Validation of a New Method for In-stack Measurement of Particulate Matter Emissions from Large Stationary Sources

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Abstract

A new method for measuring particulate matter in stationary sources has been developed by Rupprecht & Patashnick Co. (R&P). This new method, named the TEOM® Series 7000 Source Particulate Monitor, uses R&P TEOM technology to provide in situ, filter-based, direct mass measurement of particulate matter in stationary source emissions. The performance of this new monitoring method has been quantified in accordance with U.S. EPA Method 301 by making simultaneous collocated measurements with paired Series 7000 and paired EPA Reference Method 17 sample trains. R&P, with the assistance of staff from the Greater Vancouver Regional Department, Vancouver, B.C., Canada, conducted a series of tests at a coal-fired cement plant to evaluate the performance of the Series 7000. The paired Series 7000 sample trains were configured identically using the on-board Series 7000 software configuration routines and operated in accordance with standard test procedures developed by R&P. The paired manual sample trains were configured and operated in accordance with U.S. EPA Reference Method 17. Each test was made for a duration of at least one hour to ensure sufficient particulate matter was captured on the manual sample train filters. Average particulate matter mass concentrations were determined for each sampling train and used for a statistical analysis of precision and bias per U.S. EPA Reference Method 301. For each test run, the average mass concentration results for each sample train are tabulated and have been presented along with the results of the statistical analysis to determine the bias and precision for the new Series 7000 method.

Introduction

A new method for measuring particulate matter in stationary sources has been developed by Rupprecht & Patashnick Co (R&P). This new method, named the TEOM® Series 7000 Source Particulate Monitor, uses R&P TEOM technology to provide in situ, filter-based, direct mass measurement of particulate matter in stationary source emissions. The engineering design of the Series 7000 incorporates features to automate isokinetic sampling and analysis of particulate matter mass for applications such as compliance testing, process/control system optimization and calibration/certification of particulate matter continuous emissions monitoring systems. This new method has been designed for use in fixed installations or as a portable system for use at many different sources. To assess the performance of this new monitoring method, R&P, with the assistance of Air

Division staff from the Greater Vancouver Regional Department, conducted a series of tests at a coal-fired cement plant in Vancouver, British Columbia during July 2000. The performance assessment was quantified in accordance with U.S. EPA Method 301[1] by making simultaneous collocated measurements with paired Series 7000 and paired U.S. EPA Reference Method 17[1] sample trains.

BACKGROUND

Series 7000 Operation

The TEOM Series 7000 utilizes the patented R&P TEOM technology for high-resolution *direct* mass readings[2] to make in-situ measurements of particulate matter in stationary sources. For the methods validation testing reported in this paper, the instrument was set to perform short term, continuous measurements.

The Series 7000 draws flue gas through a filter while maintaining isokinetic sampling and continuously weighs the filter, resulting in a measurement of real-time particulate mass concentrations. The TEOM mass detector uses a short straight inlet tube to isokinetically sample the flue gas and transport it to the filter. Directly following the test period, the system is removed from the stack or duct, stabilized, and with flow through the system the inlet tube is brushed down with a stainless steel brush. Any particulate matter (PM) collected on the inside of the inlet (nozzle) wall during the test is loosened and captured on the filter for direct measurement by the TEOM. Desiccation of the filter is performed in-situ using the system's integrated backflow to purge the filter with dry, clean air before sampling of the flue gas is initiated and following completion of PM recovery from the inlet nozzle. PM measurements are corrected to standard conditions and reported as dry mass concentration corrected to standard conditions.

Figure 1 is a schematic diagram showing the flow through the system. Flue gas enters the sample nozzle isokinetically and passes directly through a straight inlet tube to the filter mounted on the oscillating element where all particulate mass is collected at or near stack temperature. Isokinetic sampling conditions are maintained dynamically using a positive feedback system that integrates measured stack temperature, pressure, and pressure change across an “S”-type pitot tube, along with stack gas density and moisture content. (For the purposes of this study, the gas density and moisture content were determined from pre-test measurement using EPA Methods 3 and 4.) The filtered gas proceeds through heated lines in the structural boom to a condenser located on the platform outside the stack or duct where the gas is thoroughly dried before passing through the mass flow controller and exhausted through the vacuum pump. Removal of uncombined water from the sample employs filtered dry air to desiccate the sample in the stack and after inlet recovery.

