

Evaluation of the Variability of  
GC/FID Analyses of PAMS Standards

April 1999 – January 2000

April 16, 2001

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## ***Objectives of Study***

The objectives of this study were to evaluate the reproducibility of the GC/dual FID system for the analysis of 1999 standard calibration samples taken from canisters that had been filled using a standard PAMS cylinder provided by the EPA. Data from these analyses provide information on:

- Retention time variability of individual PAMS components
- Variability in calculated quantities for individual PAMS species
- Effect of time between calibrations on quantitative results
- Quality control measures needed to detect deterioration in performance
- Methods available to set retention windows that allow reliable detection of individual components while minimizing the misidentification of peaks.

## ***Digitization of Calibration Standard Samples***

Paper chromatograms from the analysis of PAMS Standards on a daily basis from April - December 1999 were obtained from the NC Division of Air Quality and manually entered into an excel spreadsheet. There were approximately 125 samples and 250 chromatograms since each sample included results from the Porous Layer Open Tubular (PLOT) and DB1 columns respectively. An electronic copy of this file is being provided with this report.

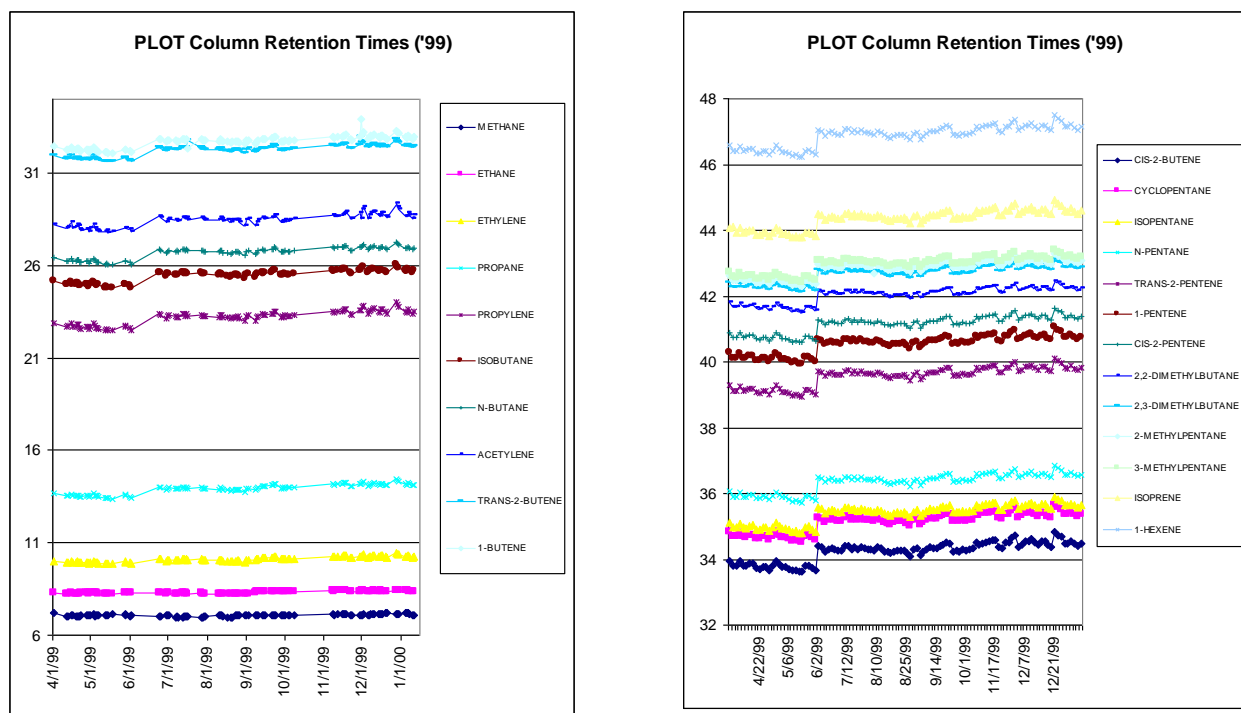
Identified compounds were entered first in retention time order; unidentified peak retention times and peak areas were entered sequentially as a separate group. This was done to allow an effective evaluation of chromatogram reproducibility.

Individual compound retention times and relative areas were plotted for the entire period. A number of chromatograms were quickly identified as having missing or unidentified peaks. These were segregated from the rest of the data. The remaining chromatograms were then used to evaluate the retention time and quantitative variability of the system in analyzing calibrations standards.

Approximately 25 of the 125 samples had either misidentified peaks or quantities that were well outside the expected range. A separate analysis of these is necessary to better understand why the system failed nearly 20% of the time with known standards at high concentrations.

