Through-the-Probe Performance Audits of Non-Methane Hydrocarbon Samplers

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ABSTRACT

In 1997, the Quality Assurance Section (QAS) of the California Air Resources Board (CARB) initiated through-the-probe (TTP) performance audits of non-methane hydrocarbon (NMHC) samplers. The NMHC TTP audit procedure was developed to support the Photochemical Assessment Monitoring Station (PAMS) program. CARB has been conducting TTP performance audits since 1981. TTP performance audits entail introducing an audit gas at the air monitoring station's probe inlet. By conducting audits at the probe inlet, the QAS can assess the total measurement system accuracy, which includes: errors inherent in contamination during transport, sample pump and probe effects, and laboratory bias. Prior to conducting NMHC TTP audits, the QAS was limited to assessing laboratory operations. Conducting both TTP and laboratory performance audits, the QAS is able to identify system-wide areas that may need improvement.

This paper presents the methodology and equipment used to conduct NMHC TTP performance audits. Additionally, the paper presents audit results and future applications with carbonyl samplers.

INTRODUCTION

The QAS of the CARB conducts TTP performance audits of NMHC samplers in support of the PAMS program. TTP performance audits enable the QAS to assess the total measurement system accuracy, which includes: errors inherent in contamination during transport, sample pump and probe effects, and laboratory bias. Prior to conducting NMHC TTP audits, the QAS was limited to assessing laboratory operations. When developing the NMHC TTP audit procedure the goal was to provide a sample at conditions similar to an ambient air sample. As a result, the QAS investigated the effects of pressure, humidity, and canister residence time and found that humidified canisters[1] and in-line humidification[2] improved recovery rates for NMHC compounds.

NMHC TTP performance audits are conducted using an in-line humidification system. The humidified audit sample is introduced at the probe inlet using a tee connector. The tee connector allows the sample to be introduced without influencing the sampler's normal operating conditions. Once a sample is collected, it is either analyzed on-site by a gas chromatograph (GC) or sent to a laboratory. Five separate laboratories support California's PAMS program. Each laboratory reports the audit results to the QAS, and a report is generated comparing the measured and assigned concentrations. If the CARB's +/- 20% control limits are exceeded, the responsible agency and laboratory are requested to investigate the problem. The QAS also conducts a network evaluation by summarizing and comparing the results to the laboratory performance audit results. This assists the QAS in determining where and how to further improve the data quality.

AUDIT PROCEDURES

General Information

NMHC TTP performance audits are conducted annually at each PAMS site. All samplers in California's network collect samples through a probe inlet into stainless steel canisters. The type of analysis system, whether it is on-site GC or subsequent laboratory analysis, does not affect the TTP audit procedure. Sample containers are filled with known concentrations of audit gases over a three-hour period. The sampler is operated, whenever possible, in conditions duplicating a routine ambient run. The QAS requests the analytical results and calculates the percent difference for each compound.

The audits are conducted using a National Institute of Standards and Technology (NIST) high concentration multi-component traceable standard. The purpose of using a high concentration multi-component gas is to be able to provide an audit sample at the probe inlet over the required time period and to allow variability in compound concentrations by appropriate dilutions.

System Equipment

The equipment needed to perform NMHC TTP performance audits includes the following:

1) Environics 2014 computerized gas dilution system.
2) Environics in-line humidification system.
3) Advanced Pollution Instrumentation (API) 701 zero air system.
4) NIST traceable high concentration audit cylinder (see Table 1 for a list of compounds and concentrations).
5) Silcosteel fused silica lined stainless steel tubing and fittings.
6) 6-liter stainless steel canisters (samplers only).

System Set-up

The Environics dilution unit is designed to precisely blend gases. The unit contains three mass flow controllers (MFC) to blend the zero air and high concentration audit gas cylinder. The MFCs and their respective flow ranges are listed below:

- MFC #1 - 0 to 10,000 cubic centimeters per minute (CCM)
- MFC #2 - 0 to 1,000 (CCM)
- MFC #3 - 0 to 150 (CCM)

MFC #1 is used for the zero air source and MFCs #2 and #3 are used for the audit gas. The desired dilution ratio determines which MFC is used for the audit gas. The MFCs are calibrated quarterly to ensure the dilution unit's precision. The in-line humidification attachment (see Figure 1) humidifies the sample between 55% and 75% (relative humidity). Previous studies have shown that humidity is a critical factor in recovering hydrocarbon compounds from stainless steel canisters. To prevent sample contamination, Nano-pure grade water is used. QAS has conducted studies to verify the water purity. In addition, humidified blank samples are run to verify that no contamination is present in the audit system. The humidifier is mounted on the back of the dilution unit and consists of a 12" water permeable internal gas path and water reservoir. It contains an outer shell and an inner water permeable tube. Using the reservoir, water is fed to the tube. Water vapor permeates the internal tube and is blended with the incoming gas.