The mass measurement is made using the tapered element oscillating microbalance (TEOM) which is housed in the mass transducer case. The mass transducer is a hollow tube, clamped at one end and free to oscillate at the other. An exchangeable filter cartridge is placed in the tip of the free end. This “tapered element” oscillates at precisely its natural frequency. An electronic control circuit senses its oscillation and, through positive feedback, adds sufficient energy to the system to overcome losses. An automatic gain control circuit maintains the oscillation at constant amplitude. A precise electronic counter measures the frequency, which has a direct relationship with mass.

As sampled particulate matter begins to accumulate on the filter element, the change in mass (Δm) of the filter over a given time period can be calculated by measuring the frequencies f_1 and f_2 where f_1 is the frequency at time a, and f_2 is the frequency at time b.

$$\Delta m = K_0 \left(\frac{1}{f_b^2} - \frac{1}{f_a^2}\right) \qquad (1)$$

where K_0 is the calibration constant for the tapered element.

The calibration constant for each tapered element is determined empirically in the laboratory using filters of known mass[2]. The tapered element is made of nonfatiguing inert material and retains its calibration indefinitely. The starting frequency, f_a, can be defined at any arbitrary time, and a mass measurement does not depend on the knowledge of the previous loading of the filter. Tracking frequency with time yields the mass rate, and when combined with the flow rate through the filter, produces the mass concentration. The sample stream through the mass transducer is held a few degrees above the stack temperature to provide the frequency stability necessary for measurement of small mass changes with high temporal resolution.

Field Test Methods

To evaluate the performance of the TEOM Series 7000, concurrent samples were taken by collocating two Series 7000 systems with two EPA Method 17 sample trains. A sample period of approximately one hour was selected for each run to ensure sufficient gas volume and particulate matter were collected by each Method 17 sample train. This sample period was more than sufficient to ensure sufficient gas volume and particulate matter were collected by each TEOM Series 7000 system to obtain a representative sample and analysis.

The sample ports were located on the stack carrying emission gases from the plant's electrostatic precipitator. Probe placement was made such that the inlet tips were arranged as close to the center point of the stack at the sample port locations while minimizing the potential for impacting the sampling by adjacent probes. Due to the geometry of the TEOM Series 7000 inlets when configured in their normal sampling positions, the inlet nozzle tips of the each TEOM Series 7000 were approximately 40 cm upstream of the inlet nozzle tips for each of the Method 17 sample filter holders. The sample ports used for the tests were found to be located in accordance with EPA Method 1[1] meeting the criteria that the ports be at least eight stack diameters downstream and two diameters upstream of the nearest flow disturbance.

The manual sampling systems were configured and operated by engineers from the Greater Vancouver Regional District Air Division in accordance with the EPA Method 17[1] protocols.

The TEOM Series 7000 systems were operated by engineers from R&P's source emissions products development group. The Series 7000 systems were configured to sample continuously and collect and store measurement data every 3.3 seconds. Continuous data from the on-board stack gas temperature and velocity sensors were combined with manual inputs for flue gas molecular weight and moisture content measured prior to each run to control the isokinetic sampling rates. Calculation and automatic control of isokinetic sample rates is performed by the Series 7000's system operating software running on the systems' integrated PC-104/80486 computer processing platform.

Gas analysis for determination of stack gas dry molecular weight and stack gas moisture content were performed following U.S. EPA Methods 3[1] (Orsat method) and 4[1], respectively. These analyses were used for both the Series 7000 and Method 17 measurements.

The same filtration media was used for all sampling trains. Pre- and post-sampling filter conditioning and gravimetric analysis of the U.S. EPA Method 17 sample train filters was performed in the GVRD's Air Resources filter laboratory. Conditioning of the TEOM Series 7000 filters was performed in situ immediately before sampling was initiated and immediately after sampling was completed using the TEOM Series 7000's integrated filter purge air system.

