

Final Technical Report

on

Photochemical Assessment Monitoring Stations (PAMS):  
Data Assessment

for

Environmental Protection Agency  
Office of Air Quality Planning and Standards  
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## EXECUTIVE SUMMARY

Following the 1990 Clean Air Act Amendments, the U.S. EPA required that ozone and its precursors be monitored more extensively in all areas considered to be in serious, severe, or extreme non-attainment for ozone. Subsequently, States have established ambient air monitoring sites in these areas called Photochemical Assessment Monitoring Stations (PAMS). The PAMS program collects and reports detailed data for volatile organic compounds (VOCs), nitrogen oxides, ozone, and meteorological parameters. The main objective of this enhanced ozone monitoring program is to produce a data base in support of evaluating, tracking, and refining control strategies for ozone attainment. Specifically, PAMS data are providing the EPA and the States with valuable information for improving our understanding of the causes of ozone pollution, which is important for developing effective solutions to the problem, identifying true environmental improvements when they occur, and making decisions regarding attainment or non-attainment.

This report provides results from an assessment of PAMS data that were generated during the years 1996, 1997, and 1998. Twenty compounds are considered in the assessment, ranging in retention time from Ethane to Cyclopentane in the Propane group (i.e., compounds eluting from the PLOT column), from *n*-Hexane to *o*-Xylene in the Benzene group (i.e., compounds eluting from the BP1 column), and including Propane and Benzene. Three general types of PAMS data are evaluated: (1) calibration data, or retention time standards, provided by States (normally used as a quality control check), (2) co-located PAMS data downloaded from AIRS, and (3) National Performance Audit Program (NPAP) data. Each of the three data sources includes some benchmark, which allows us to assess the relative bias, or recovery, and measurement variability of PAMS data from different perspectives. The assessment includes comparisons of data across years, sites, PAMS site types, EPA Regions, and analytical methods.

The major findings from the assessment of State retention time calibration standards are the following (see Chapter 3 for further details):

- While there is considerable variability from site to site, the recoveries for the late Benzene group compounds averaged 5 to 10 percent lower than the recoveries for the other elution groups, and the recoveries for the late Propane group are sometimes up to 5 percent higher. (Note that this result is consistent with that found for the NPAP data.)
- The recoveries for all compounds and sites tended to be higher in 1997 than in 1996 and 1998, with the later eluting groups being affected the most. (Note that this result is consistent with that found for the co-located AIRS data.)
- When aggregated across sites, the coefficients of variation (CVs) for all elution groups were less than 10 percent in 1998. In 1996, the CVs for both the late elution groups were above 15 percent and, in 1997, the CV for the late Propane group was about 15 percent. (Note that for the NPAP data, the CVs for the late elution groups were markedly higher in 1998 versus 1996 or 1997.)

The major findings from the assessment of data from co-located PAMS samples downloaded from AIRS are the following (see Chapter 4 for further details):

- Daily concentration averages calculated from 1-hour samples tend to be greater than 24-hour canister samples (n-Hexane, Benzene, 2-Methylhexane, Ethane, Cyclopentane, and n-Pentane) and daily averages calculated from 3-hour samples tend not to differ significantly from 24-hour canister samples.
- Ratios of daily concentration averages calculated from 1-hour data relative to 24-hour data tend to be significantly higher in 1997 compared to either 1996 or

1998 (by 15 percent or more, on average), however, 1996 and 1998 ratios do not differ significantly. (Note that this result is consistent with the higher 1997 recoveries found for the State retention time data.)

- Ratios of daily concentration averages calculated from 3-hour data relative to 24-hour data do not differ significantly according to the 3-hour AIRS method code.

The major findings from the assessment of NPAP data are the following (see Chapter 5 for further details):

- For the later eluting compounds, the results in 1998 are much more variable than those in 1996 or 1997, in part due to outliers, but mostly due to the high variability in 1998 of 1,2,4 trimethylbenzene (the late Benzene group) and propane and propylene (in the late Propane group). (Note that the State retention time data indicated lower variability for the late elution groups in 1998 compared to 1996 or 1997.)
- There are statistically significant differences in the mean recoveries for the various elution groups within and across years. The recoveries for the late Benzene group compounds are roughly 4 to 10 percent lower than the recoveries for the other elution groups, and the recoveries for the late Propane group are roughly 4 to 10 percent higher. (Note that this result is consistent with that found for the State retention time data.)
- The Nafion dryer had a significant impact overall (its use lowers the recovery), and in 1996 in particular.

It is important to remember that statistical significance does not always imply practical significance. Therefore, the results highlighted above, along with those provided throughout the report, should be tempered by a numerical and visual assessment of the accompanying tables and figures.

In general, the goal of our effort in this work assignment was to highlight the behavior, good or bad, of various data associated with the PAMS program. The goal was not to explain the causes underlying the findings. Future PAMS data assessment efforts might focus on certain results for which an answer to the question “Why?” is important. For example, why does 1997 tend to stand out as somewhat different from 1996 and 1998? Or, future assessments might consider alternative sources of data, such as existing “round-robin” data, to conduct more detailed intergroup/interlaboratory comparisons. Finally, future assessments might simply extend the current findings to cover additional compounds, years, and/or States.

## 1.0 INTRODUCTION

### 1.1 Background

Following the 1990 Clean Air Act Amendments, the U.S. EPA required that ozone and its precursors be monitored more extensively in all areas considered to be in serious, severe, or extreme non-attainment for ozone. Subsequently, States have established ambient air monitoring sites in these areas, called Photochemical Assessment Monitoring Stations (PAMS). PAMS collect and report detailed data for volatile organic compounds (VOCs), nitrogen oxides, ozone and meteorological parameters. The collection and analysis of these data are providing the EPA and the States with valuable information for improving our understanding of the causes of ozone pollution. A better understanding of the causes of ozone pollution is crucial, both for developing solutions to the problem and identifying true environmental improvements when they occur.

The main objective of enhanced ozone monitoring is to produce a data base in support of evaluating, tracking and refining (if necessary) control strategies for ozone attainment. Measurements of ambient ozone concentrations and its precursors are important for making decisions regarding attainment or non-attainment. Additionally, such data will be helpful in monitoring VOC and NO<sub>x</sub> emission inventories, characterizing ozone problems, and identifying air quality trends. PAMS data also will be important for the continuing air quality management process. For example, the States can use these data to make sure the types of regulatory controls being implemented are cost-effective.

In developing the PAMS network, EPA used the Data Quality Objectives (DQOs) process, which is a seven-step procedure for characterizing environmental decision making and the data required to support it. In other words, DQOs are statements tying the quality of environmental data to the amount of uncertainty decision-makers are willing to accept. In most cases, DQOs are developed prior to the existence of data that are directly related to the issues at

hand. Various assumptions must be made about the expected nature of the data that eventually will be generated through environmental measurements. As such, it is not possible to guarantee future data will fully satisfy a set of specified DQOs. Furthermore, when monitoring objectives evolve and/or environmental data are obtained for evaluation, a need to update the program and/or its initial set of DQOs may become apparent. An assessment of existing data is an important part of making such a determination.

## 1.2 Scope of Report

The purpose of this report is to provide an assessment of data generated under the PAMS program during the years 1996, 1997, and 1998. Three sources of data associated with the PAMS program are evaluated. The first source is calibration data and retention times provided by the states of New Jersey, New York, Maryland, and the District of Columbia (State data). These data are from the periodic analysis of so-called “retention time standards,” which serve the dual purpose of peak area quantification and quality control of peak identification (i.e., via retention time). Data also include PAMS 1-hour or 3-hour sample duration data co-located with 24-hour canister samples, which were obtained via a download from the AIRS data base conducted during the week of August 28, 2000 (AIRS data). Finally, data from the National Performance Audit Program (NPAP) are considered as well (NPAP data). The following 20 compounds are included in the assessment:

- *n*-Hexane
- 2,4-Dimethylpentane
- Benzene
- 2-Methylhexane
- Toluene
- *n*-Octane
- *m/p*-Xylene
- *o*-Xylene
- Ethane
- Ethylene
- Propane
- Propylene
- *n*-Butane
- Acetylene
- 1-Butene
- Cyclopentane

- 1,2,4-Trimethylbenzene
- Isopentane
- *n*-Decane
- *n*-Pentane

The 20 compounds selected include 10 compounds that elute from the BP1 column (Benzene group) and 10 compounds that elute from the PLOT column (Propane group). This list was generated by considering the most prevalent compounds in 1996, 1997, and 1998 audit samples received from New Jersey. For each year, we identified the 20 most abundant compounds, by total concentration, within all the audit samples. The selected compounds were based on the number of years each showed up in the top 20 and the total overall concentration. The list was then presented to OAQPS technical personnel for final confirmation.

The assessment includes comparisons of data across years, sites, PAMS site types, EPA Regions, and analytical methods. Each of the data sources (State, AIRS, and NPAP) include some benchmark, which allows us to assess the relative bias, or recovery, and measurement variability of PAMS data from three different perspectives. Specifically, for the 20 compounds studied, we address:

- What is the distribution of recovery (i.e., ratio of measurement to truth) and recovery variability observed in State calibration data (i.e., retention time standards)?
- What is the distribution of relative bias (i.e., ratio of measurement to benchmark) and measurement variability observed between daily averages calculated from 1-hour and 3-hour sample intervals versus co-located 24-hour canister samples?
- What is the distribution of recovery (i.e., ratio of measurement to target concentration) and recovery variability observed in NPAP data?

For example, for the 20 compounds studied, how do recoveries on retention time standards compare from year-to-year? Or, for the 20 compounds studied, how does the bias between daily averages calculated from 1-hour samples and co-located 24-hour canister samples vary depending on PAMS site type?

The assessment is limited in scope from several aspects. First, years other than 1996, 1997, or 1998 are not considered. Next, although representative, only 20 compounds were studied. In particular,  $\text{NO}_x/\text{NO}_y$  data were not assessed. Finally, only a limited number of states, and, hence, EPA regions, are represented by the state calibration data assessment.

Finally, it has been speculated that deviations in automated gas chromatograph (auto-GC) retention times may lead to misidentification of compounds. If so, it is important to obtain a better understanding of the auto-GC retention time process and the factors that influence it. Therefore, in addition to the three major questions summarized above, a case study of New Jersey data was conducted to break down and describe the process underlying retention times generated from an auto-GC instrument over the course of a PAMS season. Variations in the process and their causes are identified. The potential impact on reported concentrations is also discussed.

### 1.3 Organization of Report

Chapter 2 of this report provides a detailed description of the data used for this assessment, along with the issues associated with obtaining and processing the data. Chapter 3 summarizes the assessment approach and findings with respect to recovery and variability observed in State calibration data. Chapter 4 summarizes the assessment approach and findings with respect to bias and measurement variability observed between daily concentration averages calculated from 1-hour or 3-hour sample intervals versus co-located 24-hour canister samples. Chapter 5 summarizes the assessment approach and findings with respect to recovery and variability observed in NPAP data. Appendix A contains additional tables and figures of results based on State calibration data. Appendix B details the retention time case study using data

reported by New Jersey. Finally, note that each chapter's figures have been placed at the end of the associated chapter.

## 2.0 DATA TYPES AND SOURCES

This assessment considers data that were generated as part of the PAMS program during the years 1996, 1997, and 1998. Three general types of PAMS data are evaluated, including calibration data (or retention time standards) provided by States, co-located PAMS data downloaded from AIRS, and National Performance Audit Program (NPAP) data. In addition to concentrations, the state of New Jersey provided actual retention time data. Data provided by the States led to the results summarized in Chapter 3 and the appendices of this report. Data downloaded from AIRS led to the Chapter 4 results. NPAP data led to the Chapter 5 results.

### 2.1 State Retention Time Calibration Data

The states of New Jersey, New York, Maryland, and the District of Columbia each were contacted for data. This outreach effort was limited by both resources and timing. Initial contact was made by a representative of EPA (John Silvasi or Avraham Teitz). During this initial contact, a description of the PAMS data assessment objectives was provided to the State and permission was received for further contact by the contractor, Battelle. Battelle then made follow-up contact with an appropriate State PAMS representative, as identified during the initial contact. During this follow-up communication, Battelle gave a description of the type of data required for the assessment, which included data from running retention time standards and actual retention times for any of the State's sites that were operating during the PAMS seasons 1996, 1997, or 1998. The State representative then determined the means by which the data could be provided.

With the exception of Washington, D.C., all State data were provided to Battelle via e-mail in Microsoft Excel spreadsheet format. Washington, D.C., provided hard copy information via Federal Express, which were transferred to electronic copy through data entry. Processing of the provided data included reducing the information to that needed for this

assessment and transforming it into SAS<sup>®</sup> data sets for analysis. In some cases, data questions and/or quality assurance (QA) issues arose, which prompted further contact with the States in order to achieve final resolution.

The first type of data provided by the States were results from retention time standards that were analyzed on their auto-GC systems. Retention time standards are used for peak identification and calibration. They are made up of a quantitative mixture of known hydrocarbon compounds, and are used to determine gas chromatographic peak retention times and quantitative factors. Mixtures include all target volatile organic compounds (VOCs) at specified concentration levels. The standards are used during the routine operation of an auto-GC system as a quality control (QC) standard for verifying retention times. Usually, a common mixture is used throughout a PAMS season.

Because retention time standards contain a known mixture of compounds, the results of their analyses yielded data for assessing site-specific recovery (i.e., ratio of measurement to truth) and recovery variability over a PAMS season. Combining the data from multiple sites and seasons allowed for an assessment of year-to-year or site-to-site differences in recoveries, by compound. Chapter 3 of this report summarizes assessment results based on the States' retention time standard data.

The second type of data provided by the States was the retention times for all sample concentration results. A retention time is the time at which a component elutes from the analytical column (BP1 or PLOT) and passes through the detection device (auto-GC). The rigorous sampling frequency requirements of PAMS rely on the practical use of retention times for peak identification. Sample components are identified by matching their retention times in a standard with those observed from the sample. Retention times are widely applied in chromatography and provide adequate confidence, according to PAMS network requirements, that the correct peak is identified. Once the components have been distinguished according to retention time, concentrations can be calculated by comparing the sample area to the retention

time standard area of the associated peak. Retention time data could not be readily provided by most States. Appendix B of this report summarizes assessment results (a case study) based on New Jersey retention times recorded at the Rutgers site throughout the 1998 PAMS season.

## 2.2 AIRS Co-Located Data

Aerometric Information Retrieval System (AIRS) data is a database of information about airborne pollution as collected by monitoring sites across the United States and various World Health Organization member countries. AIRS data were obtained by Battelle via access through IBM SecureWay Host On-Demand 4.0 (HOD) to connect to the EPA mainframe system located in Research Triangle Park, North Carolina.

Within the AIRS data base, Battelle used the Air Quality Subsystem (AQS). AQS contains measurements of ambient concentrations of air pollutants from many monitoring stations located throughout the United States. After conferring with representatives from the EPA, it was determined that the AMP350 - Raw Data Listing was the appropriate file to retrieve. The AMP350 extraction was done to create the files from the AIRS/AQS data base that were needed for this assessment. A data dictionary for the AMP350 file is available at <http://www.epa.gov/ttn/airs/airsmans.html#AQS>. Consistent with the scope of this assessment, this extraction was completed for all PAMS monitoring sites and for all parameters collected from January 1, 1996, through December 31, 1998.

The data extraction was completed by year for two intervals: interval "7" (daily data) and interval "L" (combined 1-hour and 3-hour data). Note that 1-hour interval data actually represents a 40-minute sampling time frame. Each year/interval combination required two data extractions to obtain all parameters for every PAMS monitoring site. Submitted datasets were retrieved via HOD file transfers from the EPA mainframe to a local PC. The data were downloaded as ASCII text files and were converted to SAS<sup>®</sup> data sets for analysis. For daily data (i.e., 24-hour sample intervals), one record was created for each day of monitoring. Hourly and

three-hourly data (i.e., 1-hour and 3-hour sample intervals) contained one record for each interval for each day. Only 20 parameters of interest (i.e., compounds) were included in the final SAS<sup>®</sup> data sets used in this assessment.

Merging all days containing data for both 24-hour samples and 1-hour or 3-hour samples provided a means for comparing and assessing the bias and measurement variability of daily averages calculated from shorter sample intervals relative to 24-hour samples. Chapter 4 of this report summarizes assessment results based on the downloaded AIRS 24-hour, 3-hour, and 1-hour sample interval data.

### 2.3 NPAP Data

The National Performance Audit Program, NPAP, is a voluntary auditing program for the PAMS sites. The U.S. EPA directs the preparation of canisters/cylinders with known mixtures of PAMS target compounds. These are distributed to participating sites approximately three times per season. The site then analyses the mixture and reports their findings back to EPA. Finally, EPA shares with the site the concentrations of the prepared mixture.

EPA's Mark Shanis coordinated the delivery of the NPAP data. The data were provided electronically to Battelle as tab delimited text files. A separate e-mail indicated which files contained the standard concentration and which contained the measured concentrations. These files were then converted to SAS<sup>®</sup> datasets for the analyses.

The data given to Battelle were limited to the reported concentration and a standard concentration for any of the 20 compounds used in this study, in addition to several META variables for the years 1996, 1997, and 1998. The META data included a date, whether or not a Nafion dryer was used, or whether the site used a humidification procedure. The site and reporting organization were indicated by random values, where each site and reporting

organization could be assigned several random values within a year. Chapter 5 of this report summarizes assessment results based on NPAP data.

### 3.0 RESULTS: STATE RETENTION TIME CALIBRATION DATA

#### 3.1 Data Availability

The retention time standards give the State its view of how well their approach to monitoring the target compounds in the PAMS program is working. The intent of this work is to assess the variability of this view and eventually contrast it with the view obtained by the NPAP program. Table 3-1 shows the list of State agencies that EPA and Battelle contacted to obtain retention time standard/calibration data (see detailed discussion in Section 2.1).

Table 3-1. Sites and years in the study of State data

State Contacted	Data Included		
	Site	Years	Average Number of Calibrations in a Season
Maryland	Essex	1996-1998	24
	Lake Clifton	1996	44
	Living Classroom	1998	27
New Jersey	Camden	1997-1998	14
	Rider	1996-1998	14
	Rutgers	1996-1998	16
New York	Bronx Garden	1996	23
Washington DC	Washington DC	1996-1997	11

Once converted to SAS<sup>®</sup> data sets, the data were analyzed in two ways. First, within site and year, summaries were generated for the 20 target compounds chosen and grouped by analytical column. The compounds measured with the PLOT column are labeled the Propane group and the compounds measured with the BP1 column are labeled the Benzene group. The data from Rutgers 1998 are highlighted in this chapter, the corresponding tables and graphs for the other sites and years examined are in Appendix A. It was expected that there might be a pattern in percent recovery as the retention times increased. To see any relationship between the recoveries and the overall retention time, the information in this chapter, and generally throughout this report, is presented in increasing order of retention times. The data included zero recoveries for Cyclopentane at two sites. These were treated as missing data in the numerical summaries, but were included as zeros in the plots for each site and year.

For the second set of analyses, each analytical column grouping was split into an early and late eluting group for a total of four groups. The recoveries were then analyzed across sites and years within each group. The suggested grouping for this analysis is shown in Table 3-2. Grouped in this manner, however, the data for the middle two groups are highly skewed. To better fit the assumptions of the statistical analyses, Acetylene and *m/p*-Xylene were excluded because of their tendency to exhibit very low recoveries. The results of the first set of analyses show that for most sites these two compounds do not seem to represent typical behavior within the rest of the groupings.

Table 3-2. Suggested elution groupings

<b>Early Propane Compounds</b>	<b>Late Propane Compounds</b>	<b>Early Benzene Compounds</b>	<b>Late Benzene Compounds</b>
Ethane	Propane	n-Hexane	1,2,4-Trimethylbenzene
Ethene	Propene	2,4-Dimethylpentane	<i>n</i> -Decane

	<i>n</i> -Butane	Benzene	
	Acetylene *	2-Methylhexane	
	1-Butene	Toluene	
	Cyclopentane	<i>n</i> -Octane	
	Isopentane	<i>m/p</i> -Xylene *	
	<i>n</i> -Pentane	<i>o</i> -Xylene	

\* Acetylene and *m/p*-Xylene were excluded from the groups in the analysis.

## 3.2 Data Summary

This section describes the summary data generated from the Rutgers 1998 calibration data and discusses the features noted for that site during the 1998 PAMS season compared with the other years and sites. Appendix A contains the corresponding tables and graphs for each of the sites and years noted in Table 3-1.

For most sites, only Propane and Benzene are used for calibration. Hence, these two compounds are the most important from the point of view of the operator. The data for these two compounds are necessarily good, since otherwise the GC would have been recalibrated. This has an effect on the other compounds. The assumption is made that the other compounds have the same response factors. Hence, it would not be expected to see great differences in recoveries from one compound to another within an analytic group. This is the generally observed trend. In effect, the main point to this analysis is to show where that trend does not hold.

Tables 3-3 and 3-4 show the number of times each compound was reported with a non-zero concentration in a retention time calibration, the average retention time, the concentration of the standard, the mean recovery, a 95 percent confidence interval for the mean recovery, the coefficient of variation (as a percent of the mean), a 90 percent confidence interval for the coefficient of variation, and the bias for the compound recovery ( $= \text{mean recovery} - 100\%$ ). The boxplots, Figures 3-1 and 3-2, show a box around the 25th and 75th percentiles with a line for the median and whiskers out to the minimum and maximum recovery values within 1.5 times the interquartile range (IQR) of the median. Recoveries above or below the median by more than 1.5 times the interquartile range are indicated with asterisks. The scatter plots, Figures 3-3 and 3-4, show the recovery data values plotted against the retention times for each observation. The mean recoveries for each compound are connected by a line in the scatter plots.

Table 3-3. Statistical summaries of the recoveries for the Benzene group of the Rutgers 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	16	13.114	30.1	111.3%	(100.5,122.2)	18.3%	(12.3,31.4)	11.3%
2,4-Dimethylpentane	16	15.826	39.9	103.8%	(102.4,105.3)	2.6%	(1.9,4.1)	3.8%
Benzene	16	17.701	30.03	98.5%	(97.1,99.9)	2.7%	(2.0,4.3)	-1.5%
2-Methylhexane	16	19.121	25.23	95.8%	(94.7,96.9)	2.2%	(1.6,3.4)	-4.2%
Toluene	16	25.896	38.85	114.7%	(112.8,116.7)	3.2%	(2.3,5.1)	14.7%
n-Octane	16	28.666	29.9	99.6%	(98.5,100.6)	1.9%	(1.4,3.0)	-0.4%
m/p-Xylene	16	32.241	39.43	70.6%	(59.2,82.0)	30.4%	(19.3,56.1)	-29.4%
o-Xylene	16	33.454	24.66	97.6%	(96.0,99.1)	2.9%	(2.1,4.6)	-2.4%
1,2,4-Trimethylbenzene	16	38.371	39.49	92.8%	(91.4,94.2)	2.8%	(2.0,4.4)	-7.2%
n-Decane	16	38.739	30.89	95.7%	(94.0,97.3)	3.2%	(2.3,5.0)	-4.3%

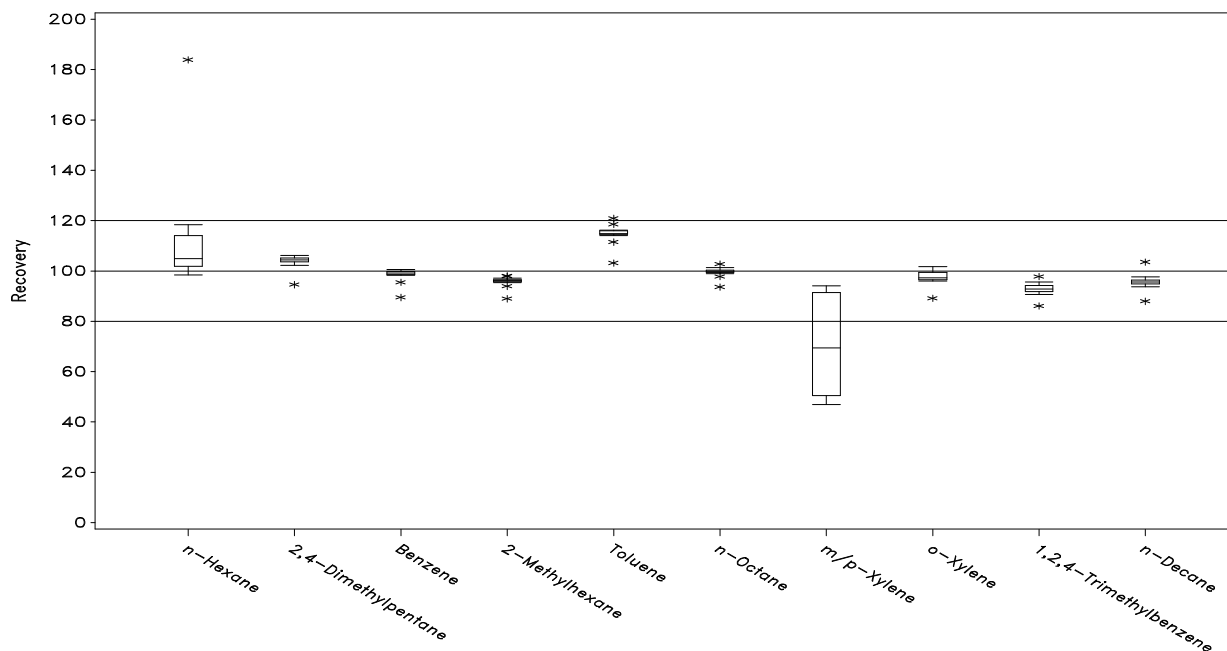


Figure 3-1. Boxplots of the recoveries for the Benzene group of the Rutgers 1998 retention time standard data by compound.



Table 3-4. Statistical summaries of the recoveries for the Propane group of the Rutgers 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	16	7.653	28.8	91.1%	(89.9,92.3)	2.5%	(1.8,4.0)	-8.9%
Ethylene	16	8.487	26.84	93.2%	(91.2,95.1)	3.9%	(2.8,6.2)	-6.8%
Propane	16	10.734	43.27	98.4%	(97.2,99.6)	2.3%	(1.7,3.6)	-1.6%
Propylene	16	18.359	23.74	95.0%	(93.7,96.2)	2.5%	(1.8,3.9)	-5.0%
n-Butane	16	22.276	43.47	102.4%	(101.2,103.6)	2.1%	(1.6,3.3)	2.4%
Acetylene	16	24.446	37.93	9.9%	(8.5,11.4)	27.7%	(17.8,50.3)	-90.1%
1-Butene	16	28.370	32.84	101.8%	(100.3,103.3)	2.7%	(2.0,4.3)	1.8%
Cyclopentane	16	30.870	20.13	98.3%	(97.3,99.4)	2.0%	(1.5,3.2)	-1.7%
Isopentane	16	31.061	42.04	102.4%	(101.2,103.6)	2.2%	(1.6,3.4)	2.4%
n-Pentane	16	31.951	25.63	99.7%	(98.8,100.6)	1.7%	(1.2,2.6)	-0.3%

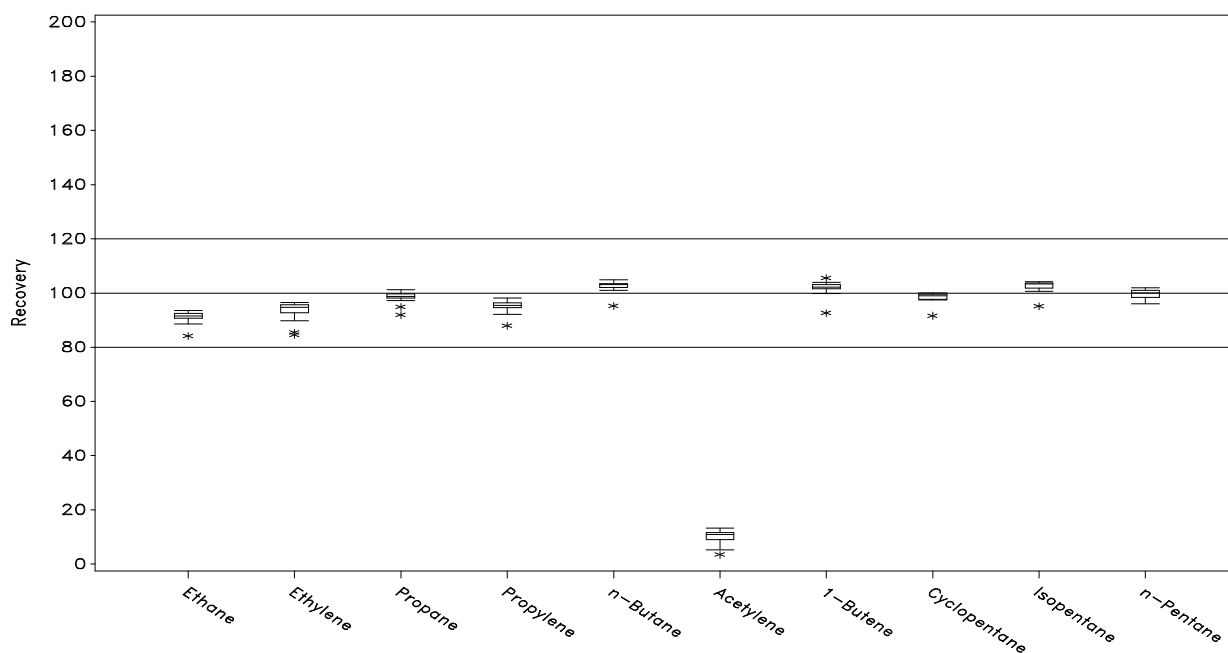


Figure 3-2. Boxplots of the recoveries for the Propane group of the Rutgers 1998 retention time standard data by compound.

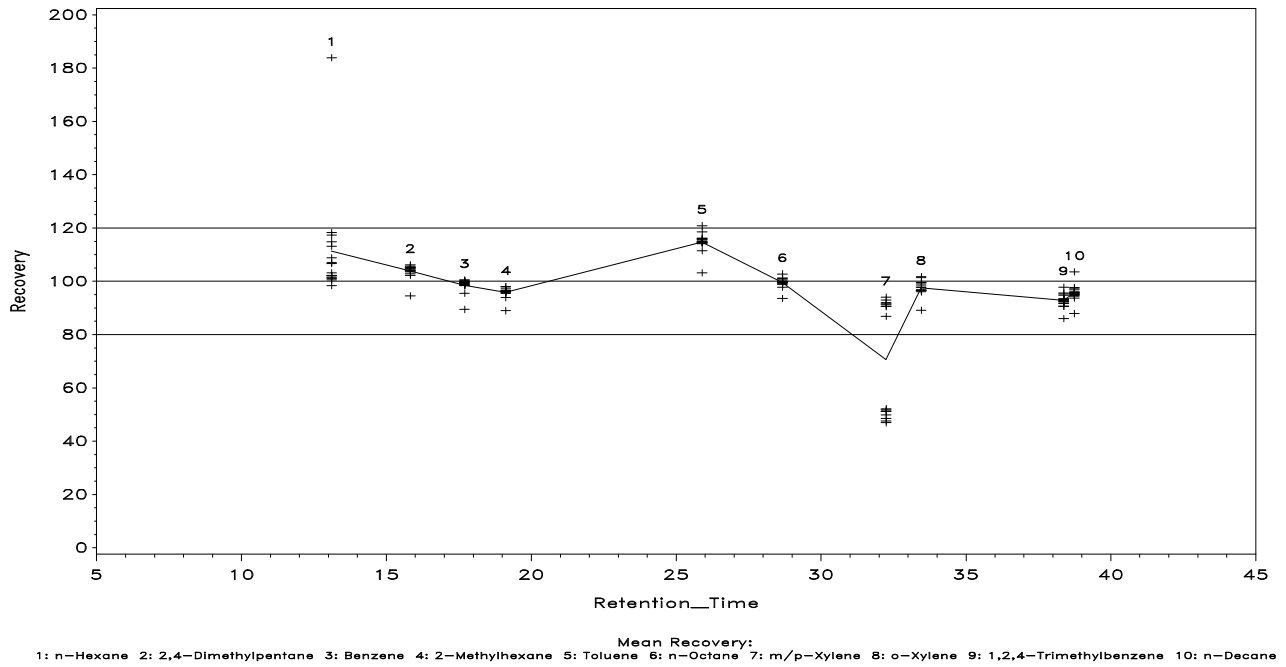


Figure 3-3. Scatter plot of the recoveries for the Benzene group of the Rutgers 1998 retention time standard data versus the retention time.

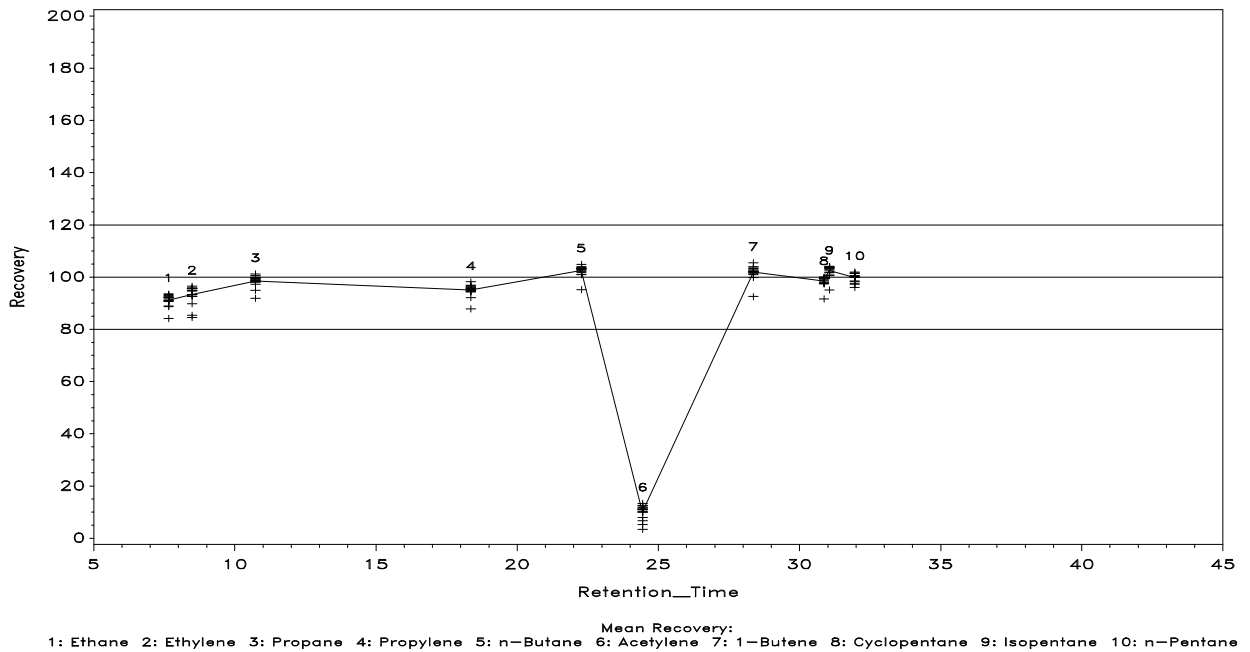


Figure 3-4. Scatter plot of the recoveries for the Propane group of the Rutgers 1998 retention time standard data versus the retention time.

There are several things to note from the graphs and tables. First, the recovery rate for Acetylene was much lower than for the other compounds, 9.9 percent. It also had a rather high coefficient of variation (CV) of 27.7 percent. (EPA has consistently noted poor stability of Acetylene in the retention time cylinders across years and organizations.) This case is typical of the other sites and years investigated. The NPAP data do not show such dramatic negative biases (see Chapter 5). Next, the *m/p*-Xylene recoveries are clustered about two very distinct values (see the scatter plot in Figure 3-3). This was a fairly common occurrence from across sites and years. (Look for boxplots that show a very wide interval between the 25th and 75th percentiles for *m/p*-Xylene.) This pattern is not seen in the NPAP data (or other round-robin analyses according to EPA), see Chapter 5. Finally, most of the minimum recovery values in the Propane group came from the same day. The scatter plot (Figure 3-4) shows a series of points that are about 7 percent lower than the mean. This case is more extreme than was typical. But it points out that what happens with Propane is representative of the rest of the compounds within the group.

Overall the Rutgers 1998 site had percent recoveries average within 90 percent to 110 percent except for Acetylene, *m/p*-Xylene, and Toluene. This is well within the 80 percent to 120 percent range that is referenced in the Technical Assistance Document for Sampling and Analysis of Ozone Precursors (TAD). The CVs also tended to be much less than 10 percent, although this is a particularly good site and year as will be seen.

Appendix A presents analogous data summaries (tables and figures) for the other sites and years included in the assessment, as listed in Table 3-1. The results for the other sites and years are similar with the following exceptions. There are two sites that have concentrations of zero reported for Cyclopentane, namely 22 of the values from Bronx Garden, 1996, and one from Essex, 1997. These were interpreted as “missing” in the numerical summaries, but were included in constructing the boxplots. Finally there are five times where the recoveries were less than 5 percent, and these cases were included in the numerical summaries and plots as valid data.

In general, the state retention time calibration data analyses parallel the NPAP data analyses. This allows the results to be compared. For example, unlike for the NPAP data, all the state data recoveries were below 200 percent.

### 3.3 Data Analysis

The recoveries for all sites and years were modeled to have separate mean recoveries for each combination of elution group and year as well as site effects, with distinct variances for each combination of elution group and year. A likelihood ratio test was used to test the significance of using separate variances for each combination of elution group and year versus a simpler model that only used distinct variances for each year. The result was highly significant,  $p\text{-value} < 0.0001$ , indicating the model with separate variances was more appropriate than the simpler common variance model.

Within this variance structure the effects of site, elution group, and year, and all the associated interactions, test significant at the 1 percent level or stronger. This means that while there may be some general statements that can be made about the recoveries, they may not apply to all site and year combinations. Hence, there may not be a sufficient variety of sites to be able to draw general conclusions on the magnitude of the effects for the network as a whole from these data alone. However, when taken with the NPAP data these data can provide insight to the network as a whole by corroborating some patterns seen in the NPAP data and indicating possible difficulties with the NPAP data.

Further, statistical significance does not imply practical significance. The practical significance (of say, the difference in the recoveries between the early and late elution groups) is best judged by first considering the statistical test results (in this case significant). Next, examine the plots or data summaries of all the retention time data for practical differences where statistical differences are noted. Finally, should the overall trend be of practical significance, examine

several of the site specific summaries to get an understanding of the practical significance of the site-to-site variability.

As mentioned, there are patterns that are confirmed in the NPAP data (the recoveries for the late eluting compounds in the Benzene group are lower) and some that seem to be contradicted (in particular the trends in the CVs from year to year). The differences may be due to the differences in the way that the data were generated (i.e., the way that samples were prepared). The purpose of this data analysis was to uncover these commonalities and differences, not to explain them. Further investigation may be valuable.

The recoveries for all the compounds within an elution group (except Acetylene and *m/p*-Xylene) were averaged to get an average compound group recovery for each site and year. Acetylene and *m/p*-Xylene were excluded because their recoveries were often very low, making them outliers relative to the other compounds studied. Acetylene recoveries were consistently low, while *m/p*-Xylene recoveries were near 100 percent about one-half of the time, and near 50 percent the other half of the time.

The CVs for each compound were combined by taking a weighted average of the squares of the CVs and then taking the square root of the result, where the compound CVs were weighted by the number of observations used to generate the compound CV. This is the procedure outlined in CFR 40 part 58. This yields a mean recovery and aggregate CV for each compound group and each site and year. These mean recoveries and the associated aggregated CVs are compared across sites and years. The results are plotted in Figures 3-5 and 3-6 and tabulated in Table 3-5. The plots show either the mean recovery or the aggregated CV plotted against the year, with the values from a given site connected by a line.

Figure 3-5 shows that the mean recoveries for each group were approximately the same in 1996 and 1998, but higher for four groups in 1997. Figure 3-6 shows a rather dramatic change in CVs across years. This should be contrasted with the CVs from the NPAP data that are sharply higher in 1998 (see Figure 5-10).



Table 3-5. Elution group mean recoveries and CVs for each site and year.

Year	Site	Early Propane		Late Propane		Early Benzene		Late Benzene	
		Mean Recovery	CV	Mean Recovery	CV	Mean Recovery	CV	Mean Recovery	CV
1996	Bronx Garden	100.1%	3.3%	90.1%	20.7%	98.6%	4.2%	98.2%	3.3%
	Essex	95.9%	5.7%	103.8%	3.3%	100.3%	8.9%	94.3%	13.7%
	Lake Clifton	98.3%	3.8%	103.1%	14.0%	92.9%	14.1%	70.1%	11.5%
	Rider	92.7%	4.1%	97.8%	3.4%	99.6%	6.8%	106.6%	11.5%
	Rutgers	89.5%	5.0%	97.3%	2.5%	99.1%	5.3%	92.1%	4.8%
	Washington DC	87.7%	12.6%	97.2%	12.3%	97.7%	15.4%	92.1%	16.5%
1997	Camden	91.7%	10.3%	100.3%	14.2%	99.0%	6.9%	93.2%	5.9%
	Essex	103.9%	9.8%	103.9%	8.3%	102.9%	5.5%	96.4%	5.0%
	Rider	103.7%	4.7%	101.1%	15.2%	99.0%	10.3%	101.9%	6.4%
	Rutgers	98.7%	9.9%	119.7%	16.3%	101.6%	13.3%	95.5%	9.9%
	Washington DC	100.3%	2.6%	105.3%	4.6%	100.6%	14.2%	95.5%	10.3%
1998	Camden	98.1%	8.4%	101.4%	7.3%	101.7%	8.7%	86.7%	13.7%
	Essex	101.3%	3.6%	98.7%	6.1%	95.3%	5.5%	84.6%	4.3%
	Living Classroom	98.6%	4.6%	101.3%	3.3%	96.0%	4.6%	87.8%	3.0%
	Rider	95.8%	3.9%	98.3%	10.5%	100.8%	6.3%	86.1%	5.1%
	Rutgers	92.1%	3.5%	99.7%	3.4%	103.1%	10.1%	94.2%	3.3%
All	Bronx Garden	100.1%	3.3%	90.1%	20.7%	98.6%	4.2%	98.2%	3.3%
	Camden	94.9%	9.9%	100.9%	11.3%	100.4%	8.0%	89.8%	11.0%
	Essex	100.3%	7.4%	101.9%	6.6%	99.2%	7.6%	91.3%	10.6%
	Living Classroom	98.6%	4.6%	101.3%	3.3%	96.0%	4.6%	87.8%	3.0%
	Lake Clifton	98.3%	3.8%	103.1%	14.0%	92.9%	14.1%	70.1%	11.5%
	Rider	97.6%	6.4%	99.1%	11.3%	99.8%	8.1%	97.8%	12.1%
	Rutgers	94.4%	8.5%	107.9%	15.5%	101.5%	11.0%	94.3%	7.3%
	Washington DC	97.6%	7.8%	103.5%	7.5%	99.8%	14.5%	94.6%	12.1%

The boxplots for each year of recovery by elution group (Figures 3-7 through 3-10) have notched boxes around the middle 50 percent of the data within the given category with a line at the median and “plus” indicating the mean. The notch is an approximate 95 percent confidence interval for the median. A pair of boxes with non-overlapping notches can be taken to indicate significantly different medians for the two different groups. The whiskers for these boxes extend outward from the quartiles to either 1.5 times the interquartile range, IQR, if there are data outside that range or to the furthest data value from the median within 1.5 times the IQR from the quartile. Any data values outside the whiskers are plotted with an asterisk. Isolated points outside the whiskers are often treated as outliers. Most of the cases shown in the figures are not isolated, and should not be considered outliers. Rather, they show that extreme values occur with some regularity in these data. Figures 3-7 through 3-10 should be compared with the corresponding figures in Chapter 5, Figures 5-5 through 5-8.

While there is considerable variability from site to site, the recoveries for the late Benzene group compounds are consistently lower than the recoveries for the other elution groups and the recoveries for the late Propane group are somewhat higher. Also, the recoveries for all compounds and sites tended to be higher in 1997 than in the other two years, with the later eluting groups being affected the most. Finally, the CVs for 1998 are generally much better than the other two years. This last point is the opposite of that found for the NPAP data.

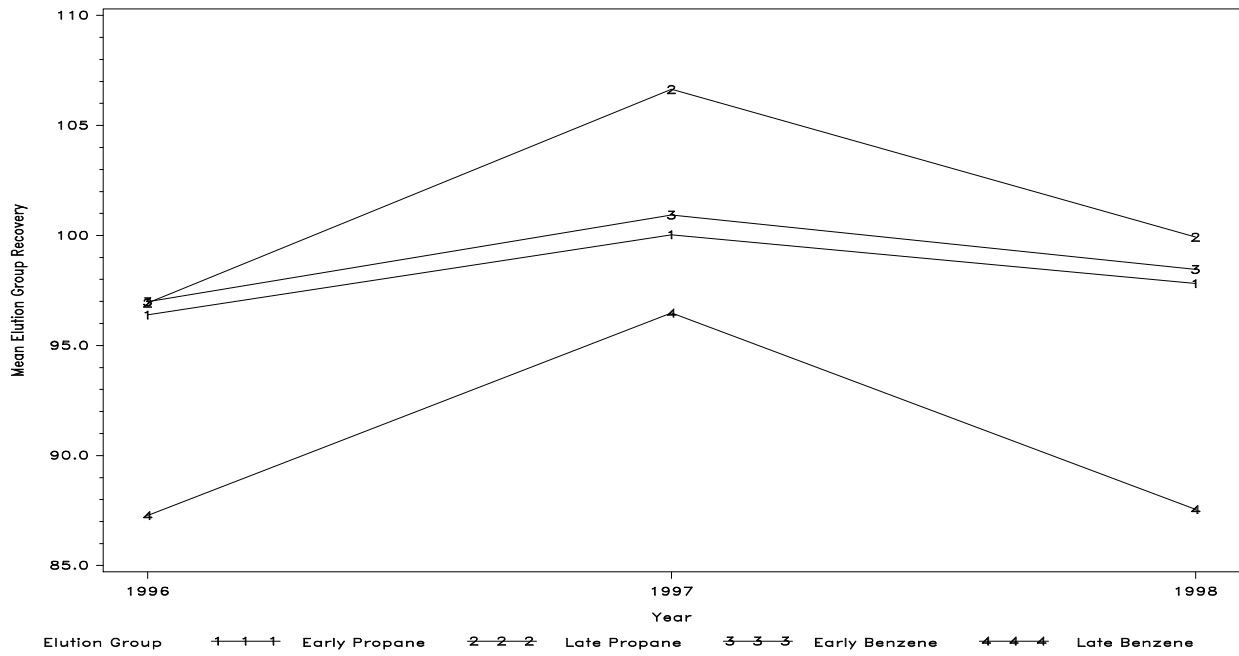


Figure 3-5. Scatter plot of the mean recoveries for each elution group by year.

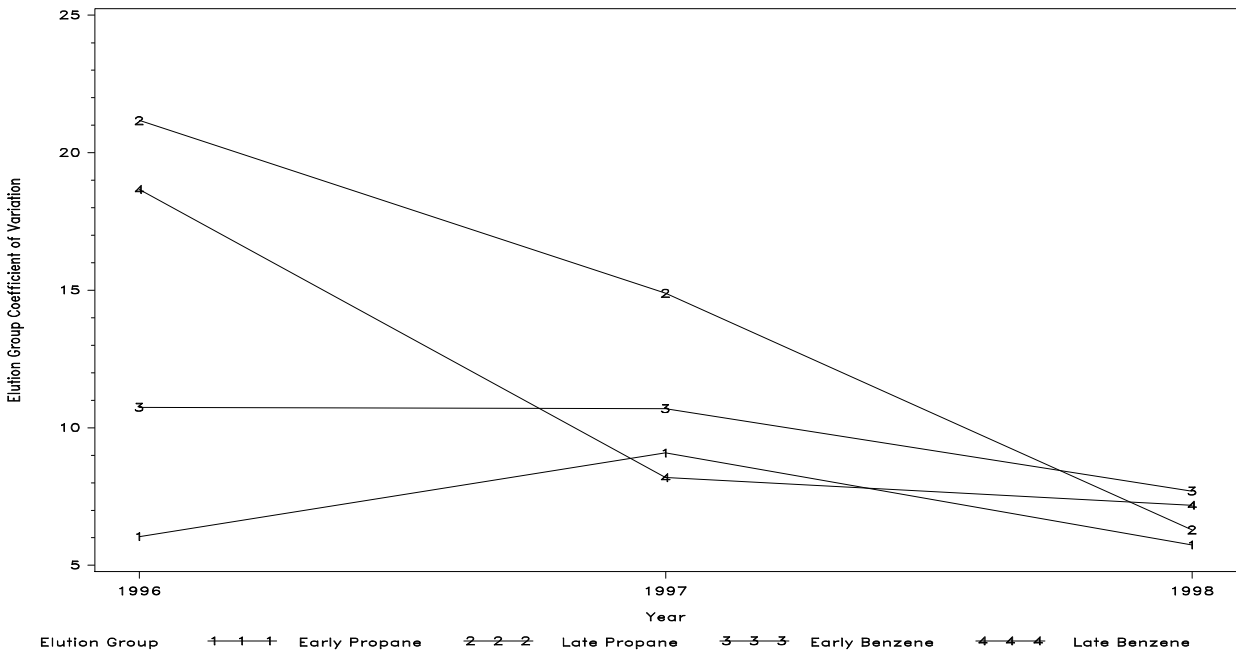


Figure 3-6. Scatter plot of the aggregated CVs for each elution group by year.

