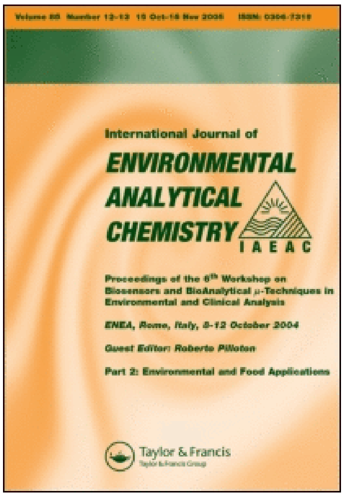

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AN EVALUATION OF INTEGRATING TECHNIQUES FOR MEASURING ATMOSPHERIC NITROGEN DIOXIDE

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Two integrating techniques for measuring ambient NO_2 were evaluated. Both techniques involved quantitative collection of NO_2 in a reagent coated cartridge, specifically triethanolamine (TEA)-coated silica gel and diphenylamine (DPA)-coated Florisil. The evaluation of these techniques consisted of laboratory and field studies. The laboratory studies of the TEA method indicated collection and reaction efficiencies of 100 and 90%, respectively. A positive interference occurred when O_3 and NO were passed through the cartridge simultaneously. PAN was found to produce a 67% positive interference. The ambient concentrations determined using the TEA method were approximately a factor of two higher than those determined using TDLAS. For the DPA method the collection and reaction efficiencies were determined to be 100 and 64%, respectively. O_3 produced a negative interference by reacting with the NO_2-DPA products. PAN produced a 42% positive interference. A regression of the DPA versus TDLAS determined ambient NO_2 concentrations yielded a slope of .91±.08 (r^2=0.990.). Neither method was found suitable for network use in its present form.

KEY WORDS: Nitrogen dioxide, triethanolamine, diphenylamine, atmospheric samples.

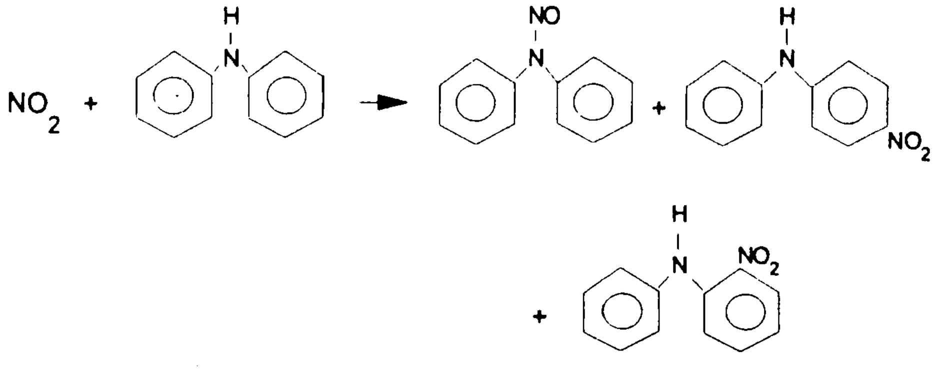
INTRODUCTION

NO_2 is an important trace gas in the atmospheric environment. It is the only significant photochemical source of ozone and contributes to acid precipitation as a precursor to HNO_3[1]. Thus, knowledge of the spatial and temporal distribution of NO_2 is required for a complete description of tropospheric photochemical processes. To monitor spatial and temporal trends of oxidant concentrations and to improve our understanding of factors leading to elevated oxidant levels, numerous monitoring networks have been established worldwide. Unfortunately, due to lack of an affordable and reliable NO_2 measurement technique these networks are unable to fulfil the basic needs of nitrogen oxides monitoring.

Ideally a measurement technique for use in a network system would be inexpensive, simple to operate, sensitive and selective. A variety of methods exist for measuring atmospheric NO_2 including: long path FTIR[2], Tunable Diode Laser Absorption Spectrometry (TDLAS)[3], Differential Optical Absorption Spectrometry (DOAS)[4], chemiluminescent based techniques that operate on either the NO-O_3 reaction using photolytic[5] converters, or the chemiluminescent reaction of luminol and NO_2[6]. However, due to a number of reasons including expense, difficulty in operation and/or interference from other trace species[5,6], none of these methods are ideal for network use. Two techniques recently developed appear to be suitable for use in a network system. Both are integrating techniques involving solid sorbent sampling. One method involves drawing sample air through a tube containing triethanolamine (TEA) coated silica gel[7,8]. The NO_2 reacts with the surface sorbed TEA, ultimately yielding NO_2^-(nitrite) and NO_3^- (nitrate) ions which are separated and quantified using ion chromatography. The mechanism for the conversion of NO_2 to NO_2^- and NO_3^- remains uncertain[9,10,11]. The second method involves pumping air through a tube containing diphenylamine (DPA) coated Florisil[12]. The NO_2 reacts with the DPA to produce nitro and nitrosodiphenylamines which are separated and quantified by high performance liquid chromatography (HPLC). Solid adsorbents as reagent substrates provide an attractive alternative for network measurements as cartridges may be transported by mail to remote sites and no lengthy field calibrations are required.

