former reference or alkaline method[2] are also described.

INTRODUCTION

The analysis of nitrogen dioxide (NO_2) in ambient air is a subject of great current interest because the Environmental Protection Agency stated in the Federal Register[3] that the alkaline method for NO_2 is unreliable and presented three tentative NO_2 methods as temporary substitutes. The former reference method involves the collection of NO_2 by bubbling ambient air for twenty-four hours through an aqueous solution of 0.1N NaOH to form a stable solution of sodium nitrite. The nitrite ion formed in the absorbing

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solution is then reacted with sulfanilamide and N-(1-napthyl)ethylenediamine dihydrochloride in acid media to form an azo dye which is measured colorimetrically.

The primary deficiencies of the alkaline method as shown by our data[1] is the variable NO_2 collection efficiency ranging from 70% at 30 $\mu g/m^3$, 30% at 180 $\mu g/m^3$ to 15% at 540 $\mu g/m^3$, and the positive interference to nitric oxide. This positive NO interference which was previously reported by Merryman[4] is further enhanced by the presence of atmospheric hydrogen donors (such as phenols) and reducing agents. During the last few years, many researchers namely Purdue,[5] Blacker,[6] Huess,[7] Meadows,[8] Ng[9] *et al*, have re-evaluated the reference method and have come up with a variety of conclusions as to its value. Several investigators attempted to improve the collection efficiency of the alkaline method by the addition of other chemicals. Huygen[10] added R-salt (disodium 2-naphthol-3, 6-disulfonate) and triethanolamine. Nash[11] added o-methoxyphenol (guaiacol) and Christie[12] added sodium arsenite. Levaggi[13] reported that triethanolamine in water was an efficient absorber for NO_2 either as a liquid or impregnated on a solid.

The main goal of our research was to find a NO_2 absorbing reagent that had better than 90% collection efficiency with no interferences. The purpose of this paper is to present data on the deficiencies of the alkaline method, and to report data on new absorbers for the manual twenty-four hour NO_2 collection method, using a varied assortment of analytical methods for NO_2 in ambient air.

EXPERIMENTAL

Photometers

A Beckman model B spectrophotometer and a Cary 14 were used to make the colorimetric measurements using 1 cm cells. Both instruments were calibrated with alkaline potassium chromate ($KOH-K_2CrO_4$)[15,16].

Reagents†

All chemicals used were reagent grade.

H_2O_2—0.2 ml of 30% H_2O_2 per 250 distilled water.

AA—2.0 g p-aminoacetophenone per 100 ml (13.5 ml concentrated acetic acid + 95.5 ml concentrated hydrochloric acid).

AZ—0.2% azulene in concentrated acetic acid.

ANSA—0.1% 8-anilino-1-naphthalenesulfonic acid in absolute methanol.

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† Mention of a specific product or company name does not constitute endorsement by the Environmental Protection Agency.

SA-NED[2]—2.0 g sulfanilamide + 5.0 ml 85% phosphoric acid per 100 ml distilled water.

SA-ANSA—2.0 g sulfanilamide + 33 ml concentrated hydrochloric acid per 100 ml distilled water.

NED—0.5 g N-(1-naphthyl)ethylenediamine dihydrochloride per 500 ml distilled water.

Dilution air was compressed house air, cleaned with activated charcoal (6–16 mesh), 5A molecular sieve and indicating silica gel (6–16 mesh). A background of 1 ug NO_2/m^3 was found using the TGS-ANSA method described later in this paper.

The nitric oxide standard was certified to contain 97 ppm NO and was verified by gas phase titration.[17] The NO Standard was found to contain 3% NO_2 as determined by a chemiluminescent monitor. Ozone was produced with a calibrated ozone generator.[18] Sulfur dioxide was obtained from a gravimetrically calibrated permeation device. Reagent grade ammonium hydroxide was used to simulate ammonia concentrations and water was double distilled using an all glass apparatus. Extra dry nitrogen (99.99%) was used as the flushing gas for the NO_2 permeation device. Carbon monoxide was 99.97% pure.

Standards

In evaluating any method for the detection of an air pollutant a procedure is needed to generate accurate static and dynamic concentrations of the pure pollutant. With most manual methods for the detection of NO_2 at ambient air levels the nitrite ion is used to represent the direct relationship of the NO_2 present in ambient air.

