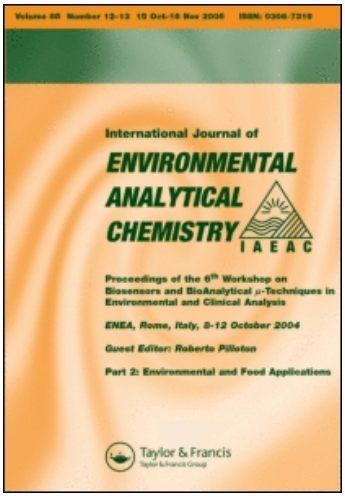

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THE DETERMINATION OF TOTAL NITRITE AND N-NITROSO COMPOUNDS IN ATMOSPHERIC SAMPLES

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A group-selective method for the determination of total N-nitroso compounds in air samples was developed. N-nitroso compounds in collected samples are selectively decomposed to yield nitric oxide, which is chemiluminescently detected using a thermal energy analyzer (TEA). The detection system is rapid, reproducible and sensitive, with a detection limit of 0.8 pmol. The method requires only 1–3 microliters of sample extract solution and can be used to analyze aqueous solutions. Nitrites interfere with the determination. However, by analyzing samples before and after treatment with sulfamic acid, total nitrite concentration can be measured from the difference in the two determinations.

The analytical technique was applied to the analysis of three collocated samples with a quartz filter followed by an XAD-II trap. The average concentration of total N-nitroso compounds collected on the quartz filters was 12.7 ± 2.4 pmol/m^3. The concentration of N-nitroso compounds collected by XAD-II was 19.1 ± 3.3 pmol/m^3. The total nitrite concentrations were 28.2 ± 3.4 pmol/m^3 and 25.5 ± 18.1 pmol/m^3 for material collected on the quartz filter and XAD-II, respectively. A fourth collocated sample spiked with diethylamine on the quartz filter gave higher concentrations of N-nitroso compounds in both the filter and the XAD-II bed. This increase indicates that artifact formation of N-nitroso compounds occurred during sampling. It is recommended that these artifacts be avoided in future sample collection by the use of diffusion denuders to remove the gas phase species before the collection of particles for accurate N-nitroso compounds analysis in ambient air.

Keywords: Total N-Nitroso compounds; total nitrite compounds; denitrosation reagents; thermal energy analyzer (TEA); atmospheric samples

INTRODUCTION

Over 300 N-nitroso organic compounds (NOC) have been tested for carcinogenicity and more than 90% of them show biological activity.[1] Hence great interest in NOC has been generated in the fields of cancer research and envi-

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ronmental analysis. Because of the ubiquity of the precursors of N-nitroso compounds and their ease of formation, they have been found in foods, cosmetics, rubber, drugs, explosives, biosamples, drinking water and air.[2] Humans may be exposed to these potential carcinogens both through ingestion or inhalation of pre-formed compounds and through in-vivo nitrosation.[3] Several methods have been established for total N-nitroso organic compound determination.[4–7] Generally they are based on chemical denitrosation and chemiluminescence detection of the released nitric oxide. Usually, these methods are quite sensitive and selective. However, the applicability of these developed methods to the analysis of atmospheric samples has not been established.

Atmospheric samples are complex. The determination of N-nitroso compounds is expected to be complicated by the presence of interfering species such as nitrites and nitrite esters. In addition, there are expected to be many different NOC with quite different structures and volatility in atmospheric samples. The structural differences among NOC could result in variations in the denitrosation process.[8] As a result, denitrosation reagents used successfully for other matrices might have serious tailing and other problems in the analysis of atmospheric samples. In addition, NOC pollutants in air are present at trace levels, requiring extraction and preconcentration of collected samples. Therefore a method with high sensitivity and requiring very small sample volume is desired for the measurement. Previously reported methods for NOC in environmental samples require 2–20 mL of sample even though some of the techniques have low detection limits.[9] Finally, atmospheric samples will contain water. Thus, an effective method for atmospheric sample analysis should also be tolerant to water. So far, few measurements of total NOC have been reported for ambient air,[10] partially because of the above mentioned reasons.

EXPERIMENTAL

Apparatus

Treatment of NOC in acid solution in the presence of an appropriate nucleophile results in the formation of the corresponding amines and free nitrous acid.[8] This denitrosation reaction is reversible. If the solution contains a trap for the nitrous acid or if nitric oxide is promptly removed from the solution, this denitrosation reaction can be made quantitative.

