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EVALUATION OF TRIETHANOLAMINE PROCEDURE FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

Office of Research and Development
National Environmental Research Center
U.S. Environmental Protection Agency
Research Triangle Park, N.C. 27711

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EVALUATION OF TRIETHANOLAMINE PROCEDURE FOR DETERMINATION OF NITROGEN DIOXIDE IN AMBIENT AIR

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ABSTRACT

A detailed method write-up describing the triethanolamine (TEA) manual procedure for measurement of nitrogen dioxide in ambient air was developed. The method involves sampling for 24 hours with a fritted bubbler immersed in 0.1N TEA collecting solution. The range of the method is approximately 20 to 700 $\mu g/m^3$.

The method was evaluated to determine its usefulness for measuring nitrogen dioxide in ambient air. This involved a review of the procedure as developed and subsequent laboratory experiments to better define some obscure points in the procedure. The constancy of the method's collection efficiency, the addition of n-butanol to enhance the collection efficiency and the need to use fritted bubblers as gas dispersers to assure high collection efficiency were the main points investigated in these experiments. The results indicated a constant collection efficiency over the method's range both with and without any added n-butanol using either frits or restricted-orifice bubblers; however, the collection efficiency using frits is about 80%, while the efficiency drops to about 50% using restricted-orifice bubblers.

Further work on the method does not seem warranted at this time because the availability of other methods which show more promise for the measurement of NO_2 in ambient air.

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The authors wish to thank Mr. Dario Levaggi and others at the San Francisco Bay Area Air Pollution Control District for assistance and helpful discussions during the procedure review.

SECTION I

CONCLUSIONS

The TEA method has a high collection efficiency of 80% using fritted bubblers for gas dispersion. The use of a frit is a disadvantage to the method, because the frit porosity needs to be checked periodically and these bubblers are easily broken under normal usage. The collection efficiency obtained by using the more preferable restricted-orifice bubbler is 50%, too low to warrant its use. Other manual NO_2 methods[4,5] are available that have high collection efficiencies of 80% or greater using restricted-orifice bubblers. Since Methods Standardization Branch plans to standardize only the most promising methods for NO_2 measurements, it appears that further work on the TEA method is not justified at this time.

SECTION II

INTRODUCTION

The Methods Standardization Branch (MSB) of the Quality Assurance and Environmental Monitoring Laboratory (QAEML), has the responsibility to evaluate and standardize various methods for measuring air pollutants to determine their utility. In the case of nitrogen dioxide, the Federal Register reference Method[1] has been shown to be highly inadequate.[2,3] In light of this, the reference method for measuring nitrogen dioxide was withdrawn and the Environmental Protection Agency (EPA) chose three tentative methods[4] for replacement of the original reference method. Interested persons were asked to comment on the three procedures as well as to offer suggestions of other methods for consideration. Additional manual methods[5,6] were suggested; one of these was the TEA liquid-absorber method.

In the TEA method,[6] air is pulled through an aqueous solution of triethanolamine (TEA) and a small amount of n-butanol; nitrogen dioxide present in the sampled air volume is absorbed by the solution. A subsequent colorimetric analysis of the exposed collecting solution indicates the concentration of NO_2 in the air sample. This report describes a laboratory evaluation of the TEA method.

SECTION III

EXPERIMENTAL

All reagents and procedures used in this evaluation are described in Appendix A. The method write-up therein is a slightly modified version of the TEA method developed by Levaggi and co-workers.[6]

A. Test Atmosphere Generation

Test atmospheres containing known concentrations of NO_2 were generated by diluting the effluent from a NO_2-permeation device with controlled volumes of purified air. This procedure has been well documented.[7,8,9] Three permeation devices of the FEP-teflon sleeve, glass reservoir type[10] developed jointly by NBS and EPA were employed in the study. They were gravimetrically calibrated[11] throughout the study period and all showed a constant permeation rate at constant temperature. Device No. 25-7 with a low permeation rate, 0.690 ± .003 $\mu g NO_2$/min, was used for generating NO_2 concentrations up to 300 $\mu g/m^3$. The other devices (Nos. 25-2 and 19-2) were used simultaneously to create the high NO_2 concentrations (300 to 700 $\mu g/m^3$) and have a combined permeation rate of 1.952 $\pm$ .003 μg/min.

For sampling and calibration, the permeation device was housed in a water-circulated condenser maintained at 25.0 ±0.1°C by a constant temperature bath. A stream of dry nitrogen at approximately 100 cm^3/min was passed over the device to flush the NO_2 from the condenser into a dilution chamber. The dilution air was compressed (housed) air purified by passage through silica gel for drying, air filters for particle removal, and finally a mixture of activated charcoal (6-14 mesh), molecular sieve (6-16 mesh, type 4A), and silica gel (6-16 mesh) for removal of any NO_2 and hydrocarbons.

A blank consisting of a 24-hour sampling of dilution air plus flushing nitrogen with no permeation device in the system, showed a NO_2 background of less than 2.5 μg NO_2/m^3. Thus the generation system was free of NO_2 interference.

B. Sampling

Samples were collected in quintuplicate according to the method described in Appendix A.

C. Flow Measurement

The flow rate for each absorption tube was measured before and after sample collection with a soap-bubble flow meter. The total flow rate into the inlet manifold was also measured immediately before and after sampling for comparison with the sum of the individual flows to detect any system leaks. Samples with a final flow that differed by more than 10% from the initial flow were rejected. Total dilution air flows in the NO_2 generation system were measured before and after sampling using a wet test meter (1 ℓ/rev or 10 ℓ/rev). The dilution air flow never varied more than one percent in any 24-hour sampling period.

D. Bubblers

Fritted bubblers with a porosity of 60 to 100 μm were used for dispersion as described by the method. The restricted-orifice bubblers used in some experiments were 0.5 - 0.7 mm I.D.

