Monitoring Network Performance for NMHCs Across 35 Monitors in Texas

Carol J. Meyer
carol@orsat.com
TCEQ AutoGC Networks

<table>
<thead>
<tr>
<th>Network</th>
<th># of Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>Houston Regional Monitoring Group</td>
<td>4</td>
</tr>
<tr>
<td>Extended Industry Monitoring Sites</td>
<td>3</td>
</tr>
<tr>
<td>North Texas Commission</td>
<td>13</td>
</tr>
<tr>
<td>University of Texas CEER</td>
<td>4</td>
</tr>
<tr>
<td>Harris County Pollution Control</td>
<td>1</td>
</tr>
<tr>
<td>TCEQ</td>
<td>12</td>
</tr>
<tr>
<td>Total AutoGC Sites</td>
<td>37</td>
</tr>
</tbody>
</table>

AutoGC Sites in Operation by Year
AutoGC Systems: Hourly Sample Collection and Separation

Basic System for the Separation of NMHCs from Ambient Air

Sample → Drier → Thermal Desorber → Gas Chromatograph → Data System

Dry gas
Additional Automation for Introduction of Quality Control Samples

- Automatic introduction of QC samples
  - Dynamically diluted check standard
  - Analytical blank
- Manual dilution of multipoint calibration curve
- Dilution from 100 ppbv or 1 ppmv multi-component standard
C2-C6 Alumina PLOT Separation

Ethane to 1-Hexene
0.5 ppbv PAMS Standard

3.0 pA fs
C6+ Dimethylsiloxane (Boiling Point) Separation

n-Hexane to n-Dodecane
0.5 ppbv PAMS Standard

3.0 pA fs
Analytical Blank

PLOT column
3.0 pA fs

Boiling point column
3.0 pA fs
Ambient Air - PLOT Column
Ambient Air - Boiling Point Column

16.0 pA fs

3.0 pA fs
<table>
<thead>
<tr>
<th>Quality Control Check</th>
<th>Composition</th>
<th>Purpose</th>
<th>Frequency</th>
<th>Acceptance Criteria</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retention Time Standard (RTS)</td>
<td>Mixture containing all target compounds ideally between 1-5 ppbC</td>
<td>To help assess retention time shifts and optimize processing methods</td>
<td>Twice a month or weekly</td>
<td>100% of the compounds are identified correctly in the multicomponent RTS</td>
</tr>
<tr>
<td>Calibration Verification Standard (CVS)</td>
<td>Mixture of 15 reference compounds including Propane and Benzene used for calibration</td>
<td>To assess the instrument drift and ensure continued instrument calibration</td>
<td>Daily</td>
<td>1) Propane and Benzene % recoveries within 75% - 125% and all other calibrants within 55 - 145%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2) Data must be bracketed by valid CVS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Method (Analytical) Blank</td>
<td>Humidified, clean air</td>
<td>To assess system contribution to the measurement</td>
<td>Daily</td>
<td>1) All target compounds &lt; 2.0 ppbC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2) TNMHC &lt; 20 ppbC</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3) Data must be bracketed by valid blanks</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Precision Check</td>
<td>Mixture used for CVS</td>
<td>To assess analytical precision</td>
<td>Weekly</td>
<td>Propane and Benzene %RPD &lt; 20% in two consecutive CVS runs</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Laboratory Calibration Standard (LCS)</td>
<td>Mixture of 15 reference compounds including Propane and Benzene used for calibration</td>
<td>Second source standard, statically blended 5 ppbv</td>
<td>Twice a month or weekly</td>
<td>Propane and Benzene % recoveries within 70-130%</td>
</tr>
</tbody>
</table>
Recoveries in Daily Check Standard at 0.5 ppbv

Check Standard % Recovery - C3/C6 Average Response Factor

PLOT Column

BP Column

% Recovery

0 20 40 60 80 100 120 140 160 180 200

Ethane  Ethylene  Propane  Isobutane  n-Butane  Acetylene  trans-2-Butene  cis-2-Butene  Cyclopentane  Isopentane  n-Pentane  trans-2-Pentene  cis-2-Pentene  2,2-Dimethylbutane  2,3-Dimethylbutane  2-Methylpentane  3-Methylpentane  2,2,4-Trimethylpentane  n-Heptane  Methylcyclopentane  2,4-Dimethylpentane  Benzene  Cyclohexane  2-Methylhexane  3-Methylhexane  2,2,4-Trimethylpentane  n-Undecane  n-Dodecane

Methylcyclohexane  2,3,4-Trimethylpentane  2-Methylheptane  3-Methylheptane  1,3,5-Trimethylbenzene  1,2,4-Trimethylbenzene  m-Diethylbenzene  p-Diethylbenzene  1,2,3-Trimethylbenzene  1,3,5-Trimethylbenzene  n-Proplybenzene  m-ethyltoluene  p-Ethyltoluene  o-Ethyltoluene  n-undecane  n-Dodecane  1,2-Trimethylbenzene  m-Diethylbenzene  p-Diethylbenzene
Network Quality Control - 25 AutoGC Sites