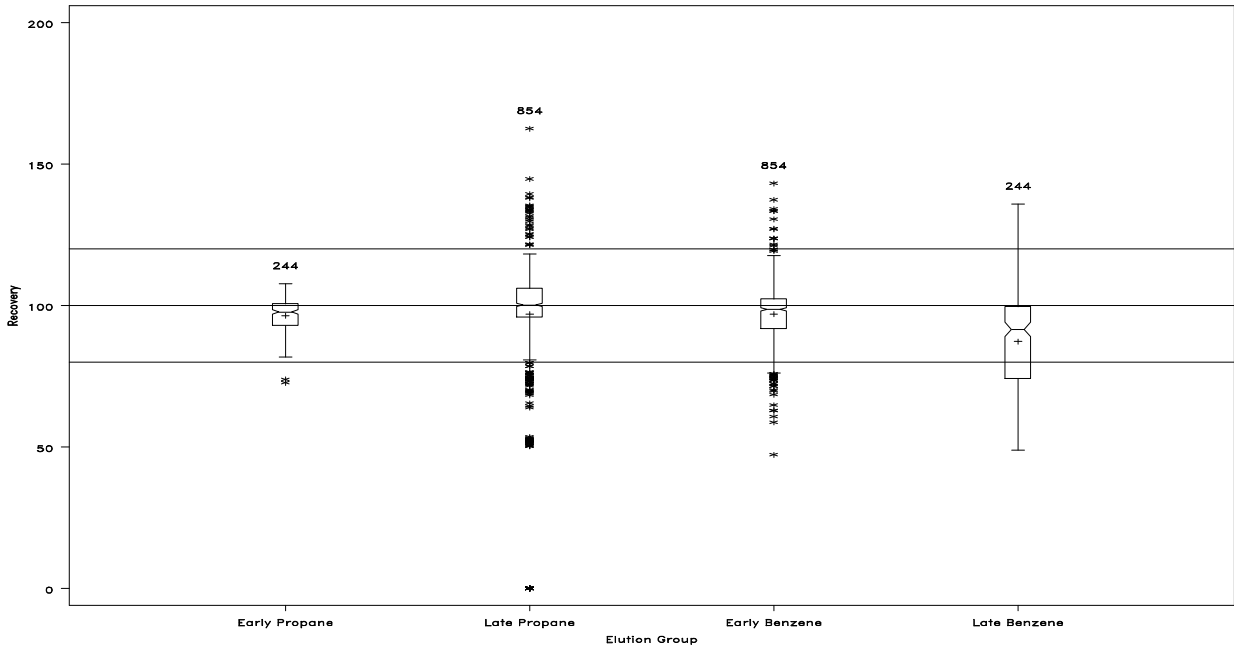


Figure 3-7. Boxplot of the 1996 elution group recoveries for the retention time data.

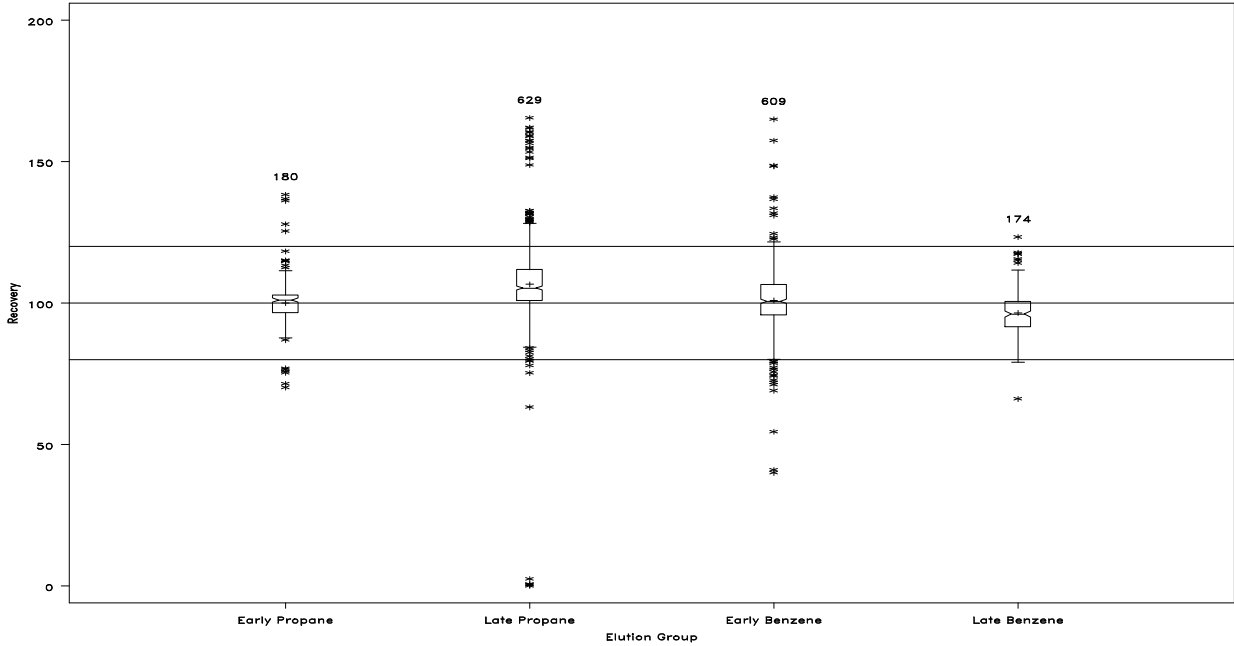


Figure 3-8. Boxplot of the 1997 elution group recoveries for the retention time data.

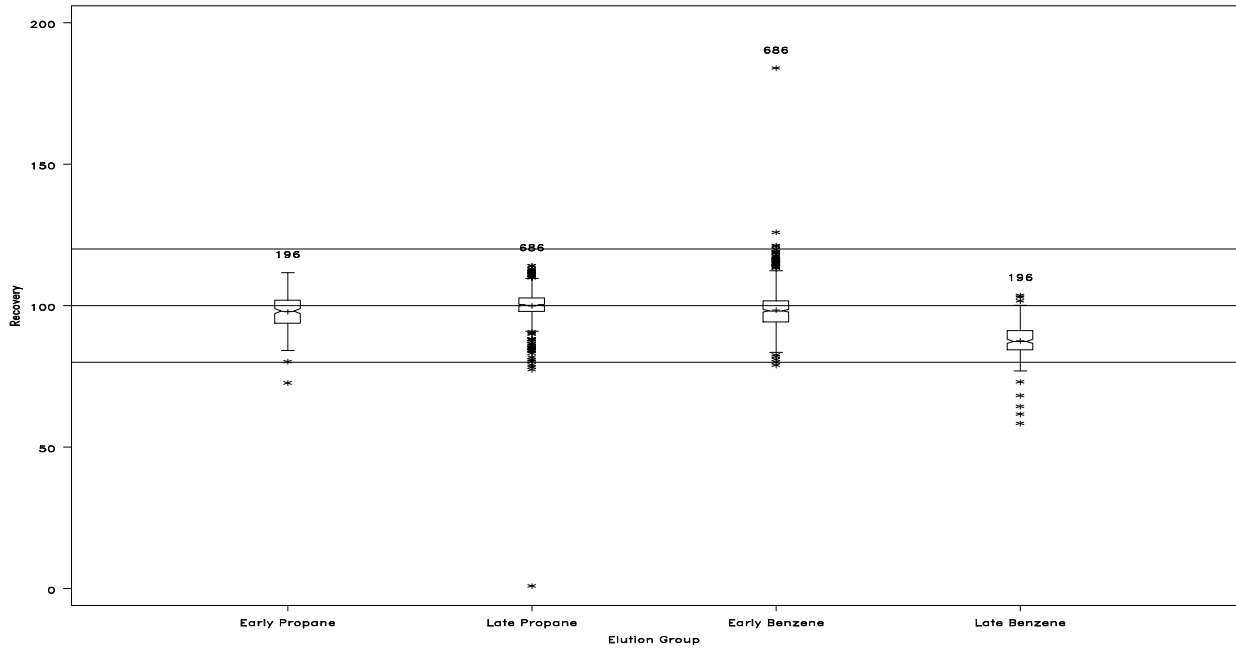


Figure 3-9. Boxplot of the 1998 elution group recoveries for the retention time data.

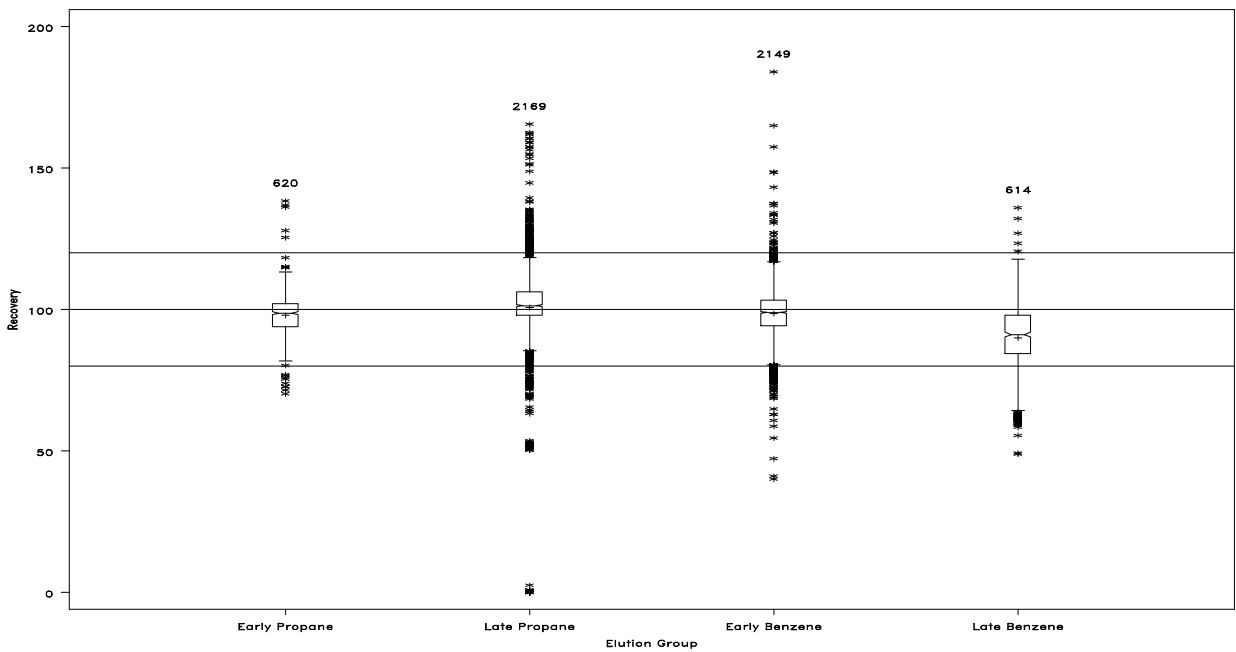


Figure 3-10. Boxplot of the retention time data elution group recoveries for all years.



## 4.0 RESULTS: AIRS CO-LOCATED DATA

### 4.1 Data Availability

The first step in comparing co-located 1-hour and 3-hour samples with 24-hour canister samples was to obtain a suitable data base. This was accomplished via a download of 1996, 1997, and 1998 PAMS data from AIRS conducted on the week of August 28, 2000. (Chapter 2 describes the download details.) Table 4-1 summarizes the initial amount of data obtained from AIRS prior to conducting data processing, data management, or quality assurance (QA)/quality control (QC) activities. Some limited downloaded data did not possess an associated date and are excluded from the summary of Table 4-1. In general, Table 4-1 provides a best case scenario summary of the amount of data (in terms of number of sites) that might be available for comparison.

For each of the 20 compounds studied, the first three “Number of Sites with Data” columns of Table 4-1 indicate the number of sites containing at least one day with a measurement of the associated sample duration (i.e., 24-hour, 3-hour or 1-hour). The last two columns indicate the number of sites containing at least one day of co-located [24-hour, 3-hour] or [24-hour, 1-hour] measurements, respectively. Comparing the first three “Number of Sites with Data” columns to the last two in Table 4-1 highlights the amount of initially-downloaded data that can not be used because they are not co-located. For example, downloaded Benzene data include 40 sites of 24-hour data and 45 sites of 3-hour data, yet only 20 sites contain one or more days of potentially useable co-located [24-hour, 3-hour] measurements.

Table 4-1. Number of sites with 24-hour, 3-hour, 1-hour, co-located [24-hour, 3-hour], and co-located [24-hour, 1-hour] data, by compound

Group	Compound	Number of Sites with Data				
		24-hour	3-hour	1-hour	24- and 3-hour	24- and 1-hour
Benzene	<i>n</i> -Hexane	34	45	34	15	13
	2,4-Dimethylpentane	27	45	39	14	7
	Benzene	40	45	39	20	12
	2-Methylhexane	28	45	34	15	7
	Toluene	41	45	34	19	14
	<i>n</i> -Octane	39	45	39	19	12
	<i>m/p</i> -Xylene	41	43	39	17	15
	<i>o</i> -Xylene	43	45	39	20	15
	1,2,4-Trimethylbenzene	38	45	39	18	15
	<i>n</i> -Decane	36	45	38	16	13
Propane	Ethane	29	45	39	16	8
	Ethylene	37	45	39	17	12
	Propane	38	45	34	17	11
	Propylene	38	45	39	17	13
	<i>n</i> -Butane	36	45	34	16	12
	Acetylene	34	45	39	17	8
	1-Butene	38	41	39	17	11
	Cyclopentane	33	45	33	18	8
	Isopentane	39	45	33	17	12
	<i>n</i> -Pentane	37	45	39	18	12

Once the data were obtained from AIRS, the next step was to create a level playing field for comparing the different sample durations. This was done by averaging a day's set of 1-hour

or 3-hour samples (up to 24 or 8, respectively) to create a one-number summary representing the daily average concentration. The resulting endpoint is appropriate for making “apples-to-apples” comparisons between 1-hour or 3-hour samples and 24-hour canister samples. It is important to recognize that some information is lost in this process, such as the diurnal variability of the given compound. However, an understanding of hourly variations is ancillary to the assessment at hand.

Some of the data could not be used in the assessment due to a lack of completeness or quality in one form or another. First, there were cases in both the 1-hour/3-hour samples or 24-hour canister samples where the concentration or the MDL value was missing. These cases were dropped. Also, observations were dropped when the measured concentration was not greater than the associated MDL. These cases were considered unreliable given that the quality of the measurements was in question. For the remaining 1-hour and 3-hour data, a criterion of 75 percent completeness was applied with regard to calculating the daily averages. Specifically, in order for a given compound’s daily average to be used in this assessment, above-MDL concentrations must remain for at least 18 of the 24 hours (or six of the eight 3-hour periods) and, if so, they are then averaged and associated with a co-located 24-hour canister sample.

Finally, there were 30 cases where two co-located 24-hour canister samples were analyzed using different analytical methods. These 30 pairs of observations were analyzed and found to be consistent (within a pair), so it was decided that both 24-hour measurements would be included in the analysis data base for association with the appropriate 1-hour or 3-hour daily average. Table 4-2 summarizes the final set of complete quality controlled (QC’d) daily data available for assessment.

Table 4-2. Number of sites and observations with co-located [24-hour, 3-hour] or [24-hour, 1-hour] complete and Quality Controlled daily data, by compound

Group	Compound	24-hour and 3-hour		24-hour and 1-hour	
		Number of Sites	Number of Observations	Number of Sites	Number of Observations
Benzene	<i>n</i> -Hexane	6	79	7	117
	2,4-Dimethylpentane	4	8	4	7
	Benzene	9	105	9	90
	2-Methylhexane	5	17	6	35
	Toluene	9	76	10	142
	<i>n</i> -Octane	5	29	3	15
	<i>m/p</i> -Xylene	6	99	12	63
	<i>o</i> -Xylene	8	46	10	45
	1,2,4-Trimethylbenzene	6	40	6	45
	<i>n</i> -Decane	4	64	6	31
Propane	Ethane	8	96	4	36
	Ethylene	7	102	6	60
	Propane	8	99	7	54
	Propylene	7	80	9	43
	<i>n</i> -Butane	7	41	6	81
	Acetylene	8	80	6	59

1-Butene	6	52	6	20
Cyclopentane	4	10	5	20
Isopentane	9	109	8	75
<i>n</i> -Pentane	7	52	6	52

For each of the 20 compounds studied, the “Number of Sites” columns in Table 4-2 indicate the number of sites containing at least one day of co-located [24-hour, 3-hour] or [24-hour, 1-hour] complete and QC’d daily data. The “Number of Observations” columns indicate the total number of days of co-located complete and QC’d daily data, summed across sites. Compare the respective “Number of Sites” columns in Table 4-2 to the last two columns of Table 4-1. This comparison highlights the additional sites’ worth of data deemed incomplete or unreliable for this effort, based on applying the criteria described above. For example, 20 sites (Table 4-1) contain co-located [24-hour, 3-hour] Benzene data, but only nine of these sites (Table 4-2) contain any complete and QC’d daily data (105 total observations). In comparison, 12 sites (Table 4-1) contain co-located [24-hour, 1-hour] Benzene data, and nine of these sites (Table 4-2) contain some complete and QC’d daily data (90 total observations).

#### 4.2 Overall Data Summary and Analysis

Using the available data as summarized in Table 4-2, we conducted an initial analysis to summarize how daily measurements based on 1-hour and 3-hour sample durations compare with measurements based on 24-hour canister samples. The endpoint of concern is the ratio of the 1-hour or 3-hour daily average to the 24-hour measurement. For example, a ratio of 0.95 indicates that a daily average measurement calculated from 1-hour or 3-hour data is 95 percent of the associated co-located 24-hour measurement. Values consistently different from 1.00 suggest a potential bias between the two sample durations being compared.

Figures 4-1 and 4-2 provide a visual summary of the data in the form of side-by-side boxplots (box and whisker plots) for the ratios of co-located [1-hour, 24-hour] and [3-hour, 24-hour] data. Figure 4-1 presents results for the ten compounds studied from the Benzene group and Figure 4-2 presents results for the ten compounds studied from the Propane group. Any ratios lying above or below the median ratio by more than  $1.5 \times \text{IQR}$ , where  $\text{IQR} = 3\text{rd quartile of data} - 1\text{st quartile of data}$ , are treated as outliers and show up as asterisks in the plots. The outer whiskers of the plots extend to the most extreme lower and upper ratios not flagged as outliers. The lines of the main box indicate the 1st quartile (bottom), median (center), and 3rd quartile (top) of the set of ratios. The horizontal axis distinguishes compounds and whether the numerator of the ratios is derived from 1-hour or 3-hour data. Horizontal lines at a ratio of 1.00 and  $\pm 20$  percent are included for reference.

Tables 4-3 and 4-4 provide corresponding summary statistics for the sets of ratios. Table 4-3 presents results for the ten compounds studied from the Benzene group and Table 4-4 presents results for the ten compounds studied from the Propane group. The tables provide side-by-side results for the 24-hour versus 3-hour and the 24-hour versus 1-hour comparisons. The summary statistics in the tables include the number of observations, the geometric mean of the daily concentrations calculated from 1-hour, 3-hour, and 24-hour measurements, the geometric mean of the ratios, the geometric standard deviation of the ratios, and a 95 percent confidence interval (CI) for the mean ratio.

Geometric means and standard deviations were reported because the distributions of concentrations and ratios tended to be skewed toward larger values. Each geometric mean and standard deviation pair is calculated by transforming the data via the natural logarithm function, deriving the arithmetic mean and standard deviation of the log-transformed data, then exponentiating the results. For skewed data, the geometric mean is often a better measure of central tendency than the arithmetic mean, as it is more resistant to the influence of extreme values. In fact, for log-normally distributed data, the geometric mean provides an unbiased estimate of the data's median on the original untransformed concentration (or ratio) scale. Also, if it is desired to use normal distribution theory in calculating CIs of skewed data, it is often more

appropriate to first generate the CIs on the log-transformed scale, then transform the CI endpoints back to the original scale via exponentiation (as was done for Tables 4-3 and 4-4).

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Table 4-3. Summary statistics for the ratio of the daily average calculated from 1-hour or 3-hour interval data relative to 24-hour interval data, for compounds in the Benzene group<sup>1</sup>

Compound	3-hour/24-hour						1-hour/24-hour					
	N	Mean of Concentrations		Mean of Ratios	Standard Deviation of Ratios	95% CI for Mean of Ratios	N	Mean of Concentrations		Mean of Ratios	Standard Deviation of Ratios	95% CI for Mean of Ratios
		3-hour	24-hour					1-hour	24-hour			
<i>n</i> -Hexane	79	2.76	2.99	0.93	1.60	(0.83, 1.03)	117	3.17	2.37	1.33	1.82	(1.20, 1.49)
2,4-Dimethylpentane	8	0.78	0.87	0.90	1.25	(0.75, 1.08)	7	1.43	1.25	1.15	6.36	(0.21, 6.34)
Benzene	105	2.70	2.52	1.07	1.39	(1.01, 1.14)	90	3.20	2.73	1.17	2.01	(1.01, 1.36)
2-Methylhexane	17	1.19	1.30	0.91	1.36	(0.78, 1.07)	35	1.54	1.19	1.29	1.60	(1.10, 1.52)
Toluene	76	3.72	3.87	0.96	1.62	(0.86, 1.07)	142	9.29	8.35	1.11	1.87	(1.00, 1.23)
<i>n</i> -Octane	29	1.21	1.69	0.72	1.93	(0.56, 0.92)	15	0.48	0.49	1.00	1.67	(0.75, 1.32)
<i>m/p</i> -Xylene	99	2.27	2.67	0.85	1.68	(0.77, 0.95)	63	3.10	2.79	1.11	1.87	(0.95, 1.30)
<i>o</i> -Xylene	46	1.71	1.86	0.92	1.96	(0.75, 1.12)	45	1.07	0.99	1.08	1.78	(0.91, 1.29)
1,2,4-Trimethylbenzene	40	1.09	1.25	0.87	2.17	(0.68, 1.11)	45	1.61	1.56	1.03	2.97	(0.74, 1.43)
<i>n</i> -Decane	64	0.36	0.46	0.80	3.01	(0.61, 1.05)	31	0.50	0.67	0.75	2.49	(0.54, 1.05)

<sup>1</sup> Means and standard deviations are calculated as geometric means and geometric standard deviations, respectively.

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Table 4-4. Summary statistics for the ratio of the daily average calculated from 1-hour or 3-hour interval data relative to 24-hour interval data, for compounds in the Propane group<sup>1</sup>

Compound	3-hour/24-hour						1-hour/24-hour					
	N	Mean of Concentrations		Mean of Ratios	Standard Deviation of Ratios	95% CI for Mean of Ratios	N	Mean of Concentrations		Mean of Ratios	Standard Deviation of Ratios	95% CI for Mean of Ratios
		3-hour	24-hour					1-hour	24-hour			
Ethane	96	9.06	9.09	1.00	1.19	(0.96, 1.03)	36	12.26	9.85	1.24	1.80	(1.02, 1.52)
Ethylene	102	3.53	3.49	1.01	1.19	(0.98, 1.04)	60	4.65	5.09	0.91	1.74	(0.79, 1.05)
Propane	99	9.24	9.12	1.01	1.14	(0.99, 1.04)	54	10.23	9.68	1.06	1.62	(0.93, 1.21)
Propylene	80	2.82	2.87	0.98	1.49	(0.90, 1.07)	43	2.71	2.94	0.92	1.71	(0.78, 1.09)
<i>n</i> -Butane	41	5.62	5.80	0.97	1.86	(0.80, 1.18)	81	13.01	12.07	1.08	1.58	(0.98, 1.19)
Acetylene	80	2.42	2.27	1.06	1.43	(0.98, 1.15)	59	2.67	2.56	1.04	1.84	(0.89, 1.22)
1-Butene	52	1.76	1.95	0.91	1.47	(0.82, 1.01)	20	0.52	0.68	0.77	1.88	(0.57, 1.03)
Cyclopentane	10	1.51	1.55	0.97	1.21	(0.85, 1.11)	20	0.55	0.39	1.43	1.43	(1.21, 1.69)
Isopentane	109	5.19	5.58	0.93	1.42	(0.87, 0.99)	75	9.11	8.63	1.06	1.93	(0.91, 1.23)
<i>n</i> -Pentane	52	2.90	2.66	1.09	1.37	(1.00, 1.19)	52	5.58	4.48	1.25	1.77	(1.06, 1.46)

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<sup>1</sup> Means and standard deviations are calculated as geometric means and geometric standard deviations, respectively.

For a given compound, any CI in Table 4-3 or 4-4 that does not include the value 1.00 is suggestive of a statistically significant overall bias in daily concentrations due to sample duration (1-hour or 3-hour) relative to the 24-hour measurement. Generally, Tables 4-3 and 4-4 suggest that 3-hour/24-hour ratios tend to be near (or possibly below) 1.00, while 1-hour/24-hour ratios tend to be above 1.00. In other words, summarizing across the 20 compounds studied,

*Daily averages calculated from 1-hour samples tend to be greater than 24-hour canister samples and daily averages calculated from 3-hour samples tend not to differ significantly from 24-hour canister samples.*

More specifically, of the 20 compounds studied, the mean of the 3-hour/24-hour daily average ratios is statistically:

- significantly less than 1.00 for n-Octane, m/p-Xylene, and Isopentane,
- significantly greater than 1.00 for Benzene, and
- not significantly different from 1.00 for the remaining 16 compounds studied.

The mean of the 1-hour/24-hour daily average ratios is statistically:

- significantly less than 1.00 for no compounds,
- significantly greater than 1.00 for n-Hexane, Benzene, 2-Methylhexane, Ethane, Cyclopentane, and n-Pentane, and
- not significantly different from 1.00 for the remaining 14 compounds studied.

#### 4.3 Factor-Specific Data Summary and Analysis

For the overall comparisons of Section 4.2, enough data were available to compute simple confidence intervals by duration and compound, which provided the overall analysis results that concluded the section. To conduct analyses specific to the factors of concern [EPA Region, year,

PAMS site type, and AIRS analytical method], various subsets of the data were used, depending on the factor, to ensure that enough data were present for valid comparisons. Given that fewer total observations were available for factor-specific analyses, and the fact that the data are essentially stratified by factor levels (e.g., year = 1996, 1997, or 1998) when conducting such analyses, we turned to a model-based statistical approach to determine the possible effect of each factor. In other words, not enough data exist to calculate confidence intervals specific to each (sample duration  $\times$  compound  $\times$  factor combination) and, therefore, a model-based approach was necessary to pool the data for comparison. Section 4.3.1 describes how the data were subsetted and provides summary boxplots for the data used in the factor-specific analyses. Section 4.3.2 describes the modeling approach and provides results.

#### 4.3.1 Summary of Data Used in Factor-Specific Analyses

When considering EPA Region, we retained for analysis only those compounds that had at least 10 observations of both [1-hour, 24-hour] and [3-hour, 24-hour] co-located data spanning two or more regions. Furthermore, one of these regions, itself, had to possess at least 10 observations of both [1-hour, 24-hour] and [3-hour, 24-hour] co-located data. The compounds that met these criteria were *n*-Hexane, Benzene, Toluene, Propane, Propylene, Acetylene, and Isopentane. Figures 4-3 through 4-9 visually present the data for each compound as side-by-side boxplots of the ratios of 1-hour or 3-hour daily average to 24-hour concentration, by EPA Region.

When considering year, we retained for analysis only those compounds with at least two years with at least 10 observations of both [1-hour, 24-hour] and [3-hour, 24-hour] co-located data, and where at least two of the years fitting this criterion provided both [1-hour, 24-hour] and [3-hour, 24-hour] co-located data. For instance, if a compound had at least 10 observations of [1-hour, 24-hour] co-located data in 1996 and 1997, and the same for 1997 and 1998 with respect to [3-hour, 24-hour] co-located data, it would not meet the criteria because it does not have at least two of the years present for both 1-hour and 3-hour data (i.e., only 1997 provides data in both cases). The set of compounds with sufficient data include *n*-Hexane, Benzene, Toluene, Ethane,

Propane, Acetylene, and Isopentane. Figures 4-10 through 4-16 visually present the data for each compound as side-by-side boxplots of the ratios of 1-hour or 3-hour daily average to 24-hour concentration, by year.

The [1-hour, 24-hour] co-located data showed very little variability in terms of PAMS site type, in that only PAMS #2 sites ever had more than 10 observations. Therefore, for site type only the [3-hour, 24-hour] co-located data were considered, and a compound was included for analysis when it had at least two site types with at least 10 observations present in each. Fourteen compounds met this criterion: *n*-Hexane, Benzene, Toluene, *m/p*-Xylene, *o*-Xylene, 1,2,4-Trimethylbenzene, *n*-Decane, Ethane, Ethylene, Propane, Propylene, Acetylene, 1-Butene, and Isopentane. Results are displayed as side-by-side boxplots of the ratio of the 3-hour daily average to 24-hour concentration, by PAMS site type and compound, with compounds in the Benzene group displayed in Figure 4-17 and those from the Propane group in Figure 4-18.

The [1-hour, 24-hour] co-located data showed very little variability with regard to AIRS analytical method, with the vast majority of observations represented by AIRS method 128 — the only method that ever had more than 10 observations. Therefore, similar to the approach for PAMS site type, only the [3-hour, 24-hour] co-located data were considered and only compounds with at least two methods having at least 10 observations were included for analysis. This left the following nine compounds: *n*-Hexane, Benzene, Toluene, *o*-Xylene, Ethane, Propane, Propylene, Acetylene, and Isopentane. Results are displayed as side-by-side boxplots of the ratio of the 3-hour daily average to 24-hour concentration, by AIRS analytical 3-hour method and compound, with Benzene compounds displayed in Figure 4-19 and Propane compounds in Figure 4-20. For further clarity, Table 4-5 indicates the AIRS description provided along with each numerical method code.

Table 4-5. AIRS analytical 3-hour method codes and their associated descriptions.

AIRS Method Code	Method Description
101	Canister Multi Detector GC
120	Sorbant Gas Chromatograph with Flame; GC FID
122	6L Dual FID - PAMS
123	6L Dual FID - PAMS
126	SS Cryogenic Preconcentration GC/FID
136	Instrumental Entech 2000 with MS/FID
146	6L PE8700; Auto GC; Subambient, Dual FID
149	6L Entech Precon - SP GC/FTIR/MSD

#### 4.3.2 Results from Factor-Specific Analyses

The statistical analysis approach is based on a general linear model that simultaneously considers the effect on mean ratios of sample duration (i.e., 1-hour or 3-hour interval), compound, and the factor of concern, as well as the interaction of each of these effects (i.e., a complete three-way analysis of variance (ANOVA) model). Each factor-specific model assumes that data variability differs by sample duration (1-hour or 3-hour), but uses a pooled variance estimate across the compounds. Visual assessment of the boxplots in Figures 4-1 through 4-20 suggests that ratio variability probably differs by both sample duration and compound; however, some pooling of the data was necessary in order to draw meaningful conclusions. Separate variances by sample duration were not necessary for modeling the effect of PAMS site type and analytical method since only 3-hour/24-hour ratio data are used in those assessments.

An initial examination of the statistical model assumptions revealed that the log-transformed ratios of daily concentrations based on 1-hour or 3-hour data relative to 24-hour samples are suitable to be modeled using the three-way ANOVA model described above. Therefore, the analysis was performed on the log-transformed ratio data using the Proc Mixed procedure in the SAS<sup>®</sup> System software package. All references to statistical significance are at the 0.01 level unless otherwise specified. The interpretation is that any effect or difference identified as statistically significant can be considered so with 99 percent confidence. Because such a large number of comparisons are being made, the 0.01 level was chosen over the other common significance level of 0.05 in order to reduce the chance of incorrectly claiming statistical significance.

To determine whether there are significant differences in ratios between EPA Regions, if the overall effect of EPA Region was found to be statistically significant, then pairwise comparisons of regions (i.e., differences in mean ratios by EPA Region) were made. The same approach was used to determine whether there are significant differences between years. The analysis approach was somewhat simplified for PAMS site type and analytic method because the model in these cases did not include the sample duration, as no 1-hour data were involved in the analysis. Thus, in these two cases, the analyses were simplified to a complete two-way analysis of variance (ANOVA) model, which considers the effect of PAMS site types (analytic methods), and the interaction of compound and PAMS site type (analytic method). Pairwise comparisons of PAMS site type effects (analytic method effects) were performed if the overall effect of PAMS site types (analytic methods) was found to be significant.

For each factor (EPA Region, year, PAMS site type, or analytic method), the statistical analysis model described above was applied to the corresponding subset of data described in Section 4.3.1. Significant differences were observed for all the factors except analytical method. Therefore, pairwise comparisons were performed within each corresponding fitted model for the effects of EPA Region, year, and PAMS site type, but not for analytical method. The statistically significant pairwise comparison results are reported in Table 4-6, according to factor.

For a particular factor, the second to last column in Table 4-6 estimates the percent difference between the effects of two different levels of a factor, averaged across the impacts of sample duration and compound. These estimates were obtained by exponentiating the modeled differences between the means for the two given factor levels. For example, the mean of the ratios of concentrations in EPA Region 1 is 21 percent higher than the mean for those in EPA Region 6. Looking back at Figures 4-3 through 4-9, this result is mostly due to the fact that EPA Region 1 ratios for n-Hexane, Toluene, and Propylene tended to be above 1.00 while EPA Region 6 ratios for Benzene, Propane, Propylene, Acetylene, and Isopentane tended to be near 1.00. As another example, the second column of Table 4-5 indicates the mean of the ratios of concentrations in 1996 is only 78 percent of that for 1997. Similarly, 1997 ratios are, on average, 15 percent higher than 1998 ratios.

Table 4-6. Summary of the statistically significant effects of EPA Region, year, PAMS site type, and analytical method on ratios of daily averages

Factor	Comparison	Ratio Between Two Compared Levels	P-value <sup>1</sup>
Region	Overall Factor Significance	NA	<0.0001
	1 vs. 6	1.21	0.0018
	1 vs. 9	1.69	<0.0001
	3 vs. 9	1.45	<0.0001
	5 vs. 6	1.23	0.0005
	5 vs. 9	1.72	<0.0001
	6 vs. 9	1.40	<0.0001
Year	Overall Factor Significance	NA	0.0002
	1996 vs. 1997	0.78	<0.0001
	1997 vs. 1998	1.15	0.003
Site Type	Overall Factor Significance	NA	0.009
	# 2 vs. # 3	0.92	0.008
Analytical Method	Overall Factor Significance	NA	0.013

<sup>1</sup> P-values indicate the statistical strength of a factor's effect (or the difference in effects between a factor's levels), with smaller p-values implying a more significant effect. Any effect with a p-value < 0.01 is deemed statistically significant.

The following general observations can be made about the daily averages calculated from 1-hour samples or 3-hour samples, relative to the 24-hour samples (from Table 4-6):

- EPA Region 9 ratios, on average, are significantly lower than ratios in any other EPA Region studied (1, 3, 5, and 6), while EPA Region 1 and 5 ratios are, on average, significantly higher than EPA Region 6 ratios;

- 1997 ratios, on average, are significantly higher than both 1996 and 1998 ratios, however, 1996 and 1998 ratios do not differ significantly (note that the higher 1997 ratios are typically the 1-hour/24-hour ratios, and this is consistent with the finding from the State retention time data that recoveries tended to be higher in 1997 relative to 1996 and 1998.);
- PAMS #2 site ratios, on average, are statistically significantly lower than PAMS #3 site ratios;
- ratios do not differ significantly by analytical method; and
- 1-hour/24-hour ratios are approximately twice as variable as 3-hour/24-hour ratios (see Figures 4-1 and 4-2).

As a final note, it is important to remember that statistical significance does not always imply practical significance. A careful comparison of the modeling results of this section with the graphical display of results in Figures 4-3 through 4-20 will provide a more thorough and accurate understanding of the effects of the factors studied. For example, the result that, overall, EPA Region 9 ratios tend to be significantly less than those from other EPA Regions is based on just 23 total EPA Region 9 data points spanning only n-Hexane and Propylene, none of which are 1-hour/24-hour ratios. In summary, any results highlighted in this section should be tempered by a visual assessment of Figures 4-3 through 4-20.

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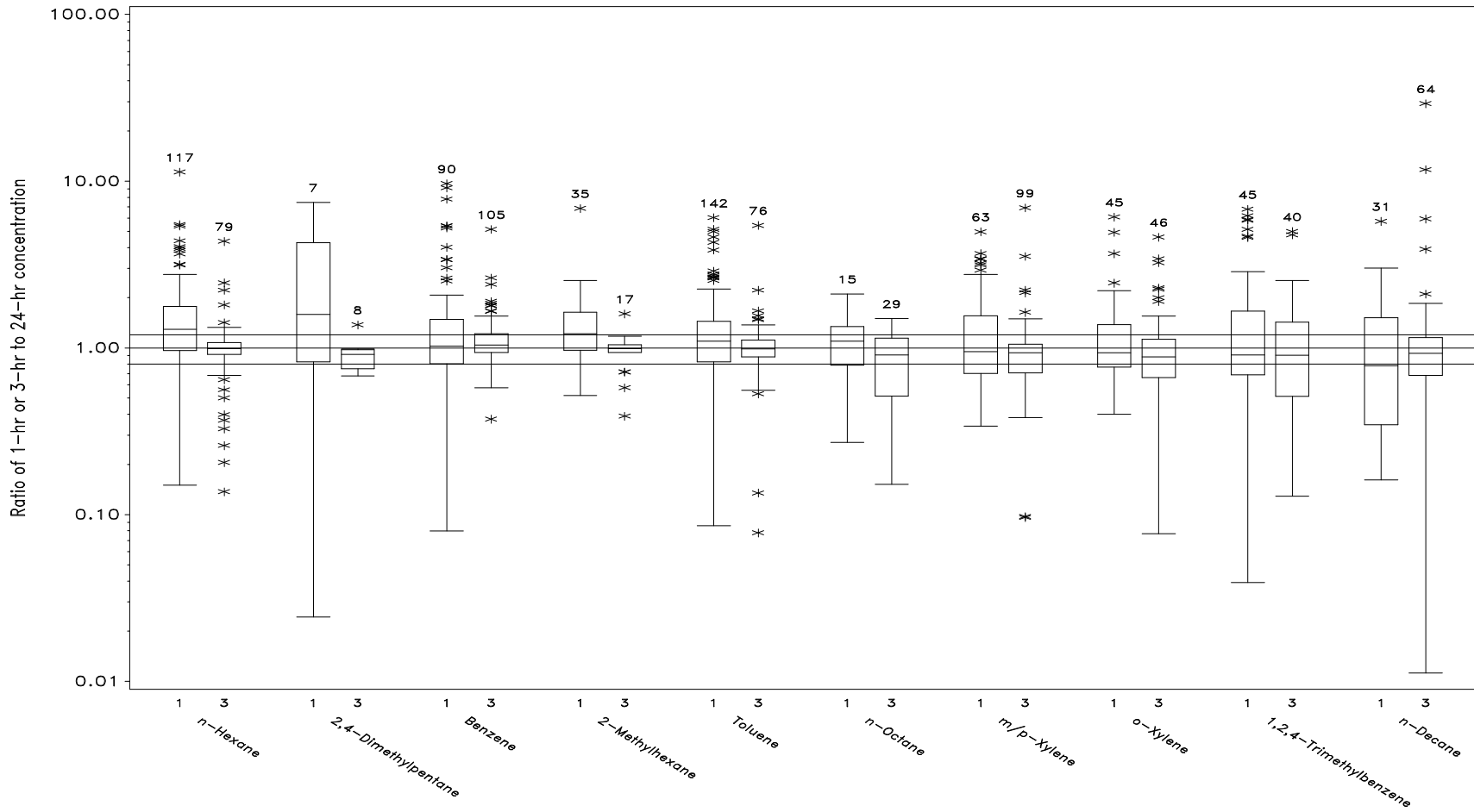


Figure 4-1. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for compounds in the Benzene group.

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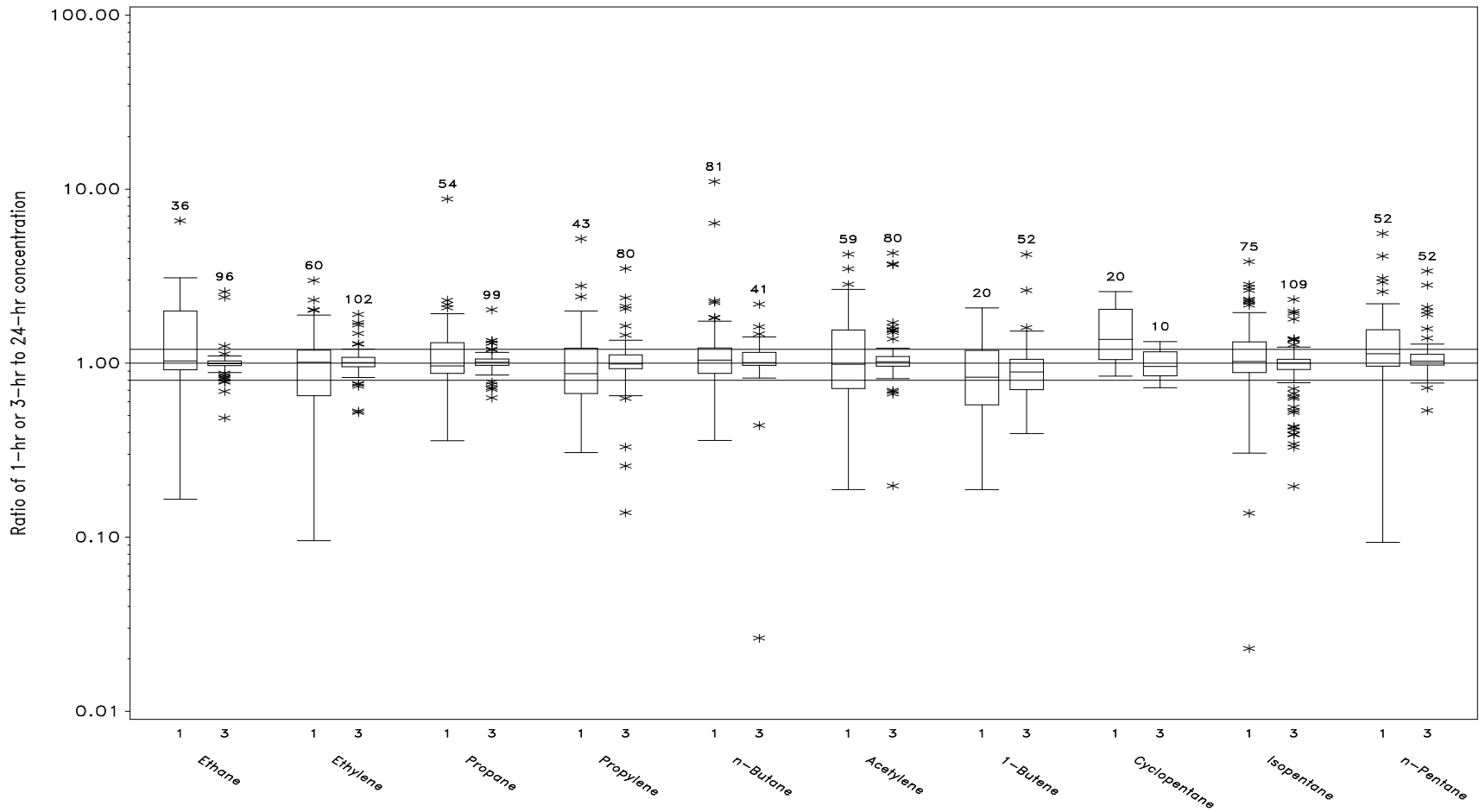


Figure 4-2. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for compounds in the Propane group.

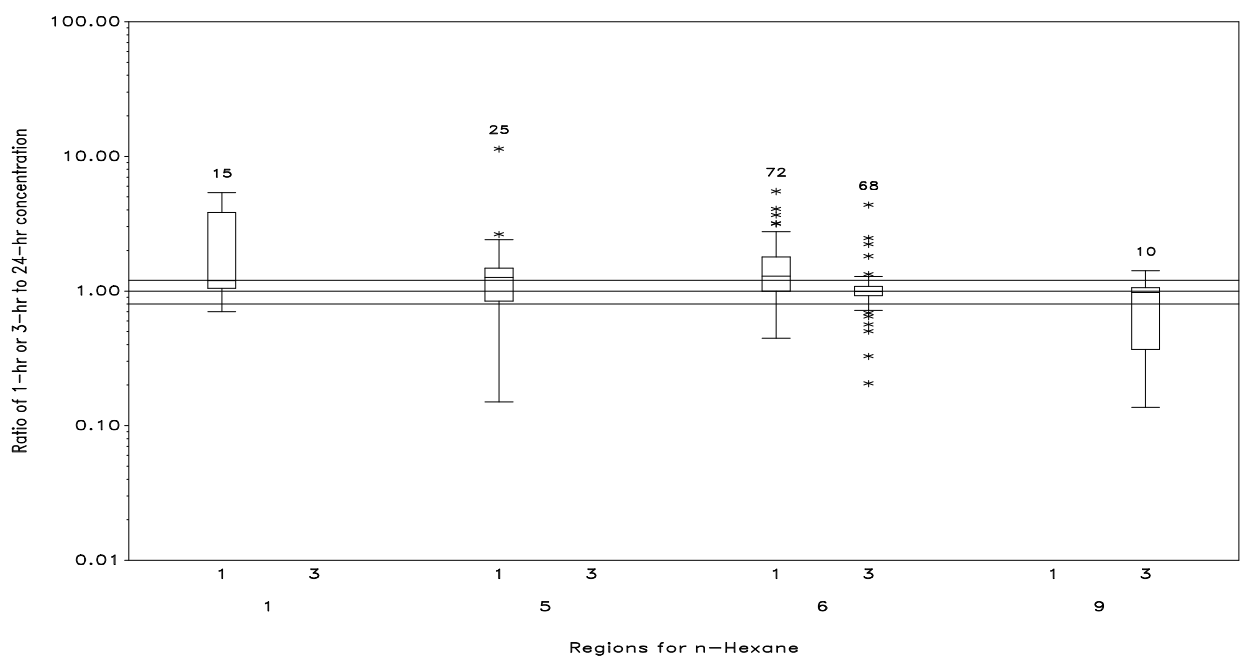


Figure 4-3. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for n-Hexane by EPA Region.

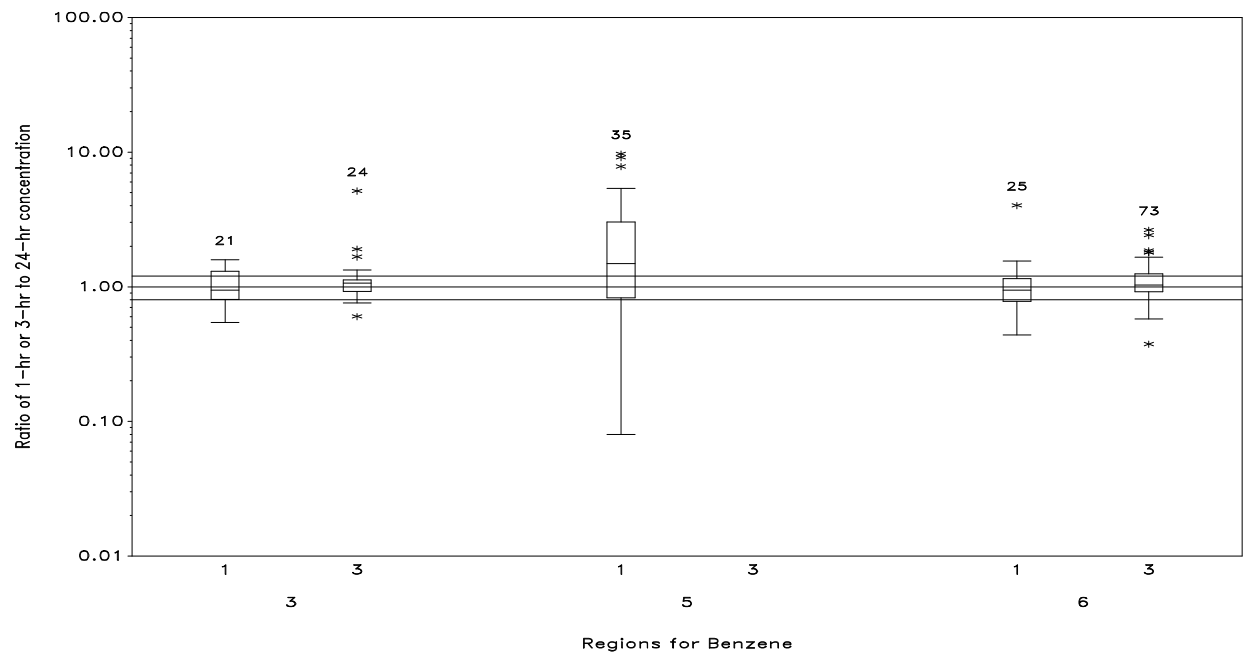


Figure 4-4. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Benzene by EPA Region.

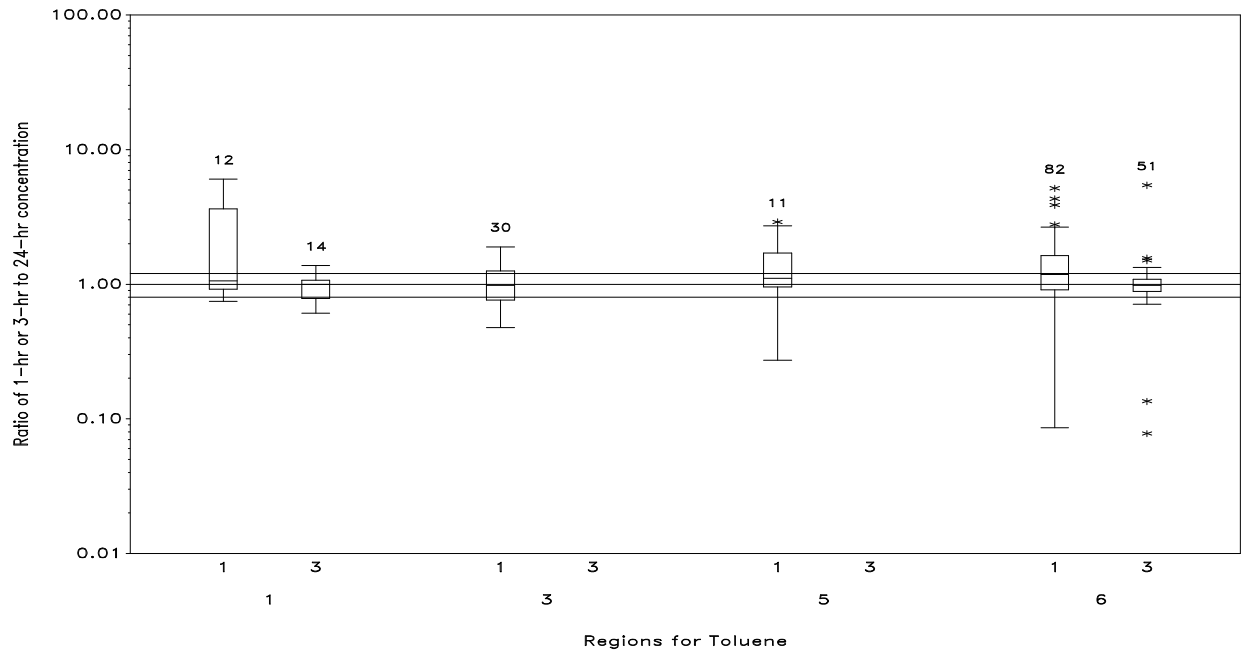


Figure 4-5. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Toluene by EPA Region.