E. Analysis

After sampling the tubes were disconnected from the sample manifold. Water lost by evaporation was replaced and an aliquot of the sample was analyzed as described in the method. A Beckman Model "B" Spectrophotometer was used for the absorbance measurements.

SECTION IV

RESULTS AND DISCUSSION

The first phase of method standardization by MSB is a procedure review and subsequent laboratory evaluation, if necessary. The former involves assessing the method developers' recommended procedure as to its potential for making meaningful measurements. Accordingly, a visit was made to the developers of the TEA method to gain insight into the method's development and to see how the method performed under optimum conditions, i.e. when used by persons trained in the method. The results of the visit indicated that a laboratory evaluation would be necessary. In particular, further study was needed to determine the constancy of the collection efficiency over the useful range, 0-700 $\mu gNO_2/m^3$; to determine the effect of n-butanol on the collection efficiency of the TEA solution; and to investigate replacement of the recommended fritted bubblers by restricted-orifice bubblers as gas dispersers.

The collection efficiency is of utmost importance because it is a measure of the overall method response to sampling NO_2. It includes both the method's absorption efficiency (percentage of NO_2 trapped chemically or physically in the absorbing solution during sampling) and stoichiometric factors (equivalency of nitrogen dioxide gas to nitrite ion in the absorbing solution). Mathematically the collection efficiency (percent) is expressed as the ratio of the concentration of NO_2 detected to the concentration of NO_2 sampled multiplied by 100. The slope from a plot of collection efficiency vs. concentration of NO_2 sampled indicates how the

collection efficiency varies with concentration. If the slope is significantly different from zero, the method has no utility because its response would depend on NO_2 concentration. On the other hand, if the collection efficiency is essentially constant, then the slope from a plot of concentration detected vs. concentration sampled gives the average collection efficiency directly.

Two series of experiments were designed for the laboratory evaluation of the TEA method. In the first series, three TEA absorbing solutions were exposed to NO_2 over the range 30-700 $\mu gNO_2/m^3$ using the fritted bubblers recommended by the method; in the second series restricted-orifice bubblers replaced the fritted bubblers. The three absorbing solutions were 0.1N TEA with n-butanol added at three concentrations levels (3ml/l, 0.5ml/l and 0.0ml/l).

The collection efficiency as a function of NO_2 concentration is shown in Figure 1 for the three TEA absorbing solutions using the fritted bubblers. The slope for each curve from a least squares linear regression fit is essentially zero thus, indicating a constant collection efficiency across the range of interest. The collection efficiency is also independent of n-butanol level studied as evidenced by the near superposition of the three curves in Figure 1.

To obtain the average collection efficiency over the pertinent concentration range for each absorbing solution, the slope from a plot of NO_2 concentration detected vs. NO_2 concentration sampled is determined for each solution. From the slope of the least squares linear regression curve in Figure 2, the average collection efficiency for the TEA-0.0ml n-butanol/l

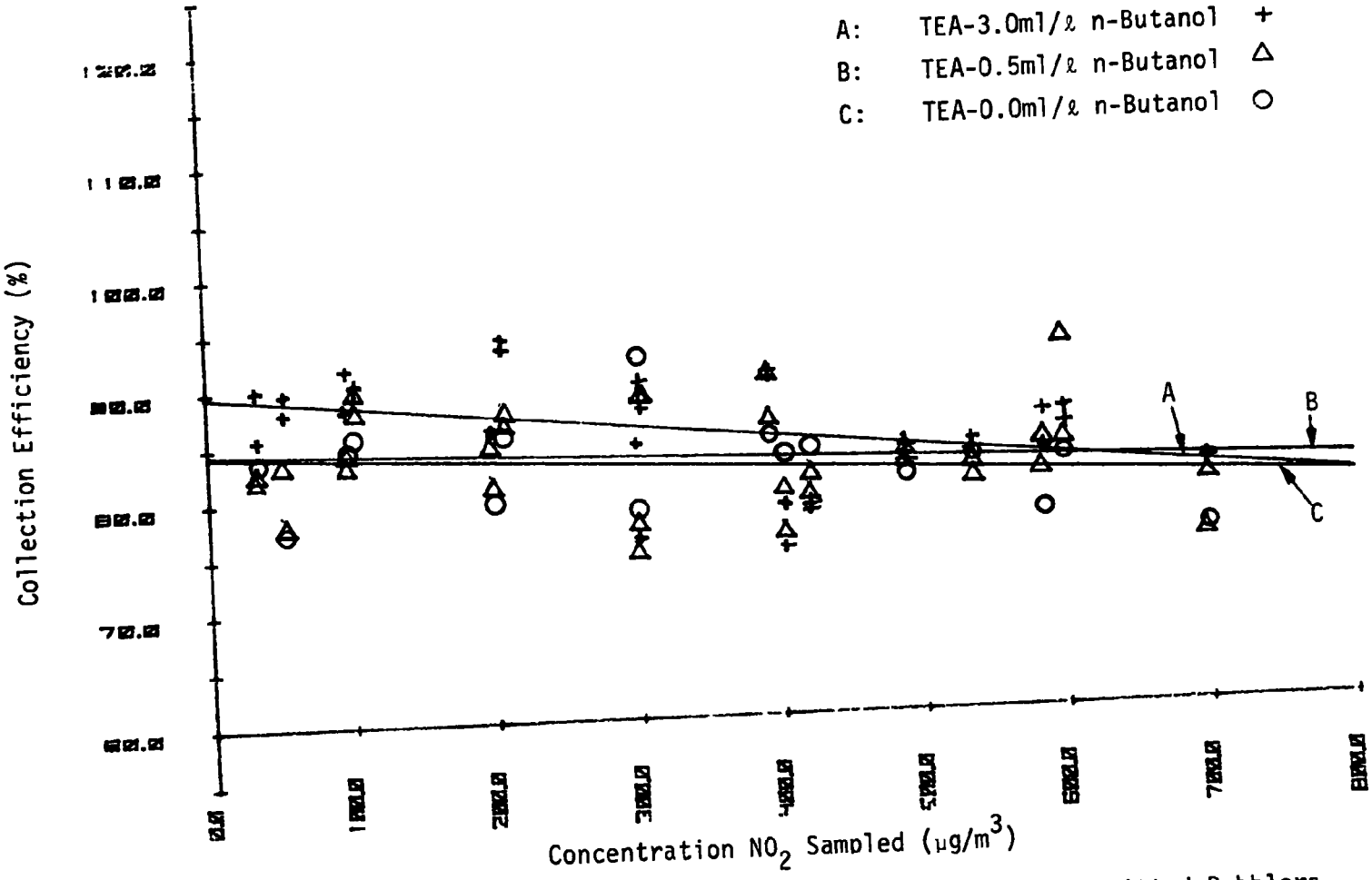

Figure 1. Collection Efficiency vs. NO_2 Concentration Using Fritted Bubblers.

