Measurement of NO_y and Potential Artifacts

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Background

Oxidized nitrogenous species play a critical role in the formation of ozone in the atmosphere. For both smog chambers and ambient air, a knowledge of the mass balance of such species is useful for the development and validation of methods to model ozone formation. The term NO_y has been developed to represent such species although the definition depends on whether it is used by a modeler or an analyst. The modeler would like a measure of the total reactive nitrogen oxides, or odd nitrogen, while the analyst uses an operational definition as the response of a chemiluminescent NO analyzer after the sample is treated with a converter that reduces more highly oxidized species to NO. The term $(NO_y)_i$ has been used to designate this operational definition from that of NO_y. These definitions, though slightly different, should be quite similar based on our knowledge of the individual oxidized nitrogenous species typically found in ambient air. Other definitions in general use are NO_x ($NO + NO_2$) and NO_z ($NO_y - NO_x$).

It is generally agreed that NO_y consists primarily of nitric oxide (NO), nitrogen dioxide (NO_2), peroxyacetyl nitrates (PacNs, primarily peroyactyl nitrate (PAN) and peroxyproyl nitrate (PPN)) , nitric acid (HNO_3), particulate nitrate, and nitrous acid (HONO) roughly in that order of importance. Commercial converters have been shown to readily reduce these gaseous species while they have no efficiency for N_2O or organic nitro compounds, species which modelers do not consider photochemically reactive (Winer et al., 1974). The reduction efficiency for particulate nitrate may vary with converter design, although little quantitative work has been reported in this area.

Most converters for nitrogen oxide reduction use either heated gold or molybdenum surfaces. Although they may be designed to minimize the collection of particulate nitrate (PN), ammonium nitrate is the most prevalent form of PN in ambient air. The high temperature of the converter will easily volatilize it into ammonia and nitric acid, the former being readily reduced to NO within the converter. Other converters have been constructed with ferrous sulfate at ambient temperature and vitrous carbon at high temperature. High temperature stainless steel has also been used, but the temperatures necessary for high reduction efficiency result in a significant efficiency for ammonia reduction to NO.

$(NO_y)_i$ converters are typically placed outside while the detector assembly remains in an air-conditioned environment. This is done to insure that the sampling lines do not adsorb nitric acid. This is a major problem when the humidity is increased when the sample is transported to a lower temperature in an air-conditioned shelter. To prevent the adsorption of nitric acid, $(NO_y)_i$ sampling must be conducted without a particulate filter using the shortest possible PFA Teflon inlet line to the converter. If NO is also to be measured and the switching valve remains in the analyzer, a separate sample line is run between the inlet and the cycling valve. Calibration gases are introduced at this inlet. Depending on the distance from the analyzer, sample flow rate, and cycling time (between $(NO_y)_i$ and NO modes) of the instrument, bypass flow may be required due to the distance between the converter and the detector.

The objective of this paper is to describe some of the interferences, biases, and idiosyncrasies that we and others have observed when measuring NO_y. It is important to note that much of the reported $(NO_y)_i$ measurement studies have focused on unpolluted air, while we have been making measurements on relatively polluted air in which NO_x was often a minor component of the $(NO_y)_i$. It should also be noted that he sub ppb sensitivity of the new generation of commercial NO analyzers have made these measurement artifacts more noticeable.

Interferences

One of the problems when using a chemiluminescent analyzer to measure NO is that water quenches the chemiluminescence. This results in a small zero bias and a larger span bias, up to 10% (Fahey et al., 1985). This raises the question of what type of air to use to assess the zero and span response. Ideally the air should be scrubbed of all species that would cause an instrumental response, but this is unlikely to be achieved. The method of standard addition is an approach that has been previously employed. In this approach, known amounts of calibration gases are added to the air being sampled by the analyzer. The calibration gases' concentrations are much higher than the desired calibration point, thus the flow rate of the calibration gas is small compared with the analyzer's flow rate. This method works best in a rural environment where concentrations are not rapidly changing. A potential solution to the rapid changes in an urban environment would be to capture ambient air in an inert flexible container (such as a Teflon bag), mix it well, and then use it as a diluent for a cylinder of NO calibration gas.