The denitrosation system used in this study is shown in Figure 1. N-nitroso compounds were denitrosated in a conical vial containing 1 or 2 mL of the denitrosation reagent. An inert gas, such as helium, was introduced through a

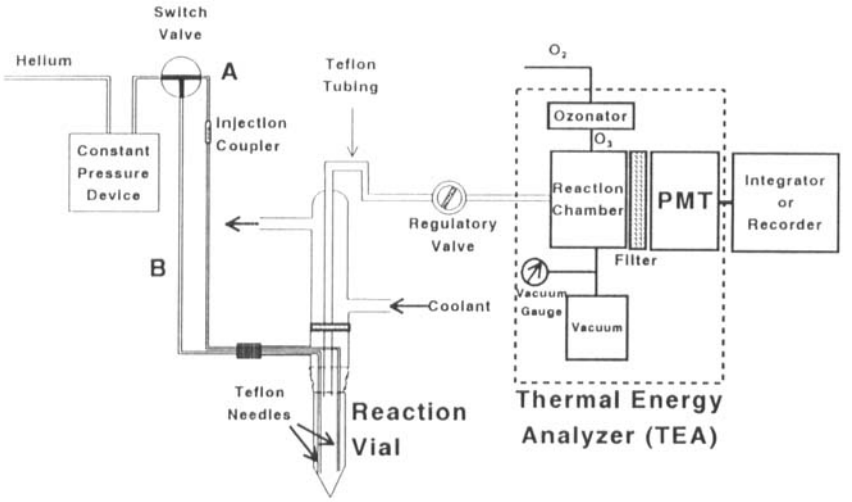


FIGURE 1 Schematic of the analysis system.

0.5 mm i.d. Teflon needle (either A or B in Figure 1) to sweep the released nitric oxide from the solution in the reaction vial into the detector. The amount of nitric oxide released is measured by a thermal energy analyzer (TEA model 543, Thermedics Inc., MA, U.S.A.). The TEA is a sensitive and selective chemiluminescence detector for the nitrosyl group.[11] All the tubing and connectors between the denitrosation vial and the TEA shown in Figure 1 are made of Teflon.

Reagents and Standards

Analytical grade reagents and standards were obtained from Aldrich, Mallinckrodt and E.M. Science: N-methyl-N-nitroso-p-toluenesulfonamide, N-nitrosodiphenylamine, diethylamine hydrochloride, and acetic acid (glacial). The explosive residue standards: nitrotoluene, nitroglycerine, 2,6-dinitrotoluene, N-nitrosodiphenylamine, 2,4-dinitrotoluene, 1-nitronaphthalene-d_p, pentaerythritol tetranitrate (PETN), 2-nitronaphthalene, 2,4,6-trinitrotoluene (TNT), 2-nitrodiphenylamine, 1,3,5-trinitrobenzene (TNB), tetryl, hexahydro--1,3,5-trinitro-1,3,5-triazine (RDX), 1-nitronaphthalene and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) were obtained from Mountain States Analytical (Salt Lake City, UT, U.S.A.). They were a mixture in acetyl nitrile solution with 5 ng/μl of each component. Stock methanol solutions of NOC were freshly made up gravimetrically to a nominal concentration of 1000 ng/μl. Standard calibration solutions were prepared by successive dilutions of the stock solutions.

Several denitrosation reagents were evaluated: (1) A solution of 3% (wt) HBr in glacial acetic acid was prepared in the same way as previously described.[4] (2) A 3% HBr-HOAc solution mixed with a concentrated inorganic acid, either phosphoric acid or sulfuric acid, in the volume ratio of 1/4 was prepared as described by Frank et al.[12] (3) A 3% (wt) NaI solution in glacial acetic acid. (4) A 3% (wt) HBr solution in glacial acetic acid was mixed at volume ratio of 1:5 with ethyl acetate.[7] (5) The solution in (4) with both hydrogen bromide (2% wt) and sodium iodide (1% wt) added with 10% (wt) phosphoric acid. All of the above denitrosation reagents were freshly prepared before an experiment.

Since many N-nitroso compounds such as N-methyl-N-nitroso-p-toluenesulfonamide and N-nitrosodiphenylamine used in this experiment are potential carcinogens, the solutions were all prepared and used in a hood with appropriate precautions to avoid direct contact with or inhalation of these chemicals. In addition, since all of the NOC standards are unstable under heat and UV light, the reagents and solutions were stored at $-10°C$ in amber bottles or vials.