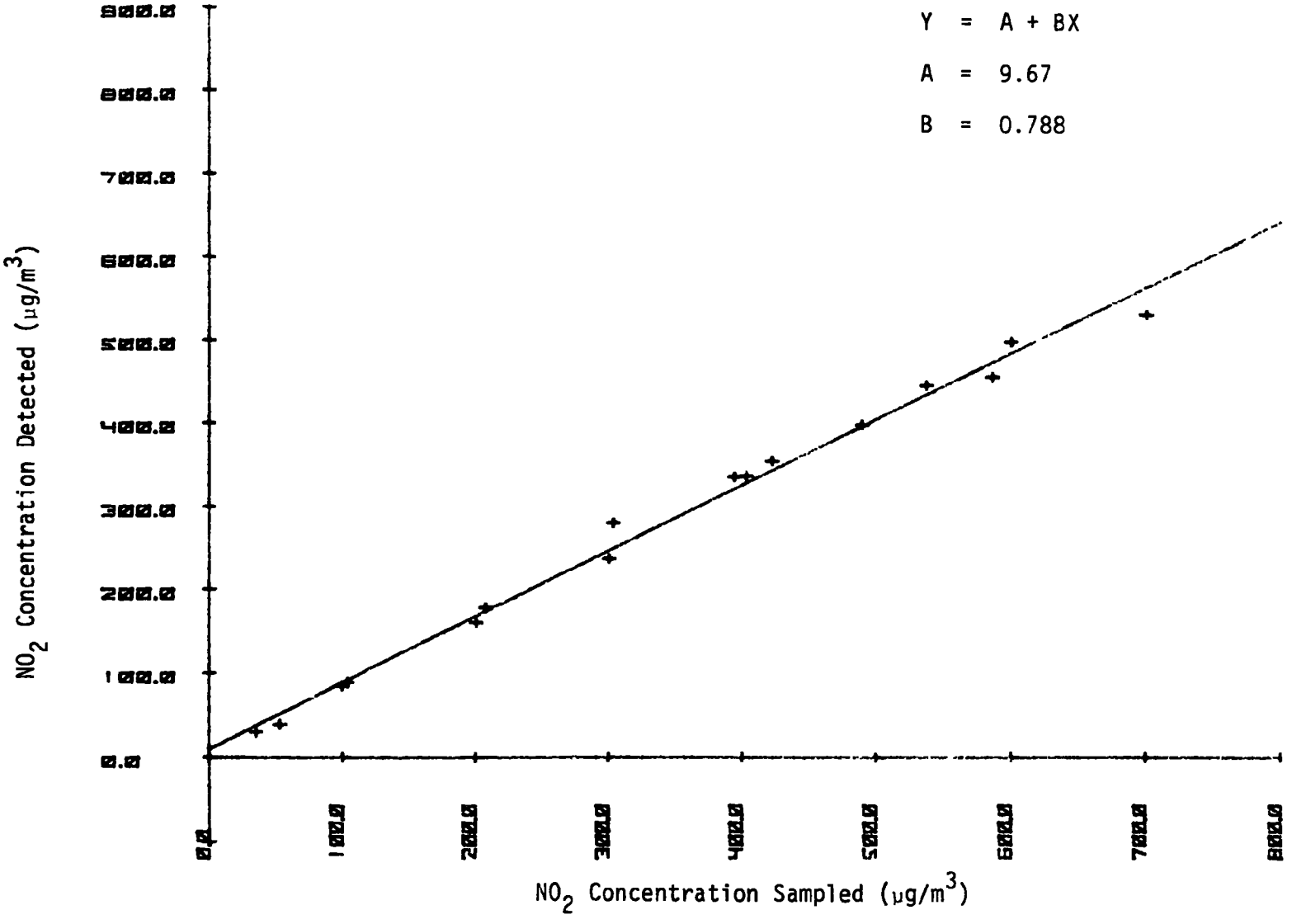

Figure 2. NO_2 Concentration Detected vs. NO_2 Concentration Sampled for TEA (frits).

solution is 78.8%. Similar plots also indicate average collection efficiencies of about 80% for the other two TEA solutions. This method for obtaining the average collection efficiency is to be preferred over using the y-intercept value from a plot like Figure 1 as the average collection efficiency. The curve in Figure 2 not only provides a direct and accurate average collection efficiency, but also its linearity is indicative of the constancy of the collection efficiency over the concentration range of interest. Associated with a linear regression analysis, an often-used indicator of the strength of the linear relationship between the two variables under consideration (in this case concentration detected vs. concentration sampled) is the correlation coefficient or r value. The closer the $|r|$ is to 1.0 then the stronger is the linear correlation between the two variables. In the case of Figure 2, $r = 0.996$.

The results of the experiments using restricted-orifice bubblers as seen from Figure 3 again show a constant collection efficiency independent of NO_2 concentration sampled or of n-butanol level in the TEA absorbing solution. Though constant, the average collection efficiency drops by about 30% when using restricted-orifice bubblers. This lower collection efficiency (47%) is shown in Figure 4 for the TEA-0.0 ml n-butanol/l.

