Hourly Photochemical Assessment Monitoring Station (PAMS) Monitoring of NMHCs by AutoGC

Building Networks of AutoGCs and Monitoring Performance

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Effects of new NAAQS Ruling on PAMS VOC Monitoring

The analysis of ozone precursors has been a feature of the EPA air quality surveillance regulations since 1992 with the establishment of Photo-chemical Assessment Monitoring Stations (PAMS) as part of State Implementation Plans (SIP) for ozone non-attainment areas classified as serious, severe or extreme. At that time, guidance documentation allowed for the measurements of VOC precursors either by canister sampling or by continuous measurement using a GC-FID with a Thermal desorber collecting hourly samples. Only a few agencies chose to do continuous sampling and since that time a lot has been learned about the issues associated with the continuous field measurement of VOCs.

In 2011 the EPA initiated an effort to re-evaluate the PAMS requirements and the technology being used for continuous field measurements in conjunction with upcoming changes to the National Ambient Air Quality Standards (NAAQS) for ozone. With guidance from Clean Air Science Advisory Committee Air Monitoring Methods Subcommittee (CASAC AMMS) and National Association of Clean Air Agencies (NACAA) Monitoring Steering Committee (MSC) the EPA has promulgated revisions to the network design and is evaluating newer technology for continuous measurements. Since the primary use of this data is for photochemical modeling the new EPA ruling has recommended a redistribution of PAMS sites in an effort to increase the spatial coverage of this data for modeling performance evaluations. More agencies may find themselves responsible for implementing continuous hourly Volatile Organic Carbon (VOC) monitoring in conjunction with the existing NCORE network. While this type of hourly AutoGC monitoring represents a significant increase in complexity in both implementation and data management, systems have been developed and deployed to fully automate and streamline data collection and management.

AutoGC Systems for PAMS Monitoring

Figure 1 shows the basic system used for continuous field measurement of PAMS NMHCs. These systems generally require the concentration of 600—1000 mL of ambient air collected over a 40 minute period. The sample is collected on a dual phase trap which must be cryogenically cooled to trap the light C2 gases.

These chromatographic systems are most often configured with Flame Ionization Detectors (FID) because of their stability, linearity, robustness and carbon-response. Calibration can be achieved utilizing certified standards of only propane and benzene making the cost of standards significantly lower than those used for other detectors.

While there are a number of systems capable of this analysis, continuous air monitoring requires a degree of automation to facilitate the routine analysis of quality control checks to enable continuous review of performance. In addition, data systems used ideally must provide output of the data which allows users to rapidly explore and review their data as well as facilitate submission to the EPA Air Quality System (AQS).

Quality Controls to Maintain Network Data Quality Objectives

Simplification of the quality control strategies as well as calibration requirements will play a key role in the success of any monitoring plan. The identification and quantitation of up to 56 non-methane hydrocarbon (NMHC) species hourly requires a quality control strategy which is easy to implement and maintain. While a number of commercially available systems are currently being evaluated for use in PAMS monitoring activities, the PerkinElmer Ozone Precursor system has been used in Texas for the Texas Commission on Environmental Quality (TCEQ) since 1992 and there are now currently 35 of these AutoGCs

