Performance of a Non-Methane Organic Compound Analyzer - EPA Method 25 and South Coast AQMD Method 25.3

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INTRODUCTION

Measurement of total non-methane organics in ambient air and source samples permits a rapid assessment of potential release of contributors to photochemical smog. All possible volatile organics are separated from methane, carbon dioxide, and carbon monoxide. Then the group is oxidized to carbon dioxide and subsequently reduced to methane, to become an effective count of the total carbon atoms in the sample. Native methane, carbon dioxide and carbon monoxide are not included in this grouping, as they are not significantly active in photochemical reactions. Conversion of all organics to carbon dioxide and then to methane to yield the composite peak for non-methane non-ethane compounds makes the measurement an effective carbon counter. Propane can then be used to generate a response factor that then is applied to all organics. Results are reported as "ppmCarbon". Any other unit designation is not appropriate.

The protocol was originally developed by South Coast Air Quality Management District (South Coast AQMD), Diamond Bar, CA, nearly 50 years ago and has been adopted by the US EPA as EPA Method 25.[1] It has undergone several revisions since, and is now updated as South Coast AQMD Method 25.3.[2] This method now provides a better separation of carbon dioxide from the other organics, especially for low levels of non-methane non-ethane organics and very high levels of carbon dioxide. However, the specified column set does not achieve enough separation from carbon dioxide for ethane, ethene and ethyne, and these three must be allowed to elute on the tail of the carbon dioxide in the foreflush mode. Their concentrations are mathematically added to the non-methane, non-ethane organic compounds, measured from the backflush peak. Since the detector responses for these three hydrocarbons are equal,[3] concentrations for them can be calibrated against any one of them and the response factor can be applied to the others.

This report discusses performance enhancements achieved in a non-methane organic compounds (NMOC) Analyzer developed by Lotus Consulting (Long Beach) with a Scion 456 Gas Chromatograph (Austin, Texas). The design and method updates have dramatically improved readily achievable linear range, lower detection limits, and cleaner blanks. Other components are added to the target list, including oxygen, nitrogen, methane, carbon monoxide and a very wide concentration range of carbon dioxide. Provisions are included in the hardware for an easy switch between measurements with EPA Method 25 and the mandates in South Coast AQMD Method 25.3. These enhancements are often a result of improvements in instrumentation and computer power, tightening of regulatory limits and advanced automation capabilities.

Performance required for measuring non-methane organic compounds is being pushed to lower detection limits. Emissions generated by new power turbines have reduced organic releases, but still have a major impact on atmospheric chemistry, due to the very high volumes of exhaust flow. The current reference method detection limit of 1 ppmCarbon with South Coast AQMD Method 25.3 needs to be lower to allow more accurate reporting of these high-volume low-emission levels.

EXPERIMENTAL CONDITIONS

The Scion 456 Gas Chromatograph includes one reduction catalyst and flame ionization detector for reporting carbon dioxide (and ethane/ethane/ethyne for Method 25.3). A second reduction catalyst after an oxidation catalyst and second flame ionization is configured for the backflush of non-methane organic compounds for Method 25, and non-methane non-ethane organic compounds for Methods 25.3, and low levels of methane and carbon monoxide. A thermal conductivity detector is set up to report oxygen, nitrogen and higher levels of methane and carbon monoxide. All actions in the system are fully automated, including a column-switching valve to readily insert the column set for either protocol, and a valve for sample volume selection, without manual hardware changes.

A sixteen-position automated sampler to allow multiple samples to be loaded. Heated sample lines are provided to ensure sample components remain volatile during introduction. Special valving is installed to allow a mixture of Tedlar™ sample bags and pressurized sample canisters to be processed without operator intervention. And sample loops are maintained at a constant elevated temperature (to 0.1 $^{\circ}$C tolerance), 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 needed for pressure variations, due to effects of Charles' Law.

Provisions are included for selection of 1 ml or 3 ml sample loops without manual hardware changes. High level Carbon Dioxide concentrations are processed with a separate sample loop of 0.1 ml, at the option of the user.