In summary, the collection efficiency over the concentration range studied, is constant and independent of n-butanol level in the absorbing solution using either frits or restricted-orifice bubblers; however, the collection efficiency using frits is about 80%, while the efficiency drops to about 50% for restricted-orifice bubblers. Since there appears to be no

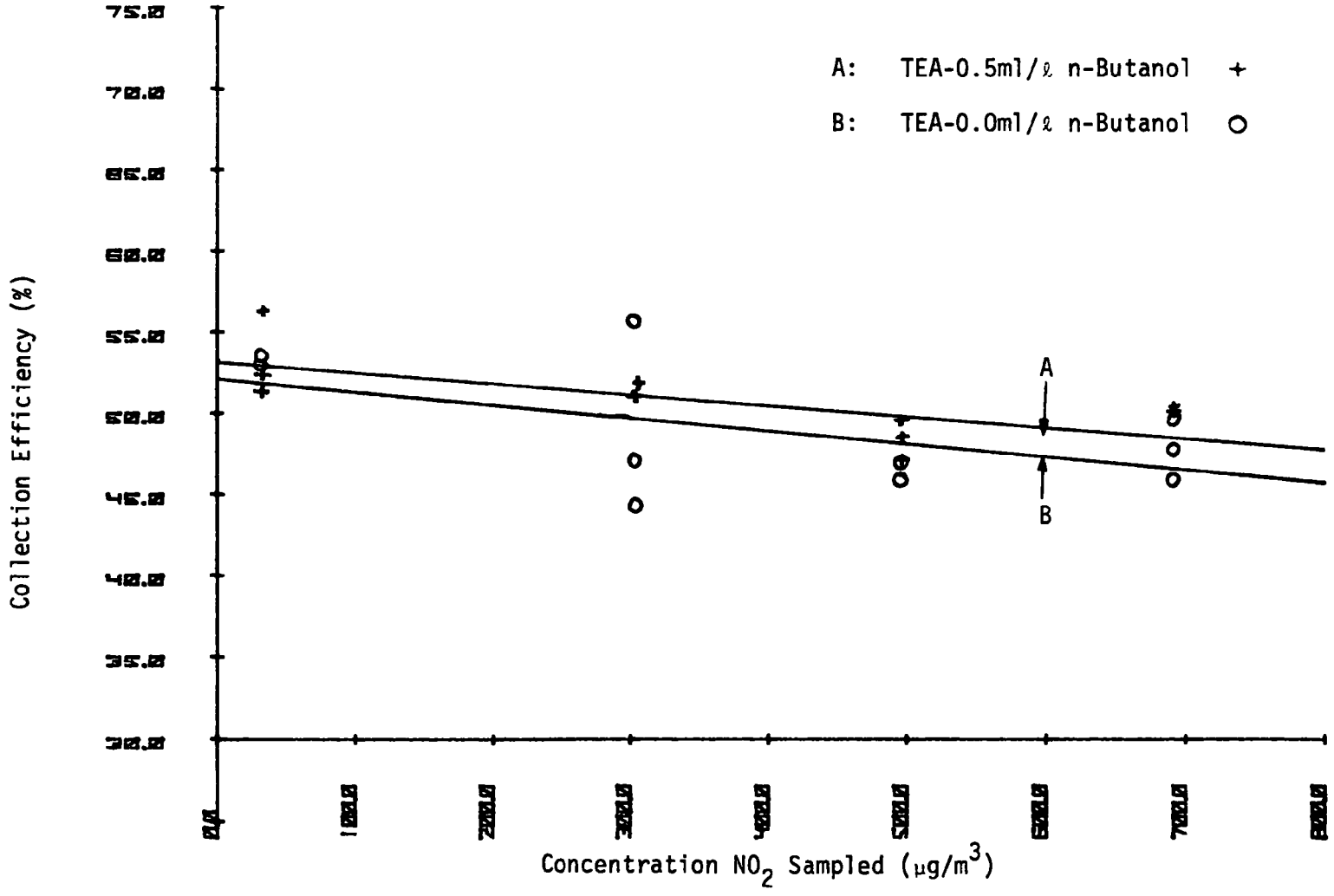

Figure 3. Collection Efficiency vs. NO_2 Concentration Using Restricted-Orifice Bubblers.