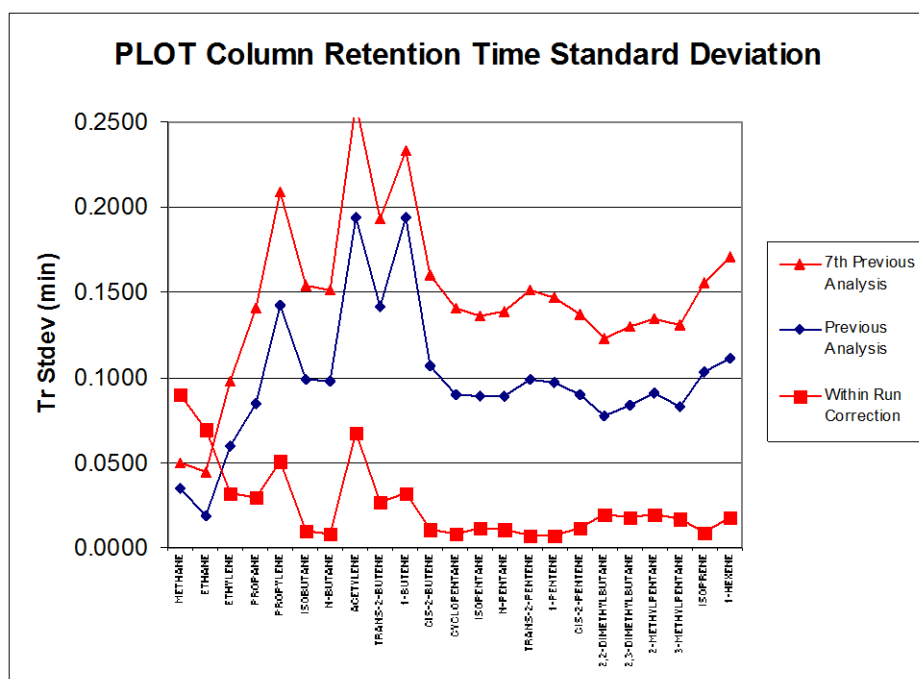
## ***Reproducibility of Retention Times***

**Figure 1** portrays the variability of retention times by component for the PLOT column for the period April to December 1999. As instrument operating conditions change, retention times shift. Among components, there is a noticeable consistent pattern to these shifts, with the major fluctuations in retention times primarily resulting from differences between days. On a given day, all the retention times appear to be shifted by a similar amount. Much of the retention variability could be eliminated by adjusting for the average shift for that run. If retention windows for each component are not adjusted for day-to-day fluctuations, then they would have to be set wide to account for these changes. This increases the probability of mistakenly identifying another peak that falls within the wide window as the target compound.



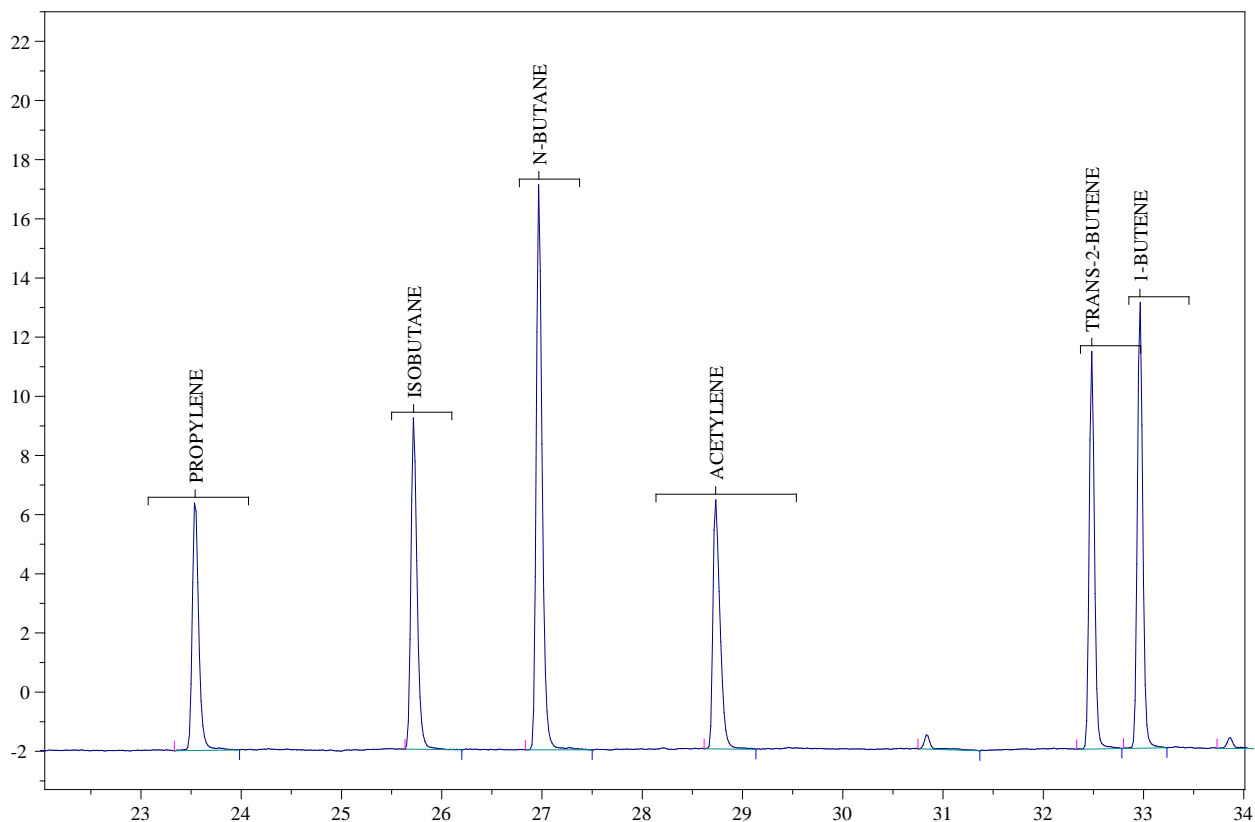
**Figure 1.** Retention Times for all components of the PLOT column during the April-December 1999 period for the analysis of a PAMS standard.