TEA has been investigated as an NO_2 trapping solution coated on the following surfaces: firebrick[9], molecular sieves[13], glass fibre filters[14,15] and Sep-Pak C_{18} cartridges[7,8,16]. The results of these studies are generally in agreement that 90–100% of the NO_2 is trapped on the TEA coated surface, except in the case of TEA coated Sep-Pak C_{18} cartridges, where the study of Nishikawa *et al*[7] reported 90–100% recovery of the NO_2 as nitrite and nitrate, while Peschke *et al*[16] reported only 50% recovery.

Diphenylamine coated Thermosorb-F (florisil) has been investigated as an NO_2 trapping reagent[12,16]. This method was developed after it was determined that secondary amines react with nitrogen oxides to form nitrosamines[17]. DPA is expected to react with NO_2 to form N-nitrosodiphenylamine, as well as 4-nitrodiphenylamine and 2-nitrodiphenylamine[12] as shown below.



This study involved a comparison of these two recently developed solid sorbent integrating sample techniques for measuring NO_2 with the ultimate goal of determining the feasibility of using them in an air monitoring network. The sampling procedures used for the DPA method were essentially as described by Lipari[12]. However, for the TEA method we chose to investigate the possibility of using silica as the solid sorbent rather than C_{18} coated silica gel [7,8,16] because of concerns regarding retention of TEA on the C_{18} surface during sampling, and because of impurities associated with the C_{18} surface that might adversely affect the attainable detection limit. We also felt that PAN might yield a smaller interference on a polar substrate because of its lipophilic nature. The laboratory studies involved determination of the collection efficiencies (percent of the NO_2 that was trapped on the cartridge) and the reaction efficiencies (percent of trapped NO_2 that was detected as the products measured) for both methods. In addition, possible interferences from water, NO, O_3 and PAN were also investigated. Two field studies were conducted at Egbert, Ontario in March and April, 1990 and October, 1990. The field studies involved comparing the ambient NO_2 concentrations determined by each method to values determined by an independent technique, TDLAS.

EXPERIMENTAL

Reagents and materials

All reagents used were analytical or HPLC grade. Sep-Pak silica cartridges (Waters, Mississauga, Ont.) are constructed of polyethylene, are 1×3 cm long, and are filled with 37–53 μm silica gel. Standards were made from dried sodium nitrite and sodium nitrate. Thermosorb-F cartridges (ThermoElectron Corp., Waltham, MA) are also constructed of polyethylene, are 1.5×2 cm long and are filled with 60/80 mesh florisil. Standards were made from purchased 99% pure N-nitrosoDPA, 4-nitroDPA and 2-nitroDPA (Aldrich Chemical, Milwaukee, WI).

Cartridge preparation

Sep-Pak TEA-coated silica cartridges were prepared as described by Nishikawa *et al*[7,8] using a 20% v/v solution of TEA in methanol. The coated cartridges were dried by placing them in a vacuum desiccator at a pressure of 50 mm Hg for 30 minutes and then passing 100 ml/min of He through them for 30 minutes. Cartridges could be reused by washing with 20 ml methanol followed by preparation as described above.

Thermosorb-F cartridges were first washed with 5 ml methanol and then coated using 4 ml of 0.02M solution of DPA in methanol. Cartridges were dried as described above. It was determined that if the cartridges were not dried immediately, the seams of the moulded plastic shell became prone to leaks. Cartridges could be reused by washing with 20 ml methanol, followed by preparation as described above.

Both types of cartridges were kept refrigerated before and after sampling. Analysis of duplicate samples determined that no degradation occurred over a period of two weeks.

Quantitative analysis

TEA method Sampled TEA coated Sep-Pak cartridges were eluted as described by Nishikawa *et al*[7,8]. It was determined that 5ml of eluent was sufficient when eluting even the most concentrated samples. The components of the eluate were separated by an ion chromatography system consisting of a 100 µl sample loop, a Hamilton PRP-X100 guard column, a Dionex anion fibre suppressor, a Dionex AS-4 ion exchange column and a Waters Conductivity Detector Model 430. Optimal separation was obtained with a mobile phase of 1.4mM $NaHCO_3$/1.1mM Na_2CO_3 at a flow rate of 1.9 ml/min. The anion exchange solution for the suppressor was a 16 mM H_2SO_4 solution delivered at approximately 1 ml/min. Under these conditions NO_2^-, NO_3^-, and $SO_4^=$ elute at 2.5, 4.7 and 10 minutes respectively. Calibrations were conducted using standards made from the analyte dissolved in the 4mM Na_2CO_3/1.5 mM $NaHCO_3$ cartridge extract solution. Standards exchanged with an independent Environment Canada Ion Chromatography lab yielded agreement to within 8%.

The excess TEA in the sample cartridges increased the pH of the eluate, which caused a constant 15±2% positive error in the concentrations of both the nitrite and the nitrate ions at concentrations ranging from 2.5nmole/ml to 200nmoles/ml. All NO_2^- and NO_3^- concentrations were thus divided by 1.15 to account for this effect.

The DPA method The sampled DPA coated Thermosorb-F cartridges were eluted with 5 ml methanol opposite to the sampling direction. To the eluate 0.25 ml 1N HC1 was added. The HPLC system consisted of a 20 µl injection loop, a Hewlett Packard Series 1050 chromatographic pump, a 250 mm × 4.6 mm id reverse phase C-18 column (Supelco, Oakville, Ont.) and a variable wavelength UV/VIS detector. Optimal separation was obtained using a ternary isocratic system of water, methanol and tetrahydrofuran(55/35/10) at a flow rate of 1.1 ml/min. This procedure yielded much improved separation relative to the conditions used by Lipari[12] with N-nitrosoDPA, 4-nitroDPA, DPA and 2-nitroDPA eluting at approximately 12, 14, 17.5 and 20 minutes, respectively. The detector was generally operated at 254 nm, but was occasionally programmed to change to 430 nm after 15 minutes to ensure detection of the 2-nitroDPA product in the presence of excess DPA.