The zero air source is an API 701 totally self-contained system. The purity of the air was tested and found to be below 1 part per billion carbon (ppbC) for all compounds. The total hydrocarbon level did not exceed 20 ppbC. The zero air system is connected to the dilution unit (MFC #1) using ¼" Teflon tubing. The NIST traceable audit cylinder is connected to the dilution unit using ¼" Silcosteel silica lined stainless steel tubing. The silica lined tubing is used to prevent potential hydrocarbon losses that can occur with Teflon tubing. The same tubing is used to deliver the audit sample to the NMHC sampling inlet port. The audit tubing is connected to the inlet using a tee connector that is also silica lined. The tee connector allows the audit sample to be introduced at the sampler's inlet port without influencing its normal operation. The audit sample is collected into a 6-liter canister and sent to the laboratory for analysis or is collected and analyzed real time by an auto GC. See Figure 2 for a complete diagram of the audit set-up.

System Operation

The dilution unit is the central component of the TTP performance audit system. Using the unit's flow mode, the user manually programs the target flow rates for each MFC. The selected flow rates are based on the desired dilution ratio. The dilution ratio determines the actual concentrations of the compounds listed in Table 1. The dilution ratio is defined as follows:

$$\text{Dilution Ratio} = \frac{\text{Gas Flow Rate}}{\text{Air Flow Rate + Gas Flow Rate}} \quad \text{(Equation 1)}$$

The ratio is calculated prior to the audit and depends on several factors, including assigned cylinder concentrations, required minimum air flow rate, gas flow rate (cannot exceed 1,000 CCM), and the requirement to generate concentrations greater than the minimum detection limit to permit quantitative laboratory analysis. In general, the desired compound concentrations are in the range of 1.0 to 15.0 ppbC. Once the concentration is selected, the dilution ratio and required flow settings are determined according to the following example for ethane.

Desired Gas Concentration (Assigned Value): 11.0 ppbC

Assigned NIST Cylinder Value: 1,100 ppbC

$$\text{Dilution Ratio (calculated)} = \frac{11.0 \text{ ppbC}}{1{,}100 \text{ ppbC}} = \frac{1}{100}$$

Note: The established dilution ratio for ethane will also be used to determine the final concentration of the other compounds in the audit cylinder. For this example, an ethane concentration of 4 ppbC or greater must be selected to permit quantitative analyses of the remaining compounds.

If the probe inlet flow rate measures 3.5 liters per minute (LPM) and a 1.0 LPM bypass is required, the air flow rate needed is as follows:

Air Flow Rate = 3.5 LPM + 1.0 LPM

Air Flow Rate = 4.5 LPM = 4500 CCM (True)

To determine the gas flow rate, solve Equation 1 with the known values listed above.

$$\text{Dilution Ratio} = \frac{\text{Gas Flow Rate}}{\text{Air Flow Rate + Gas Flow Rate}}$$

$$\frac{1}{100} = \frac{\text{Gas Flow Rate}}{\text{4500 CCM + Gas Flow Rate}}$$

Gas Flow Rate = 45.5 CCM (True)

The gas and air target flow rates are calculated by applying the certification (Equation 2) from the latest calibration report. The dilution unit is certified on a quarterly basis to ensure its precision when blending gases. Below are the results from a typical calibration:

Target Flow Rate (Display) = Slope * (True Flow) + Intercept (Equation 2)

Gas Target Flow Rate (Display) = 1.0947 * (45.5 CCM) + 0.3180

Gas Target Flow Rate (Display) = 50.1 CCM

Air Target Flow Rate (Display) = 1.1 * (4,500 CCM) + 9.8

Air Target Flow Rate (Display) = 4,960 CCM

Based on a dilution ratio of 1 to 100 and a minumum required flow rate of 4500 CCM, the dilution unit would be programmed with the following target flow rates:

- MFC #1 = 4,960 CCM
- MFC #3 = 50.1 CCM

Prior to initiating the audit, the system is purged and checked for leaks. MFC #1 is programmed with a flow rate of 4,960 CCM and the system is purged with zero air for one hour. MFC #3 is programmed with a flow rate of 50.1 CCM and an additional 30-minute gas purge is conducted. After the system purge, the sampling system is checked for leaks. Upon completion of the system purge and leak checks, a sample container is filled with the audit gas for three hours.

Data Reporting

The audit sample is analyzed on-site by an auto GC or is shipped to the laboratory for analysis. The analysis results are sent to the QAS for evaluation. A percent difference for each compound is calculated using the following equations:

Assigned Concetration = Dilution Ratio * True Cylinder Concentration (Equation 3)

$$\text{Percent Difference} = \frac{\text{Average Concentration} - \text{Assigned Concentration}}{\text{Assigned Concentration}} \times 100 \quad \text{(Equation 4)}$$

The results are presented in a report shown in Figure 3.

