I am here to talk about PAMS AutoGC Monitoring. My company Orsat, 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. We have worked with TCEQ since then to configure, deploy, operate and validate data from the TCEQs AutoGC network.
1. TCEQ has been operating PAMS AutoGC systems since the mid 90’s after completion of the initial Coastal Oxidant Assessment Study in Texas (COAST) study.
2. The map represents the current AutoGC networks in Texas and
3. the graph below shows the growth of the networks since 1996. Through various networks the TCEQ receives data from 35 continuous monitors collecting speciated concentration data on 48 VOCs hourly year round. This data is available on their website hourly.
The systems used in Texas are configured from the PerkinElmer Ozone Precursor System along with additional automation supplied by Orsat. 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.
1. Our sites have a dilution system which allows the dilution of a 1 ppmv standard for 
2. Automatic introduction of daily Calibration Verification Standard as well as an analytical or system blank. 
3. Allows manual multi point calibration curves 
4. And is capable of diluting either from a 100 ppbv or 1 ppmv standard 

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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.
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.
To show the typical system response across all 56 PAMS targets components using a simple carbon response factor, an average response factor from a 3-point calibration curve based on propane and benzene response from 0.5 ppbv to 60 ppbv was used. Then a daily check standard generated by the dilution of a 100 ppbv 56 component standard diluted to 0.5 ppbv was run daily. This graph shows the distribution of the % recovery of all targets in a daily check standard 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
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%
This data represents the results of **two separate audit test series**. Both test canisters contained all targets at nominally **4 ppbv**. The bias on the blends were less than 5% and laboratory results represent the averaged values for the two separate canisters which had a RPD of generally less than 30% with exceptions including acetylene, ethylene, 2-methylpentane, n-decane, 1,2,3-trimethylbenzene and n-Undecane. However bias in AutoGC results were generally within 30% with exceptions being acetylene and n-undecane.
This performance audit of the 7 AutoGCs in the Houston/Galveston Extended Industry Monitoring Network was based on an audit canister concentration of nominally 5 ppbv. This data represents two separate audits whose blends were not as close as with other tests shown, blend error was about 12%. %Bias in laboratory results was generally less than 30% with the exception of acetylene, n-nonane and n-undecane. These AutoGCs are some of the oldest in the network with over 10 years of continuous service. %Bias of AutoGC results was less than 30% with the sole exception of n-undecane.
In order to compare all sites regardless of network the results were normalized as percent bias from the theoretical values for each test. This represents bias across 32 AutoGC sites on a single audit test series (5 sites not included in audit program). The graph also shows the plus and minus 30% control limits.
Minimum Detection Limits are calculated on each site yearly to assure that all systems are performing well after yearly maintenance has been performed. Detection limits across all networks are maintained by rigorous attention to instrument setup and operation insuring that responses are maintained within specified limits at the time of maintenance. Since the consumption of gas and time required to run 7 duplicate runs at an acceptable low level presents a significant challenge, our procedure involves “spiking” several minutes of a 40 ppbC PAMS standard on to the analytical trap followed by the remainder of the 40 minute sample period with blank humidified air from our dilution system. This can all be done remotely and automatically so operators are not required to blend canister and spend hours running samples.

This graph shows the results of the MDL method across 34 AutoGC sites showing that all detection limits are below 1 ppbC and most below the 0.4 ppbC TCEQ quality objective. (3 sites had not had MDL's for the year pending maintenance)
Rigorous attention to instrumentation settings and response allows these systems to perform consistently not only across multiple networks but also over the years. This data represents the results of the same MDL method on a single instrument over a 10 year period. The blue squares are the average MDL value at this site with error bars representing the minimum and maximum values seen over that period. The Red diamond represents the average for all sites from the previous data set. Again detection limits are well below 1 ppbC.
The importance of maintaining MDL is made more obvious by this representation of the typical distribution of ambient data concentrations across 3 ½ months.

1. This log scale clearly shows that approximately 35% of the ambient data falls below 1 ppbC. Thus it is crucial that instrumentation be maintained and operated with MDL’s in mind. Generation of synthetic concentrations of low levels sufficient to truly measure MDLs is difficult at best given the limitations of canisters and humidification requirements. However some test results suggest that our ability to accurately measure instrument detection limits may be limited by our ability to make sufficient challenge samples from humidified canisters.
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 36 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.
I would like to acknowledge the folks who have been instrumental in the various AutoGC networks in Texas

1. AECOM previously URS has operated the Houston/Galveston Extended Industry Monitoring Network for over 10 years and I would like to thank Marty Hale for his performance audit data and Program director Scott Jenkins.

2. The University of Texas Center for Energy and Environmental Research has operated the Corpus Christi Monitoring Network as well as several of the initial systems in the Eagle Ford Shale monitoring activities. We want to thank Dave Sullivan for his continued help and support.

3. And all the Monitoring Groups at the TCEQ from the director Cory Chism down have worked tirelessly to maintain the quality of these activities. Our continued gratitude go to Cindy Maresh and Melanie Hotchkiss who struggle with the ongoing quality issues of such a large network and who have helped to develop a strong QAPP and supporting documents and to Patti De La Curz whose direction of monitoring operations has allowed us to maintain a robust network.
PAMS AutoGC: Monitoring Network Performance of NMHCs Across 35 Monitors in Texas

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