Atmospheric Samples

Four collocated ambient air samples were collected for a three-day period from Aug. 31 to Sep. 3, 1995 in Provo, Utah at a flow rate of ~ 170 sLpm (standard liters per minute at 1 atm and 25°C). The inlet to each system was a virtual impactor[13] with a cut of 2.5 μm D_p. Following the inlet, particles smaller than 2.5 μm were collected on 47 mm quartz fiber filters, and gas phase components were captured in a trap with 50 mL of XAD-II. The quartz filters were baked at 800°C for 4 hours and then stored in a clean glass bottle at $-10°C$. The XAD-II resin were ultrasonically extracted with dichloromethane (DCM) (HPLC grade, Mallinckrodt) for five times and each time 30 minutes. The last time extract was analyzed to find none detectable NOC. Then the resin was vacuumed to dryness and stored in a closed bottle at ambient temperature.

Initial analysis of test samples collected on quartz filters and XAD-II traps involved extraction three times by sonication for 30 minutes with 20 mL of dichloromethane, and sonication three times with 20 mL of methanol (HPLC grade, Curtin Matheson Sci., Inc.), as previously described.[13] The combined extracts were concentrated to 0.6 mL in a K-D tube. The initial extracts of dichloromethane and methanol for ambient samples were analyzed separately for total NOC and nitrite concentrations. The concentrations of both NOC and nitrite in methanol were over four times higher than those in DCM. Therefore, we changed the solvent to a 1:2 (v/v) DCM-methanol mixture for analysis of the collocated samples. Using this solvent mixture, all samples were extracted three times with sonication for 30 minutes each time. To examine the complete-

ness of extraction, we extracted both the quartz filters and XAD-II traps for a fourth time with 20 mL of the solvent mixture and concentrated these extracts to 0.6 mL. The amount of NOC or nitrite found on this fourth extract was below the detection limit. In addition, blank quartz filter and XAD-II samples were also treated in the same way as the air samples.

Analysis Procedure

In each total NOC determination 1.0 mL of the denitrosation reagent was added to the reaction vial. The three-way valve, Figure 1, was set open to Teflon needle B, with Teflon needle A closed. The flow of helium was set at about 50 mL/min. When a stable baseline was seen on the TEA detector, the system was ready for an analysis. The injection coupler was then separated and a 1–3 μl sample was injected into needle A using an air-tight syringe with a fused silica needle (0.17 mm o.d. $\times$ 11.5 cm, Hamilton). The injection coupler was replaced and the sample liquid plug in needle A was swept into the denitrosation reagent by switching the three-way valve. The TEA response peak usually was seen in less than 5 minutes. The time to peak elution, the peak shape and the peak area are functions of the rate and completeness of the denitrosation reaction. Ideally, the elution time should be short and the peak should be sharp and symmetrical.

RESULTS AND DISCUSSION

Optimization of Conditions

The TEA was operated under the same conditions as previously described.[14] The reaction chamber pressure was 0.55–0.80 mmHg, and the ozone flow-rate was 2.5–12.0 mL/min. The helium gas flow had two counteracting effects. The helium was used to degas nitric oxide from the denitrosation solution. For this purpose, the helium flow should be kept high enough to degas efficiently. However, in the TEA reaction chamber the electronically excited nitrogen dioxide may decay to its ground state through both photo emission (detected by the PMT in the TEA) and collisional deactivation. At pressures below 1 atm, the only significant non-emitting decay route is deactivation through collisions with other molecules or the chamber wall.[11] Therefore, the flow of helium carrier gas into the reaction chamber should be as low as possible. The overall effect of helium flow on TEA sensitivity is shown in Figure 2. The signal reproducibility related to resetting a constant flow is illustrated by an error bar in Figure 2. Once the instrument is set and stable, the signal response is constant. Based