The sample injection to the column set in the forward direction is directed to a reduction catalyst a flame ionization detector for measurement of carbon dioxide, ethane, ethene and ethyne. An oxidation catalyst is not required here as none of these has to be oxidized for proper quantitation. Then the column set flow is reversed with a second independent flow source. The eluting analytes for non-methane non-ethane organic compounds are combined into a single peak and passed on to an oxidation catalyst, a second reduction catalyst and a second flame ionization detector. This separate flow allows a higher rate to sharpen the non-methane peak shape. This sequence assures that a tailing peak from a huge level of Carbon Dioxide is not contributing erroneously to the non-methane peak.

Oxygen, nitrogen, methane and carbon monoxide are measured with a separate column pathway involving a Hayesep N stripper column plumbed in-series with a Molecular Sieve 5A column. Column effluent is directed to an included thermal conductivity detector for measurement of oxygen, nitrogen, and high levels of methane and carbon monoxide. Since the thermal conductivity detector is not destructive and as the second flame ionization detector has no analytes during the elution times of methane and carbon monoxide, the exit from the thermal conductivity detector is connected to the second reduction catalyst and second flame ionization detector for measurement of low levels for these two. The Molecular Sieve 5A column is mounted in a separate independent-controlled column oven to facilitate its reconditioning at elevated temperatures.

Oxidation of target analytes results in gradual loss of surface oxygen capacity in the oxidation catalyst. It must be occasionally recharged with oxygen. This operation is performed by a valved setup to bypass the catalyst and pass air over its surface in a "standby" mode.

Tests are required to validate performance of the catalysts by measuring peak sizes with and without catalysts. Valving is provided to allow this operation without manual reconfigurations.

Operating parameters for analyzer are listed in Table I.

Table I. Instrument Settings for Analyzer

Sample Injection Volume	1 ml, 3 ml, or 0.1 ml, user selection
Fixed Gases Sample Injection Volume	0.25 ml
Sample Loop Loading	0.01 – 0.75 minutes
Sample Injection	1.00 minute
Backflush	14.00 minutes
Heated Sample Lines	50 ºC
EPA Method 25 Column Set	Unibeads 1S, 0.3 m, and Carbosieve G, 0.6 m
SCAQMD Method 25.3 Column Set	Tenax TA, 0.3 m, and Chromosorb 106, 2 m
Fixed Gases Column Set	Hayesep N, 2 m + Mol Sieve 5A, 2m
Column Temperature	50 ºC, hold 14 minute
Column Ramp	100 ºC/minute to 150 ºC, hold 5.00 minutes
Mol Sieve Column Oven	90 ºC, isothermal
Foreflush Carrier (Argon)	10 ml/minute
Backflush Carrier (Argon)	20 ml/minute
Fixed Gases Carrier Flow (Argon)	20 ml/minute
Valve Ovens	120 ºC
Oxidation Catalyst	650 ºC
Reduction Catalyst	380 ºC
Reduction H_2 Flow	10 ml/minute
Flame Ionization Detectors	140 ºC
FID Range	10^{-12} A/mV to 10^{-9} A/mv, full scale, autoranging
Thermal Conductivity Detector	130 ºC, Filaments 250 ºC
TCD Range	0.5