Basic System for the Separation of NMHCs from Ambient Air

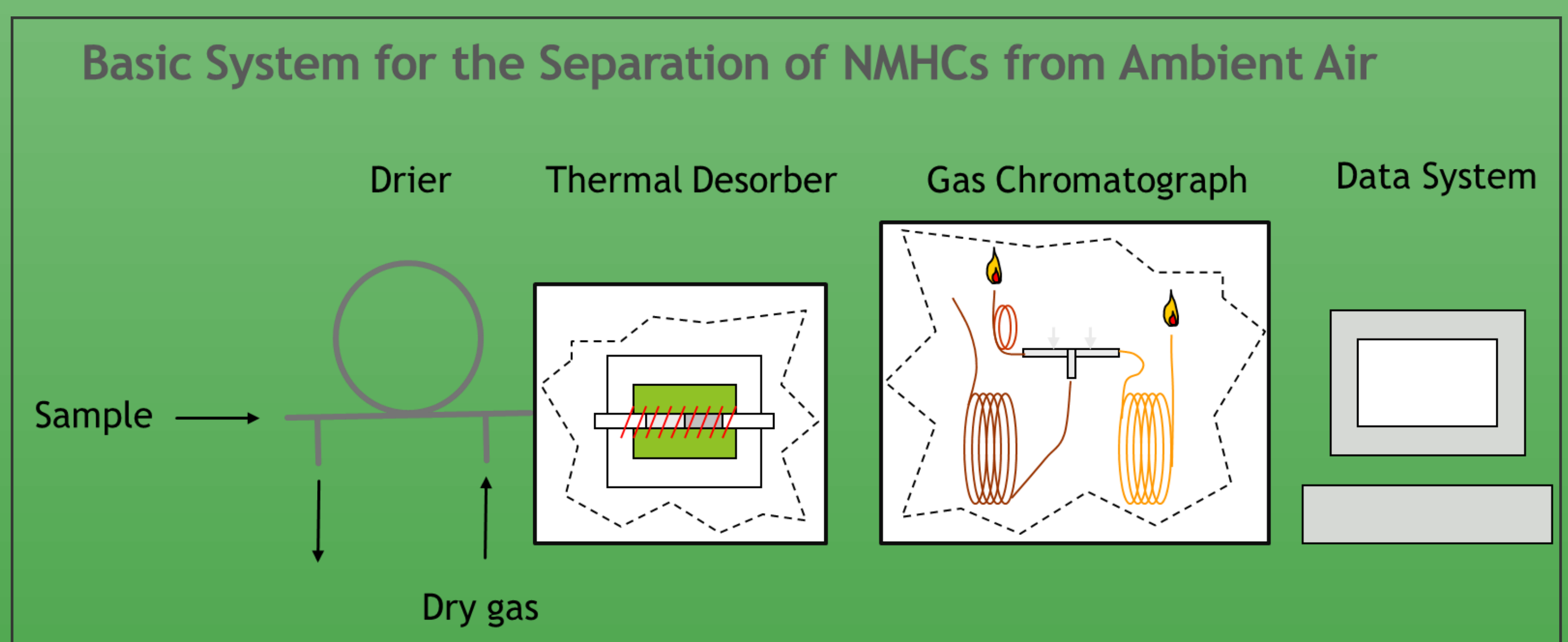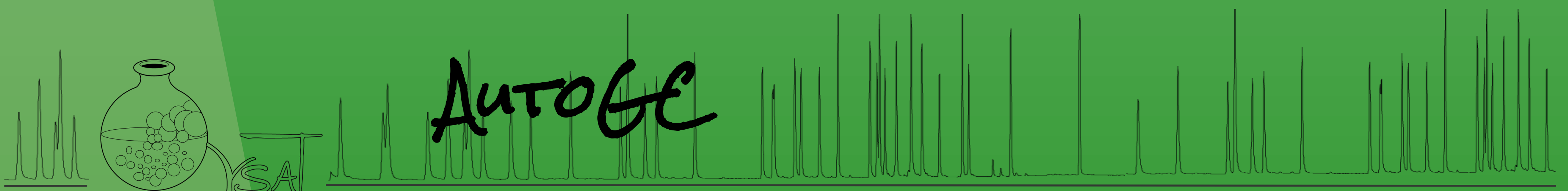Drier   Thermal Desorber   Gas Chromatograph   Data System

Sample

Dry gas

Figure 1: Basic System for the Separation of NMHCs from Ambient Air

collecting data hourly across the state. The PerkinElmer Ozone Precursor system comprised of the Turbomatrix Thermal Desorber in conjunction with a Clarus Dual FID Gas Chromatograph equipped with a dean's switch has been used extensively in operations in Texas for over 20 years. This system has been completely automated using the Totalchrom Data System in conjunction with automation software supplied by Orsat, LLC. .