Laboratory studies

Known concentrations of NO in air were prepared by metering dry air and certified NO in N_2 gas (Scott Specialty Gases) through a calibrated Tylan mass flow controller, and mixing the streams in the ¼″ OD teflon tube. The NO stream was oxidized to NO_2 with the use of a CrO_3 trap[9] consisting of 1″ OD teflon tubing filled with 20/30 mesh non acid washed Chromasorb-A (Mandel Scientific, Guelph, Ont.) that had been coated with a 17% CrO_3 in water solution and dried ad 150°C. The air stream was then passed through a nylon filter, which is known to remove particulate nitrate and nitric and nitrous acids[18]. Complete conversion of NO to NO_2 was verified with a Monitor Labs model 8840 nitrogen oxides analyzer. The sample stream was then passed through three cartridges placed in parallel to determine analytical precision, and a second cartridge placed in series with each to evaluate collection efficiencies. A fourth set of cartridges was used to obtain the dilution air blank. Sample air was pumped through the cartridges, and the flow rate was monitored with calibrated Hastings flow meters. A flow rate of 1 l/min was used for the TEA method, which was the maximum achievable due to the pressure drop across the cartridges, while a 4 l/min flow was employed for the DPA method. Sample times varied from 30 minutes to 24 hours.

For the interference experiments moist air, NO, O_3, PAN and NO+O_3 were diluted with the dry air stream and subsequently sampled. O_3 was synthesized using a PCI Ozone Generator and diluted with dry air. The O_3 concentration was monitored using a Model 1003-AH Dasibi Environmental Corporation Ozone Monitor. PAN was synthesized using the method developed by Neilson *et al*[19], followed by extraction of PAN into dodecane[20]. The synthesized PAN was purified to produce gas phase PAN as described by Blanchard *et al*[21]. PAN and NO concentrations were monitored using the NO_x analyzer.

Field studies

The two field studies were conducted at the Centre for Atmospheric Research Experiments maintained by the Atmospheric Environment Service located in a rural setting approximately 50 km northwest of Toronto. The first study was part of the EMEFS (Eulerian Model Evaluation Field Study) 1990 study, which was conducted from March 20, 1990 to April 27, 1990. During this field study numerous trace species were monitored including NO, NO_2, HNO_3, particulate nitrate, PAN, organic nitrates, O_3, SO_2, and NH_3. The second study was an intercomparison study of NO_2 measuring techniques which was conducted from October 2 to November 6, 1990.

For both studies, the inlet line (¼″ OD teflon tubing) for cartridge sampling was fixed to a railing on the roof on the west side of the air monitoring station at a height of approximately 4m. The inlet air passed first through a nylon filter situated at the inlet under a rain bonnet. The ambient air was then passed through the two cartridges in series at room temperature inside the monitoring station. The flow rate was monitored using calibrated Hastings flow meters. Integrated samples were obtained from roughly noon to noon each day. The length of tubing between the inlet and the first cartridge was approximately 6m. Field blanks were obtained using cartridges handled exactly as for the sample cartridges, but which were not sampled.

For the purpose of this study, tunable diode laser absorption spectrometry (TDLAS) was used as the independent reference technique. Because of the very narrow bandwidth of the laser employed and the sharp rotation line chosen in the IR spectrum, there are no known interferences for this method of measuring NO_2[3]. However, the absolute calibration of the TDLAS is conducted using a permeation source which must be independently calibrated. This calibration determines the absolute uncertainty of the method. For this comparison the TDLAS concentrations were averaged to yield a 24 hour average NO_2 concentration, for the same time period as for the cartridge samples.

RESULTS AND DISCUSSION

Laboratory results-TEA method

Throughout this study 46 blank TEA cartridges were analyzed. The average quantities and standard deviations of NO_2^- and NO_3^- were 3.8±1.6 and 4.0±2.6 nmoles, respectively, which corresponds to a detection limit of 0.2 ppb NO_2 for a 24 hour integrated sample at a flow rate of 1 l/min. The detection limit is defined as three times the standard deviation of the blank. This remains higher than NO_2 levels in remote areas[22].

Table 1 shows a summary of the reaction efficiency experiments. Each experiment represents a mean of the three cartridges placed in parallel and the errors represent the 95% confidence interval of the mean. The collection efficiency of this method was determined to be 100% since no detectable NO_2^- or NO_3^- was found on the back of the two cartridges in series. This result is in agreement of the finding of Nishikawa *et al.*[7,8], but not with that of Peschke *et al.*[16] who reported efficiencies as low as 91%.

The average reaction efficiency, defined as the fraction of the NO_2 that was detected as the sum of NO_2^- and NO_3^-, was determined to be 90 ± 19% and was independent of NO_2 loading. This result is comparable to the 87% and 98% reported by Sickles *et al.*[15] and Nishikawa *et al.*,[7,8] respectively, for TEA coated glass fibre filters and TEA-coated Sep-Pak C_{18} cartridges, but is much larger than the roughly 50% reported by Peschke *et al*[16] for TEA coated Sep-Pak C_{18} cartridges.