Propane standard used to measure detection limits is generated from a 5.1 ppmCarbon NIST Primary Standard (Gaitherburg, Maryland) and diluted to 0.35 ppmCarbon with Environics Dilutor (Toronto, Ontario). Other standards used in the work are from Scott-Marrin, Inc. (Riverside, California).
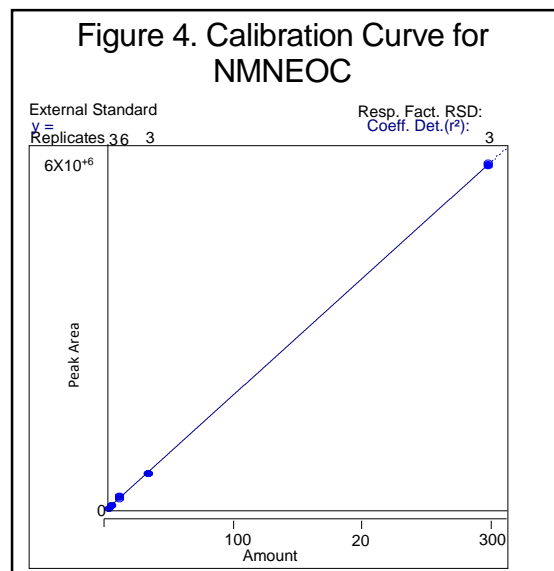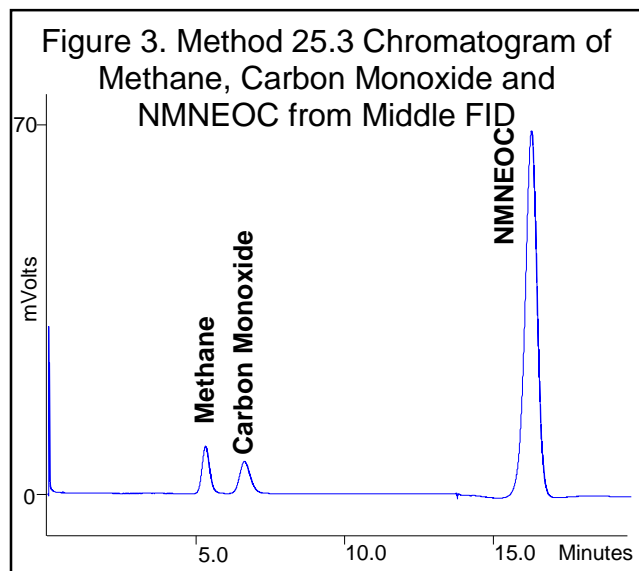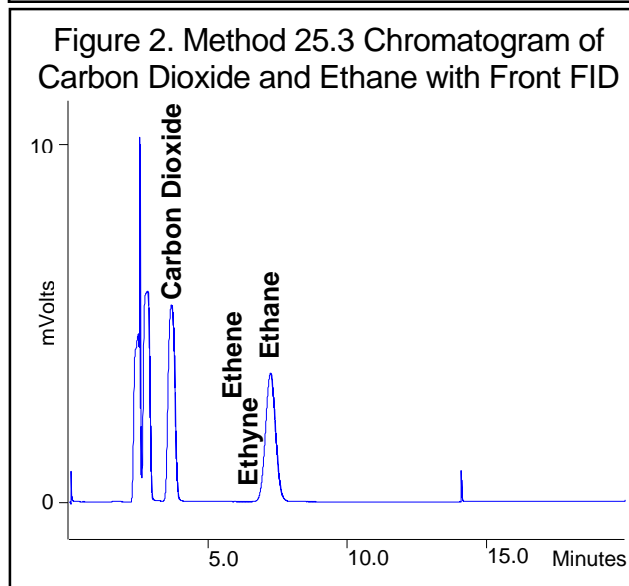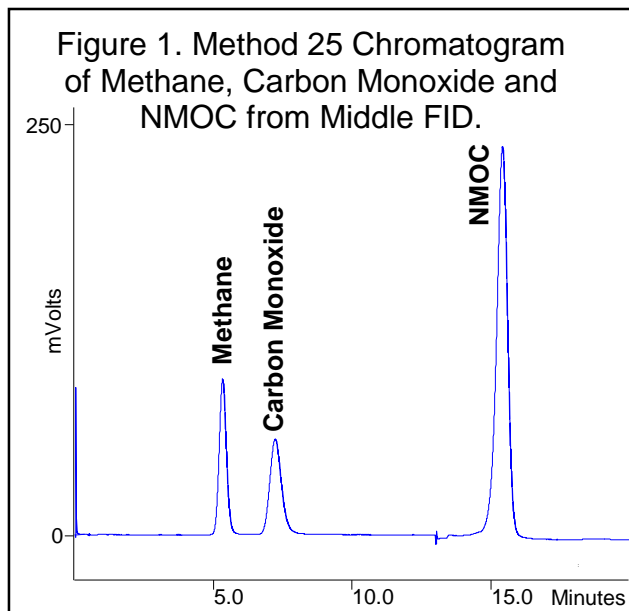
RESULTS AND DISCUSSIONS