Table 1 shows the quality controls used in the TCEQ Network to insure consistency across multiple instruments. These quality controls have been automated to make data available daily on the performance to each instrument to allow for adjustment if necessary and thus reduce data losses.

Quality Control Check	Composition	Purpose	Frequency	Acceptance Criteria
Retention Time Standard (RTS)	Mixture containing all target compounds ideally between 1-5 ppbC	To help assess retention time shifts and optimize processing methods	Twice a month or weekly	100% of the compounds are identified correctly in the multicomponent RTS
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) TNMHC < 20 ppbC 3) Data must be bracketed by valid blanks
Precision Check	Mixture used for CVS	To assess analytical precision	Weekly	Propane and Benzene %RPD < 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%

Table 1: Quality Controls for PAMS AutoGC Network

Automation for Continuous Unattended Operation

Orsat has over 20 years of experience automating PerkinElmer Ozone Precursor Systems for the Texas Commission on Environmental Quality. In addition, the Agilent PAMS system which includes an Agilent gas chromatograph and the Markes Unity 2 Thermal Desorber has been automated as well. Automation includes the Merlin MicroScience Dilution system shown in Figure 2 for generating daily check standards and system blanks daily as well as providing multiple levels for calibration. Additional valves are used to automate additional quality control checks including a second source canister statically diluted to confirm the dynamic dilution system as well as a retention time standard to confirm that the system is identifying all targets correctly and consistently. Because of the limited range of concentrations seen in ambient air and the FID carbon based response, calibration is accomplished by using a simple average response factor generated from a three level calibration curve accomplished using the dilution system when necessary.

Figure 2: Merlin MicroScience **Dilution System**

Chromatographic Data Systems

The chromatographic data system is a key element of the AutoGC system. It controls the system introduction of samples, identifies and quantitates all the components to be analyzed and generates the output which will ultimately be used to generate files compatible with the EPA Air Quality System. The basic requirements for field systems include:

- Data portability, the ability to easily move the data from the field workstation to a central location for validation.
- The ability to reconstruct the original processing method from the result file for reprocessing if necessary
- Use of retention time references to accommodate diurnal peak shifting
- Use of response factors and calibration by reference for unidentified HCs
- The ability to name files for easy identification of site, date, time, hour of the day and sample type
- The ability to schedule and control introduction of routine quality control samples
- The ability to recover from simple power failures and continue hourly sampling

Both the PerkinElmer Totalchrom Data System and the Agilent OpenLab EZChrom CDS have been successfully configured to meet the requirements of continuous field sampling. Orsat can provide specialized software which allows the generation of sequences that will generate descriptive filenames which make handling the large numbers of data files more efficient in addition to archiving and facilitating automated polling of data.

Calibration by Carbon Response

Because the FID response is proportional to the carbon content of most if not all the PAMS target components, the system can be calibrated based on a carbon response factor. Thus the values reported are generally reported as ppbC instead of ppbv. This type of calibration is easier than target specific linear regressions which are generally used in laboratories using GC-MS, a technique which does not have a proportional response for all analytes. It eliminates the necessity of expensive certified standards containing all targets. Generally only propane and benzene are used as calibrants to generate response factors for each FID. A multipoint calibration is done using the dynamic dilution system and an average carbon response factor is used for all targets.