Table 1 also shows that 74±6% of the NO_2 signal was in the form of NO_2^-. This value is slightly lower than the 83% reported by Nishikawa *et al*[7]. In contrast, the values reported by Peschke *et al*[16] ranged from 35 to 78%.

Water was found to produce no interference as exposure of TEA coated cartridges to humid air did not produce higher blank values. In addition increased humidity also did not effect the collection or reaction efficiencies for NO_2/humid air samples. NO and O_3 were shown to produce no interferences individually. However, when a 10 ppb NO/40 ppb O_3 mixture was sampled, a positive interference corresponding to approximately 15% of the NO resulted. This finding is believed to be the result of O_3 adsorption onto the silica gel[23], thereby increasing the local O_3 concentration to allow the oxidation, perhaps heterogeneously, of NO to NO_2.

Table 1 Reaction and collection efficiency results – TEA Method.

NO_2 Concentration (ppb)	*Sampling Time (hours)*	*Reaction Efficiency (%)*	*% of Product as NO_2^-*
5	4.0	84±5	80±14
15	18.0	94±7	71±9
20	1.0	79±4	78±7
20	6.0	83±5	74±6
40	0.5	107±11	68±8
Average:		**90±19**	**74±6**

Table 2 PAN interference results for the TEA method.

PAN Concentration (ppb)	*Sampling Time (hours)*	*Interference (%)*	*% of Product as NO_2^-*
5.8	22.5	62±7	42±2
10.8	12.7	73±5	13±3
22.0	6.0	57±7	20±2
23.0	6.0	65±4	16±2
50.7	2.6	77±6	12±1
Average		**67±8**	**21±12**

Table 2 shows that PAN was found to produce a significant positive interference. The experiments, each done with three cartridges in series, yielded an average 67% interference, with the degree of interference being independent of PAN concentration. On average, 21% of the signal was detected as NO_2^-, which is significantly lower than the 74% determined for NO_2 samples. These results are in agreement with the findings of Sickles *et al*[15] for glass fibre filters. In contrast, Hisham and Grosjean[24] reported that, for TEA coated C_{18} cartridges, 73–110% of the PAN was detected as nitrite with no nitrate formation. Although the reason for the difference remains unclear it is likely due to the difference in the reagent substrates. Because PAN concentrations can exceed NO_2 concentrations in remote settings[22], this interference may have serious implications.

To determine if the observed interference is caused by a direct PAN-TEA reaction, or the thermal decomposition of PAN to NO_2 and the peroxyacetyl radical,[25] we exposed a group of four cartridges, half of which were cooled to 0°C, to identical PAN concentrations. No significant difference in the PAN interference between the two sets was observed which suggests that thermal decomposition is not the dominant mechanism. However when PAN was passed through an uncoated silica cartridge and eluted, approximately 20% of the PAN was detected as NO_2^- and NO_3^- which suggests that some adsorption and subsequent decomposition of PAN onto silica gel does occur.

Laboratory results-DPA method

The average of 45 blank values for N-nitrosoDPA, 2-nitroDPA and 4-nitroDPA were 1.9±0.72, 0.56±0.50 and 0.62±0.36 nmoles, respectively, corresponding to a detection limit of 0.03 ppb NO_2 for a 24 hour integrated sample at a flow rate of 4 l/min, as defined for TEA. This detection limit is close to a factor of 10 better than the detection limit estimated for the TEA method, and may be sufficiently low to allow measurements at remote sites.

The reaction efficiency experiments are summarized in Table 3, where each experiment represents the mean of three cartridges placed in parallel and the errors represent the 95% confidence limit. The collection efficiency was found to be 100% for all experiments, as no detectable amount of products was found on the back cartridges. The average reaction efficiency is 64±5%, which appears to be independent of total NO_2 loading. 61% of the recovered products, or 39% of the NO_2, was in the form of N-nitrosoDPA. These results are

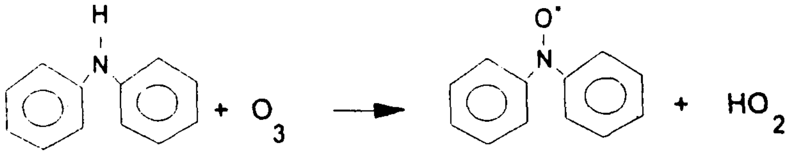
Table 3 Reaction and collection efficiency results – DPA method.

NO_2 Concentration (ppb)	*Sampling Time (hours)*	*Reaction Efficiency (%)*	*% Product as N-NitrosoDPA*
14.9	1.7	64±15	56±6
14.9	4.2	67±8	61±4
14.9	6.5	57±6	63±4
14.9	19.5	57±7	64±3
29.0	2.0	68±6	62±8
36.0	1.0	69±7	60±5
Average:		**64±5**	**61±3**

in conflict with the 80 and 98% reaction efficiencies respectively reported by Peschke *et al* [16] and Lipari[12]. Lipari[12] also reported that 94–98% of the total reaction product was in the form of N-nitrosoDPA. The reason for this difference remains unclear since the cartridges were prepared and eluted in a nearly identical manner. Although this result suggests that another product or products are formed in the NO_2/DPA reaction, no new peaks were observed in the chromatogram in comparison to the standard. Hence, any other products formed either do not absorb 254 nm light or do not elute from the column. Past studies[12,16] suggested that 4-nitrosoDPA could be formed in the reaction, though both studies found this to be an insignificant product, which we confirmed as well using standard samples. Recently Stine[26] detected 2,4′ dinitroDPA as a nitration product of DPA when DPA concentrations approached zero, and NO_2 reaction with the products becomes important. That condition was never satisfied in this study, hence no 2,4′-dinitroDPA was expected.