EPA Method 25

This method was designed originally to measure higher levels of non-methane from emissions from power station stacks and landfills. The specified method detection limit is listed as 50 ppmCarbon. The primary trouble with this method is its difficulty in handling high concentrations of carbon dioxide generated from modern power turbines and from sewage treatment digester gases. And power turbines are much cleaner emission sources than conventional engines, and require lower limits for non-methane. Some regulatory agencies still specify this method for measurements of emission sources.

South Coast AQMD Method 25.3

This Southern California developed this method to handle properly low level non-methane organics and high levels of carbon dioxide (Figure 2 and 3). Linearity is demonstrated in Figure 4 to extend the measurement range from 0.05 ppmCarbon to greater than 300 ppmCarbon.

Figure 1. Method 25 Chromatogram of Methane, Carbon Monoxide and NMOC from Middle FID.

Figure 2. Method 25.3 Chromatogram of Carbon Dioxide and Ethane with Front FID

Figure 3. Method 25.3 Chromatogram of Methane, Carbon Monoxide and NMNEOC from Middle FID
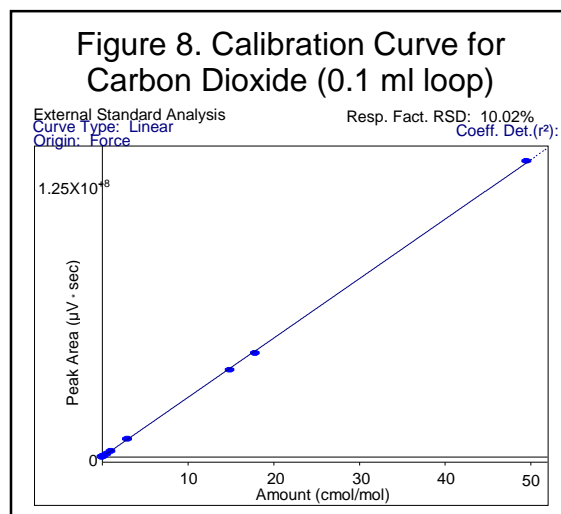
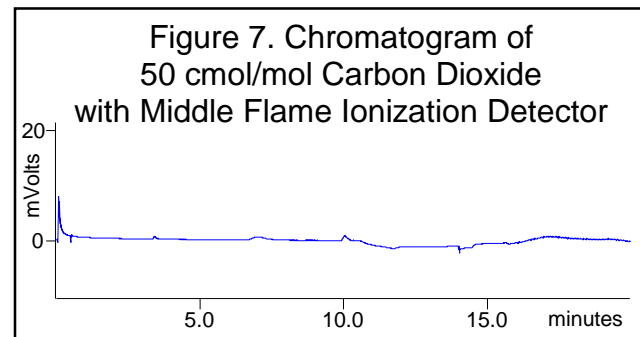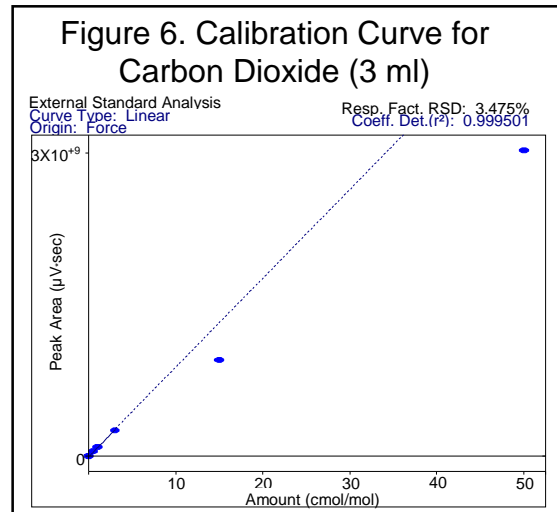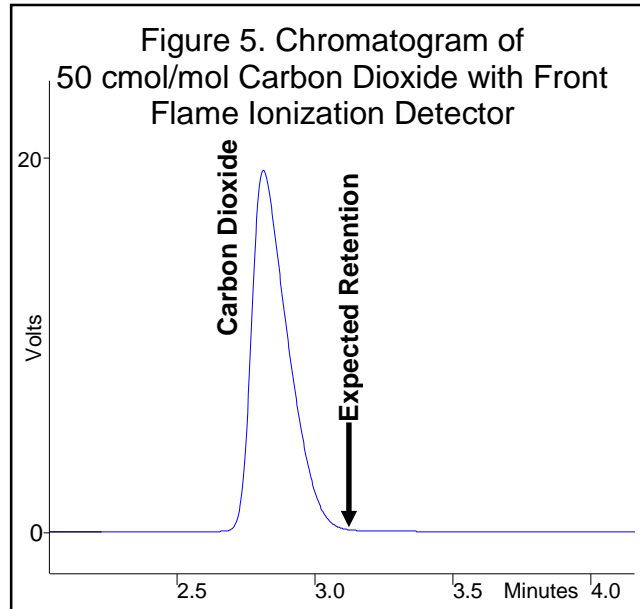Figure 4. Calibration Curve for NMNEOC