Appropriate quality assurance procedures were followed for each sample train including pre- and post-test sample and pitot pneumatic line leak checks, and flow sensor calibrations before and after the visit to the test site.

Data Analysis Methods

To assess the performance of the TEOM Series 7000 by comparison to EPA Reference Method 17, EPA Reference Method 301[1], "Field Validation of Pollutant Measurement Methods from Various Waste Media", was used to determine and document the precision and bias of measured particulate matter concentrations. A brief description of the methods used to assess the bias and precison of the TEOM Series 7000 method are given below.

Precision Analysis

Evaluation of the TEOM Series 7000 method's variance with respect to the variability of Method 17 was conducted per the statistical analysis procedures described in EPA Method 301 for quadreplet sampling systems. The variance of the TEOM Series 7000 method with respect to Method 17 is calculated using Method 301 equation 301-11:

$$\text{Variance } (S^2) = \frac{(\Sigma d_i^2)}{2n} \qquad \text{(eq. 301-11)}$$

where: d_i is the difference between TEOM Series 7000 average concentrations for the ith replicate measurements.

Using the F-test, the variance of the TEOM Series 7000 method is evaluated to determine if the method was more variable than Method 17. The experimental F-value is calculated using Method 301 equation 301-8:

Experimental F-Value $= S_p^2 / S_v^2$ (eq. 301-8)

where: S_p^2 is the variance of TEOM Series 7000 method = $(\Sigma d_i^2)/2n$, d_i's are the differences between the paired TEOM Series 7000 values.

S_v^2 is the variance of Method 17 = $(\Sigma d_i^2)/2n$; d_i's are the differences between the paired Method 17 values.

Per Method 301, the critical value of F = 1.

Bias Analysis

The bias (mean of the differences between the TEOM Series 7000 method and Method 17) and the standard deviation of the difference is determined as described in Section 6.2.2.4 of Method 301. The t-statistic is then calculated to test the bias of the TEOM Series 7000 method with respect for statistical significance at an 80 percent confidence level.

The bias (mean of the differences between TEOM Series 7000 method and Method 17) is calculated by using Method 301-1 equation 310-12 (shown below) to first calculate the differences.

$d_i = ((V_{1i} + V_{2i})/2) - ((P_{1i} + P_{2i})/2)$ (eq. 301-12)

where: V_{1i} = First measured value of Method 17 in the *i*th test sample.

P_{1i} = First measured value of the TEOM Series 7000 method.

The standard deviation of the differences (SD_d) is determined using Method 301, equation 301-2 substituting d_i calculated using equation 301-12 for S_i.

$$SD_d = \sqrt{\sum (d_i - d_m)^2 / 2n} \quad \text{(eq. 301-2)}$$

where: d_m is the mean of the differences (d_i) determined using equation 301-12.

The t-statistic is calculated using Method 301 equation 301-9 to test the bias for statistical significance at the 80% confidence level.

$$t = \frac{SD_d}{\sqrt{n}} \quad \text{(eq. 301-9)}$$

Results

Test Results

A total of six valid sample runs were obtained over a three-day period thereby resulting in the collection of 6 sets of replicate samples (a total of 24 samples). Throughout the testing, the plant was operated per its normal production level and schedule. No extraordinary actions were taken by plant operations personnel to maintain plant capacity at a specified level. Table 1 presents a summary of results for each system for each run. Figure 2 presents a plot of average mass concentrations determined by each method for each test run. Continuous two minute (rolling) average mass concentrations measured by each Series 7000 system for each run are plotted in Figures 3 – 8. The data plot for each run also includes the average mass concentration reported for each sampling system.

