Optimum Parameters for Detection of Long-Lived Green House Gases in Ambient Air

Randall Bramston-Cook and **Edward Bramston-Cook**
Lotus Consulting
5781 Campo Walk, Long Beach, Ca 90803
310/569-0128

Presented at 2010 EPA/AWMA Symposium on
Air Quality Measurement Methods and Technology,
Los Angles, California
November 2, 2010

Optimum Parameters for Detection of Long-Lived Green House Gases in Ambient Air

Extended Abstract # 54

Randall Bramston-Cook and Edward Bramston-Cook
Lotus Consulting, 5781 Campo Walk, Long Beach, California 90803

INTRODUCTION

Long-lived greenhouse gases continue to impact global surface temperatures. Carbon dioxide is considered to be the main culprit and is determined to contribute about 63% to radiative forcing.[1,2] The so-called "stealth gases" make up the remainder, including methane (18%), halocarbons plus sulfur hexafluoride (13%), and nitrous oxide (6%). These stealth gases are generally out of public awareness, and while they are significantly lower in concentrations in ambient air, their radiative efficiency factors $\left({}^{Watts}\!/_{m^2 \times ppbV}\right)$ can be 10,000 higher for many halocarbons than for carbon dioxide. This aspect alone makes them significant contributors to the overall consequences of greenhouse gases.

All of these gaseous components need to be considered in describing the influences of greenhouse gases on global warming. NASA Advanced Global Atmospheric Gases Experiment uses two measuring systems (MEDUSA for halocarbons[3] and GCMD for methane, nitrous oxide and a limited group of halocarbons[4]) for long-term deployment at remote stations. MEDUSA uses a proprietary coolant trap to concentrate halocarbons into detection range. Other studies[5,6] have monitored only carbon dioxide, methane and nitrous oxide, while excluding the important halocarbons.

All halocarbons in ambient air have concentrations in the pptV range with some even below 10 pptV. Direct measurement by most mass spectrometers cannot reach this level. Cryogenic trapping of large-volume air samples is mandated for halocarbons to approach the operating range of high performance mass spectrometers.[7] Measurement of these gases needs to be as accurate and reproducible as possible, as subtle changes in concentrations can have a major impact on their effects on the atmosphere. Accuracy is very dependent both on the correct labeling of the standards employed and on the reproducibility of reported concentrations. Precision is enhanced by maximizing the detector signals and optimizing the chromatography involved.

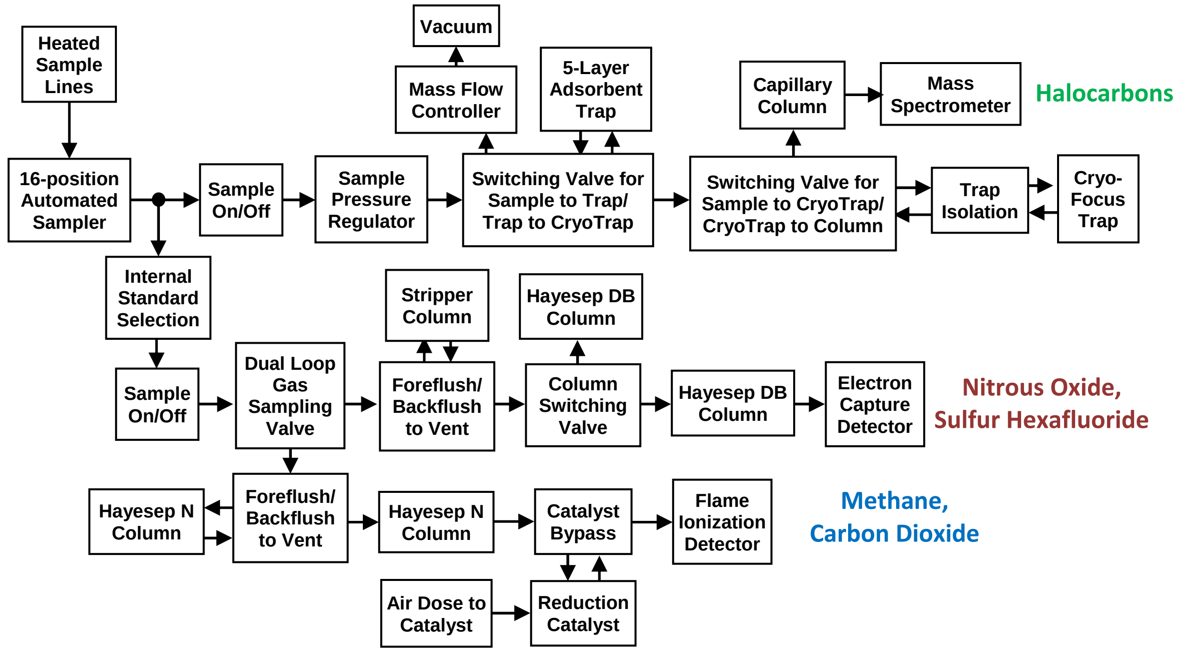
This paper reports on the most favorable conditions for detection of the complete list of long-lived greenhouse gases in an urban industrial park using a single instrument method and data collection system. The instrument is fully automated for sample collection as determined intervals, and makes its measurements by employing (1) chromatography with reduction catalyst and flame ionization detection for carbon dioxide and methane, (2) chromatography with electron capture detection for nitrous oxide and sulfur hexafluoride, and (3) capillary chromatography with mass spectrometry in full scan electron impact mode for positive identification and measurement of all halocarbons involved.

