Method for the Determination of Nitrous Oxide in Ambient Air and Vehicle Exhaust Using Gas Chromatography and Electron Capture Detection

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INTRODUCTION

Measurement of nitrous oxide emissions from motor vehicle sources has been and will continue to be a concern for regulatory agencies. This interest will expand with continued growth in the atmospheric levels of nitrous oxide, and with mounting impacts in climate change that are attributed, at least in part, to anthropogenic sources of nitrous oxide. This concern is strongly shown by California law AB1493 (2002)[1] which provides for future regulation of greenhouse gas emissions from motor vehicles, and by California law AB32 (2006)[2] which is more encompassing and requires long range control and reporting of greenhouse gas emissions in all sectors of the economy thru the year 2050. Together, these regulations form the basis for future control of greenhouse gases from motor vehicles by the California Air Resources Board.

Current methods for nitrous oxide measurement used in motor vehicle studies generally employ infrared instrumentation[3, 4] or gas chromatographic instrumentation.[5, 6] Missing in many references on methods using infrared is the indication of the spectral interferences from carbon monoxide that must be compensated for when quantifying nitrous oxide. Gas chromatographic techniques for nitrous oxide measurement have been used because of the sensitivity of the electron capture detector (ECD) for nitrous oxide and because of its selectivity in detection of certain compound types, including nitrous oxide. Additional selectivity for a gas chromatographic method is derived from the selection of the analytical column, which also eliminates or reduces potential interferences.

The electron capture detector is the workhorse detector for nitrous oxide analysis since its development in the 1960's.[7] Both the electron capture detector and the helium pulsed discharge detector (Valco Instruments, Inc., Houston, Texas) have a similar detection limits for nitrous oxide. The selection of the electron capture detector is based on convenience. The Varian electron capture detector (Varian, Inc, Walnut Creek, CA), used in this experiment, can employ either 5% methane in argon or high purity nitrogen (such as boil-off from liquid nitrogen) as carrier and make-up gas. Significant enhancement of detection has been reported with use of argon blended with 5% methane.[8] This same reference cites difficulties with drifting signals and non-linear response with electron capture detection.

In this paper, we report on the advancement of a new gas chromatographic technique for nitrous oxide measurement that is being adapted for motor vehicle emissions testing. The method uses an optimized gas chromatographic procedure that was developed after extensive testing. This approach involves multiple columns to select the nitrous oxide peak through a "heart-cut" method. The protocol uses a stripper column to select the target peak for analysis from heavier peaks, such as Freons and hydrocarbons. These late eluters can contaminate the detector, especially over time. The elution times for heavier hydrocarbons also require a much longer analysis to ensure that they are off the column before the next run. Results are shown for stable detector responses over time and differences in performance with argon/methane and nitrogen. Linearity and detection limits are provided. Examples are shown for measurements with vehicle emissions and ambient air.

EXPERIMENTAL

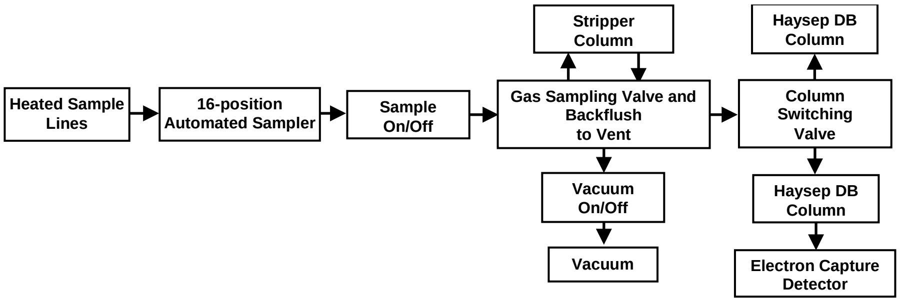
Nitrous oxide is determined with a Varian 3800 Gas Chromatograph (Varian Inc., Walnut Creek, Ca) equipped with a “general licensed” pulsed ^{63}Ni electron capture detector. Instrument operating parameters are provided in Table 1. This system also includes a thermal conductivity detector and a flame ionization detector with reduction catalyst, for simultaneous measurement of oxygen, nitrogen, carbon monoxide, carbon dioxide and methane.

Table 1. GC-ECD parameters for nitrous oxide analysis

Column Oven	80 ^{o}C
Carrier Gas	Nitrogen, 10 ml/min
Make-up Gas to ECD	Nitrogen, 10 ml/min
Detector	ECD at 340 ^{o}C
Detector Range	1
Sample Size	3.2 ml

All valves are Valco Series 1/16” WE type, with purged housings and special leak testing to less than 10^{-8} cc-atm/sec. These valves are equipped with micro-electric actuators controlled through timed events in the chromatograph. A valve oven, holding most valves, is maintained at 80 ^{o}C. A sixteen position automated sampler (Valco Multiposition Valve CSD Type with heated sample lines) is included to allow unattended operations with multiple samples. All data is collected, processed and reported with the Varian Star Workstation, with full control of most operating parameters and the automated sampler, including all Varian 3800 operations. Valving system is designed and assembled by Lotus Consulting (Long Beach, Ca). A block diagram of the valving is given in Figure 1.