Water was determined not to interfere for this method as blank values did not increase upon exposure to humid air, and the reaction and collection efficiencies were unchanged for humidified NO_2/air samples. NO and O_3 also did not produce higher blank values when passed individually through DPA coated cartridges.

It is known that O_3 reacts with secondary amines[27] such as DPA as shown below.



The mechanism of the reaction and the yield and fate of the nitroxyl radical remain unclear. The O_3-DPA reaction does not produce NO_2-DPA reaction products as higher blanks were not produced upon exposure to O_3. However, the possibility of the NO_2-DPA reaction products, which are also secondary amines, reacting with O_3 was also examined by coating 24 cartridges with equivalent amounts of a standard containing the reaction products and an excess of DPA and exposing half of them to various concentrations of O_3. Figure 1 shows that exposure to O_3 reduced the concentration of the products on the cartridge. However the decrease in product concentration is not dependant on O_3 concentration for constant O_3

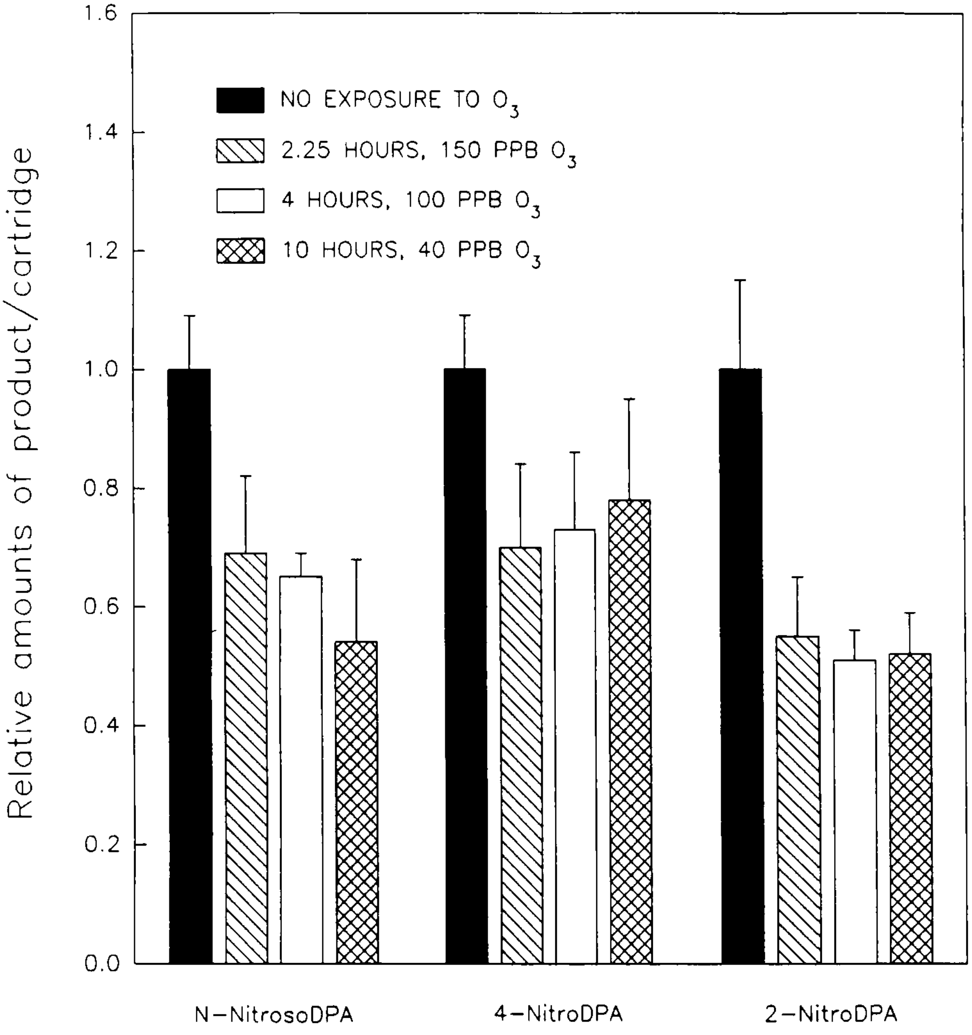


Figure 1 Ozone interference results for the DPA method.

loadings. Evaluation of the chromatograms reveals peaks at approximately 6 and 13 minutes that were not previously observed. To determine if these new products were unique to exposure to O_3, similarly coated cartridges were exposed to dry air, moist air and NO in dry air. There was no identifiable loss of products observed, nor were any new products identified in any case. Another investigation involved sampling 15 ppb NO_2 through two cartridges, while simultaneously sampling a 15 ppb NO_2/100 ppb O_3 mixture through two other cartridges in parallel. The product concentrations on the cartridges exposed to O_3 were 63% lower than on the control cartridges indicating that O_3 produces a significant negative

Table 4 PAN interference results for the DPA method.

