Hello, my name is Carol Meyer and I am here to talk about Photochemical Assessment Monitoring Stations. My company Orsat, LLC has been working in the state of Texas since 1992 on VOC monitoring required by the Clean Air Act for areas which have failed to meet the ozone attainment goals set by the National Ambient Air Quality Standards or NAAQS rules.
On October 1, 2015, Administrator McCarthy signed a rulemaking action that revises the current national ambient air quality standards (NAAQS) for ozone to 70 parts per billion. Changes which have affected many aspects of state and local responsibilities for monitoring.

**Need and impact of the lower ozone standard**, the EPA determined a number of areas in which PAMS VOC monitoring should be changed to better meet the needs of the regulatory community. Based on feedback from agencies and scientists the EPA had issued additional rulings designed to increase the spacial resolution and data frequency for PAMS VOC data.

Changes include:

1) a **redistribution of monitoring sites** by requiring PAMS monitoring at Ncore sites in Core Based Statistical Areas with greater than 1 million population regardless of their ozone attainment status. Additional sites will be based on required Enhances Monitoring Plans required for areas which are classified as non-attainment.
2) **Continuous hourly monitoring** using hourly AutoGC where previously canister composite collections had been allowed.
3) Hourly monitoring will be required **only during the designated ozone season**.
The analysis of NMHCs is basically done based on two sampling strategies

1) **Field collection with either canisters or sorbent tubes** and subsequent analysis by either GC-FID or GC-MS in the laboratory. This generally was less frequent sampling of either 3 hour or 8 hour composite samples on a 6 day schedule. This generally results in a delay in results of weeks.

2) Or **Continuous field sampling and analysis using an AutoGC** which is generally a GC-FID system, collecting and analyzing hourly samples with immediate results.
When Continuous Field monitoring is the goal there are basically two methods generally considered.

1) **GC-FID** which is less expensive, more stable and has a response relative to the carbon content of the compound which thus allows the use of a carbon-based response factor which can be used for all compounds. This results in data which can be characterized by its relative carbon reactivity across targets and is generally reported as ppbC. The FID has a linear response over a large dynamic range, is not sensitive to oxygen, nitrogen or moisture in the injected sample and its only downfall is its reliance on retention time to identify specific compounds resulting in possible interferences where multiple hydrocarbon components co-elute.

2) The **GC-MS** on the other hand is more expensive and more complex both in operation and the data set it generates. It requires more frequent calibration due to its inherent drift and instability and because it does not respond uniformly to the hydrocarbons based on carbon content and its inherent non-linear response, it requires a compound-specific calibration. Thus calibration curves have to be generated for all compounds to be identified. It is also sensitive to any oxygen, nitrogen or moisture which may be injected along with the sample. However, it is often used for instance with air toxics because it does have the ability to handle interferences by virtue of ion selectivity.
1. **AutoGC Monitoring involves continuous field sampling and analysis** by drawing a sample through a multi bed sorbent trap at cryogenic temperatures for 40 min of each hour. The cryogenic trapping allows quantitative collection of C2 HCs but requires humidity control to eliminate freezing of moisture in the trap. This is generally accomplished using a Nafion permeable membrane. The collection and analysis times can be overlapping allowing the collection of the next sample during the analysis of the last sample.

2. **Separation is accomplished on a multi-dimensional gas chromatographic system.** The trap is heated and the sample injected into the boiling point dimethyl siloxane column which is connected by a Deans switch to an alumina PLOT column and the first FID. Once the C2 to C6 HCs have eluted from the boiling point column on to the PLOT column, the deans switch is activated sending the remainder of the C6-C12 HCs to the second FID.

3. **The work horse of the system is the Chromatographic Data System which identifies and quantitates all the peaks detected by the two FIDs each hour.**
Simple overview of the basic AutoGC system.

1. The sample enters the system through the drier which has a counter flow of dry air to remove the ambient moisture from the sample prior to trapping.
2. The sample is then pulled through the trap at -30ºC by the sample pump.
3. Once the sample is collected the flow is reversed on the trap and it is rapidly heated into the gas chromatograph which is equipped with the boiling point and PLOT columns where the C2-C12 HCs are then separated.
4. And the Chromatographic data system records the FID signals, identifies an quantitates the detected peaks. While the 48 minute chromatogram is collected and quantitated by the data system the thermal desorber returns to -30ºC and begins to collect the next sample.
Would that it were this simple. There is a bit of ancillary equipment required for this including the necessary Air supply.