The potentially more important source of interference is the reduction converter. Although these were designed to reduce NO_2 to NO, it is well known that they reduce most of the nitrogen oxides except organic nitro compounds and nitrous oxide. Due to the high natural background of nitrous oxide, all potential converters must be shown to have virtually no reduction efficiency for this compound. Commercial NO-NO_x analyzers generally used converters based on molybdenum. Complete conversion is obtained at a temperature of 350 °C rather than the 500 °C or more required for stainless steel. Although these lower temperature converters should minimize the reduction of ammonia, we have found converter efficiencies that varied from 5 to 25% for this species as shown in Table 1. The efficiency did not correlate with the converter temperature. A representative of the manufacturer stated that these conversion efficiencies are normal and that they usually rise as the converter ages due to the production of molybdenum trioxide (Kieta, 1999). Hot spots caused by the heater design may also lead to molybdenum decompositions (Williams, et al., 1998).

Hydrocarbons have also been shown to affect converter efficiency, and a memory effect after sampling high NO_y concentrations has been observed by us and others (Fehsenfeld et al., 1987). The memory effect results in a significant and decreasing background after the zero is supplied to the converter after sampling polluted ambient air. We have observed concentrations as high as 6ppb on zero air that gradually fall to zero after many hours of sampling zero air. Bypassing the converter eliminates this memory artifact. The memory effect can be reduced by daily bakeout at 600 °C (Fehsenfeld et al. 1987), although this is inconvenient and can lead to early converter failure.

We have also observed a selective degradation of converter efficiencies in $(NO_y)_i$ analyzers. In this case converter temperatures were adjusted to achieve near 100% efficiency for NO_2, PAN, HONO, HNO_3 , and n-propyl nitrate (NPN). After the instruments were used for one summer to measure ambient air concentrations at locations of varying air quality they were brought together to sample air during photochemical oxidations conducted in our environmental chamber. Figure 1 shows the results of $(NO_y)_i$ measurement during one experiment. In the dark, when only NO and NO_2 are in the chamber, all of the instruments show nearly the same concentrations. After the lights are turned on NO (measured by a chemiluminescent analyzer without a converter) drops rapidly, the NO_2 (measured by a tunable diode laser absorption spectrometer, TDLAS) rises to a maximum then drops, and the $(NO_y)_i$ concentrations slowly diverge as more oxidized $(NO_y)_i$ species are formed.

Catalysts consisting of heated gold tubing have been reported in a number of research applications, particularly in rural areas (Bollinger et al., 1983). Either CO or H_2 is added to the sample stream to facilitate the reduction of $(NO_y)_i$. The conversion efficiencies of this type of converter for NH_3 and HCN was found by Fahey and co-workers (1986) to be significant with dry air but negligible with ambient levels of water vapor. These converters have been shown to have the potential for significant efficiency for ammonia and cyanides and to be dependent on water, ozone concentration and previous sampling history. Converter design and temperature profiles are also likely to affect the conversion efficiency for these compounds. The conversion efficiency is also affected by relative humidity and pressure of the air sampled (Crosly, 1996). Kliner and co-workers (1997) reported a detailed laboratory study of gold and other metallic converter and found gold to be the best material for tube construction. H_2 was preferred over CO as losses of the latter were observed on the stainless steel components of the converter and was not as efficient at converting NPN. They reported substantial conversion efficiencies for HCN and NH_3 to NO, especially under dry conditions. Measurement artifacts due to impurities in the CO source have also been reported (Wang et. al., 1996). Frequent cleaning is apparently needed under ambient sampling to maintain high $(NO_y)_i$ conversion efficiency and in one case full efficiency could not be restored by cleaning (Bollinger et al. 1983; Fahey et al. 1986;Wang et al., 1996; Williams et al., 1998).

Both gold and molybdenum-based converters of different designs have been used in a variety of $(NO_y)_i$ intercomparison studies (Fehsenfeld, 1987, Williams et al. 1998). These converters have been found to generally give similar $(NO_y)_i$ measurements although some groups systematically reported lower concentrations. Selective loss of nitric acid conversion efficiency has been observed for both types of converters (Williams et al., 1998). This study also showed that ammonia conversion efficiencies ranged from zero to twelve per cent. William et al. conclude that $(NO_y)_i$ measurements require constant attention from experienced personnel, frequent converter efficiency checks (including on-site nitric acid and ammonia), and redundant instruments.