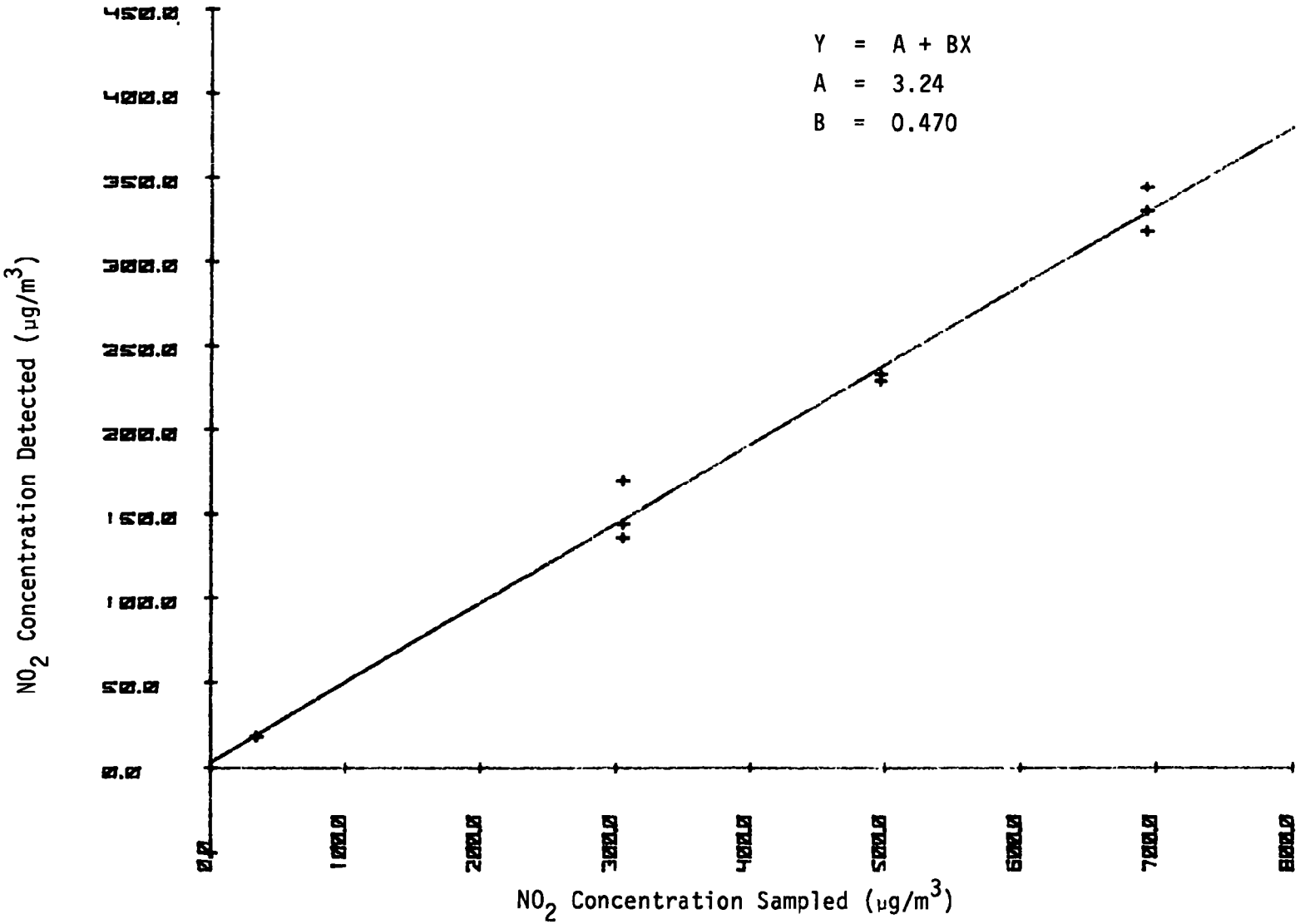

Figure 4. NO_2 Concentration Detected vs. NO_2 Concentration Sampled for TEA (restricted-orifice bubblers).

advantage to adding n-butanol to the TEA absorbing solution, its addition is not recommended in the method write-up in Appendix A. The recommended TEA procedure uses fritted bubblers and has an average collection efficiency of 78.8% over the range 0-700 $\mu g/m^3$ NO_2. Experimental data are found in Appendix B.

SECTION V

ADDITIONAL EXPERIMENTS & RESULTS

During the course of the laboratory evaluation, it was a simple matter to collect stability data on the absorbing solutions. Collected samples were analyzed immediately, then again at one week and three week intervals after collection. There were no significant differences noted in the amount of NO_2 detected for any of the analyses (Table 1). Additionally, the TEA absorbing solutions were all found to be stable for at least a month after preparation when stored in glass containers placed on the bench top.

A large number of the collected samples were also analyzed by an alternate colorimetric procedure.[5] The collection efficiencies obtained by the sulfanilamide - 8-Anilino-1-naphthalenesulfonic acid Ammonium salt (S-ANSA) procedure were consistently about 10% higher than those obtained by the method's recommended analytical procedure[6] - diazotization of sulfanilamide and coupling to N-(1-Naphthyl)-ethylenediamine Dihydrochloride (S-NEDA). Results comparing the two analytical procedures are shown in Table 2. Though somewhat puzzling, no explanations can be given for the differences noted between the two analytical procedures and no further investigations seem warranted at this time, because the scope of the evaluation of the TEA method did not call for optimization.

Table 1. Effect of Sample Age on Collection Efficiency.

NO_2 Sampled ($\mu g/m^3$)	n-Butanol Level (mℓ/ℓ)	Collection Efficiency (%) Analysis Time: Immediately	1st week	3rd week	Mean(%)
35.7[a]	0.0	83.8	91.7	97.8	91.1
	0.5	82.9	89.8	94.1	88.9
	3.0	88.0	100.	99.9	95.9
99.9	0.0	84.3	89.2	90.1	87.9
	0.5	84.2	87.4	91.6	87.7
	3.0	89.9	95.1	91.9	92.3
201[a]	0.0	79.7	87.5	89.6	85.6
	0.5	82.9	91.9	95.0	89.9
	3.0	86.0	92.1	95.5	91.2
304	0.0	92.2	94.6	89.7	92.2
	0.5	88.8	92.1	88.1	89.7
	3.0	89.0	90.6	87.2	88.9
395	0.0	85.0	84.6	81.6	83.7
	0.5	88.7	85.1	87.6	87.1
	3.0	90.5	86.7	86.1	87.8
490	0.0	81.1	83.2	85.4	83.2
	0.5	82.6	85.4	85.6	84.5
	3.0	82.7	85.0	84.5	84.1
587	0.0	77.5	76.5	85.6	79.9
	0.5	82.5	78.5	85.1	82.0
	3.0	84.9	81.1	87.3	84.4
701	0.0	75.6	80.4	80.5	78.8
	0.5	77.9	81.6	82.7	80.7
	3.0	81.3	83.7	85.0	83.3

a: Samples were not properly sealed initially and evaporative losses caused the seemingly increased results with aging.

Table 2. Comparison of S-NEDA and S-ANSA Analytical Systems.