Static

With nitrogen dioxide, the most common static standard used is sodium nitrite. The chemical specifications of the static standard must be known. The sodium nitrite used in this evaluation was assayed by Baker Chemical at 99.99%. This assay was verified titrimetrically by the permanganate-ferrous ammonium sulfate procedure.[19]

The sodium nitrite static standard was always prepared in the specific absorbing solution under study. Calibration curves as determined by colorimetric analysis were then prepared. Beer's law was followed from 0.04 μg/ml to 15 μg/ml. As an example, the following regression equation was obtained with the TGS*-ANSA-SA procedure

$$Y = 0.471X - 0.003$$

using the unexposed absorbing reagent as the blank.

Dynamic

National Bureau of Standards prototype NO_2 permeation devices[20] such as the one shown in Figure 1 were used as dynamic calibration standards. NO_2 permeates from this device at a constant temperature dependent rate. The rate of NO_2 effusion was determined gravimetrically by weighing the device at one to three day intervals. A least squares linear regression curve of at least five points was then plotted of the weight loss per unit time as shown in Figure 2. The slope of this curve gave the weight loss in μg/min.

Equation 1 was used to calculate the theoretical concentration of NO_2 in the test atmospheres that were generated.

Equation 1

$$C_T = \frac{PR}{TDA} \times 1000$$

C_T = Theoretical concentration of NO_2, $\mu g/m^3$

PR = Permeation rate of NO_2 device, μg/min

TDA = Total dilution air, liters/min

1000 = Conversion of liters to m^3

Absorbing solutions

Alkali Method—4 g NAOH per liter of distilled water.

TG—20 g triethanolamine + 0.5 g guaiacol per liter of distilled water.

TGS—20 g triethanolamine + 0.5 g guaiacol + 0.025 g sodium metabisulfite per liter of distilled water.

TGS*—20 g triethanolamine + 0.5 g guaiacol + 0.250 g sodium metabisulfite per liter of distilled water.

Calibration procedure

NO_2 Test Atmosphere Generator

Figure 3 is a schematic of the apparatus[21] used for generation of known NO_2 test atmospheres and for calibration of the NO_2 permeation device. The apparatus consisted of a NO_2 permeation device housed in a water-cooled condenser which was supplied with water at ±0.1°C from a constant temperature bath. Clean dry N_2 continuously passed over the device at 50 ml min^{-1}. Additional purified air was added at known flow rates to obtain the desired concentrations of NO_2. The NO_2 test atmosphere was continuously monitored by a chemiluminescence NO_2 monitor. The monitor was