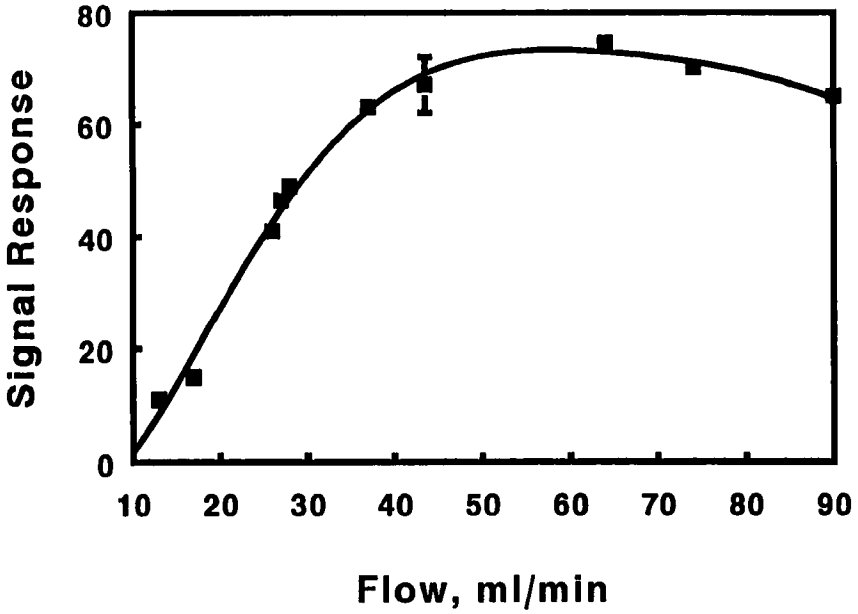


FIGURE 2 Effects of helium flow on sensitivity.

on the data in Figure 2, a constant helium flow in the range of 45–75 mL/min was used in the various experiments.

Denitrosation Reagents

Even though all NOC will denitrosate under acidic conditions in the presence of a nucleophilic catalyst, the NOC denitrosation rate is dependent on the compound structure, and the nucleophile and solvent used.[8] Usually, aromatic compounds (including alkyl or aryl-aniline derivatives) are more reactive, while dialkyl- and heterocyclic nitrosamines are less reactive in HBr-HOAc solution. The relative reactivities of the nucleophiles follow the sequence $Cl^- < Br^- < SCN^- < SC(NH_2)_2$ in water and 10% acetic acid, but change to $Cl^- < SCN^- < SC(NH_2)_2 < Br^-$ in 80% acetic acid. A good denitrosation reagent should have rapid and comparable reaction rates for a wide variety of N-nitroso compounds. An example of the desired detector response is illustrated in Figure 3(a). In this analysis, the peak was sharp and symmetrical. The denitrosation reaction was complete and degassing efficiency was high.

However, the situation was not as ideal for the atmospheric samples with very complex matrices. The responses of these samples to different denitrosation re-

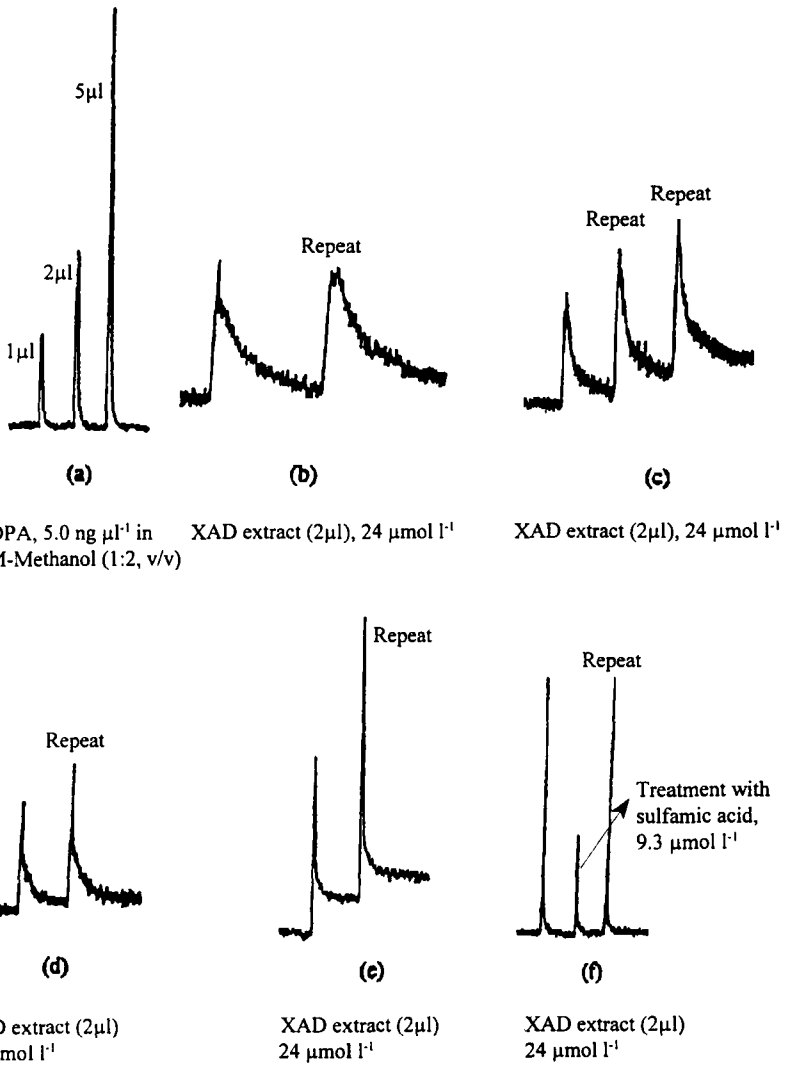
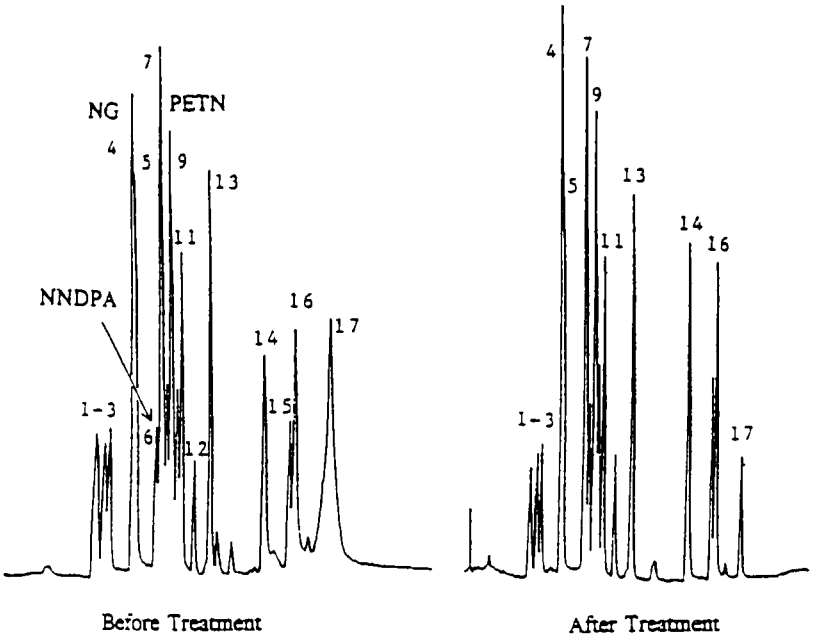