The column set specified in the method is unable to fully elute high concentrations of carbon dioxide before light hydrocarbons start coming through the columns. As a result, the method allows ethane, ethene and ethyne to come out in the foreflush, and then these concentrations are mathematically added to the total Non-Methane Non-Ethane result. Ethane, ethene and ethyne have equal responses with a high performance flame ionization detector, so only one is required to generate response factors for all three.[1]

Carbon Dioxide

Common emission sources releasing high levels of carbon dioxide are landfills (50 cmol/mol),[4] digester gas (35-40 cmol/mol) and gas turbines (up to 85 cmol/mol), especially turbines with oxygen deployed in the combustion processes.

An enlarged sample loop (3 ml) for enhanced detection of the non-methane component puts pressure on measurement of these high levels of carbon dioxide by causing overloading of the analytical columns and reduction catalyst (Figure 5). This effect creates severe non-linearity at carbon dioxide above 10 cmol/mol and a shift in peak retention (Figure 6). Despite the huge carbon dioxide eluting off the front flame ionization detector, no non-methane peak is found on the middle

Figure 5. Chromatogram of 50 cmol/mol Carbon Dioxide with Front Flame Ionization Detector

Figure 6. Calibration Curve for Carbon Dioxide (3 ml)

External Standard Analysis
Curve Type: Linear
Origin: Force
Resp. Fact. RSD: 3.475%
Coeff. Det.(r²): 0.999501

Figure 7. Chromatogram of 50 cmol/mol Carbon Dioxide with Middle Flame Ionization Detector

Figure 8. Calibration Curve for Carbon Dioxide (0.1 ml loop)