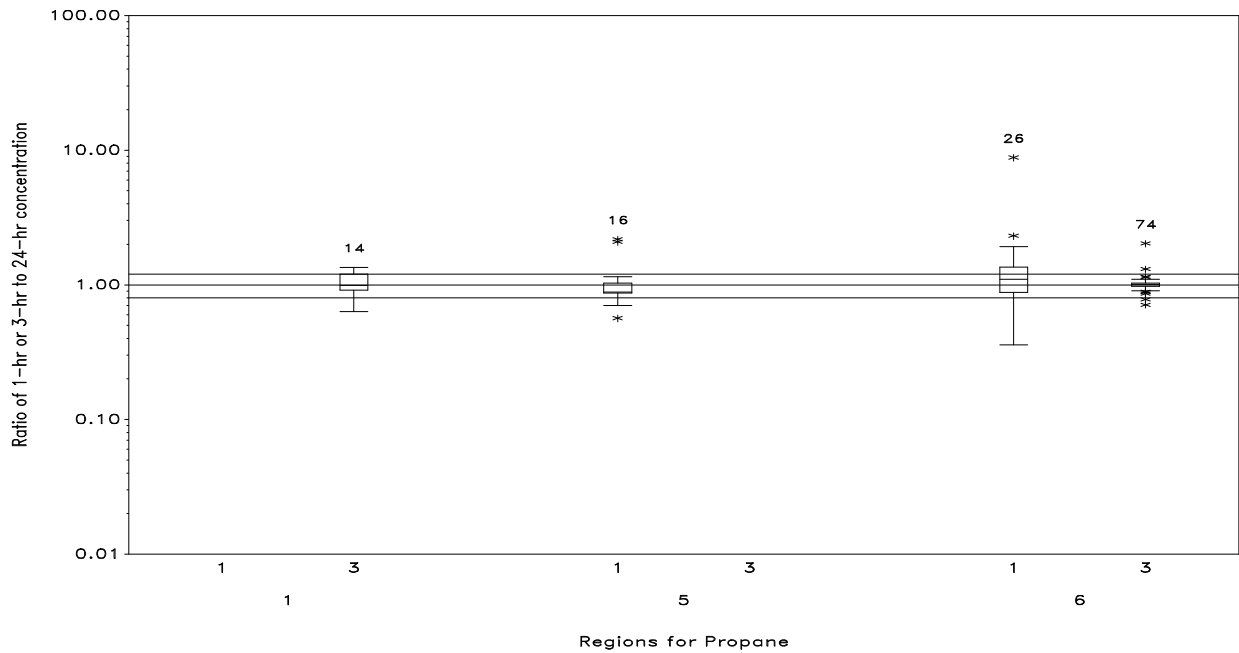


Figure 4-6. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Propane by EPA Region.

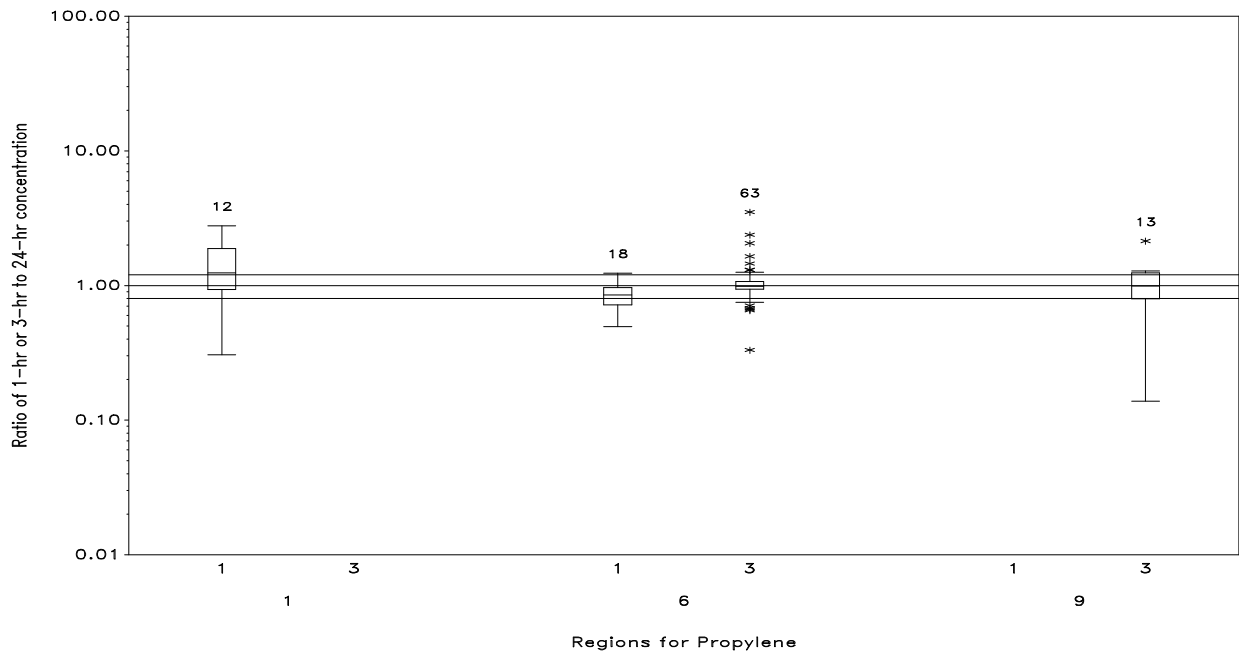


Figure 4-7. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Propylene by EPA Region.

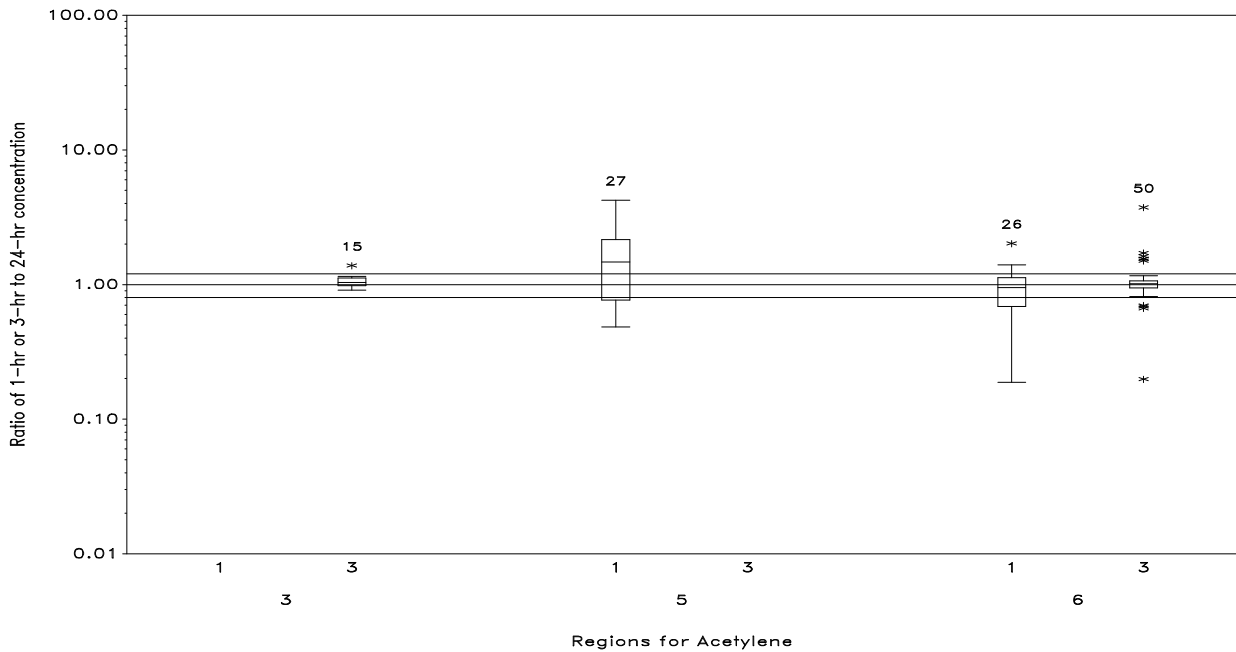


Figure 4-8. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Acetylene by EPA Region.

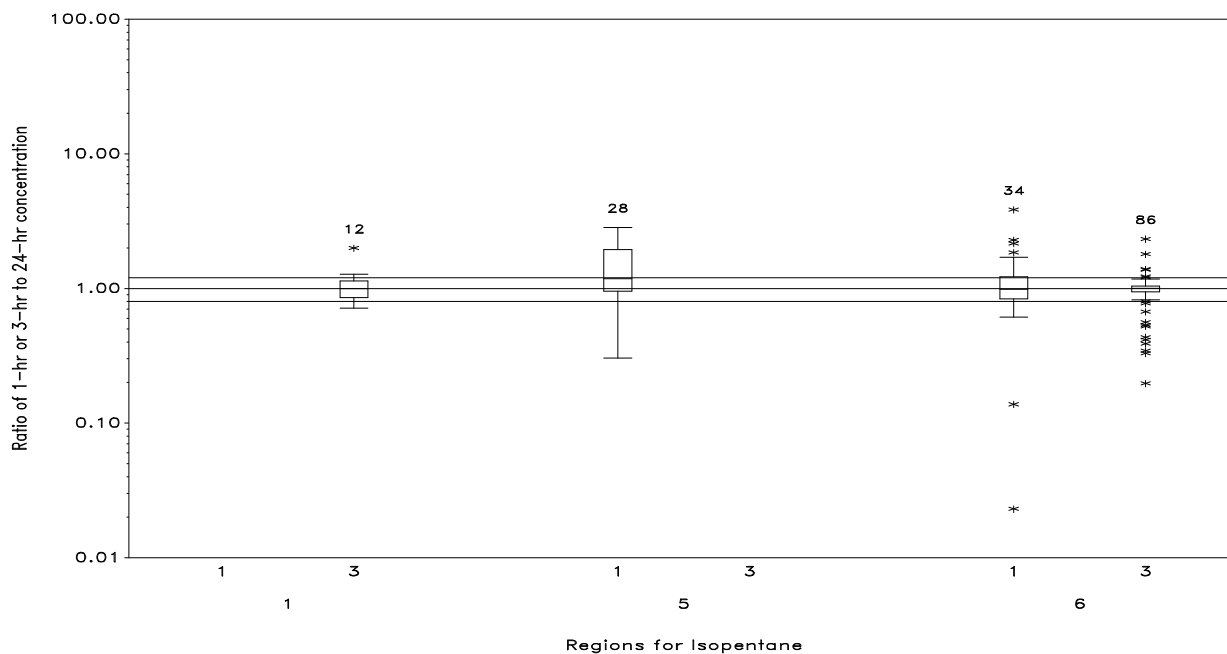


Figure 4-9. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Isopentane by EPA Region.

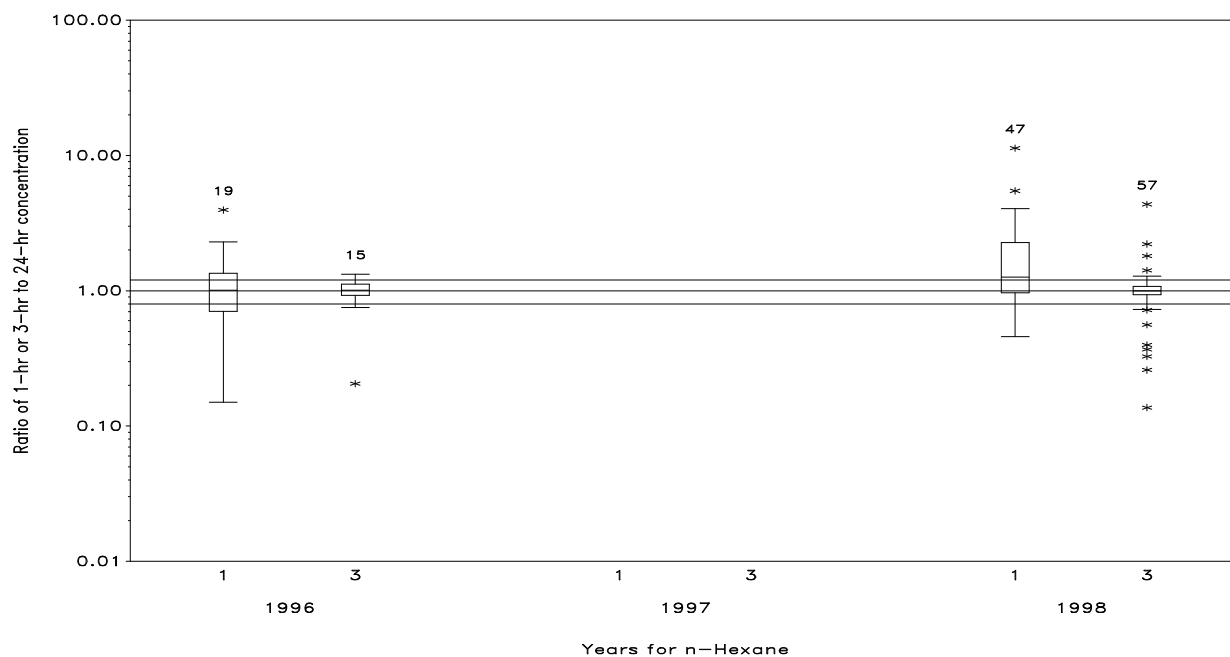


Figure 4-10. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for n-Hexane by year.

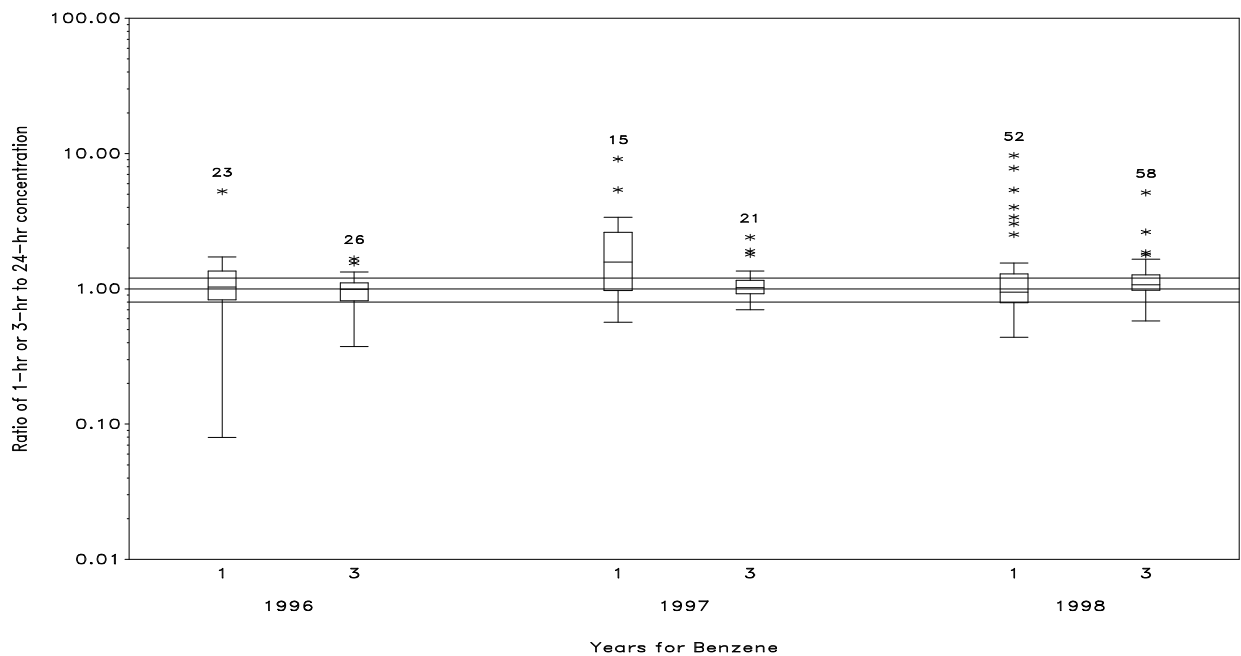


Figure 4-11. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Benzene by year.

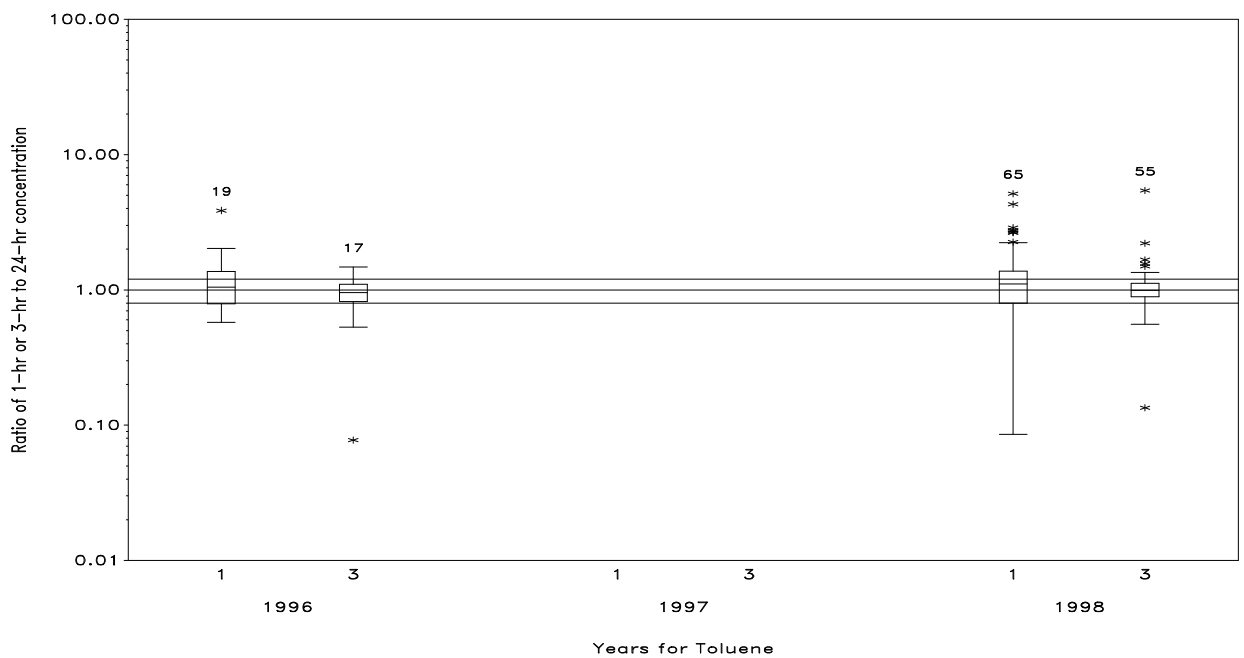


Figure 4-12. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Toluene by year.

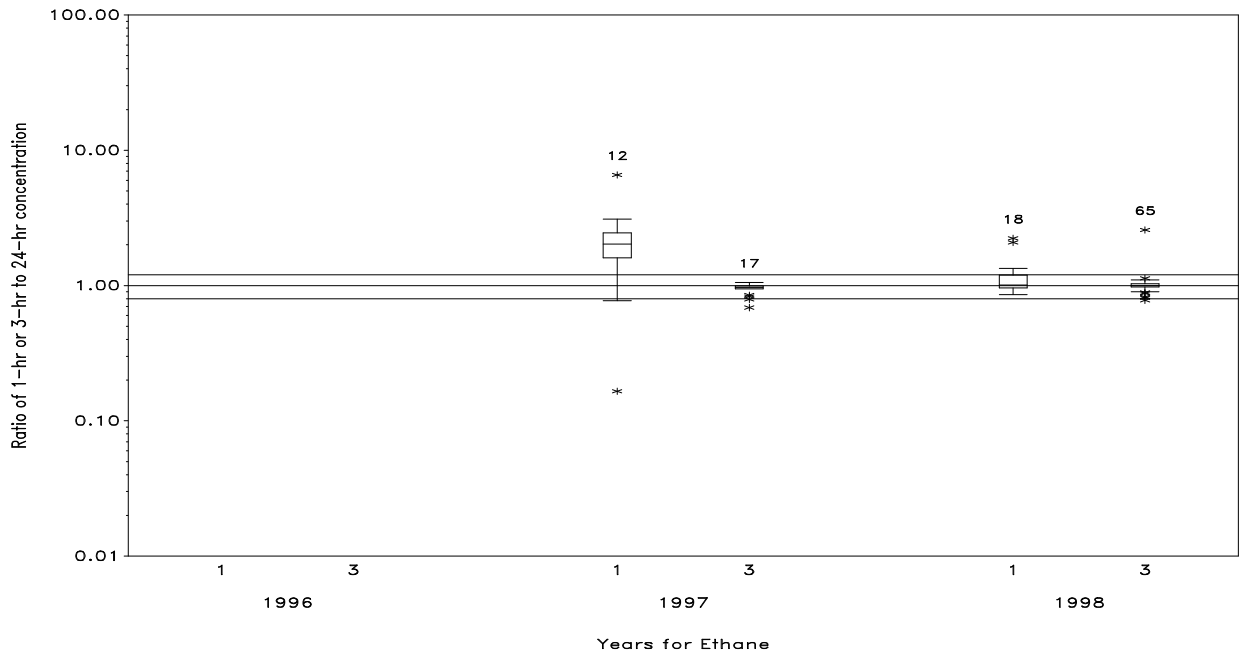


Figure 4-13. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Ethane by year.

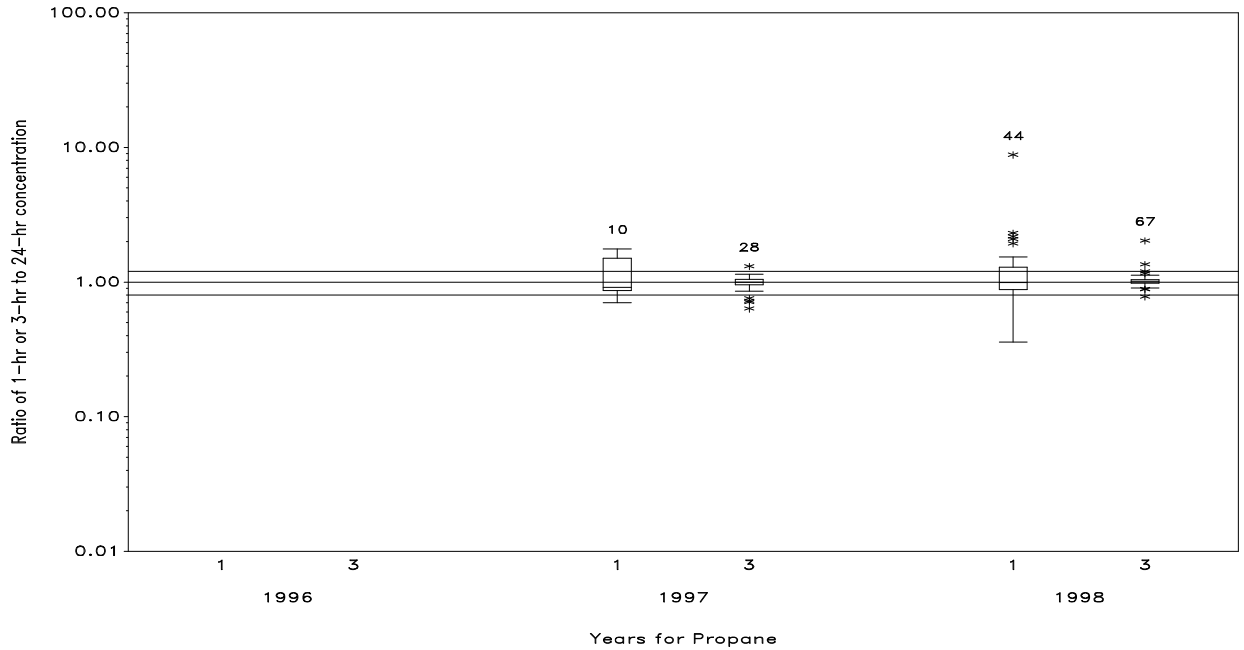


Figure 4-14. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Propane by year.

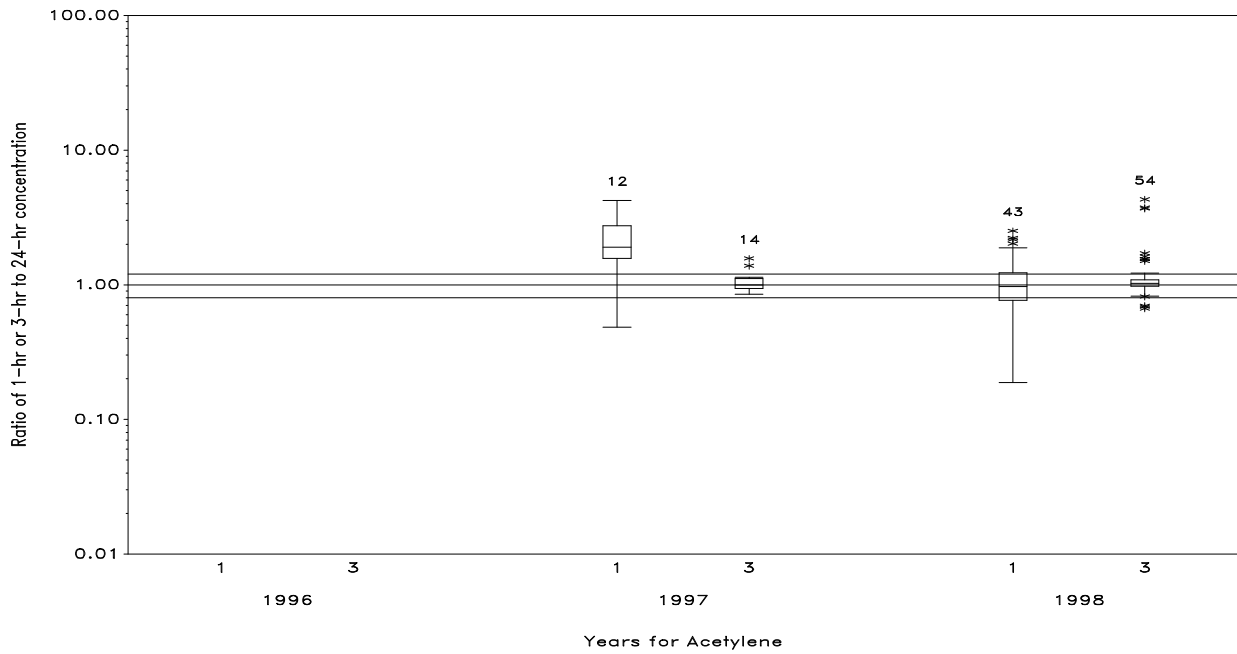


Figure 4-15. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Acetylene by year.

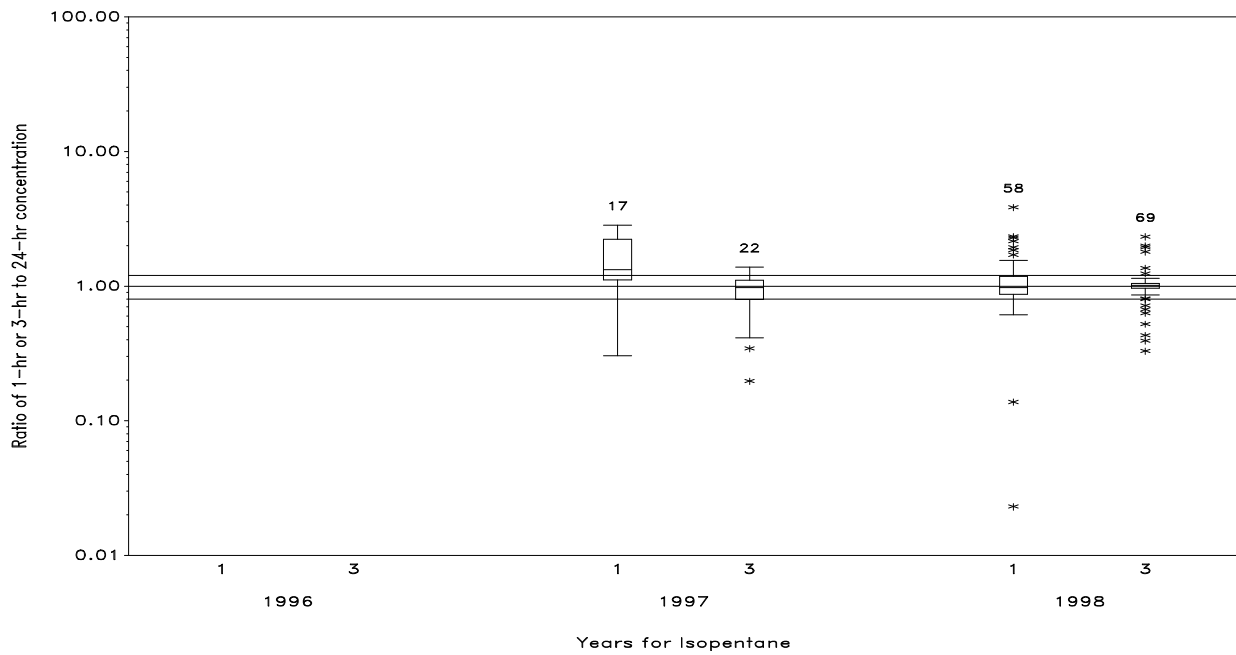


Figure 4-16. Summary boxplots for the ratio of the daily average calculated from 1-hour or 3-hour data relative to 24-hour data, for Isopentane by year.

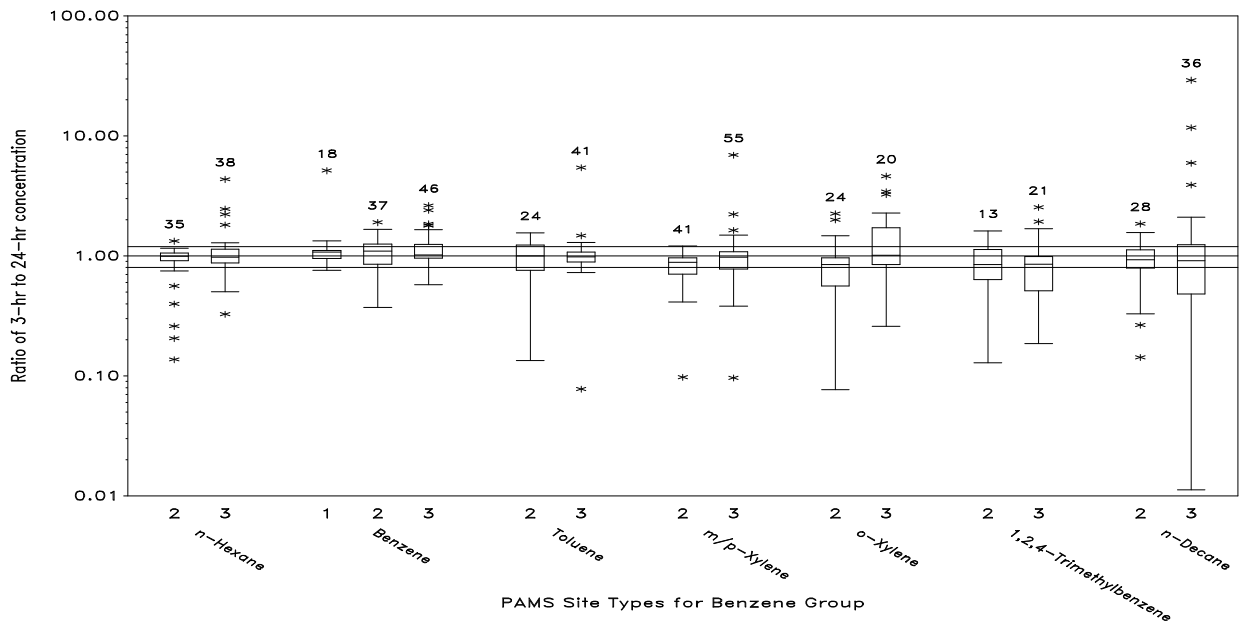


Figure 4-17. Summary boxplots for the ratio of the daily average calculated from 3-hour data relative to 24-hour data, by Benzene group compound and PAMS site type.

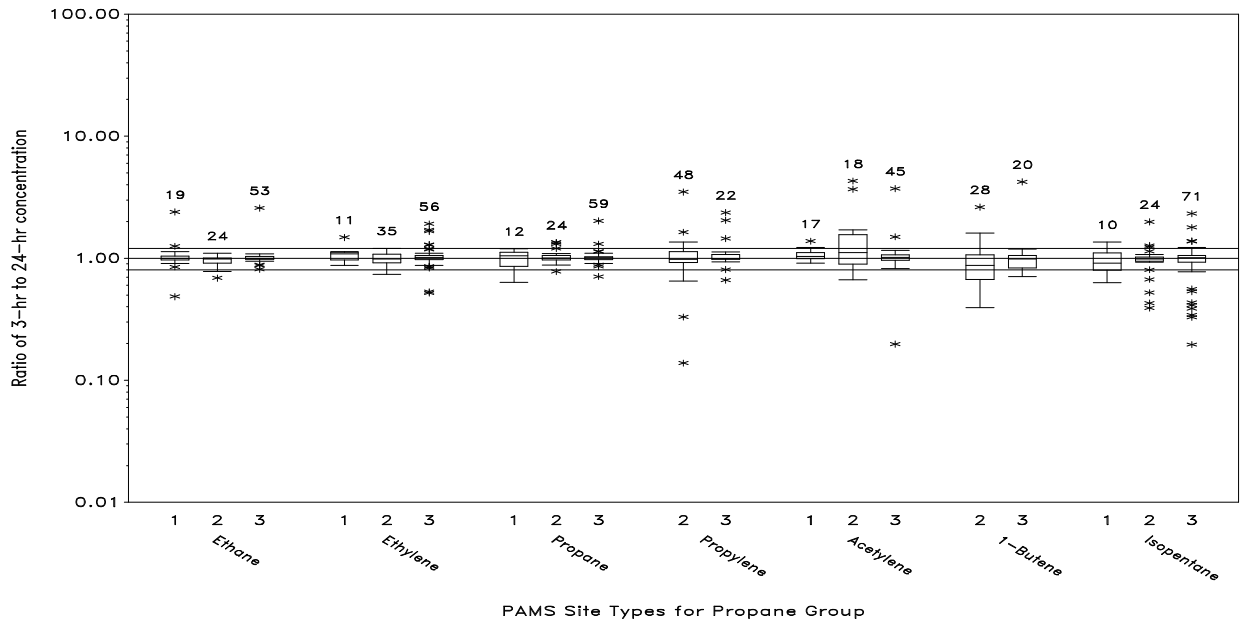


Figure 4-18. Summary boxplots for the ratio of the daily average calculated from 3-hour data relative to 24-hour data, by Propane group compound and PAMS site type.

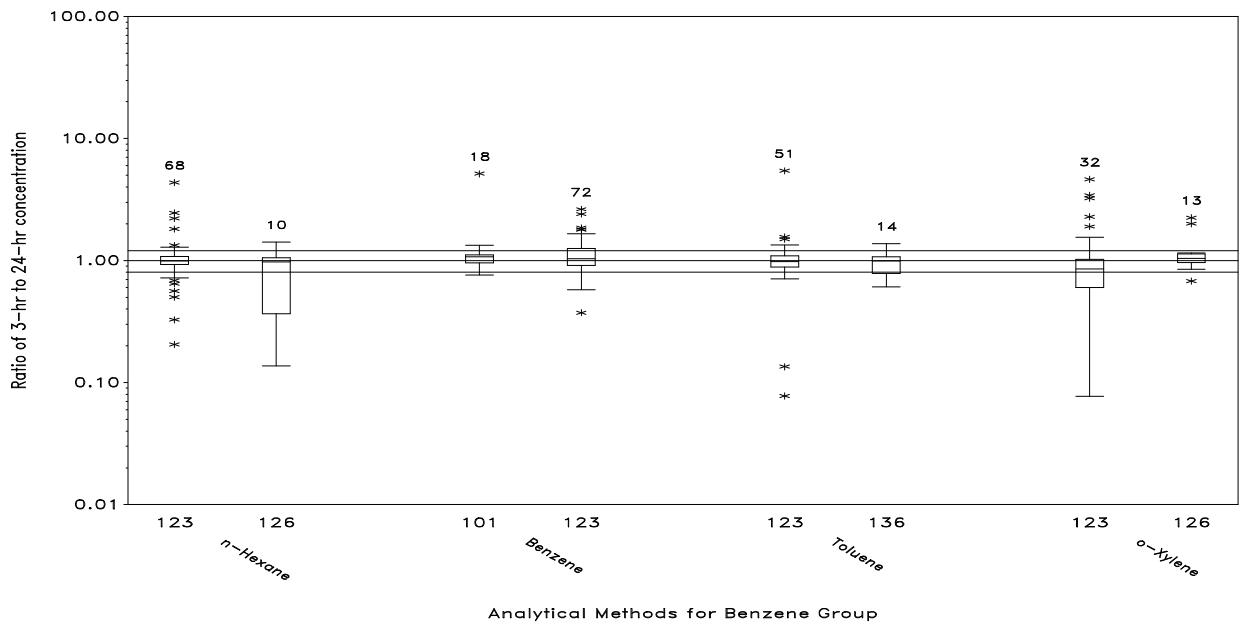


Figure 4-19. Summary boxplots for the ratio of the daily average calculated from 3-hour data relative to 24-hour data, by Benzene group compound and 3-hour AIRS method.

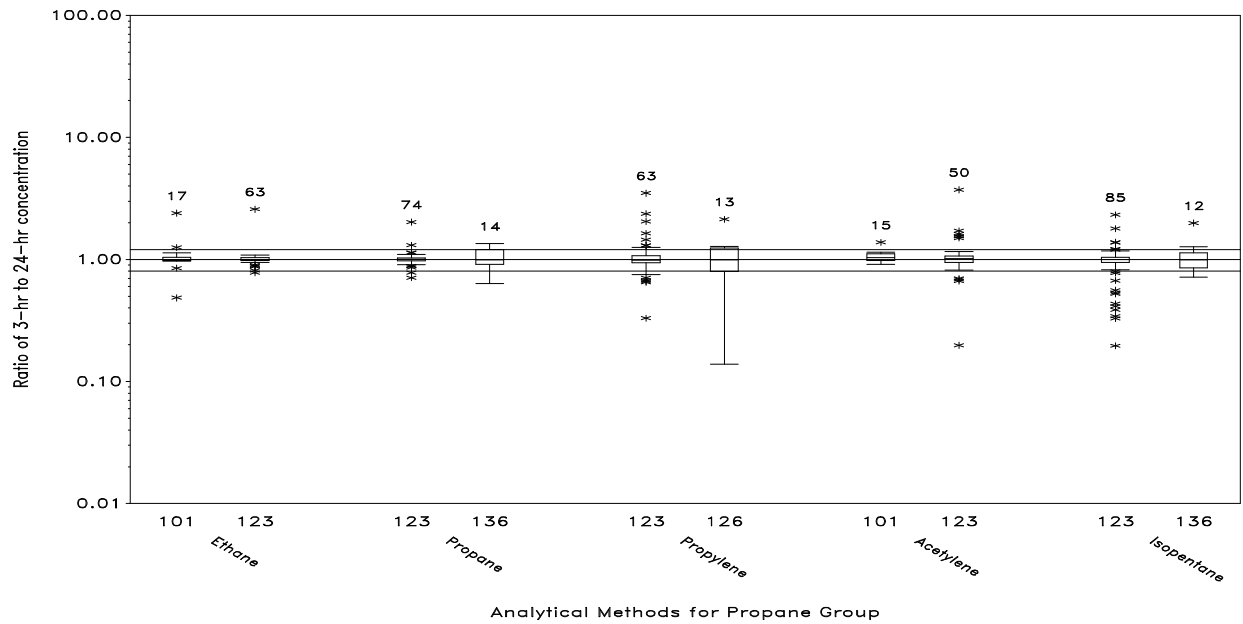


Figure 4-20. Summary boxplots for the ratio of the daily average calculated from 3-hour data relative to 24-hour data, by Propane group compound and 3-hour AIRS method.



## 5.0 RESULTS: NPAP DATA

### 5.1 Data Availability

The National Performance Audit Program, NPAP, is an auditing program for the PAMS sites. Cylinders with a mixture of PAMS target compounds are distributed to participating sites approximately three times per season. The site then analyzes the mixture and reports their findings back to EPA. The data given to Battelle included the reported concentration and a standard concentration<sup>1</sup> for any of the 20 compounds<sup>2</sup> used in this study, in addition to several META variables for the years 1996, 1997, and 1998. In addition to the concentrations, the data included a date, whether or not a Nafion dryer was used, and whether or not a humidifier was used. The site and reporting organization were indicated by random values, where each site and reporting organization could be assigned several random values within a year. Hence, there could be no comparisons between, nor data summaries for, sites or reporting organizations. The data summaries given in Tables 5-1 through 5-9 are for the nation as a whole. They are broken down by compound, year, and elution group. For comparison with the state retention time data, Acetylene and *m/p*-Xylene are excluded from the elution groups. (See Table 3-2 for the groupings.) The data summaries by compound indicate that excluding these data would not have been necessary for analyses restricted to this data set.

The NPAP program typically restricts the analysis to data that are at least 5 ppbC. (The same cutoff is applied to all compounds.) However, approximately 9 percent of the data have a

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<sup>1</sup> For different years the method for generating the target concentration has changed. Sometimes it has been the value based on the amount of dilution and sometimes it has been based on the value obtained by EPA lab analysis of the mixture after dilution. This may account for the year to year effect noted in our analysis of the data.

<sup>2</sup> There are no data for *n*-Decane, so the analyses are based on the remaining 19 compounds.

standard concentration that is less than 5 ppbC and a reported value greater than the MDL. Except as noted below, all of these data were included in the summaries and analyses.

## 5.2 Data Summary

The data summaries by compound follow the format for the state retention time data. The compounds are listed in their elution order within their analytical column group, Propane or Benzene. Tables 5-1 through 5-8 show the number of samples with non-missing target concentrations and reported concentrations above the MDL. (No MDLs were reported so all data reported as “below the MDL” were treated as missing data. This is unlikely to bias the data significantly since the audit samples were usually spiked with concentrations well above these values.) Mean recoveries with 95 percent confidence intervals and the coefficients of variation with 90 percent confidence intervals are also shown. The summaries shown in Tables 5-1 through 5-8 and the analyses in Section 5.3 are for data with a strictly positive standard concentration (i.e., non-missing), strictly positive reported concentration (i.e., non-missing and above the MDL), and with a recovery, calculated as the reported concentration divided by the standard concentration, that was less than 10. This latter restriction excluded three data points, two for 1998 that were above 150 and one for 1997 that was approximately 20. Tables 5-1 through 5-6 break down the data by year for the years 1996-1998. The last two tables, Tables 5-7 and 5-8, show the combined results for all three years.

Note that while the recoveries for Acetylene are low and the CV is high compared to the other compounds, the performance is not as poor as the retention time standards indicate (i.e., see Figure 3-4). The same is also true for *m/p*-Xylene. The poor overall performance of *n*-Hexane is due to the extremely variable results in 1998. Specifically, in 1996 and 1997 the upper bound for the 90 percent confidence interval on the CV for *n*-Hexane is about 25 percent, while for 1998 the lower bound is above 150 percent. The confidence interval for the mean for 1998 was truncated at zero.

### 5.3 Data Analysis

The statistical analyses of the NPAP data are accompanied by a series of plots, mainly notched boxplots. These boxplots have notches around the middle 50 percent of the data within the given category, with a line at the median and “plus” indicating the mean. The notch is an approximate 95 percent confidence interval for the median. A pair of boxes with non-overlapping notches can be taken to indicate significantly different medians for the two different groups. The whiskers for these boxes extend outward from the quartiles to either 1.5 times the interquartile range, IQR, if there are data outside that range, or to the furthest data value from the median within 1.5 times the IQR from the quartile. Any data values outside the whiskers are plotted with an asterisk. Isolated points far outside the whiskers are often treated as outliers. Most of the cases in the figures are not isolated and, thus, should not be considered outliers. Rather, they show that extreme values occur with some regularity in these data. As noted above, there were three data points that were excluded from these analyses; each appeared to be far from a typical response.

The plots and the summaries by year and elution group, or whether or not a Nafion dryer was used, show interesting behavior and depict the results found through statistical modeling. The results should be interpreted by first considering what was found to be statistically significant, and then examining the plots to see whether the statistically significant results are of practical significance.

The data were fit with a heterogeneous ANOVA model using the SAS<sup>®</sup> Proc Mixed procedure with fixed effects for separate mean recoveries for each elution group for each year, and whether or not a Nafion dryer was used. The residuals were modeled with distinct variances for each combination of year and elution group. This model was tested against simpler models. The likelihood ratio test comparing the 11 different variances versus three distinct variances (one for each year) was highly significant ( $p\text{-value} < 0.0001$ ). Visually, the need for distinct variances is clear from looking at the boxplots of each elution group by year (Figures 5-13

through 5-16) and the plot of the estimated CVs for each elution group by year (Figure 5-18). The different groups and years have quite different errors. With the appropriate variance structure chosen, the fixed effects were estimated and tested, indicating the following:

- The test of the significance of the Nafion dryer shows its use significantly lowers the recovery (the effect is mainly observed in the 1996 data). See Figures 5-9 through 5-12. Perhaps just as important as a relative bias, there is no significant change in variability between data generated with the use of a Nafion dryer and those generated without one. It is possible that the main effect of its use is dependent on site conditions. It was not possible to evaluate whether this was the case, due to the confidential nature of the data. Also note that there is some confounding due to the fact that there were fewer compounds included in the 1996 data (see Tables 5-1 through 5-6).
- The test for the additive effect of humidifying was not statistically significant ( $p$ -value  $> 0.8$ ). It is possible that the main effect is highly dependent on site conditions. It was not possible to evaluate whether this was the case.
- There are statistically significant differences among the various combinations of year and elution group. The late Benzene group had a lower response in 1997, but overall the issue is clouded because the responses were so much more variable in 1998. See Figures 5-13 through 5-18 and Table 5-9, which summarize the recovery means and CVs by year and elution group.

Compare the NPAP elution group recovery boxplots, Figures 5-9 through 5-16, with the State retention time boxplots, Figures 3-7 through 3-10. Compare the scatter plots of the mean recovery and CV for each elution group, Figures 5-17 and 5-18, with the corresponding plots of the State retention time data, Figures 3-5 and 3-6.

The results from the analysis of the NPAP data show several significant trends for the nation as a whole. First, for the later eluting compounds, the results in 1998 were much more

variable. This goes against the trend seen with the State retention time data, where the CVs show improvement in the measurement precision from year to year. Second, there are also statistically significant differences in the mean recoveries for the various elution groups within and across years. However, 1996 NPAP had no late eluting Benzene data and there were no *n*-Decane data at all, so the results are not entirely comparable with the results from the State data. It should also be pointed out that the State retention time data indicates that there are significant differences from site to site, so the general trends seen for the nation as a whole may not apply to many individual sites.

Table 5-1. Summary statistics for the NPAP recoveries for the Benzene analytical group in 1996

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
n-Hexane	15	13.0	14.8	99.0%	(90.8, 107.3)	15.0%	(10.1,25.8)
2,4-Dimethylpentane	16	17.9	18.0	99.3%	(91.2, 107.4)	15.4%	(10.5,25.9)
Benzene	0	.	.	.	.	.	.
2-Methylhexane	20	10.0	12.0	101.5%	(95.8, 107.1)	11.8%	(8.5,18.3)
Toluene	0	0.2	.	.	.	.	.
n-Octane	34	10.1	11.0	96.3%	(86.4, 106.1)	29.4%	(21.5,43.1)
m/p-Xylene	15	12.6	19.6	89.1%	(79.2, 99.0)	20.0%	(13.2,35.5)
o-Xylene	0	0.9	.	.	.	.	.
1,2,4-Trimethylbenzene	0	0.5	.	.	.	.	.
n-Decane	0	35.2	.	.	.	.	.

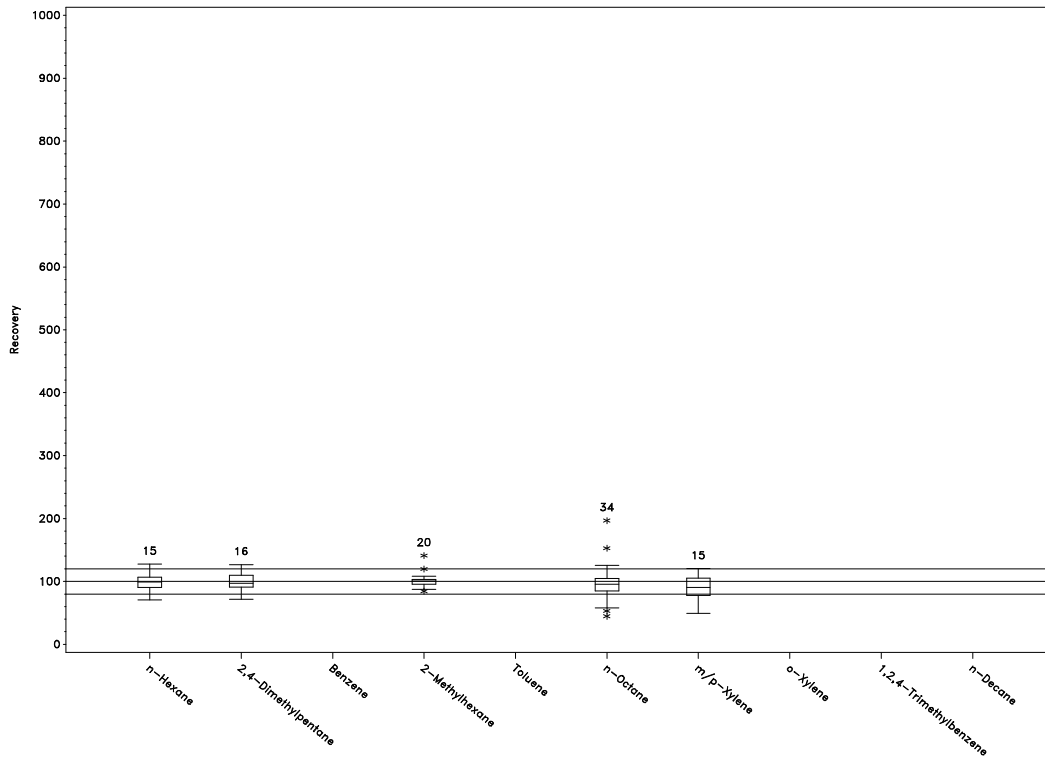


Figure 5-1. Boxplots of the NPAP recoveries for the Benzene analytical group in 1996.

