

**Measurement of Carbon Dioxide, Methane,  
Nitrous Oxide, Sulfur Hexafluoride  
and Halocarbons in Ambient Air  
at an Industrial Park  
in Huntington Beach, California**

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# **Measurement of Carbon Dioxide, Methane, Nitrous Oxide, Sulfur Hexafluoride and Halocarbons in Ambient Air at an Industrial Park in Huntington Beach, California**

**Extended Abstract: 2011-A-748-AWMA**

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## **INTRODUCTION**

Carbon Dioxide is often featured as the major culprit in global warming, but it only has an impact of about 2/3 of the total human contributions toward the effects of greenhouse gases. So-called Stealth Gases make up the rest, including Methane (18%), Halocarbons (13%), and Nitrous Oxide (6%).<sup>1</sup> Even though these are out of public awareness, and while they are significantly lower in concentrations in ambient air than carbon dioxide, their radiative efficiencies [watts/(m<sup>2</sup> \*ppbV)] can be 10,000 higher for many halocarbons than carbon dioxide. These factors make them significant contributors to the consequences of greenhouse gases. All of these components need to be considered in describing influences of greenhouse gases on global warming.

This paper reports on an hourly appraisal of the complete list of long-lived greenhouse gases in an urban industrial park, using a fully automated, simultaneous measurement system employing chromatography with reduction catalyst and flame ionization detection for carbon dioxide and methane, chromatography with electron capture detection specifically for nitrous oxide, and capillary chromatography with mass spectrometry operating in electron impact. All of this is performed within a single instrument method and data collection system set up for automated sample collection at predetermined time intervals.

Trends in concentrations for these analytes are presented, synchronized with observations of the immediate surroundings to relate changes in gas concentrations with neighborhood events and activities, such as local factory delivery operations, nearby manufacturing functions, and local weather conditions.

## **EXPERIMENTAL METHODS**

All measurements are performed with a Bruker 450 Gas Chromatograph (Fremont, Ca) equipped with an electron capture detector (pulsed ECD - <sup>63</sup>Ni, 15 millicuries, active cell volume - < 300 µl, 330 °C, Range - 1) for nitrous oxide and sulfur hexafluoride detection, a flame ionization detector (FID, Range -10<sup>-12</sup> Amperes/mV) with reduction catalyst, to monitor both methane and carbon dioxide, and a Bruker 320 Triple Quadrupole Mass Spectrometer set up with cryofocusing 1 liter samples 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 are provided by Lotus Consulting (Long Beach, Ca). Experimental details are presented in Reference 2. 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.

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 MS 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.

## RESULTS AND DISCUSSION

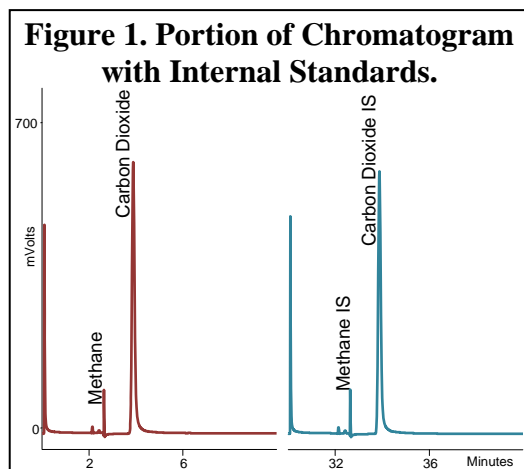
**Corrections for Variations in Temperature and Barometric Pressure** - Changes in temperature and pressure of the contents of the sample loop at injection can have significant impacts on the precision of the measurement. From Charles-Gay-Lussac Law, a 1 °C change in the loop temperature will yield a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

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.

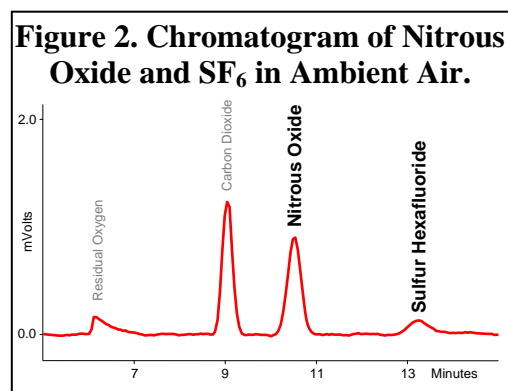
However, changes in atmospheric pressure can still impart changes in the results. If the calibration process occurs when the atmospheric pressure is elevated, and samples are run later when the pressure drops, the effect can be as much as 1% lower results. Possible variations over a single summer day in Southern California can impact 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.