NO_2 Sampled ($\mu g/m^3$)	Collection Efficiency (%) TEA - 0.0 mℓ n-Butanol/ℓ	
	S-NEDA	S-ANSA
35.7	83.8	96.2
53.2	77.2	89.5
99.9	84.3	91.1
201	79.7	88.6
208	85.6	91.8
301	78.7	94.0
304	92.2	97.8
395	85.0	88.3
423	83.7	96.4
490	81.1	87.8
587	77.5	90.1
602	82.4	91.9
701	75.6	82.9

SECTION VI

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SECTION VII

APPENDICES

APPENDIX A

TENTATIVE METHOD FOR THE DETERMINATION OF NITROGEN DIOXIDE IN THE ATMOSPHERE (TRIETHANOLAMINE PROCEDURE)[a]

[a]A tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization Branch and has undergone extensive laboratory evaluation. The method is still under investigation and, therefore, is subject to revision.

1. Principle and Applicability

1.1 Nitrogen dioxide is collected by bubbling air through an aqueous triethanolamine[1] solution. The nitrite ion produced during sampling is determined colorimetrically via diazotization of sulfanilamide and subsequent coupling with N-(1-naphthyl)-ethylenediamine to form an azo dye.

1.2 The method is applicable to collection of 24-hour samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 0.04 to 2.0 μg NO_2^-/ml. Beer's law is obeyed throughout this range (0 to 1.0 absorbance units). With 50 ml of absorbing reagent and a sampling rate of 200 cm^3/min for 24-hours, the range of the method is 20 to 700 $\mu g/m^3$ (0.01 to 0.4 ppm) nitrogen dioxide.

2.2 A concentration of 0.04 μg NO_2^-/ml will produce an absorbance of approximately 0.016 with 1 cm cells.

3. Interferences

3.1 Nitric oxide at concentrations as high as 740 $\mu g/m^3$ in the presence of 40 - 170 $\mu g/m^3$ NO_2 does not affect the NO_2 analyses.[1]

3.2 The potential SO_2 interference is eliminated by converting it to sulfate ion with hydrogen peroxide prior to analysis.[2]

3.3 Ozone at atmospheric concentrations does not affect analysis for NO_2.

4. Precision, Accuracy and Stability

4.1 Precision. Insufficient data are available to state the precision of the method.

4.2 Accuracy. No accuracy data are available.

4.3 The absorbing reagent is stable for up to 5 weeks without refrigeration. Collected samples are stable for at least 3 weeks prior to analysis.

5. Apparatus.

5.1 Sampling. A diagram of a suggested sampling apparatus is shown in Figure 1.

5.1.1 Probe. Teflon, polypropylene, or glass tube with a glass or polypropylene funnel at the end.

5.1.2 Absorption Tube. Polypropylene tubes 164 x 32 mm, equipped with polyproylene two-port closures. A gas dispersing tube with a fritted end of 60 to 100 μm porosity is used in conjunction with the tube. Frits need be screened as to exact porosity only for initial usage. The maximum useable pore diameter is about 160 μm.

5.1.2.1 Measurement of Maximum Pore Diameter of Frit. Carefully clean the frit with dichromate-concentrated sulfuric acid cleaning solution and rinse well with distilled water. Insert through one hole of a two-hole rubber stopper and install in a test tube containing sufficient distilled water to cover the fritted portion. Attach a vacuum source to the other hole of the rubber stopper and measure the vacuum required to draw the first perceptible stream of air bubbles through the frit. Apply the following equation:

$$\text{maximum pore diameter, } \mu m = \frac{30s}{P}$$

s = Surface tension of water (dynes/cm) at the test temperature (73 at 18°C, 72 at 25°C and 71 at 31°C).

P = Measured vacuum, mmHg.

5.1.3 Moisture Trap. Polypropylene tube equipped with two-port closure. The entrance port of the closure is fitted with tubing that extends to the bottom of the trap. The unit is loosely packed with glass wool to prevent moisture entrainment.

5.1.4 Membrane Filter. 0.8-2.0 μm porosity to protect the flow control device from particulate matter. The filter should be replaced after collecting ten samples.

5.1.5 Flow Control Device. Any device capable of maintaining a constant flow through the absorbing solution between 180-220 cm^3/min. A typical flow control device is a 27-gauge hypodermic needle,[3] three-eights inch long.

5.1.6 Air Pump. Capable of maintaining a pressure differential of at least 0.6 - 0.7 atm across the flow control device. This value includes the minimum useful differential,[3] 0.53 atm, plus a safety factor to allow for variations in atmospheric pressure.

5.1.7 Calibration Equipment. Flow meter for measuring air flows up to 275 cm^3/min within $\pm$ 2%, stopwatch, and a soap-bubble flow meter (100 ml).

5.2 Analysis

5.2.1 Glassware. Appropriate vol. flasks, pipets, graduated cylinders and test tubes to prepare reagents and standard solutions and to perform colorimetric analyses.

5.2.2 Spectrophotometer. Instrument capable of measuring absorbance at 530 nm.*

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* The wavelength of maximum absorbance for the azo dye should be determined. Different manufacturers' lots of NEDA have different absorption peak maximas.

6. Reagents

6.1 Sampling

6.1.1 Triethanolamine [$N(C_2H_4OH)_3$]. Reagent grade.

6.1.2 Absorbing Solution. Dissolve 15g of triethanolamine (TEA) in 500 ml of distilled H_2O. Dilute to one liter with distilled water. The solution is stable for at least one month without refrigeration.

6.2 Analysis

6.2.1 Hydrogen Peroxide (H_2O_2). ACS reagent grade, 30%.

6.2.2 Sulfanilamide [$4\text{-}(H_2N)C_6H_4SO_2NH_2$] melting point 165-167°C.

6.2.3 N-(1-Naphthyl)-ethylenediamine dihydrochloride (NEDA). Best grade available.

6.2.4 Sodium Nitrite, ($NaNO_2$). ACS reagent grade. Assay of 97% $NaNO_2$ or greater.

6.2.5 Phosphoric Acid (H_3PO_4). ACS reagent grade, 85%.

6.2.6 Hydrogen Peroxide Solution. Dilute 0.2 ml of 30% H_2O_2, to 250 ml with distilled water. The solution may be used for a month if protected from light and refrigerated.