Table 5-2. Summary statistics for the NPAP recoveries for the Propane analytical group for 1996

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
Ethane	34	8.4	7.9	106.2%	(101.0, 111.5)	14.1%	(10.9,19.6)
Ethylene	34	9.4	9.3	99.3%	(93.0, 105.7)	18.3%	(13.9,25.7)
Propane	36	9.4	9.0	104.4%	(97.9, 110.8)	18.2%	(13.9,25.3)
Propylene	20	12.7	12.2	104.0%	(99.2, 108.9)	10.0%	(7.3,15.3)
n-Butane	20	11.0	10.1	108.4%	(104.1, 112.6)	8.3%	(6.1,12.7)
Acetylene	0	.	.	.	.	.	.
1-Butene	16	8.3	9.7	96.1%	(78.4, 113.9)	34.6%	(21.6,65.6)
Cyclopentane	0	12.7	.	.	.	.	.
Isopentane	20	12.7	12.8	106.9%	(103.3, 110.6)	7.3%	(5.4,11.0)
n-Pentane	0	0.2	.	.	.	.	.

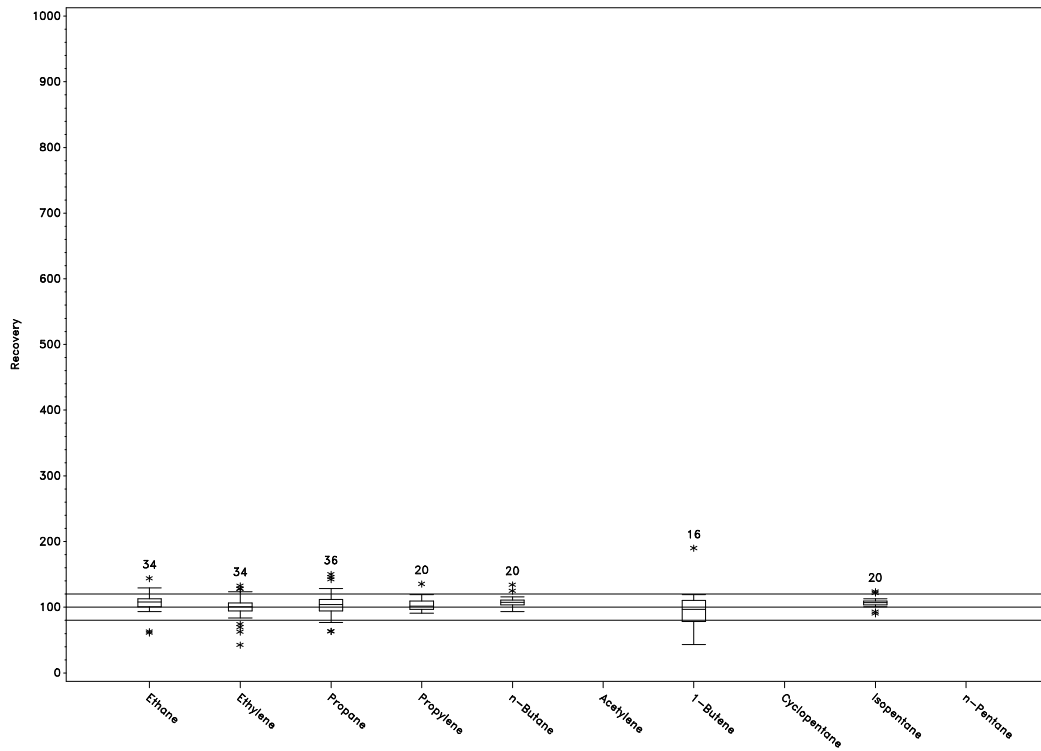


Figure 5-2. Boxplots of the NPAP recoveries for the Propane analytical group in 1996.

Table 5-3. Summary statistics for the NPAP recoveries for the Benzene analytical group in 1997

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
n-Hexane	66	17.3	19.0	100.8%	(96.0, 105.7)	19.5%	(15.9,24.7)
2,4-Dimethylpentane	64	18.8	20.0	97.8%	(95.4, 100.1)	9.6%	(8.0,11.9)
Benzene	70	10.1	11.4	93.9%	(91.1, 96.7)	12.6%	(10.5,15.5)
2-Methylhexane	30	10.2	14.1	90.4%	(85.0, 95.8)	16.0%	(12.0,22.9)
Toluene	70	9.9	11.2	92.9%	(90.1, 95.7)	12.5%	(10.4,15.4)
n-Octane	26	18.1	38.5	91.4%	(85.8, 96.9)	15.0%	(11.1,22.0)
m/p-Xylene	66	15.1	19.0	94.6%	(90.2, 99.1)	19.2%	(15.6,24.3)
o-Xylene	28	7.4	10.0	89.6%	(76.4, 102.9)	38.1%	(26.2,60.8)
1,2,4-Trimethylbenzene	39	4.0	6.6	74.2%	(66.8, 81.5)	30.5%	(22.7,43.6)
n-Decane	0	42.2	.	.	.	.	.

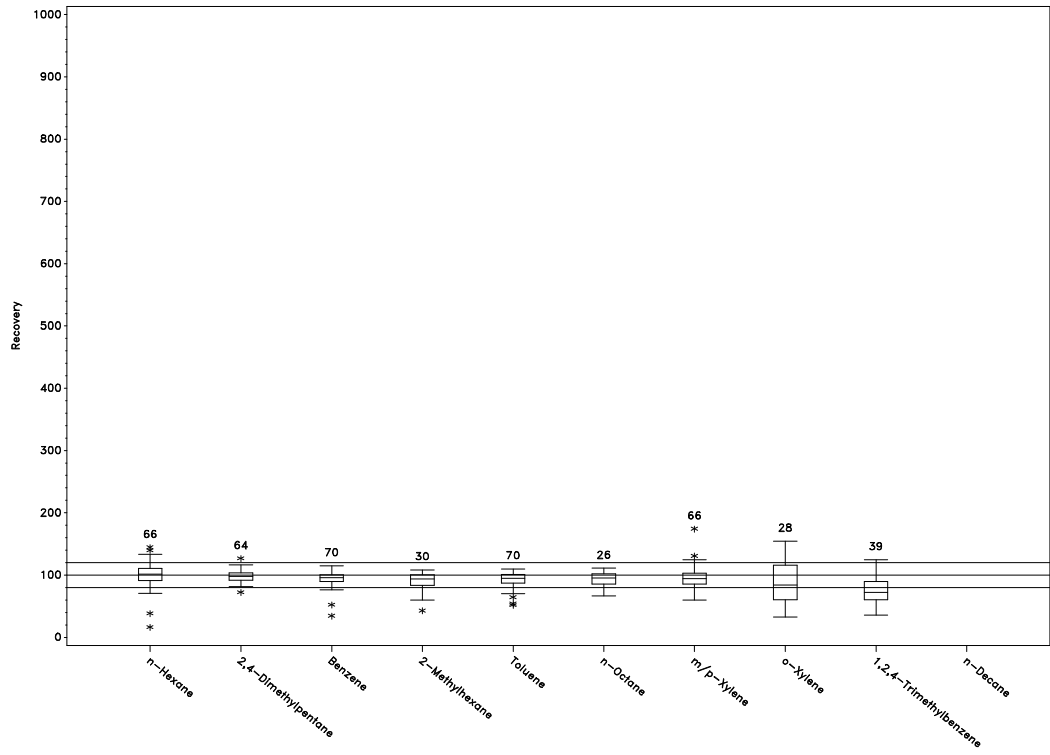


Figure 5-3. Boxplots of the NPAP recoveries for the Benzene analytical group for 1997.

Table 5-4. Summary statistics for the NPAP recoveries for the Propane analytical group for 1997

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
Ethane	60	24.1	25.7	99.8%	(95.8, 103.9)	15.6%	(12.7,19.8)
Ethylene	23	6.9	10.2	98.5%	(94.4, 102.6)	9.6%	(7.1,14.2)
Propane	66	17.2	19.1	98.1%	(95.4, 100.9)	11.6%	(9.6,14.4)
Propylene	30	4.2	5.7	101.1%	(95.1, 107.0)	15.7%	(11.8,22.5)
n-Butane	70	14.2	13.7	112.1%	(85.1, 139.1)	101.1%	(69.8,159.8)
Acetylene	28	2.7	3.0	101.8%	(85.5, 118.1)	41.2%	(28.1,66.7)
1-Butene	26	9.7	19.1	74.5%	(61.0, 88.1)	44.9%	(29.8,75.7)
Cyclopentane	68	12.6	12.7	97.5%	(94.7, 100.3)	12.0%	(10.0,14.8)
Isopentane	30	7.5	10.2	104.2%	(98.3, 110.1)	15.1%	(11.4,21.5)
n-Pentane	70	10.9	11.8	99.6%	(96.6, 102.6)	12.6%	(10.5,15.6)

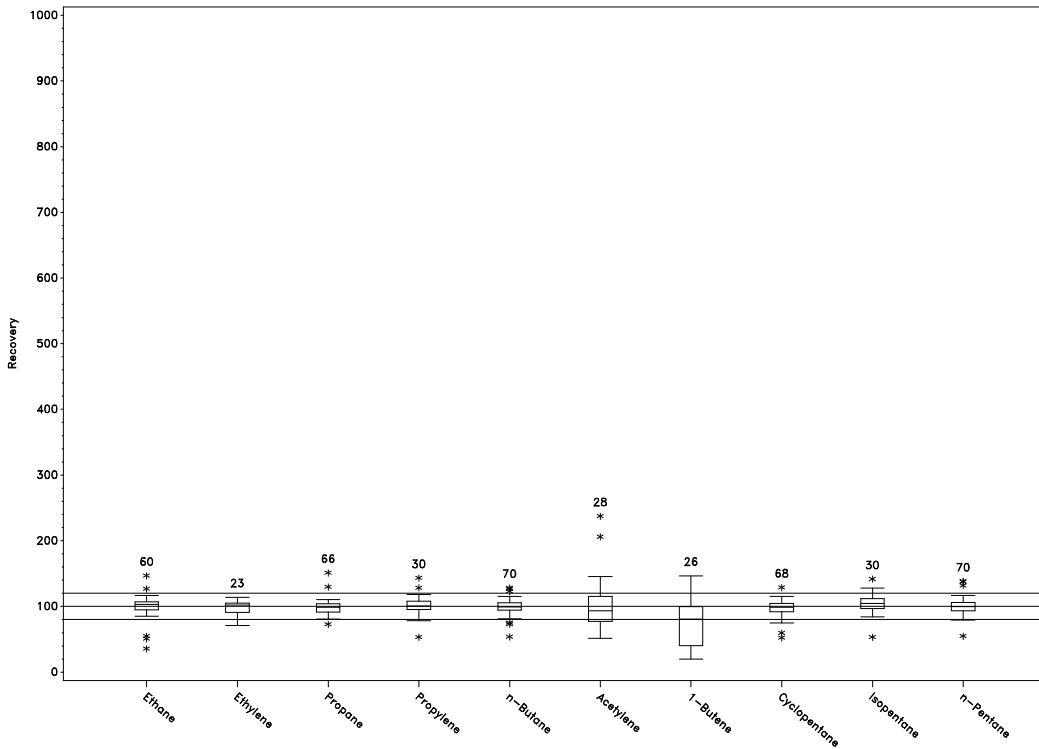


Figure 5-4. Boxplots of the NPAP recoveries for the Propane analytical group for 1997.

Table 5-5. Summary statistics for the NPAP recoveries for the Benzene analytical group in 1998

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
n-Hexane	51	16.3	9.5	713.3%	(-149.2, 1575.7)	429.9%	(162.8,-2555.4)
2,4-Dimethylpentane	37	22.9	23.3	100.9%	(98.8, 103.1)	6.4%	(5.1,8.5)
Benzene	137	15.6	16.1	96.7%	(94.7, 98.7)	12.2%	(10.7,14.1)
2-Methylhexane	101	14.9	15.2	105.0%	(97.3, 112.6)	36.8%	(30.1,46.1)
Toluene	57	12.0	14.5	95.1%	(92.6, 97.5)	9.6%	(7.9,12.1)
n-Octane	41	4.3	5.0	99.4%	(88.4, 110.3)	35.0%	(25.9,50.4)
m/p-Xylene	42	3.2	3.3	103.4%	(93.4, 113.4)	31.1%	(23.3,43.9)
o-Xylene	43	11.5	15.2	91.1%	(82.7, 99.4)	29.9%	(22.6,41.8)
1,2,4-Trimethylbenzene	50	2.8	1.8	108.5%	(81.8, 135.3)	86.6%	(58.0,143.1)
n-Decane	0	38.7	.	.	.	.	.

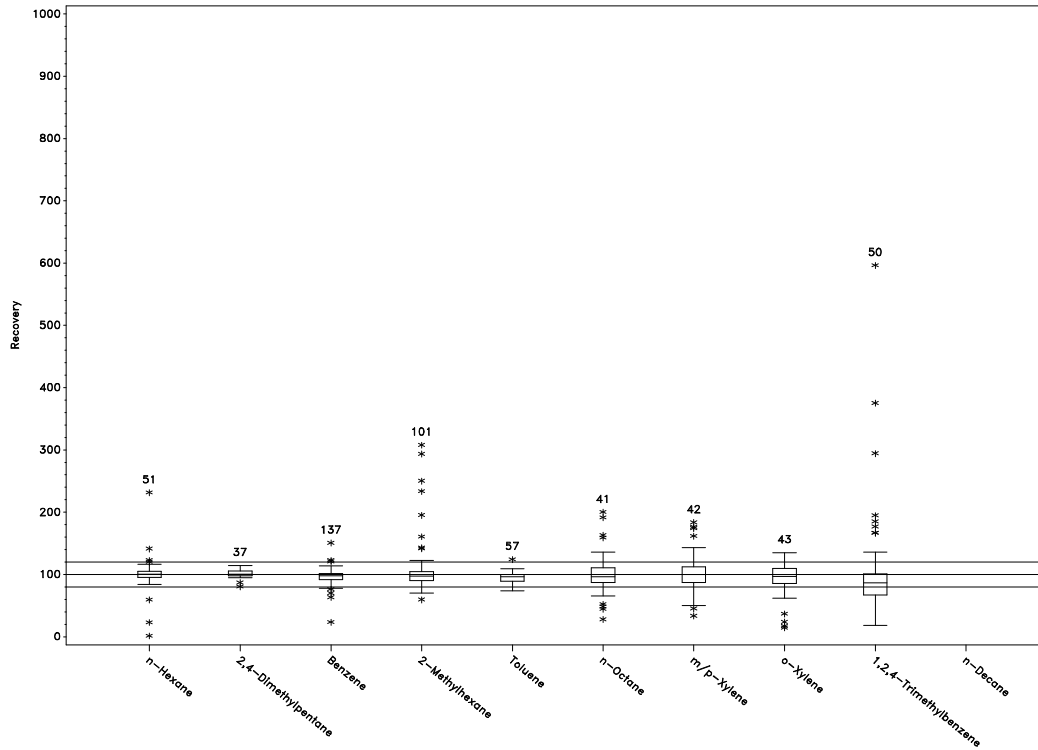


Figure 5-5. Boxplots of the NPAP recoveries for the Benzene analytical group for 1998.

Table 5-6. Summary statistics for the NPAP recoveries for the Propane analytical group for 1998

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
Ethane	33	25.7	26.7	104.6%	(99.4, 109.9)	14.2%	(10.9,19.8)
Ethylene	39	18.0	13.6	94.2%	(91.3, 97.1)	9.4%	(7.5,12.5)
Propane	41	26.7	14.1	179.4%	(114.8, 243.9)	114.0%	(68.8,227.9)
Propylene	58	16.2	17.4	111.8%	(92.2, 131.5)	66.8%	(48.0,99.2)
n-Butane	38	24.4	28.4	103.3%	(100.9, 105.7)	7.0%	(5.6,9.3)
Acetylene	53	29.8	42.3	76.2%	(70.0, 82.3)	29.2%	(22.7,39.3)
1-Butene	43	11.6	14.1	93.3%	(89.7, 97.0)	12.8%	(10.2,16.9)
Cyclopentane	56	21.5	24.0	97.8%	(93.7, 101.9)	15.8%	(12.8,20.3)
Isopentane	136	9.7	9.3	103.1%	(98.5, 107.6)	26.2%	(22.4,31.1)
n-Pentane	56	11.2	14.2	98.6%	(95.9, 101.4)	10.6%	(8.7,13.4)

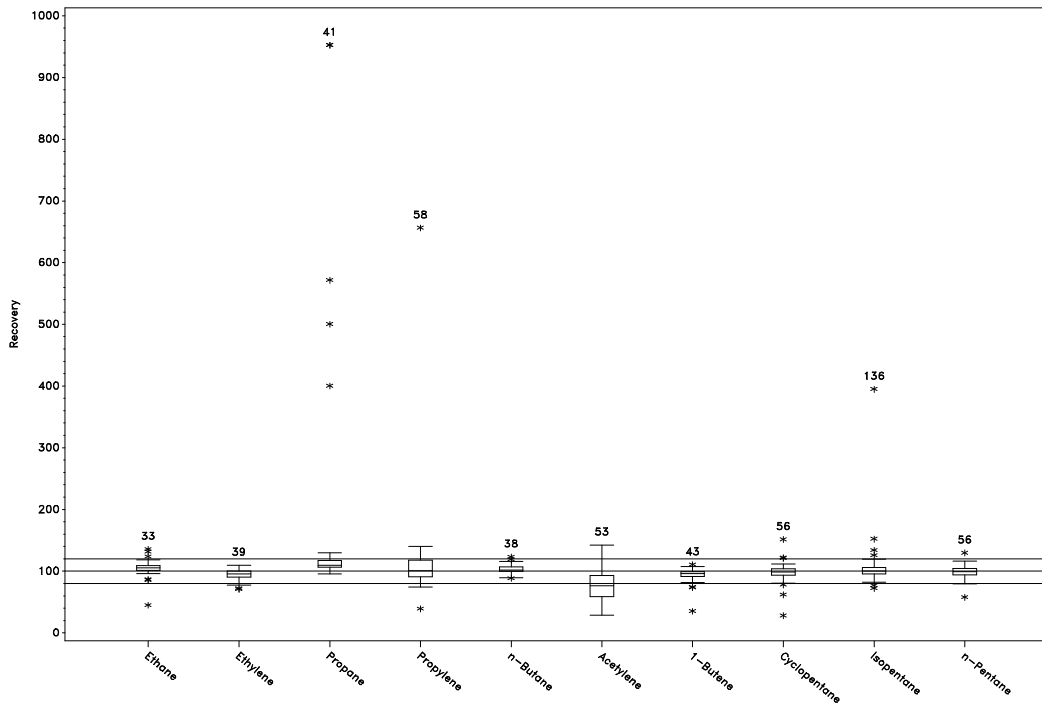


Figure 5-6. Boxplots of the NPAP recoveries for the Propane analytical group for 1998.

Table 5-7. Summary statistics for the NPAP recoveries for the Benzene analytical group for 1996-1998

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
n-Hexane	132	16.4	13.4	337.3%	(7.0, 667.5)	568.7%	(256.4,31127.9)
2,4-Dimethylpentane	117	19.9	20.8	99.0%	(97.2, 100.7)	9.7%	(8.5,11.4)
Benzene	207	13.7	14.5	95.7%	(94.1, 97.4)	12.3%	(11.1,13.9)
2-Methylhexane	151	13.1	14.6	101.6%	(96.3, 106.9)	32.4%	(27.7,38.6)
Toluene	127	10.7	12.7	93.9%	(92.0, 95.7)	11.2%	(9.8,13.1)
n-Octane	101	10.7	14.9	96.3%	(90.7, 101.9)	29.5%	(24.5,36.3)
m/p-Xylene	123	10.3	13.0	97.0%	(92.6, 101.3)	24.9%	(21.2,29.8)
o-Xylene	71	8.6	13.3	90.5%	(83.4, 97.6)	33.0%	(26.3,43.0)
1,2,4-Trimethylbenzene	89	3.2	2.9	93.5%	(77.9, 109.0)	78.9%	(58.9,110.9)
n-Decane	0	39.5	.	.	.	.	.

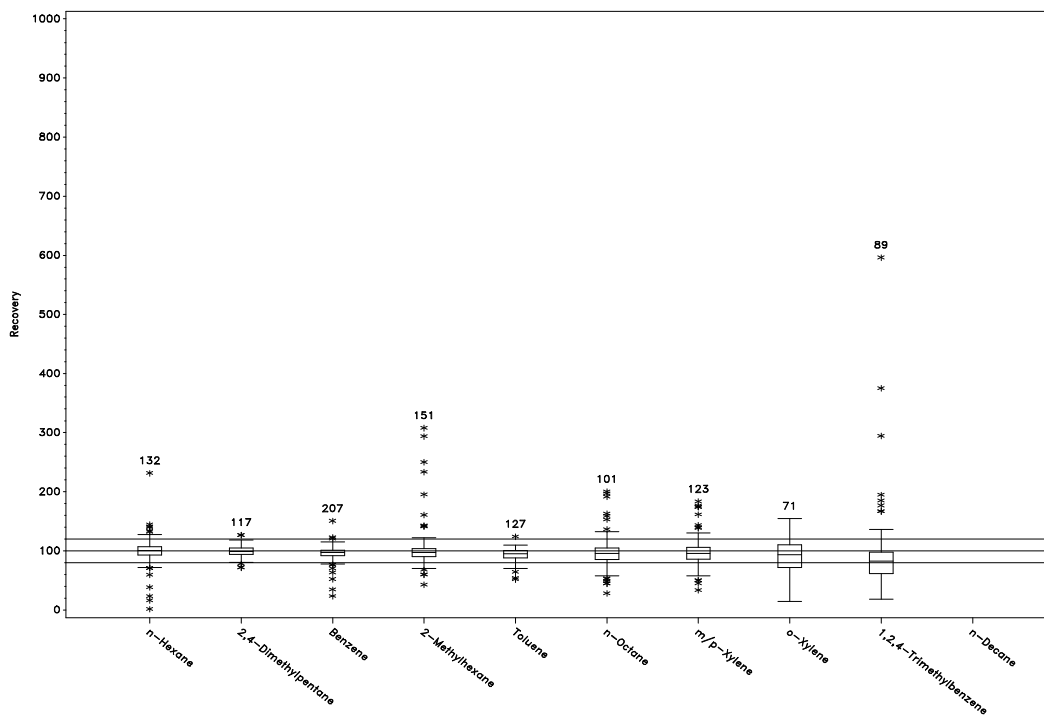


Figure 5-7. Boxplots of the NPAP recoveries for the Benzene analytical group for 1996-1998.

Table 5-8. Summary statistics for the NPAP recoveries for the Propane analytical group for 1996-1998

Compound	N	Mean Std. Conc. (ppbC)		Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision
		Reported	Actual				
Ethane	127	20.6	21.4	102.8%	(100.1, 105.5)	15.0%	(13.0,17.5)
Ethylene	96	12.0	11.7	97.0%	(94.4, 99.7)	13.5%	(11.5,16.2)
Propane	143	18.6	14.8	123.0%	(104.0, 142.0)	93.5%	(72.5,125.1)
Propylene	108	11.8	13.3	107.4%	(96.8, 118.0)	51.7%	(41.5,66.2)
n-Butane	128	17.1	17.6	108.9%	(94.3, 123.6)	76.9%	(60.4,101.3)
Acetylene	81	20.0	28.8	85.0%	(77.8, 92.2)	38.4%	(30.7,49.6)
1-Butene	85	10.3	14.8	88.1%	(82.5, 93.8)	29.7%	(24.3,37.4)
Cyclopentane	124	16.7	17.8	97.6%	(95.2, 100.0)	13.8%	(12.0,16.1)
Isopentane	186	9.5	9.8	103.7%	(100.2, 107.1)	23.2%	(20.4,26.7)
n-Pentane	126	10.7	12.9	99.2%	(97.1, 101.2)	11.7%	(10.2,13.7)

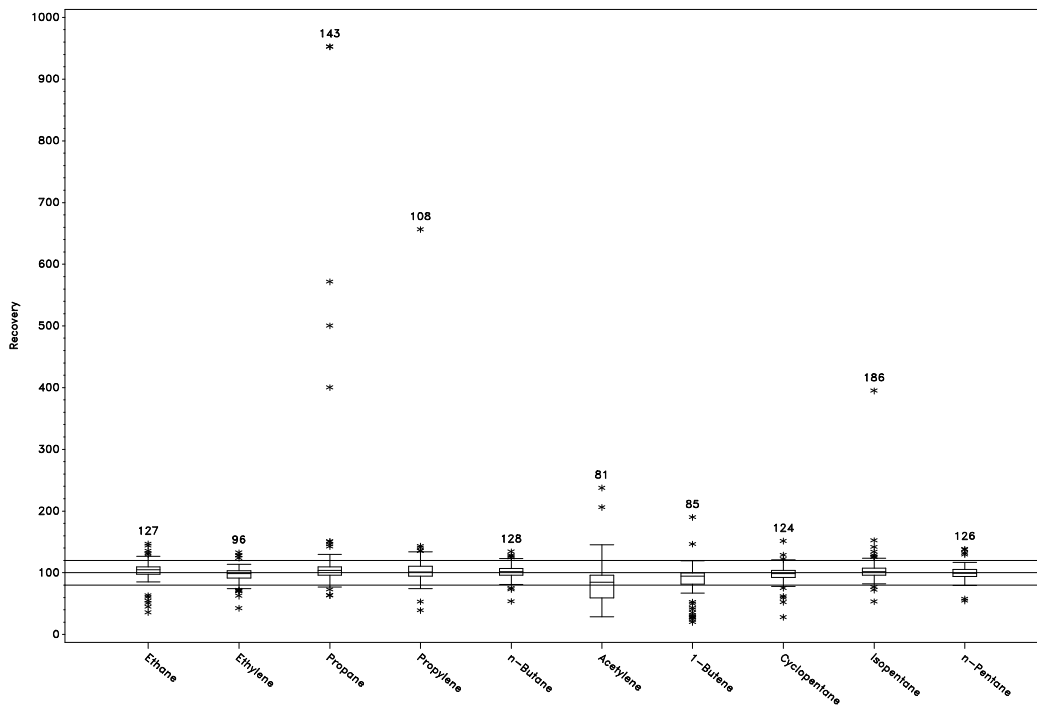


Figure 5-8. Boxplots of the NPAP recoveries for the Propane analytical group for 1996-1998.

Table 5-9. NPAP recovery means and CVs for each elution group

Year	Early Propane		Late Propane		Early Benzene		Late Benzene	
	Mean Recovery	CV	Mean Recovery	CV	Mean Recovery	CV	Mean Recovery	CV
1996	102.8%	16.4%	104.3%	17.1%	98.6%	21.0%	.	.
1997	99.5%	14.2%	97.4%	16.8%	94.9%	17.4%	74.2%	30.5%
1998	99.0%	13.1%	109.3%	67.8%	98.7%	25.8%	108.5%	86.6%
All	100.3%	14.7%	104.0%	50.8%	97.2%	22.6%	93.5%	78.9%

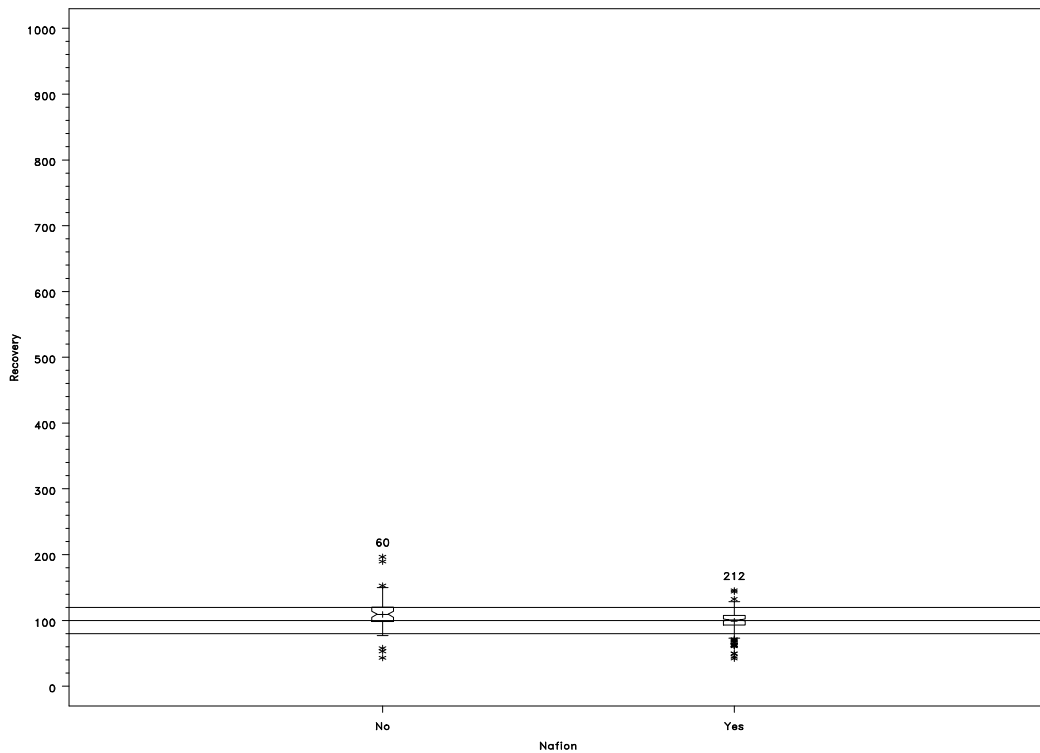


Figure 5-9. Boxplot of the NPAP recoveries for 1996 by whether or not a Nafion dryer was used.

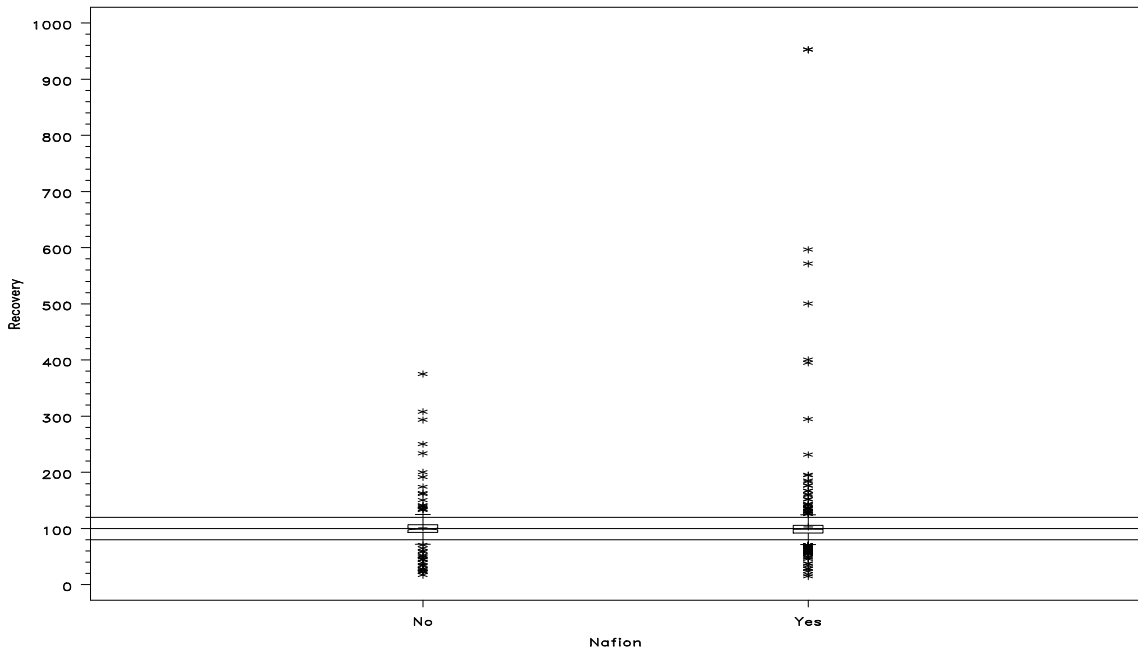


Figure 5-10. Boxplot of the NPAP recoveries for 1997 by whether or not a Nafion dryer was used.

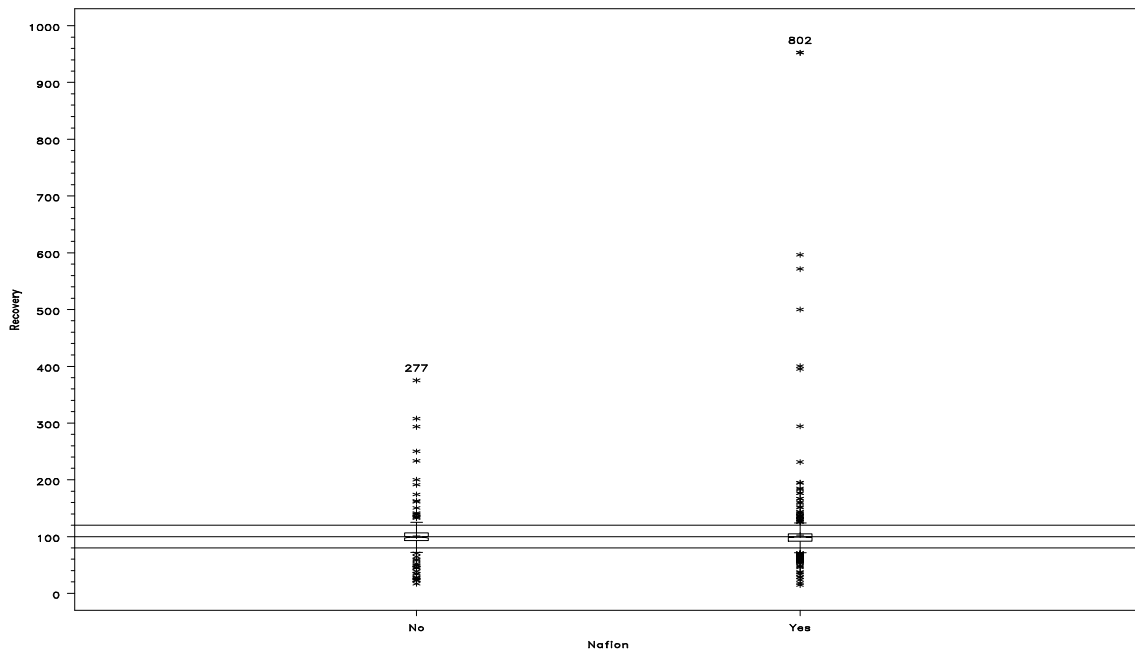


Figure 5-11. Boxplot of the NPAP recoveries for 1998 by whether or not a Nafion dryer was used.

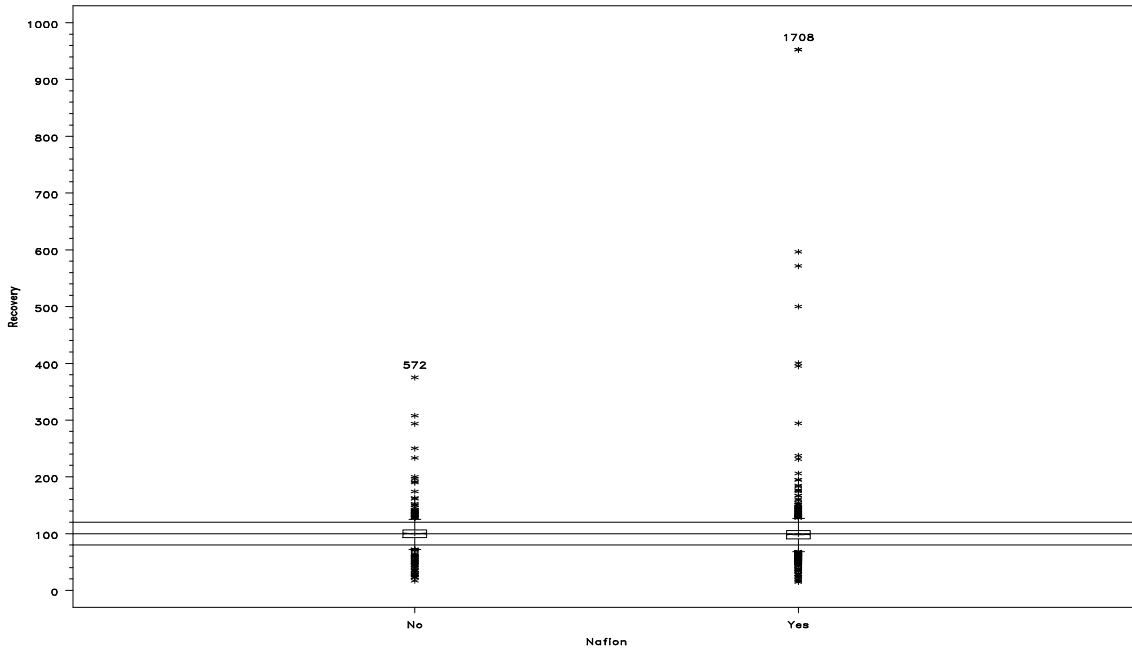


Figure 5-12. Boxplot of the NPAP recoveries for all years by whether or not a Nafion dryer was used.

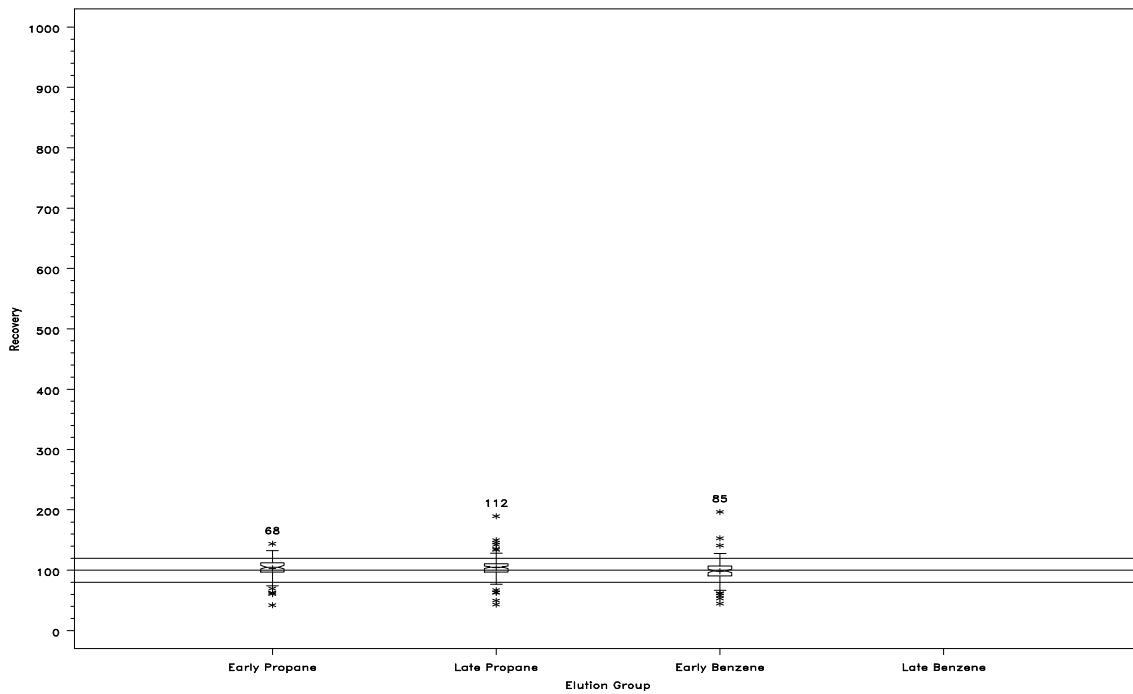


Figure 5-13. Boxplot of the NPAP recoveries for 1996 by elution group.

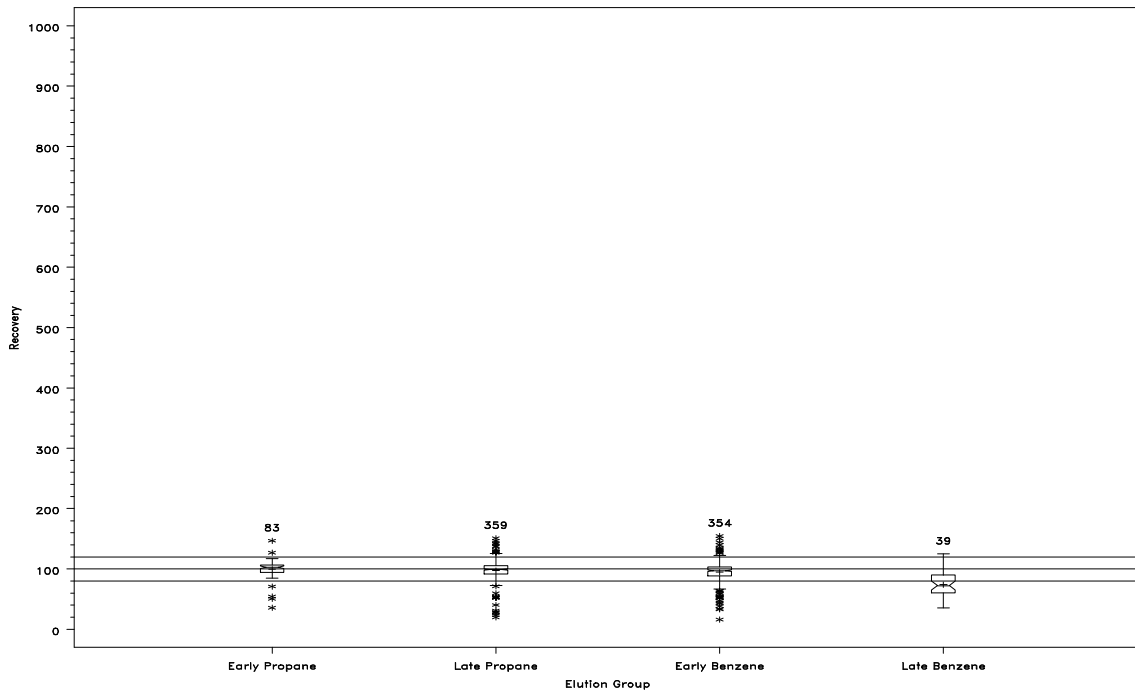


Figure 5-14. Boxplot of the NPAP recoveries for 1997 by elution group.

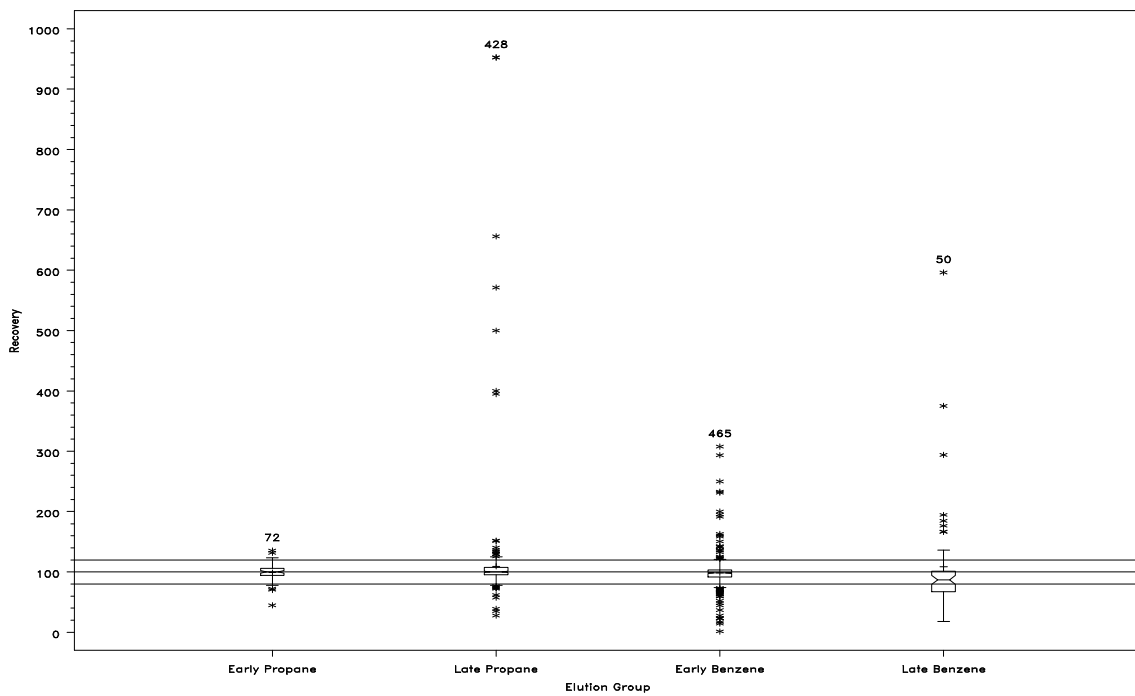


Figure 5-15. Boxplot of the NPAP recoveries for 1998 by elution group.

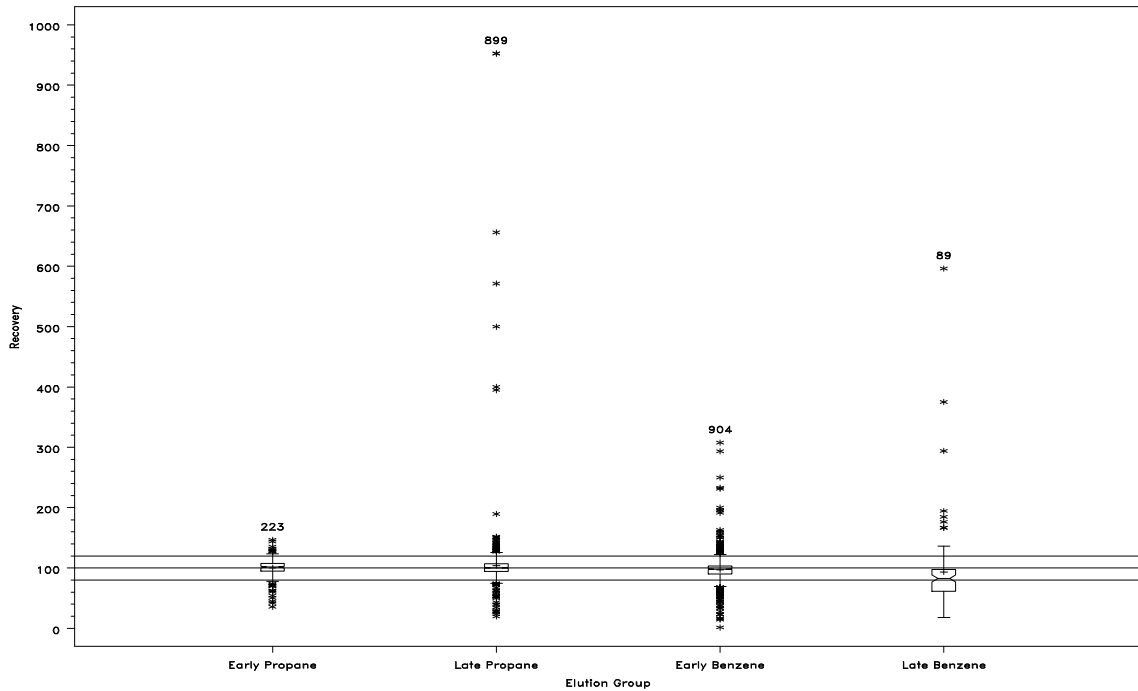


Figure 5-16. Boxplot of the NPAP recoveries for all years by elution group.

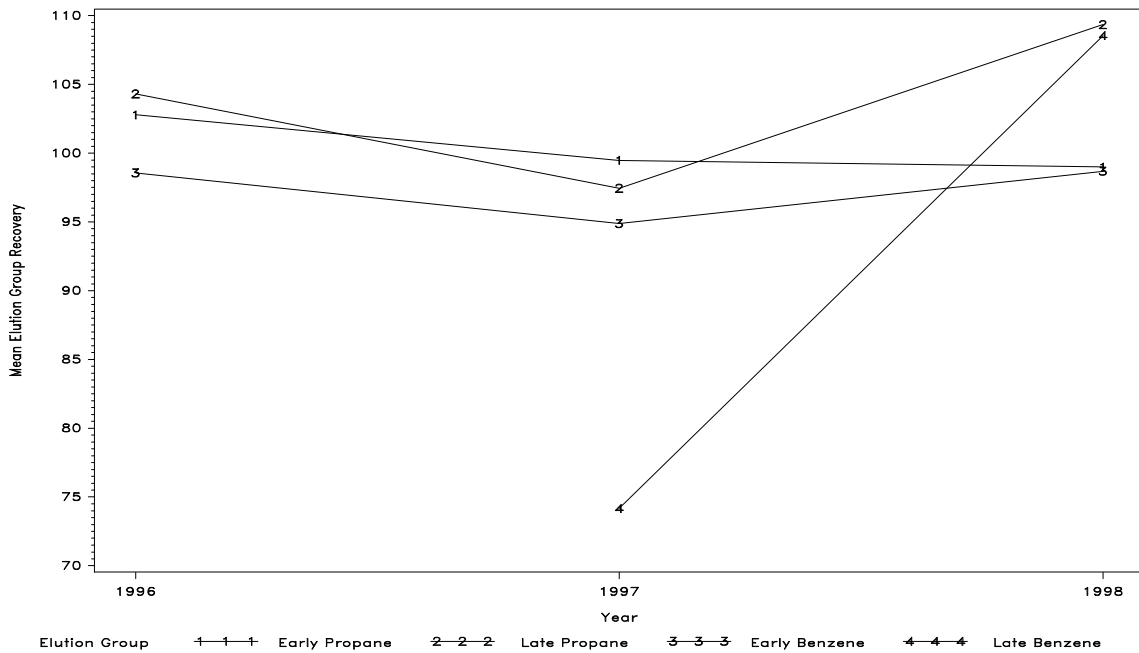


Figure 5-17. Scatter plot of the NPAP recoveries versus year for each elution Group.

