FACT SHEET FOR NO_y MONITORING

Introduction

Reactive nitrogen compounds (NO_y) have been identified as precursors for both ozone and fine particulate matter ($PM_{2.5}$). The National Ambient Air Monitoring Strategy (NAAMS) calls for deployment of NO_y monitors at approximately 75 locations. OAQPS has begun an effort to gain knowledge and experience with NO_y monitoring in order to resolve a number of technical issues that have been identified with NO_y monitoring, as well as to be prepared to provide support to State and Local monitoring agencies as they begin to purchase, install, and operate NO_y monitors.

Definition of NO_y

NO_y consists of all oxides of nitrogen in which the oxidation state of the N atom is +2 or greater, ie, the sum of all reactive nitrogen oxides including NO_x ($NO + NO_2$) and other nitrogen oxides referred to as NO_z. The major components of NO_z include nitrous acids [nitric acid (HNO_3), and nitrous acid (HONO)], organic nitrates [peroxyl acetyl nitrate (PAN), methyl peroxyl acetyl nitrate (MPAN), and peroxyl propionyl nitrate, (PPN)], and particulate nitrates.

$$NO + NO_2 + NO_z = NO_y$$

Principle of Operation

The current recommendation for the measurement of NO_y is the use of a thermal converter to convert reactive nitrogen species to NO followed by detection of NO by its chemiluminescence reaction with an excess of O_3. NO is measured by bypassing the converter. The combination of NO_2 and NO_z can be then determined by difference. This procedure is similar to the current methodology used to measure NO_x, however, the converter temperature is higher in order to more completely convert NO_z species, and the converter has been moved to very near the sample inlet to avoid line losses of "sticky" NO_y species such as HNO_3.

Literature Search

Based on the results of a literature search, three manufacturers of trace level NO_y monitors have been identified. The specifications for the three analyzers are provided in Table 1. The price for these analyzers are in the range of $15,000 and $20,000. See the internet websites below for additional information on these analyzers, and vendor contacts in your area:

http://www.teledyne-api.com/products/index.asp
http://www.thermo.com/
http://www.ecotech.com.au/ml9800.htm

Trace Level Modifications

A number of modifications are typically made to the standard NOx/NOy monitor to improve the detection limit for trace gas monitoring. Depending on the particular make, modifications may include the following:

- Pre-reactor to eliminate non-NOy interferent,
- Increase sample flow rate, and
- Improved temperature controls in photomultiplier tube.

Calibration and Zero

Calibration and zero tests should be performed through the remote converter. The Thermo NO_y analyzer has a separate connection for the calibration gas at the inlet of the converter. An adequate supply of calibration gasses must be supplied to ensure that excess calibration gas passes out the inlet. Currently, OAQPS recommends that a zero and span check be performed daily, and multi-point calibrations be performed on a monthly basis. OAQPS is currently conducting a study to determine if more frequent checks are needed, or if less frequent checks are acceptable.

Issues with the Method

1) Reaction of NO with ambient ozone.

It is well known that ambient ozone will react with NO in the sample line, resulting in a reduction in the NO reading. For this reason, it is recommended that the residence time in the sample line be as short as possible, and no more than 2 seconds. For a 1/4 inch OD, 1/8 inch ID tubing and a total sample rate of 1.5 liters per minute, the maximum sample line length is approximately 20 feet. Thick wall tubing and increased bypass flow can be used if longer sampling lines are needed.

2) Conversion efficiency of converter.

The molybdenum converter is consumed, and has an average life of approximately 1 year. The efficiency of the converter will reduce over time, and as such must be checked periodically. At this time, differences of opinion exist between researchers as to the appropriate NO_y species to use to check converter efficiency. Potential species include NO_2, HNO_3, isopropyl nitrate, and n-propyl nitrate. OAQPS is performing a study to determine which species should be used in the NCore program to test converter efficiency.

3) Ammonia interference.

Depending on the converter temperature, the converter may convert a small amount of NH_3 to NO, resulting in increased NO readings. However, under normal circumstances NH_3 concentrations are low compared to NO and this positive interference is negligible. Nonetheless, care should be taken when siting the monitor to be sure that it is not located near significant NH_3 sources which could cause elevated NH_3 concentrations (e.g., concentrated animal feeding

operations).

Table 1. Summary of Commercially Available NO_y Monitors

Instrument Make/Model	Lowest Range	LDL	Response Time	Zero Drift	Span Drift	Auto Ranging	Precision	Approximate Price
API 501NOY	0-5ppb	50 ppt	120	<0.1 ppb/day	<0.5% FS	Yes	0.5%	$15-19,000
Thermo 42C-YNOy	0-5ppb	50 ppt	120	Neg.	+/- 1% FS	Yes	NA	$19,490
EcoTech EC9841A-NOy	0-20ppb	50 ppt	Variable	<0.1 ppb/day	+/- 1% FS	Yes	50ppt, or 0.5% of reading above 50 ppb	NA