Figure 1. Block diagram for Greenhouse Gas Analyzer



The stripper column is Hayesep N, 1/8”, 6 feet, 60/80 mesh (Hayes Separations, Bandera, Tx). The two “heart-cut” columns are matched with Hayesep D, 1/8”, 12 feet, 80/100 mesh. All columns are located in the conventional GC column oven and maintained at an isothermal temperature of 80 ^{o}C throughout the run.

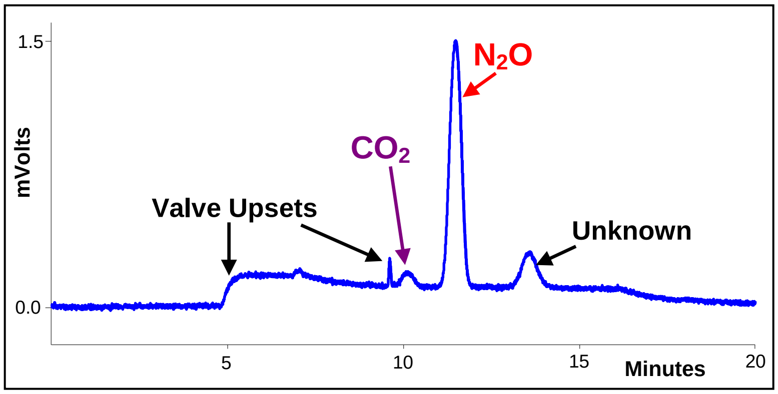
The sample loading process is carefully executed with attention to the consistency of the sample loop pressure and temperature to ensure that effects from changes in effective loop volume from Boyle’s and Charles’ Gas Laws are minimized.

The high concentration nitrous oxide standard (10.0 ppmV) is NIST Standard Reference Material (NIST, Gaithersburg, Md); lower concentration standards (5 and 1 ppmV) are provided by Scott-Marrin, Inc. (Riverside, Ca); these standards are used for all calibrations. Multiple level calibrations are accomplished by dilution of the standards with an Environics Model 4040, Computerized Gas Dilution System (Environics, Tolland, Ct) into Tedlar bags.

Most runs reported here are performed with nitrogen carrier gas, with this nitrogen derived from the headspace of liquid nitrogen to ensure absolute purity from all organics.

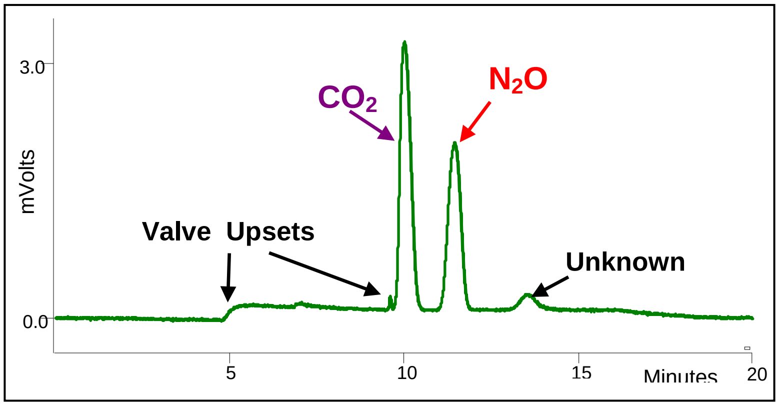
RESULTS

Figure 2. Chromatogram of 0.33 ppm N_2O in Ambient Air



A typical chromatogram of ambient air is given in Figure 2. Oxygen is obviously fully excluded from the chromatogram through careful optimization of the "heart-cut" operation. Carbon dioxide elutes prior to nitrous oxide and does not interfere with the target peak. Valve upsets are minimized with use of balancing restrictors to maintain steadiness in the pneumatic flows when valves are actuated. Vehicle exhausts normally have nitrous oxide concentrations a bit higher. A typical result for an in-use vehicle is shown in Figure 3.

Figure 3. Chromatogram of 0.51 ppm N_2O in Vehicle Exhaust



To evaluate reports of enhancements with argon/methane carrier, several experiments are performed to compare results. Figure 4 and Table 2 show the resulting peaks for nitrous oxide with both carriers.