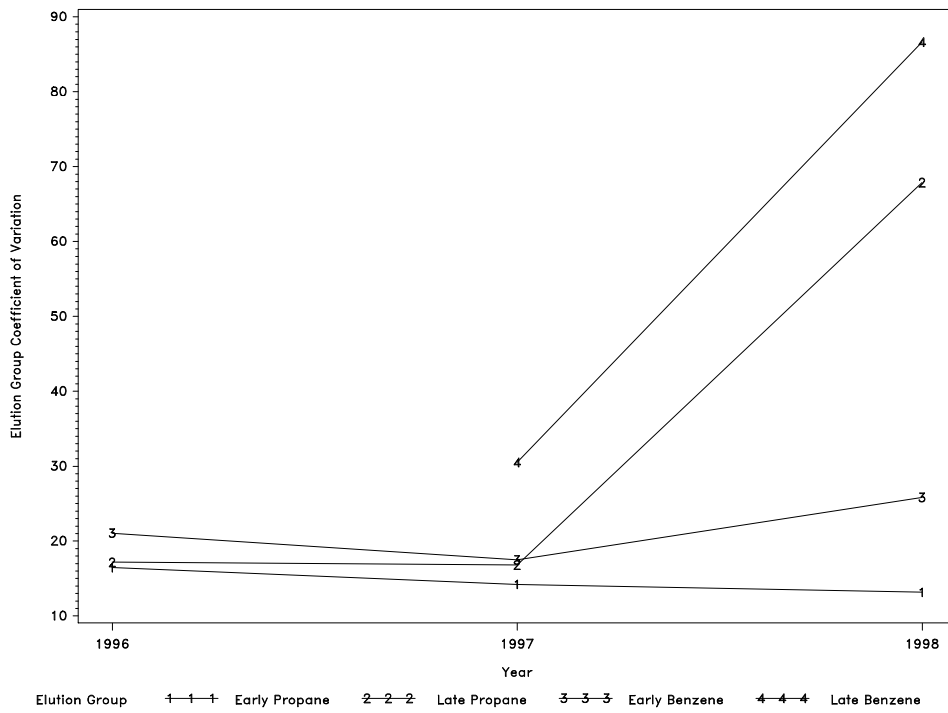


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APPENDIX A:

SUMMARY TABLES AND FIGURES OF  
STATE RETENTION TIME CALIBRATION DATA

January 23, 2001

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## APPENDIX A: SUMMARY TABLES AND FIGURES OF STATE RETENTION TIME CALIBRATION DATA

The materials in this Appendix follow the discussion in Chapter 3. For each site and year indicated in Table A-1, there are either two or three pages of summary information, depending on whether or not the state provided the retention time information with calibration data (only New Jersey provided this information).

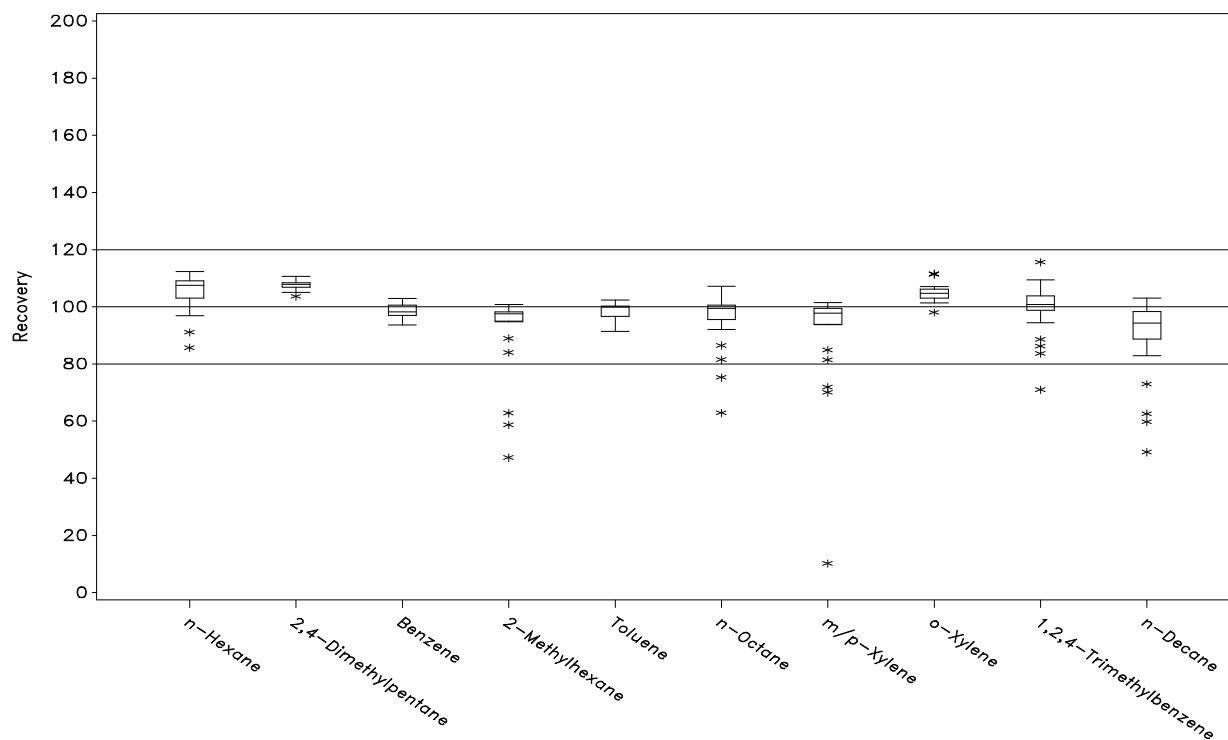
In order to see any relationship between the recoveries and the overall retention time, there are a pair of scatter plots of the raw recovery data plotting the recoveries versus the retention time for the New Jersey sites and boxplots of the recoveries for each compound shown in increasing order of the retention time. The recovery information is tabulated as well, with the compounds listed in the order of the retention time and grouped by analytic column. To improve the readability of the boxplots, the spacing between each compound is uniform. The uniform spacing of the boxplots could distort the nature of any trend, but would still show the existence of a trend. For the non-New Jersey sites, the boxplots and tables have the same order as the New Jersey sites, namely by the retention time within the analytic column grouping.

Table A-1. Sites and years in the study of State data

State	Data Included		
	Site Name	Years	Includes Scatter Plots
Maryland	Essex	1996-1998	No
	Lake Clifton	1996	No
	Living Classroom	1998	No
New Jersey	Camden	1997-1998	Yes
	Rider	1996-1998	Yes
	Rutgers	1996-1998	Yes
New York	Bronx Garden	1996	No
Washington, DC	Washington, DC	1996-1997	No

Table A-2. Statistical summaries of the recoveries for the Benzene group of the Essex 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	24	.	33.71	105.1%	(102.4,107.8)	6.1%	(4.6,8.8)	5.1%
2,4-Dimethylpentane	24	.	44.92	107.7%	(107.1,108.4)	1.5%	(1.1,2.1)	7.7%
Benzene	24	.	34.27	98.6%	(97.6,99.6)	2.5%	(1.9,3.5)	-1.4%
2-Methylhexane	24	.	28.08	91.5%	(85.5,97.5)	15.6%	(11.4,23.4)	-8.5%
Toluene	24	.	43.3	98.5%	(97.2,99.7)	3.0%	(2.3,4.3)	-1.5%
n-Octane	24	.	33.35	96.0%	(91.7,100.3)	10.5%	(7.8,15.5)	-4.0%
m/p-Xylene	24	.	43.16	91.0%	(82.9,99.1)	21.2%	(15.1,32.6)	-9.0%
o-Xylene	24	.	26.91	104.9%	(103.5,106.3)	3.1%	(2.4,4.4)	4.9%
1,2,4-Trimethylbenzene	24	.	40.17	99.3%	(95.4,103.3)	9.4%	(7.0,13.7)	-0.7%

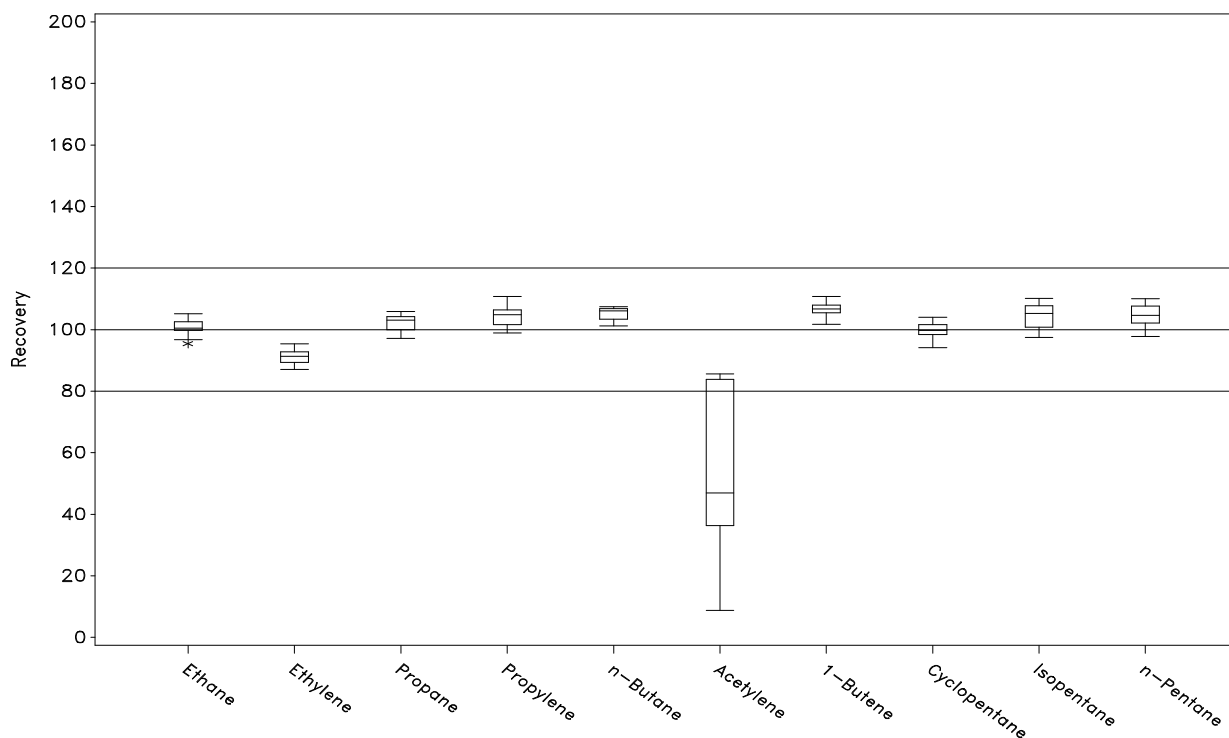


n-Decane	24	.	33.21	89.3%	(83.3,95.3)	15.9%	(11.6,23.9)	-10.7%
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Figure A-1. Boxplots of the recoveries for the Benzene group of the Essex 1996 retention time standard data by compound.

Table A-3. Statistical summaries of the recoveries for the Propane group of the Essex 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	24	.	28.92	100.8%	(99.8,101.8)	2.4%	(1.9,3.4)	0.8%
Ethylene	24	.	23.83	91.1%	(90.1,92.0)	2.5%	(1.9,3.5)	-8.9%
Propane	24	.	45.73	102.1%	(101.1,103.2)	2.5%	(1.9,3.5)	2.1%
Propylene	24	.	26.43	104.2%	(103.0,105.4)	2.7%	(2.1,3.9)	4.2%
n-Butane	24	.	44.08	105.1%	(104.3,106.0)	1.9%	(1.4,2.6)	5.1%
Acetylene	24	.	46.88	55.8%	(44.6,66.9)	47.4%	(30.7,83.1)	-44.2%
1-Butene	24	.	32.27	106.5%	(105.5,107.5)	2.2%	(1.7,3.1)	6.5%
Cyclopentane	24	.	23.03	99.9%	(98.9,100.9)	2.4%	(1.9,3.4)	-0.1%
Isopentane	24	.	44.77	104.2%	(102.5,106.0)	3.9%	(3.0,5.6)	4.2%



n-Pentane	24	.	28.55	104.5%	(103.0,106.0)	3.4%	(2.6,4.8)	4.5%
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Figure A-2. Boxplots of the recoveries for the Propane group of the Essex 1996 retention time standard data by compound.

Table A-4. Statistical summaries of the recoveries for the Benzene group of the Essex 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	22	.	32.59	110.3%	(109.3,111.4)	2.1%	(1.6,3.1)	10.3%
2,4-Dimethylpentane	22	.	43.95	110.7%	(109.9,111.5)	1.6%	(1.2,2.3)	10.7%
Benzene	22	.	34.57	99.2%	(98.4,100.0)	1.8%	(1.4,2.6)	-0.8%
2-Methylhexane	22	.	27.57	96.5%	(95.7,97.3)	1.9%	(1.4,2.7)	-3.5%
Toluene	22	.	42.34	101.4%	(100.1,102.6)	2.8%	(2.1,4.0)	1.4%
n-Octane	22	.	31.7	103.7%	(102.8,104.5)	1.9%	(1.5,2.8)	3.7%
m/p-Xylene	22	.	42.59	96.2%	(95.0,97.5)	2.9%	(2.2,4.2)	-3.8%
o-Xylene	22	.	27.12	99.0%	(97.7,100.2)	2.8%	(2.1,4.0)	-1.0%
1,2,4-Trimethylbenzene	22	.	41.37	98.1%	(96.2,100.1)	4.4%	(3.3,6.4)	-1.9%
n-Decane	22	.	30.14	94.6%	(92.5,96.6)	4.9%	(3.7,7.2)	-5.4%

Figure A-3. Boxplots of the recoveries for the Benzene group of the Essex 1997 retention time standard data by compound.

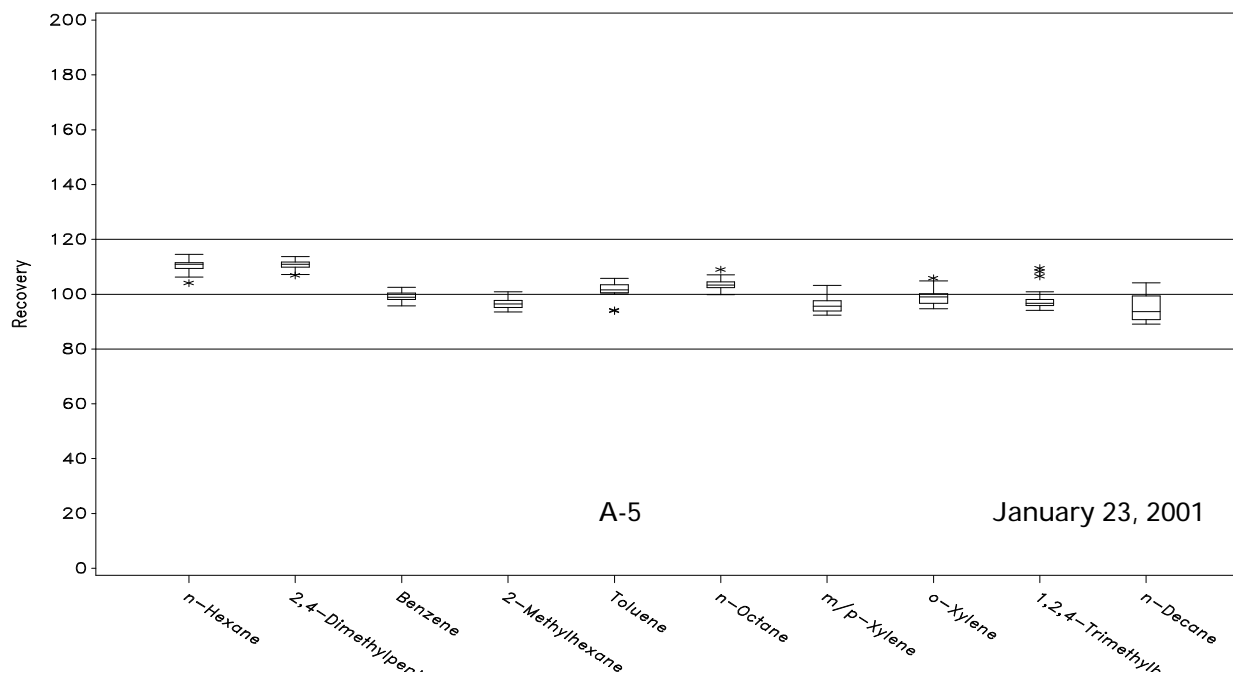


Table A-5. Statistical summaries of the recoveries for the Propane group of the Essex 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	22	.	28.55	102.5%	(101.6,103.3)	1.9%	(1.5,2.7)	2.5%
Ethylene	22	.	21.13	105.3%	(99.0,111.6)	13.5%	(9.8,20.6)	5.3%
Propane	22	.	46.11	100.6%	(99.8,101.4)	1.8%	(1.4,2.6)	0.6%
Propylene	22	.	25.19	104.8%	(103.8,105.9)	2.3%	(1.7,3.3)	4.8%
n-Butane	22	.	43.99	105.2%	(104.0,106.3)	2.5%	(1.9,3.7)	5.2%
Acetylene	22	.	59.25	48.7%	(40.8,56.6)	36.5%	(24.2,62.3)	-51.3%
1-Butene	22	.	32.06	106.7%	(105.1,108.2)	3.3%	(2.5,4.7)	6.7%
Cyclopentane	21	.	22.57	89.7%	(87.5,91.9)	5.4%	(4.0,8.0)	-10.3%
Isopentane	22	.	40.87	114.8%	(109.7,119.9)	10.1%	(7.4,15.0)	14.8%
n-Pentane	22	.	26.9	104.6%	(104.1,105.2)	1.3%	(1.0,1.8)	4.6%

Figure A-4. Boxplots of the recoveries for the Propane group of the Essex 1997 retention time standard data by compound.

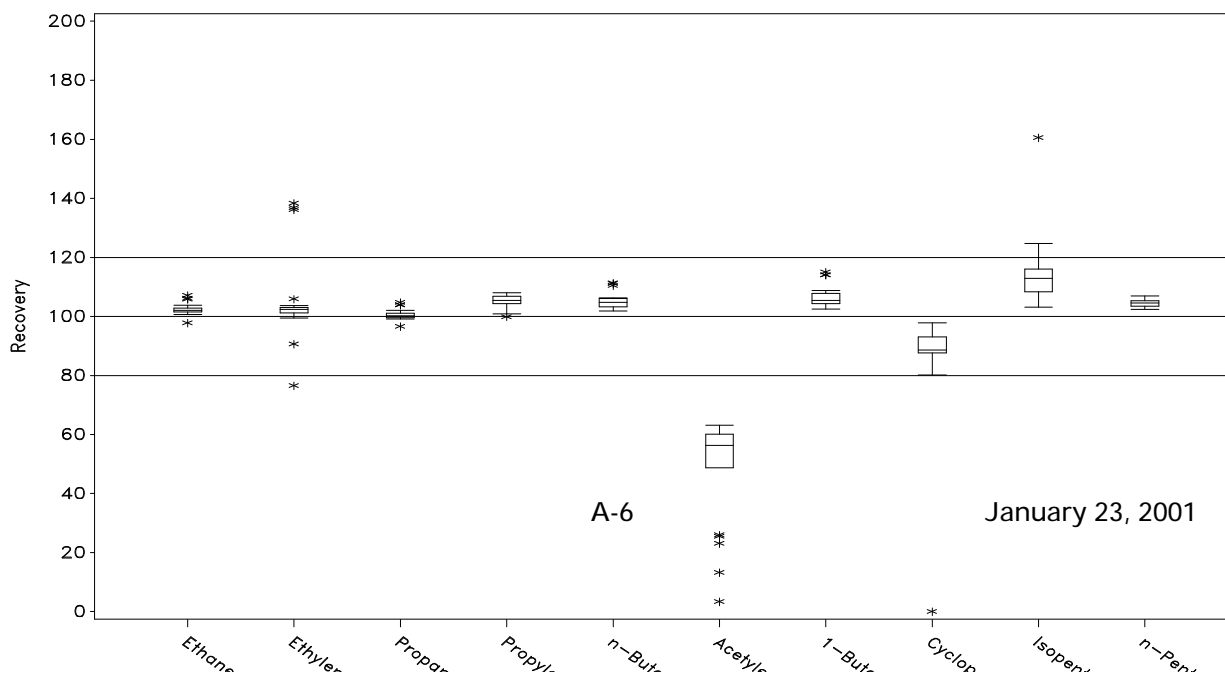


Table A-6. Statistical summaries of the recoveries for the Benzene group of the Essex 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	27	.	30.09	98.3%	(97.6,99.0)	1.8%	(1.4,2.4)	-1.7%
2,4-Dimethylpentane	27	.	39.72	101.6%	(100.6,102.5)	2.3%	(1.8,3.2)	1.6%
Benzene	27	.	30	92.6%	(91.8,93.5)	2.4%	(1.9,3.3)	-7.4%
2-Methylhexane	27	.	25.1	87.2%	(86.3,88.0)	2.4%	(1.9,3.4)	-12.8%
Toluene	27	.	38.7	100.8%	(99.8,101.8)	2.6%	(2.0,3.6)	0.8%
n-Octane	27	.	29.74	94.1%	(93.4,94.8)	1.8%	(1.4,2.5)	-5.9%
m/p-Xylene	27	.	39.3	84.6%	(78.9,90.3)	17.1%	(12.6,25.1)	-15.4%
o-Xylene	27	.	24.7	92.2%	(91.4,93.0)	2.2%	(1.7,3.0)	-7.8%
1,2,4-Trimethylbenzene	27	.	39.61	86.2%	(84.9,87.6)	3.9%	(3.0,5.4)	-13.8%
n-Decane	27	.	30.86	82.9%	(81.6,84.1)	3.8%	(3.0,5.3)	-17.1%

Figure A-5. Boxplots of the recoveries for the Benzene group of the Essex 1998 retention time standard data by compound.

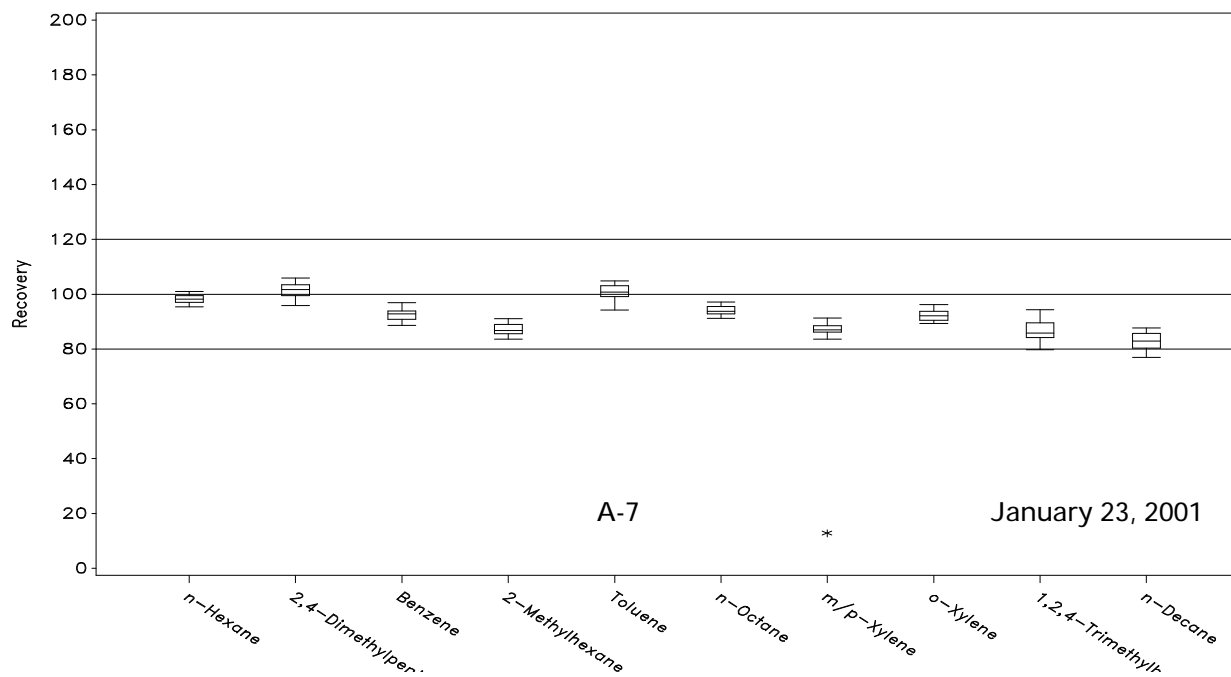


Table A-7. Statistical summaries of the recoveries for the Propane group of the Essex 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	27	.	28.58	98.5%	(97.7,99.4)	2.2%	(1.7,3.0)	-1.5%
Ethylene	27	.	28.05	104.0%	(103.0,105.0)	2.5%	(2.0,3.5)	4.0%
Propane	27	.	43.71	100.8%	(99.9,101.7)	2.3%	(1.8,3.1)	0.8%
Propylene	27	.	23.99	96.6%	(95.9,97.4)	2.0%	(1.6,2.7)	-3.4%
n-Butane	27	.	43.65	100.2%	(99.3,101.2)	2.3%	(1.8,3.2)	0.2%
Acetylene	23	.	35.51	8.4%	(7.1,9.8)	37.3%	(24.8,62.9)	-91.6%
1-Butene	27	.	33	99.1%	(98.3,99.9)	2.1%	(1.6,2.9)	-0.9%
Cyclopentane	27	.	20.11	87.3%	(86.2,88.5)	3.3%	(2.6,4.6)	-12.7%
Isopentane	27	.	42.1	106.5%	(105.0,108.0)	3.6%	(2.8,5.0)	6.5%
n-Pentane	27	.	25.7	100.3%	(99.3,101.3)	2.5%	(1.9,3.4)	0.3%

Figure A-6. Boxplots of the recoveries for the Propane group of the Essex 1998 retention time standard data by compound.

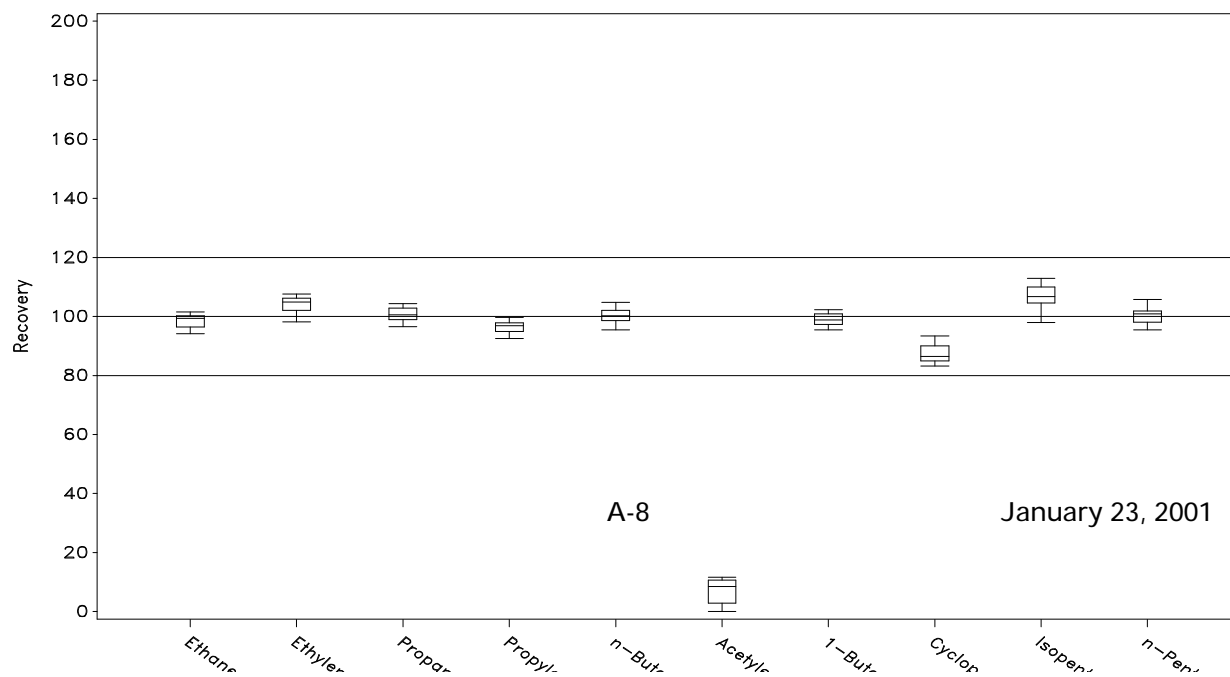


Table A-8. Statistical summaries of the recoveries for the Benzene group of the Lake Clifton 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	44	.	33.71	95.1%	(92.2,98.1)	10.2%	(8.1,13.3)	-4.9%
2,4-Dimethylpentane	44	.	44.92	101.2%	(97.0,105.5)	13.9%	(11.0,18.4)	1.2%
Benzene	44	.	34.27	108.2%	(105.2,111.2)	9.0%	(7.3,11.8)	8.2%
2-Methylhexane	44	.	28.08	79.7%	(78.2,81.3)	6.3%	(5.1,8.1)	-20.3%
Toluene	44	.	43.3	97.4%	(95.6,99.2)	6.1%	(4.9,7.9)	-2.6%
n-Octane	44	.	33.35	81.1%	(78.9,83.2)	8.7%	(7.0,11.4)	-18.9%
m/p-Xylene	36	.	43.16	74.3%	(64.6,84.0)	38.6%	(27.7,58.0)	-25.7%
o-Xylene	44	.	26.91	87.6%	(85.8,89.4)	6.8%	(5.5,8.8)	-12.4%
1,2,4-Trimethylbenzene	44	.	40.17	77.0%	(75.8,78.2)	5.3%	(4.3,6.8)	-23.0%
n-Decane	44	.	33.21	63.2%	(61.9,64.4)	6.5%	(5.2,8.4)	-36.8%

Figure A-7. Boxplots of the recoveries for the Benzene group of the Lake Clifton 1996 retention time standard data by compound.

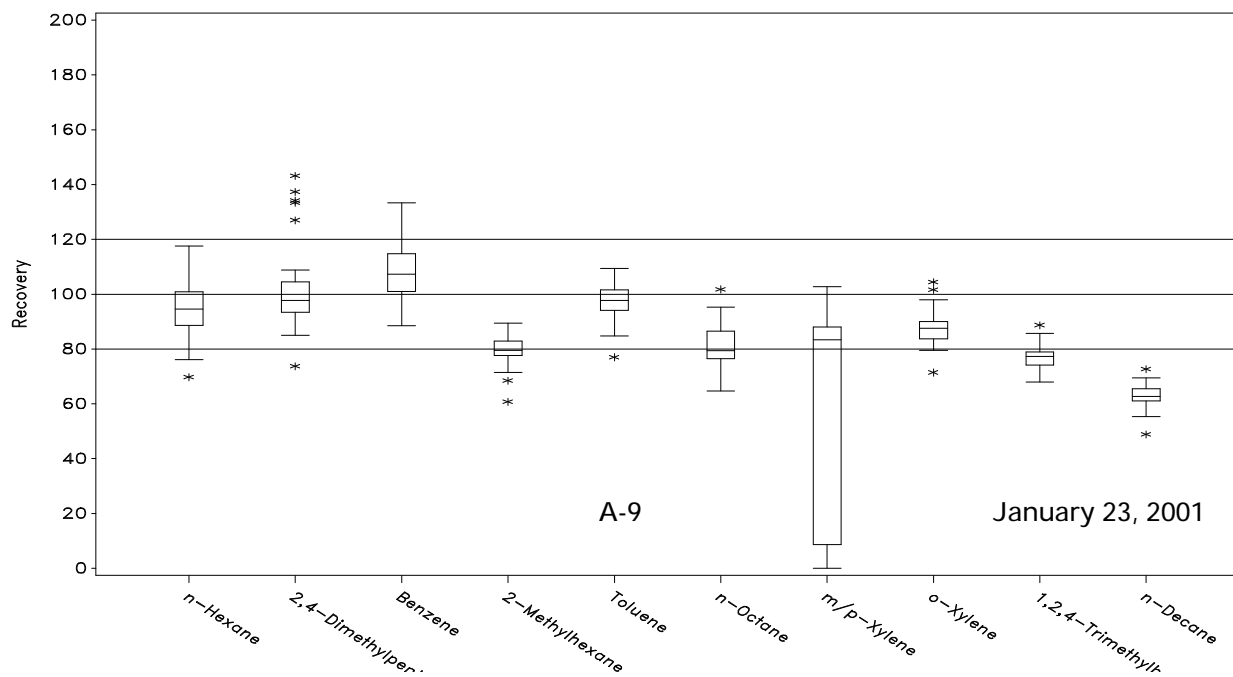


Table A-9. Statistical summaries of the recoveries for the Propane group of the Lake Clifton 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	44	.	28.92	96.7%	(95.6,97.8)	3.7%	(3.0,4.8)	-3.3%
Ethylene	44	.	23.83	99.9%	(98.9,100.9)	3.3%	(2.7,4.2)	-0.1%
Propane	44	.	45.73	102.9%	(101.7,104.1)	3.9%	(3.2,5.1)	2.9%
Propylene	44	.	26.43	106.4%	(104.9,107.9)	4.6%	(3.8,6.0)	6.4%
n-Butane	44	.	44.08	107.7%	(106.8,108.6)	2.8%	(2.3,3.6)	7.7%
Acetylene	44	.	46.88	66.0%	(58.4,73.6)	37.7%	(27.9,53.9)	-34.0%
1-Butene	44	.	32.27	123.0%	(118.9,127.2)	11.1%	(8.8,14.5)	23.0%
Cyclopentane	44	.	23.03	104.3%	(100.9,107.7)	10.8%	(8.6,14.1)	4.3%
Isopentane	44	.	44.77	89.6%	(86.2,93.1)	12.7%	(10.1,16.7)	-10.4%
n-Pentane	44	.	28.55	88.0%	(84.5,91.6)	13.3%	(10.5,17.5)	-12.0%

Figure A-8. Boxplots of the recoveries for the Propane group of the Lake Clifton 1996 retention time standard data by compound.

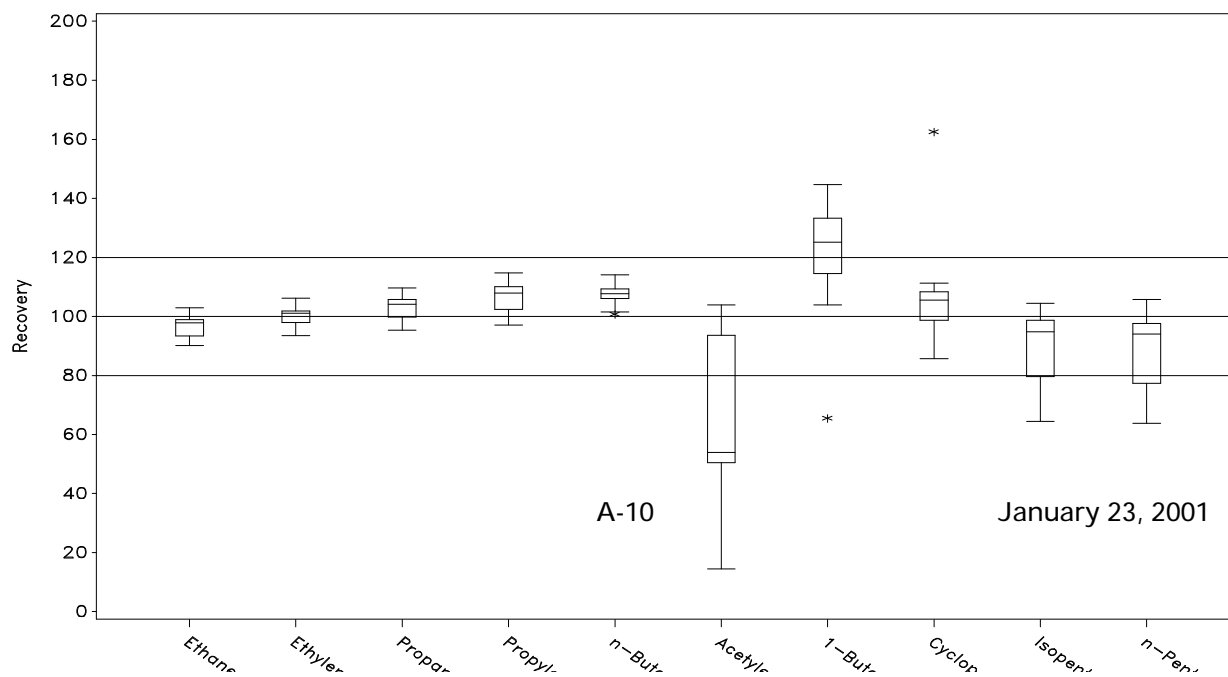


Table A-10. Statistical summaries of the recoveries for the Benzene group of the Living Classroom 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	27	.	30.09	98.7%	(97.7,99.6)	2.4%	(1.9,3.3)	-1.3%
2,4-Dimethylpentane	27	.	39.72	100.6%	(100.0,101.3)	1.7%	(1.3,2.3)	0.6%
Benzene	27	.	30	95.9%	(95.1,96.7)	2.2%	(1.7,3.0)	-4.1%
2-Methylhexane	27	.	25.1	90.9%	(89.8,91.9)	3.0%	(2.4,4.2)	-9.1%
Toluene	27	.	38.7	100.3%	(99.8,100.9)	1.4%	(1.1,1.9)	0.3%
n-Octane	27	.	29.74	95.8%	(95.2,96.4)	1.5%	(1.2,2.1)	-4.2%
m/p-Xylene	27	.	39.3	90.5%	(86.7,94.3)	10.5%	(8.0,15.1)	-9.5%
o-Xylene	27	.	24.7	90.1%	(89.4,90.9)	2.1%	(1.6,2.8)	-9.9%
1,2,4-Trimethylbenzene	27	.	39.61	86.8%	(85.8,87.7)	2.8%	(2.2,3.9)	-13.2%
n-Decane	27	.	30.86	88.8%	(87.8,89.8)	2.8%	(2.2,3.9)	-11.2%

Figure A-9. Boxplots of the recoveries for the Benzene group of the Living Classroom 1998 retention time standard data by compound.

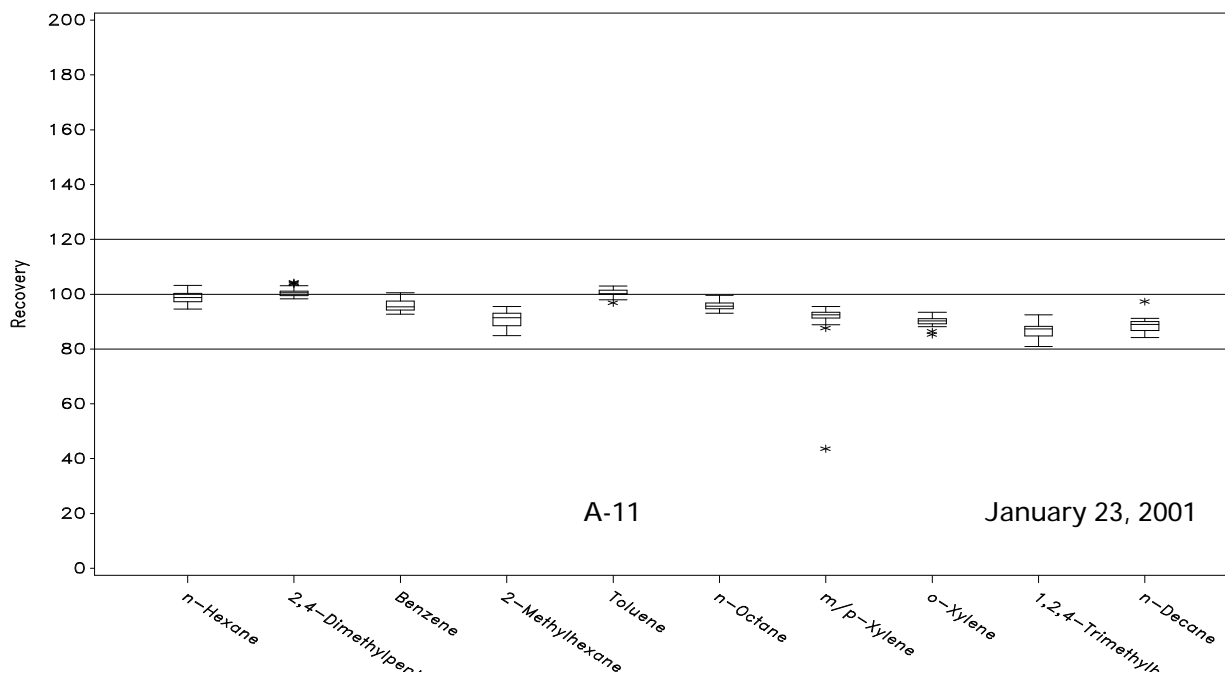


Table A-11. Statistical summaries of the recoveries for the Propane group of the Living Classroom 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	27	.	28.58	94.4%	(93.9,94.9)	1.4%	(1.1,1.9)	-5.6%
Ethylene	27	.	28.05	102.8%	(102.1,103.5)	1.7%	(1.4,2.4)	2.8%
Propane	27	.	43.71	99.2%	(98.6,99.9)	1.7%	(1.3,2.3)	-0.8%
Propylene	27	.	23.99	99.1%	(98.4,99.7)	1.6%	(1.2,2.2)	-0.9%
n-Butane	27	.	43.65	103.1%	(101.6,104.6)	3.7%	(2.8,5.1)	3.1%
Acetylene	27	.	35.51	9.1%	(8.4,9.7)	17.3%	(12.8,25.5)	-90.9%
1-Butene	27	.	33	103.1%	(101.6,104.6)	3.6%	(2.8,5.0)	3.1%
Cyclopentane	27	.	20.11	100.0%	(98.8,101.3)	3.1%	(2.4,4.3)	0.0%
Isopentane	27	.	42.1	102.9%	(101.6,104.2)	3.1%	(2.4,4.3)	2.9%
n-Pentane	27	.	25.7	101.8%	(100.7,102.9)	2.7%	(2.1,3.7)	1.8%

Figure A-10. Boxplots of the recoveries for the Propane group of the Living Classroom 1998 retention time standard data by compound.

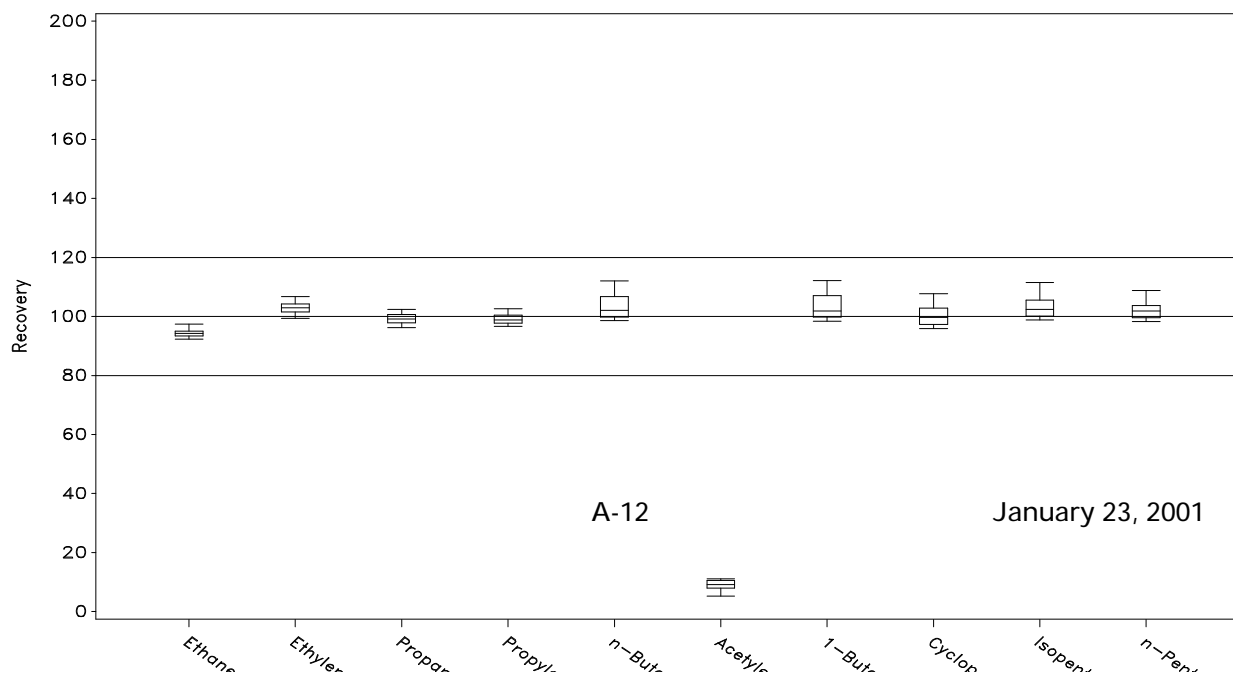


Table A-12. Statistical summaries of the recoveries for the Benzene group of the Camden 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	13	12.676	33.64	106.0%	(103.0,109.0)	4.6%	(3.2,7.8)	6.0%
2,4-Dimethylpentane	13	15.310	45.17	104.8%	(100.5,109.1)	6.7%	(4.6,11.6)	4.8%
Benzene	13	17.228	35.27	96.8%	(93.6,100.1)	5.6%	(3.9,9.5)	-3.2%
2-Methylhexane	13	18.662	28.42	99.7%	(97.5,101.8)	3.6%	(2.5,6.1)	-0.3%
Toluene	13	25.568	43	96.5%	(93.9,99.2)	4.5%	(3.2,7.7)	-3.5%
n-Octane	13	28.384	32.32	97.6%	(94.6,100.6)	5.1%	(3.5,8.6)	-2.4%
m/p-Xylene	13	31.978	42.67	62.8%	(45.5,80.2)	45.8%	(25.7,104.4)	-37.2%
o-Xylene	13	33.233	27.25	91.6%	(88.2,95.0)	6.1%	(4.3,10.5)	-8.4%
1,2,4-Trimethylbenzene	13	38.204	40.96	91.1%	(88.0,94.1)	5.5%	(3.8,9.4)	-8.9%
n-Decane	13	38.579	30.28	95.4%	(92.3,98.5)	5.4%	(3.8,9.3)	-4.6%

Figure A-11. Boxplots of the recoveries for the Benzene group of the Camden 1997 retention time standard data by compound.