PAN Concentration (ppb)	*Sampling Time (hours)*	*Interference (%)*	*% Products as N-NitrosoDPA*
5	21.5	45±7	62±6
10	12.0	44±11	65±4
18	6.0	40±5	59±5
30	2.0	41±8	62±4
Average:		**43±2**	**62±3**

interference in this method. This interference was not reported in the studies of Lipari[12] or Peschke *et al*[16].

PAN was determined to produce a significant positive interference. Table 4 shows PAN produces a 43±2% positive interference independent of PAN concentration, which is in agreement with the 45% and 50% positive PAN interferences reported by Peschke *et al*[16] and Lipari[12], respectively. Table 4 also shows that 62% of the total reaction product was in the form of the N-nitrosoDPA product, which is not significantly different than the 61% reported for the NO_2 experiments. Cooling of the cartridges exposed to PAN to 0°C did not affect the degree of interference, indicating that as for the case of TEA, PAN reacts directly with DPA.

Field results-TEA method

The TEA method was evaluated during both field studies. Throughout the intercomparison study of October 1990 duplicate samples were taken to determine method precision. A linear regression of one set against the other yielded a slope of 1.02±.04 (r^2=0.991), and an intercept of 0.38±1.4 ppb. For the intercomparison with the TDLAS, the average concentration obtained from the duplicate samples was used.

PAN was measured during both field studies. PAN concentrations were determined by gas chromatography with electron capture detection during the EMEFS study, and with luminol detection during the intercomparison study. These measurements allowed a correction for the PAN interference to be applied to the data. The correction consisted of subtracting 67% of the average daily PAN concentration from the NO_2 concentration determined by the ion concentrations.

The results of the two field studies are shown in Figure 2, where the ratio of the TEA and TDLAS determined NO_2 concentrations are plotted against the TDLAS value. There is a significant amount of scatter in the data with ratios of the TEA and TDLAS NO_2 concentrations ranging from 0.9 to 3.4 over the two field studies. However, it is clear that on average the TEA method overestimates the NO_2 concentration, as the average ordinate values were 2.1±0.6 and 2.0±0.2 for the EMEFS and intercomparison studies, respectively.

To investigate if the previously discussed O_3/NO interference is the cause of the NO_2 concentration overestimation by the TEA method we did a regression analysis of the

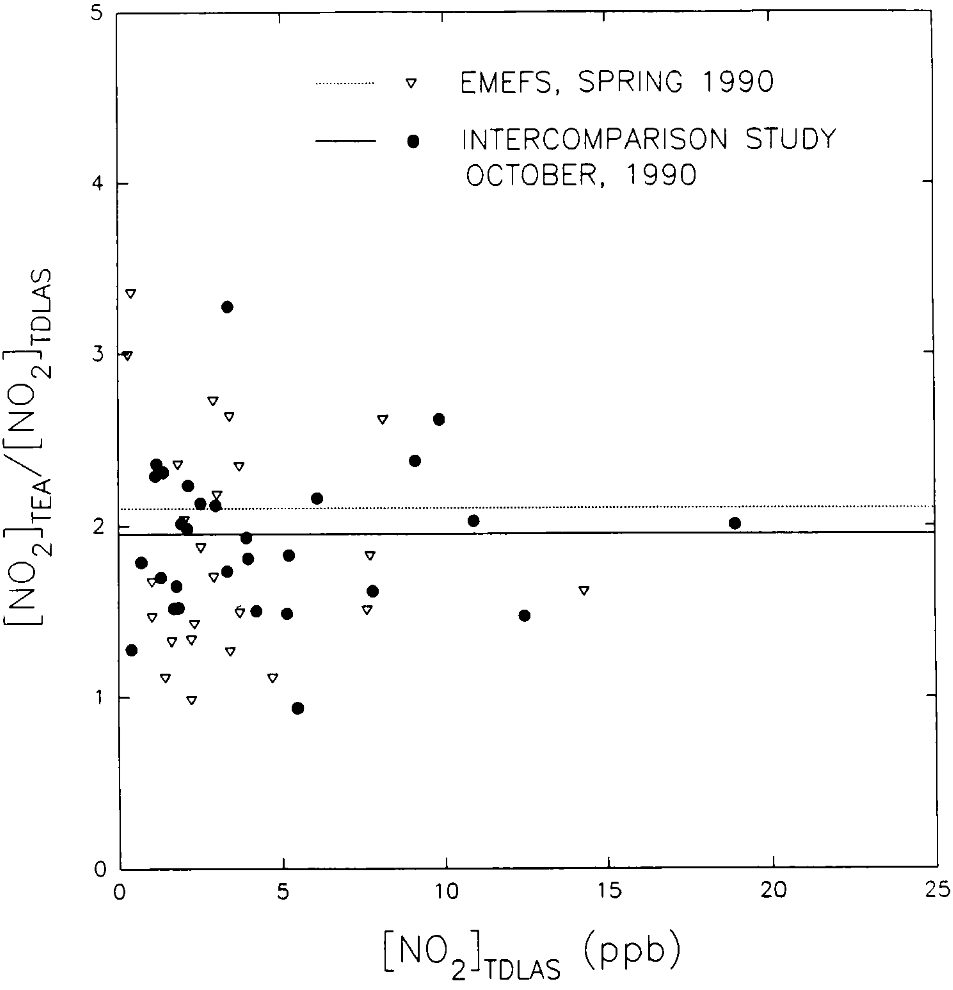


Figure 2 Ratio of TEA and TDLAS ambient measurements versus TDLAS measurement.