Figure 4. Comparison of responses of differing carrier gases to nitrous oxide in ambient air

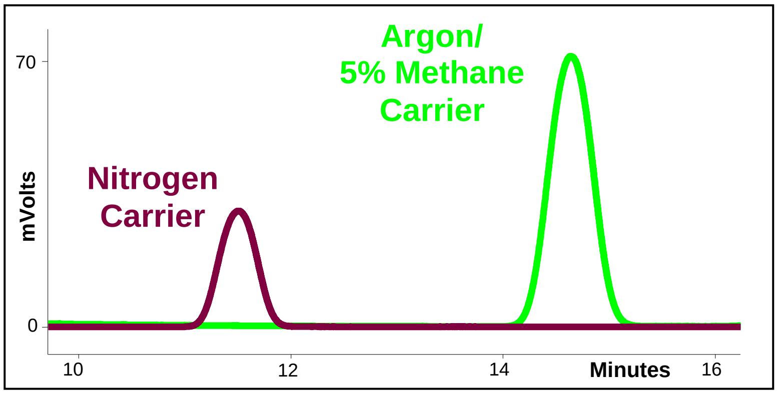


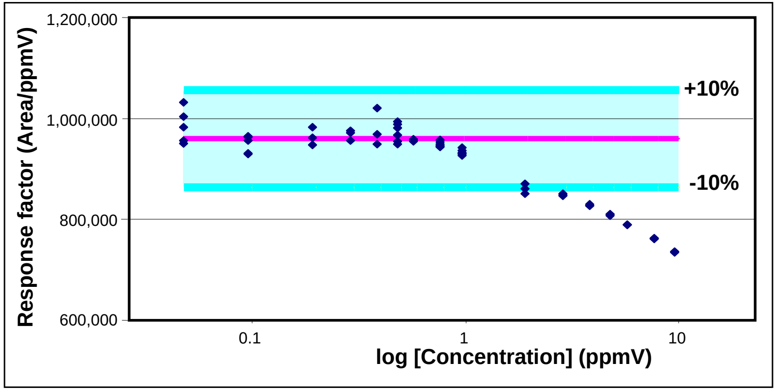
Table 2. Data for comparison of responses with different carrier gases

Carrier Gas	Area Counts for N_2O
Argon/Methane	88,565
Nitrogen	31,445

Experimental conditions are identical, and the system is allowed to be purged with the new carrier for at least overnight before running with new carrier. The area with argon/methane is 2.8 times the area with nitrogen as carrier.

Multi-point calibration is performed by diluting the NIST Standard Reference Material (SRM) gas into Tedlar bags from 0.0500 ppmV to 10.0 ppmV, over 16 levels, with 61 data points. Results are displayed in Figure 5. Ten percent error bars from the average over the range 0.05 to 1 ppmV are given to indicate linearity without multi-order curve fittings. The average response factor from 0.05 to 1 ppmV is 960,754 area counts/ppmV.

Figure 5. Response factor versus log[concentration] plot for nitrous oxide from



Detection limit is determined from 5 consecutive runs of the lowest standard used in the multi-point calibration (0.0500 ppmV) and is calculated following protocols given in California Air Resources Board Method 1002.[9] Table 3 lists the raw areas for the series and computations to yield a preliminary detection limit of 0.6 ppb V (0.0006 ppmV).

Table 3. Detection Limit Calculation

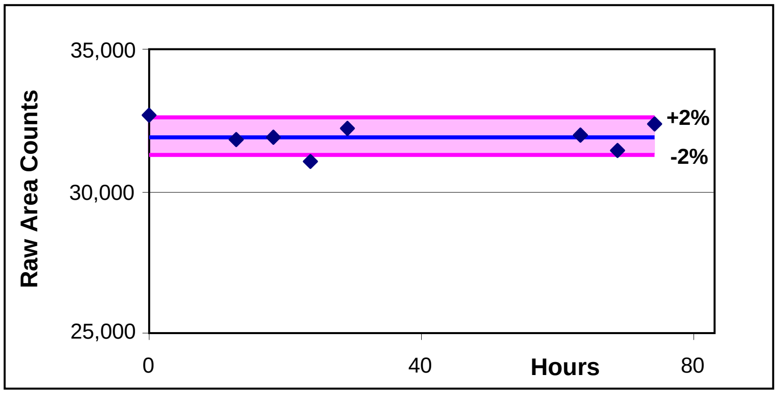
Raw Area Counts
4,913
5,157
4,751
5,022
4,781

$$LOD = \frac{t*s}{m} = \frac{3.4*169}{960{,}754} = 0.0006\, ppmV/V$$

where m = average response factor
t = t-factor for 99% confidence level; 3.4 for 5 replicates
s = standard deviation of at least five replicates

Stability of raw area measurements for nitrous oxide in ambient air is demonstrated in Figure 6 illustrates a constancy of near 2% over 74 hours without changes to the instrument.

Figure 6. Consistency of raw area counts for nitrous oxide in ambient air over 74 hours.