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 1). Then conventional “internal standard” computations can be used to generate final results. Maximum variations in pressure over a typical 30 minute interval are 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.

**Nitrous Oxide** - Nitrous oxide and sulfur hexafluoride are readily separated to baseline and away from carbon dioxide (Figure 2) with the column conditions used. Attempts to enhance peak sizes by using larger injection volumes show that even though the measured areas did grow, peak shapes deteriorate from the sample volume still filling the column when the first portion is eluting from the column. 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.



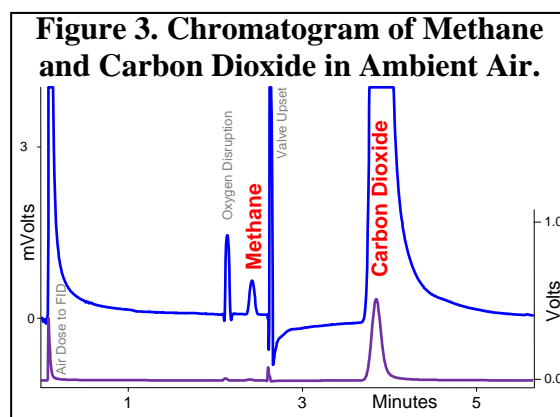
An unusual effect with ECD detection of nitrous oxide is the dependence of its response on detector temperature. A setting of 330 °C for final measurements is selected to minimize thermal stress on the detector. This temperature must be maintained within  $\pm 0.1$  °C to limit its impact on peak area to less than 0.15%.



Since the ECD signals are inherently noisy at the levels analytes are measured, and automatic baseline assignments can greatly impact peak areas, results can be reported relative to peak heights. Here baseline changes have less impact on quantitation. With nearly 100 runs of 350 ppbV Nitrous Oxide standard over three days, the area is 1,456,254  $\mu$ V-sec with a precision of 1.0%. Using peak heights instead yields an average of 4,550  $\mu$ V with a reduced precision to 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 2). A 9.8 pptV standard generates precisions over a 2 day span of 7.8% for area, with an average of 5,298  $\mu$ V-sec, and 1.2% for peak heights with an average of 1,160  $\mu$ V.

**Methane** - This analyte is properly detected at expected ambient levels when appropriate baseline signals are achieved both before and after its elution (Figure 3). 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. Typical area counts are 22,200  $\mu$ V-sec for 1.976 ppmV standard. Measurements of the same standard over a 3-day span yield a variation of area counts of  $\pm 1.8\%$ , and the deviation lowers to  $\pm 0.3\%$  with internal standard operations outlined above.



**Carbon Dioxide** - Ambient levels of carbon dioxide are readily monitored by flame ionization detection with in-series reduction catalyst to convert CO<sub>2</sub> to methane. Typical area counts are 4,600,000 μV-sec for a 400 ppmV standard. Measurements over a 3-day run series yield a raw precision of 0.60% that becomes 0.23% with internal standards.

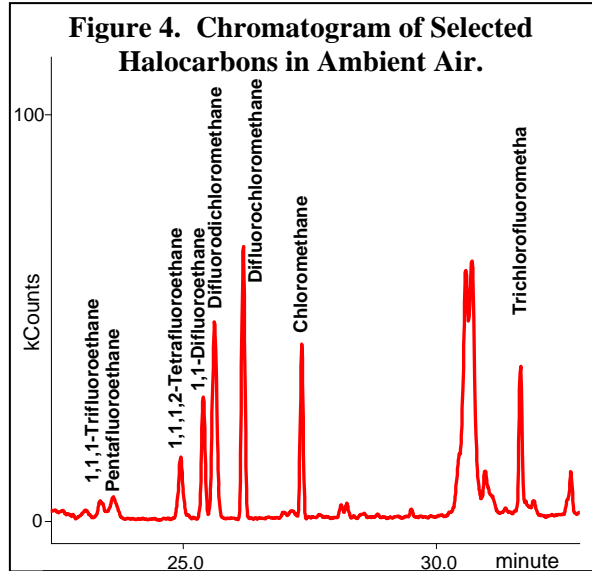
**Halocarbons** - Most halocarbons elute early in the chromatography of ambient air due to their inherent volatility (Figure 4). To get them into the detection range of the spectrometer and to achieve proper separations, cryogen must be used both for trapping and for cooling down the column. Detection limits for selected analytes by MS 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.

**Hourly Monitoring of Ambient Air at Huntington Beach, Ca** – Measurements for all long-lived greenhouse gases are made at an industrial park every hour for nearly 10 days, along with wind speed and temperature readings.

