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Enthalpy Analytical
Standard Operating Procedure

Analysis of Canisters for Ozone Precursors (PAMS)

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Author	David M. Berkowitz	Date Written	July 14, 2010
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Pages 7

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1.0 Scope and Application

This document describes the procedures for sample preparation, analysis, and QC of volatile organic compound ozone precursors in ambient air samples. Air samples are collected in 6L or 1.4L canisters at pressures above or below atmospheric pressure. The compounds determined using this SOP are listed in Table 15.1.

2.0 Summary of Method:

The samples are analyzed using a cryogenic concentrator and a gas chromatograph equipped with a flame ionization detector. Sample analysis begins by employing a three stage sample concentration technique using a series of cryogenically cooled traps. The sample is desorbed and refocused at the head of the analytical column for enhanced chromatographic resolution.

It is the responsibility of the qualified analytical staff of Enthalpy Analytical, Inc. to follow the procedures set forth in this SOP.

3.0 Definitions:

3.1 FID – Flame Ionization Detector
3.2 ppbC – Part per billion Carbon
3.3 VOCs - Volatile Organic Compound Ozone precursors
3.4 Batch – A batch consists of up to 16 samples over a 24 hour period.
3.5 LCS – Laboratory Control Sample (Propane only)
3.6 ICAL – Initial Calibration, Initial multipoint calibration
3.7 ICV – Initial Calibration Verification, Second source verification of initial propane calibration
3.8 RTS – Retention Time Standard, daily analysis of 57 component standard
3.9 CCV – Continuing Calibration Verification, daily midpoint calibration standard
3.10 PAMS – Photochemical Assessment Monitoring Stations
3.11 TNMOC – Total Non-methane Organic Compounds
3.12 RPD – Relative Percent Difference
3.13 Zero Air – Hydrocarbon free air

4.0 Safety:

4.1 Appropriate personal protective equipment should be worn including a lab coat, gloves and safety glasses during standard preparation and sample analysis.

5.0 Equipment and Supplies:

5.1 Gas Chromatograph (GC) –Agilent 5890 or 6890N series or equivalent equipped with an FID.
5.2 GC Column – 60 m, 0.32 mm, 1.0 um film thickness fused silica capillary column coated with 100% dimethyl polysiloxane. Restek® Rtx-1 or equivalent.

5.3 Concentrator – Entech 7100A Preconcentrator or equivalent; it utilizes a 3-stage concentration to eliminate water vapor, methane and CO_2.

5.4 Data system – Agilent ChemStation or equivalent is used for data acquisition and processing. This system is capable of continuous acquisition and storage of chromatographic data obtained throughout the run.

5.5 Entech 4600A Dynamic diluter equipped with a 5L/min and a 50cc/min for standard preparation.

6.0 Reagents and Standards:

6.1 PAMS Retention Time Standard 57 component – A certified cylinder containing 57 ozone precursor hydrocarbon compounds at various concentrations.

6.2 Calibration standards – A NIST traceable 1ppm (3000 ppbC) Propane stock calibration gas cylinder is purchased from a vendor. Intermediate gas standards are prepared in clean canisters at 7 ppbC and 141 ppbC, using the stock standard. These standards are diluted to create a calibration curve ranging from 0.7 ppbC to 3000 ppbC propane.

6.3 Initial Calibration Verification Standard (Second Source Standard) – The Certified 57 component Retention Time Standard will serve as a second source propane standard

6.4 Zero-air – for standards prep, blanks and sample dilution. High purity Nitrogen may be substituted if sufficiently clean air is not available.

7.0 Sample Preservation, Storage, and Handling:

7.1 Samples are stored in the ambient secure sample storage area, prior to, and after analysis.

7.2 VOCs are stable for at least 30 days after collection in canisters.

8.0 Calibration:

8.1 Initial Calibration:

8.1.1 Analyze a multipoint initial calibration consisting of a minimum of 5 concentration levels. One of the calibration levels must be the same as the daily continuing calibration. (See tables 15.2 and 15.2 for typical GC and pre-concentrator operating conditions.)

8.1.2 Two humidified canister standards containing propane, one at 141 ppbC and one at 7.0 ppbC, are prepared. These canisters are analyzed at various load volumes to yield concentrations between 0.7 ppbC up to 141 ppbC. The certified 3000 ppbC (1 ppm) propane standard can be used as well to extend the range of the calibration.

