Novel Approach to Measuring Non-Methane Organic Compounds (NMOC) with Cryo-Trapping

Extended Abstract # ME83

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INTRODUCTION

Measurement of total non-methane organics in ambient air and source samples requires the complete separation of other carbon-based analytes, including methane, carbon monoxide, and carbon dioxide from all other organics. EPA Method 25[1] and South Coast AQMD Method 25.3[2] accomplish the task with packed column chromatography. Performance with this approach is limited by the allowable sample injection volume to avoid overloading the columns, and to properly handle the tailing peak from high concentrations of carbon dioxide that could erroneously be included in the non-methane composite peak.

Frequently, these methodologies are not sensitive enough to properly measure low levels of non-methane organic compounds. EPA Method 25 lists the required minimum detection limit as 50 ppmCarbon. The protocol for South Coast AQMD is lower – down to 1 ppmCarbon. Results below these levels are then reported as "not detectable" or "less than detection limit". Often samples from clean sources need to have reported measurements lower than these limits.

A different approach is to direct the sample loading to a multi-bed adsorbent trap, made of hydrophobic carbon materials held at an initial temperature of -40 °C during loading. This trap does not retain oxygen, nitrogen, carbon monoxide, methane, and carbon dioxide, and these pass through the trap to vent. Non-methane organics, required for the assessment, are all retained on the trap. The trap is then rapidly heated, and a transfer gas flow directs the analytes to a cryofocus trap to concentrate these into a small volume. This second trap is then heated and a third flow directs the composite peak to an oxidation catalyst to convert all carbon atoms to carbon dioxide. Then the peak is passed on to a reduction catalyst to convert them to methane that represents all of the non-methane carbons in the sample. Detection is by flame ionization to provide a quantitative result for all non-methane organics. Detection is dramatically enhanced due to the larger injection volume and the much sharper peak generated.

EXPERIMENTAL METHODS

Calibration Standards

Propane standard used in these experiments is generated from a 2.9 ppmCarbon standard (Scott-Marrin, Inc., Riverside, California) and diluted to lower levels by both dilution and smaller injection volumes.

Chromatographic Conditions

Analytical measurements are performed with a Scion 450 Gas Chromatograph (Scion Instruments, Austin, Texas) equipped with an oxidation catalyst, reduction catalyst and flame

ionization detector. Results were computed and reported using Scion MS Workstation Version 8.0. This system is modified by Lotus Consulting (Long Beach, CA) to perform these measurements. An optional multi-position stream selector valve is available to provide automated, unattended switching between sample, blank and standard streams. To prevent possible condensation of analytes in the interconnecting lines after the sample attachment, all lines are heated to a minimum of 90 ºC. All valving is accomplished with Valco series C_WE valves with microelectric actuators (Valco Instruments, Houston, TX).

A fixed volume sample loop loading of typically 10 ml sample is set up to load into a multi-bed adsorbent trap held initially at -40 ºC. Oxygen, nitrogen, methane, carbon monoxide and carbon are allowed to pass on through to vent, as the trap temperature is warm enough to not snare these components. After the dose is fully loaded and flushed with helium, the contents are passed onto a cryofocus trap to reduce the effective analyte volume. The trap contents are isolated while the cryofocus trap heated up. Then the full trap contents are injected into the oxidation catalyst, and then to the reduction catalyst and flame ionization detector. Figure 1 displays flow path for system measurements.

