Hello, my name is Carol Meyer and I am here to talk about PAMS AutoGC. My company Orsat, has been working in the state of Texas since 1992 on VOC monitoring for Photochemical Assessment Monitoring Sites (PAMS). Although we use the PE system for most of our monitoring we are also familiar with several other systems. I am going to give an overview of the basic strategy for hourly continuous monitoring, some basics about the differences in some of the equipment. I hope to also address some of the issues we have found which affect the success of this type of monitoring as well as some of the suggestions for SOPs and guidance to monitor system performance.
PAMS AutoGC is referred to as continuous monitoring for VOC’s but it is not continuous in the fashion of Ozone or NOx analysis. In fact it is actually a mix of discrete sampling and composite collection of ambient air. In an attempt to collect data which could be related to current hourly averages for other criteria measurements and meet the necessary detection limits, these systems collect a composite sample of enough of the single hour period to be representative of the hour. But it is a single composite sample for each hour. It is more like running multiple canisters, one collected each hour but doing it in near real-time. Ultimately it is a large number of discrete data points.

- Sample collected on sorbent trap
- Separation of 48-56 NMHCs on a chromatograph and detected by either FID, MS or PID
- Separation generally occurs while the next sample is collected allowing sample collection of 40 min each hour.
Multiple instruments are available which can achieve the necessary separation and detection limits. They are differentiated by their method of sample collection and resulting analysis.

Collection on Single Trap with multi-dimensional separation of the single sample

Collection and separation on two separate chromatographic systems with separate traps and columns
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) **GC-PID** – less expensive than MS but has some selectivity and sensitivity which reduces some interferences however it like MS does not have a uniform detector response and thus usually requires species specific calibration

3) 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.
Simple overview of the basic Single instrument 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.
Simple overview of the Dual Chromatograph AutoGC system.

1. C2-C6 Chromatograph uses a cryogenically cooled trap and requires a drier to remove atmospheric moisture. The sample is injected onto a pre-column which will require backflush to separate and discard the heavier components which will not be put into the analytical column.

2. C6+ Chromatograph does not require a cryogenic trap and may use a dry purge instead of a Nafion™ drier to eliminate moisture. The trap is desorbed onto a methyl silicone column for separation of all compounds.

3. Both systems may be connected to the same data system which identifies and quantitates all the target compounds.
Would that it were this simple. There is a bit of ancillary equipment required for this including the necessary Air supply for the FID

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, a dual FID system requires ~ 800 mL/min of HC free air for operation. Some systems may require an additional 150-300 mL/min HC free air for the dilution of standards for calibration and check standards.

2. Additional gases required for the FID 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 and possibly detector make-up gas

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.
The sampling system for these chromatographic systems are similar to those used with other ambient air monitoring but have some specialized requirements. A standard glass manifold with blower is used to bring the sample into the station. These should be heated and cleaned with de-ionized water on a regular basis.

Sample lined from the manifold should be SS or, Silcosteel™ they should be heated to avoid condensation and should be 1/8” or less if sample flows are below 50 sccm.

Problems associated with sample lines include
- Losses of heavy components due to inadequate humidification
- Contamination
- Carry-over
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 should be capable of recovery from simple power failures and be able to continue hourly sampling. This feature is rarely simply achieved if at all.
In our current network of 36 field instruments we use TotalChrom and the strategy for calibration is the same as for most chromatographic data systems. Data systems generally have two functions, to control the instrument (temperatures, flows and data acquisition parameters) and to provide the necessary information for identification and quantification of the peaks of interest. Retention time windows are used to identify components, peaks are quantitated by their areas and either a response factor or linear regression used to determine the amount in each sample.
Calibration can be accomplished in either of two ways and the detector will determine which way is suitable

1. **Carbon Response factor** – this method is only used for FID systems. It relies on the FID's ability to respond uniformly to the carbon content of the component. Thus a single component can be used on each column to provide a response factor for all components detected.

2. **Target Specific Linear Regression** is the method commonly used in laboratories using GS/MS methods such as TO-15. This method requires the generation of a multipoint calibration curve for each of the 48-56 components in the analysis.
Mass Spectrometry or PID detection may require calibration across a larger dynamic range as these detectors have a more limited linear range. They do not have a uniform detector response so each target must have its own response factor or regression. This means the calibration mixture must contain all targets.