8.1.2.1 Analyzing a 500cc aliquot of the 141 ppbC standard canister is an undiluted analysis, resulting in a 141 ppbC standard concentration. Analysis of a 150cc aliquot of the 141 ppbC standard canister is a 3-fold dilution of the standard, resulting in a 42 ppbC standard concentration.

8.1.3 Enter the concentration of each level of propane, in ppbC, into the calibration table when new standards are prepared. A linear regression curve should have a correlation coefficient of $\geq$0.995. A single point calibration is entered for each of the other 56 components in the cylinder such that the slope is entered as the amount (concentration) and the area is entered as 1.00. This will calculate all compounds in ppbC using the propane response factor.

8.1.4 Initial Calibration Verification/LCS:

8.1.4.1 Analyze an initial calibration verification standard (or second source standard) after the acceptable analysis of an initial calibration. The second source standard is the Propane in the 57 component Retention Time Marker standard.

8.1.4.2 The results of the analysis of the second source standard for propane should be within 20% of its tag value. The RPD between the propane in the RTS and the initial calibration should be within 10%. The retention time of the propane in the RTS should be within 0.1 minutes of the propane in the initial calibration. If the second source standard does not meet these criteria, reanalyze the standard. If reanalysis fails, check the initial calibration for errors and recalibrate if necessary.

8.2 Daily/Continuing Calibration Verification (CCV):

8.2.1 Analyze a mid-level continuing calibration at the beginning and end of analytical sequence. The results of the analysis of the CCV should be 90 to 100%.

8.2.2 Analyze the Retention Time Standard (RTS) to establish the daily windows for each component.

8.3 Following a passing LCS, a system blank must be analyzed to ensure the analytical system is not contaminated. See blank acceptance criteria in section 10.

8.4 Sample analysis may begin once the system has meet initial or continuing calibration, LCS and blank acceptance criteria.

9.0 Procedure:

9.1 Canister Cleaning (see SOP ENT-089 "PAMS Canister Cleaning" for canister cleaning procedures):

9.2 Sample Preparation:

9.2.1 Measure and record the pressure of each canister in mmHg, prior to analysis. Use a calibrated test gauge. Pressurize the canister using zero air. Document the final pressure in mmHg. (Canisters are usually pressurized to a gauge reading of approximately 700 mmHg for an approximate 2-fold dilution of the sample. The canister may be pressurized more or less based on the test program data quality objectives.)

9.2.2 The Entech concentrator is equipped with a vacuum pump that will allow samples received at ambient pressure to be analyzed without additional pressurization, if a lower detection limit is required.

9.2.3 Initial and final canister pressures, temperature and barometric pressure are recorded on Tank Pressurization forms in addition to client name, project number, client sample ID, canister number, analysts initials and the date.

9.3 Sample Analysis

9.3.1 Samples are analyzed in the same manner as calibration standards. If the sample is to be analyzed with no instrument dilution factor a 500mL aliquot of the sample is analyzed. If the sample is expected to be high level, then a smaller sample volume may be analyzed. See section 8.1.2.1 for an explanation of instrument dilutions.

9.3.2 The concentration of target compounds in the sample analysis must fall within the established instrument calibration range. If any target compound concentration exceeds the calibration range, the sample must be reanalyzed at a dilution.

9.3.2.1 When more than one compound concentration exceeds the instrument's calibration range, dilute the sample based on the highest compound concentration.

9.3.2.2 Dilute the sample in the same manner described in section 8.1.2.1, until the highest concentrated target compound falls within the instrument's calibration range.

9.3.2.3 Target compound concentrations that exceed the instrument's calibration range are flagged with an "E", denoting an estimated concentration.

9.3.2.4 Report the undiluted (or least diluted) analysis and the diluted analysis that brings the highest concentrated target compound within the calibration range. All target analytes are reported from the undiluted (or least diluted) analysis. Only target compounds that exceeded the calibration range in the undiluted (or least diluted) analysis are reported from the diluted analysis.

9.4 Once the samples have been analyzed, process each sample using the data analysis software. Use the daily calibration Retention Times Standard to identify target compounds based on retention time window.

9.5 Affix the printed analytical sequence tables to the instrument logbook pages. Record all information associated with instrument calibration and sample analysis on the instrument logbook pages.