Figure 1. Block Diagram
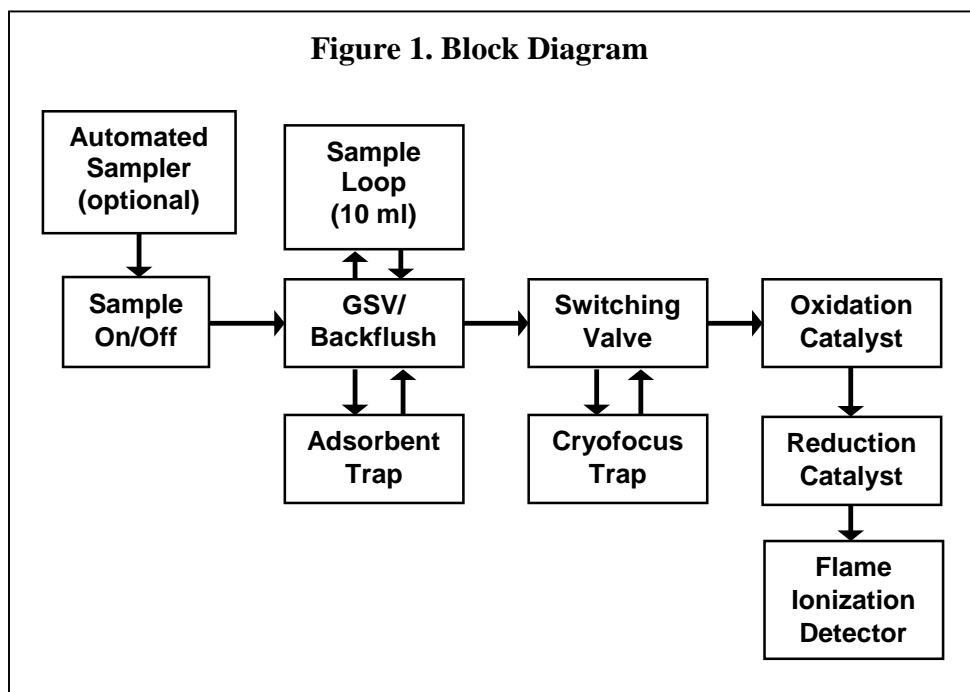
Special valving is installed to allow a mixture of Tedlar™ sample bags and pressurized sample canisters to be processed without operator intervention. And the sample loop is maintained at a constant elevated temperature (130 ºC ± 0.1 ºC), to provide adherence to Boyle's Law. Excess pressure is released to atmosphere to yield equal sample loop pressures at time of injection, independent of sample source, and to eliminate any mathematical corrections for pressure variations due to effects of Charles' Law.

Concentrator Parameters

Adsorbent Trap: multi-layer hydrophobic mixed bed

Initial Temperature: -40 ºC, hold 4.10 minutes
Temperature Ramp: +200 ºC/min
Final Temperature: +250 ºC, hold 2.61 minutes

Cryofocus Trap: 90 µl empty trapping
Initial Temperature: +80 ºC, hold 1.00 minutes
Temperature Ramp: -200 ºC/min
Temperature: -180 ºC, hold 5.10 minutes
Temperature Ramp: +200 ºC/min
Temperature: +200 ºC, hold 0.25 minutes

Instrument Conditions

Transfer from Sample Loop to Adsorbent Trap: Helium, 20.0 ml/min with EFC Type 23
Transfer from Adsorbent Trap to Cryofocus Trap: Helium, 10.0 ml/min with EFC Type 23
Transfer Flow from Cryo Trap to Catalysts and FID: Helium, 20.0 ml/min with EFC Type 23

Valve Oven: 130 ºC
Oxidation Catalyst: 575 ºC
Reduction Catalyst: 380 ºC
Reduction H_2 Flow: 10 ml/minute
Flame Ionization Detector: 140 ºC
FID Range: 10-12 A/mV to 10-9 A/mv, full scale, autoranging
Time constant: fast
Data Rate: 50 Hertz

The oxidation catalyst is mounted in an external oven, held at 575 ºC. This temperature is adequate for oxidation of all organics, except methane. Since methane is vented off before the sample components reach the oxidation catalyst, a higher temperature is not required.
The Scion 450 Gas Chromatograph includes one reduction catalyst and flame ionization detector. All actions in the system are fully automated. Figure 2 illustrates actions performed to achieve this measurement.

RESULTS AND DISCUSSIONS

A typical chromatogram for 2.9 ppmCarbon Propane is shown in Figure 3. This technique generates extremely sharp peaks that enhance detection by making the peak much taller.