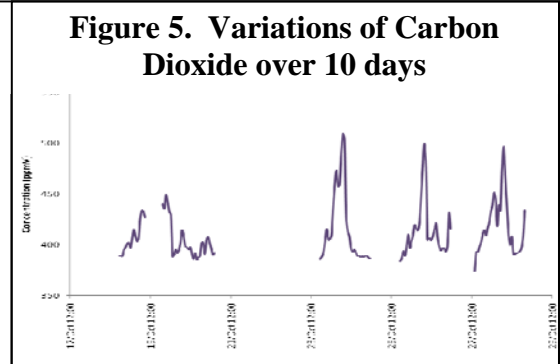
Carbon dioxide and methane both spiked three mornings during the measurement sequence around 8 am, with wind speed near zero, correlating with normal morning truck deliveries in the neighborhood.

Many halocarbons monitored, including octafluoropropane (R218), often are elevated late in the afternoon (after 5 pm), and are observed also at noticeably higher levels on one Saturday evening. Several electronic manufacturers in the area are likely to be contributors, but surprisingly at off-hours.

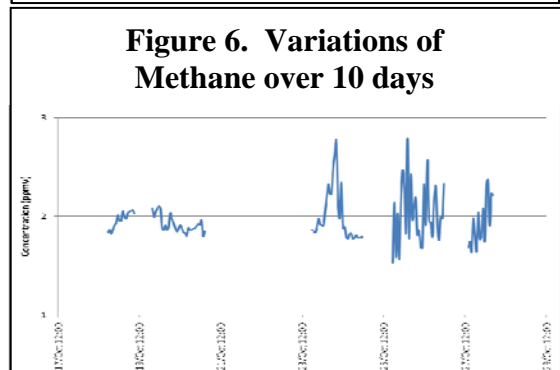
Nitrous oxide and sulfur hexafluoride remain quite stable over the testing interval, at an average of 356.4 ppbV for nitrous oxide and an average of 0.0078 ppbV for sulfur hexafluoride.



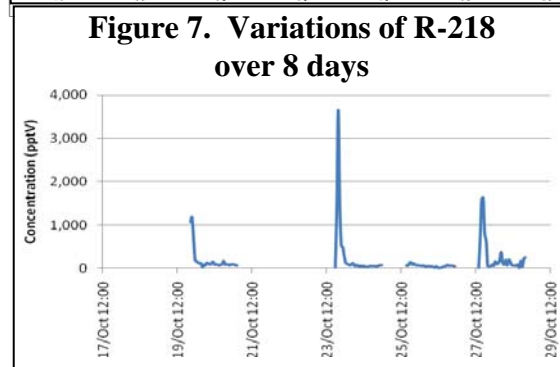
**Figure 4. Chromatogram of Selected Halocarbons in Ambient Air.**



**Figure 5. Variations of Carbon Dioxide over 10 days**



**Figure 6. Variations of Methane over 10 days**



**Figure 7. Variations of R-218 over 8 days**

## SUMMARY

The ability to report concurrently the full complement of long-lived greenhouse gases permits complete assessment of possible sources and their effects on global warming. Just an examination of one or two components cannot provide an adequate evaluation of all potential impacts on our environment.

Data and discussions presented demonstrate that ambient levels of all long-lived greenhouse gases can be measured with enough precision and stability to pick up changes in ambient concentrations over extended sampling intervals. These influences over one day can often be overwhelmed by the inherent imprecisions of both ECD and FID detectors, but become 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 well above established detection limits and are not likely to be lowered soon. More important considerations relate to the reproducibility and accuracy of results, as concentration trends are the essential consideration.

Variations in concentrations are an important aspect of monitoring these gases, and precision of results must be minimized to detect subtle variations. A novel addition of internal standards to the every chromatographic run greatly improves the reproducibility by self-correcting for changes in chromatographic conditions and for variations in injection loop temperatures and barometric pressures due to environmental surroundings of the instrument. Ambient pressure and temperature changes have little effect with the measurement of halocarbons due to the employment of a mass flow controller to measure sample volumes.

## ACKNOWLEDGEMENTS

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## 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](http://www.ipcc.ch/ipccreports/ar4-wg1.htm) (accessed September 2010).
2. Bramston-Cook, E., Bramston-Cook, R. "Optimum Parameters for Detection of Long-Lived Green House Gases in Ambient Air", 2010, A&WMA Symposium on Air Quality Measurement Methods and Technology, Los Angeles, CA.

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