Other converters have been reported but not widely used. Ferrous sulfate effectively reduces NO_2 (Helas et al., 1981), but has variable efficiency for other $(NO_y)_i$ components (Fehsenfeld et al., 1987) and a significant memory effect (Dickerson, 1985). A former NO-NO_x analyzer manufacturer used a heated vitrous carbon converter, but no studies of potential interferences have been reported.

Regardless of the type of converter used, $(NO_y)_i$ must be sampled without a particulate filter. The efficiency for conversion of particulate nitrate to NO has not been quantified and will depend on the cation and most likely a number of environmental variables. Also complicating the evaluation is the difficulty in removing nitrogenous species from the particulate matter or vice versa due to the equilibium between nitric acid, ammonia, and ammonium nitrate and the affinity of the ammonia and nitric acid to adsorb on surfaces and collected particulate matter.

Compound X

Studies where the major individual NO_y species are measured (NO, NO_2, PAN, PPN, HNO_3, NO_3^-) and added together result in a summation that is typically significantly less than the measured $(NO_y)_i$. This missing species has been dubbed compound X and the significance of this missing species appears to be location and method dependent. Fahey et al. (1986) speculated that this compound X was an organic nitrate other than PAN of PPN. Further evidence of missing $(NO_y)_i$ species have been reported by others (Roberts, 1990; Ridley, 1991; Parrish et al., 1993; Nielsen et al., 1995).

Crosley (1996) summarized the evidence for compound X and conclusions from a panel of $(NO_y)_i$ measurement experts. They concluded that the excess $(NO_y)_i$ could likely be due to adsorption/desorption of nitric acid in the inlet to the converter. Williams et al. (1997) observed that the missing $(NO_y)_i$ correlated directly with the ratio of NO_x to NO_y O_3 and aerosols and inversely with temperature suggesting that one or more individual NO_y species were not being measured (perhaps a compound X).

Experiments that we recently performed on dual converter $(NO_y)_i$ analyzers have shown that some or all of the compound X may be due to ammonia. These instruments were designed to measure nitric acid by the difference between the response of the $(NO_y)_i$ channel and a similar channel from which the nitric acid is removed with a sodium chloride coated filter. After using two instruments to measure nitric acid for a summer, we conducted a quality control test in which the sodium chloride filters were removed and the instruments set up to sample air from which nitric acid had been removed using a sodium chloride coated filter. Figure 2 shows the results of measuring the difference between the two channels for several days in Riverside, California. Rather than a response near zero (all nitric acid has been removed prior to the sample inlet and the analyzers did not have filters to remove nitric acid), we saw negative peaks each day in the afternoon. In the afternoon Riverside is usually downwind of a large concentration of dairies. Significant ammonia concentrations have routinely been observed in Riverside. Based on these findings and our laboratory testing of the conversion efficiency of ammonia, we feel that ammonia was causing this measurement artifact. In this case, the converters that were used on the channel scrubbed of nitric acid were more efficient in converting ammonia than the $(NO_y)_i$ converters, thus resulting in a negative concentration when the difference is taken.

Molydenum Converter Idiosyncrasies-note that sub ppb sensitivity has exacerbated the idiosyncrasies

- Lag time with various species- especially nitric acid, but ambient air in general.
- Zero bias or memory effect, especially for $(NO_y)_{i.}$
- Converter hysteresis – show Riverside HNO_3 scrubbed air- this may explain some of the inconsistencies reported in the literature.
- Lowered efficiency when placing the converter at the sample inlet ahead of the flow control capillary.

Conclusions

- There are considerable conflicting reports with respect to convert efficiencies for $(NO_y)_i$ compounds and interfering compounds.
- The use of presently used converters result in significant biases and interferences which center on more highly oxidized species such as HNO_3 .
- Better converters need to be developed.
- Until better converters are developed frequent zero checks (perhaps every hour or two) are needed as well as routine assessment of converter efficiency for both NO_y and ammonia.
- Acid coated diffusion denuders may be useful in removing ammonia so that it does not interfere with $(NO_y)_i$ measurements. It will be necessary to thoroughly test such a denuder to insure that it does not remove a significant amount of $(NO_y)_i$ species.

References

Bollinger, M.J., Sievers, R.E., Fahey, D.W., and Fehsenfeld, F.C. (1983) Conversion of nitrogen dioxide, nitric acid, and n-propyl nitrate to nitric oxide by gold-catalyzed reduction with carbon monoxide. *Anal. Chem.* **55,** 1980-1986.