DATA INTERPRETATION/TROUBLESHOOTING

Performing both laboratory and TTP performance audits enables the QAS to identify system-wide problems as well as to pinpoint what portions of the system (sample collection, laboratory analysis) require closer evaluation. The individual audit reports show the results for a specific monitoring station. The QAS summarizes these results to interpret the station and laboratory performance. If the CARB's +/- 20% control limits are exceeded, the responsible agency and laboratory are requested to investigate their sampling and analysis system. They must also report the findings of their investigation and any corrective action taken. The corrective action normally involves recalibrations, instrument maintenance, and system cleanings; however, data action has been taken when appropriate. Since December 1997, 11 TTP performance audits have been performed.

The TTP audit results are also compared to the annual laboratory performance audits to help identify system problems. The laboratory performance audits entail sending an audit gas cylinder to each of California's laboratories. Again, the results are evaluated both individually and collectively. Comparing the TTP and laboratory audit results enables the QAS to interpret California's overall network performance. Figures 4 through 7 graphically display both the TTP and laboratory audit results since December 1997.

As one would expect, the TTP results tend to show slightly more variability compared to the laboratory audit results. This indicates that the delivery, sampling, and/or transport system could be affecting the data quality. The sampling configuration can be an issue if multiple PAMS samplers are connected to one sample probe line/manifold. If one or more samplers are idle, leaks can occur. Agencies using this configuration have changed largely to single dedicated probe lines.

Another concern resulting from the audit results is the significant variability in percent difference for ethane. Investigations have shown that the variability is primarily due to the differences in laboratory methodologies (column selection, single versus dual columns, column temperature). The greatest descrepancy in audit results is for heavier molecular weight NMHC compounds (ethylbenzene, xylenes, 1,2,4-trimethylbenzene, decane, etc.). The U.S. Environmental Protection Agency (U.S. EPA), CARB, and local districts are working to improve the recovery rates of these compounds.

CONCLUSION

Conducting NMHC TTP performance audits enables the QAS to assess the total measurement system accuracy. TTP performance audits entail a sample being introduced at the probe inlet without the audit affecting the normal operating procedures. Studies have shown that when samples are collected through stainless steel probes and into canisters, in-line humidity is required to achieve the best hydrocarbon recovery rates. Using a dilution unit, humidification system, zero air system, high concentration cylinder, and silica-lined tubing, an audit sample can be delivered to the sampling system without influencing the sampler's normal operation. The dilution unit is used to generate compound concentrations from 1 ppbC to 50 ppbC.

Overall, TTP audit results tend to show slightly higher variability compared to the laboratory audit results. This indicates potential problems with the delivery, sampling, and/or transport system. One potential problem relates to systems having multiple samplers using one sample probe line/manifold. Dedicated probe lines are recommended. There was also significant variability in the percent difference for ethane audit samples that appear to be primarily due to differences in laboratory methodologies. Laboratories experiencing large percent differences for ethane are taking action to correct the problem. Lastly, the audit results showed poor recovery for the heavier molecular weight hydrocarbon compounds. This is a continuing problem that the U.S. EPA, CARB, and local districts are working to improve.

FUTURE APPLICATIONS

The dilution unit is equipped with a permeation oven. The permeation oven was incorporated into the dilution unit to enable the QAS to perform PAMS carbonyl TTP performance audits. Using a certified permeation tube, the QAS is investigating our ability to assess the accuracy of the sampling system, cartridge, and laboratory. Preliminary testing has shown the output sample to be unstable (+/- 50%). Future tests and investigations using other permeation tubes, concentrations, sources, etc. are planned to investigate the causes of the instability.

AKNOWLEDGMENTS

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REFERENCES

1. Michael G. Miguel; "A Comparison Study to Determine the Effects of Pressure, Relative Humidity, and Canister Residence Time on NMHC recovery Rates from Stainless Steel Canisters", Presented at the U.S. EPA/Air & Waste Management Association Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, North Carolina, May 16 - May 18, 1995.

2. Alice Westerinen; "Study to Determine the Effect of Moisture on Volatile Organic Compound Recovery Rates for Thru-the-Probe Audits into Stainless Steel Canisters", Presented at the U.S. EPA/Air & Waste Management Association Symposium on Measurement of Toxic and Related Air Pollutants, Research Triangle Park, North Carolina, May 7 – May 9, 1996.

DISCLAIMER

Mention of trade names and/or commercial products does not constitute endorsement or recommendation for use.

Table 1. List of compounds and concentrations – audit cylinder.

