Low Level TNMHC Measurements

(Total Non-Methane Hydrocarbons)

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Introduction

- **Exhaust emission testing has become increasingly important to both manufacturers and operators of any form of equipment relying on the combustion of Fossil Fuels as emission limits are being drastically reduced and fines for non-compliance steadily rising**

The following key compounds have the most stringently regulated emissions due to their effects on atmospheric chemistry

Nitrogen & Sulfur Oxides (NOx, SOx)

Carbon Monoxide &Carbon Dioxide

Total Non-Methane Hydrocarbons

Particulate Matter

With the goal of adhering to Federal Clean Air Act standards, the need for accurate quantification of low level TNMHC has moved to the forefront of source testing and analysis

Current emissions standards for Combustion Turbines subject to the 2.0 ppmC (TNMNEOC) BACT limit has created the need of a new sampling and analysis protocol able to accurately measure TNMNEOC at this level.

The following is a brief summary of the current Methodologies available

- **EPA method 25A**
- **Uses portable GC/FID**
- **Has response factor issues**
- **Susceptible to many interferences**

- **EPA Method 25**
- **Uses a sampling tank and steel trap**
- **Analysis by GC/FID (TCA) Total Carbon Analyzer**
- **Oxidation & Reduction Catalyst System**
- **Capable of quantifying emissions >50 ppmC**
- **Sampling done in triplicate consecutively**

- **SCAQMD method 25.1**
- **Modified version of EPA method 25**
- **Re-designed steel trap**
- **Oxidation & Reduction Catalyst System**
- **Sampling done in duplicate simultaneously**
- **Generally accepted Reporting limit >50 ppmC**
- **More stringent QA/QC requirements**

- **SCAQMD method 25.3**
- **Modified version of SCAQMD 25.1**
- **Aqueous impinger trap**
- **Oxidation & Reduction Catalyst System**
- **Sampling done in duplicate simultaneously**
- **Generally accepted upper Reporting limit ~50 ppmC**
- **More stringent QA/QC requirements**

- **EPA method TO-12**
- **Ambient air method**
- **Summa canister sampling**
- **GC/FID analysis with cryo-concentration**
- **No Oxidation & Reduction Catalyst System**
- **ppbC Reporting limit**
- **Riddled with problems**

- **EPA method TO-12 PAMS Protocol**
- **Modification of original TO-12**
- **C2 to C12 speciated Hydrocarbons**
- **GC/FID analysis with cryo-concentration**
- **No Oxidation & Reduction Catalyst System**
- **Generally accepted Reporting limit 1.0 ppbC**

- **Interferences**
- **Difficulties with existing methods arise from interfering combustion products and condensation due to the temperature drop between stack and ambient conditions.**
- **Carbon Dioxide is the major interference in the measurement of TNMOC using EPA 25 or SCAQMD 25.1. These methods are not reliable for emissions <50.0 ppmC**

In-field methods such as EPA 25A are not suitable, as they utilize FID's or NDIR's which have major response factor issues for various VOC's.

Cryogenic concentration techniques such as those used in EPA TO-12 have major water management issues resulting in FID flame blowouts and baseline interferences.

EPA TO-12 PAMS protocol utilizes modern cryofocusing as well as CO2 and H20 management techniques, has the capability to report down to 1.0 ppbC with little to no interferences.

This method does not utilize a oxidation/reduction catalyst system and is therefore susceptible to bias low response factors for things such as carbonyls.

This method does however speciate 59 hydrocarbons between C2 and C12 giving superior resolution especially for exempt compounds such as Ethane.

SCAQMD method 25.3 offers reliable quantitation < 50.0 ppmC TNMNEOC and is not prone to bias response factors.

The PQL for this method is almost entirely based upon the volume of air collected and the background concentration of VOC's in the equipment and water used in the impingers.

SCAQMD has a proposed MDL of 1.0 ppmC

The PQL for the Tank portion of the sampling train is 1.0 ppmV as propane

(lowest point in the curve)

The PQL in the Aqueous Trap portion is 4.0 ug/sample (1.0 ppmC x 4 ml)

If you assume an 8.0L tank filled to 7.0L and pressurized to 900mmHg, using the method PQL's you obtain a final reporting limit between 5.0 – 6.0 ppmC

This is approximately 3x higher than the RL needed for the current BACT limit of 2.0 ppmC for Turbines

In order to meet the RL, you would need to report down to the MDL which carries with it the potential for a large amount of error.

This would require certification of every piece of equipment, including the water, to the MDL level as well which may still leave the potential of reporting background levels as false positive detects.

In summary, there are currently thousands of Combustion Turbines subject to the 2.0 ppmC BACT emissions limit with no approved method capable of accurately measuring to that level.

Thus the need for method development and performance evaluation is at a critical level.