Calibration standards of 2.9, 0.29, 0.029 and 0.0029 ppmCarbon are displayed in a x-y Cartesian plot in Figure 4. Due to the very large concentration range, only the higher concentrations are visible on this graph, and the low ones are all bunched together and not separately discernable. A better plot is computed response factors versus log[concentration] and are shown in Figure 5. Linearity and dynamic range for the measurement are more readily viewable and ascertained.
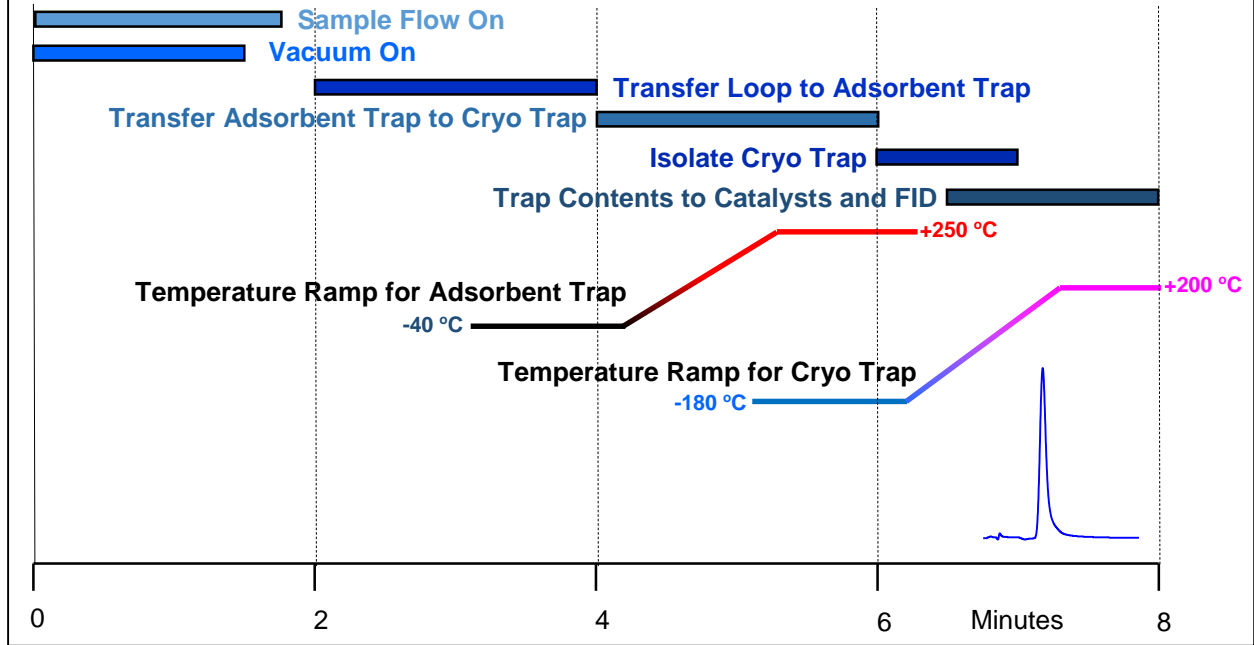
Figure 2. Timed Actions for Operations

Sample Flow On
Vacuum On
Transfer Loop to Adsorbent Trap
Transfer Adsorbent Trap to Cryo Trap
Isolate Cryo Trap
Trap Contents to Catalysts and FID

+250 °C

Temperature Ramp for Adsorbent Trap
-40 °C

+200 °C

Temperature Ramp for Cryo Trap
-180 °C

0   2   4   6   Minutes   8

Figure 3. NMOC Chromatogram of Propane at 2.9 ppmCarbon.

200

mVolts

Peak Width
= 0.78

0

7.05   7.10   7.15   7.20   7.25 Minutes

Figure 4. Calibration Curve for NMOC.

Resp. Fact. RSD: 29.72%
Coeff. Det.(r²): 0.99294

Replicates 3   3   3

150,000
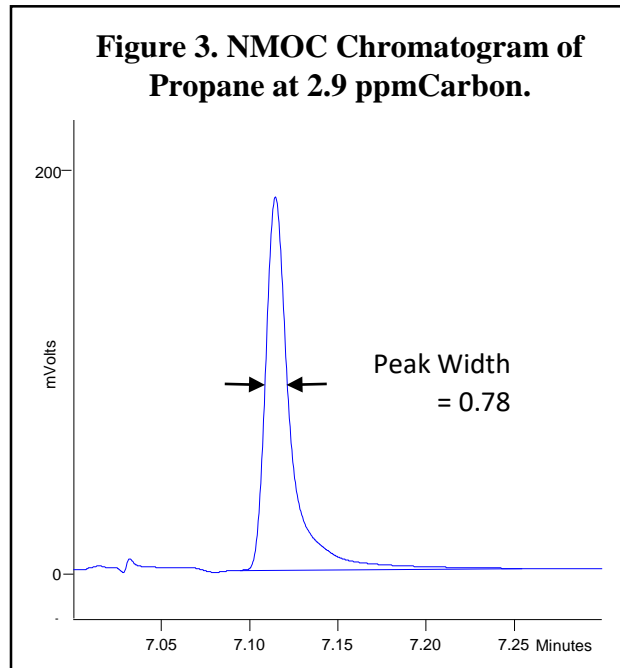
Area Counts (µV * sec)