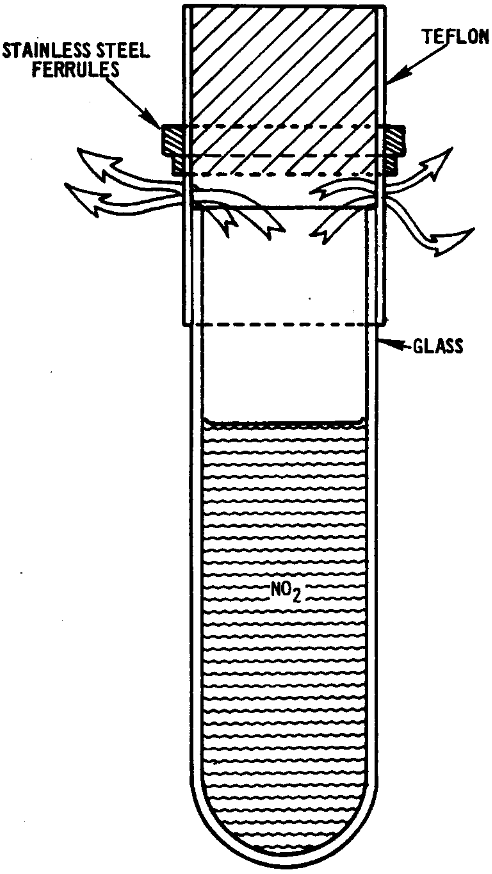

FIGURE 1

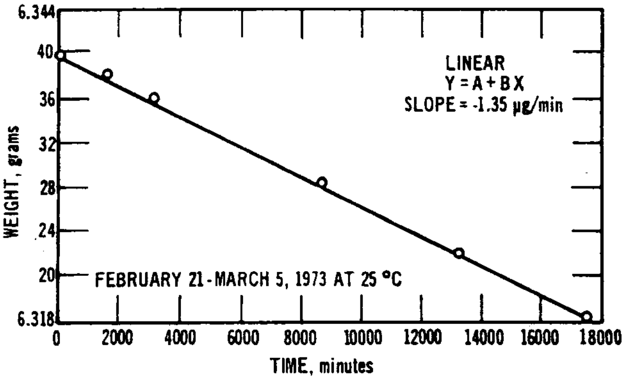

FIGURE 2

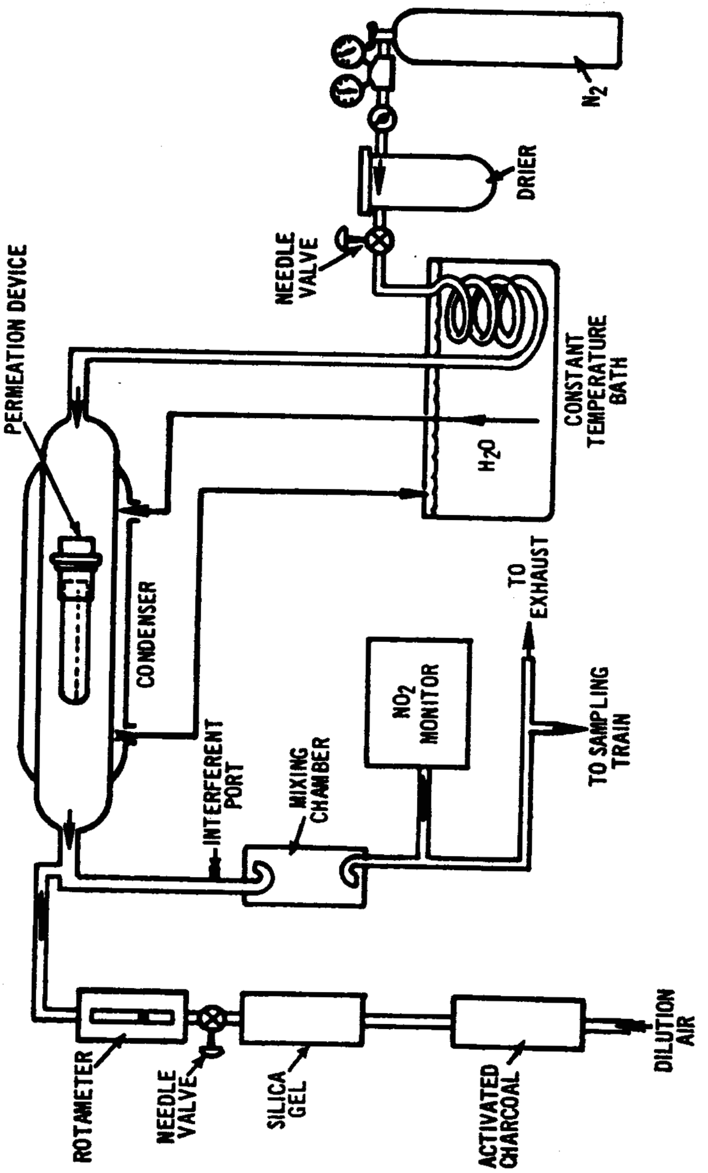
PERMEATION DEVICE
CONDENSER
INTERFERENT PORT
MIXING CHAMBER
NO_2 MONITOR
TO EXHAUST
TO SAMPLING TRAIN
H_2O
CONSTANT TEMPERATURE BATH
NEEDLE VALVE
DRIER
N_2
ROTAMETER
NEEDLE VALVE
SILICA GEL
ACTIVATED CHARCOAL
DILUTION AIR

FIGURE 3

calibrated by a means independent of the permeation device (gas phase titration) which gave an added level of confidence in the NO_2 concentration. The NO_2 monitor also served as in indicator of possible upsets in flows, temperatures, etc, during the sampling period.

Sampling procedure

The basic sampling unit shown in Figure 4 was used to evaluate the alkaline method. The unit consisted of a fritted glass bubbler (70 to 100 μm porosity) immersed in 0.1 N NAOH, a trap to remove any entrained moisture, a critical orifice (#27 hypodermic needle) and a vacuum pump capable of pulling 16" of Hg. The pump pulls air through the collecting solution at approximately 200 ml/min as controlled by the critical orifice. If the critical orifice is not calibrated with the frit with which it is to be used, a 6 to 7% negative error occurs in flow measurement. Five of these sampling units were assembled in parallel by means of a glass manifold in order to obtain the precision of each method studied.