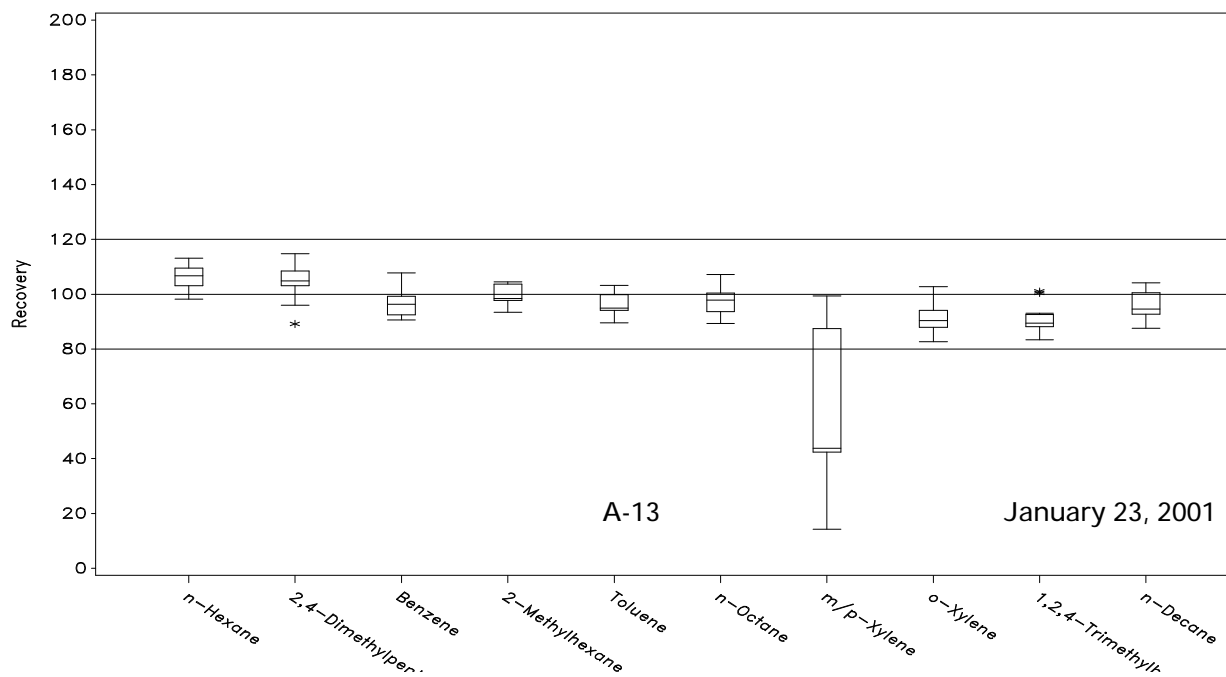
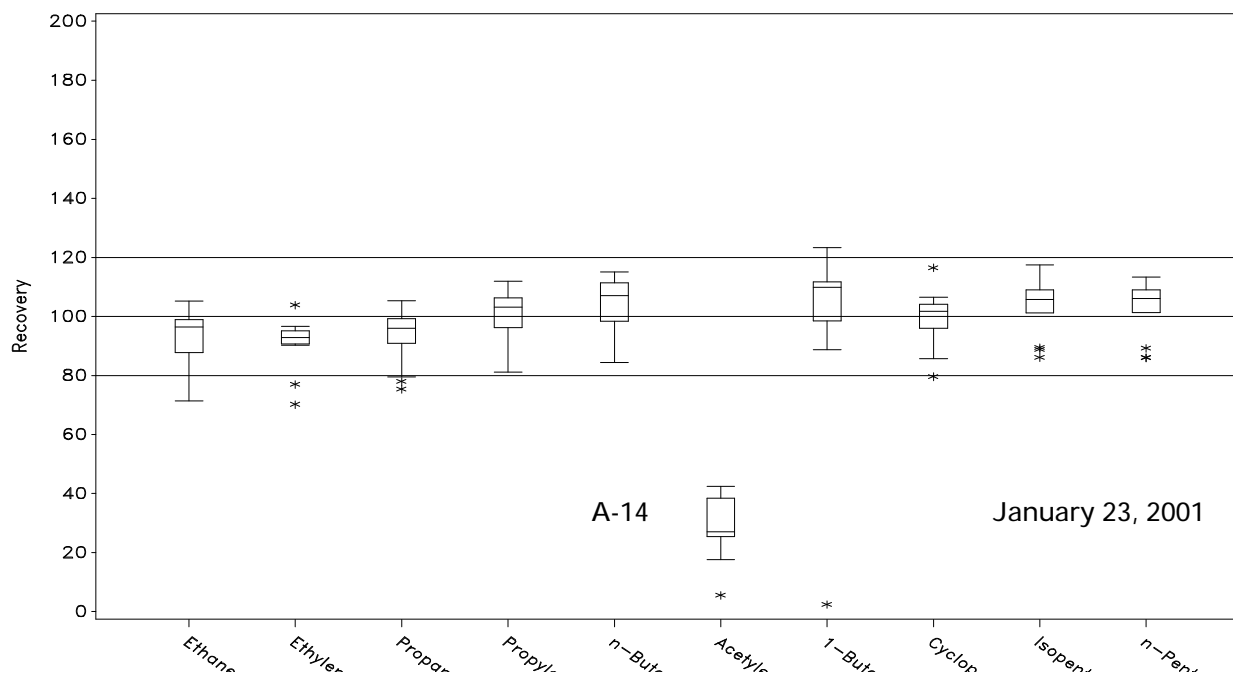


Table A-13. Statistical summaries of the recoveries for the Propane group of the Camden 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	14	7.599	29.42	92.2%	(86.0,98.4)	11.7%	(7.9,20.2)	-7.8%
Ethylene	14	8.400	22.1	91.1%	(86.3,95.9)	9.1%	(6.3,15.5)	-8.9%
Propane	14	10.621	47.3	93.2%	(87.8,98.5)	9.9%	(6.8,16.9)	-6.8%
Propylene	14	17.840	26.4	99.8%	(94.5,105.2)	9.3%	(6.4,15.8)	-0.2%
n-Butane	14	21.754	45.3	103.4%	(97.4,109.4)	10.1%	(6.9,17.2)	3.4%
Acetylene	13	23.667	54.47	28.9%	(22.5,35.2)	36.4%	(21.4,77.0)	-71.1%
1-Butene	14	27.743	33.27	99.9%	(82.7,117.1)	29.7%	(18.4,57.9)	-0.1%
Cyclopentane	14	30.259	23.16	99.0%	(93.6,104.4)	9.5%	(6.5,16.1)	-1.0%
Isopentane	14	30.394	42.09	103.4%	(97.9,108.8)	9.2%	(6.3,15.6)	3.4%
n-Pentane	14	31.308	27.7	103.3%	(97.9,108.8)	9.1%	(6.3,15.5)	3.3%

Figure A-12. Boxplots of the recoveries for the Propane group of the Camden 1997 retention time standard data by compound.



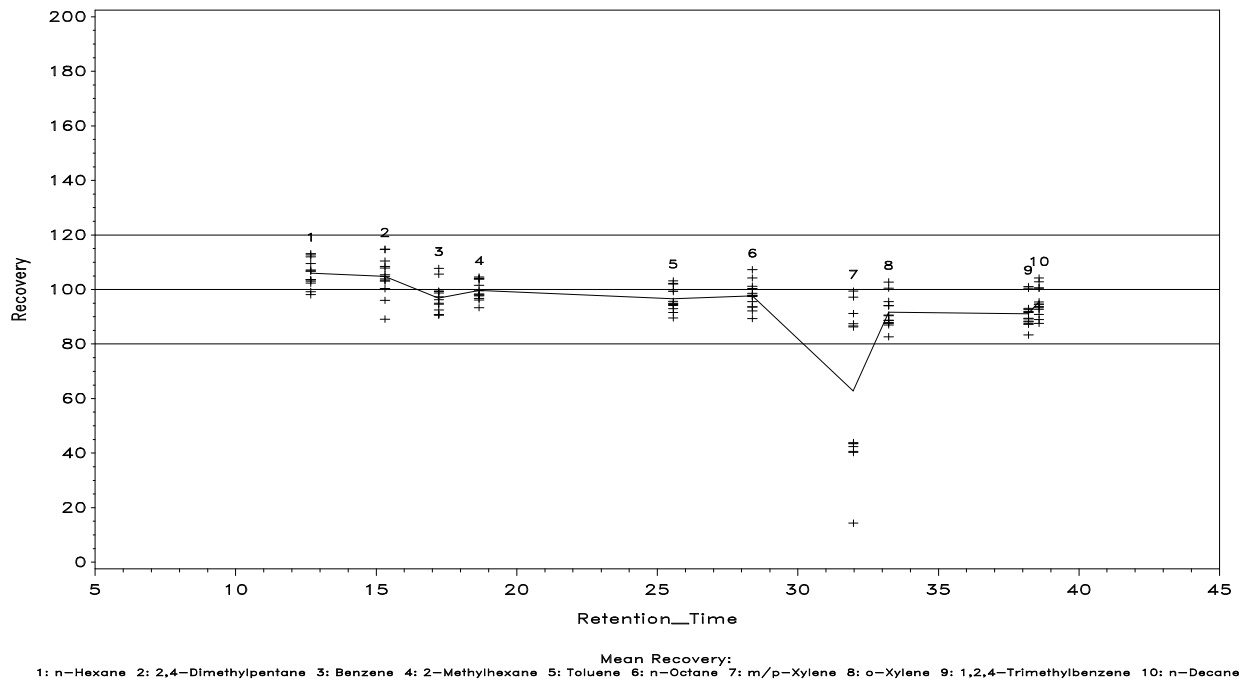


Figure A-13. Scatter plot of the recoveries for the Benzene group of the Camden 1997 retention time standard data versus the retention time.

Figure A-14. Scatter plot of the recoveries for the Propane group of the Camden 1997 retention time standard data versus the retention time.

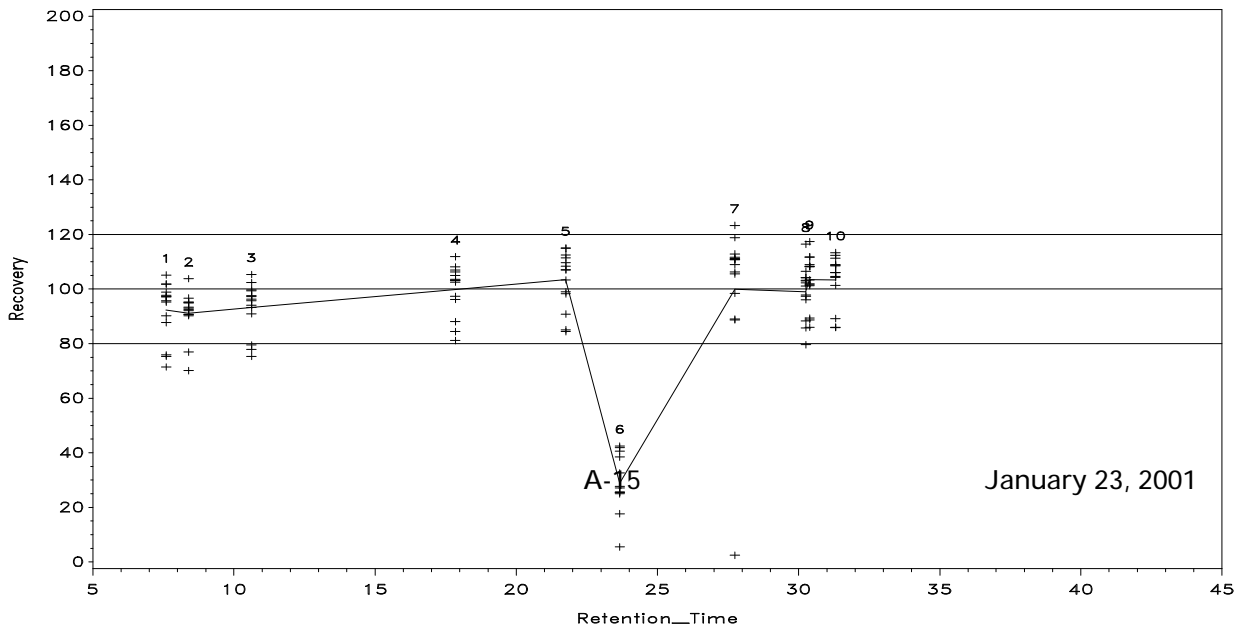


Table A-14. Statistical summaries of the recoveries for the Benzene group of the Camden 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	14	13.352	30.1	105.0%	(101.9,108.1)	5.2%	(3.6,8.6)	5.0%
2,4-Dimethylpentane	14	16.019	39.9	102.0%	(96.6,107.3)	9.0%	(6.2,15.4)	2.0%
Benzene	14	17.885	30.03	96.6%	(93.4,99.8)	5.8%	(4.0,9.6)	-3.4%
2-Methylhexane	14	19.266	25.23	98.9%	(95.3,102.5)	6.2%	(4.4,10.4)	-1.1%
Toluene	14	26.095	38.85	113.2%	(108.5,117.9)	7.2%	(5.0,12.0)	13.2%
n-Octane	14	28.872	29.9	100.4%	(96.7,104.0)	6.3%	(4.4,10.5)	0.4%
m/p-Xylene	14	32.478	39.43	58.1%	(43.8,72.3)	42.5%	(24.8,90.9)	-41.9%
o-Xylene	14	33.740	24.66	95.5%	(91.2,99.8)	7.8%	(5.4,13.1)	-4.5%
1,2,4-Trimethylbenzene	14	38.721	39.49	82.2%	(74.2,90.2)	16.8%	(11.1,30.1)	-17.8%
n-Decane	14	39.075	30.89	91.1%	(86.7,95.6)	8.4%	(5.8,14.2)	-8.9%

Figure A-15. Boxplots of the recoveries for the Benzene group of the Camden 1998 retention time standard data by compound.

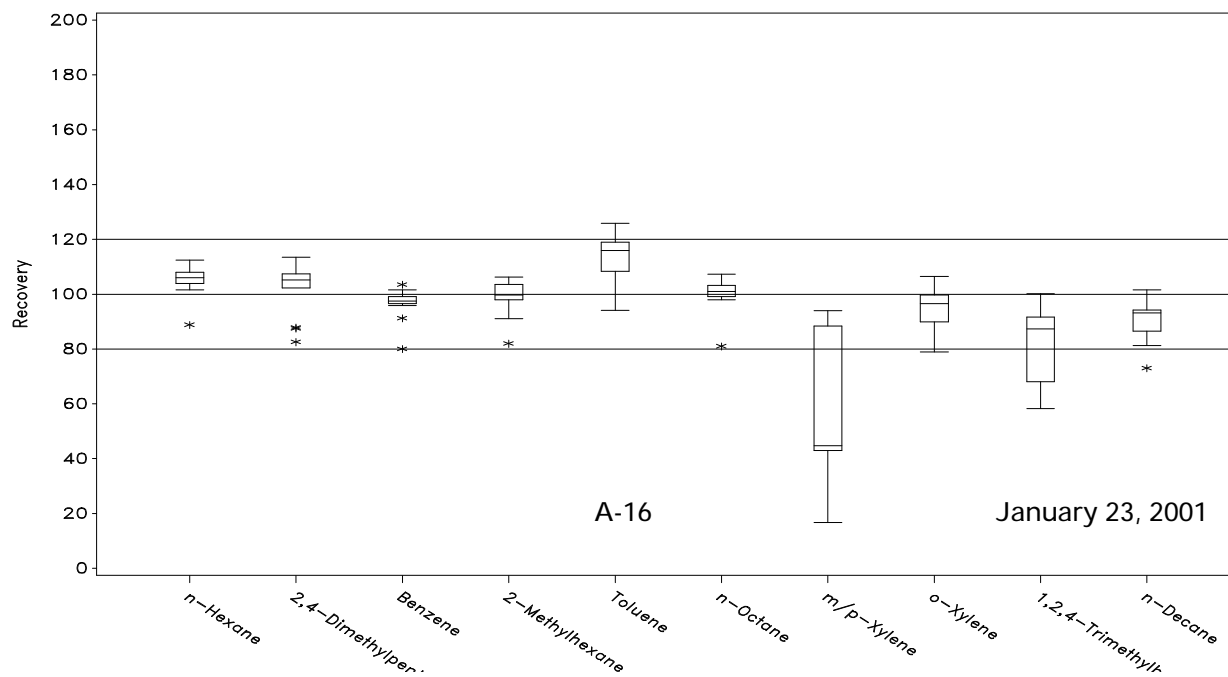
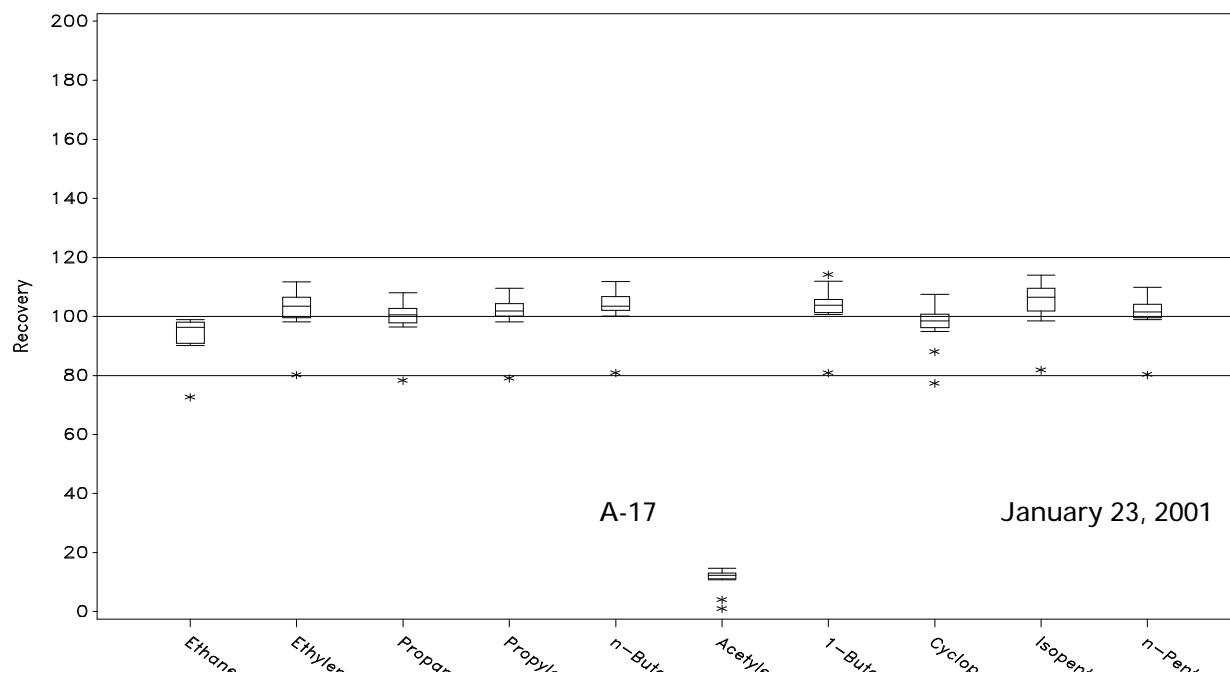


Table A-15. Statistical summaries of the recoveries for the Propane group of the Camden 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	14	7.645	28.8	94.0%	(90.0,98.0)	7.3%	(5.1,12.3)	-6.0%
Ethylene	14	8.462	26.84	102.2%	(97.9,106.6)	7.4%	(5.1,12.4)	2.2%
Propane	14	10.623	43.27	99.4%	(95.4,103.3)	6.8%	(4.8,11.4)	-0.6%
Propylene	14	17.982	23.74	100.9%	(96.9,105.0)	6.9%	(4.8,11.6)	0.9%
n-Butane	14	21.670	43.47	103.1%	(98.9,107.4)	7.1%	(4.9,11.9)	3.1%
Acetylene	14	23.906	37.93	11.1%	(8.9,13.4)	35.1%	(21.2,70.9)	-88.9%
1-Butene	14	27.633	32.84	103.4%	(99.0,107.7)	7.3%	(5.1,12.3)	3.4%
Cyclopentane	14	30.077	20.13	97.3%	(93.0,101.5)	7.6%	(5.2,12.7)	-2.7%
Isopentane	14	30.194	42.04	104.9%	(100.3,109.5)	7.6%	(5.2,12.7)	4.9%
n-Pentane	14	31.099	25.63	101.0%	(97.0,105.0)	6.9%	(4.8,11.5)	1.0%

Figure A-16. Boxplots of the recoveries for the Propane group of the Camden 1998 retention time standard data by compound.



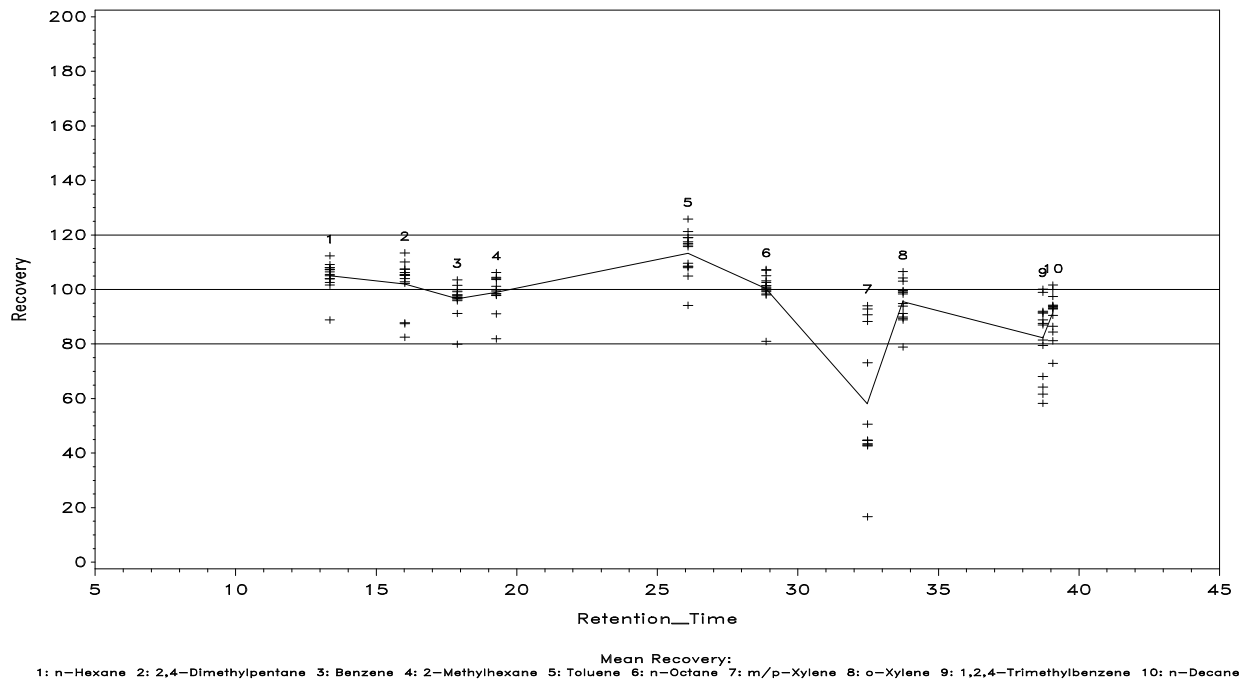


Figure A-17. Scatter plot of the recoveries for the Benzene group of the Camden 1998 retention time standard data versus the retention time.

Figure A-18. Scatter plot of the recoveries for the Propane group of the Camden 1998 retention time standard data versus the retention time.

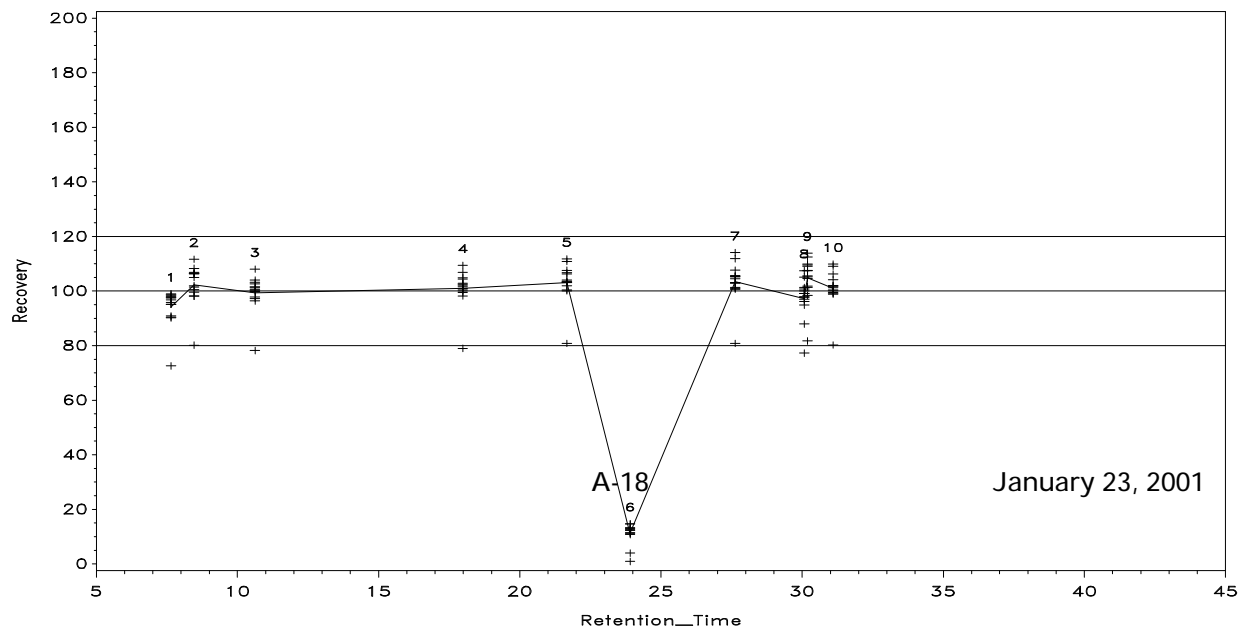


Table A-16. Statistical summaries of the recoveries for the Benzene group of the Rider 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	12	15.187	35.37	88.5%	(85.4,91.6)	5.5%	(3.8,9.7)	-11.5%
2,4-Dimethylpentane	12	17.807	46.31	97.7%	(96.4,99.0)	2.1%	(1.5,3.6)	-2.3%
Benzene	12	19.619	36.02	95.4%	(94.4,96.4)	1.6%	(1.1,2.8)	-4.6%
2-Methylhexane	12	20.913	29.31	99.5%	(98.3,100.7)	1.9%	(1.3,3.2)	-0.5%
Toluene	12	27.606	45.14	104.4%	(102.4,106.4)	3.0%	(2.1,5.2)	4.4%
n-Octane	12	30.307	34.88	105.1%	(103.5,106.7)	2.4%	(1.7,4.2)	5.1%
m/p-Xylene	12	33.954	45.15	47.6%	(25.2,69.9)	73.9%	(35.6,236.8)	-52.4%
o-Xylene	12	35.240	28.03	106.5%	(103.1,109.8)	4.9%	(3.4,8.6)	6.5%
1,2,4-Trimethylbenzene	12	40.253	42.42	106.5%	(103.8,109.2)	4.0%	(2.8,7.0)	6.5%
n-Decane	12	40.532	34.73	106.6%	(95.7,117.6)	16.2%	(10.4,30.6)	6.6%

Figure A-19. Boxplots of the recoveries for the Benzene group of the Rider 1996 retention time standard data by compound.

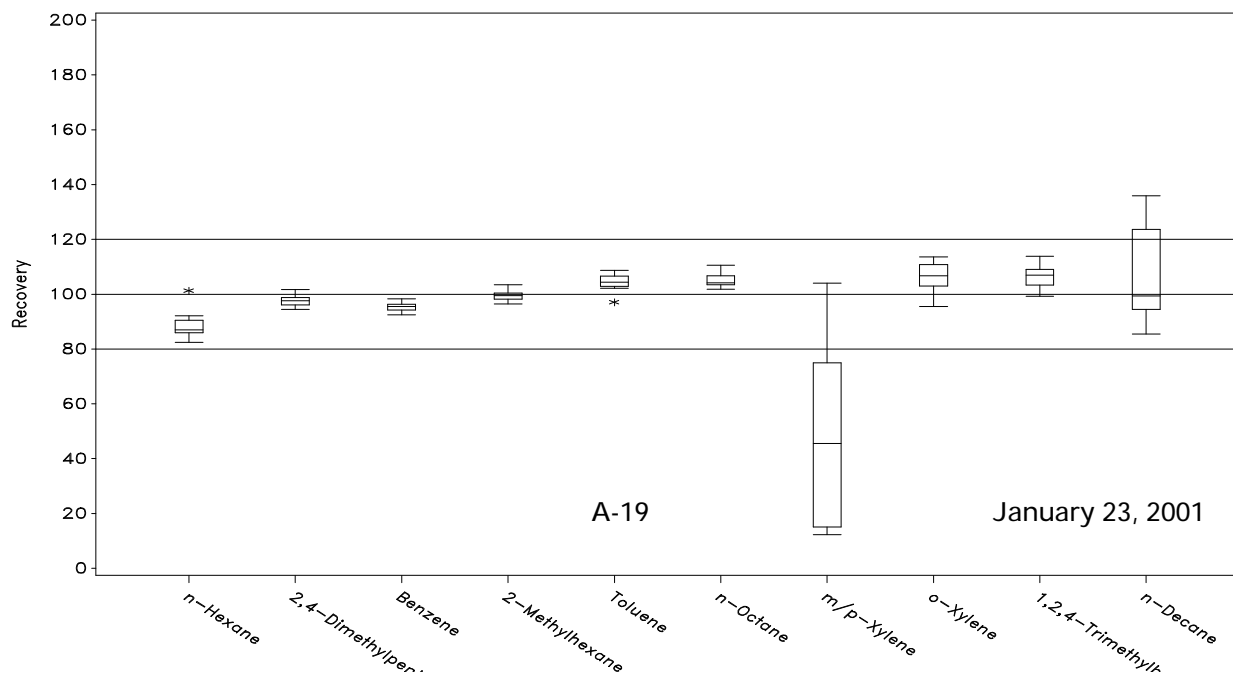
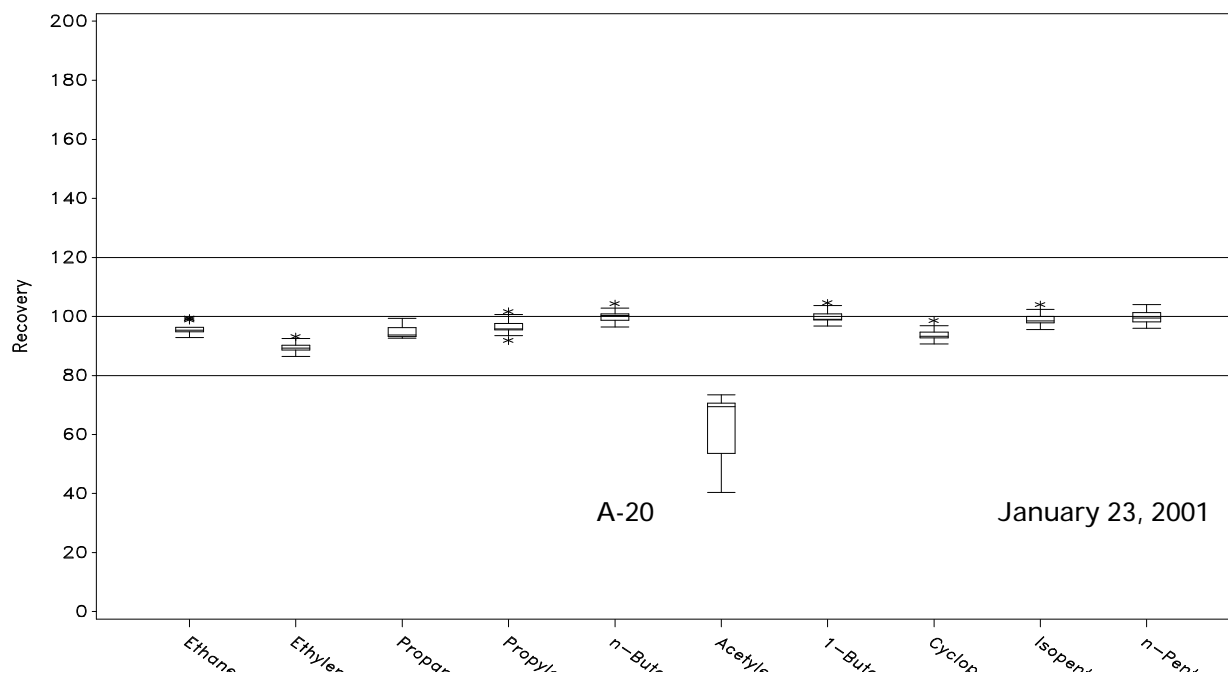
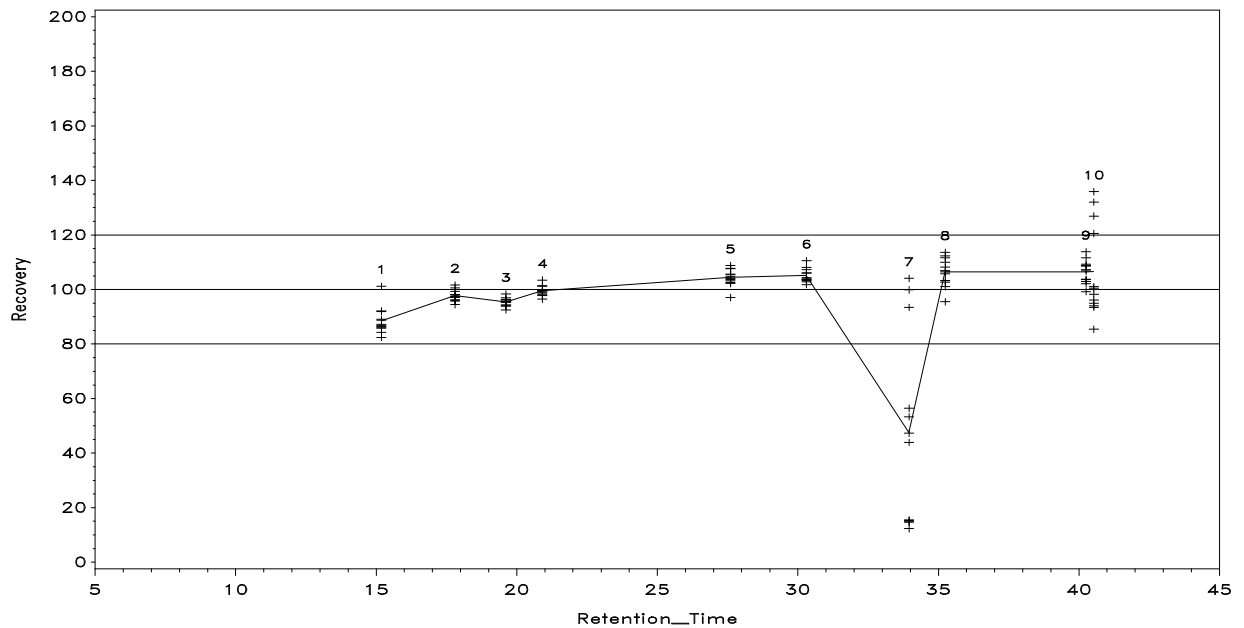


Table A-17. Statistical summaries of the recoveries for the Propane group of the Rider 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	13	8.489	29.06	95.8%	(94.6,97.1)	2.1%	(1.5,3.6)	-4.2%
Ethylene	13	9.288	23.82	89.5%	(88.3,90.6)	2.1%	(1.5,3.6)	-10.5%
Propane	13	11.491	46.13	94.9%	(93.6,96.3)	2.3%	(1.7,3.9)	-5.1%
Propylene	13	18.382	26.7	96.5%	(94.9,98.2)	2.8%	(2.0,4.7)	-3.5%
n-Butane	13	22.010	43.62	100.2%	(98.9,101.5)	2.1%	(1.5,3.6)	0.2%
Acetylene	13	23.905	48.03	62.3%	(55.4,69.1)	18.2%	(11.8,33.8)	-37.7%
1-Butene	13	27.773	32.47	100.0%	(98.6,101.4)	2.3%	(1.6,3.8)	0.0%
Cyclopentane	13	30.260	24.11	93.9%	(92.6,95.2)	2.3%	(1.6,3.8)	-6.1%
Isopentane	13	30.367	47.25	99.1%	(97.8,100.5)	2.2%	(1.6,3.8)	-0.9%
n-Pentane	13	31.258	29.87	99.6%	(98.3,101.0)	2.3%	(1.6,3.8)	-0.4%

Figure A-20. Boxplots of the recoveries for the Propane group of the Rider 1996 retention time standard data by compound.

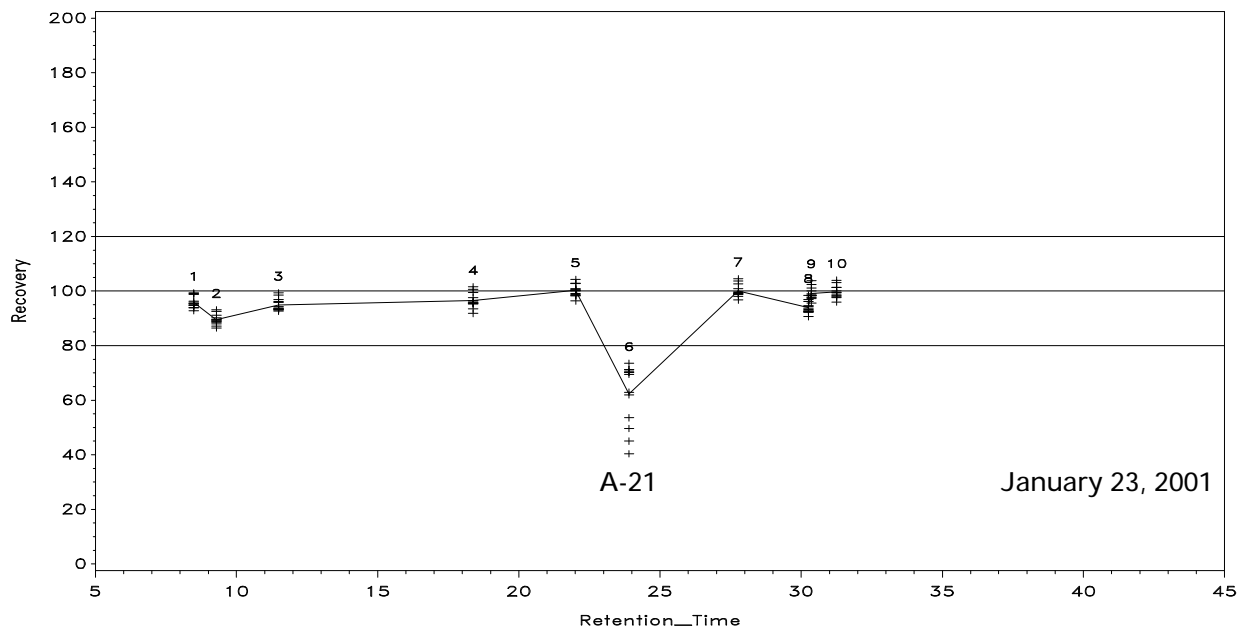




Mean Recovery:  
 1: n-Hexane 2: 2,4-Dimethylpentane 3: Benzene 4: 2-Methylhexane 5: Toluene 6: n-Octane 7: m/p-Xylene 8: o-Xylene 9: 1,2,4-Trimethylbenzene 10: n-Decane

Figure A-21. Scatter plot of the recoveries for the Benzene group of the Rider 1996 retention time standard data versus the retention time.

Figure A-22. Scatter plot of the recoveries for the Propane group of the Rider 1996 retention time standard data versus the retention time.



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Table A-18. Statistical summaries of the recoveries for the Benzene group of the Rider 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	15	15.965	33.64	78.1%	(74.6,81.5)	7.9%	(5.6,13.1)	-21.9%
2,4-Dimethylpentane	15	18.535	45.17	100.1%	(97.4,102.8)	4.9%	(3.5,8.0)	0.1%
Benzene	15	20.335	35.27	97.7%	(95.3,100.1)	4.5%	(3.2,7.2)	-2.3%
2-Methylhexane	15	21.599	28.42	103.4%	(101.1,105.7)	4.0%	(2.9,6.4)	3.4%
Toluene	15	28.263	43	104.9%	(102.7,107.2)	3.9%	(2.8,6.3)	4.9%
n-Octane	15	30.935	32.32	107.7%	(105.3,110.0)	4.0%	(2.9,6.5)	7.7%
m/p-Xylene	15	34.617	42.67	73.2%	(53.6,92.8)	48.4%	(27.9,104.3)	-26.8%
o-Xylene	15	35.891	27.25	100.9%	(98.7,103.2)	4.1%	(2.9,6.6)	0.9%
1,2,4-Trimethylbenzene	15	40.856	40.96	99.5%	(96.5,102.6)	5.6%	(3.9,9.0)	-0.5%
n-Decane	15	41.104	30.28	104.2%	(100.5,107.9)	6.4%	(4.5,10.5)	4.2%

Figure A-23. Boxplots of the recoveries for the Benzene group of the Rider 1997 retention time standard data by compound.

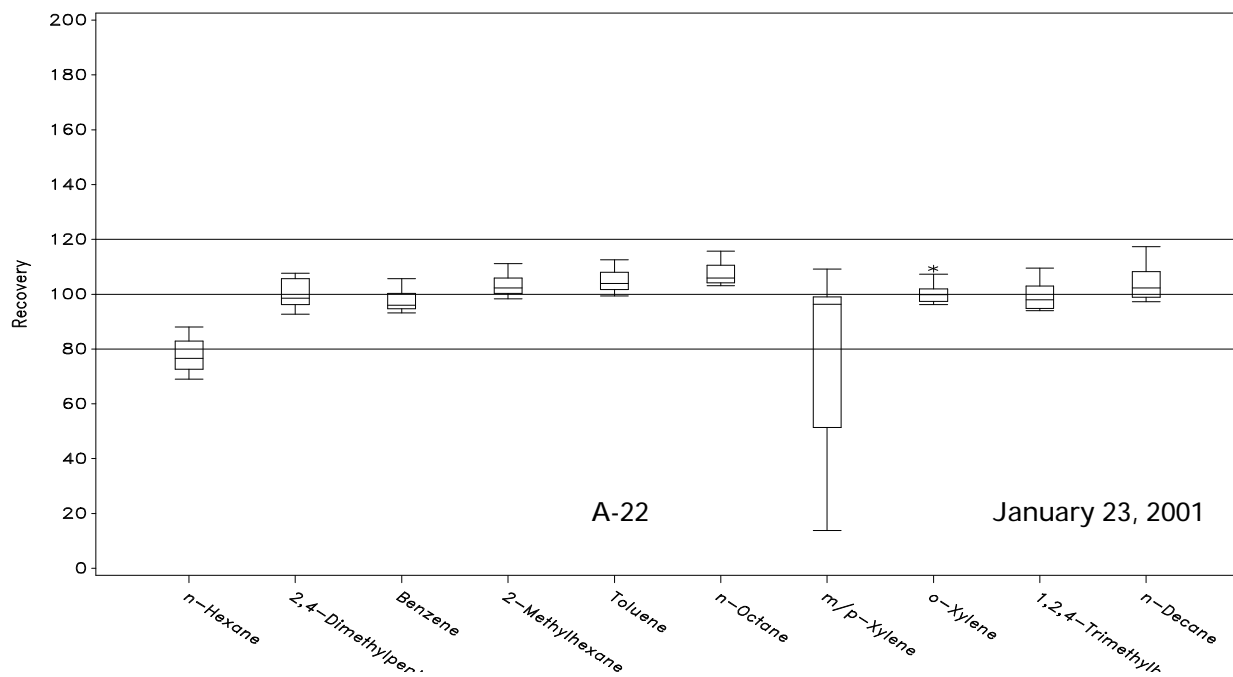
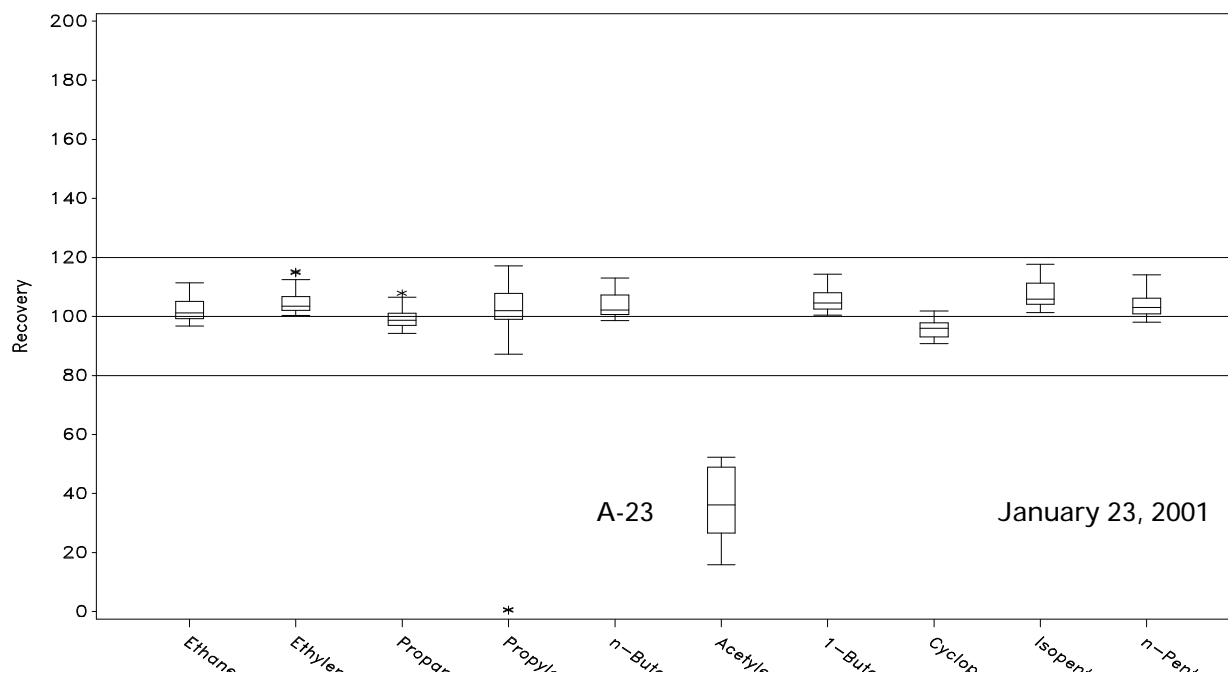
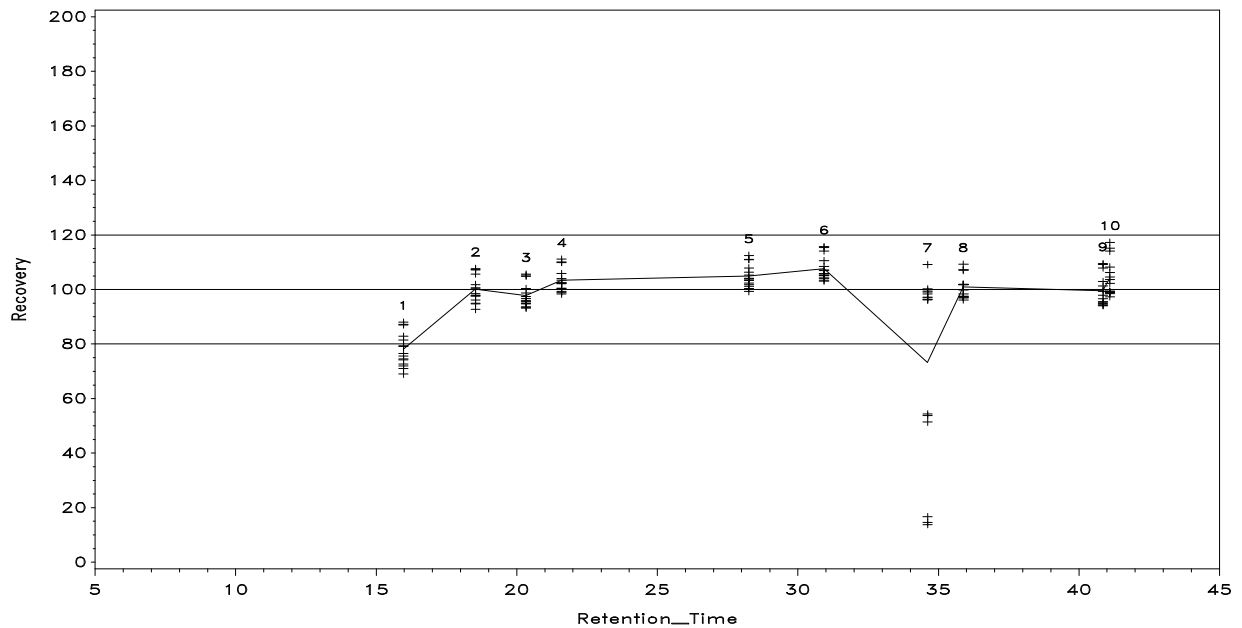


Table A-19. Statistical summaries of the recoveries for the Propane group of the Rider 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	15	8.778	29.42	102.0%	(99.6,104.5)	4.3%	(3.1,7.0)	2.0%
Ethylene	15	9.589	22.1	105.3%	(102.6,108.0)	4.6%	(3.3,7.5)	5.3%
Propane	15	11.829	47.3	99.8%	(97.5,102.1)	4.2%	(3.0,6.7)	-0.2%
Propylene	15	18.728	26.4	90.4%	(69.8,111.0)	41.1%	(24.5,83.9)	-9.6%
n-Butane	15	22.186	45.3	103.8%	(101.1,106.4)	4.6%	(3.3,7.4)	3.8%
Acetylene	15	24.190	54.47	36.5%	(29.7,43.2)	33.3%	(20.6,64.4)	-63.5%
1-Butene	15	27.865	33.27	105.8%	(103.4,108.2)	4.1%	(3.0,6.7)	5.8%
Cyclopentane	15	30.333	23.16	96.0%	(94.0,98.0)	3.8%	(2.7,6.1)	-4.0%
Isopentane	15	30.401	42.09	107.5%	(104.5,110.5)	5.0%	(3.6,8.1)	7.5%
n-Pentane	15	31.289	27.7	104.5%	(101.7,107.3)	4.8%	(3.5,7.8)	4.5%

Figure A-24. Boxplots of the recoveries for the Propane group of the Rider 1997 retention time standard data by compound.

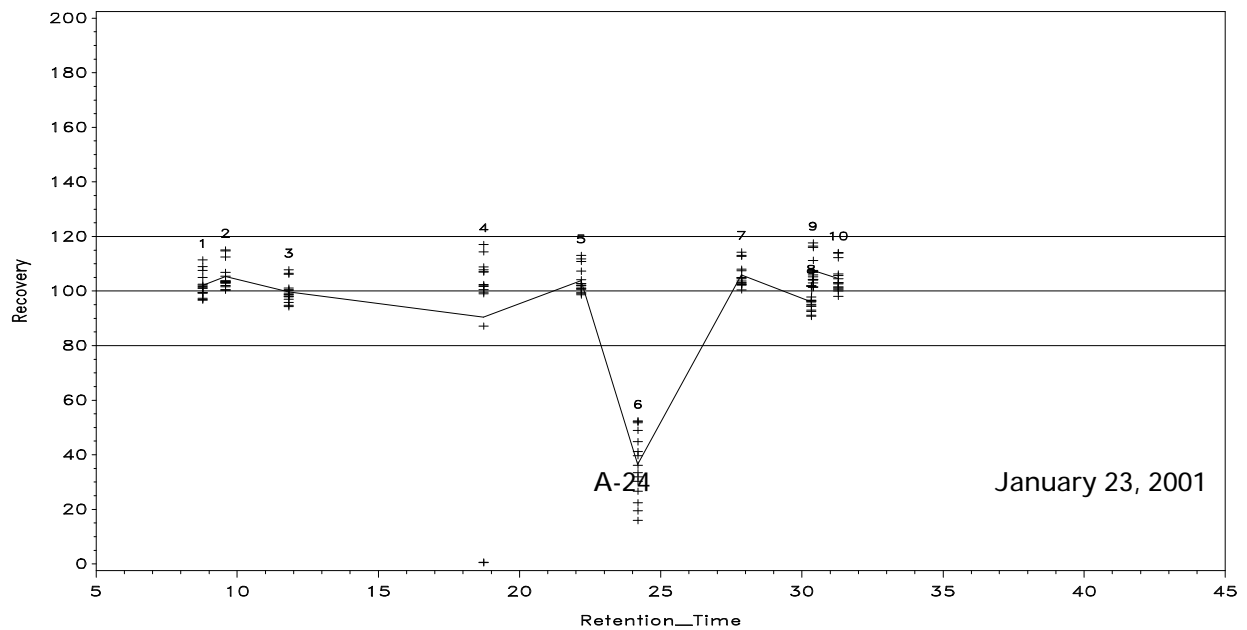




Mean Recovery:  
 1: n-Hexane 2: 2,4-Dimethylpentane 3: Benzene 4: 2-Methylhexane 5: Toluene 6: n-Octane 7: m/p-Xylene 8: o-Xylene 9: 1,2,4-Trimethylbenzene 10: n-Decane

Figure A-25. Scatter plot of the recoveries for the Benzene group of the Rider 1997 retention time standard data versus the retention time.