Crosley, D.R. (1996) NO_y blue ribbon panel. J. *Geophys. Res.* **101** 2049-2052.

Dickerson, R.R. (1985) Reactive nitrogen compounds in the Arctic. *Geophys. Res.* **90**, 10,739-10743.

Fahey, D.W., Eubank, C.S., Hubler, G., and Fehsenfeld, F.C. (1985) Evaluation of a catalytic reduction technique for the measurement of total reactive odd-nitrogen NO_y in the atmosphere *J. Atmos. Chem*. **3,** 469-489.

Fahey, D.W., Hubler, G., Parrish, D.D., Williams, E.J., Norton, R.B., Ridley, B.A., Singh, H.B., Liu, S.C. and Fehsenfeld, F.C. (1986) Reactive nitrogen species in the troposphere: measurements of NO, NO_2, HNO_3, particulate nitrate, peroxyacetyl nitrate (PAN), O_3, and total reactive odd nitrogen (NO_y) at Niwot Ridge, Colorado. *J. Geophys. Res.* **91** 9781-9793.

Fehsenfeld, F.C., Dickerson, R.R., Hubler, G., Luke, W.T., Nunnermacker, L.J., Williams, E.J., Roberts, J.M., Calvert, J.G., Curran, C.M., Delany, A.C., Eubank, C.S., Fahey, D.W., Fried, A., Gandrud, B.W., Langford, A.O., Murphy, P.C., Norton, R.B., Pickering, K.E., and Ridley, B.A. (1987) A ground-based intercomparison of NO, NO_x, and NO_y measurement techniques. J. *Geophys. Res.* **92,** 14,710-14,722.

Helas, G., Flanz, M., and Warneck, P. (1981) Improved NO_x monitor for measurements in tropospheric clean air regions. *Intern. J. Environ. Anal. Chem*. **10,** 155-166.

Kita, D. (1999) Personal communication.

Kliner, D.A.V., Daube, B.C., Burley, J.D., and Wofsy, S.C. (1997) Laboratory investigation of the catalytic reduction technique for measurement of atmospheric NO_y. J. *Geophys. Res.* **102,** 10,759-10,776.

Nielsen, T. (1995) Observations of particulate organic nitrates and unidentified components of NO_y. *Atmos. Environ*. **29,** 1757-1769.

Parrish, D.D., Buhr, M.P., Trainer, M., Norton, R.B., Shimstock, J.P., Fehsenfeld, F.C., Anlauf, K.G., Bottenheim, J.W., Tang, Y.Z., Wiebe, H.A., Roberts, J.M., Tanner, R.L., Newman. L., Bowersox, V.C., Olszyna, K.J., Bailey, E.M., Rodgers, M.O., Wang, T., Berresheim, H., Roychowdhury, U.K., and Demerjian, K.L. (1993) The total reactive oxidized nitrogen levels and the partitioning between the individual species at six rural sites in eastern North America. J. *Geophys. Res.* **98,** 2927-2939.

Ridley, B.A. (1991) Recent measurments of oxidized nitrogen compounds in the troposphere. *Atmos. Environ*. **25A,** 1905-1926.

Roberts, J.M. (1990) The atmospheric chemistry of organic nitrates. *Atmos. Environ.*, Part A, **24,** 243-287.

Wang, T, Carroll, M.A., Albercock, G.M., Owens, K.R., Duderstadt, K.A., Markevitch, A.N., Parrish, D.D., Holloway, J.S., Fehsenfeld, F.C., Forbes, G., and Ogren, J. (1996) Ground-based measurements of NO_x and total reactive oxidized nitrogen (NO_y) at Sable Island, Nova Scotia, during the NARE 1993 summer intensive. *J. Geophys. Res.* **101,** 28,991-29,004.

Williams, E.J., Roberts, J.M., Bauman, K., Bertman, S.B., Buhr, S., Norton, R.B., and Fehesenfeld, F.C. (1997) Variations in NO_y composition at Idaho Hill, Colorado. J. *Geophys. Res.* **102** 6297-6314.

Williams, E.J., Bauman, K., Roberts, J.M., Bertman, S.B., Norton, R.B., Fehsenfeld, F.C., Springston, S.R., Nunnermacker, L.J., Newman, L., Olszyna, K., Meagher, J., Hartsell, B., Edgerton, E., Pearson, J.R., and Rodgers, M.O. (1998) Intercomparison of ground-based NO_y measurement techniques. J. *Geophys. Res.* **103** 22,261-22,280.