Compound	Certified Concentration (ppbC)
Ethane	1100
Ethene	958
Propane	1914
Propene	567
n-Butane	1392
1-Butene	354.8
2-Methylbutane	1500
n-Pentane	765
2,3-Dimethylbutane	561.6
2-Methylpentane	1002
Hexane	553.8
Methylcyclopentane	403.8
Benzene	996
3-Methylhexane	323.4
2,2,4-Trimethylpentane	800
Methylcyclohexane	305.9
2,2-Dimethylhexane	307.2
Toluene	1596
Octane	316
Ethylbenzene	596
m/p-Xylene	1400
o-Xylene	567.2
1,2,4-Trimethylbenzene	381.6
Decane	480

Figure 1. Environics in-line humidification set-up.

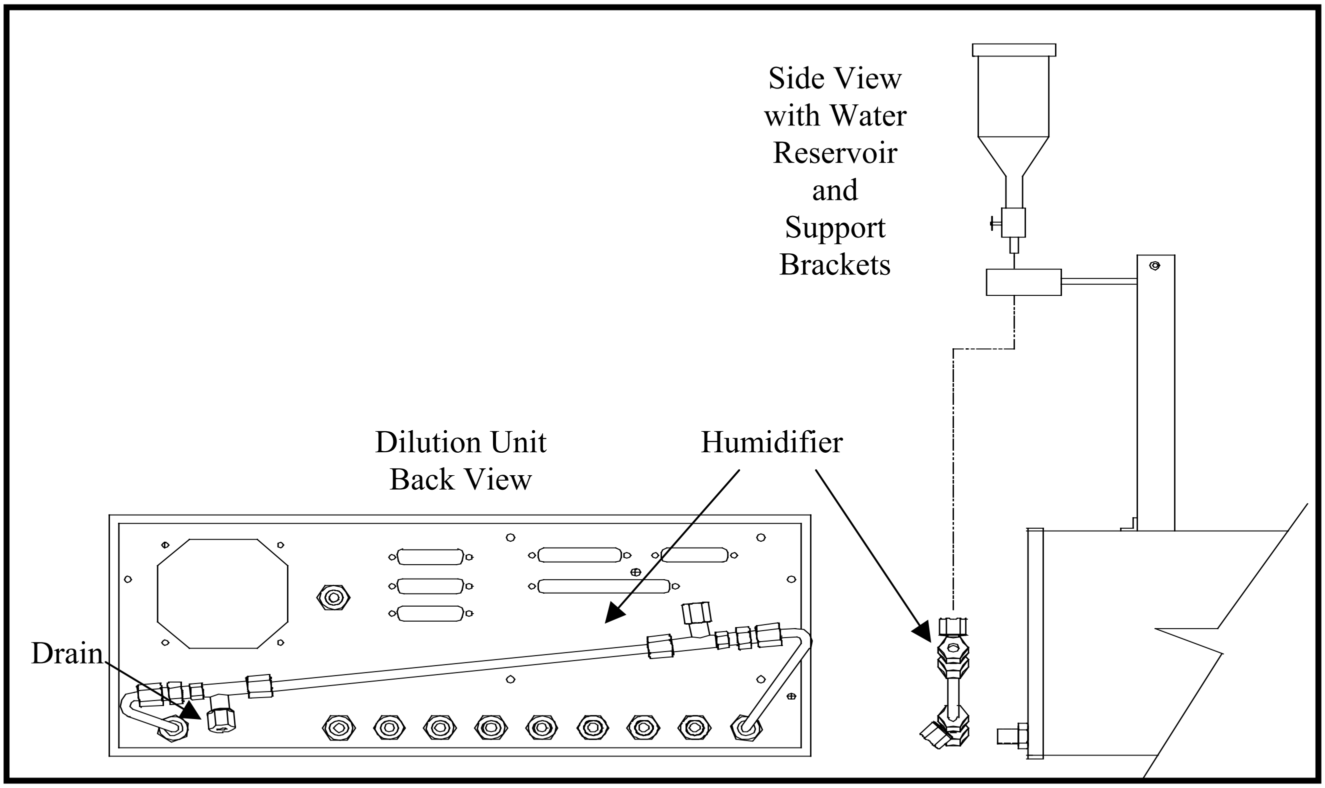


Figure 2. NMHC through-the-probe audit set-up.