DISCUSSION

The system linear range is readily within ±10% over the important concentration range from 0.05 ppmV to 1 ppmV; a second order fit provides an improved fit to the data. Higher concentrations are handled properly with a second order fit to the upper standards.

The initial detection limit is computed to be 0.6 ppbV, but following procedures of the California Air Resources Board[9], it is elevated to 10 ppb V - a factor of 5 below the lowest standard used (50 ppbV).

The "heart-cut" configuration employed in this report is optimized for ease of use by making the operation fully automated. This methodology is found to be an advantage over traditional two-column, stripper techniques that remove only the later eluting peaks from the analysis. The additional removal of oxygen from the electron capture detector appears to enhance the stability of the baseline and adds longevity to the detector.

A factor found to be important for optimizing this method is the maintenance of extreme instrument cleanliness by employment of high purity nitrogen as the carrier and detector make-up gases, the use of relatively low column temperatures to reduce contamination from reaching the detector, and the utilization of valving that can be purged with nitrogen to minimize the influence of minor leaks on the detector. The longevity of the detector now is being evaluated over extended intervals for robustness of the method.

The choice of nitrogen for carrier gas is one of cost and elimination of gas cylinders, with some sacrifice in peak size, but nitrogen does not reduce signal as much as reported elsewhere. The active volume for the ^{63}Ni cell in the Varian electron capture detector is 50 microliters.[10] Since these detectors are "concentration-type" detectors, a smaller cell enhances the effective concentration of the analyte in the detector, giving a larger peak over cells with larger volumes. Secondly, β-electrons from ^{63}Ni are active over a limited distance in nitrogen. The smaller cell shortens the distance between the ^{63}Ni foil and collector, allowing nitrogen to maintain the activity of the β-electrons. Larger cells often need 5% methane in argon to enhance the electron lifetime over the distances involved, to allow capture by nitrous oxide. The anticipated enhancement of a factor of 100 was not realized with the Varian detector using the more expensive alternate carrier gas.

The stability performance of approximately 2% for a long time interval provides confidence in the data quality when monitoring subtle changes in nitrous oxide concentrations over extended periods.

SUMMARY

The system performance readily meets the measurement requirements for measuring nitrous oxide in ambient air and vehicle exhaust. The calibration range is nearly linear from 0.05 ppmV to 1 ppmV, with an excellent second order fit of the data to 10 ppmV. The method detection limit is less than 0.01 ppmV.

Potential interferences of oxygen, carbon dioxide and carbon monoxide are eliminated or adequately separated away from the nitrous oxide peak.

The instrument is very stable over long time periods, and is a perfect tool for measuring nitrous oxide in gaseous samples.

REFERENCES

1. California Assembly Bill AB 1493 (2002); www.leginfo.ca.gov/pub/01-02/bill/asm/ab_1451-1500/ab_1493_bill_20020722_chaptered.pdf.

2. California Assembly Bill AB 32 (2006); www.leginfo.ca.gov/pub/05-06/bill/asm/ab_0001-0050/ab_32_bill_20060927_chaptered.pdf.

3. Becker, K. H., Lorzer, J. C., Kurtenbach, R. Wiesen, P., Jensen, T. E., and Wallington, T. J.; "Nitrous Oxide (N2O) Emissions from Vehicles," *Environ. Sci. Technol.*, ***33***, 4134-4139 (1999).

4. Behrentz, E., Ling, R., Rieger, P., and Winer, A.M.; "Measurements of Nitrous Oxide Emissions from Light-Duty Motor Vehicles: a Pilot Study," *Atmos. Environ.*, ***38***, 4291-4303 (2004).

5. Dasch, J. M.; "Nitrous Oxide Emissions from Vehicles", *J. Air Waste Manage. Assoc.*, ***42***, 63-67 (1992).

6. Graham, L. A., Rideout, G., Rosenblatt, D., Hendren, J.; "Greenhouse Gas Emissions from Heavy-Duty Vehicles," *Atmos. Environ.*, ***42***, 4665-4681 (2008).

7. Wentworth, W.E., Freeman, R. R., "Measurement of Atmospheric Nitrous Oxide Using an Electron Capture Detector in Conjunction with Gas Chromatography", *J. Chrom.*, ***79*** 322-324 (1973).

8. Crill, P.M., Butler, J. H., Cooper, D. J., Novelli, P. C., in *Biogenic Trace Gases: Measuring Emissions from Soil and Water*, Matson, P. A, Harriss, R. C., Eds., Blackwell Science Ltd; London, 1995, pp 190-193.

9. California Air Resources Board SOP Method 1002; www.arb.ca.gov/msprog/levprog/cleandoc/clean_nmogtps_final.pdf.

10. Private communication, Bob Belair, Varian Inc, September 2, 2008.