Winer A.M., Peters, J.W., Smith, J.P., and Pitts, J.N. Jr. (1974) Response of commercial chemiluminescent NO-NO_x analyzers to other nitrogen-containing compounds. *Environ. Sci. Technol.* **8**, 1118-1121.

Table 1. $(NO_y)_i$ converter efficiency for ammonia (56ppb) for a variety of $(NO_y)_i$ analyzers with molybdenum-based converters.

% NH_3 Conversion	**Converter Temperature, °C**
14.8%	315
26.8%	313
5.2%	360
4.5%	376
10.4%	359
10.4%	374
7.7%	361
26.6%	314
5.2%	370
9.5%	365
2.5%	301
11.2%	**Average**

Figure 1. Response of $(NO_y)_i$ analyzers to synthetic polluted air generated in a smog chamber.

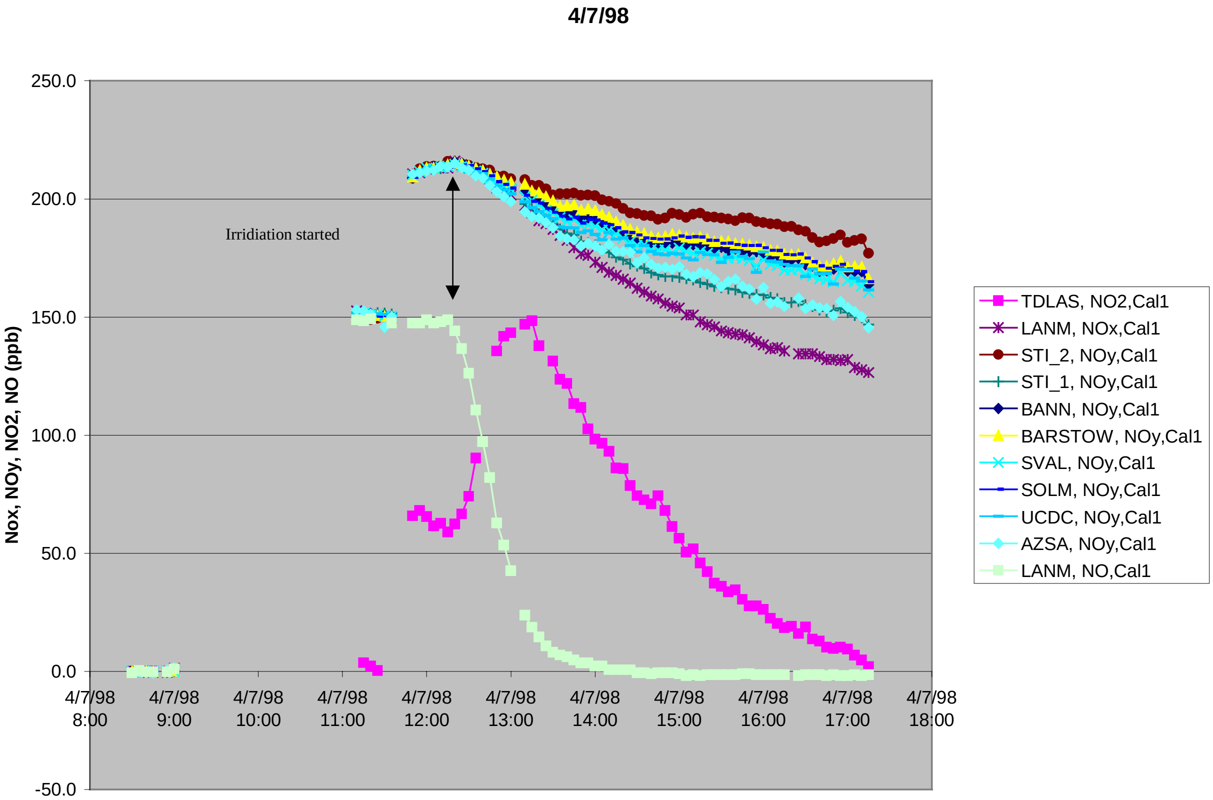

Figure 2. Nitric acid channel (NA) response (ppb) to filtered ambient air with nitric acid removed.