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Using the relative carbon response method of calibration assumes 100% recovery for all species and will reflect systematic losses as lower recoveries. Target specific calibrations do not readily reflect the system losses for any specific target. Figure 3 shows the typical daily recoveries seen for 56 PAMS targets using a carbon response factor over a period of 2.5 months. This reflects losses to the analytical system caused by inadequate humidification, adsorption on steel surfaces and in the adsorbent trap itself. Monitoring these losses is a key element in the quality control process that allows users to maintain consistent recoveries across multiple instruments.
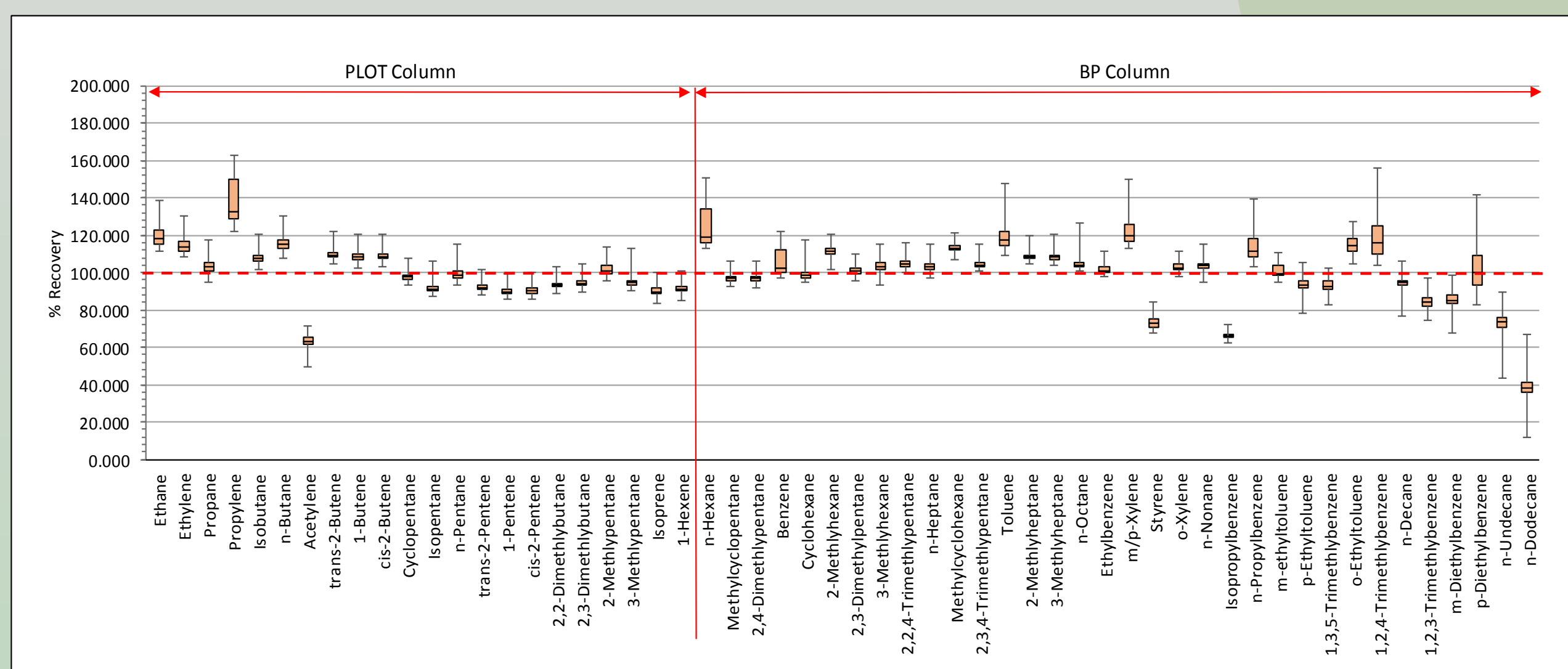

Figure 3: Distribution of Check Standard % Recovery

Some common recovery issues include higher than normal recovery for targets which can accumulate in the Nafion® drier such as propylene in particular, as well as lower than expected recoveries for targets such as acetylene and heavier hydrocarbons which are often lost to steel surfaces due to inadequate humidification of canister samples. Some losses such as higher than expected recoveries of hexane are not a function of sampling but rather is due to poorly integrated peaks. Hexane is the first peak to elute after the effluent of the boiling point column is switched and thus integration of the peak can be affected by any upset caused by this flow change.