difference in the NO_2 concentrations determined by the TEA and TDLAS methods versus the product of the NO and O_3 concentrations, for the intercomparison study of October, 1990. This difference was a highly scattered function of the product $[O_3]$ [NO] (r^2=0.32), indicating no significant correlation between the two. Therefore, this interference does not appear to be the source of the error in the field values. Over the field study the average NO concentration was approximately 0.7 ppb, while the average daily NO_2 concentration was approximately 4.4 ppb, hence it is unlikely that NO caused a significant fraction of the overestimated NO_2 concentration.

Since nitric and nitrous acids and particulate nitrate are removed from the sample air[18], and we have corrected for the PAN interference, and ruled out NO, it is not evident what species caused the positive interference. Organic nitrates present in the atmosphere are typically 0–7% of the total reactive nitrogen[28,29], and therefore are not likely to be the source of an interference of this magnitude. To determine if the interference is caused by an unaccounted for nitrogen containing species, the difference in NO_2 concentrations determined by the TDLAS and the TEA method were compared against the residual nitrogen concentration. The residual nitrogen concentration was determined by subtracting the NO, NO_2, PAN and nitric and nitrous acid concentrations from the total reactive nitrogen (NO_y) concentration which was measured with a modified Monitor Labs model 8840 nitrogen oxides analyzer equipped with a gold converter[30]. It was determined that the residual reactive nitrogen concentration was, on average, not significantly non-zero, within the scatter of the measurements. There was no significant correlation between the difference in the TEA and TDLAS determined NO_2 concentrations and the residual nitrogen concentrations. Hence the overestimation by the TEA method does not appear to be a result of an unknown odd nitrogen species.

During the intercomparison study integrated weekly TEA samples were also taken. The results of the weekly samples were consistent with the daily samples. For the weekly samples collection efficiencies were consistently 100%. The average ratio of the summed (over 1 week) TEA daily sample concentration to the average TDLAS concentration was 1.9, while the average ratio for the weekly TEA samples was also 1.9.

It has been shown that the TEA method overestimates the ambient NO_2 concentration by approximately a factor of 2. This result is in contrast to the field study results reported by Sickles *et al*[15] for TEA coated filters, and with Nishikawa *et al*[7] for TEA coated C_{18} silica cartridges. Sickles *et al*[15] reported the TEA coated filters gave values only slightly higher than the TDLAS for similar ambient conditions, while Nishikawa *et al*[7] reported the TEA method yielded ambient concentrations similar to a modified Greiss-Saltzman technique for urban air. It is unclear why our results are systematically high. PAN, nitric acid, particulate nitrate, NO and O_3 were determined not to be the sources of this large error. No other reactive odd nitrogen species were identified that might cause a positive interference. However, the laboratory studies for NO/O_3 mixtures and these field studies indicate that the TEA-coated silica gel cartridge method is not suited to ambient air measurements.

Field studies-DPA method

The DPA method was evaluated in the field only during the intercomparison study of October 1990. Due to leakage problems encountered with cartridges, samples were obtained on only seven days. DPA samples were obtained in duplicate throughout the study. There was good agreement between the two sets of samples, with the regression yielding a slope of .94±.16 (r^2=0.97) and an intercept of .51±1.1ppb.

The reaction efficiency for this method (i.e. for conversion of NO_2 to the three measured products) was determined to be 64%. Therefore the ambient NO_2 concentration was determined by summing the concentrations of the NO_2-DPA reaction products and dividing by 0.64. A correction for PAN interference was also applied to the data, by subtracting 42% of the measured PAN concentration from the reaction efficiency corrected NO_2 concentration.

The results of the DPA method are plotted in Figure 3, where the ratio of the DPA and TDLAS determined NO_2 concentrations are plotted against the TDLAS concentration. The average ratio is 0.93±.25, with values ranging from 0.52 to 1.3 over the seven data points.

The product distribution for the ambient samples was considerably different than that observed for laboratory samples. For ambient samples, 90–100% of the products were detected in the form of N-nitrosoDPA, as opposed to 61% determined for the laboratory samples. This result suggests that the chemistry occurring between NO_2 and DPA in the laboratory differs from the chemistry under ambient conditions. Lipari[12] reported that approximately 90% of the products were consistently detected in the form of N-nitrosoDPA, under laboratory and field conditions. No reason for this difference could be identified as the cartridges were prepared and eluted in a manner identical to that used by Lipari. The