9.6 Record instrument maintenance in the instrument's maintenance logbook.

10.0 Quality Control

10.1 Humidified Method Blank:

10.1.1 Analyze one method blank per batch following the initial or continuing calibration standard(s) to assess system background and carryover.

10.1.2 Analyze the method blank in the same manner as the calibration standards.

10.1.3 The method blank must not contain more than 10 ppbC TNMOC or any target compounds at concentrations greater than 3 times the MDL value.

10.2 Laboratory Control Sample (LCS)

10.2.1 The LCS is an analysis of the initial calibration verification standard at a concentration that falls within the initial calibration range.
10.2.2 Analyze the LCS with each batch.
10.2.3 The LCS analysis is acceptable if the propane recovery is 80 to120% of its tag value. If the LCS fails, reanalyze. If the LCS continues to fail, check for problem with the instrument or standards; recalibrate if necessary.
10.2.4 Method blank and sample analysis may begin once a passing LCS is achieved.
10.2.5 Evaluate the LCS at program startup and once weekly to verify sample trapping and transfer efficiency. A minimum of one target compound per carbon number should be evaluated for recovery. Recovery should be within 80-120%.

10.3 Laboratory Duplicate:
10.3.1 Analyze one field sample in duplicate per sample batch
10.3.2 The results of the duplicate analysis should be within 25% RPD for target concentrations greater than 5 times the Method Detection Limit (MDL).

11.0 Data Analysis and Calculations:

11.1 Calculate the RPD between the average sample analysis and the duplicate for all analytes greater than 5 times the MDL:

$$\left(\frac{Conc_{init} - Conc_{dup}}{Conc_{init}}\right) * 100$$

Where:
Conc $_{init}$ = Concentration of initial analysis
Conc $_{dup}$ = Concentration of duplicate analysis

11.2 If the canister is pressurized prior to analysis, a tank dilution factor is calculated and included in the calculation for "as sampled" analyte concentrations. The following formula is used to calculate tank dilution factors:

$$\frac{(GPF + PbarF)}{(TempF + 460)}$$

$$\overline{\left(\frac{GPI + PbarI}{TempI + 460}\right) - \left(\frac{GPP + PbarP}{TempP + 460}\right)}$$

Where:
GPF = Final Gauge Pressure, mmHg
PbarF = Final Barometric Pressure, mmHg
TempF= Final Temperature, degrees F
GPI = Initial Gauge Pressure, mmHg
PbarI = Initial Barometric Pressure, mmHg
TempI = Initial Temperature, degrees F
GPP = Pretest Gauge Pressure, mmHg
PbarP = Pretest Barometric Pressure, mmHg
TempP = Pretest Temperature, degrees F

11.3 Conc. as sampled = Conc as analyzed * Tank Dilution Factor * Analytical Dilution Factor

12.0 Method Performance:

12.1 Method performance is demonstrated through MDL studies and demonstrations of capability performed by the analyst. Follow procedures detailed in SOP ENT027, "Minimum or Method Detection Limits (MDLs) and Limits of Quantitation (LOQ) – Chemical Measurement Division

(CMD)" for determining MDLs. Follow the procedures detailed in SOP ENT005, "Training" for performing demonstrations of capability.

12.2 Interferences:

12.2.1 Contamination may occur in the sampling system if canisters are not properly cleaned before use. Additionally, all other sampling equipment (e.g., pump and flow controllers) should be thoroughly cleaned to ensure that the filling apparatus will not contaminate samples.

12.2.2 Very volatile compounds, such as the C_2 and C_3 hydrocarbons can display peak broadening and co-elution with other species if the compounds are not delivered to the GC column in a small volume of carrier gas. Refocusing of the sample after collection on the primary trap, either on a separate focusing trap or at the head of the gas chromatographic column mitigates this problem.

12.2.3 Interferences in canister samples may result from improper use or from contamination of: (1) the canisters due to poor manufacturing practices, (2) the canister cleaning apparatus, and (3) the sampling or analytical system. Attention to the following details will help to minimize the possibility of contamination of canisters. Canisters should be stored in a contaminant-free location and should be capped tightly during shipment to prevent leakage and minimize any compromise of the sample.

12.2.4 Impurities in the calibration dilution gas (if applicable) and carrier gas, organic compounds out-gassing from the system components ahead of the trap, and solvent vapors in the laboratory account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running humidified zero air blanks. The use of non-chromatographic grade stainless steel tubing, non-PTFE thread sealants, or flow controllers with Buna-N rubber components must be avoided.