External Standard Analysis
Curve Type: Linear
Origin: Force
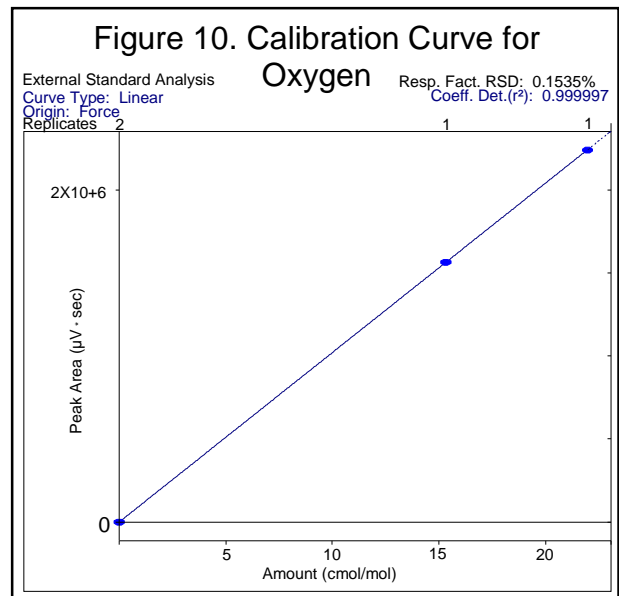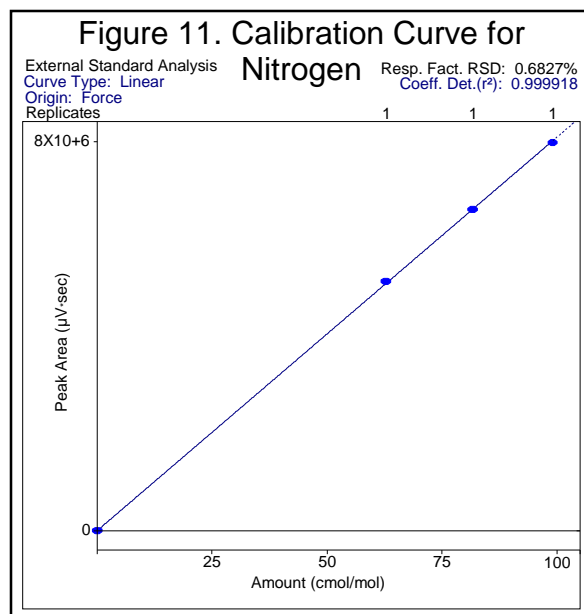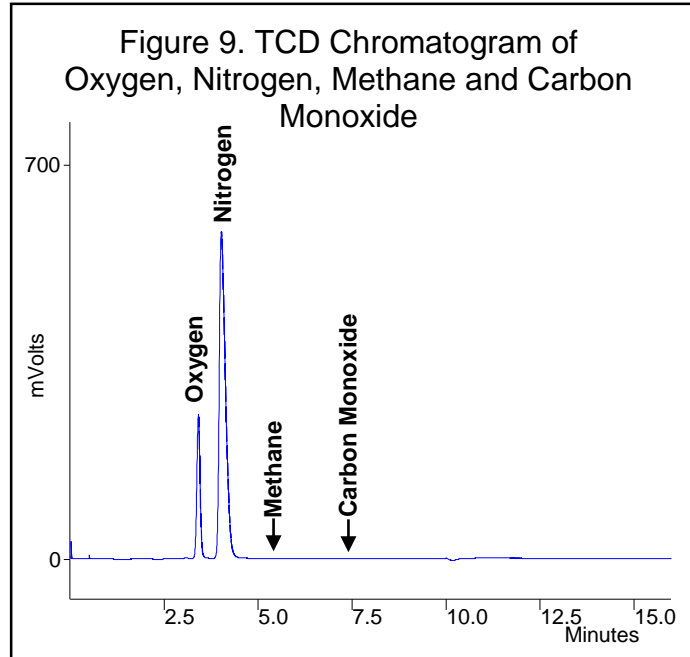Resp. Fact. RSD: 10.02%
Coeff. Det.(r²):

flame ionization detector (Figure 7). An additional gas sampling pathway with a 0.1 ml sample loop brings the linearity in to be appropriate over a much wider concentration range (Figure 8). This secondary injection can be performed concurrently with the standard measurement.

Other Fixed Gases (Oxygen, Nitrogen, Methane and Carbon Monoxide)

Emission samples can always possess other gases that are not part of the non-methane grouping, but are often requested. Oxygen is an important indicator that the sampling process is executed appropriately. For example, samples from landfill sources will have a reduced concentration of oxygen. If instead the sample yields oxygen concentration near ambient air (~21 cmol/mol), then the sample was not collected from a subterranean source and was instead ambient air.