FIGURE 3 Typical responses of (a) NOC standards in HBr-HOAc 3% (wt) solution and extracted atmospheric samples using (b) HBr-HOAc 3% (wt), (c) HBr-HOAc 3% (wt) and 1/4 (v/v) phosphoric acid (conc.), (d) NaI-HOAc 3% (wt) and 1/4 (v/v) phosphoric acid (conc.), (e) HBr-HOAc 3% (wt) mixture with ethyl acetate at the ratio of 1:5 (v/v) and (f) HBr (2%)-NaI (1%)-HOAc mixture with ethyl acetate at the ratio of 1:5 (v/v) and 10% (wt) concentrated phosphoric acid added as denitrosation reagents.

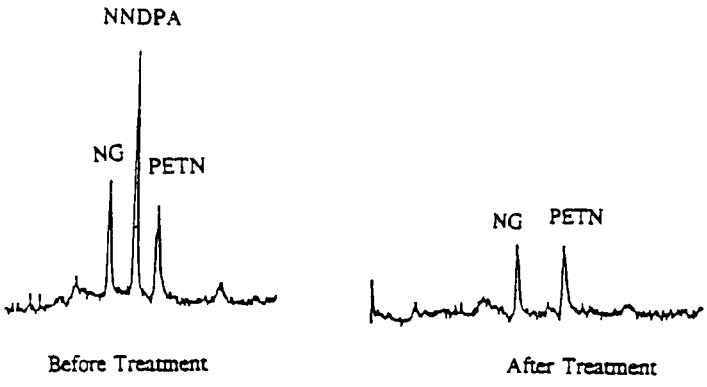
agents are illustrated in Figure 3(b)–(f). Only (f) had a good peak shape and stable baseline. In this denitrosation reagent, two halide ions (Br^- and I^-) were used simultaneously. They are complementarily effective for different kinds of NOC in acetic acid solution, so that all NOC could undergo denitrosation efficiently at the same time. Water in the solution was believed to improve the degassing efficiency of the system. As a result, the signal could return to its baseline more readily and quickly.