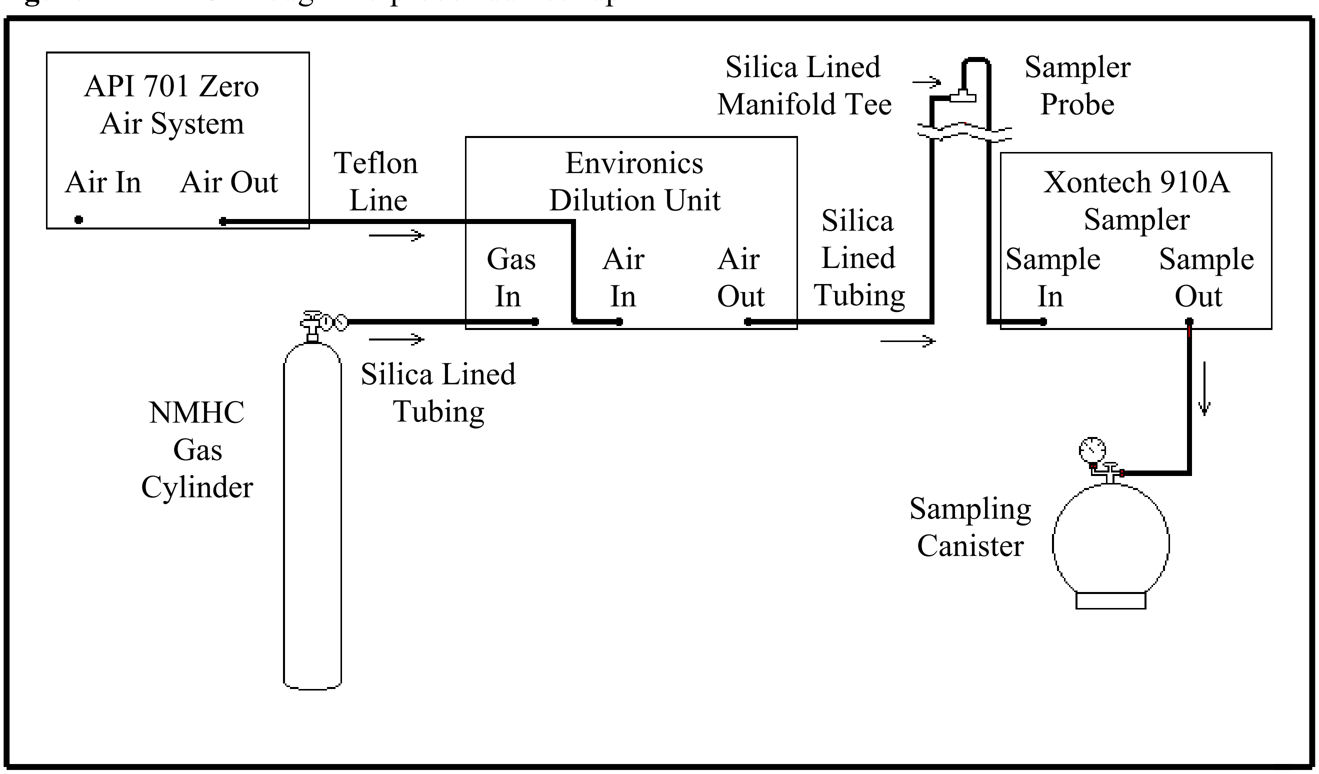


Figure 3. Audit report.

CALIFORNIA AIR RESOURCES BOARD
THROUGH-THE-PROBE NON-METHANE HYDROCARBON
PERFORMANCE AUDIT RESULTS
BY
QUALITY ASSURANCE SECTION
MONITORING AND LABORATORY DIVISION

Manager: Alice Westerinen *Phone #: (916) 324-6191*

SITE: SACRAMENTO-BRUCEVILLE *SITE #: 34310* *AUDIT DATE: 11/20/97*

LABORATORY: CALIFORNIA AIR RESOURCES BOARD

Compound	True Conc. (ppbC)	Dilution Ratio	Assigned Conc. (ppbC)	Measured Conc. (ppbC) Run 1	Measured Conc. (ppbC) Run 2	Average Measured Conc. (ppbC)	Percent Difference
Ethane	1100	1/114	9.6	9.9	10.0	10.0	4.2
Ethene	958	1/114	8.4	9.0	9.0	9.0	7.1
Propane	1914	1/114	16.8	17.0	17.1	17.1	1.8
Propene	567	1/114	5.0	5.7	5.7	5.7	14.0
Butane	1392	1/114	12.2	12.0	12.0	12.0	-1.6
1-Butene	354.8	1/114	3.1	3.0	3.1	3.1	0.0
2-Methylbutane	1500	1/114	13.2	13.0	13.1	13.1	-0.8
Pentane	765	1/114	6.7	6.6	6.7	6.7	0.0
2,3-Dimethylbutane	561.6	1/114	4.9	4.9	4.9	4.9	0.0
2-Methylpentane	1002	1/114	8.8	8.6	8.6	8.6	-2.3
Hexane	553.8	1/114	4.9	4.8	4.9	4.9	0.0
Methylcyclopentane	403.8	1/114	3.5	3.6	3.6	3.6	2.9
Benzene	996	1/114	8.7	8.7	8.7	8.7	0.0
3-Methylhexane	323.4	1/114	2.8	3.2	3.1	3.2	14.3
2,2,4-Trimethylpentane	800	1/114	7.0	7.2	7.2	7.2	2.9
Methylcyclohexane	305.9	1/114	2.7	2.7	2.7	2.7	0.0
2,2-Dimethylhexane	307.2	1/114	2.7	2.8	2.9	2.9	7.4
Toluene	1596	1/114	14.0	13.7	13.7	13.7	-2.1
Octane	316	1/114	2.8	3.0	3.0	3.0	7.1
Ethylbenzene	596	1/114	5.2	4.9	5.1	5.0	-3.8
m/p-Xylene	1400	1/114	12.3	11.3	11.6	11.5	-6.5
o-Xylene	567.2	1/114	5.0	4.7	4.8	4.8	-4.0
1,2,4-Trimethylbenzene	381.6	1/114	3.3	3.4	3.2	3.3	0.0
Decane	480	1/114	4.2	4.6	4.8	4.7	11.9