0

0.5   1.0   1.5   2.0   2.5   3.
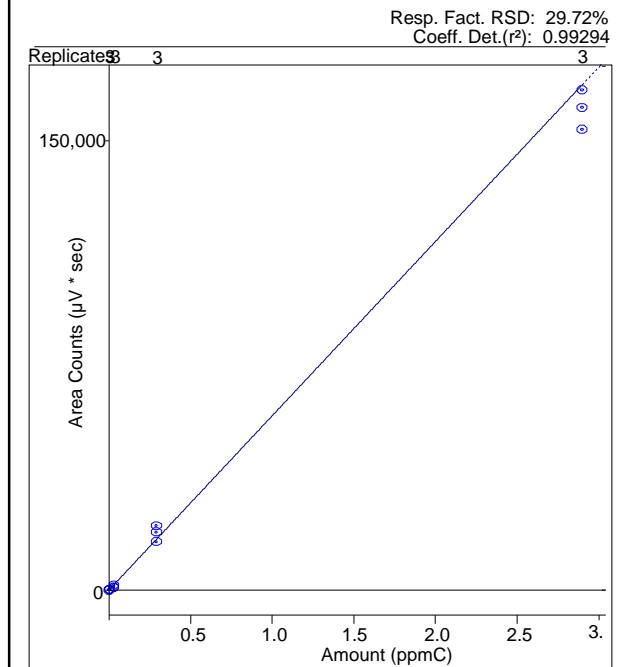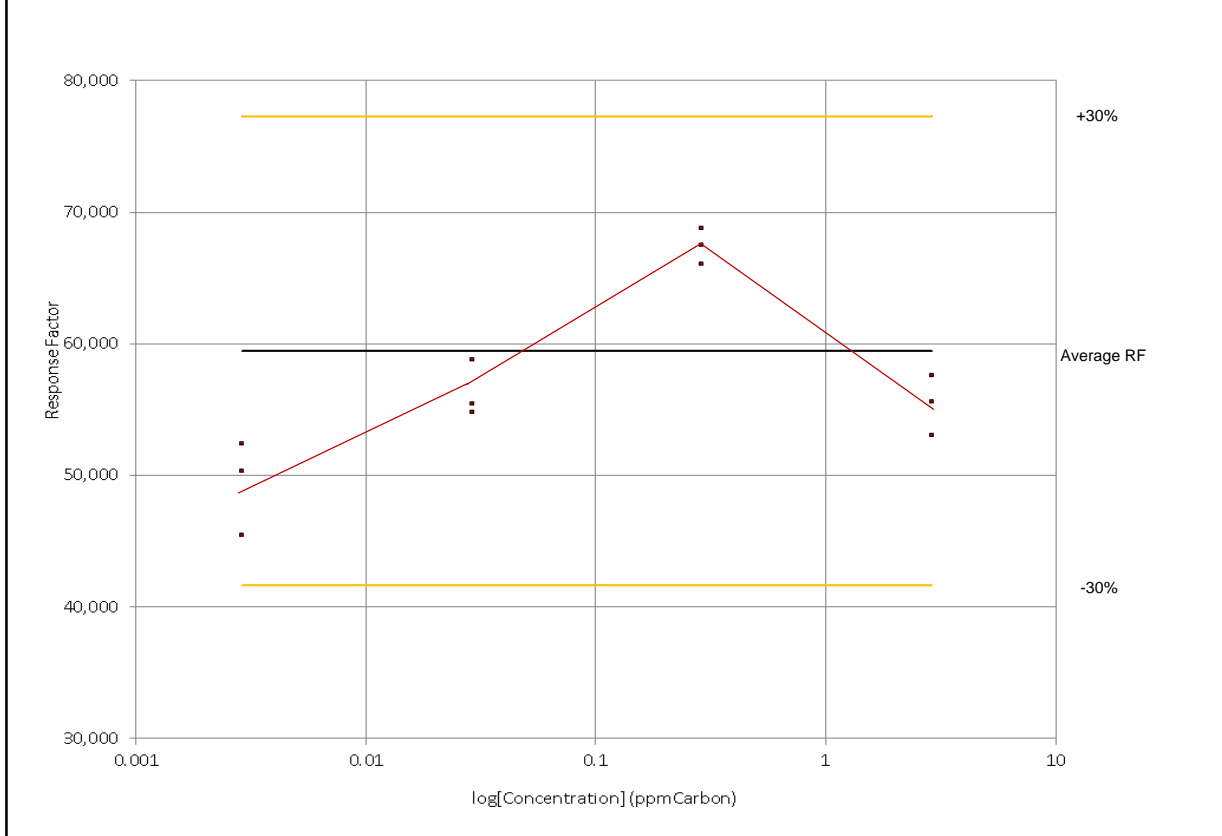
Amount (ppmC)