Oxygen, nitrogen, methane and carbon monoxide are properly separated with a molecular sieve column, with a porous polymer column configured to strip off all other components to vent, and measured with a thermal conductivity detector (Figure 9). Argon is present in ambient air at 0.93 cmol/mol,[5] and has the same presence in most samples analyzed with this method. With molecular sieve columns, under normal operating conditions, oxygen and argon coelute. This overlap becomes a major contributor to significant errors in measuring lower levels of oxygen. By utilizing argon as a carrier gas, the detection of argon is cancelled out and only oxygen is determined are reported.

Figure 9. TCD Chromatogram of Oxygen, Nitrogen, Methane and Carbon Monoxide

Figure 10. Calibration Curve for Oxygen

External Standard Analysis
Curve Type: Linear
Origin: Force
Replicates   2

Resp. Fact. RSD: 0.1535%
Coeff. Det.(r²): 0.999997

Figure 11. Calibration Curve for Nitrogen

External Standard Analysis
Curve Type: Linear
Origin: Force
Replicates

Resp. Fact. RSD: 0.6827%
Coeff. Det.(r²): 0.999918

Methane and carbon monoxide are measured with both a thermal conductivity detector and a flame ionization detector with a reduction catalyst plumbed in series with the thermal conductivity detector. High levels are reported from results from the thermal conductivity. The flame ionization detector provides values for low levels for methane and carbon monoxide. Chromatography for these four components occurs in a region when no other target analyte is eluting, and offers no interference in the final results. Linearity for oxygen and nitrogen are provided in Figures 10 and 11.

Catalyst Performance Checks

Results for nearly all of the analytes relies heavily on the efficient conversions of the catalysts. Any degradation in performance will yield reported concentrations lower than their actual values. All catalysts employed are impacted by presence of sulfur gases in samples, such as hydrogen sulfide, and by depletion of surface oxygen, in the case of the oxidation catalyst. Regular monitoring of these catalysts is required. The process is very simple. All catalysts are first bypassed and a known concentration of propane is injected. Its area counts becomes the basis for comparisons. Then the oxidation catalyst is included, but the reduction catalyst is bypassed, and the propane standard is injected again. Propane should be fully converted to carbon dioxide and any detected area represents the loss of efficiency with this catalyst.

The appropriate reduction catalyst is brought back in series and propane is injected a third time. The loss in area when compared with the original measurement is amount of degradation of the reduction catalyst. Figure 12 and Table II summarize typical results. Method requirement for the oxidation catalyst is greater than 99%, and for the reduction catalyst is greater than 95%.
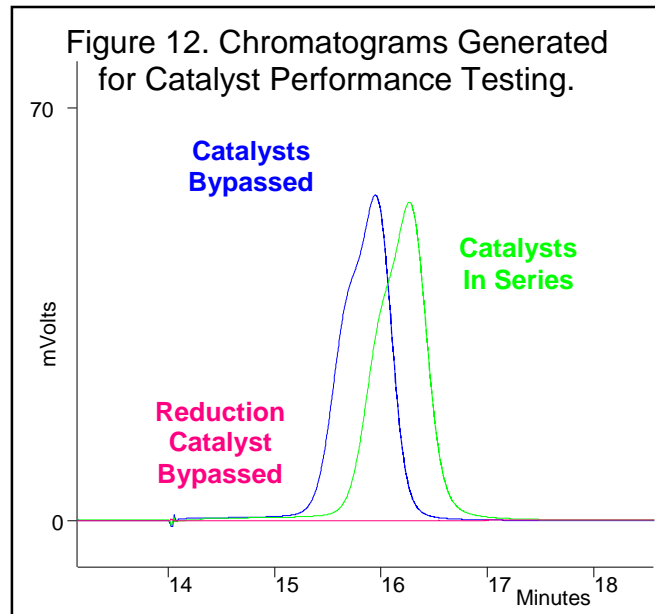

Figure 12. Chromatograms Generated for Catalyst Performance Testing.