Specificity Test and Calibration

A series of experiments were conducted using denitrosation reagent (5) as described in Figure 3(f) (mixture of HBr and NaI) to test the specificity for N-nitroso compounds in the presence of nitro and nitrate compounds. An explosive standard, which contains a variety of nitro, nitroso and nitrate compounds, was analyzed by SFC-TEA before and after treatment with the denitrosation reagent. The denitrosation treatment was accomplished by adding 2 μl of the denitrosation reagent (described in Figure 3(f)) to 30 μl of the explosive standards solution. The mixture was then kept in an amber vial for at least 2 hours before it was injected onto the SFC column. The chromatographic conditions were the same as those previously described[14] and are given in Figure 4. For the results shown in Figure 4(a), the TEA pyrolyzer temperature was set at 800°C. At this pyrolysis temperature all of the nitro- and nitroso-compounds should give a response on the TEA detector. As expected, all compounds were detected. Included in the mixture in order of elution are (1)–(3) the three isomers of nitrotoluene, (4) nitroglycerine (NG), (5) 2,6-dinitrotoluene, (6) N-nitrosodiphenylamine (NNDPA), (7) 2,4-dinitrotoluene, (8) 1-nitronaphthalene-d_p, (9) pentaerythritol tetranitrate (PETN), (10) 2-nitronaphthalene, (11) 2,4,6-trinitrotoluene, (12) 2-nitrodiphenylamine, (13) 1,3,5-trinitrobenzene, (14) tetryl, (15) cyclotrimethylene trinitramine (RDX), (16) 1-nitronaphthalene, and (17) octogen (HMX). When the pyrolyzer temperature was 400°C, Figure 4(b), only NG, NNDPA and PETN gave measurable TEA responses. The response to the nitroso compound, NNDPA, was identical at the two temperatures as expected.[14] In addition, response to most nitro compounds was not present at the lower pyrolysis temperature as expected.[14] A significantly reduced response to the two hydroxylated nitro and nitrate compounds, NG and PETN, was observed. By comparing the two pairs of chromatograms in Figure 4(a) and (b), it is obvious that only the N-nitroso compound (N-nitrosodiphenylamine, NNDPA) was quantitatively decomposed in the denitrosation reagent. Thus, the interference from nitro compounds usually present in N-nitroso determination



(a)



(b)

FIGURE 4 SFC-TEA chromatograms for the analysis of a standard explosive mixture. Conditions: CO_2, 75 atm to 125 atm at 50 atm/min, then 5 atm/min to 220 atm, then 15 atm/min to 410 atm for 30 min, 68°C for 20 min, then 4°C/min to 120°C for 30 min, 10 m × 50 μm i.d. capillary column with p,p-cyanobiphenyl stationary phase, 0.25 μm film thickness. (a) pyrolyzer at 800°C, (b) pyrolyzer at 400°C. Treatment with the denitrosation reagent as described in Figure 3 (f).

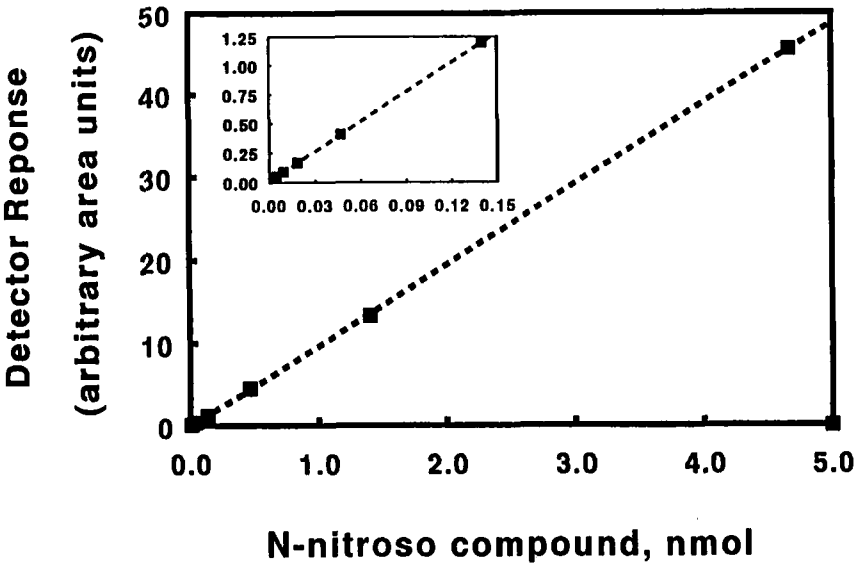


FIGURE 5 Calibration curve for NOC using N-methyl-N-nitroso-p-toluenesulfonamide as a probe.

with TEA is eliminated by the separate denitrosation procedure used in the developed analysis technique, Figure 1.