Although the quality control samples show lower recovery for some NMHCs, previous comparisons of data from a system calibrated using compound specific calibrations versus carbon response factors did not show significant differences in the measurements of ambient air[1]. This suggests that the losses in recovery shown here are more closely related to the generation of humidified standards and may not accurately reflect the actual recoveries in ambient air samples.

Quality Control for Uniform Network Performance

Establishing a strong quality control strategy enhances data quality and data return by insuring consistency across multiple instruments. The TCEQ has a network of over 30 AutoGCs collecting hourly data year round which uses automation configured by Orsat and utilizes the quality controls listed in Table 1. In addition Orsat provides technical assistance for instrumental failures as well as an annual maintenance program designed to keep all instrumentation performing based on standardized testing and configuration criteria. This insures that all instrumentation is configured for the same performance and tested each year after maintenance to insure each instrument is returned to the same performance level. At least annually a single performance evaluation should be done to challenge all systems in the network with a single test sample designed to evaluate the network performance.
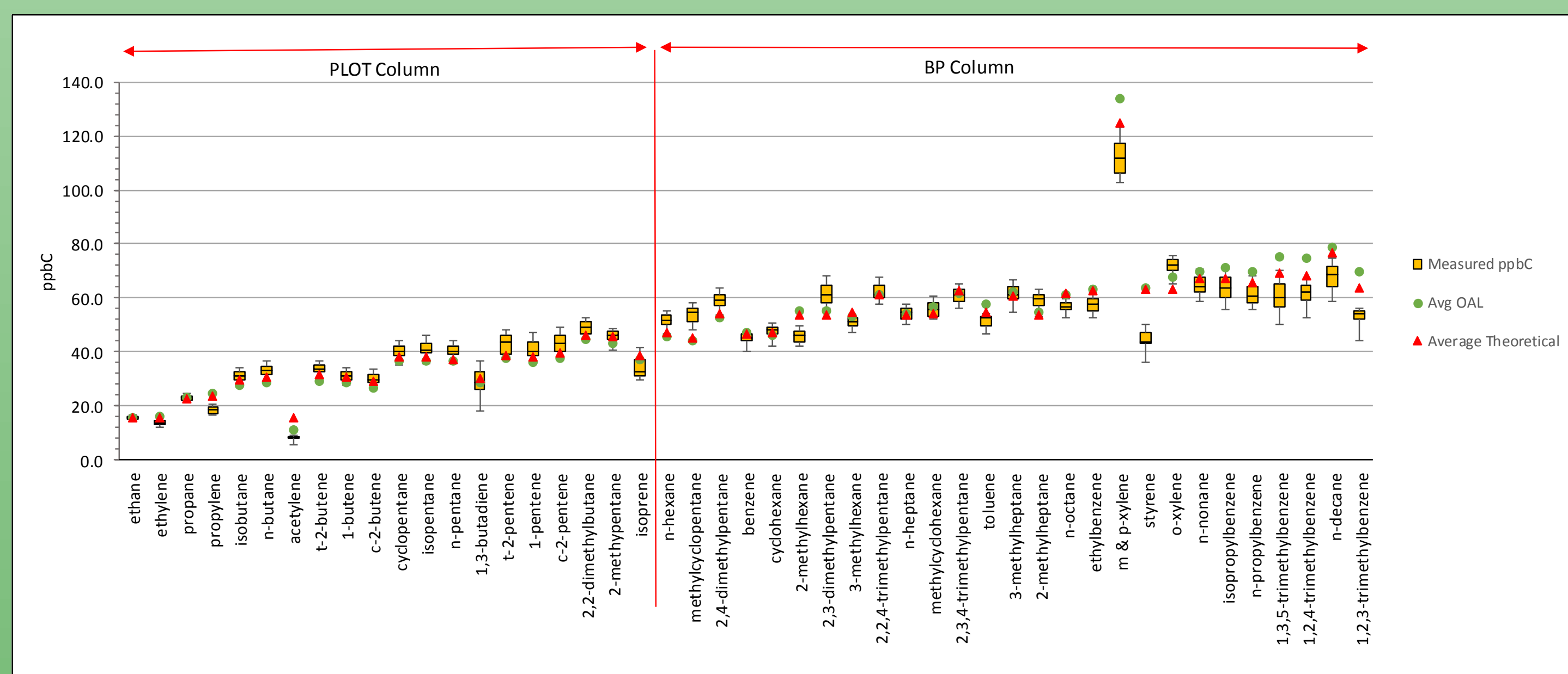