Method Development

Over the past year, AAC, in conjunction with SCAQMD, has begun trials with a modified version of SCAQMD method 25.3

SCAQMD method 25.3 modified

- The major modification began with altering the sampling train in which the impinger was removed leaving only the sampling tank and probe.
- In order to prevent condensation within the tank stemming from moisture in the emissions, a flow controller is used to fill a little over half of the tank in one hour.

- Upon receipt at the laboratory, the tank is then pressurize with dry UHP helium or Nitrogen in order to distribute the moisture and prevent condensation.
- The analytical sample loop was also doubled in order to achieve lower reporting limits.

All of the other analytical specs including the oxidation and reduction catalysts remained the same.

An initial calibration curve was established from 0.1 to 5.0 ppmV as propane. This is approximately 10x lower than the original method.

SCAQMD Method 25.3 modified Calibration Curve

Theoretical Concentration (ppmv)	Retention time (min)	Response Area	RPD from initial result (+/- 20%)	Std Deviation	Theoretical Concentration (ppmv)	Response Area (mean)	Calculated Concentration (From Mean)	Recovery (+/- 15 %)
0.10	6.90	5839						
0.10	6.91	5892	0.9	37.48	0.10	5866	0.11	103
0.26	6.90	14348						
0.26	6.92	15361	6.8	716.30	0.26	14855	0.27	104
0.52	6.90	30570						
0.52	6.89	29195	4.6	972.27	0.52	29883	0.54	105
1.04	6.90	59520						
1.04	6.89	62017	4.1	1765.65	1.04	60769	1.11	106
2.60	6.90	151366						
2.60	6.90	148755	1.7	1846.26	2.60	150061	2.73	105
5.20	6.90	285876						
5.20	6.90	276256	3.4	6802.37	5.20	281066	5.12	98
Avg RT	6.90	RT Window	+/- 0.20 min			Calb. Type	Linear	*Y=MX+B*
						R2 value:	0.9980	*Must be > 0.990*
Calibration Verification Standards:						Intercept (B)	0.00	*Included*
						Lin Const (M)	54921.60	
CCV	Retention Time	Result (ppmv)	% Rec					
2.5 ppmv	6.89	2.60	100.0					
2.5 ppmv dp	6.90	2.59	99.6					

The QA/QC analyses were then targeted to the expected concentrations in the samples around 0.25 ppmV as propane

An MDL study was then conducted in order to evaluate the existing curve and system reproducibility which resulted in a 0.016 ppmV detection limit.

SCAQMD method 25.3 modified MDL Study

Analyte:	Conc.	MDL #1	MDL #2	MDL #3	MDL #4	MDL #5	MDL #6	MDL #7
TNMNEOC	0.050	0.047	0.056	0.043	0.053	0.047	0.056	0.048
Analyte:	Mean	Std Dev	MDL	MRL				
TNMNEOC	0.050	0.005	0.016	0.047				
Analyte:	LOD	LOQ	Conc./MDL	M % Rec	S:N Ratio			
TNMNEOC	0.015	0.050	3.0	100	9.93			
Analyte:	PQL	RL						
TNMNEOC	0.100	0.100						

- The overall resultant PQL established using a 6.0L summa canister and pressurizing to 900 mmHg, including the 1.086 bias correction factor from the original method is < 1.0ppmC

- Several successful sampling events have been conducted since November of 2011

- The following table shows 5 duplicate runs which were analyzed by both SCAQMD 25.3 modified and for comparison purposes, EPA TO-12 PAMS protocol.

Comparison of TNMNEOC measurements

	25.3 mod(ppmc)	PAMS(ppmc)
Run 1	0.21	0.07
Run 1 dp	0.16	0.18
Run 2	0.24	0.10
Run 2 dp	0.22	0.08
Run 3	0.22	0.07
Run 3 dp	0.17	0.06
Run 4	0.44	0.24
Run 4 dp	0.25	0.18
Run 5	0.17	0.13
Run 5 dp	0.20	0.07

The table shows a fairly consistent 2x to 3x higher result for the 25.3 analysis when compared to the PAMS analysis.

This is believed to be due to PAMS being biased low for oxygenated and halogenated compounds in addition to the 25.3 modified analysis being biased high due to elevated levels of water and CO2 which produce a small baseline hump at the TNMNEOC RT making integration very difficult at this level.

SCAQMD method 25.3 modified could be the resolution to low level TNMNEOC emissions measurements with further method development and many more comparative samples and analyses.

Future goals include the possibility of further modifying this method to include advanced cryofocusing instrumentation utilizing water and CO2 management techniques.

Conclusions

- **AAC laboratory has successfully developed and validated a cost effective method to measure low level TNMNEHC (2ppmc).**
- **This method meets the recent BACT regulations for Turbine emissions.**
- **This method does not suffer from interferences.**

Thank You,

On behalf of everyone at

Atmospheric Analysis and Consulting Inc.