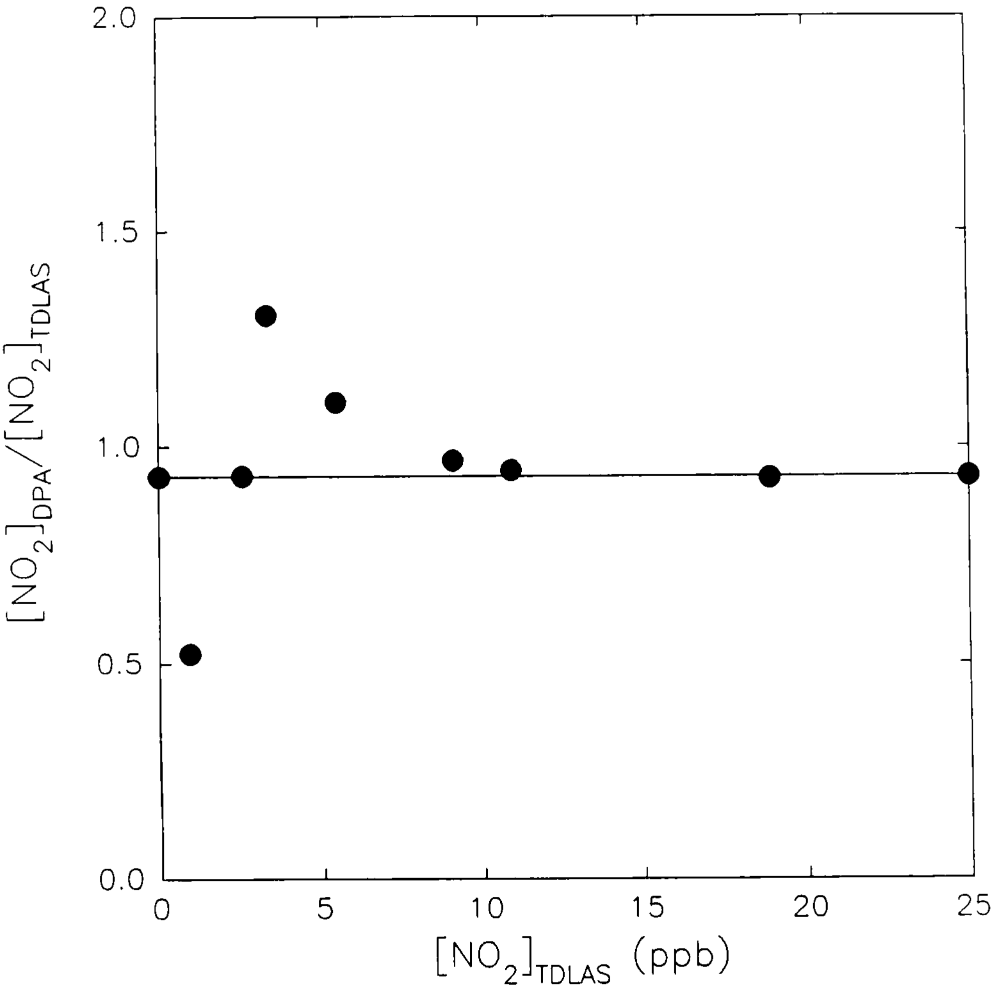


Figure 3 Ratio of DPA and TDLAS ambient measurements versus TDLAS measurement.

principal difference between the two cases is humidity, yet for laboratory conditions when NO_2/air standards were humidified no change was observed in the product distribution.

We determined from laboratory studies that O_3 reacts with the NO_2-DPA products to produce new products that were seen to elute at 6 and 13 minutes. These new peaks also appeared in the chromatograms for ambient samples. To investigate whether O_3 was producing an important interference in the field we did a regression of the difference between the TDLAS and DPA determined NO_2 concentrations versus the daily average O_3 concentrations. The regression yielded a slope of -0.065±0.047 (r^2=0.72), where the uncertainty represents the 95% confidence interval. Since we would have expected a positive slope, this result is difficult to understand. However, the data set covers a limited range of O_3 concentrations (≈15–40 ppb), yielding only a weak inverse correlation.

Although the field results of the DPA method are encouraging, a more extensive data set is required for a complete evaluation of the method. Although no correlation could be found between the difference in the NO_2 concentrations determined by the TDLAS and the DPA method and the ambient O_3 concentrations for the limited data set, the laboratory results clearly indicate that O_3 can be a source of significant negative interference.

CONCLUSIONS

This study involved a comparison of two solid sorbent integrating sampling techniques with the aim of determining the feasibility of using them in regional monitoring networks such as the Canadian Air and Precipitation Monitoring Network (CAPMoN). Collection and reaction efficiency experiments indicate satisfactory performance for the TEA method for laboratory samples. The detection limit of the TEA method was estimated to be 0.2 ppb for a 24 hour integrated sample, at 1 l/min. However, the finding that NO/O_3 mixtures result in a positive interference makes this method unacceptable for ambient air monitoring. We found that the TEA method overestimated the actual ambient NO_2 concentrations, although it is unclear what caused the interference. This method may, however, be useful for indoor air measurements, where O_3 concentrations are relatively low, and NO_2 concentrations can be much higher[31] (e.g. tens of ppb) than those found in our ambient samples.

The detection limit for the DPA method, estimated at .018 ppb for a 24 hour integrated sample at 4 l/min, is a factor of 10 better than for the TEA method, and is adequate for clean ambient air. Since the laboratory studies determined the collection efficiency to be 100%, and the reaction efficiency was determined to be relatively constant at 64±5%, this method shows promise. However, O_3 does react with the NO_2-DPA products resulting in a significant negative interference, for concentrations comparable to ambient polluted conditions. The field study of the DPA method yielded a limited but encouraging data set. Since O_3 interferes in both measurements, these or similar experiments should be repeated with the use of an ozone scrubber at the sample inlet. If the ozone interference can be removed, the DPA technique may offer a promising alternative for clean air monitoring sites, as well as for indoor air measurements.

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