To quantitatively assess the required widths for retention windows when using various retention time updating procedures, an analysis of the variability in retention behavior was conducted. Each analysis was compared with one approximately 7 days earlier, with the previous day's run, and the within-run average shift. **Figure 2** illustrates the results of this analysis for each of the PLOT column components. Accounting for within-run shifts dramatically reduces variability.



**Figure 2.** Comparison of retention time variability from: 1) 7<sup>th</sup> previous analysis, 2) previous day, and 3) within-run. Note the dramatic reduction for using within-run retention shifts.

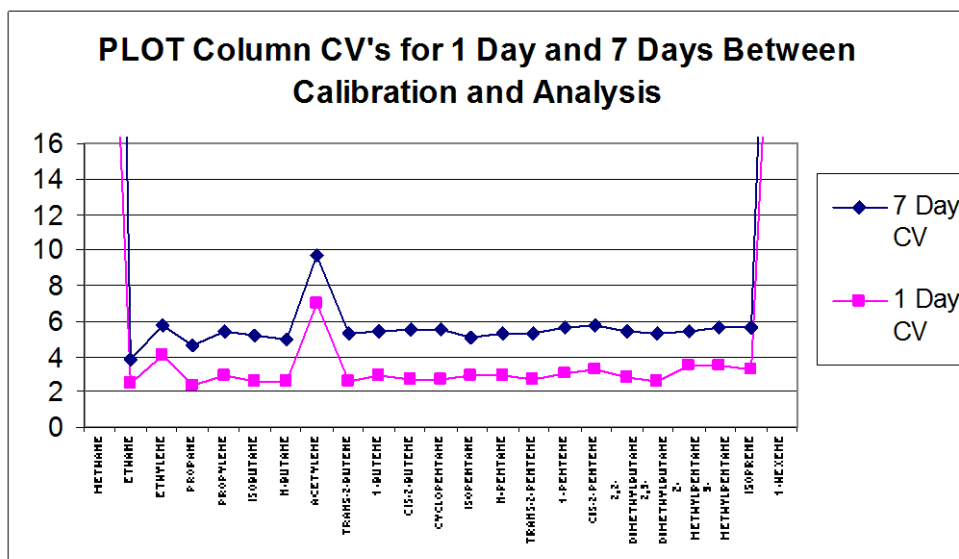
It is also apparent that certain target PAMS compounds (particularly acetylene, and to a lesser extent propylene and 1-butene) have large retention time variability. As seen in **Figure 3**, while 1-butene elutes just past trans-2-butene, neither acetylene nor propylene have other PAMS components that are near their retention. It appears that these small compounds, all with a double or triple bond, interact differently with the analytical column on various days in a manner that causes greater variability in retention. Retention windows for these substances necessarily should be set wider to account for their greater variability in retention times.