Figure 4: Distribution of Reported Results from 12 TCEQ Sites on 2014 Fall PE Audit

A challenge sample containing all targets is manufactured at nominally 5 ppbv concentration in a canister and this sample is run at all sites. In the case of TCEQ, several canisters are required to test all the systems in their network. Figure 4 shows the distribution of reported results of the 2014 performance evaluation (PE) audit of 12 TCEQ sites (additional sites from other networks which report to the TCEQ system have independent performance audits). Theoretical concentrations as well as analytical results are reported and include pre and post distribution analysis. The pre and post distribution analytical results as well as theoretical concentrations based on the gravimetric production are averaged across the two separate canisters which were manufactured for testing. The relative percent difference between pre and post distribution results were less than 20% (frequently less than 10%) with the exception of acetylene which deteriorated significantly across the 4 month period from pre to post testing. These results verify that these 12 monitors are performing similarly and generally agree with the laboratory GC-MS results when operated using a carbon based calibration scheme.

Summary

The new NAAQS requirements for continuous PAMS VOC monitoring will require accurate hourly collection and analysis of up to 56 NMHCs using equipment which is technically more sophisticated than other air monitoring activities generally required of most state air monitoring agencies. Establishing a sound quality control strategy along with sufficient automation will enable the successful operation of systems such as the PerkinElmer Ozone Precursor System and the Agilent PAMS Monitoring System. Challenges for the successful implementation of PAMS monitoring include not only the implementation and operation of the equipment to collect and analyze ambient air but also the organization necessary to generate the required quality control samples and review and validate the resulting data.

[1] Meyer, C.. "The Analysis of Ozone Precursors by AutoGC: The Role of Calibration and Quality Control Strategies in Data Management for Fully Automated TD-GC-FID Systems.", Presentation, Air Quality Measurement Methods and Technology, Chapel Hill, NC, March 15-17, 2016..
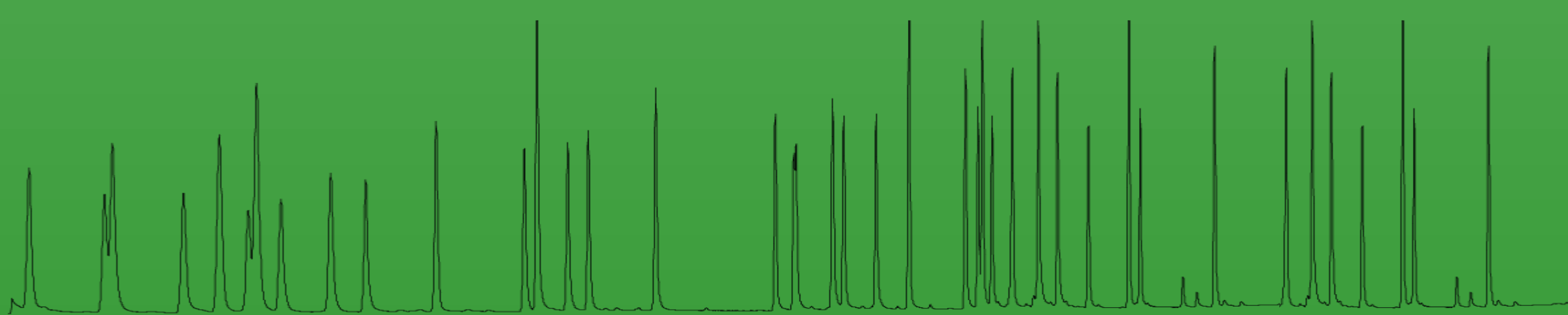
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