1. This generally includes an air compressor and the necessary purification systems to supply dry air at < 1 ppm moisture for use with the nafion drier and to blanket the Peltier thermo-electric coolers used to control the low trap temperature which would ice up if left in ambient air. In addition, the dual FID system requires ~ 800 mL/min of HC free air for operation. For our systems we required an additional 150-300 mL/min HC free air for the dilution of standards for calibration and check standards.

2. Additional gases required include ~80 mL/min of Hydrogen which can be either from cylinder gas or hydrogen generator.

3. And carrier Helium of ~ 10-15 mL/min.

4. Other equipment includes the necessary sample manifold and blower for pulling in outside air and a sample pump to pull the sample from the manifold through the trap.

5. Canisters for standards as well as a dilution system for dynamic dilution of calibration standards and generation of daily blanks and check standards are recommended in lieu of frequent replacement of statically diluted check standards.

<table>
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<tr>
<th>Ancillary Equipment Requirements</th>
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<tr>
<td><strong>Air supply - Compressor</strong></td>
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<td>- Purification Systems to supply</td>
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<tr>
<td>- Dry air &lt; 1ppm moisture for Peltier cooler and nafion drier ~ 350 mL/min</td>
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<tr>
<td>- Hydrocarbon-free air for FID support gas ~ 800 mL/min</td>
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<td>- Dilution gas for dilution system ~ 150 - 300 mL/min</td>
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<tr>
<td><strong>Hydrogen</strong></td>
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<tr>
<td>- Cylinder gas or Hydrogen generator ~ 80 mL/min</td>
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<td><strong>Carrier gas - Helium</strong> ~ 10-15 mL/min</td>
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<tr>
<td><strong>Sample manifold and pump</strong></td>
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<td><strong>Canisters and dilution system</strong></td>
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<td>- Calibration curves</td>
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<td>- Check standards</td>
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Our sites have a dilution system which allows the dilution of a 1 ppmv standard for generating calibration curves as well as provides the automated daily Calibration Verification Standard as well as an analytical or system blank.
This is an example of the separation achieved on the PLOT column of a standard containing all 56 PAMS targets. The standard was generated on a molar basis and diluted to 0.5 ppbv and you can see the relative carbon response for each of the targets as their respective carbon content increases. Propane is used to generate a carbon response factor which is applied to all components of the PLOT chromatogram including unidentified totals.
Plotted on the same scale as the previous, this is the chromatogram from the **boiling point column** of the remaining targets in the PAMS 56 standard. Targets in this standard vary from **1 to 5 ppbC**. Benzene is used to generate a carbon response factor which is applied to all the components on the boiling point chromatogram and its totals. While this system has good sensitivity, this can be mitigated by the difficulties of determining the contribution of the system to the measurement. The boiling point column is responsible for the **more difficult separation** and due to the complex nature of ambient samples is more likely to exhibit potential interferences.
Generating a good system blank is a challenge in its own right. Here is the blank generated from the same dilution system used to dilute the 100 ppbv PAMS standard to 0.5 ppbv. This shows the ultimate contribution to that diluted sample as this reflects the diluent. This humidified blank represents not only the contribution of the zero gas from the dilution system but also any contribution of the sampling system, trap or columns. The large peak on the PLOT column corresponds to iso-butylene which is not uncommonly seen where systems have parts containing buna o-rings of any type. It along with propylene can accumulate as well in the nafion drier which may require regular replacement and/or cleaning.
By contrast this is a typical PLOT column ambient air sample at 5 times the scale.
And the corresponding boiling point chromatogram at the same scale showing the much lower concentrations generally encountered in the higher boiling targets. **Note the many integrated peaks at the end of the run.**

The expanded portions shows the complex separation issues seen routinely in ambient samples which can contain hundreds of components at low levels.
While a number of chromatographic systems are capable of doing this separation and sufficiently sensitive for the necessary quantification, the burden of continuous monitoring of 56 NMHCs on an hourly basis will fall exclusively on the data system and its ability to handle large quantities of data efficiently. The basic requirements for the chromatographic data system include; (all bullets one keystroke)