Please note that continuous mass concentration values reported from the TEOM Series 7000 systems' measurements are calculated by averaging the wet mass measurement and dry sample gas volume measurement readings taken every 3.3 seconds and corrected to standard conditions. The average mass concentration reported for the TEOM Series 7000 measurements are calculated by taking the dry total mass of particulate matter collected during the sample run plus the dry total mass recovered from the inlet and the total sample gas volume (dry) corrected to standard conditions. The average mass concentration reported for each Method 17 sampling train was determined in accordance with EPA Method 17.

Methods Validation Analysis

The Method 301 validation results from analyzing the test data collected using the TEOM Series 7000 method and EPA Reference Method 17 are presented in Tables 2 – 4 and summarized below. As noted previously, quadruplet sampling systems (two TEOM Series 7000 method and two Method 17 systems) were used to collect six sets of replicate samples, with each method contributing half of the sample measurements.

Precision Assessment

The variance of the TEOM Series 7000 method's average mass concentrations is as follows:

$$\text{Variance } (S^2) = (\Sigma d_i^2)/2n = 103.5/(2*6) = 8.6$$

$$\text{Experimental F-value } = \frac{S_p^2}{S_v^2} = \frac{(\Sigma d_{p_i}^2/2n)}{(\Sigma d_{v_i}^2/2n)} = \frac{(39.3/12)}{(1229.2/12)} = 0.03$$

The critical value of F is 1. The experimental F-value is less than the critical value indicating that the precision of the TEOM Series 7000 results are, at least, comparable to Method 17 results.

Table 2 presents the data and calculations for the variance. Table 3 tabulates the data and calculations of the experimental F-value.

Bias Assessment

The calculated bias of the TEOM Series 7000 method relative to the results obtained from the Method 17 sample trains following the procedures given in Method 301 are as follows.

The differences between the means of each pair of TEOM Series 7000 method test results and means of the corresponding pairs of Method 17 results is:

$$d_m = -1.1$$

The standard deviation of the differences is:

$$SD_2 = \sqrt{\frac{\Sigma(d_i - d_m)^2}{n-1}} = \sqrt{\frac{87}{(6-1)}} = 4.2$$

The t-statistic is:

$$\pm t = \frac{d_m}{(SD_d/\sqrt{n})} = \frac{-1.1}{(4.2 * \sqrt{6})} = -0.640$$

The critical value for the t-statistic specified by Method 301 at the 80% confidence interval with five degrees of freedom is 1.475. The experimental t-value is less than the critical value indicating no significant bias in the TEOM Series 7000 Method.

Table 4 presents the data and calculations for bias, standard deviation of the differences and the t-statistic.

Discussion

The statistical analysis shows that the Series 7000 method results are comparable to EPA Reference Method 17 results with respect to accuracy as there was no significant bias determined by statistical analysis of monitored data. With regard to precision, measurement data show that the Series 7000 can provide significantly enhanced measurement precision in comparison to Method 17 even under typical plant operating conditions. Additionally, the TEOM Series 7000's ability to provide direct, real-time particulate matter mass measurements can allow a user to characterize emission conditions with much greater detail than with traditional manual test methods. The data presented herein also indicate that the Series 7000 may meet the US EPA requirements as an alternative method for measurement of particulate matter in cement plant emissions. Additional methods validation testing is underway to evaluate the system's performance in other emissions sources of the same source category as well as in other source category types such as coal-fired power plants.

References

1. Code of Federal Regulations, "Test Methods", 40 CFR Part 60, Appendix A, U.S.

Government Printing Office, Washington, DC, July 1, 1999.

2. Patashnick, H.; Rupprecht, E. “Continuous PM-10 Measurements Using the Tapered Element Oscillating Microbalance”, *J. Air Waste Management Association* 1991, 41, 1079-1083.