6.2.7 Sulfanilamide Solution. Dissolve 20g sulfanilamide in 700 ml distilled water. Add, with mixing, 50 ml concentrated H_3PO_4 and dilute to one liter. The solution is stable for one month, if refrigerated.

6.2.8 NEDA Solution. Dissolve 0.5g of NEDA in 500 ml distilled water. The solution is stable for one month, if refrigerated and protected from light.

6.2.9 Standard Nitrite Solution. Prepare a liter of 100 μgNO_2^-/ml for a stock nitrite standard. The amount of $NaNO_2$ to use is calculated as follows:

$$G = \frac{1.500}{A} \times \frac{100\%}{10}$$

where

G = amount of $NaNO_2$, grams

1.500 = gravimetric factor in converting NO_2 into $NaNO_2$

A = assay per cent

10 = dilution factor

7. Procedure

7.1 Sampling. Assemble the sampling apparatus as shown in Figure 1. Components up stream from the absorption tube may be connected, where required, with teflon or polypropylene tubing; glass tubing with dry ball joints; or glass tubing with butt-to-butt joints with tygon, teflon on polypropylene. Add exactly 50 ml of absorbing reagent to the (calibrated) absorption tube. Disconnect funnel, insert calibrated flowmeter and measure flow before sampling. If flow rate before sampling is not between 180 and 220 cm^3/min, replace the flow control device and/or check the system for leaks. Start sampling only after obtaining an initial flow rate in this range. Sample for 24 hours and measure the flow after the sampling period.

7.2 Analysis. Replace any water lost by evaporation during sampling by adding distilled water up to 50 ml; mix well. Pipet 5 ml of the collected sample into a test tube; add 0.5 ml of the peroxide solution, 5 ml sulfanilamide solution and 0.7 ml NEDA solution with thorough mixing after the addition of each reagent. Prepare a blank in the same manner using 5 ml of unexposed absorbing reagent. Allow the color to develop for

10 minutes, then measure the absorbance of sample against the blank at 530 nm. Read $\mu g NO_2^-$/ml from the calibration curve (Section 8.2). Samples with an absorbance greater than 1.0 must be reanalyzed after diluting an aliquot (less than 5 ml) of the collected sample with unexposed absorbing reagent to 5 ml.

8. Calibration and Efficiencies

8.1 Sampling

8.1.1 Calibration of Flowmeter. Using a soap-bubble flow meter and a stopwatch, determine the rates of air flow (cm^3/min) through the flowmeter at a minimum of 4 different flows. Plot meter position versus flow rates.

8.1.2 Flow Control Device. The flow control device results in a constant rate of air flow through the absorbing solution and is determined in Section 7.1.

8.2 Calibration Curve. Dilute the stock standard nitrite solution (Section 6.2.9) 50:1 with TEA absorbing solution to prepare a working standard solution containing 2.0 μg NO_2^-/ml. To a series of test tubes pipet 0.1, 0.5, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard. Make the volume in each tube up to 5 ml with absorbing solution. Run standards as instructed in 7.2. Plot μg NO_2^-/ml vs. absorbance. A straight line should be obtained.

8.3 Efficiencies. An overall average collection efficiency of 79% is obtained over the range of 30 to 700 $\mu g/m^3$ NO_2.

9. Calculation

9.1 Sampling

9.1.1 Calculate volume of air sampled

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

V = volume of air sampled, m^3

F_1 = measured flow rate before sampling, cm^3/min

F_2 = measured flow rate after sampling, cm^3/min

t = time of sampling, min

10^{-6} = conversion of cm^3 to m^3

9.1.2 Uncorrected Volume. The volume of air sampled is not corrected to S.T.P., because of the uncertainty associated with 24-hour average temperature and pressure values.