We used N-methyl-N-nitroso-p-toluenesulfonamide to investigate the linear dynamic range of the denitrosation and detection system illustrated in Figure 1. The calibration linear dynamic range was found to be at least four orders of

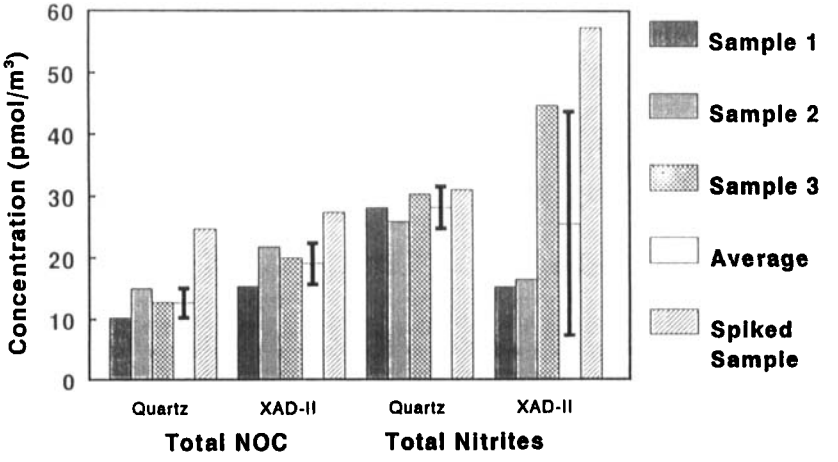


FIGURE 6 Total NOC and total nitrite concentrations in ambient air samples.

TABLE I Determination of Total Nitrites and NOC in Atmospheric Samples

Sample	*Before Treatment with Sulfamic Acid (pmol/m³)*		*After Treatment with Sulfamic Acid (NOC) (pmol/m³)*		*Total Nitrites* (pmol/m³)*	
	Filter	*XAD-II*	*Filter*	*XAD-II*	*Filter*	*XAD-II*
Blank1	N/D	54.1	N/D	N/D	—	54.1
Blank2	—	43.6	—	N/D	—	43.6
1	38.5	133.7	10.3	15.4	28.2	15.4
2	41.0	141.4	15.1	21.9	25.9	16.6
3	43.2	167.7	12.8	20.0	30.4	44.7
4	55.8	187.7	24.7	27.5	31.0	57.3

N/D not detected.

* The total nitrites were obtained by subtracting the values after treatment with sufamic acid from those before treatment.

magnitude, Figure 5. The plot was linear with a correlation coefficient of R = 0.9999. The linearity of the response demonstrates high denitrosation efficiency. The detection limit, calculated as three times the noise level, was 0.8 pmol.

Analysis of Atmospheric Samples

Of the four samples collected side-by-side in the Provo urban area Aug.31–Sep.3, 1995, three of them were replicates, whereas the fourth was spiked with diethylamine hydrochloride on the quartz filter to examine potential artifactual formation of nitrosamines during sampling. The experimental results are listed in Table I.

The direct denitrosation of the extracted environmental samples results in the determination of both NOC and nitrites (both inorganic and organic nitrites).[15] In order to distinguish between these two species, we treated the sample solutions for two hours with sulfamic acid (5% wt) in methanol solution. Nitrites will be decomposed in the sulfamic acid solution, whereas NOC will be unaffected.[5] The sum of NOC and nitrites was determined in samples not treated with sulfamic acid. The treated samples were analyzed with the denitrosation system to directly measure total N-nitroso compound concentrations. Nitrite was obtained as the difference, Table I. Nitrite and NOC in the blank quartz filter samples were below the analytical detection limit. In the blank XAD-II sorbent NOC was also not detectable, however, nitrite was detected at the level of 48.9 $\pm$ 5.3 pmol/m^3.

The total NOC results for the unspiked triplicate atmospheric samples were in good agreement. The average blank corrected NOC concentrations on the quartz filter and XAD-II trap were 12.7 $\pm$ 2.4 pmol/m^3 and 19.1 $\pm$ 3.3 pmol/m^3, respectively. The blank corrected sums of NOC and nitrite in the samples analyzed without sulfamic acid treatment were higher, 40.9 $\pm$ 2.4 pmol/m^3 and

44.6 ± 17.8 pmol/m^3 respectively on the quartz filter and XAD-II samples. The large standard deviation for XAD-II results before sulfamic acid treatment may be due to artifact formation of nitrites during sampling with the XAD-II sorbent. The total measured NOC concentrations for the fourth sample quartz filter spiked with 65.1 mg of diethylamine hydrochloride prior to sample collection were higher for both the quartz filter and XAD, Figure 5. We conclude that there is artifactual formation of nitrosamines during sampling in an amine spiked sample. The increase in the concentration of NOC in the XAD-II trap of this sample can be attributed to the lost of some of the amine or artifactual semi-volatile NOC from the spiked filter. About 40% of the artifactually formed NOC was collected by the XAD-II sorbent.