The sampling unit for the newly developed absorbing reagents had one important difference; this is the replacement of the fritted glass bubbler with the restricted orifice bubbler. The restricted orifice bubblers had several advantages: they were much less expensive; were easier to clean; had less breakage and did not require daily calibration.

Fifty milliliters of the specific absorbing reagent of interest was placed in each of the five bubblers shown in Figure 5. The flow rate through each of the bubblers was determined by a soap bubble flow meter[22] while the total dilution flow for the permeation device was measured with a wet test meter.[23]

The sampling train was then attached to the NO_2 test atmosphere generator.

At the end of the sampling period (20 to 24 hours) the flow rates were remeasured. The volume of air sampled in m^3 was calculated from Eq. 2.

Equation 2

$$V = \frac{F_1 + F_2}{2} \times T \times 10^{-6}$$

V = Volume of air, m^3

F_1 = Measured flow rate before sampling ml/min

F_2 = Measured flow rate after sampling ml/min

T = Sampling time in minutes

10^{-6} = Conversion of ml to m^3

Any water lost during the sampling period was replaced with distilled water before colorimetric analysis was performed on aliquots from each tube.

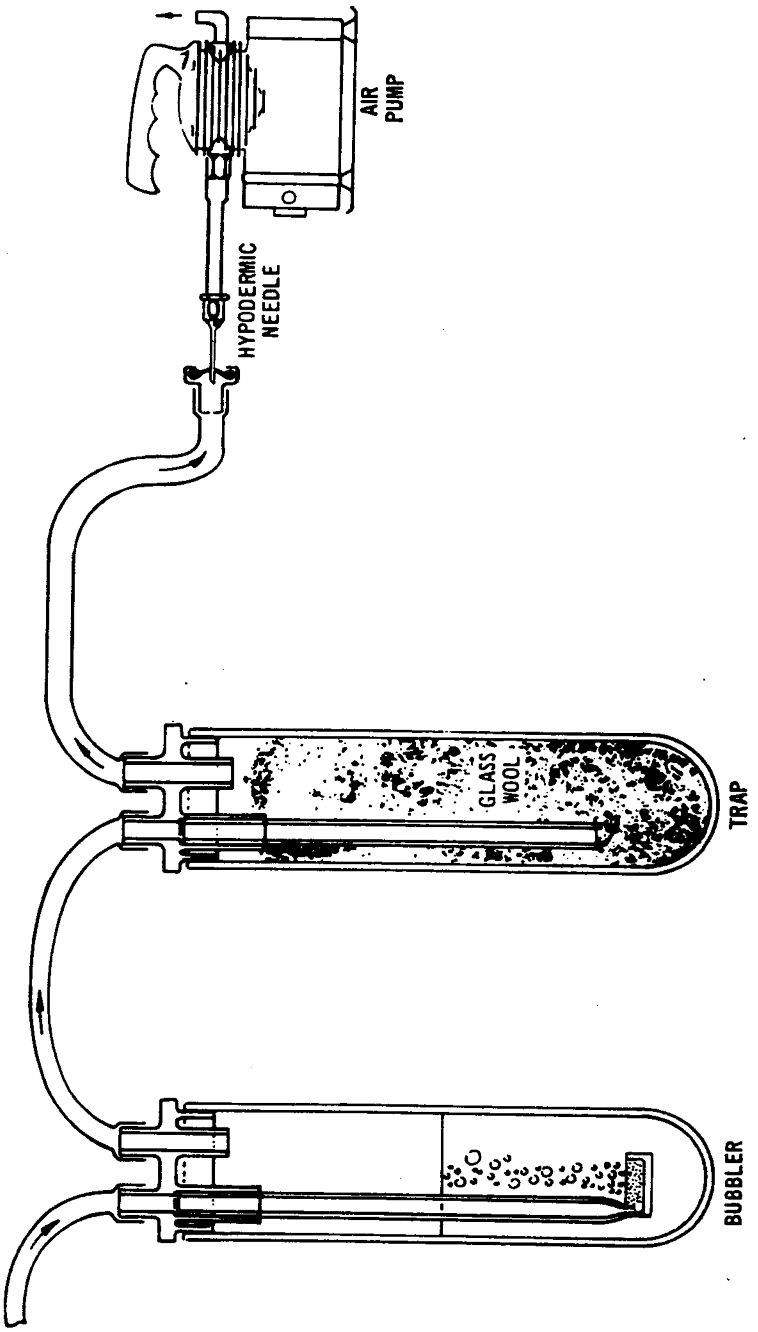

FIGURE 4

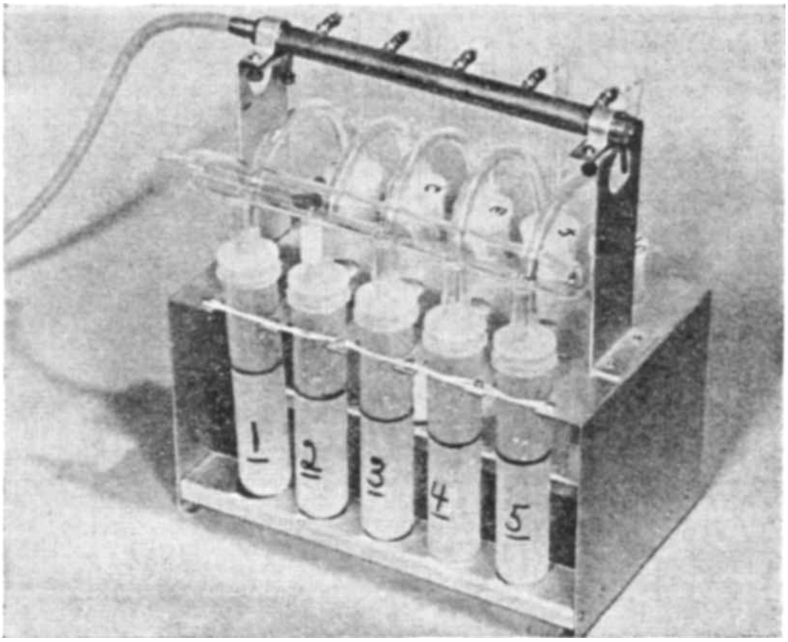

FIGURE 5

Analytical procedures

The colorimetric procedure for the alkaline method is described in Ref. 2.