9.2 Calculate the concentration of nitrogen dioxide as $\mu g/m^3 NO_2$ using:

$$\mu g/m^3 NO_2 = \frac{(\mu g/ml NO_2^-)\ 50}{V \times 0.79}$$

50 = volume of absorbing reagent used in sampling, ml

V = volume of air sampled, m^3

0.79 = collection efficiency

If desired, concentration of NO_2 may be calculated as ppm NO_2 using

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

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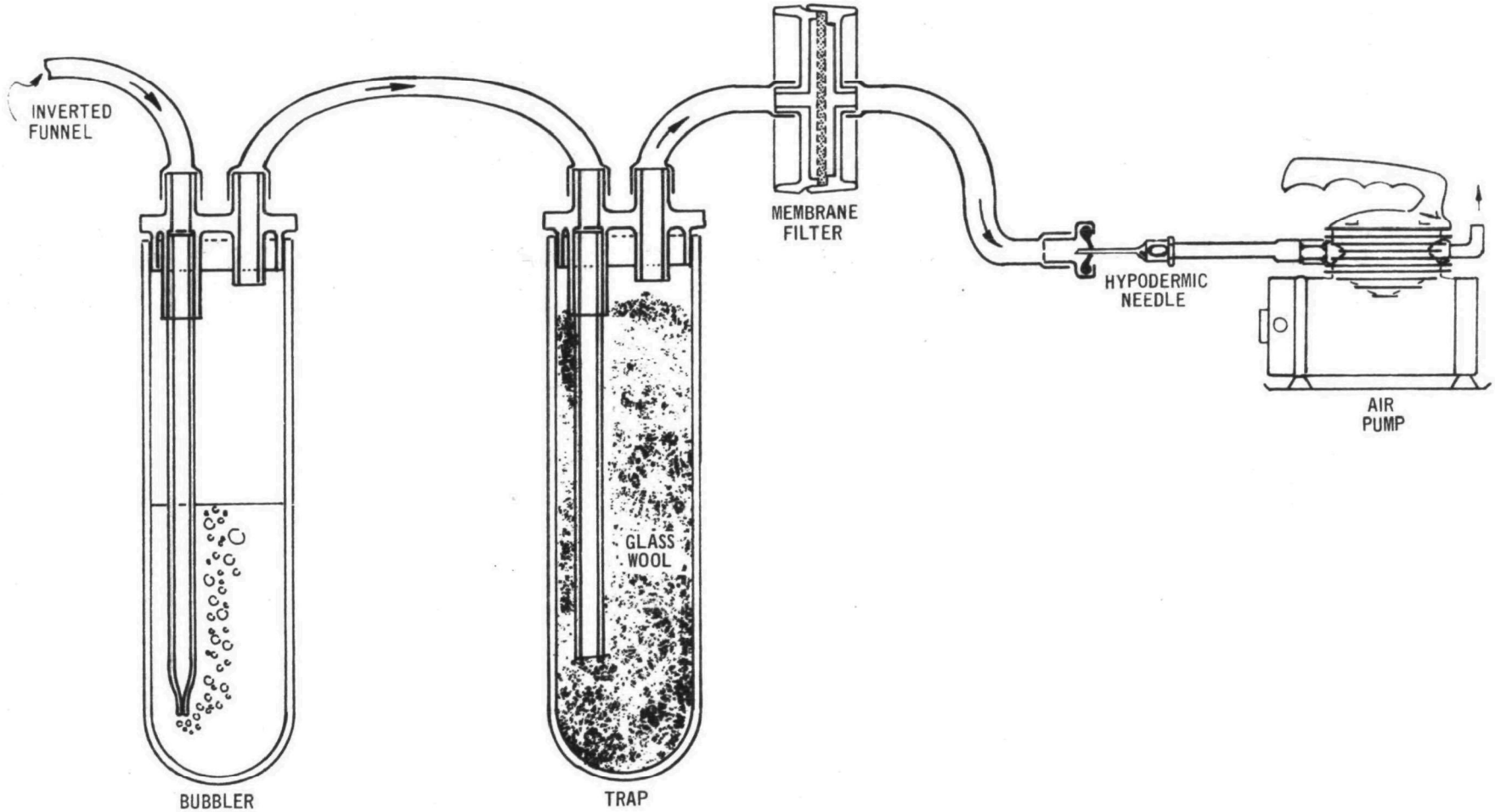

Figure 1. Sampling train.

APPENDIX B. Laboratory Evaluation Data: Fritted Bubblers.

NO_2 Sampled ($\mu g/m^3$)	NO_2 Detected ($\mu g/m^3$) at n-Butanol Level (mℓ/ℓ)			Collection Efficiency (%) at n-Butanol Level (mℓ/ℓ)		
	3.0	0.5	0.0	3.0	0.5	0.0
35.7	32.1	29.6	29.8	90.2	82.9	83.8
	30.6	29.6		85.8	82.9	
53.2	47.4	44.4	38.7	89.7	83.4	77.2
	46.8	41.3		88.0	77.6	
99.9	87.9	83.9	84.3	88.0	84.1	84.3
	91.8	84.2		91.8	84.3	
104	93.1	91.4	89.0	89.5	87.9	85.6
	93.8	93.3		90.2	89.7	
201	173	171	160	85.9	84.9	79.7
	173	163		86.1	81.0	
208	194	180	178	93.3	86.5	85.6
	196	179		94.2	86.1	
301	229	231	237	76.1	76.7	78.7
	254	228		84.4	75.7	
304	273	270	280	89.9	88.9	92.2
	268	270		88.1	88.7	
395	358	360	335	90.8	90.8	85.0
	356	342		90.2	86.5	
404	303	308	336	74.9	76.2	83.2
	318	324		78.7	80.1	
423	335	336	354	79.2	79.4	83.7
	333	344		78.7	81.3	
490	400	409	398	81.7	83.4	81.1
	410	401		83.6	81.8	
538	447	442	445	83.1	82.2	82.7
	452	435		84.0	80.9	
587	490	493	455	83.4	84.0	77.5
	508	476		86.4	81.1	
602	512	559	497	85.1	92.9	82.4
	521	506		86.5	84.0	
701	572	528	530	81.5	75.4	75.6
	569	564		81.2	80.3	

APPENDIX B. Laboratory Evaluation Data: Restricted-Orifice Bubblers.

NO_2 Sampled ($\mu g/m^3$)	NO_2 Detected ($\mu g/m^3$) at n-Butanol Level (mℓ/ℓ)		Collection Efficiency (%) at n-Butanol Level (mℓ/ℓ)	
	0.5	0.0	0.5	0.0
34.2	17.9	18.3	52.4	53.4
	17.6	18.1	51.3	52.8
	19.3		56.3	
305	158	136	51.8	55.7
	156	144	51.1	44.4
		170		47.1
497	234	229	47.1	45.9
	242	233	48.5	46.9
	247		49.5	
693	345	318	49.9	45.9
	345	344	49.8	49.7
		330		47.7

TECHNICAL REPORT DATA (Please read Instructions on the reverse before completing)		
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16. ABSTRACT A detailed method write-up describing the triethanolamine (TEA) manual procedure for measurement of nitrogen dioxide in ambient air was developed. The method involves sampling for 24 hours with a fritted bubbler immersed in 0.1N TEA collecting solution. The range ofthe method is approximately 20 to 700 $\mu g/m^3$.

The method was evaluated to determine its usefulness for measuring nitrogen dioxide in ambient air. This involved a review of the procedure as developed and subsequent laboratory experiments to better define some obscure points in the procedure. The constancy of the method's collection efficiency, the addition of n-butanol to enhance the collection efficiency and the need to use fritted bubblers as gas dispersers to assure high collection efficiency were the main points investigated in these experiments. The results indicated a constant collection efficiency over the method's range both with and without any added n-butanol using either frits or restricted-orifice bubblers; however, the collection efficiency using frits is about 80%, while the efficiency drops to about 50% using restricted-orifice bubblers.

Further work on the method does not seem warranted at this time, because the availability of other methods which show more promise for the measurement of NO_2 in ambient air.

17 KEY WORDS AND DOCUMENT ANALYSIS		
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