EXPERIMENTAL METHODS

All measurements are performed with a Bruker 450 Gas Chromatograph (Fremont, Ca) equipped with an electron capture detector (ECD - ^{63}Ni, 15 millicuries, active cell volume - < 300 µl, 330 ^{o}C, Range - 1) for nitrous oxide and sulfur hexafluoride detection, a flame ionization detector (FID, Range -10^{-12} Amperes/mV) with reduction catalyst to monitor both methane and carbon dioxide, and a Bruker 320 Triple Quadrupole Mass Spectrometer for sensitive measurements of halocarbons. All instrument operations are activated with a single method and monitored with Bruker MS Workstation (Version 7) software.

Custom valving and column configurations (Figure 1) are provided by Lotus Consulting (Long Beach, Ca). A 16-position automated sampler is included to allow easy switching between multiple calibration standards and sample streams. Each sample is concurrently loaded into three measurement channels to determine all analytes simultaneously.

Figure 1. Block Diagram for Greenhouse Gas Analyzer



Local weather conditions are monitored every 15 minutes with Ambient Weather Wireless Station Model WS-2080 (Phoenix, AZ) mounted on the roof of the test location. Temperatures, wind vectors, humidity and barometric pressures are recorded and archived for later correlations with results.

Routine hourly sampling, with intermittent calibration runs, is easily accomplished with built-in WAIT and GOTO operations set into the workstation sample list. First the WAIT function holds up the process until the next hour when the run is started. After the measurement has completed, the GOTO step cycles around to pause until the next hour. This action continues until interrupted by the operator.

Nitrous Oxide and Sulfur Hexafluoride Measurements - Details of the plumbing for nitrous oxide have been described elsewhere[8], except the two Hayesep DB columns are now 12 feet, 100/120 mesh, for added separation of carbon dioxide and nitrous oxide. Column flow is 10 ml/min nitrogen, with additional flows from detector make-up of 7 ml/min nitrogen plus 3 ml/min of 5% methane in argon. Special adaptations to exclude oxygen from carrier and sample pathways for nitrous oxide are implemented, including minimal use of polymeric fittings, extensive use of gold-plated ferrules, purged-housings for all applicable valves, and installation of nitrogen purifiers at the gas inlet to the GC and also after both column flow controllers. An exhaustive leak check of the ECD channel ensures that room-air oxygen does not diffuse into the gas pathways to degrade detector performance. The valving setup is specifically designed to strip off the major peak of oxygen to vent to minimize disruption by its huge tail into the nitrous oxide peak and also to exclude the possibility of degradation of the detector from oxidation at the nickel surface. Injection volume for routine measurements is 5 ml; column temperature is 80 ^oC; detector range is 1. Additionally, a special apparatus is installed to provide continuous nitrogen flow to the ECD in the event of a power failure to prevent back-diffusion of room air into the hot ECD causing surface oxidation on the nickel foil when the electronic flow controllers are disabled and normal detector flows are turned off.