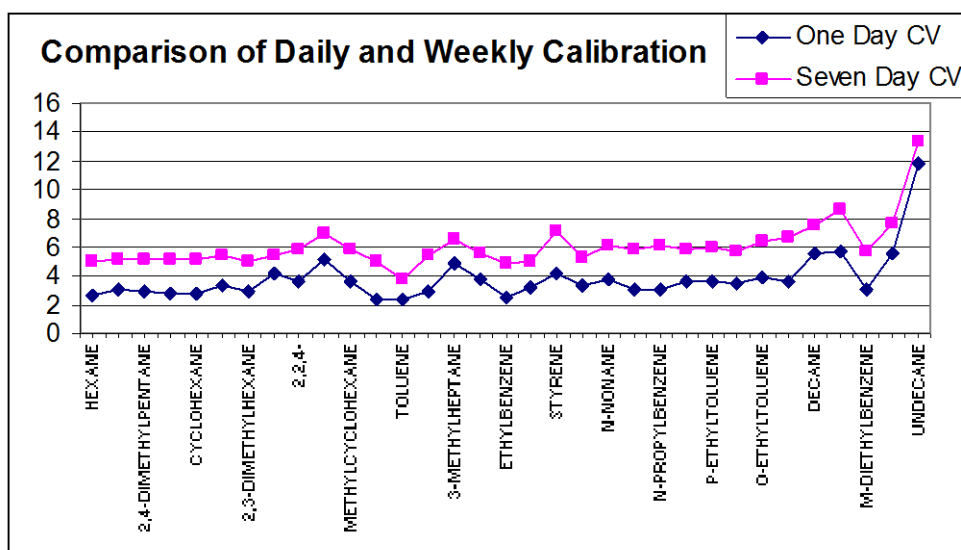
**Figure 3.** Portion of PLOT Chromatogram showing the three components—acetylene, propylene, and 1-butane—that have the greatest retention variability. Only 1-butene has another closely co-eluting peak.

### ***Variability in Quantitative Results***

Currently PAMS analyses are conducted by calibrating the system approximately once every 7-10 days. Additionally a calibration challenge analysis is conducted at the end of each batch of samples each day to provide information on the performance of the GC/FID system. Detector sensitivity changes with time due to fluctuations in gas flows, temperatures, and other factors. An analysis was carried out to evaluate the practice of quantification using a calibration run from seven days earlier versus quantification using the previous day's analysis as the calibration. **Figures 4 and 5** compare the Coefficients of Variation for analyses using detector response factors from calibrations analyses conducted one day and seven days earlier respectively.



**Figure 4.** Comparison of Coefficients of Variation (CV) for quantification using the previous day's and the 7<sup>th</sup> previous day's calibration run's response factors for each of the PLOT column components.



**Figure 5.** Comparison of Coefficients of Variation (CV) for quantification using the previous day's and the 7<sup>th</sup> previous day's calibration run's response factors for each of the DB1 column components.

For both columns, use of updated calibration detector response factors from the previous day instead of from a week prior lessens the error by approximately half. Increasing the frequency of calibration lessens the overall uncertainty in amounts measured.

## ***Recommended Quality Control Procedures***

Based on this study several recommendations are made concerning quality control procedures and the setting of retention time windows.

1. Develop and chart daily a retention parameter that shows the performance of the GC/FID system's retention reproducibility. This parameter can be the sum of absolute differences in retention times between each day's calibration check analysis and the system's current calibration file.
2. Develop and chart a retention parameter will quickly point out whether there have been shifts in individual PAMS components. This parameter can be the sum of absolute differences between each day's calibration check analysis (after it has been corrected for an average shift) and the systems current calibration file.
3. Develop and chart daily a recovery parameter that shows the changes occurring in detector response factors. The recovery for each component is the quantity found by each day's calibration check analysis divided by the amount of that component in the calibration standard. When recoveries from daily analyses of the PAMS standard fall outside of a particular range, then all samples should be reanalyzed using a more recent calibration file.
4. For retention time windows, these should be updated as much as is possible. It is recommended that the daily calibration check run be used to update retention window settings.
5. If feasible for sample analysis, it is recommended that a target compound be identified and used to update retention times for each particular sample analysis. This will require a review of the samples to determine whether there is in fact a major peak retention marker that is always present, that is representative of the average chromatogram shift, and that does not have nearby interfering peaks. The purpose of this recommendation is to provide within run retention information to allow setting the narrowest possible retention windows to minimize the possibility of an interfering substance being identified as a PAMS component (alpha error). Clearly a tradeoff must be made between this consideration and the one to ensure the retention window is sufficiently wide to prevent failing to identify a PAMS component that is present (beta error).