1) Data portability, by this I mean a file structure which makes archiving and moving the data easy
2) The ability to reconstruct the original processing method from the data result file makes the process of data validation much easier.
3) The use of Retention time references within the method will greatly assist in maintaining consistent peak identification across diurnal retention time shifting which is commonly seen
4) The ability to apply response factors to multiple peaks and/or groups and calibrate by reference will allow for flexibility in the calibration of difficult species.
5) The ability to name files in a meaningful way to easily identify each sample by site, date, time and hour as well as sample type makes handling large amounts of data more efficient
6) For unattended fully automated introduction of quality control samples the data system must be able to schedule and control events within the sequence.
7) Last but not least, the entire system must be capable of recovery from simple power failures and be able to continue hourly sampling.
We have worked with both the EZChrom data system on an Agilent System in conjunction with the Markes Unity 2 Thermal Desorber and the PerkinElmer Totalchrom Data system used with their Ozone Precursor system. Both of these data systems have successfully met these requirements. This is the EZChrom data system. It has typical chromatographic event control, peak window and reference peak identification, as well as event control. It also can accommodate either calibration by response factor, calibration by reference to other peak calibrations or target specific linear or non-linear regression.
This is the TotalChrom data system. It also has typical chromatographic event control, peak reference and window controls and the same calibration by reference, response factor or linear regression.
The typical calibration strategy used for the PAMS continuous AutoGC systems as outlined in the PAMS Technical Assistance Document is for carbon based response factors. However, this calibration strategy is not without compromise.

1. Target specific Linear regression calibration requires a calibration standard with contains all the components to be calibrated and this can be costly. It also requires vigilance on the part of the operator to insure that all 56 targets achieve a good qualified linear regression. This type of calibration is common in environmental labs using GC-MS by necessity as the GC-MS does not have a uniform response to the components of interest.

2. Carbon Based Response factors only requires certified standards for the reference components – propane and benzene. It uses the average response factor across its range and is easily applied and confirmed for all targets. This is possible only with GC-FID systems.
This data is from an Agilent system using the Markes Unity 2 Thermal desorber. Using the dynamic dilution system, the AutoGC was calibrated using an average response factor for propane and benzene using a 3-point calibration of 100 ppbv PAMS standard from 0.5 ppbv to 60 ppbv. This graph shows the distribution of the % recovery of all targets in a daily check standard diluted to 0.5 ppbv over 2.5 months. Significant deviations include:

1. Propylene – values which are high due to common contamination of nafion driers
2. Acetylene - poorly adsorbed and often lost in the sampling or analytical system
3. Hexane – again values high and larger deviations due to integration errors associated with the dean’s switch.
4. Generally Losses of heavier targets due to adsorption
This graph shows the distribution of ambient measurements across 3 ½ months. Note this is a log scale and it should be noted that a 37% of measurements occur at or below 1 ppbC.
It has been repeatedly shown based on other inter-comparisons that to insure that measurements are consistent across a network, it is important that all measurements be made in the same fashion, standards and methodologies used should be uniform and well documented. It is important for Data Quality Objective be uniformly applied to both operations and validation tasks.

1. This requires well defined operating procedures as well as well documented and controlled instrumental parameters. A fully automated system will reduce errors from operator activities. Easily identifiable and transportable data files will make errors in file transfer less likely to result in lost data. Fully automated routine quality checks will provide continuous feedback on instrumental performance and allow problems to be addressed quickly.

2. Data validation will require well defined control limits and procedures for handling data which falls outside those limits. Real time data transfer and review again will facilitate making adjustments to operations to maximize data quality and recovery. Good annual performance audits to review instrumental performance across a network is a necessity to generate a strong data population for the modeling community.
The TCEQ program which currently has 37 AutoGCs collecting hourly data year round, has well defined Operations and Validation operating procedures based around this set of Quality Control checks. With well defined acceptance criteria for each type of quality control, data can be handled accordingly and operations are driven by the quality of the data.