Daily CVS Recoveries - 25 AutoGC sites
1 week N = 9

Weekly LCS Recoveries - 25 AutoGC sites
6 weeks N = 7
TCEQ Performance Evaluation Audit
Fall 2014 - 12 AutoGCs

PLOT Column

BP Column

- Measured ppbC
- Average Lab Result
- Average Theoretical
AECOM Performance Evaluation Audits
Q2 & Q4 2015 - 13 AutoGCs North Texas Network
AECOM Performance Evaluation Audits
Q2 & Q3 2015 - 7 AutoGCs Houston/Galveston Network

Graph showing measured ppbC, average lab results, and average theoretical values for various hydrocarbons and other compounds.

- Measured ppbC
- Average Lab Results
- Average Theoretical

Compounds include:
- Ethane
- Ethylene
- Propane
- Propylene
- iso-Butane
- n-Butane
- Acetylene
- Trans-2-Butene
- 1-Butene
- Cis-2-Butene
- Cyclopentane
- iso-Pentane
- n-Pentane
- 1,3-Butadiene
- cis-2-Pentene
- 1-Pentene
- trans-2-Pentene
- 1-Methylpentane
- trans-2-Methylpentane
- 1,3-Dimethylpentane
- 1,2-Dimethylpentane
- 2,2-Dimethylbutane
- 2-Methylhexane
- 3-Methylhexane
- 2,2,4-Trimethylpentane
- 2,3,4-Trimethylpentane
- Methylcyclopentane
- 1,3,5-Trimethylbenzene
- 1,2,4-Trimethylbenzene
- 1,2,3-Trimethylbenzene
- n-Decane
- n-Undecane
- Benzene
- Methylbenzene
- Ethylbenzene
- Toluene
- Isopropylbenzene (cumene)
- n-Propylbenzene
- n-Butylbenzene
- n-Hexane
- n-Heptane
- Ethylbenzene
- M&P-Xylene
- Styrene
- O-Xylene
- n-Nonane
- Methylcyclohexane
- 2-Methylhexane
- 3-Methylhexane
- 2,3-Dimethylpentane
- 2,4-Dimethylpentane
- 2,3,4-Trimethylpentane
- 2-Methylheptane
- 3-Methylheptane
- 2,2-Dimethylbutane
- 2-Methylpentane
- 3-Methylpentane
- 2,2,4-Trimethylpentane
- 2,3,4-Trimethylpentane

ppbC measured for each compound and compared to average lab results and theoretical values.
Normalized Performance Audit Data
Fall 2014 - Spring 2015 - 32 AutoGC Sites

<table>
<thead>
<tr>
<th>Network</th>
<th># of Sites</th>
<th>Nominal ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTC</td>
<td>13</td>
<td>5</td>
</tr>
<tr>
<td>EIMS</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>TCEQ</td>
<td>12</td>
<td>7</td>
</tr>
</tbody>
</table>

![Normalized Performance Audit Data Chart](chart.png)
Minimum Detection Limits across 34 AutoGC Systems  40 CFR part 136 Appendix B

<table>
<thead>
<tr>
<th>Network</th>
<th># of Sites</th>
</tr>
</thead>
<tbody>
<tr>
<td>NTC</td>
<td>13</td>
</tr>
<tr>
<td>EIMS</td>
<td>5</td>
</tr>
<tr>
<td>TCEQ</td>
<td>11</td>
</tr>
<tr>
<td>UT</td>
<td>4</td>
</tr>
<tr>
<td>HCPCS</td>
<td>1</td>
</tr>
</tbody>
</table>
Minimum Detection Limits over 10 years on a Single AutoGC System  
40 CFR part 136 Appendix B
Distribution of Ambient Data
3.5 Months - over 1900 measurements

Ambient Data - C3/C6 Average Response Factor

35% < 1 ppbC
Summary
Requirements for Successful AutoGC

- Chromatographic Data System
  - Capable of identification and quantitation of complex samples
  - Robust and simple calibration strategy
  - Output format for easy review of data
  - Event control for automation of quality control checks

- Standard Operating Procedures
  - Daily operations for consistent data collection
  - Validation to handle deviations consistently

- Data Quality Objectives
  - Well defined control limits
  - System for identifying and correcting failures
Acknowledgements

“Without data you are just another person with an opinion.”  --- W. Edwards Deming

AECOM
Marty Hale
Scott Jenkins

University of Texas Austin
Dr. Dave Sullivan

Texas Commission on Environmental Quality
Cory Chism
Cindy Maresh
Patricia De La Cruz
Melanie Hotchkiss