The following new colorimetric procedures were developed for the new NO_2 absorbing solutions discussed in this paper. At least three and generally five simultaneous samples were collected and assayed for each test atmosphere generated.

A. Azulene (AZ) + 4′-aminoacetophenone (AA)
  1. 5 ml of test solution TGS
  2. 0.5 ml H_2O_2 solution
  3. 1 ml 4′AA
  4. 1 ml Azulene
  5. Read after 3.5 minutes at 516 nm in 1.0 cell

B. 8-Anilino-1-naphthalenesulfonic acid (ANSA) + 4′-aminoacetophenone (AA)
  1. 5 ml of test solution TGS
  2. 0.5 ml of H_2O_2 solution
  3. 2.7 ml 4′—AA
  4. 3.0 ml ANSA
  5. Read immediately at 560 nm in 1.0 cm cell

C. Azulene (AZ) + Sulfanilamide (SA)
  1. 5 ml of test solution TGS*
  2. 0.5 ml H_2O_2 solution
  3. 1 ml sulfanilamide
  4. 0.1 ml azulene
  5. Read immediately at 508 nm in 1.0 cm cell

D. 8-anilino-1-naphthalenesulfonic acid (ANSA) + sulfanilamide (SA)
  1. 5 ml of test solution TGS*
  2. 0.5 ml of H_2O_2
  3. 2.7 ml sulfanilamide
  4. 3.0 ml ANSA
  5. Read immediately at 550 nm in 1.0 cm cell

Upon addition of each reagent, the test solution must be vigorously stirred with a test tube agitator for approximately 15 seconds.

The actual quantity of NO_2 in $\mu g/m^3$ found by each collecting solution was calculated from Eq. 3.

Equation 3

$$C_F = \frac{50\,A}{V}$$

C_F = Concentration of NO_2 found, $\mu g/m^3$

50 = Volume of collecting solution, ml

V = Volume air sampled, m^3

A = Concentration, $\mu g\ NO_2^-/ml$, obtained from the calibration curve prepared for each absorbing solution.

Theoretical concentrations of NO_2 were calculated from Eq. 1.