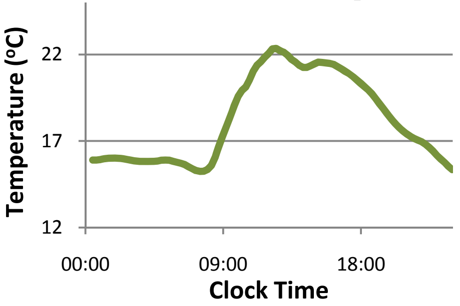
Methane Analysis - Methane is separated from oxygen and other interferences with two Hayesep N columns (6 feet, 1/8" OD, 60/80 mesh), with the first plumbed in foreflush/ backflush-to-vent to strip off heavier hydrocarbons. Although oxygen produces a small disruption peak with a flame ionization detector just prior to the elution of methane, it does not impede proper integration of the methane response. The reduction catalyst is bypassed here, as oxygen would have created a bigger baseline upset that would obscure the methane peak. Injection volume is 2 ml, column temperature is 80 ^oC, and column carrier flow (nitrogen) is 30 ml/min.

Carbon Dioxide Studies - Chromatography for carbon dioxide is performed with identical conditions as methane. A flame ionization detector combined with a reduction catalyst is used for measuring carbon dioxide to efficiently convert carbon dioxide into methane for detection. This combination generates a much larger area counts for easier quantitation than could be achieved with a thermal conductivity detector. The reduction catalyst is 10% nickel nitrate on Chromosorb GAW 100/120 mesh (Bruker, Fremont, CA), 1/8" OD stainless steel tubing, 6 inches long, and maintained at 380 ^oC. Hydrogen flow through the catalyst is set to 10 ml/min and an additional 20 ml/min hydrogen flow directly to the detector. Previous measurements have shown the conversion of carbon dioxide to methane is >99%.[9] A small dose (100 µl) of air is injected directly into the reduction catalyst at the start of every run to maintain maximum long-term performance of the catalyst by removing any carbon build up on the catalyst.

Halocarbons Assessments - To achieve detection of the full range of halocarbons, samples are measured into the trapping process with a mass flow controller set to a flow rate of 80 ml for typically 12.5 minutes, giving a loading volume of 1 liter. Water is excluded from the trap with a Nafion dryer. This initial trap (multi-layer glass beads and carbon adsorbents) is maintained at -60 ^oC during sample loading, and then heated to transfer the trapped analytes to a second low-volume trap at -160 ^oC to focus all analytes. This trap is next heated for injection into a capillary column (Varian CP-624, 0.25 mm ID, 60 m, 1.4 µ film) and on to the spectrometer operating in electronic impact mode. On-column injection occurs at 17 min. The column temperature program is -60 °C, hold for 17 min, ramp to 250 °C at 8.3 °C/min. Column flow is 1 ml/min. Total analysis time is 55 min.

Internal standard addition is not practical with these halocarbon analytes, as all possible candidates are potential greenhouse gases and could exist in ambient air samples.

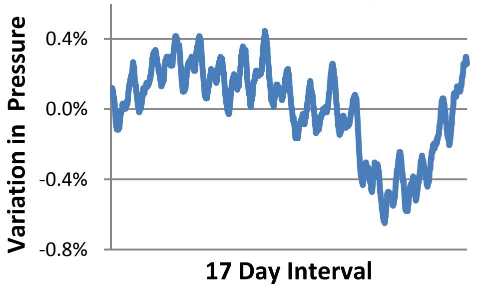
Figure 2. Typical Daily Variations inRoom Temperature