% Difference = ((Average Concentration - Assigned Concentration)/Assigned Concentration) x 100

Figure 4. Through-the-probe performance audit results.

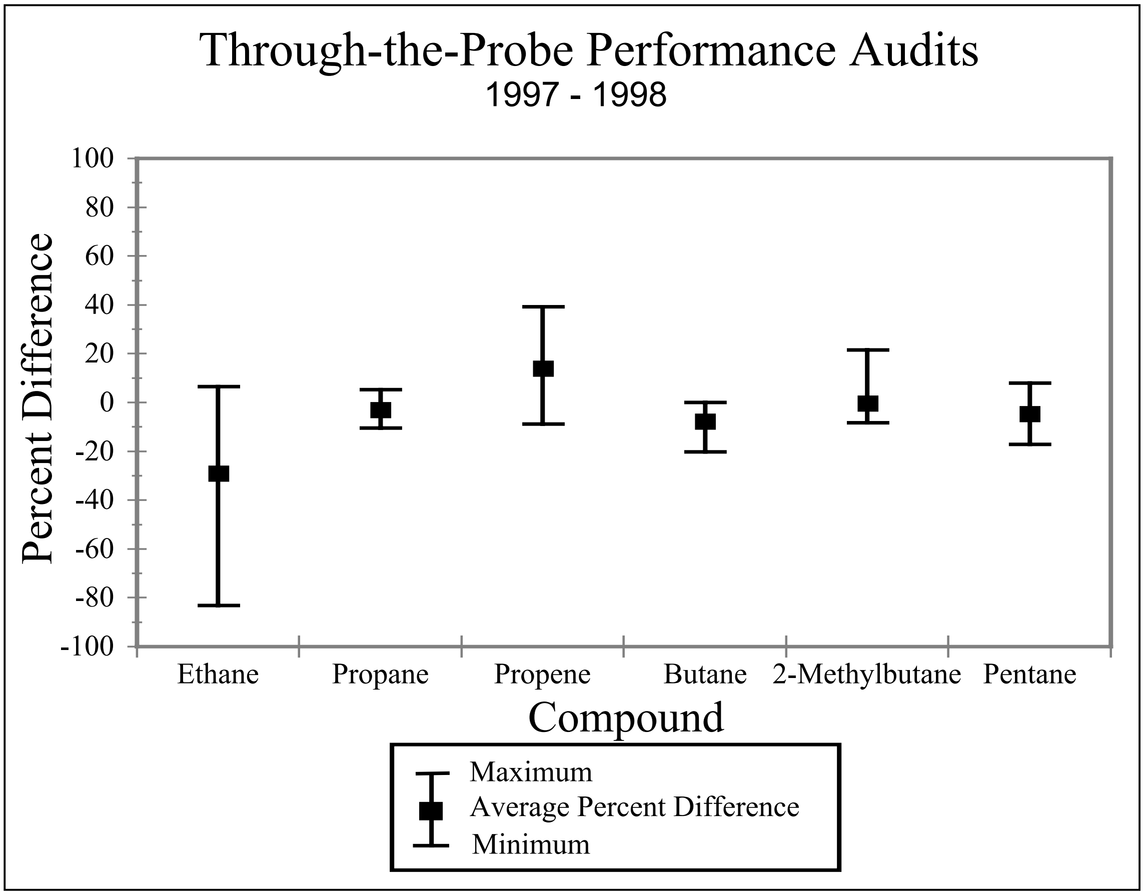


Figure 5. Laboratory performance audit results.