% efficiency was then determined by the following equation:

$$\%\ \text{efficiency} = \frac{C_F}{C_T} \times 100$$

RESULTS AND DISCUSSION

All percent recovery data reported herein depends solely on the amount of NO_2 recovered as nitrite and do not involve any stoichometric factors of any kind as used by Saltzman,[24] Morgan, *et al.*[25] However, in order to determine 100 percent NO_2, the NO_2 found in Eq. 3 would be divided by 0.93 since the collection efficiency of the TGS* ANSA Method is 93 percent.

Additional pollutants were studied as possible interferences to the reference method. At a concentration of 100 $\mu g/m^3$, the collection efficiency of the reference method is 38%. At this NO_2 concentration ammonia at 200 $\mu g/m^3$ gave an efficiency of 58%; carbon monoxide at 150,000 $\mu g/m^3$ gave 43%; formaldehyde at 500 $\mu g/m^3$ gave 68%; ozone at 1008 $\mu g/m^3$ gave 52%; and phenol at 600 $\mu g/m^3$ produced a 48% collection efficiency.

These interferences, the NO interference, and the variable collection efficiency, indicated rather strongly that a new manual twenty-four hour method for the collection and analysis of ambient NO_2 was needed if a manual twenty-four hour procedure was to be maintained as the reference method.

Our initial laboratory experiments were performed on absorbing reagents that had been recently reported in the literature. Most of these absorbers contained an alkali absorber with a hydrogen donor, e.g., a reducing agent or an organic compound containing a —C—OH group. When investigated by this laboratory they all suffered from NO interference and/or collection efficiencies of less than 90%. To reach our goal of better than 90% collection efficiency for an NO_2 absorber, we believed that combinations of some of the reported absorbing reagents without sodium hydroxide could prove to be successful.

The first absorbing solution which met our criteria of better than 90% efficiency with no interferences was triethanolamine and guaiacol in distilled water (TG).

The colorimetric procedure used in the reference method (NED) was utilized for the assay of the TG absorbing solution. A 93% average recovery over the range of 20 to 750 $\mu g/m^3$ was obtained as shown in Table I. However, the TG absorber was only good if it was used and assayed within seven days because the TG absorbing solution experienced color stability problems and a decay in efficiency after this period of time.

To overcome the color stability and decay in efficiency on standing, a reducing agent, sodium metabisulfite, was added to produce a new absorber, TGS.

New colorimetric procedures were investigated for the TGS absorbing solution because the sulfite bleached the NED dye and because naphthylamines are suspected bladder carcinogens.[26] Indications are that sulfonation of the carcinogens destroys their activity. Reagents were picked for the sampling solution which were believed to be non-carcinogenic and readily biodegradable. Arsenite was not investigated because of its known hazardous properties, its possible carcinogenicity and lack of biodegradability.

The new colorimetric procedures originally developed by E. Sawicki,[27] *et al.* were previously described as colorimetric procedures A & B in the analytical section of this paper.

TABLE I

Percentage recovery of NO_2, TG-NED—average of five determinations

NO_2 Added (μg/m^3)	Recovery (μg/m^3)	% Recovery	$S_{(REL)}$ %[a]
26	25	96	2.8
99	96	97	2.0
201	185	92	1.1
308	279	91	1.2
379	364	96	3.5
511	474	93	3.0
631	568	90	1.4
683	636	93	3.2
731	655	90	2.3
		$\bar{X} = 93$	$\bar{X} = 2.27$

[a] $S_{(REL)}\ \% = \dfrac{\text{STANDARD DEVIATION}}{\text{AVERAGE RECOVERY}} \times 100$

TABLE II

Percent recovery of NO_2, TGS-ANSA-AA
Sulfite = 0.025 g
Average of five determinations

NO_2 Added (μg/m^3)	Recovery (μg/m^3)	% Recovery	$S_{(REL)}$ %
46	43	93	4.0
100	91	91	1.1
181	167	92	2.2
250	230	92	1.5
361	336	93	1.0
446	410	92	2.9
527	509	97	2.1
591	581	98	2.9
743	705	95	1.0
		$\bar{X} = 94$	$\bar{X} = 2.1$

Turbidity problems were encountered in the TGS collection procedure with the azulene method (A) in the presence of some of the possible interferences. Therefore, the 8-anilino-1-naphthalenesulfonic acid (ANSA) procedure (B) was selected for assay of the TGS absorber. 4-Aminoacetophenone (AA) was used with both A and B methods. Table II displays the efficiency data generated with TGS-ANSA-AA procedure and indicates that the addition of the sulfite and the change in method of assay had no effect on the collection efficiency. However, the color stability problem remained on aging of the collecting solution. The sulfite was increased to 0.250 g keeping the triethanolamine and guaiacol at the same concentration. This new absorbing reagent, TGS*, with the 0.250 g sulfite resolved the color stability difficulties with no apparent effect on the collection efficiency as shown in Table III.