<table>
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<tr>
<th>Quality Control Check</th>
<th>Composition</th>
<th>Purpose</th>
<th>Frequency</th>
<th>Acceptance Criteria</th>
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<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>
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</table>
| Calibration Verification Standard (CVS) | Mixture of 15 reference compounds including Propane and Benzene used for calibration | To assess the instrument drift and ensure continued instrument calibration | Daily | 1) Propane and Benzene % recoveries within 75% - 125% and all other calibrants within 55% - 145% 
2) Data must be bracketed by valid CVS |
| Method (Analytical) Blank | Humidified, clean air | To assess system contribution to the measurement | Daily | 1) All target compounds < 2.0 ppbC 
2) TMMHC < 20 ppbC. 
3) Data must be bracketed by valid blanks |
| Precision Check | Mixture used for CVS | To assess analytical precision | Weekly | Propane and Benzene %RDP < 20% in two consecutive CVS runs |
| Laboratory Calibration Standard (LCS) | Mixture of 15 reference compounds including Propane and Benzene used for calibration | Second source standard, statically blended 5 ppbv | Twice a month or weekly | Propane and Benzene % recoveries within 70-130% |
1. In a system generating such large amounts of data, review must occur daily even if actual validation is only completed monthly. Site Operators are charged with insuring on a daily basis that the system is collecting data within the hour so it can be compared with other hourly averages. They must insure that all components are being identified correctly and that equipment parameters are within their specified ranges. A daily review of the system blank and calibration verification check standard (CVS) to insure that these are within the proposed limits is also done.

2. Validation is then completed after the month of data is completed and can be reviewed all together. The validator reviews all the quality controls and flags any data necessary. Chromatography is checked based on high hours or other observable deviations such as unusually low levels, or hours after or before lost data.
A system for the review of quality control data is helpful. Here you see our Merlin AutoGC Xplorer website which allows us to plot the daily CVS check standard over periods of time to find areas where the system may have not been performing well or to see the trend which might indicate a trap failure.
Likewise we can plot the statically diluted LCS which is run weekly over the same period. Note the deterioration of some compounds which was not evident in the CVS trend chart. This may indicate that the canister pressure for this standard which is statically blended into a 6L or 15L canister has gotten too low and it needs to be replaced.
With large amounts of data it is important for operators to have tools for reviewing data quickly. Here you see our QuickLook Email report. This report is generated automatically from data polled from each site (based on the dynamic dilution system we use at each site).
It includes concentration data for all hours, all targets but we have quality control hours highlighted in gray. We also have some pre-defined highlights for targets of concern such as benzene here which is set to be highlighted red if it exceeds 8 ppbC.
At the bottom the QC sample recoveries are calculated so operators know if anything is failing. These also will be highlighted if outside the specified ranges.
The application of consistent quality control across so many systems is reflected in the population of data. Although there is some inherent bias in the calibration method originally set forth. With fine tuned quality control procedures, these systems can be operated to produce extremely uniform results.

1. This graph shows the distribution of recoveries on 13 targets used in the TCEQ daily check standard collected over a week across 25 AutoGC sites. The small quartile limits shows that the precision across these 25 sites is good.

2. The second graph shows the same data for the statically diluted second source weekly standard across a 6 week period for the same 25 sites and again the low quartile spread indicates that these systems are generating similar quality data.
The TCEQ Performance audit requires **two separate canisters** due to the distance between sites. Canisters contained all 48 targets diluted to nominally 7 ppbv. These results represent the **average blended concentration** as well as the **average of the pre and post laboratory analysis**. With the **exception of acetylene** the analytical bias was generally less than **20% on pre and post lab analysis** with one canister being consistently less than 10%. Box plots show the distribution of 75% of the results and whiskers represent the minimum and maximum values observed. Red shadow represents 30% bias from the theoretical value expected. The bias on average AutoGC results with the exception of acetylene was less than 30%
To summarize, the general requirements for successful PAMS AutoGC operations include

1. A good Chromatographic data system capable of identification and quantitation of complex samples, a robust and simple calibration strategy, an output format for easy review of data and event control for the automation of routine quality control checks.

2. Strong uniform Standard operating procedures for both operations and validation to maintain the operations within the necessary control limits and uniformly flag data which falls outside those limits.

3. A strong set of data quality objectives with well defined control limits and a system for identifying and correcting failures.
Orsat has been configuring, operating and helping to develop quality controls to produce robust PAMS AutoGC systems since 1992. TCEQ currently collects data from 37 PAMS AutoGC systems in Texas which are operated year round. These systems post hourly data to the TCEQ website real-time with percent data recoveries of 90-95% and are operated based on the original PAMS technical assistance document which outlined using the average carbon response factor.
Acknowledgements

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

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