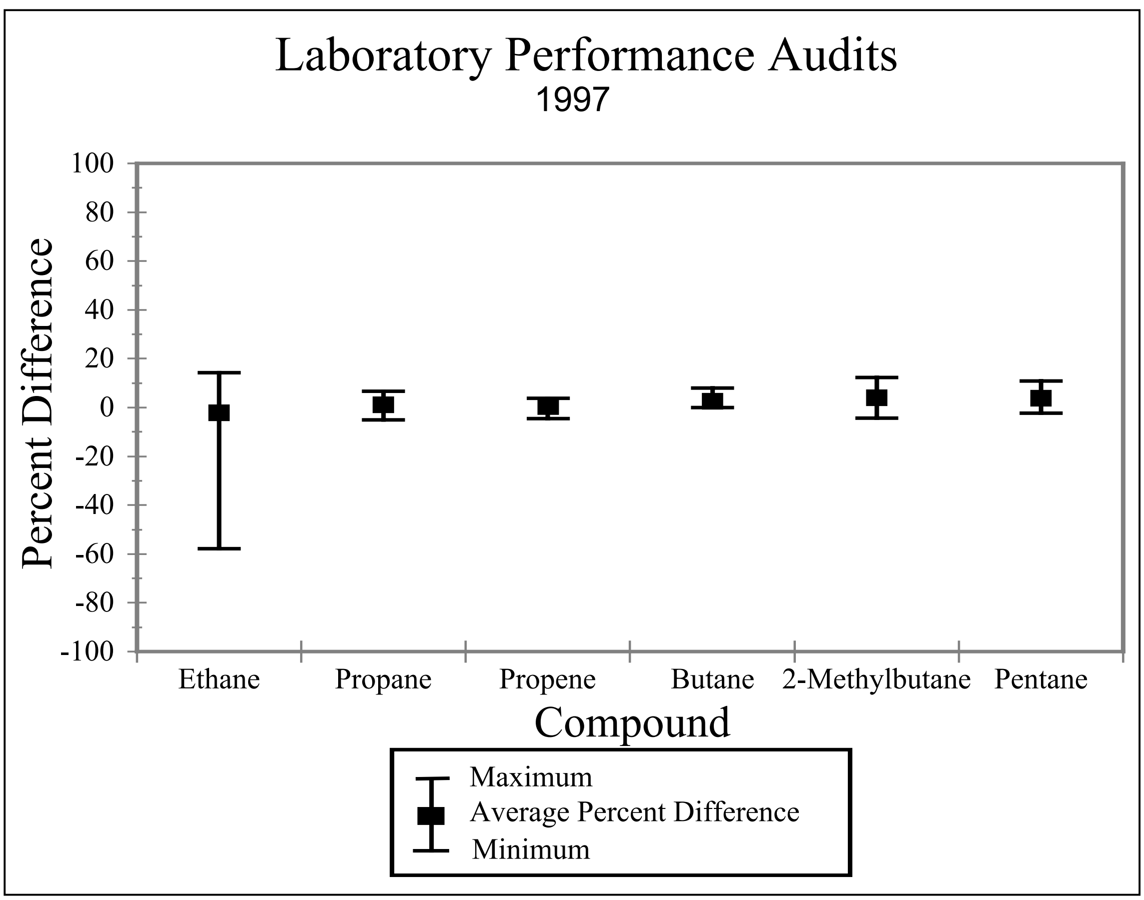


Figure 6. Through-the-probe audit results.