TABLE III

Percent recovery of NO_2, TGS*-ANSA-AA
Sulfite = 0.250 g
Average of five determinations

NO_2 Added ($\mu g/m^3$)	Recovery ($\mu g/m^3$)	% Recovery	$S_{(REL)}$ %
78	72	92	1.5
87	85	97	0.7
94	89	95	2.0
93	87	94	2.9
178	160	90	2.5
303	278	92	1.3
537	505	94	1.8
702	624	89	0.7
		$\bar{X} = 93$	$\bar{X} = 1.5$

To maintain good collection efficiency of the TGS* for three weeks before exposure to NO_2 and three weeks after NO_2 collection, the colorimetric procedure had to be modified for the TGS* absorber, because the increased amount of sulfite was causing the ANSA-AA assay to be erratic when using different batches of AA. Two colorimetric procedures (C & D) were developed where the AA was replaced with sulfanilamide (SA). Procedure (D) (sulfanilamide and ANSA) was far superior to procedure C (azulene and sulfanilamide) which experienced turbidity problems with high concentrations of possible

TABLE IV

Percent of recovery of NO_2 TGS*-ANSA-SA
Sulfite = 0.250 g
Average of five determinations

NO_2 Added $\mu g/m^3$	NO_2 Found $\mu g/m^3$	% NO_2 Recovery	$S_{(REL)}$ %
43.6	42.6	98.0	1.38
78.6	72.8	92.8	0.85
93.1	86.2	92.8	2.56
95.8	92.9	96.9	2.55
178	162	90.7	0.94
303	283	93.3	1.30
538	516	96.0	0.88
702	643	91.5	1.18
		$\bar{X} = 94.0$	$\bar{X} = 1.46$

TABLE V

Interference studies, TGS*-ANSA-SA with
100 μg NO_2/m^3
Average of five determinations

Pollutant	$\mu g/m^3$	% Recovery
		93
NO	734	94
SO_2	439	90
O_3	400	98
CO	154,000	90
NH_3	205	94
HCHO	750	90
C_6H_5OH	150	90
Temperature, 104 F		93

interferences. In Table IV are data on the overall average recovery of NO_2 for the TGS* absorber using sulfanilamide and ANSA (procedure D). These data indicate that the increase in sodium meta bisulfite in the absorber and the change to sulfanilamide in the colorimetric assay produced no deleterious effects on the efficiency.

Data shown in Table V on the TGS* absorber with the sulfanilamide + ANSA colorimetric procedure indicate that there are no apparent interferences from the pollutants studied.

It has been show in recent studies[28], where large numbers of samples have to be analyzed, that the time between diazotization and coupling is critical to the color formation. On investigation of this problem, we found that the coupling reagent should be added within six minutes after the addition of the diazotizing reagent, so as to prevent the possible decay of the diazonium salt.

CONCLUSIONS

The alkaline method for the collection and analysis of atmospheric NO_2 has been shown to have certain deficiencies such as variable collection efficiency and interference from nitric oxide, formaldehyde, phenol, carbon monoxide and ammonia. In developing the new NO_2 absorbers (TG, TGS, TGS*) and procedures for assay, an attempt was made to obtain a reasonable range in balance between biodegradability and the shelf life of the absorbing solution.

Although all three absorbers (TG, TGS, TGS*) can be used effectively under the conditions described herein, we recommend that the TGS* absorber utilizing the sulfanilamide-ANSA colorimetric procedure be the preferred method whenever the sample containing NO_2 cannot be assayed within 48 hours. However, assay by this procedure must take place within three weeks. When analyses can be done within 48 hours, then any of the collection or analytical methods can be used within the limits imposed in this paper.

The TGS*-ANSA method for the assay of NO_2 in ambient air presents several attractive features: 93 percent collection efficiency; no apparent interferences; stability both before and after collection of NO_2; and uses inexpensive and easily calibrated restricted orifice bubblers.

These features make the TGS*-ANSA method an excellent procedure for the collection and colorimetric analysis of atmospheric NO_2.

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