FID has a uniform carbon response and can be calibrated using only a simple carbon response factor. Since there can be differences in the response of each detector, a single component is used for each detector, propane for the PLOT or C2-C6 chromatogram and benzene for the BP or C6+ chromatogram. This simplifies the calibration by requiring only Propane and Benzene certified standards. The FID is extremely linear and we have found a single point is generally representative and a 3 point curve can be done as confirmation of linearity.
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 generated 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 isobutylene 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.
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 35% of measurements occur at or below 1 ppbC.
Data losses need to be minimized. 75% data completeness is required for inclusion in the AQS system. One of the largest sources of data loss is data collected where the sampling was not 75% within the sampling hour. This generally is caused by the system failing to sample on an hourly basis due to shelter temperatures or compressor failures or from power failures where systems either restart at the wrong time or fail to restart.

Poor QC results can be due to canisters, sample line contamination or carry-over, sample pump failures or collection failures due to icing traps. Losses of specific targets like the C2 hydrocarbons can be a result of trap cooling failures or sample flow issues. Contaminants in blanks due to carry-over or contaminated Nafion™ driers can also cause losses of data.
Carry-over can be a problem with extremely high ambient data or from QC samples. Recommend always running blanks after any QC samples. Carry-over on must systems is generally less than 2% so it is generally not a problem. If carry over is more than this there could be a problem with either Nafion™ driers or sample lines. Nafion™ driers can accumulate impurities such as propylene and may need to be replaced and cleaned periodically. Sample lines can cause carry-over if un-heated or have condensation. Trap material which has escaped the trap into the system can be a source of carry-over and will require cleaning of all suspect tubing associated with the trap failure. Losses and carry-over can result from graphite and graphite-vessel ferrules which are incorrectly installed.

As with carry-over – contaminants and interferences can arise which cause problems with the integration and quantitation of components of interest. The sources of contaminants in QC samples can be the canisters themselves so always check to compare your ambient to your QC when contaminants appear in QC samples. Failing air purifiers can cause contaminants if the air system is suppling blanks. Leak testing solutions are a source of contaminants and should not be used on these systems. Sometimes there are site specific interferences which cannot be resolved except by adequate separation.

Baseline issues should be addressed if baselines show aberrations which interfere with quantitation such as stair-stepping, oscillations, or high noise conditions. These may be caused by detector ferrules, air supply issues or electrical or vibration issues.
These are check standards on the BP column from 11/6 to 11/9 on the 304 SS cold line showing the drop in heavies over the three day period.
11/6 to 11/9 Blanks on SS cold line
Once the SS line was heated 11/9 Blanks after the standard run show successive recovery of missing heavies over blank runs for over 4 hours after the standard was run.
Blanks after the standard run on the cold Sulfinert™ line on 11/12 show little carry-over.
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.
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.
   1. Is it running
   2. Is sample collection 75% within hour
   3. Does ambient look like ambient
   4. Sample parameters within acceptable limits
   5. Quality controls (recovery) within acceptable limits

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.
Logbook are a must for all monitoring activities. Operators log instrument parameters, support gas usage, QC sample pressures and other relevant site observations. Notes on any observed changes in system performance or modifications to instruments such as hardware changes, cylinder changes etc.

Logs should be available for validation where site activities may have influenced data. Cloud based logs are best or logs should be included in any polling activities.

TCEQ LEADS™ system has AutoGC operator log system
TCEQ LEADS logs stored with ambient data and are polled hourly with data files. Available on TCEQ internal website.
We have also used other formats such as Google Docs for logs which are available to both validators and operators via the web. Requires broadband connection to the site computer.
Features which will help operators, validators and managers track the system performance and ultimately correct any issues quickly include:
1. Automation of routine quality control samples
2. Remote access for checking on system operations and polling data
3. Email alerts on power failures or system status.
Control Charts are a valuable tool for tracking the system performance based on routine quality control checks. TCEQ LEADS system is capable of generating control charts of recoveries for daily check standards and weekly check standards.
We also have a similar system for monitoring both QC samples and ambient data for data review. These and other similar systems will make identification of issues easier and allow operators to quickly correct issues as they show up.
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 the TCEQ Long term ESL Effects Screening Level.
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.