Table II. Middle Catalyst Efficiency Tests

|	Area Counts	Calculation	Efficiency
Propane Both Catalysts Bypassed	17,675	-	-
Reduction Catalyst Bypassed	<50	<50/17,675)	>99%
Catalysts in Series	17,355	17,355/17,675	>98%

Detection Limits

Detection limit for non-methane non-ethane organic compounds is computed from repetitive runs from a standard at or near the anticipated limit, calculating their standard deviation, and multiplying by 3, to yield a confidence level of 99% that a peak of that size can be detected.[6] Table III lists results of the measurement and Figure 13 shows overlay of eight repetitive runs.

Table III. Raw Area Counts (µV*sec) for Repetitive Runs of 0.35 ppmCarbon

7,743	7,022
7,416	6,987
6,718	7,270
7,751	7,425

NMNEOC Detection Limit - 3*Std Dev = 0.05 ppmCarbon

Figure 13. Eight Chromatograms of 0.35 ppmCarbon Propane used for Detection Limit.
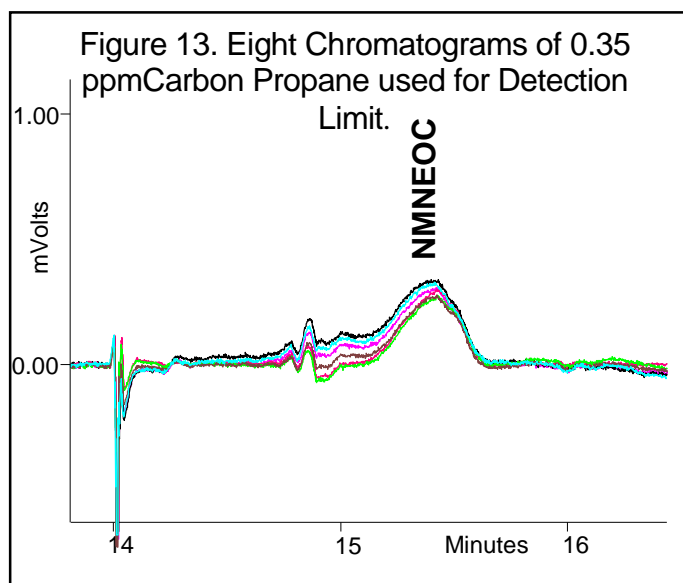
Liquid Water in Samples

Presence of liquid water in sample canisters can have detrimental effects on this measurement. Ambient air at 30 °C and 1 atmosphere contains approximately four cmol/mol.[7] At 70 °C and 1 atmosphere, approximately 28 cmol/mol of water vapor is present in gas samples. Any concentration of water above these levels in sample sources will result in liquid inside the canister, particularly when the condensate trap, indicated in South Coast AQMD Method 25.3 and usually inserted preceding the canister loading, is removed, and when the canister temperature cools to ambient. With liquid presence in the canister, water-soluble organics, such as alcohols, ketones and aldehydes will partition into the liquid water and will not be measured in the non-methane non-ethane peak.

One suggestion has been offered to only fill the canister to half total volume and then pressurize with helium or nitrogen to prevent condensation. The injection volume is doubled to compensate for this sample dilution. Then the reported detection limit doubles as well for these samples. Even then, this process only raises the saturation level to eight percent, and may not be enough to keep water in a vapor state from landfill and digester gases. And any liquid in a canister prohibits mounting canisters upside down on an automated sampler.

SUMMARY

This new approach to the measurement extends the ability to measure non-methane organic compounds to lower levels, as efforts proceed to monitor and reduce emissions from stationary sources. New regulatory measurement concentration requirements mandate lower levels, especially related to Best Available Control Technology (BACT) mandates from regulatory agencies.

This methodology for reporting non-methane organic compounds involves separate flow pathways for the foreflush and backflush actions, dramatically improves the sharpness of the non-methane non-ethane organic compounds peak, lowers detection limits to 0.05 ppmCarbon with a 3 ml sample injection, and properly handles major amounts of carbon dioxide. Oxygen, nitrogen, methane and carbon monoxide are also reported during the same measurement.

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