Figure A-26. Scatter plot of the recoveries for the Propane group of the Rider 1997 retention time standard data versus the retention time.



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Table A-20. Statistical summaries of the recoveries for the Benzene group of the Rider 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	14	14.500	30.1	101.3%	(100.0,102.6)	2.2%	(1.6,3.6)	1.3%
2,4-Dimethylpentane	14	17.186	39.9	104.7%	(103.2,106.1)	2.3%	(1.7,3.8)	4.7%
Benzene	14	18.997	30.03	97.9%	(96.4,99.3)	2.5%	(1.8,4.1)	-2.1%
2-Methylhexane	14	20.322	25.23	97.0%	(96.0,98.0)	1.8%	(1.3,3.0)	-3.0%
Toluene	14	26.974	38.85	113.0%	(110.9,115.1)	3.2%	(2.3,5.2)	13.0%
n-Octane	14	29.672	29.9	97.2%	(95.8,98.5)	2.5%	(1.8,4.0)	-2.8%
m/p-Xylene	14	33.279	39.43	84.5%	(75.5,93.5)	18.4%	(12.1,33.2)	-15.5%
o-Xylene	14	34.505	24.66	94.4%	(93.1,95.6)	2.3%	(1.7,3.8)	-5.6%
1,2,4-Trimethylbenzene	14	39.439	39.49	86.8%	(83.7,89.9)	6.2%	(4.3,10.3)	-13.2%
n-Decane	14	39.763	30.89	85.4%	(83.6,87.3)	3.7%	(2.6,6.1)	-14.6%

Figure A-27. Boxplots of the recoveries for the Benzene group of the Rider 1998 retention time standard data by compound.

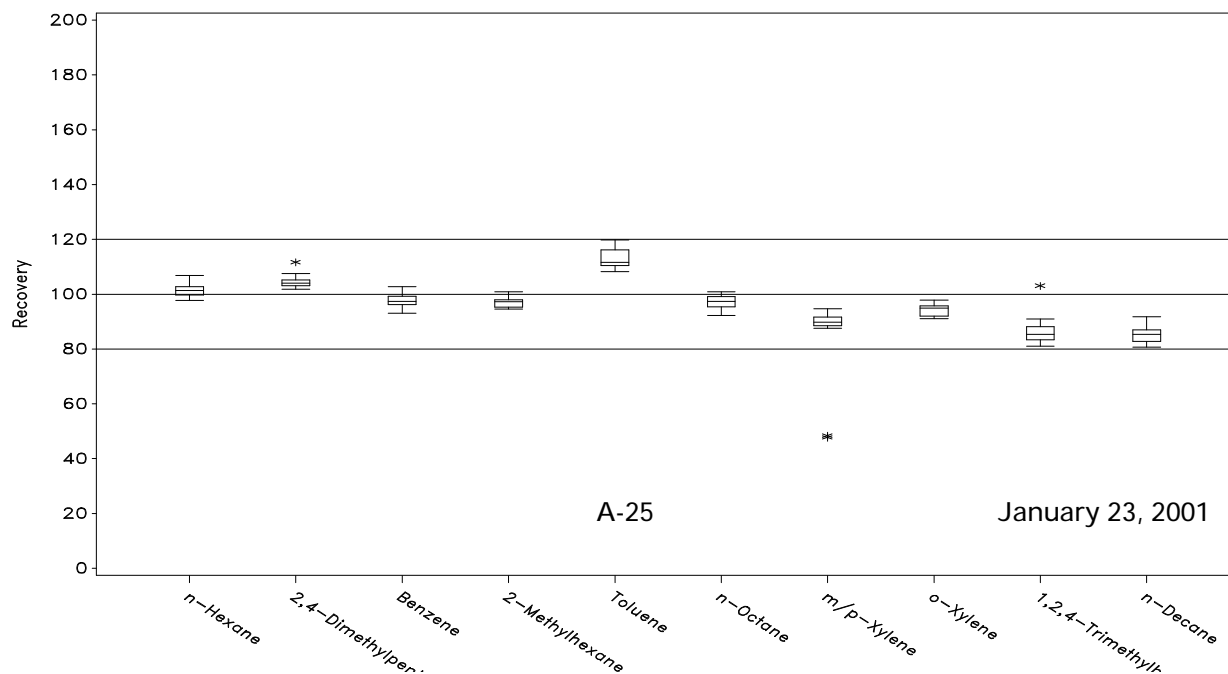
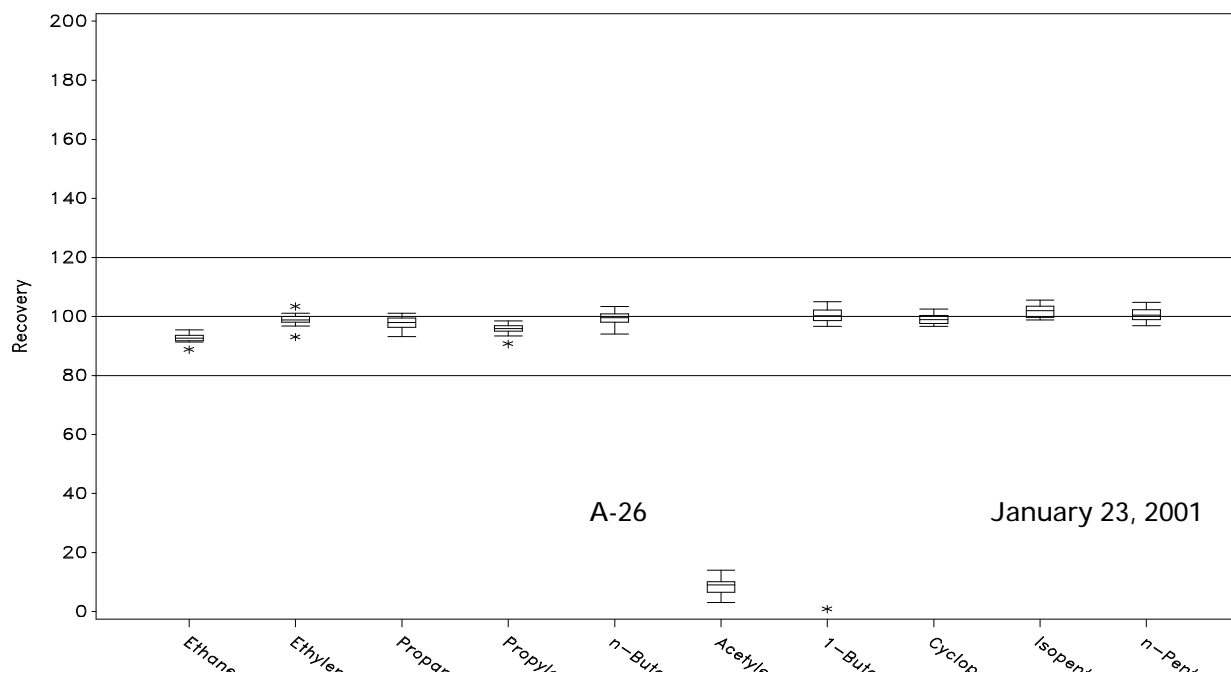
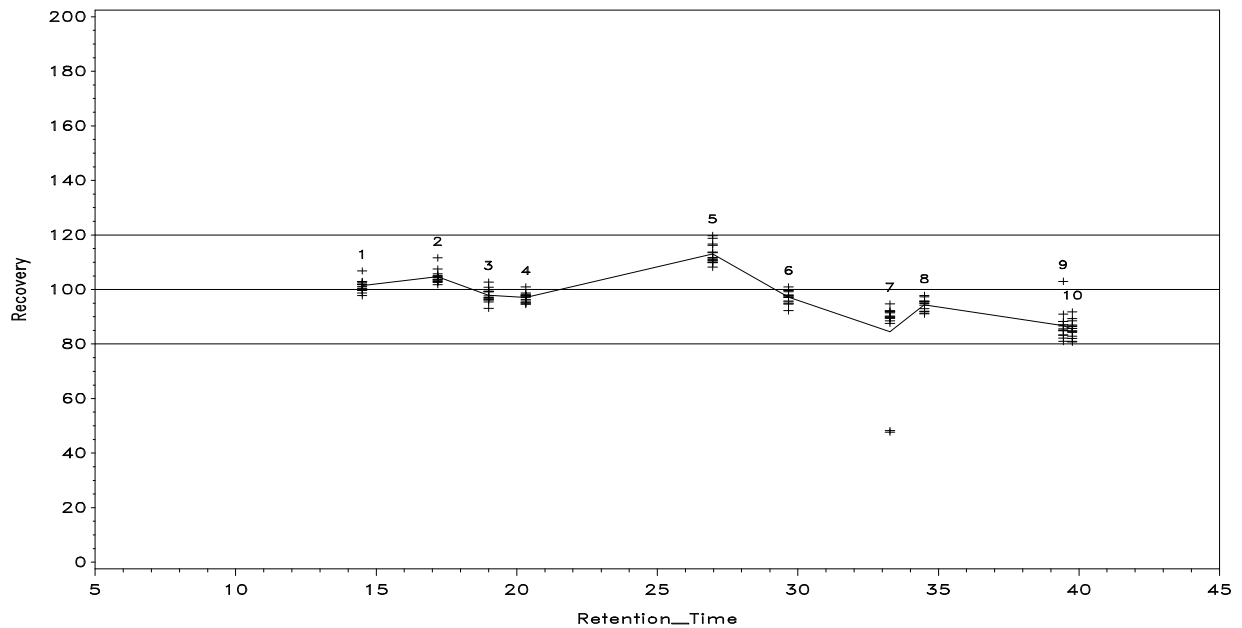


Table A-21. Statistical summaries of the recoveries for the Propane group of the Rider 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	14	8.254	28.8	92.7%	(91.7,93.6)	1.7%	(1.2,2.8)	-7.3%
Ethylene	14	9.118	26.84	98.9%	(97.6,100.3)	2.4%	(1.7,3.9)	-1.1%
Propane	14	11.442	43.27	97.8%	(96.5,99.1)	2.3%	(1.7,3.8)	-2.2%
Propylene	14	18.729	23.74	95.8%	(94.6,96.9)	2.1%	(1.5,3.4)	-4.2%
n-Butane	14	22.462	43.47	99.6%	(98.1,101.1)	2.6%	(1.9,4.3)	-0.4%
Acetylene	14	24.690	37.93	8.6%	(6.7,10.5)	38.1%	(22.7,78.8)	-91.4%
1-Butene	14	28.404	32.84	93.3%	(77.9,108.7)	28.6%	(17.8,55.2)	-6.7%
Cyclopentane	14	30.906	20.13	99.1%	(98.0,100.2)	1.9%	(1.4,3.2)	-0.9%
Isopentane	14	31.048	42.04	101.8%	(100.6,102.9)	2.0%	(1.4,3.2)	1.8%
n-Pentane	14	31.943	25.63	100.5%	(99.3,101.8)	2.1%	(1.5,3.5)	0.5%

Figure A-28. Boxplots of the recoveries for the Propane group of the Rider 1998 retention time standard data by compound.

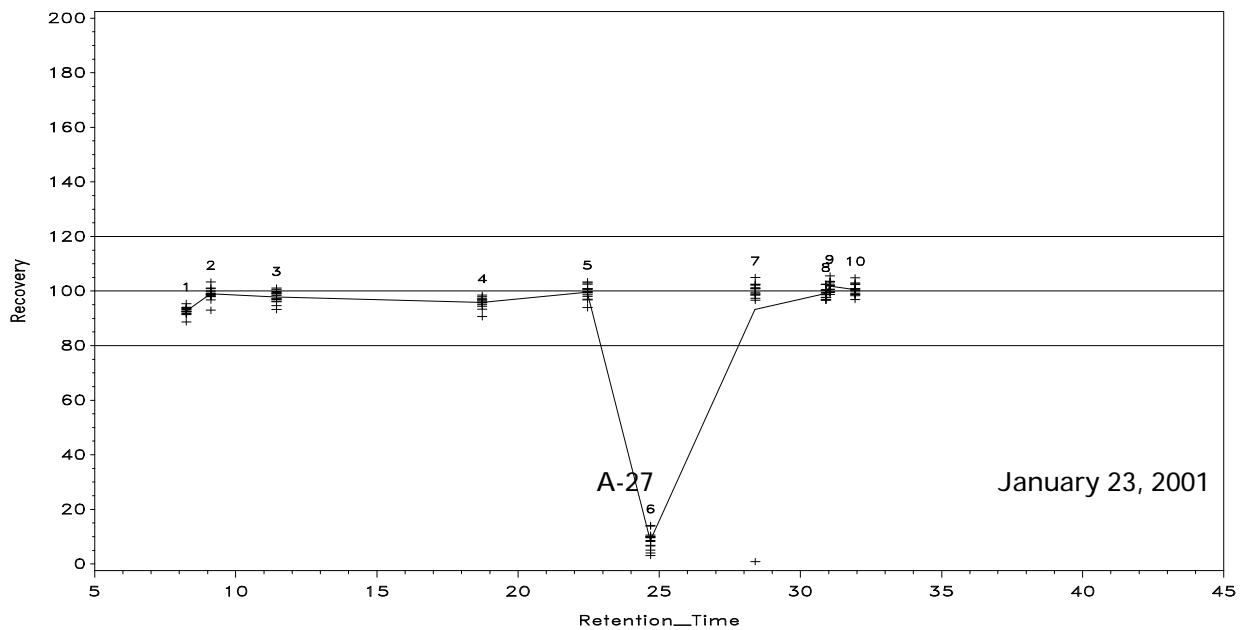




Mean Recovery:  
 1: n-Hexane 2: 2,4-Dimethylpentane 3: Benzene 4: 2-Methylhexane 5: Toluene 6: n-Octane 7: m/p-Xylene 8: o-Xylene 9: 1,2,4-Trimethylbenzene 10: n-Decane

Figure A-29. Scatter plot of the recoveries for the Benzene group of the Rider 1998 retention time standard data versus the retention time.

Figure A-30. Scatter plot of the recoveries for the Propane group of the Rider 1998 retention time standard data versus the retention time.



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Table A-22. Statistical summaries of the recoveries for the Benzene group of the Rutgers 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	11	14.135	35.37	102.2%	(100.6,103.8)	2.3%	(1.6,4.1)	2.2%
2,4-Dimethylpentane	11	16.865	46.31	106.2%	(103.9,108.6)	3.3%	(2.2,5.9)	6.2%
Benzene	11	18.715	36.02	95.8%	(93.5,98.1)	3.5%	(2.4,6.4)	-4.2%
2-Methylhexane	11	20.078	29.31	95.7%	(91.4,99.9)	6.7%	(4.4,12.2)	-4.3%
Toluene	11	26.833	45.14	97.6%	(95.5,99.8)	3.3%	(2.3,5.9)	-2.4%
n-Octane	11	29.577	34.88	98.0%	(95.1,101.0)	4.5%	(3.1,8.2)	-2.0%
m/p-Xylene	11	33.184	45.15	61.5%	(40.8,82.3)	50.1%	(26.2,132.6)	-38.5%
o-Xylene	11	34.446	28.03	98.2%	(95.5,101.0)	4.2%	(2.8,7.5)	-1.8%
1,2,4-Trimethylbenzene	11	39.429	42.42	91.5%	(88.9,94.2)	4.3%	(2.9,7.8)	-8.5%
n-Decane	11	39.763	34.73	92.6%	(89.2,95.9)	5.4%	(3.6,9.8)	-7.4%

Figure A-31. Boxplots of the recoveries for the Benzene group of the Rutgers 1996 retention time standard data by compound.

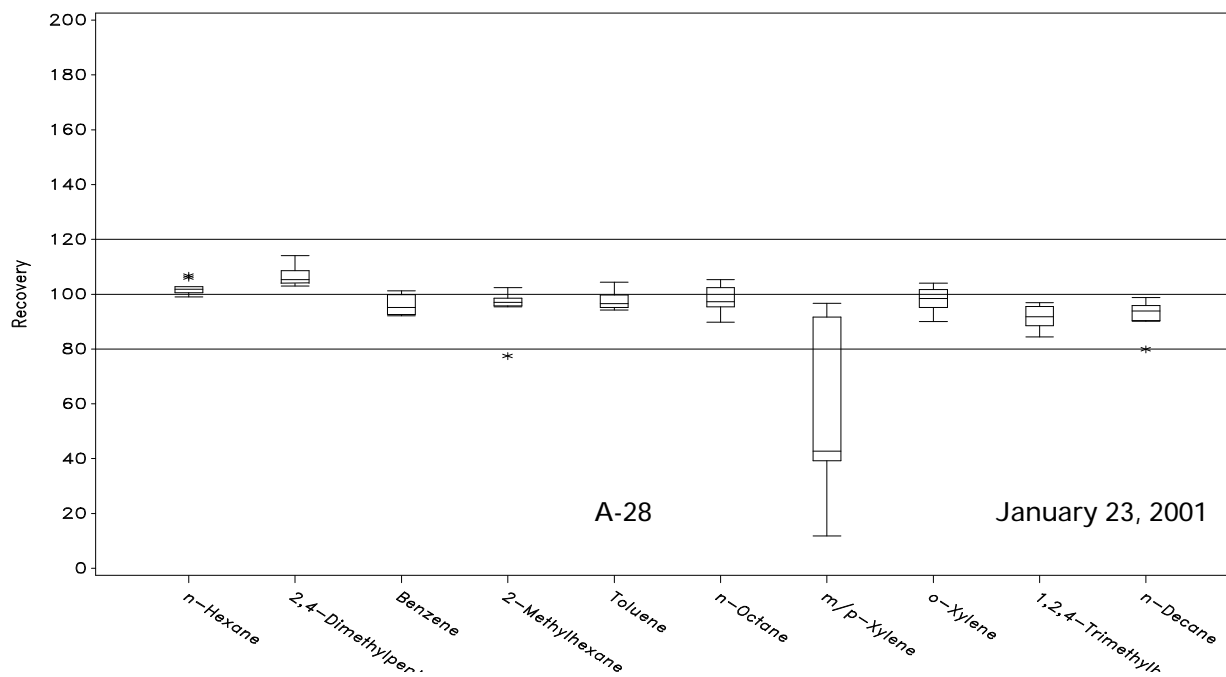
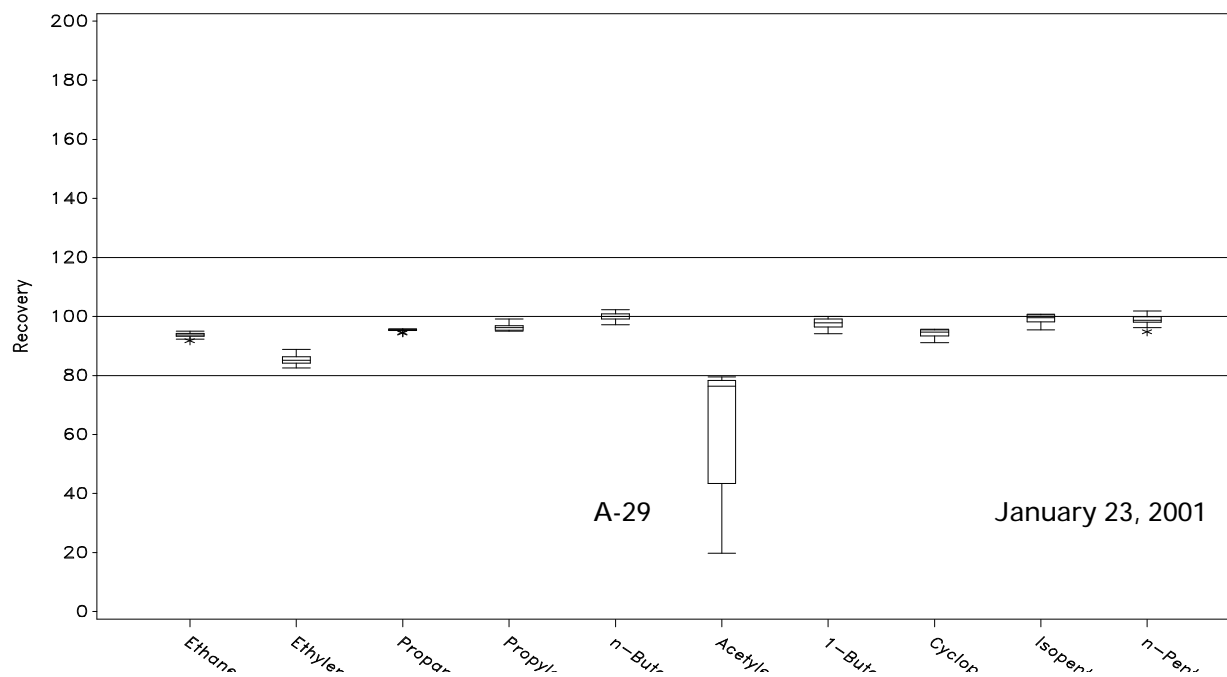


Table A-23. Statistical summaries of the recoveries for the Propane group of the Rutgers 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	11	8.365	29.06	93.6%	(93.0,94.3)	1.0%	(0.7,1.8)	-6.4%
Ethylene	11	9.295	23.82	85.3%	(84.2,86.4)	1.9%	(1.3,3.4)	-14.7%
Propane	11	11.751	46.13	95.3%	(95.0,95.6)	0.5%	(0.3,0.9)	-4.7%
Propylene	11	19.325	26.7	96.3%	(95.5,97.2)	1.3%	(0.9,2.3)	-3.7%
n-Butane	11	23.078	43.62	99.9%	(99.0,100.8)	1.4%	(0.9,2.4)	-0.1%
Acetylene	11	24.915	48.03	65.0%	(50.5,79.5)	33.1%	(18.9,74.7)	-35.0%
1-Butene	11	28.908	32.47	97.6%	(96.4,98.9)	1.9%	(1.3,3.3)	-2.4%
Cyclopentane	11	31.442	24.11	94.2%	(93.2,95.1)	1.5%	(1.0,2.7)	-5.8%
Isopentane	11	31.605	47.25	99.0%	(97.8,100.1)	1.8%	(1.2,3.2)	-1.0%
n-Pentane	11	32.494	29.87	98.6%	(97.3,100.0)	2.0%	(1.4,3.6)	-1.4%

Figure A-32. Boxplots of the recoveries for the Propane group of the Rutgers 1996 retention time standard data by compound.



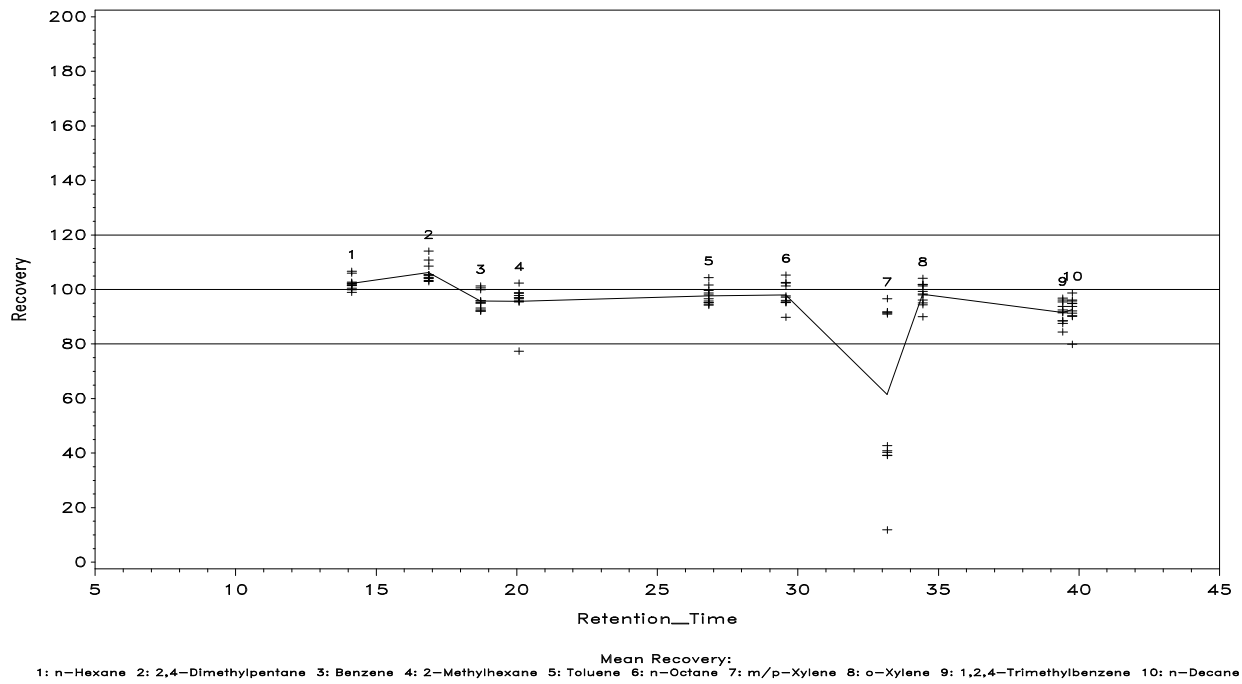


Figure A-33. Scatter plot of the recoveries for the Benzene group of the Rutgers 1996 retention time standard data versus the retention time.

Figure A-34. Scatter plot of the recoveries for the Propane group of the Rutgers 1996 retention time standard data versus the retention time.

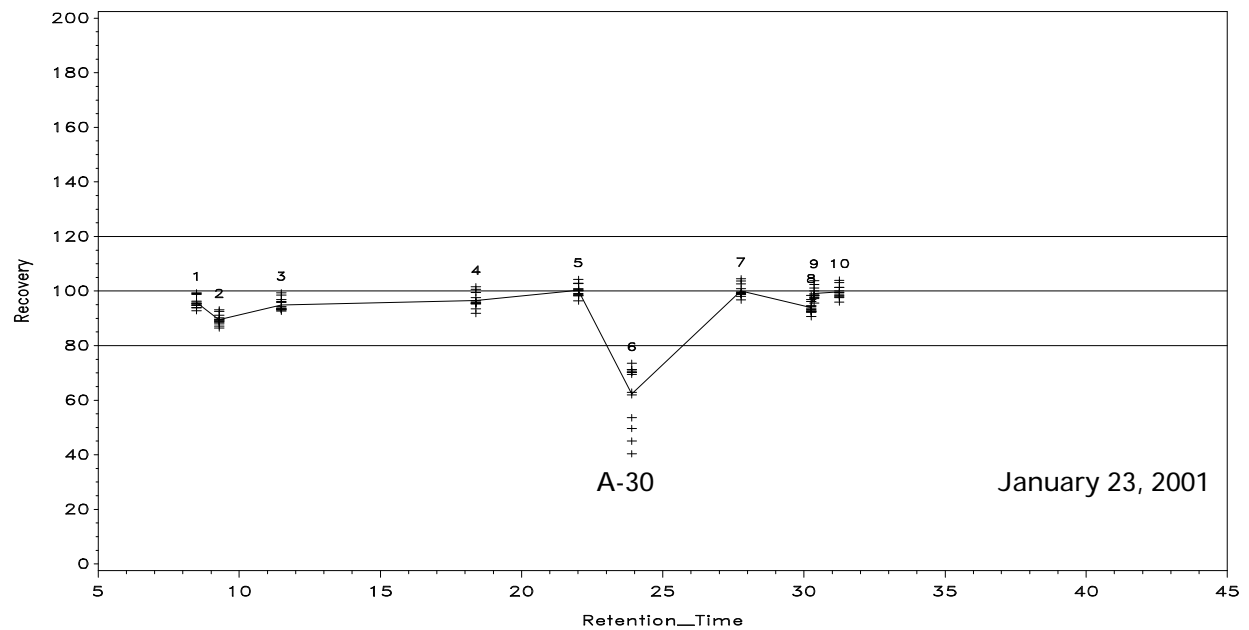


Table A-24. Statistical summaries of the recoveries for the Benzene group of the Rutgers 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	21	14.710	33.64	115.6%	(108.9,122.2)	12.7%	(9.2,19.4)	15.6%
2,4-Dimethylpentane	21	17.405	45.17	113.6%	(108.7,118.4)	9.4%	(6.9,14.2)	13.6%
Benzene	21	19.230	35.27	103.2%	(98.3,108.0)	10.3%	(7.5,15.6)	3.2%
2-Methylhexane	21	20.567	28.42	96.9%	(92.7,101.1)	9.5%	(7.0,14.3)	-3.1%
Toluene	21	27.269	43	95.7%	(91.6,99.9)	9.5%	(7.0,14.4)	-4.3%
n-Octane	21	29.980	32.32	95.5%	(91.4,99.6)	9.5%	(7.0,14.3)	-4.5%
m/p-Xylene	21	33.611	42.67	81.9%	(73.4,90.5)	22.9%	(15.9,37.0)	-18.1%
o-Xylene	21	34.847	27.25	90.9%	(87.0,94.9)	9.5%	(7.0,14.4)	-9.1%
1,2,4-Trimethylbenzene	21	39.823	40.96	91.6%	(87.9,95.3)	8.9%	(6.5,13.4)	-8.4%
n-Decane	21	40.148	30.28	99.4%	(95.2,103.6)	9.2%	(6.8,13.9)	-0.6%

Figure A-35. Boxplots of the recoveries for the Benzene group of the Rutgers 1997 retention time standard data by compound.

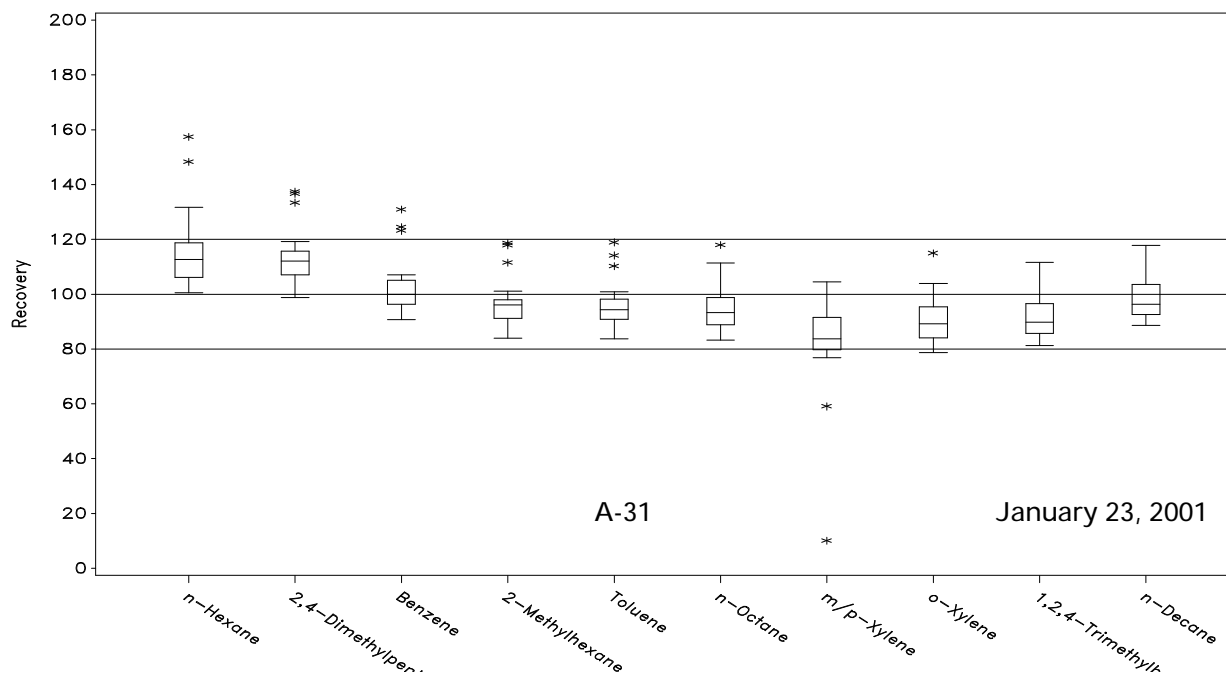
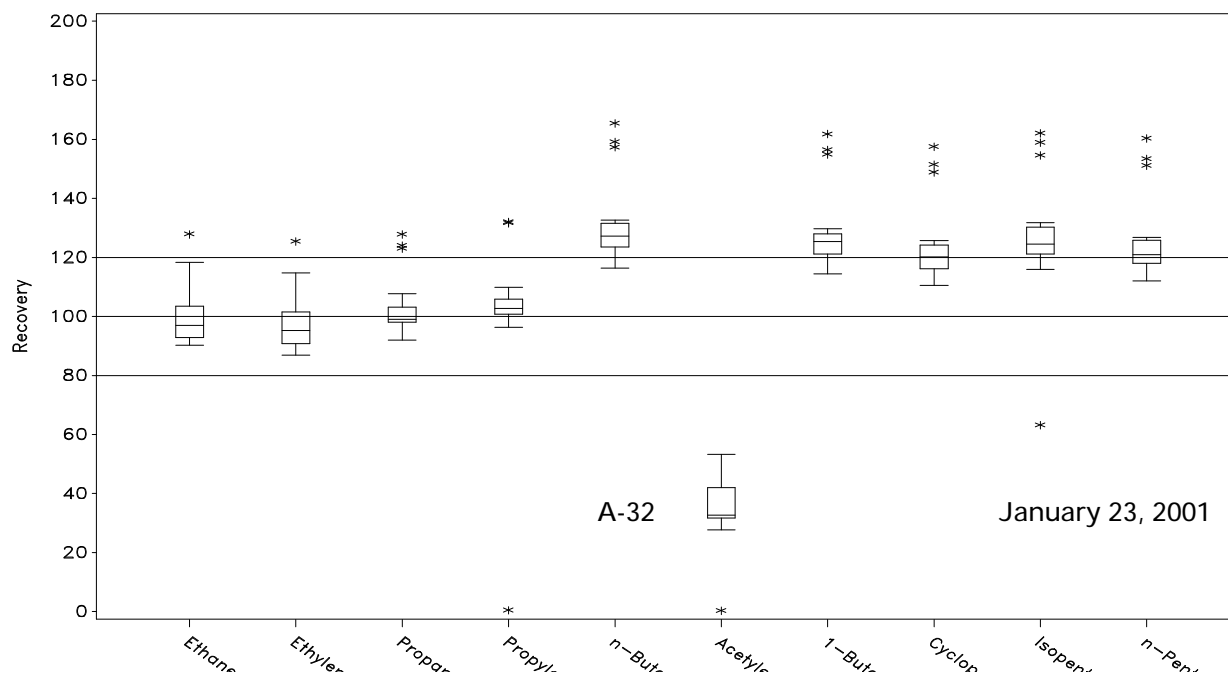


Table A-25. Statistical summaries of the recoveries for the Propane group of the Rutgers 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	21	8.439	29.42	99.7%	(95.2,104.2)	9.9%	(7.2,14.9)	-0.3%
Ethylene	21	9.318	22.1	97.8%	(93.3,102.2)	10.1%	(7.4,15.2)	-2.2%
Propane	21	11.698	47.3	102.6%	(98.0,107.2)	9.8%	(7.2,14.9)	2.6%
Propylene	21	19.070	26.4	100.7%	(89.4,112.0)	24.6%	(16.9,40.0)	0.7%
n-Butane	21	22.750	45.3	130.9%	(124.9,136.9)	10.0%	(7.4,15.2)	30.9%
Acetylene	21	24.547	54.47	35.1%	(30.1,40.1)	31.1%	(20.8,52.3)	-64.9%
1-Butene	21	28.550	33.27	128.1%	(122.2,134.1)	10.1%	(7.4,15.3)	28.1%
Cyclopentane	20	31.074	23.16	123.8%	(117.7,129.9)	10.5%	(7.6,16.2)	23.8%
Isopentane	21	31.201	42.09	126.5%	(117.7,135.3)	15.3%	(10.9,23.8)	26.5%
n-Pentane	21	32.099	27.7	125.2%	(119.2,131.2)	10.5%	(7.7,16.0)	25.2%

Figure A-36. Boxplots of the recoveries for the Propane group of the Rutgers 1997 retention time standard data by compound.



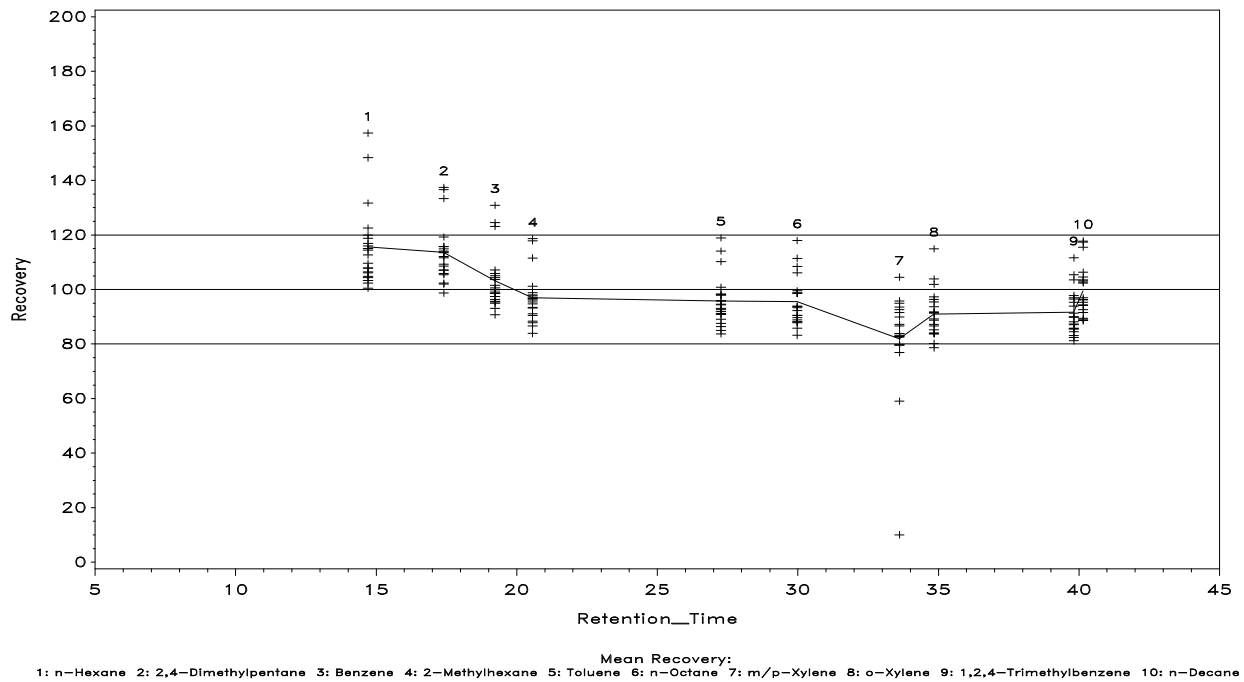


Figure A-37. Scatter plot of the recoveries for the Benzene group of the Rutgers 1997 retention time standard data versus the retention time.

Figure A-38. Scatter plot of the recoveries for the Propane group of the Rutgers 1997 retention time standard data versus the retention time.

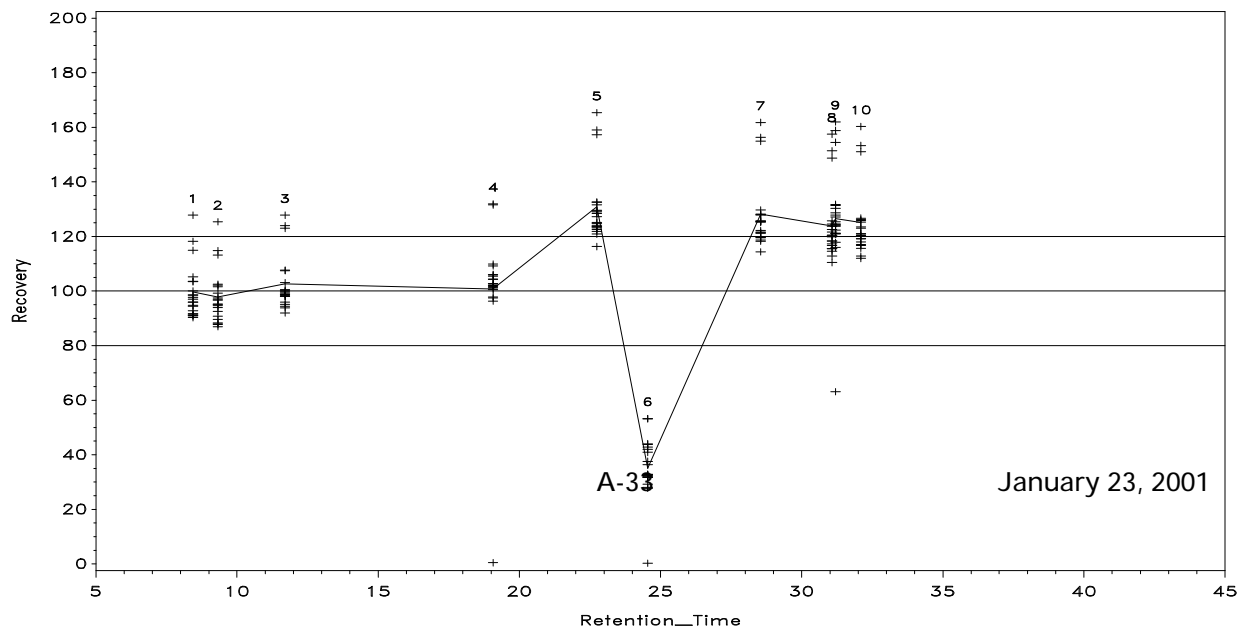


Table A-26. Statistical summaries of the recoveries for the Benzene group of the Rutgers 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	16	13.114	30.1	111.3%	(100.5,122.2)	18.3%	(12.3,31.4)	11.3%
2,4-Dimethylpentane	16	15.826	39.9	103.8%	(102.4,105.3)	2.6%	(1.9,4.1)	3.8%
Benzene	16	17.701	30.03	98.5%	(97.1,99.9)	2.7%	(2.0,4.3)	-1.5%
2-Methylhexane	16	19.121	25.23	95.8%	(94.7,96.9)	2.2%	(1.6,3.4)	-4.2%
Toluene	16	25.896	38.85	114.7%	(112.8,116.7)	3.2%	(2.3,5.1)	14.7%
n-Octane	16	28.666	29.9	99.6%	(98.5,100.6)	1.9%	(1.4,3.0)	-0.4%
m/p-Xylene	16	32.241	39.43	70.6%	(59.2,82.0)	30.4%	(19.3,56.1)	-29.4%
o-Xylene	16	33.454	24.66	97.6%	(96.0,99.1)	2.9%	(2.1,4.6)	-2.4%
1,2,4-Trimethylbenzene	16	38.371	39.49	92.8%	(91.4,94.2)	2.8%	(2.0,4.4)	-7.2%
n-Decane	16	38.739	30.89	95.7%	(94.0,97.3)	3.2%	(2.3,5.0)	-4.3%

Figure A-39. Boxplots of the recoveries for the Benzene group of the Rutgers 1998 retention time standard data by compound.

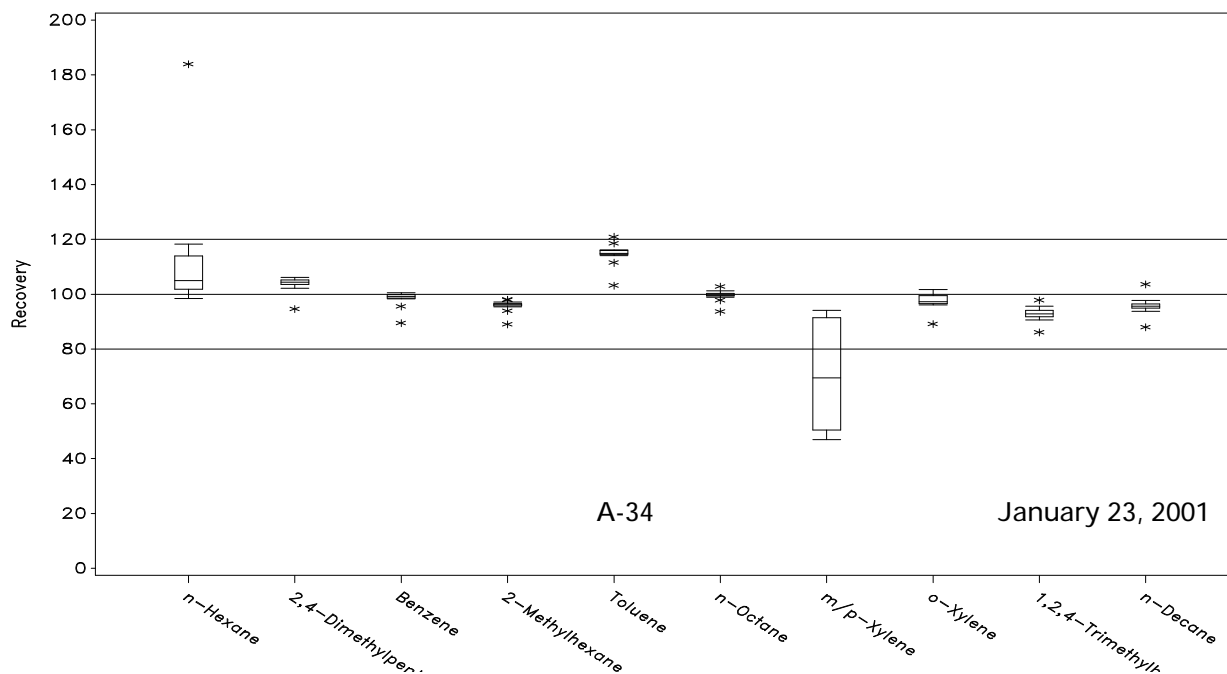
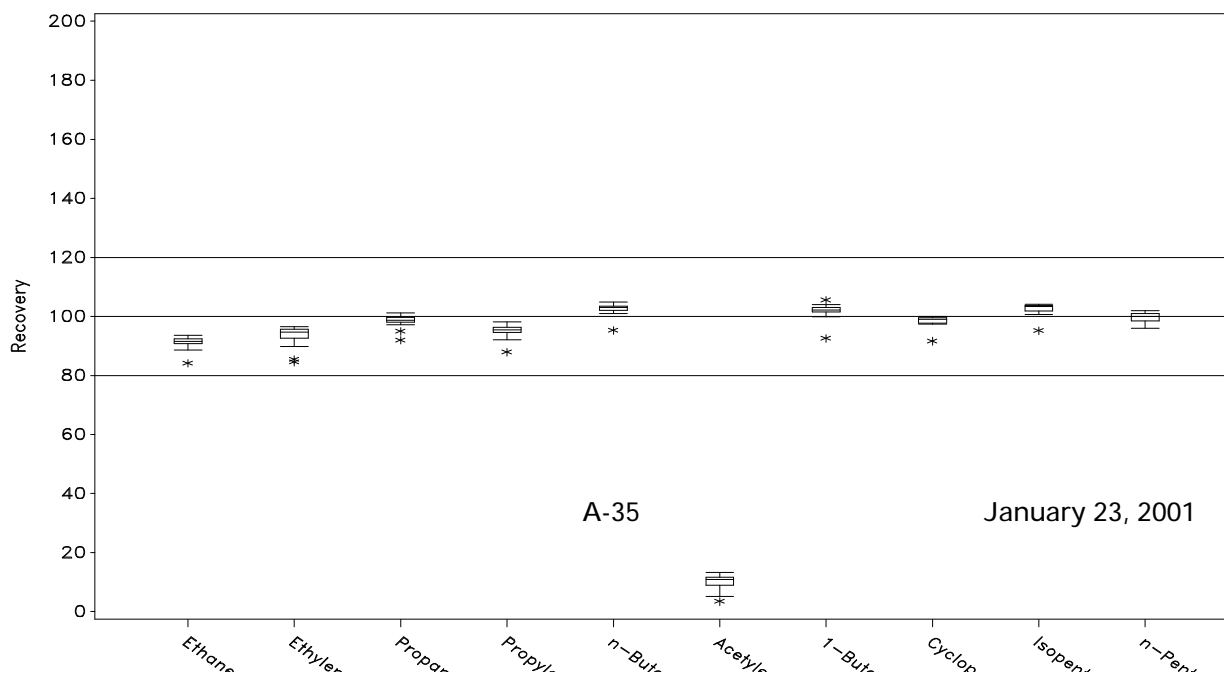
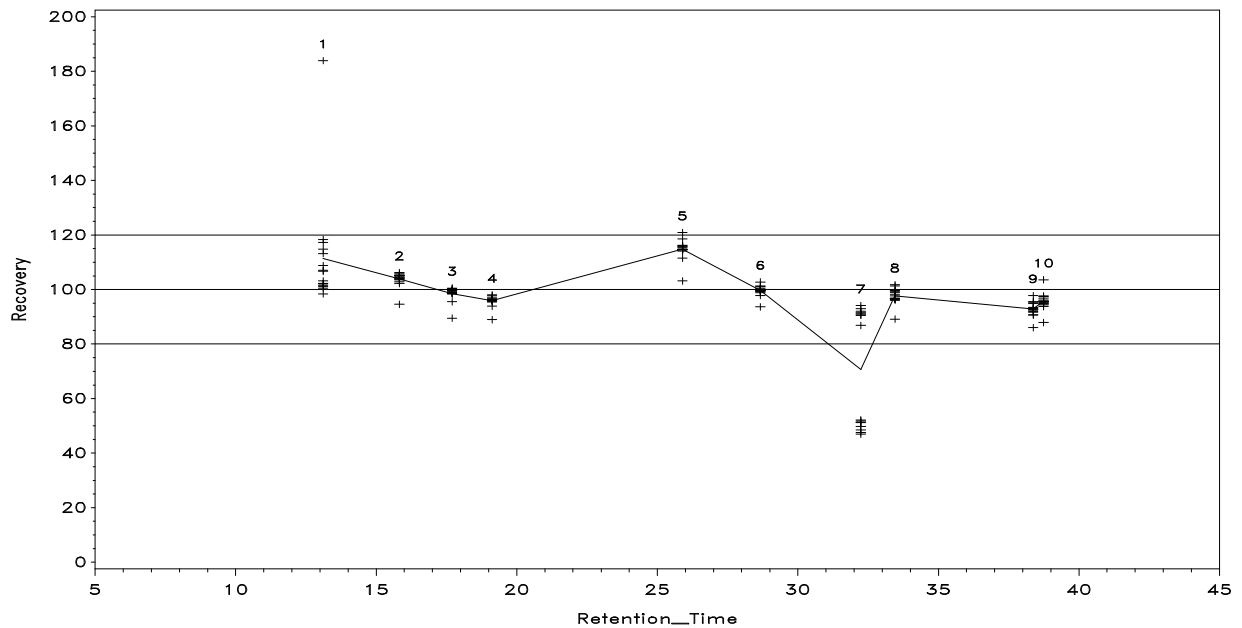


Table A-27. Statistical summaries of the recoveries for the Propane group of the Rutgers 1998 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	16	7.653	28.8	91.1%	(89.9,92.3)	2.5%	(1.8,4.0)	-8.9%
Ethylene	16	8.487	26.84	93.2%	(91.2,95.1)	3.9%	(2.8,6.2)	-6.8%
Propane	16	10.734	43.27	98.4%	(97.2,99.6)	2.3%	(1.7,3.6)	-1.6%
Propylene	16	18.359	23.74	95.0%	(93.7,96.2)	2.5%	(1.8,3.9)	-5.0%
n-Butane	16	22.276	43.47	102.4%	(101.2,103.6)	2.1%	(1.6,3.3)	2.4%
Acetylene	16	24.446	37.93	9.9%	(8.5,11.4)	27.7%	(17.8,50.3)	-90.1%
1-Butene	16	28.370	32.84	101.8%	(100.3,103.3)	2.7%	(2.0,4.3)	1.8%
Cyclopentane	16	30.870	20.13	98.3%	(97.3,99.4)	2.0%	(1.5,3.2)	-1.7%
Isopentane	16	31.061	42.04	102.4%	(101.2,103.6)	2.2%	(1.6,3.4)	2.4%
n-Pentane	16	31.951	25.63	99.7%	(98.8,100.6)	1.7%	(1.2,2.6)	-0.3%

Figure A-40. Boxplots of the recoveries for the Propane group of the Rutgers 1998 retention time standard data by compound.