RESULTS AND DISCUSSION

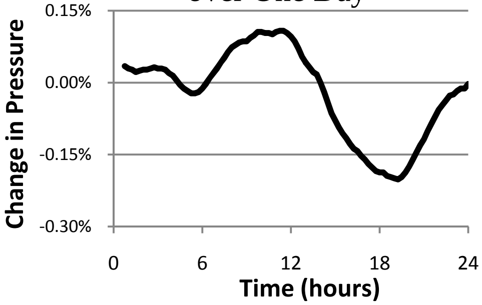
Corrections for Variations in Temperature and Barometric Pressure - Changes in temperature and pressure of the contents of the sample loop at injection can have significant impacts on the precision of the measurement. From Charles-Gay-Lussac Law, a 1 °C change in the loop temperature will yield a 0.4% change in effective volume. If sample loops were allowed to follow room temperatures at the instrument (Figure 2), results can change as much as 2.8%. By holding the temperature of the loops to 100 ± 0.1 °C, the effect is minimal at less than 0.05%.

Figure 3. Variation of Pressure over 17 Days



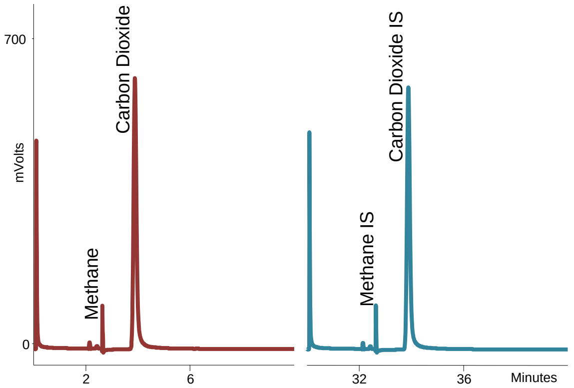
Boyle-Mariotte Law links the effective volume of a fixed-volume loop as proportional to its pressure. Changes in this pressure can impact results at expected reported precision levels for these gases. Sample loading processes executed in this system make certain that the sample loop reaches atmospheric pressure just prior to injection into the columns sets, to insure that impacts of differing sample pressures at injection are minimized.

Figure 4. Change in Pressure over One Day



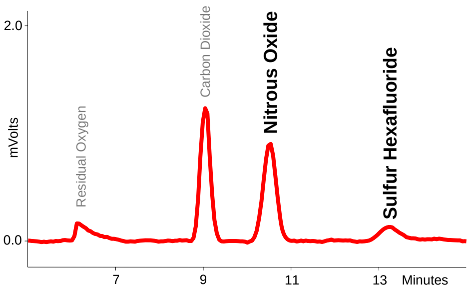
However, changes in atmospheric pressure can still impart changes in the results. Figure 3 illustrates these changes over an extended time interval. If the calibration process occurs when the atmospheric pressure is elevated, and samples are run later when the pressure drops, the effect can be as much as 1% lower results. Figure 4 demonstrates possible variations over a single summer day in Southern California, and even then, results can be altered by as much as 0.3%. This effect can be more severe with dramatic changes in an approaching or clearing storm.

Figure 5. Portions of Chromatogram with Internal Standards.



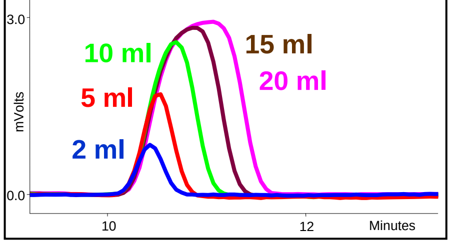
A process to correct for this variation is to compute results relative to an immediate secondary injection, within the same run, of a known standard near the measurement time of the ambient sample (Figure 5). Then conventional “internal standard” computations can be used to generate final results. Variations in pressure over a typical 30 minute interval range from 0 to 0.07%. Thus, changes in atmospheric pressures between the calibration series and the ambient air assessments are adjusted automatically, and without need to monitor pressures and then apply separate mathematical corrections.

Figure 6. Chromatogram of Nitrous Oxide and SF_6 in Ambient Air.



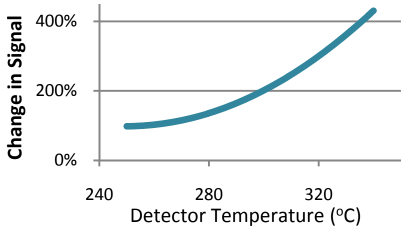
Nitrous Oxide - Nitrous oxide and sulfur hexafluoride are readily separated to baseline and away from carbon dioxide with the column conditions used (Figure 6). Attempts to enhance peak sizes by using larger injection volumes (Figure 7) show that even though the measured areas did grow, its shape deteriorates from the sample volume still filling the column when the first portion is eluting. The resulting broadness starts to overwhelm adjacent peaks. Five milliliters is used for the final measurements, as a compromise to maximize signal while still maintaining adequate peak shape.