CONCLUSIONS

An analytical technique for total N-nitroso and nitrite compounds has been developed and applied to the analysis of ambient air samples. This method provides rapid and continuous analysis (less than 5 min for a determination). The technique requires only 1–3 μl of sample extract solution. The detection limit for NOC or nitrite is 0.8 pmol. The selectivity of the detection system for NOC is excellent, with the only identified interferences being from nitrites. The concentration of nitrite compounds can be estimated by analysis of sulfamic acid treated and untreated samples. This method should also be applicable, with little adjustment, to a wide variety of samples, such as food extracts, biological fluids, etc.

Artifactual formation of NOC may be a problem in sampling with a filter and XAD-II sorbent combination. Thus, samplers employing diffusion denuders, such as the BOSS[16] and BIG BOSS,[17] should be used for the collection and determination of NOC in the atmosphere.[18]

Acknowledgements

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References

[1] R. Preussmann and B. W. Stewart, *N-Nitroso Carcinogens, ACS Monogr.*, **182** (Chem. Carcinog., 2nd Ed., Vol 2), 643–828 (1984).

[2] R. N. Loeppky, "Nitrosamine and N-Nitroso Compound Chemistry and Biochemistry: Advances and Perspectives", *Nitrosamines and Related N-Nitroso Compounds: Chemistry and Biochemistry* (American Chemical Society, Washington, D.C., 1994) pp 1–18.

[3] C. L. Walters, P. L. R. Smith and P. I. Reed, *IARC Int. Agency Res. Cancer Sci. Publ.*, **57**, 113 (1984).

[4] G. S. Drescher and C. W. Frank, *Anal. Chem.*, **50**, 2118–2121 (1978).

[5] B. Pignatelli, I. Richard, M. C. Bourgade and H. Bartsch, *Analyst*, **112**, 945–949 (1987).

[6] K. Kikuchi, T. Nagano, H. Hayakawa, Y. Hirata and M. Hirobe, *Anal. Chem.*, **65**, 1794–1799 (1993).

[7] C. L. Walters, R. J. Hart and P. L. R. Smith, *IARC Int. Agency Res. Cancer Sci. Publ.*, **45**, 295 (1983).

[8] L. R. Dix, S. M. Oh and D. L. H. Williams, *J. Chem. Soc., Perkin Trans.*, **2**, 1099–1104 (1991).

[9] B. Pignatelli, C. S. Chen, P. Thuillier and H. Bartsch, *Analyst*, **114**, 1103–1108 (1989).

[10] D. Grosjean, *J. Air Waste Manage. Assoc.*, **41**, 306–311 (1991).

[11] I. S. Krull, T. Y. Fan and D. H. Fine, *Anal. Chem.*, **50**, 698–701 (1978).

[12] C. W. Frank, P. J. Nord and R. D. Cox, *U.S. Patent* 4,256,462 (1981).

[13] H. Tang, E. A. Lewis, D. J. Eatough, R. M. Burton and R. J. Farber, *Atmos. Environ.*, **28**, 939–947 (1994).

[14] E. S. Francis, D. J. Eatough and M. L. Lee, *J. Microcol. Sep.*, **6**, 395–401 (1994).

[15] I. S. Krull, E. U. Goff, G. G. Hoffman and D. H. Fine, *Anal. Chem.*, **51**, 1706–1709 (1979).

[16] D. J. Eatough, C. L. Benner, J. M. Bayona, J. M. Caka, G. Richards, J. D. Lamb, E. A. Lewis and L. D. Hansen, *Environ. Sci. Technol.*, **23**, 679–687 (1989).

[17] D. J. Eatough, A. Wadsworth, E. A. Eatough, J. W. Crawford, L. D. Hansen and E. A. Lewis, *Atmos. Environ.*, **27**(8), 1213–1219 (1993).

[18] Y.-M. Ding, W. Cui, M. L. Lee and D. J. Eatough, *Proc. EPA/APCA Symposium on Measurement of Toxic and Related Pollutants*, Air Pollution Control Association, 12–23 (1996).