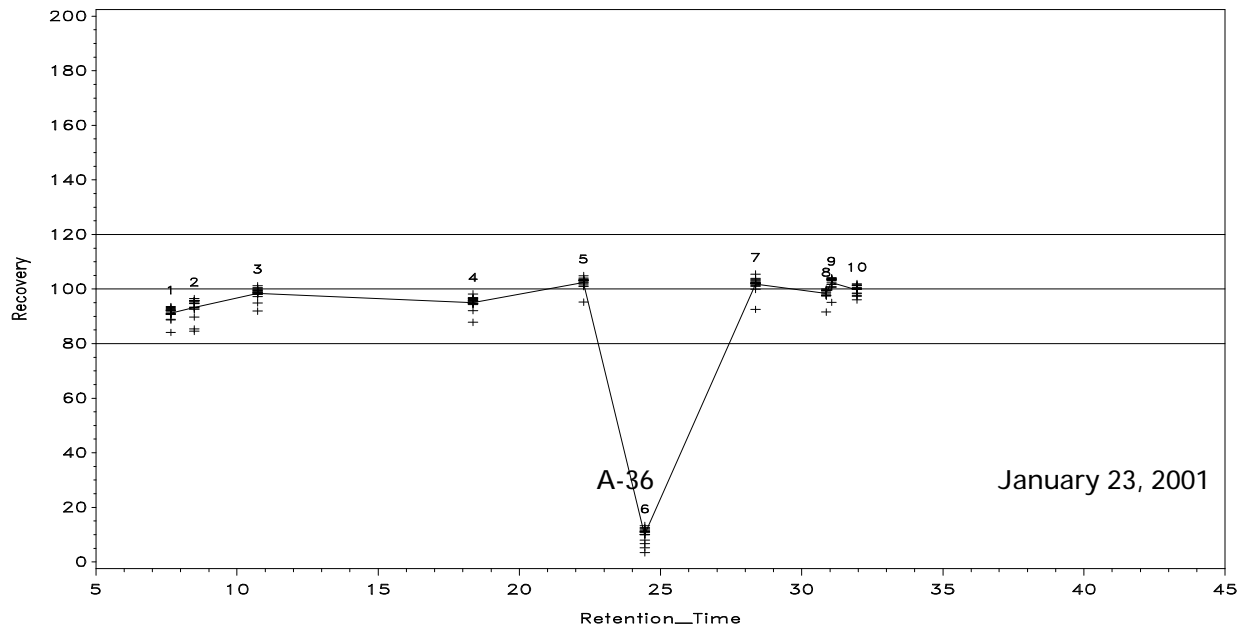




Mean Recovery:  
 1: n-Hexane 2: 2,4-Dimethylpentane 3: Benzene 4: 2-Methylhexane 5: Toluene 6: n-Octane 7: m/p-Xylene 8: o-Xylene 9: 1,2,4-Trimethylbenzene 10: n-Decane

Figure A-41. Scatter plot of the recoveries for the Benzene group of the Rutgers 1998 retention time standard data versus the retention time.

Figure A-42. Scatter plot of the recoveries for the Propane group of the Rutgers 1998 retention time standard data versus the retention time.



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Table A-28. Statistical summaries of the recoveries for the Benzene group of the Bronx Garden 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	25	.	41.8	90.7%	(88.6,92.8)	5.6%	(4.2,7.9)	-9.3%
2,4-Dimethylpentane	25	.	44.9	100.1%	(99.6,100.7)	1.4%	(1.1,2.0)	0.1%
Benzene	25	.	34.4	99.7%	(98.8,100.6)	2.2%	(1.7,3.1)	-0.3%
2-Methylhexane	25	.	28.3	99.6%	(99.0,100.3)	1.6%	(1.2,2.2)	-0.4%
Toluene	25	.	43.6	99.5%	(98.7,100.3)	1.9%	(1.4,2.6)	-0.5%
n-Octane	25	.	33.9	99.8%	(98.9,100.6)	2.1%	(1.6,2.9)	-0.2%
m/p-Xylene	25	.	43.8	100.0%	(99.2,100.8)	1.9%	(1.5,2.7)	-0.0%
o-Xylene	25	.	27.2	100.4%	(99.5,101.3)	2.3%	(1.7,3.2)	0.4%
1,2,4-Trimethylbenzene	25	.	41.3	98.1%	(96.8,99.4)	3.2%	(2.5,4.5)	-1.9%
n-Decane	25	.	33.8	98.3%	(96.9,99.7)	3.5%	(2.7,4.9)	-1.7%

Figure A-43. Boxplots of the recoveries for the Benzene group of the Bronx Garden 1996 retention time standard data by compound.

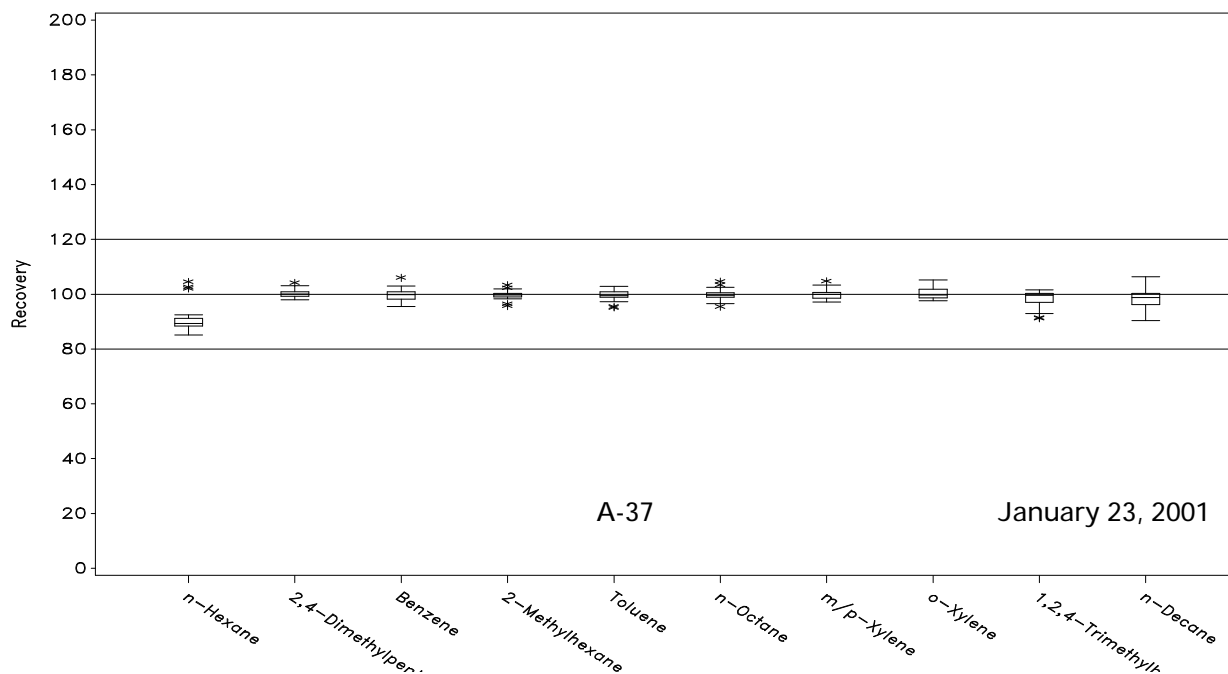


Table A-29. Statistical summaries of the recoveries for the Propane group of the Bronx Garden 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	25	.	29.4	100.4%	(99.1,101.7)	3.1%	(2.4,4.4)	0.4%
Ethylene	25	.	23.8	99.9%	(98.5,101.3)	3.4%	(2.7,4.9)	-0.1%
Propane	25	.	45	100.6%	(99.3,101.8)	3.0%	(2.3,4.3)	0.6%
Propylene	25	.	26.1	100.3%	(98.4,102.1)	4.5%	(3.5,6.4)	0.3%
n-Butane	25	.	43.4	100.2%	(98.7,101.7)	3.6%	(2.8,5.1)	0.2%
Acetylene	25	.	48	39.9%	(27.5,52.3)	75.2%	(44.8,151.8)	-60.1%
1-Butene	25	.	31.8	100.2%	(98.7,101.7)	3.7%	(2.8,5.2)	0.2%
Cyclopentane	3	.	23.4	109.9%	(108.2,111.7)	0.6%	(0.3,4.1)	9.9%
Isopentane	25	.	45.5	78.0%	(73.4,82.6)	14.3%	(10.5,21.1)	-22.0%
n-Pentane	25	.	29	58.7%	(50.8,66.6)	32.6%	(22.4,52.3)	-41.3%

Figure A-44. Boxplots of the recoveries for the Propane group of the Bronx Garden 1996 retention time standard data by compound.

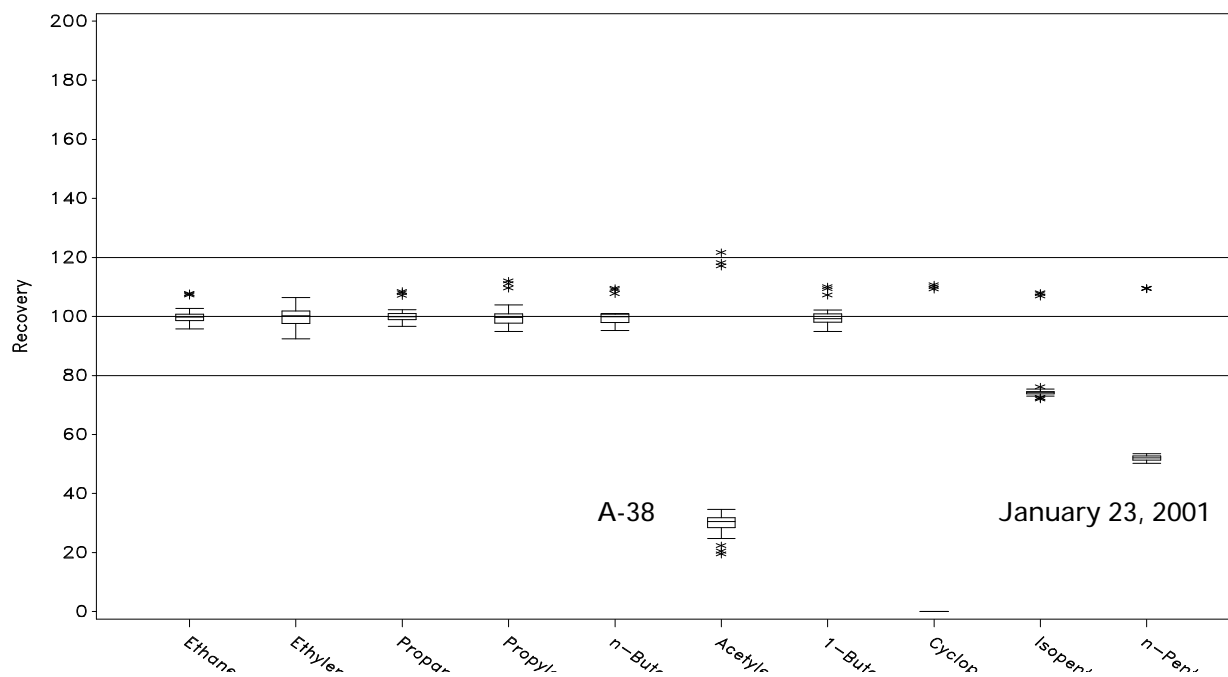


Table A-30. Statistical summaries of the recoveries for the Benzene group of the Washington, DC 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	6	.	33.71	104.5%	(86.8,122.2)	16.1%	(8.6,47.6)	4.5%
2,4-Dimethylpentane	6	.	44.92	102.6%	(87.2,118.1)	14.3%	(7.8,41.4)	2.6%
Benzene	6	.	34.27	95.0%	(80.3,109.7)	14.8%	(8.0,42.9)	-5.0%
2-Methylhexane	6	.	28.08	91.2%	(72.4,110.0)	19.6%	(10.2,60.6)	-8.8%
Toluene	6	.	43.3	94.9%	(79.4,110.4)	15.6%	(8.4,45.8)	-5.1%
n-Octane	6	.	33.35	98.2%	(80.2,116.2)	17.5%	(9.2,52.5)	-1.8%
m/p-Xylene	6	.	43.16	70.5%	(54.5,86.5)	21.6%	(11.0,68.4)	-29.5%
o-Xylene	6	.	26.91	97.7%	(83.6,111.7)	13.8%	(7.5,39.4)	-2.3%
1,2,4-Trimethylbenzene	6	.	40.17	95.2%	(81.5,108.9)	13.7%	(7.5,39.3)	-4.8%
n-Decane	6	.	33.21	89.0%	(70.3,107.7)	20.0%	(10.3,62.1)	-11.0%

Figure A-45. Boxplots of the recoveries for the Benzene group of the Washington, DC 1996 retention time standard data by compound.

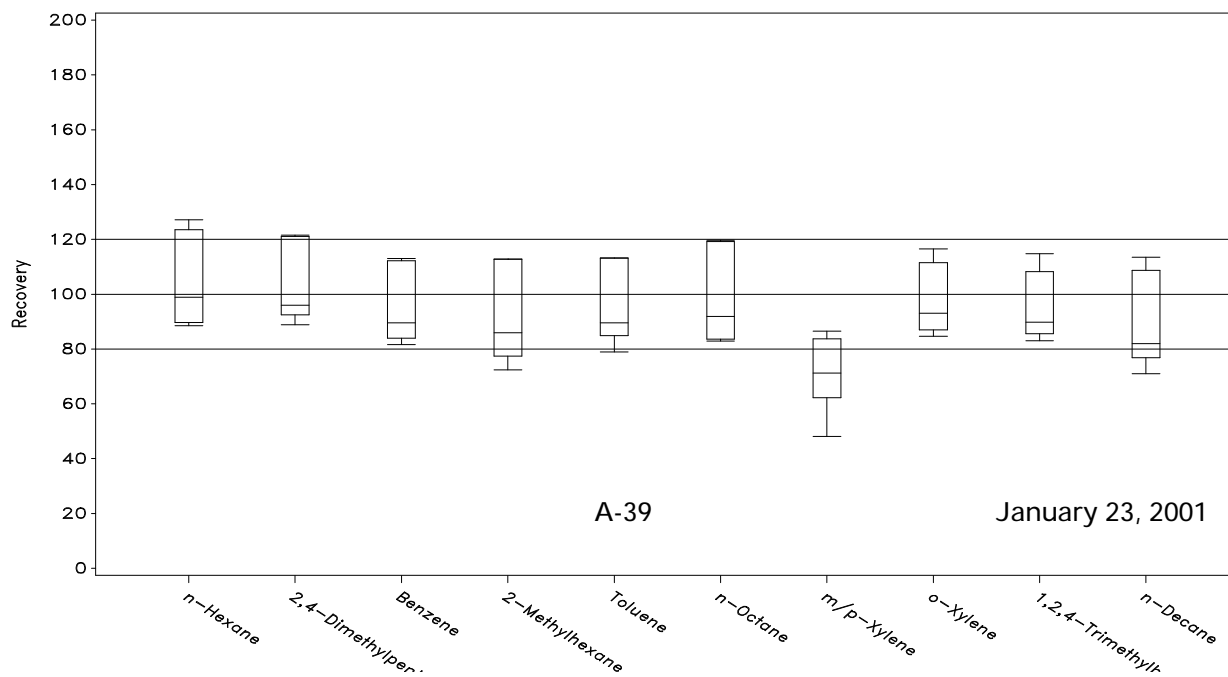


Table A-31. Statistical summaries of the recoveries for the Propane group of the Washington, DC 1996 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	5	.	28.92	91.7%	(78.3,105.0)	11.7%	(6.1,39.5)	-8.3%
Ethylene	5	.	23.83	83.7%	(70.1,97.3)	13.1%	(6.8,45.0)	-16.3%
Propane	5	.	45.73	93.3%	(79.5,107.1)	11.9%	(6.2,40.3)	-6.7%
Propylene	5	.	26.43	93.9%	(79.9,107.9)	12.0%	(6.3,40.6)	-6.1%
n-Butane	5	.	44.08	99.4%	(84.3,114.5)	12.2%	(6.4,41.4)	-0.6%
Acetylene	5	.	46.88	45.0%	(24.2,65.8)	37.2%	(15.3,199.1)	-55.0%
1-Butene	5	.	32.27	101.5%	(85.0,118.1)	13.1%	(6.8,45.1)	1.5%
Cyclopentane	5	.	23.03	94.7%	(78.4,111.0)	13.9%	(7.1,48.1)	-5.3%
Isopentane	5	.	44.77	99.5%	(82.9,116.1)	13.4%	(6.9,46.4)	-0.5%
n-Pentane	5	.	28.55	98.4%	(80.7,116.1)	14.5%	(7.3,50.7)	-1.6%

Figure A-46. Boxplots of the recoveries for the Propane group of the Washington, DC 1996 retention time standard data by compound.

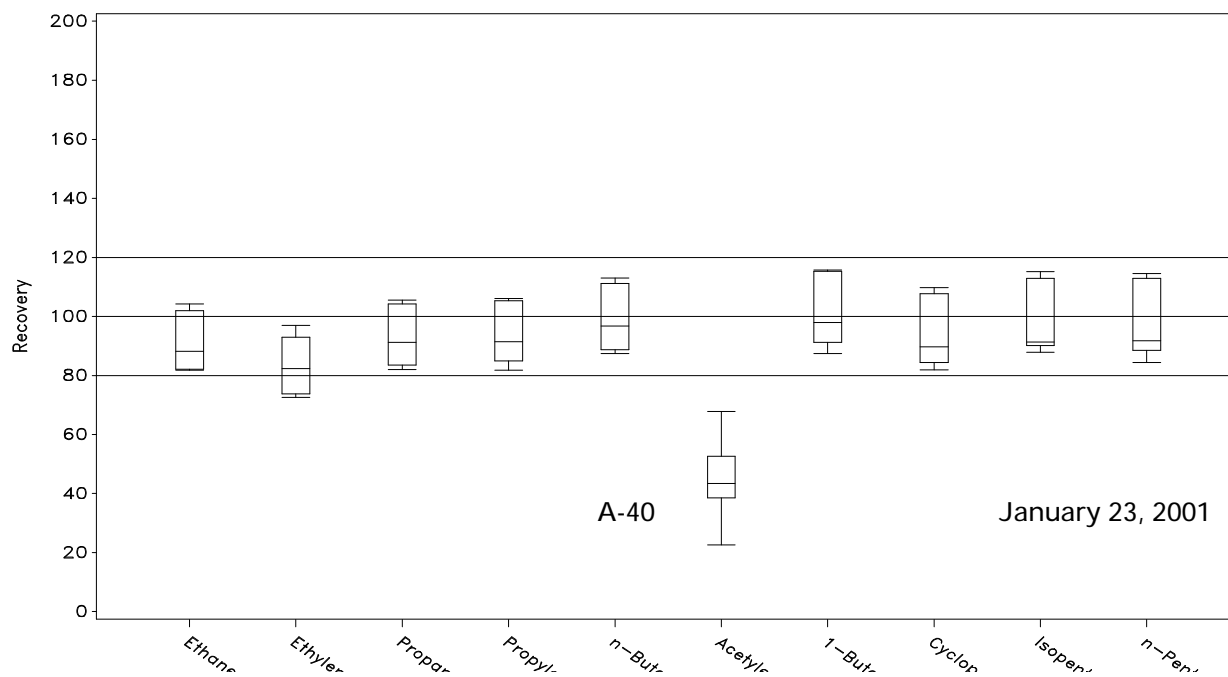


Table A-32. Statistical summaries of the recoveries for the Benzene group of the Washington, DC 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
n-Hexane	16	.	32.59	106.6%	(102.4,110.9)	7.5%	(5.3,12.1)	6.6%
2,4-Dimethylpentane	16	.	43.95	115.1%	(106.2,124.1)	14.6%	(10.0,24.5)	15.1%
Benzene	16	.	34.57	97.8%	(95.4,100.1)	4.5%	(3.2,7.1)	-2.2%
2-Methylhexane	16	.	27.57	87.5%	(75.8,99.1)	25.0%	(16.3,44.6)	-12.5%
Toluene	16	.	42.34	98.4%	(95.8,101.1)	5.1%	(3.6,8.0)	-1.6%
n-Octane	16	.	31.7	99.0%	(93.8,104.2)	9.8%	(6.9,16.1)	-1.0%
m/p-Xylene	16	.	42.59	86.8%	(78.3,95.3)	18.4%	(12.3,31.5)	-13.2%
o-Xylene	16	.	27.12	99.6%	(94.9,104.4)	8.9%	(6.3,14.5)	-0.4%
1,2,4-Trimethylbenzene	16	.	41.37	96.1%	(90.8,101.5)	10.4%	(7.3,17.1)	-3.9%
n-Decane	16	.	30.14	94.9%	(89.7,100.2)	10.4%	(7.3,17.0)	-5.1%

Figure A-47. Boxplots of the recoveries for the Benzene group of the Washington, DC 1997 retention time standard data by compound.

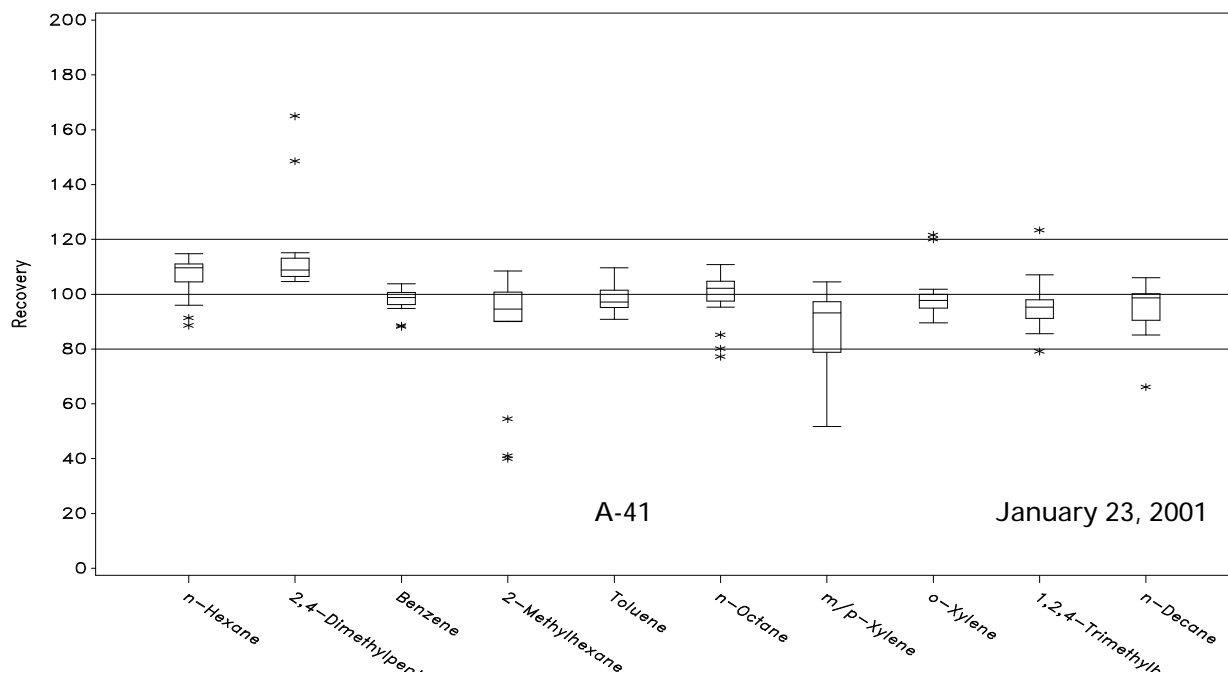
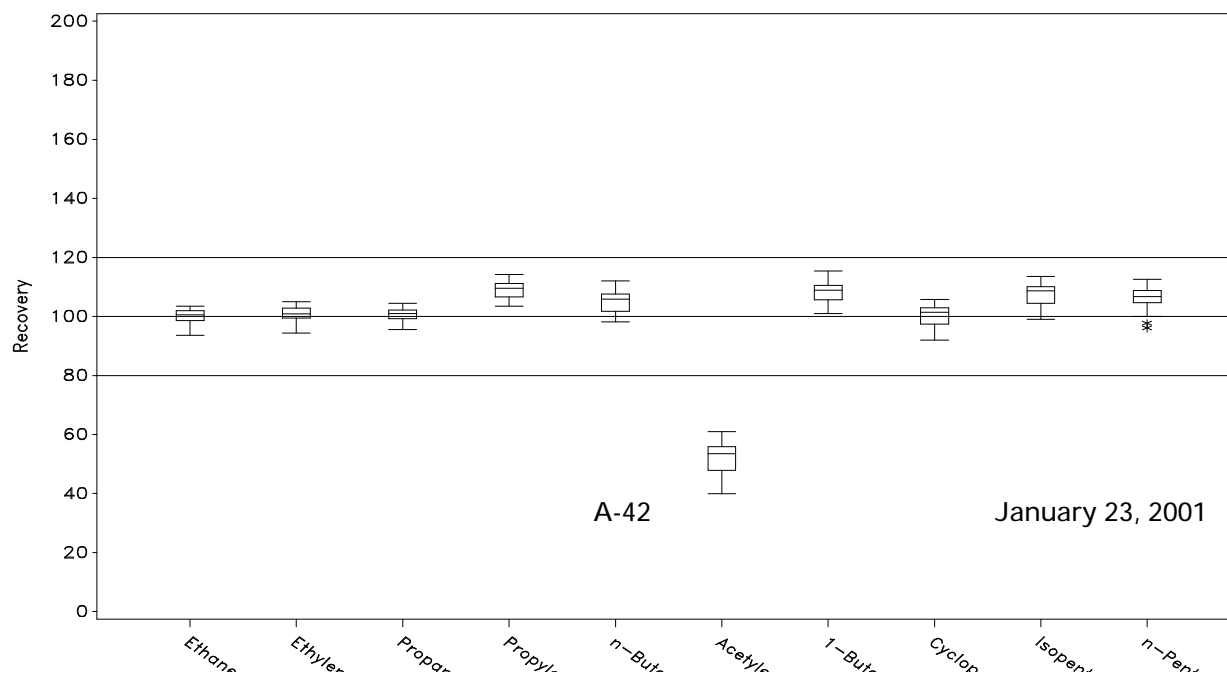


Table A-33. Statistical summaries of the recoveries for the Propane group of the Washington, DC 1997 retention time standard data

Compound	N	Mean Retention Time (Min)	Std. Conc.	Mean Recovery	95% CI for Mean Recovery	Precision (CV)	90% CI for Precision	Bias
Ethane	18	.	28.55	100.0%	(98.8,101.3)	2.5%	(1.9,3.8)	0.0%
Ethylene	18	.	21.13	100.6%	(99.2,102.0)	2.8%	(2.1,4.2)	0.6%
Propane	18	.	46.11	100.8%	(99.7,101.9)	2.2%	(1.6,3.3)	0.8%
Propylene	18	.	25.19	109.0%	(107.6,110.4)	2.6%	(1.9,3.9)	9.0%
n-Butane	18	.	43.99	105.3%	(103.4,107.2)	3.5%	(2.6,5.4)	5.3%
Acetylene	18	.	59.25	52.9%	(50.3,55.4)	9.7%	(6.9,15.3)	-47.1%
1-Butene	18	.	32.06	108.2%	(106.1,110.2)	3.8%	(2.8,5.8)	8.2%
Cyclopentane	18	.	22.57	100.3%	(98.4,102.1)	3.8%	(2.8,5.8)	0.3%
Isopentane	18	.	40.87	107.5%	(105.5,109.5)	3.8%	(2.8,5.8)	7.5%
n-Pentane	18	.	26.9	105.9%	(103.7,108.2)	4.3%	(3.2,6.6)	5.9%

Figure A-48. Boxplots of the recoveries for the Propane group of the Washington, DC 1997 retention time standard data by compound.



APPENDIX B:  
NEW JERSEY RETENTION TIMES

January 23, 2001

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## APPENDIX B: NEW JERSEY RETENTION TIMES

The New Jersey retention calibration data came with the retention times for all the samples run at each of the sites operating in New Jersey during the PAMS seasons of 1996, 1997, and 1998. This section was to take a more in depth look at the relationship between the retention times and the recoveries. However, during the quality assessment (QA) of the data, a pattern of concern arose that may limit the further use of the data as intended. The retention times for the PLOT column following a retention time standard run peak sharply. It seems to take about five to six hours for the times to return to normal. At this time it is not known whether the effect is the result of the retention time standard or the blank that is usually run immediately following the retention time standard. It is also not known why the times should peak in this manner.

The section is organized along the original planned analysis. As in the previous sections, a subset of 20 compounds were used in the analysis. The compounds considered in this section are the same as those used in the previous sections. The analysis section is further limited to the PLOT column (Propane group) since that is where the issue arose.

### B.1 Data Summary

The retention times for the 20 compounds studied are summarized in Tables B-1 and B-2. These tables show the retention time means, the standard deviations, and quartile information.

Table B-1. Retention time summaries for the Benzene group

Compound	Mean	Standard Deviation	Min	Q1	Median	Q3	Max
<i>n</i> -Hexane	13.12	0.060	13.00	13.10	13.10	13.20	13.20
2,4-Dimethylpentane	15.84	0.064	15.50	15.80	15.90	15.90	16.00
Benzene	17.71	0.062	17.60	17.70	17.70	17.80	17.80
2-Methylhexane	19.13	0.060	19.00	19.10	19.20	19.20	19.20
Toluene	25.90	0.055	25.60	25.90	25.90	25.90	26.00
<i>n</i> -Octane	28.67	0.052	28.50	28.60	28.70	28.70	28.90
<i>m/p</i> -Xylene	32.19	0.054	31.90	32.10	32.20	32.20	32.40
O-Xylene	33.45	0.053	33.10	33.40	33.50	33.50	33.50
1,2,4 Trimethylbenzene	38.37	0.055	38.20	38.30	38.40	38.40	38.60
<i>n</i> -Decane	38.74	0.052	38.30	38.70	38.80	38.80	38.90

Table B-2. Retention time summaries for the Propane group

Compound	Mean	Standard Deviation	Min	Q1	Median	Q3	Max
Ethane	7.65	0.015	7.58	7.64	7.65	7.66	7.68
Ethylene	8.48	0.016	8.40	8.47	8.48	8.49	8.53
Propane	10.73	0.023	10.7	10.7	10.7	10.7	11.0
Propylene	18.36	0.098	18.2	18.3	18.3	18.5	18.6
<i>n</i> -Butane	22.29	0.066	22.2	22.2	22.3	22.4	23.2
Acetylene	24.40	0.125	24.2	24.3	24.3	24.6	24.8
1-Butene	28.39	0.061	28.3	28.4	28.4	28.5	28.6
Cyclopentane	30.84	0.059	30.7	30.8	30.8	30.9	31.0
Isopentane	31.05	0.058	31.0	31.0	31.0	31.1	31.3
<i>n</i> -Pentane	31.93	0.060	31.8	31.9	31.9	32.0	32.1

## B.2 Data Analysis

The purpose of this section was to take a more detailed look at retention times and a possible relationship with recoveries. Time series plots of the retention times suggested that the times could be viewed as a process that varied about a slowly changing (usually increasing) average. (Generally, as an analytical column ages, the retention times for all compounds increase.) The time series plots also suggested that during any given run, the times deviated from their average in a group. So, for example, if the time for Propane was higher than the current average, then so were the times for the other compounds detected with the PLOT column. The question explored was:

*Is there a fixed underlying process that governs the pattern of deviations in retention times from the local averages that is related to the recoveries?*

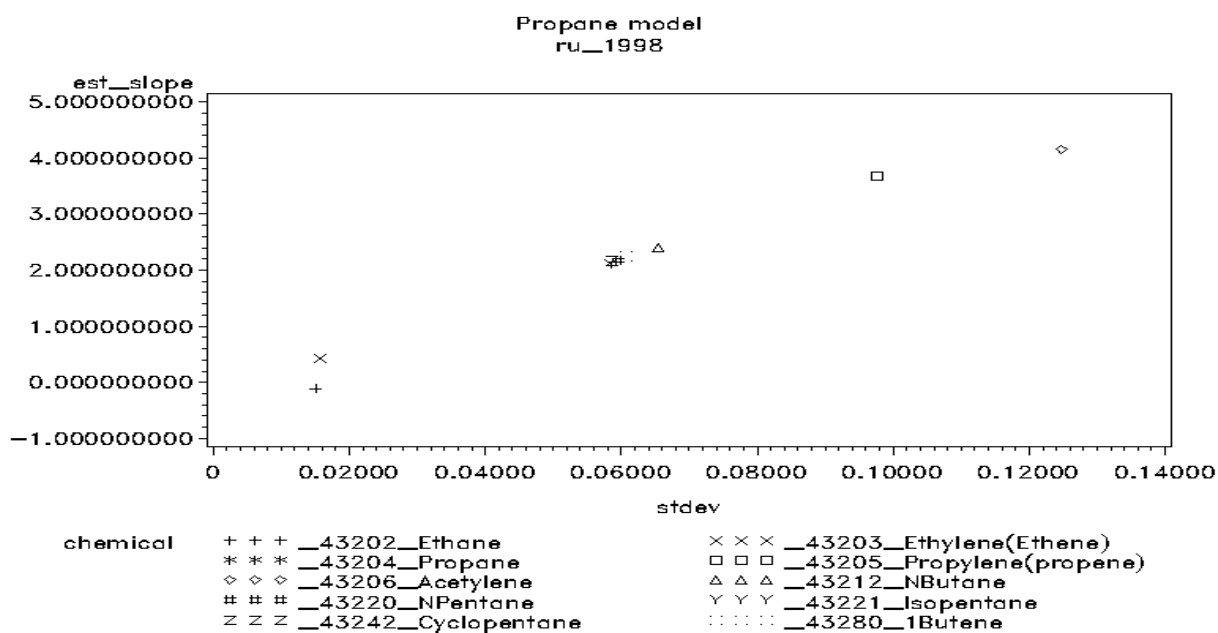
The magnitude of the range in the shifts varied from compound to compound. The times for Acetylene varied the most, up to 0.2 minutes from the average, but still followed the pattern exhibited by the other compounds within the Propane group. While this common pattern of shifts was seen in both groups, the analyses in this section were limited to the 10 compounds in the Propane group.

The concept for modeling the process is that the retention times are varying due to common external influences. The individual compounds are allowed to vary in their sensitivity to the external force. It is assumed (and graphically verified) the vast majority of the variability in the retention times is due to the common outside influence. Hence, the sensitivity can initially be estimated by the standard deviation in the retention times. The graphical verification comes from regressing the retention times for each compound on the times for Propane. Under the assumption, the slopes should be roughly proportional to the relative sensitivities (relative to the sensitivity of Propane). Table B-3 has the regression information together with the standard

deviations in the retention times. Figure B-1 plots these slopes against the standard deviations.

Table B-3. Results of regressing the retention times of each compound on those of Propane (Sorted by the slopes)

Compound	R-squared	Intercept	Slope	Mean Time	Standard Deviation
Propane	.	.	.	10.73	0.023
Ethane	0.03	8.84	-0.11	7.65	0.015
Ethylene	0.39	3.81	0.45	8.48	0.016
Isopentane	0.67	8.35	2.12	31.05	0.058
Cyclopentane	0.65	7.56	2.17	30.84	0.059
<i>n</i> -Pentane	0.68	8.54	2.18	31.93	0.060
1-Butene	0.69	4.24	2.25	28.39	0.061
<i>n</i> -Butane	0.74	-3.51	2.40	22.29	0.066
Propylene	0.73	-21.18	3.69	18.36	0.098
Acetylene	0.57	-20.19	4.16	24.40	0.125



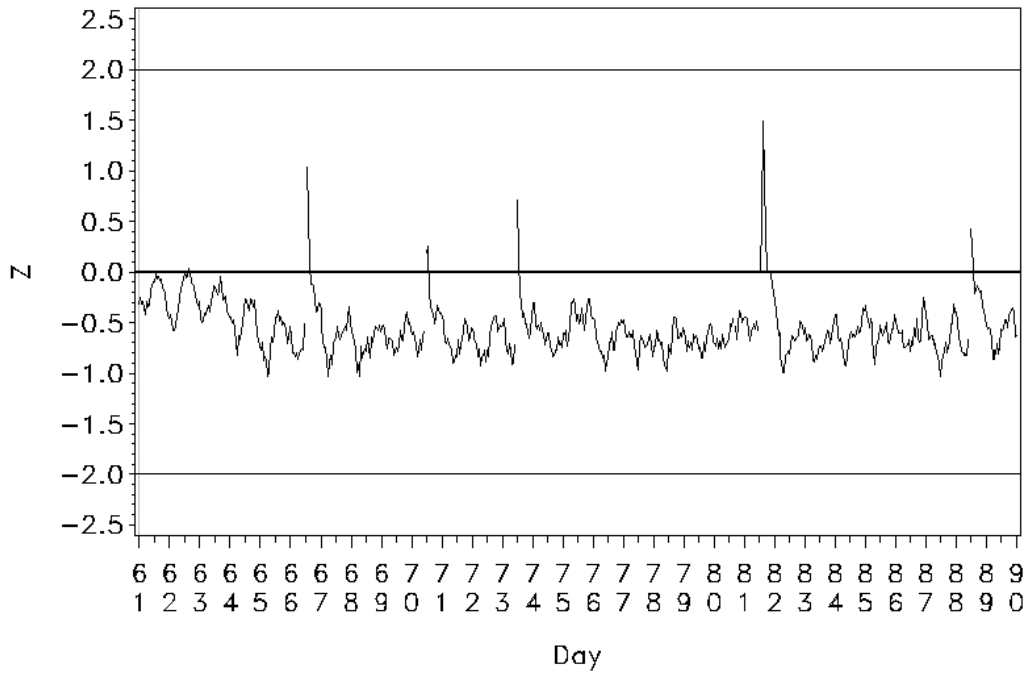
The straight line verifies the assumption that the relative sensitivities can be estimated by the standard deviations of the retention times. (Regressing one variable on another usually assumes that the dependent variable is measured without error. In this case the Propane times have as much measurement error as the times for the other compounds. Hence, the slopes are not used as the estimate of the relative sensitivities, but instead are just used as a check.)

Note that Ethane seems to be relatively independent of (or unaffected by) the overall process. This is seen in the very low r-squared value and the fact that it is not on the line in Figure B-1.

The retention times for any given compound then are modeled as a series of hour-to-hour shifts from the compound's mean retention time. The direction and relative magnitude for each shift is the same for all compounds. The absolute magnitude of the compound shift is determined by multiplying the compound's sensitivity to the process (the standard deviation) and the relative shift.

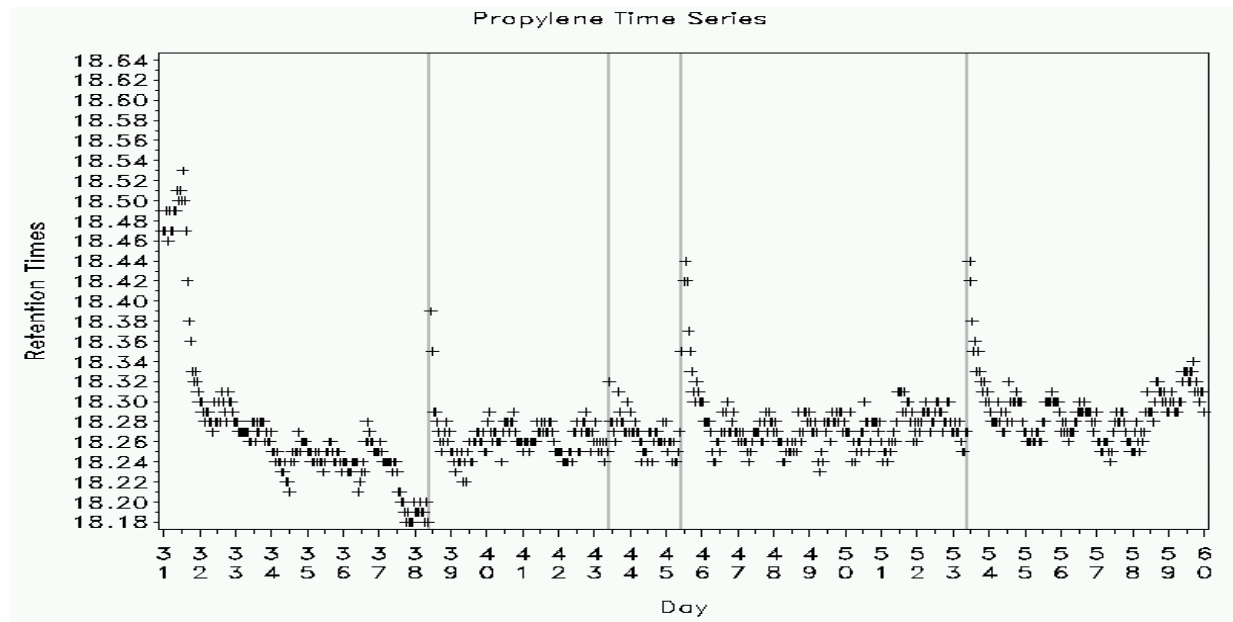
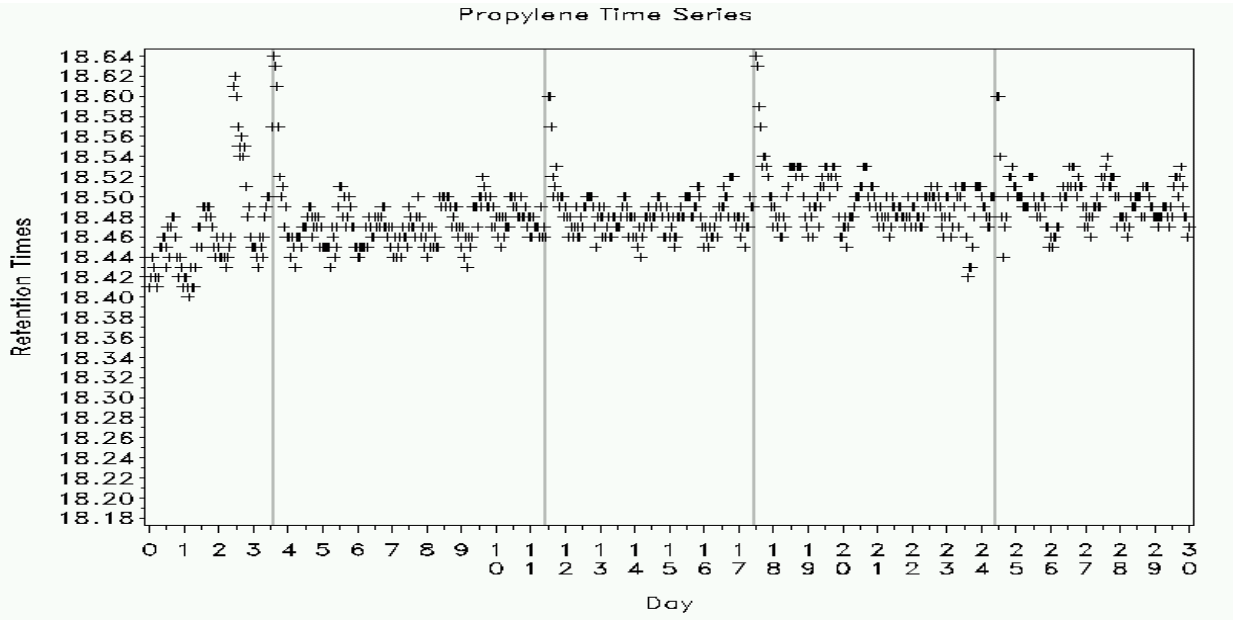
The estimates for the common retention time pattern for the last 30 days are plotted in Figure B-2. This shows several interesting points. First there is a strong diurnal pattern. (An air conditioning unit has been added to this site since these data were collected. This may help stabilize this pattern.) Note also that there does not appear to be any week-long patterns, that might be associated with operator activities. The biggest thing to note, however, are the five sharp peaks and the gaps at the start of these peaks. The gaps are from running blanks. There are no retention times associated with these times, so no pattern can be estimated for these times.

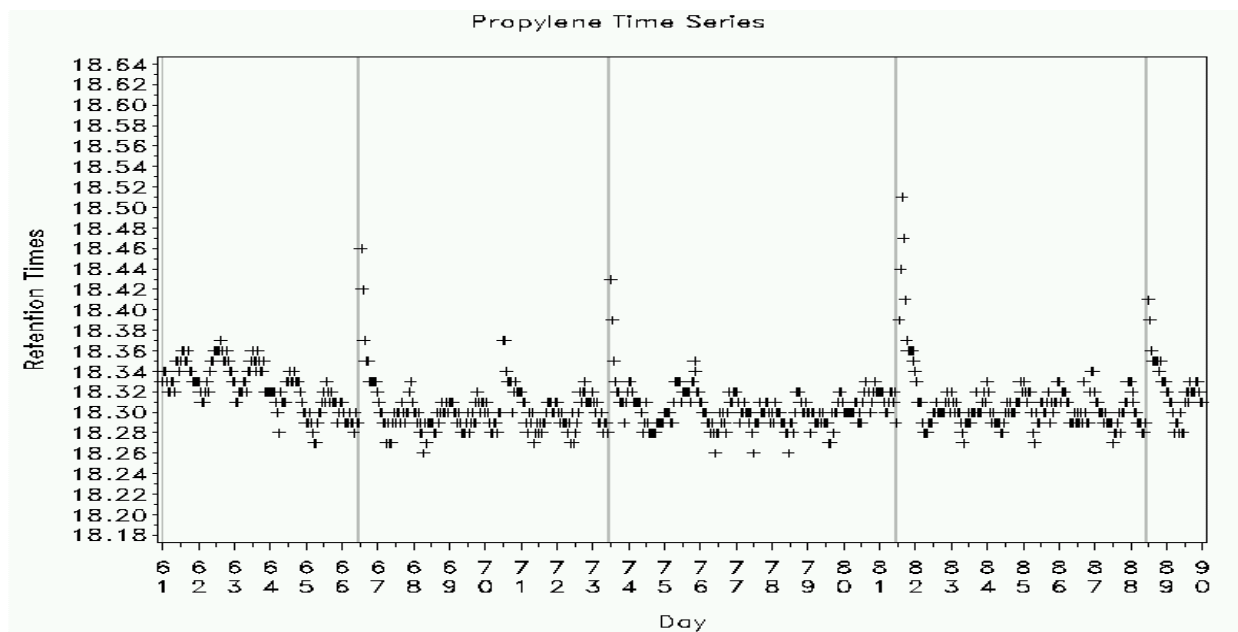
Estimated retention time pattern



Figures B-3 through B-5 show the raw retention times for Propylene with gray vertical bars at the times the retention time standards were run. All the compounds in the Propane group except for Ethane showed this pattern. From these plots it can be seen that something related to running the retention time standards has an effect on the times. Moreover, this effect lasts about five to six hours, and can continue to spike after normal sampling has resumed (see the fourth spike in Figure B-2).

There is a peak in the beginning of the year that is not associated with a retention time standard. There is also a large drop in the times between day 31 and day 32. It is not known why these are present, but the large drop would be consistent with replacing the PLOT column. (It has been noted that as a column ages the times slowly increase.) The times appear to increase until day 31, and then generally increase from day 32 until the end of the season. The diurnal pattern can also be seen in these graphs.





It was planned to test whether the common pattern modeled above had any relationship to the recoveries. However, if the process of running the check somehow disturbs the measurement device, then the retention times for the standards are not representative of the usual patterns. Hence, inferences about the relationship between the recoveries and the deviations in the retention times seen when these standards are run are valid, at best, only during the times the standards are run. Since this would defeat the purpose of the analysis, the analysis was stopped at this point.

The nature of the peaks in the retention times seen after running the standards needs further investigation. The main purpose of running the standards is to establish the times associated with the various compounds for peak identification. For this to make sense the times need to be representative of the general status of the machine. The peaks observed above indicate that this may not be the case. Although, the effect may be from the blanks, rather than the standards. Also, regardless of the cause, any carryover effect should be investigated. Data for heavier compounds following the retention time standards are sometimes invalidated, because of a known carryover effect.