Figure 7. Effects of Injection Volume on Nitrous Oxide Peak.



An unusual effect with ECD detection of nitrous oxide is the dependence of its response on detector temperature. Figure 8 displays the change over a range of temperatures. A setting of 330 °C for final measurements is selected to minimize thermal stress on the detector. This temperature must be maintained within ±0.1 °C to limit its impact on peak area to less than 0.15%.

Figure 8. Effects of Detector Temperature on Response



Electron capture detectors are “concentration” detectors, in that their response is a function of the speed of the analyte through the cell. Figure 9 illustrates the effect by changing the detector make-up flow without affecting the established chromatography. A total flow of 20 ml/min is chosen for routine measurements to keep flow high enough to minimize back-diffusion of ambient oxygen through the detector exit.[10] Argon/methane is often reported as the indicated carrier/make-up gas for measurements with ECD, especially for detectors with larger cells, to sustain an adequate flow of electrons for analyte detection. The small volume cell in the system used allows nitrogen to remain the carrier gas of choice without significant loss in sensitivity. Figure 10 illustrates enhancements with addition of 5% methane/argon make-up directly to the detector. For the Bruker ECD, the optimum portion of Argon/Methane addition for nitrous oxide detection is 2-3 ml/min.

Figure 9. ECD Response vs Total Flow

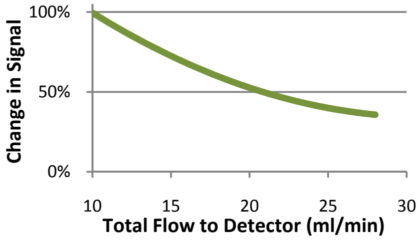
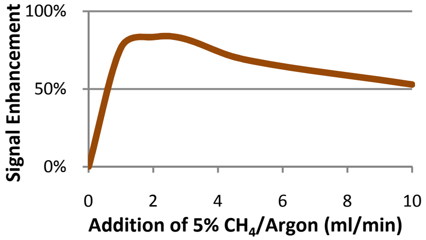


Figure 10. Changes in ECD Response with Argon/Methane

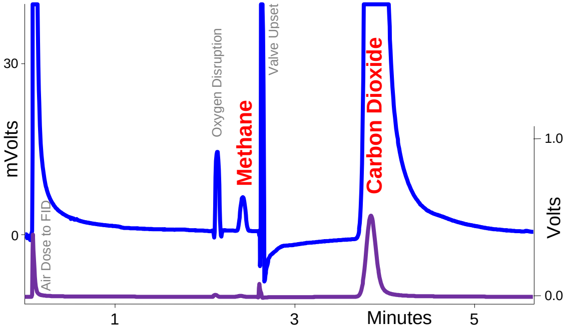


Typical area counts are 39,600 µV-sec for a 500 ppbV standard. Measurements of the same sample over a 3-day span produce a deviation in area counts of ±1.0%, and decreases to 0.8% with internal standard adjustments. Since the ECD signals at the levels analytes are measured are inherently noisy, and automatic baseline assignments can greatly impact peak areas, results can be reported in peak heights where these baseline changes have less impact. Using the same 3-day data, the typical height is 1.841 mv, with a standard deviation of ±0.7%.

Sulfur Hexafluoride - This analyte is very difficult to trap using the concentrator setup described here due to its extreme volatility, but is sufficiently sensitive enough to be monitored with the electron capture detector alongside nitrous oxide (Figure 6). A 9.8 pptV standard generates precisions over a 2 day span of 7.8% for area with an average of 5,298 µV-sec, and 1.2% for peak heights with an average of 1,160 µV.