12.2.5 Significant contamination of the analytical equipment can occur whenever samples containing high VOC concentrations are analyzed. This in turn can result in carryover contamination in subsequent analyses. Whenever a high concentration sample is encountered, if possible, it should be followed by an analysis of humid zero air blank to check for carryover contamination. Otherwise, closely examine the sample analysis following the high concentration sample for the presence of carryover. If carryover is suspected, reanalyze the affected sample.

12.2.6 In cases when solid sorbents are used to concentrate the sample prior to analysis, the sorbents should be tested to identify artifact formation.

13.0 Pollution Prevention and Waste Management

Sample canisters are purged and vented into a laboratory fume hood or a closed system manifold.

14.0 References

EPA Technical Assistance Document for Sampling and Analysis of Ozone Precursors, EPA/600-R-98/161, September 1998

15.0 Tables, Diagrams, and Flow Charts

15.1 Target Volatile Organic Compounds

Ethene (Ethylene)	3-Methylhexane
Ethyne (Acetylene)	2,2,4-Trimethylpentane
Ethane	n-Heptane
Propylene	Methylcyclohexane
Propane	2,3,4-Trimethylpentane
2-Methylpropane (isobutane)	Toluene
1-Butene	2-Methylheptane
n-Butane	3-Methylheptane
trans-2-Butene	n-Octane
cis-2-Butene	Ethylbenzene
2-Methylbutane (isopentane)	m&p-Xylene
1-Pentene	Styrene
n-Pentane	o-Xylene
2-Methyl-1,3-butadiene (isoprene)	n-Nonane
trans-2-Pentene	Isopropylbenzene
cis-2-Pentene	n-Propylbenzene
2,2-Dimethylbutane	1-Ethyl-3-methylbenzene
Cyclopentane	1-Ethyl-4-methylbenzene
2,3-Dimethylbutane	1,3,5-Trimethylbenzene
2-Methylpentane	1-Ethyl-2-methylbenzene
3-Methylpentane	1,2,4-Trimethylbenzene
1-Hexene*	n-Decane
n-Hexane	1,2,3-Trimethylbenzene
Methylcyclopentane	m-Diethylbenzene
2,4-Dimethylpentane	p-Diethylbenzene
Benzene	n-Undecane
Cyclohexane	n-Dodecane*
2-Methylhexane	TNMOC**
2,3-Dimethylpentane	PAMHC***
* These compounds have been added as calibration and retention time standards primarily for the purpose of retention time verification. They can be quantitated at the discretion of the user.	
** Total Nonmethane Organic Compounds	
*** Total Speciated PAMS Hydrocarbons	

15.2 Typical Gas Chromatographic Conditions:

Chromatography	Column	Rtx-1 (60m x 0.32-mm x 1.0 µm film thickness)
	Carrier Gas	Helium (1.5 mL/min constant flow)
Temperature Program	Initial Column Temperature	-50°C
	Initial Hold Time	4 minutes
	Program	15.0°C/minute to 10°C 4.0°C/minute to 150°C 15.0°C/minute to 240°C
	Final Hold Time	5.00 minutes (may be extended)
Flame Ionization Det.	Hydrogen	40 cc/min
	Air	450 cc/min
	N2 (make-up gas)	40 cc/min

15.3 Typical Entech 7100 Sample Pre-concentrator Conditions:

Trapping	Preflush	10 sec
	Trapping	150 cc/min
Sweep/Purge Gas	Preflush	2 sec
	Sweep gas flow	100 cc/min
	Sweep gas volume	75cc
Module 1 Settings	Trap type	Mixed media Glass Beads and Tenax - #4
	Trapping temp.	-165°C
	Desorb pre-heat	0°C
	Desorb temp.	10°C
	Bake temp.	150°C
	Bake time	20 min
Module 1 to Module 2 transfer	Flow	10 cc/min
	Volume:	40 cc
Module 2 Settings	Trap type	Tenax - #2
	Trapping temp.	-40°C
	Pre-heat	none
	Desorb temp.	180°C
	Desorb time	3 min
	Bulkhead temp.	90°C
	Bake temp	190°C
Module 3 Settings	Trapping temp	-190°C
	Inject time	2 min
Transfer line	Temperature	90°C

Revision History:

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0.0	August 2, 2010	David M. Berkowitz