Figure 5. log[Concentration] Curve for NMOC.

Detection Limit

The combination of larger injection volume and dramatically sharper peak improves the ability to measure very low levels of Non-Methane Organic Compounds. Figure 6 illustrates the enhancement with seven runs near the expected detection limit.

Detection limit for non-methane organic compounds is computed from repetitive runs from a standard at or near the anticipated limit, calculating their standard deviation, and multiplying by 3.14, to yield a confidence level of 99.7% that a peak of that size can be detected. Table I lists results of the measurement and Figure 6 shows overlay of seven replicate runs.
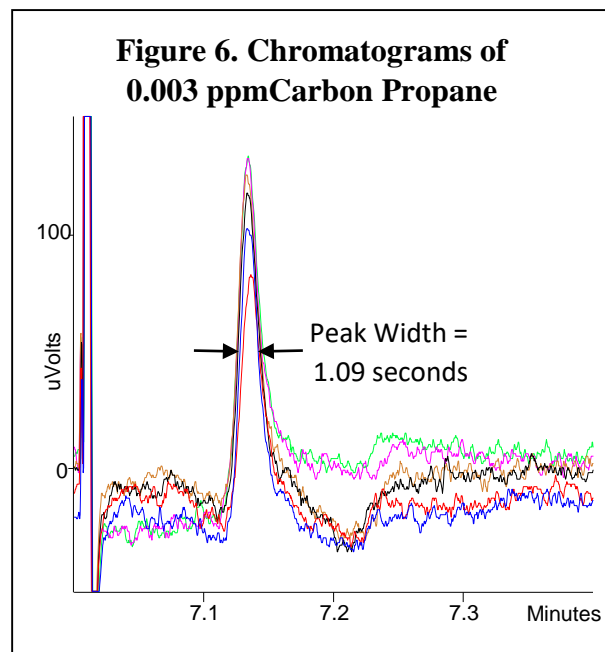

Figure 6. Chromatograms of 0.003 ppmCarbon Propane

Peak Width = 1.09 seconds

Table I. Measured Concentrations for Repetitive Runs of 0.003 ppmCarbon

0.0033	0.0033	0.0044
0.0040	0.0038	0.0030
	0.0042	

NMOC Detection Limit - 3*Std Dev = 0.002 ppmCarbon

Extreme precautions must be undertaken when setting up a system with this approach to attain the indicated performance, including:

- Locate all operations involved in this protocol away from all processes involving solvents, especially liquid-liquid extractions.
- Use dedicated canisters not previously utilized for higher concentration levels.
- Perform canister cleaning of these dedicated canisters separated from others.
- Employ very high purity helium carrier gas of 99.9999%.
- Install chromatographic-grade stainless steel tubing for all supply gases.
- Install high performance filtering of supply gases, including after pneumatic components.

SUMMARY

Advantages of this method include significantly lower detection capabilities from the larger sample volumes that can be loaded, and the very sharp detected peak, typically <2 second peak width, since broadening due to column effects is not involved. The run time for the required separation of methane, carbon monoxide and carbon dioxide from the other organics and processing the NMOC peak through the hardware is performed in a short time frame; typical analysis time is less than 8 minutes. Dynamic range for low levels is >1,000. And achievable detection limit is under 0.01 ppmCarbon, with 10 ml sample loading.

REFERENCES

1. www3.epa.gov/ttnemc01/promgate/m-25.pdf (accessed July 2017).
2. www.aqmd.gov/docs/default-source/laboratory-procedures/methods-procedures/stm-025-3.pdf (accessed July 2017).