Methane - This analyte is properly detected at expected ambient levels when appropriate baseline signals are achieved both before and after its elution (Figure 11). Efforts to use larger volumes fail to benefit the measurement as both the methane and carbon dioxide peaks become severely broader, affecting their peak integration. The FID signal is enhanced by a factor of two with nitrogen as carrier gas (compared with helium), due to the tighter and hotter flame generated. Typical area counts are 22,200 µV-sec for 1.976 ppmV standard. Measurements of the same standard over a 3-day span yield a variation of area counts of ±1.8%, and the deviation lowers to ±0.3% with internal standard operations outlined above.

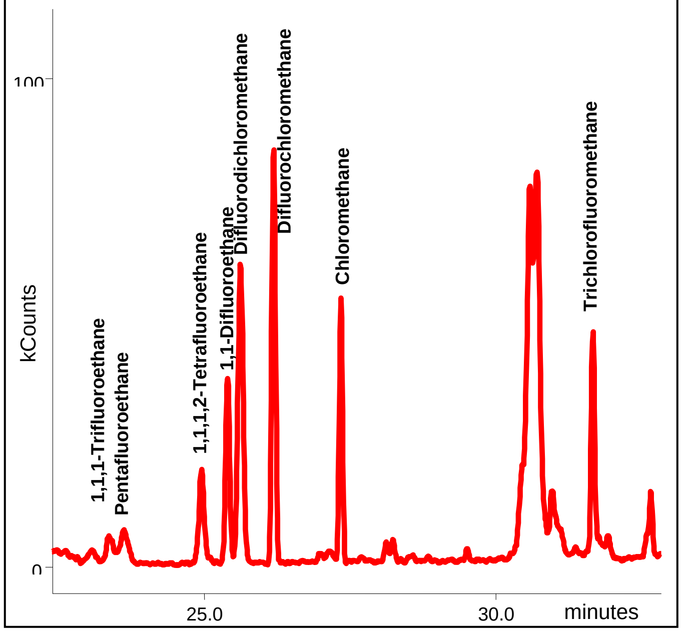
Figure 11. Chromatogram of Methane and Carbon Dioxide in Ambient Air.



Carbon Dioxide - The peak generated for carbon dioxide is quite large as expected (Figure 10) and yields areas near 4,600,000 µV-sec for a concentration of 402 ppmV. The response factor for carbon dioxide (1.15 x 10^4) matches well with that for methane (1.11 x 10^4), confirming full conversion of carbon dioxide to methane with the reduction catalyst. Measurements of the same sample over a 3-day span generate a variation in area counts of ±0.6%, and the precision reduces to ±0.2% with internal standard corrections outlined above.

Halocarbons - Most halocarbons elute early in the chromatography of ambient air due to their inherent volatility. To get them into the detection range of the spectrometer and to achieve proper separations, cryogen must be used both for trapping and for cooling down the column.

Figure 12. Selected Halocarbons in Ambient Air.

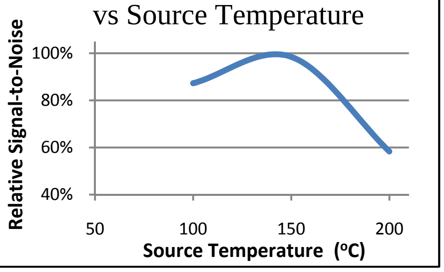


Attempts to enhance detection with negative chemical ionization with ammonia reactant are unsuccessful in getting sensitivity and selectivity for halocarbons better than the conventional electron impact mode.

The mass range of the spectrometer is set to 47 to 200 m/z in full scan to enhance identification of the halocarbons. Single ion monitoring is not used as many halocarbons have very similar fragment ions and their positive labeling requires matching up multiple ions against the NIST library, especially at very low levels found in ambient air.

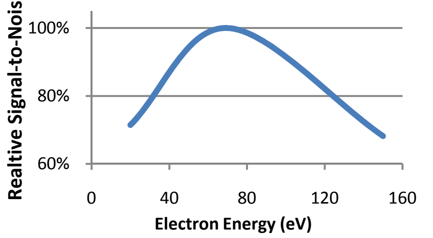
A study of peak size versus source temperature in the spectrometer found that the optimum setting is 150 ^{o}C (Figure 13). Another test series varies the filament current. Even though higher settings give larger peak counts, the noise escalates faster and the best setting is 70 eV (Figure 14). Another impact of a higher energy setting is a dramatic change in fragmentation patterns that deviate significantly from library spectra.