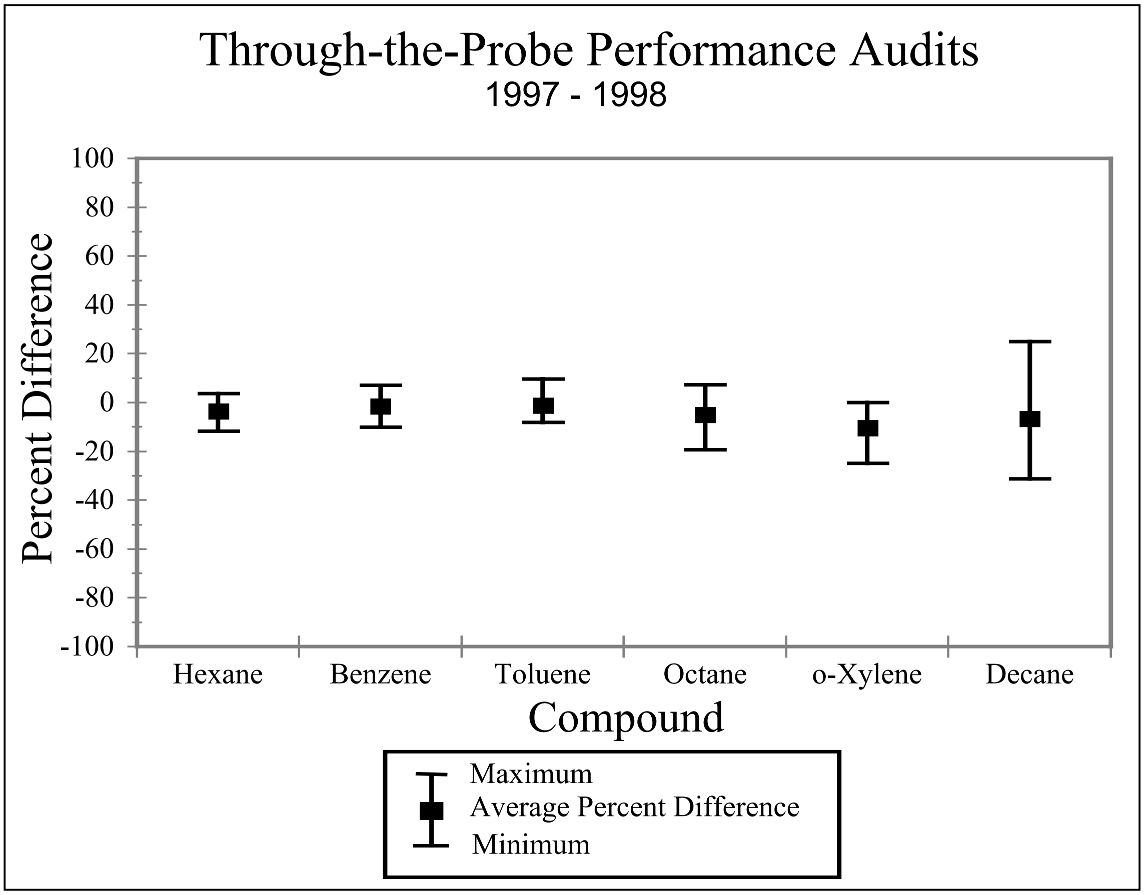
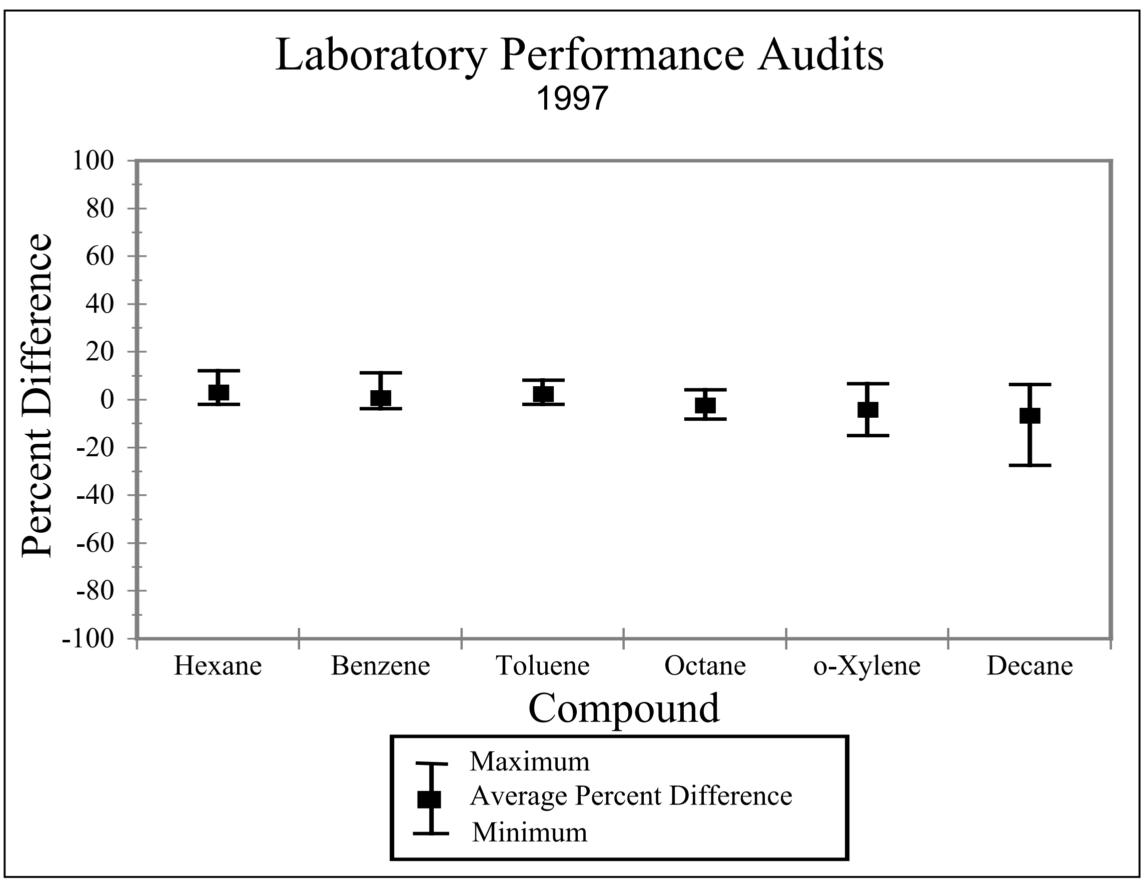


Figure 7. Laboratory performance audit results.



Key Words

Accuracy
Dilution Unit
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Performance Audits
Quality Assurance
Through-the-Probe