Figure 13. Peak Response vs Source Temperature



Detection limits for selected analytes are 1.2 pptV for 1,1-Difluoroethane, 1.4 pptV for 1,1,1,2-Tetrafluoroethane, 1.9 pptV for Difluorochloromethane, and 1.6 pptV for Pentafluoroethane. These limits are based on seven consecutive injections of 16 ml volume of a 1 ppbV NIST standard and then scaled to 1 liter injection of samples.

Figure 14. Reak Response vs Filament Current



SUMMARY

Data and discussions presented demonstrate that ambient levels of all long-lived greenhouses gases can be measured with enough precision and stability to pick up changes in ambient concentrations over extended sampling intervals. Use of a second injection for nitrous oxide, methane and carbon dioxide as an internal standard automatically corrects for variations in barometric pressure and with drift in responses with detectors. The influence over one day is often overwhelmed by the inherent imprecisions of both ECD and FID detectors, but becomes important over long-term monitoring or during dramatic changes in the barometer. Ambient pressure has little effect with the measurement of halocarbons due to the use of a mass flow controller to measure sample volumes.

Detection limits are not necessarily a determining factor in the measurement of nitrous oxide, methane and carbon dioxide, as these have minimum ambient levels that are not likely to be lower soon. More important considerations relate to the reproducibility and accuracy of results, as concentration trends are the essential consideration. Parameters affecting this performance are outlined to maximize generated signals and improve the quality of the final reporting concentrations.

REFERENCES

1. Intergovernmental Panel on Climate Change, Fourth Assessment Report, Chapter 2, p. 141, Table 2.1. See www.ipcc.ch/ipccreports/ar4-wg1.htm (accessed September 2010).

2. Carbon Dioxide Information Analysis Center, “Recent Greenhouse Gas Concentrations”, cdiac.ornl.gov/pns/current_ghg.html (accessed September 2010).

3. Advanced Global Atmospheric Gases Experiment, “MEDUSA Gas Chromatography with Mass Spectrometry”. See agage.eas.gatech.edu/instruments-gcmd.htm (accessed September 2010).

4. Advanced Global Atmospheric Gases Experiment, “Gas Chromatography- MultiDetector”. See agage.eas.gatech.edu/instruments-gcms-medusa.htm (accessed September 2010).

5. S. van der Laan, R.; Neubert, R.E.M, Meijer, H.A.J. *Atmos. Meas. Tech.*, **2009**, *2*, 549-559.

6. Thompson, R.L., et alii, Atmos. Meas. Tech. **2009**, *2*, 573-591.

7. Bilek, R., Bramston-Cook, R. “Performance of the Varian 240 Ion Trap Mass Spectrometer in the Measurement of Volatile Organic Compounds by EPA Method TO-15”, **2008**, A&WMA Symposium on Air Quality Measurement Methods and Technology, Chapel Hill, NC.

8. Bramston-Cook, R. “Method for the Determination of Nitrous Oxide in Ambient Air and Vehicle Exhaust Using Gas Chromatography and Electron Capture Detection”, **2008**, A&WMA Symposium on Air Quality Measurement Methods and Technology, Chapel Hill, NC.

9. Bramston-Cook, R., Baltensperger, B, Strittmatter, W. “Non-Methane Organic Compounds – EPA Method 25 Revisited”, **1998**, A&WMA Measurement of Toxic and Related Air Pollutants”, Cary, NC.

10. Kellogg, C., Bruker CAD, Private Communication, 2009.

ACKNOWLEDGEMENTS

The authors thank Charlie Schmidt, Carlos Warner and John Mills of Bruker Chemical Analysis Division, Dennis Carroll of Valco Instruments, and Jack Marrin of Scott-Marrin, Inc., for their help with this project.

Lotus Consulting
310/569-0128 Fax 714/898-7461
email ebramstoncook@msn.com

5781 Campo Walk
Long Beach, California 90803