Figures

Figure 1
Schematic of
TEOM Series 7000

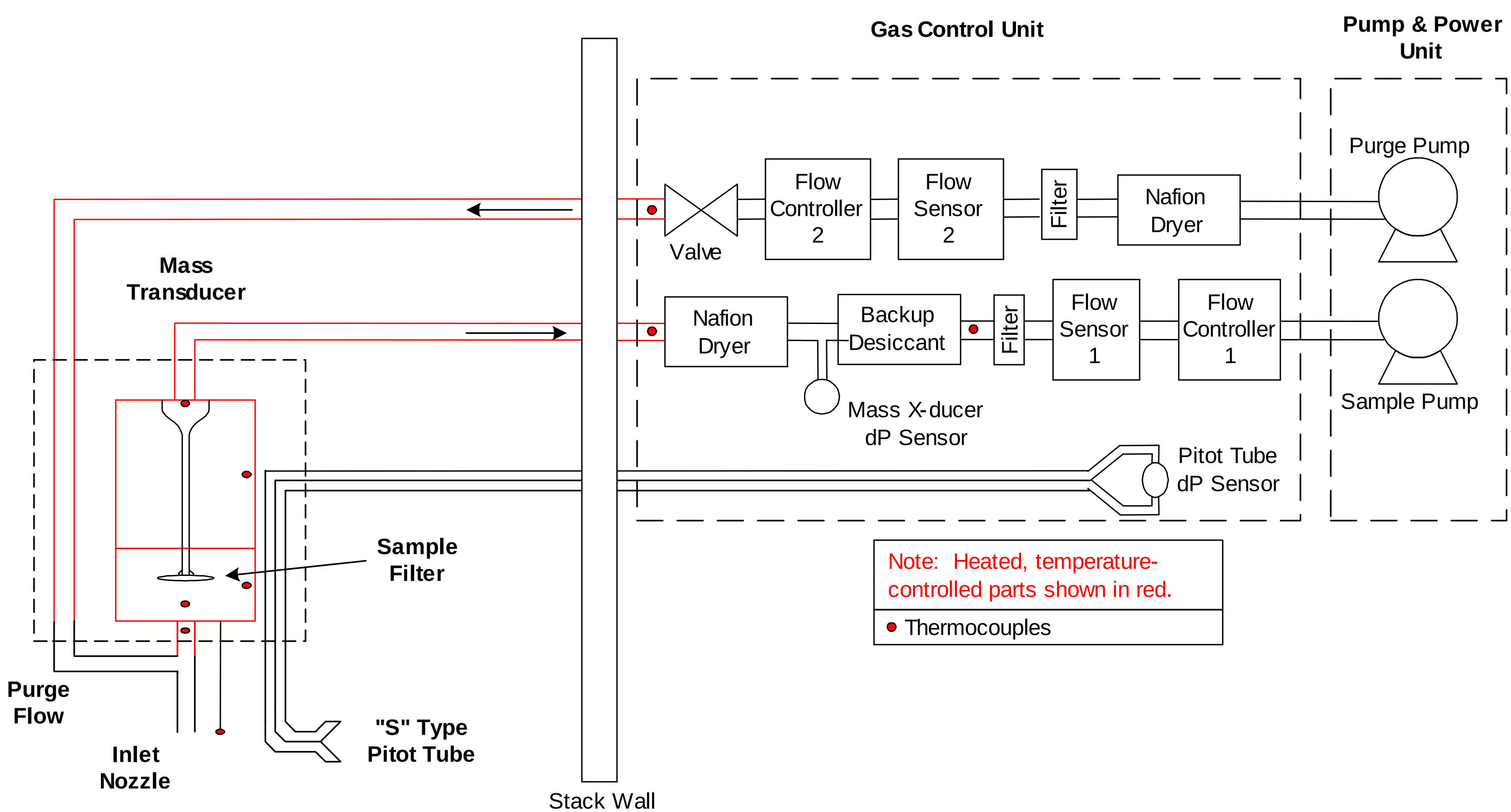


Figure 2

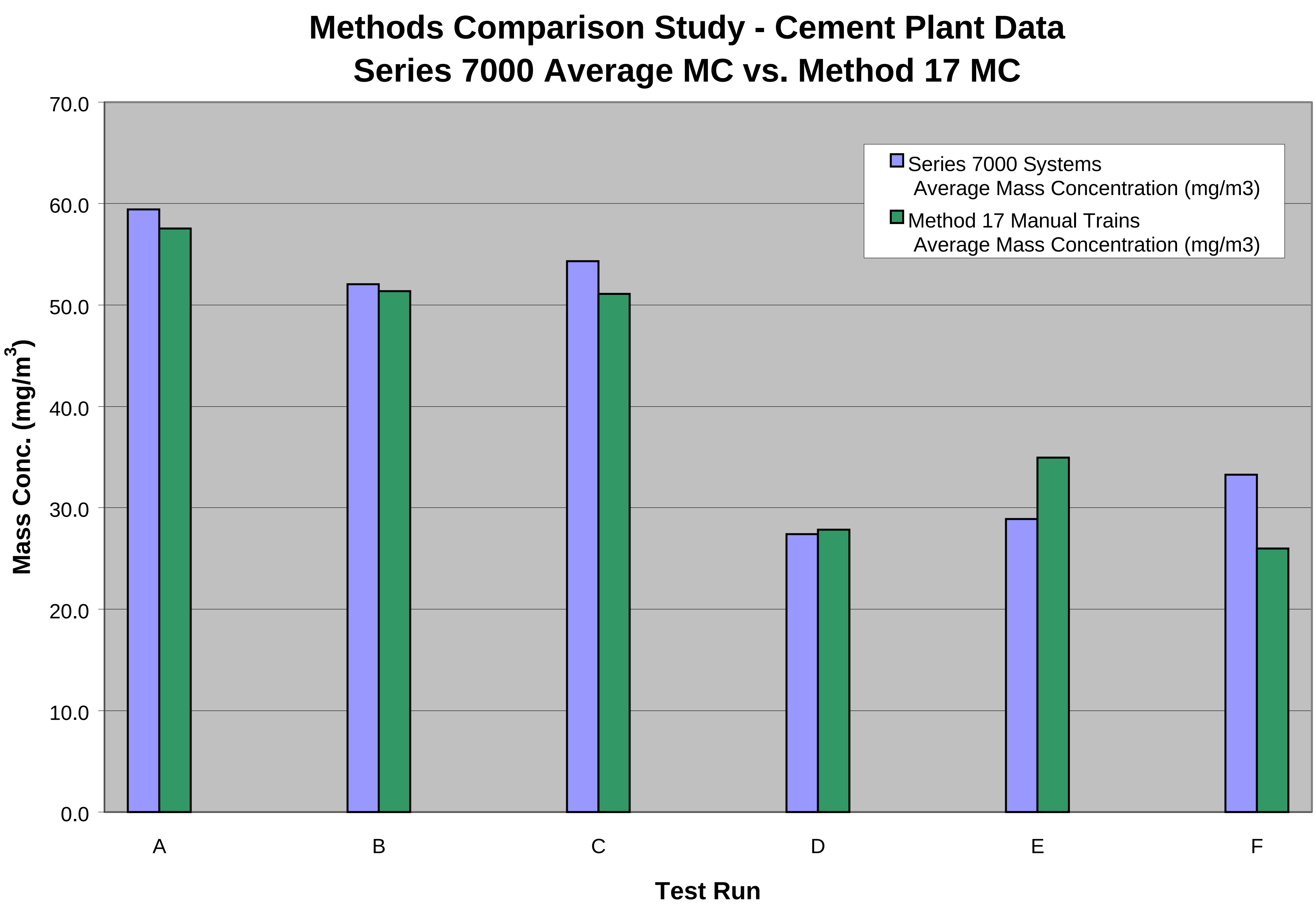

Methods Comparison Study - Cement Plant Data
Series 7000 Average MC vs. Method 17 MC
Series 7000 Systems Average Mass Concentration (mg/m3)
Method 17 Manual Trains Average Mass Concentration (mg/m3)
Mass Conc. (mg/m3)
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0.0
A
B
C
D
E
F
Test Run

Figure 3

Methods Comparison Study - Cement Plant Data
R&P Series 7000 System M1 & M2 Results
Mass Concentration vs. Time
Run A 7/12/00 16:04 - 17:06

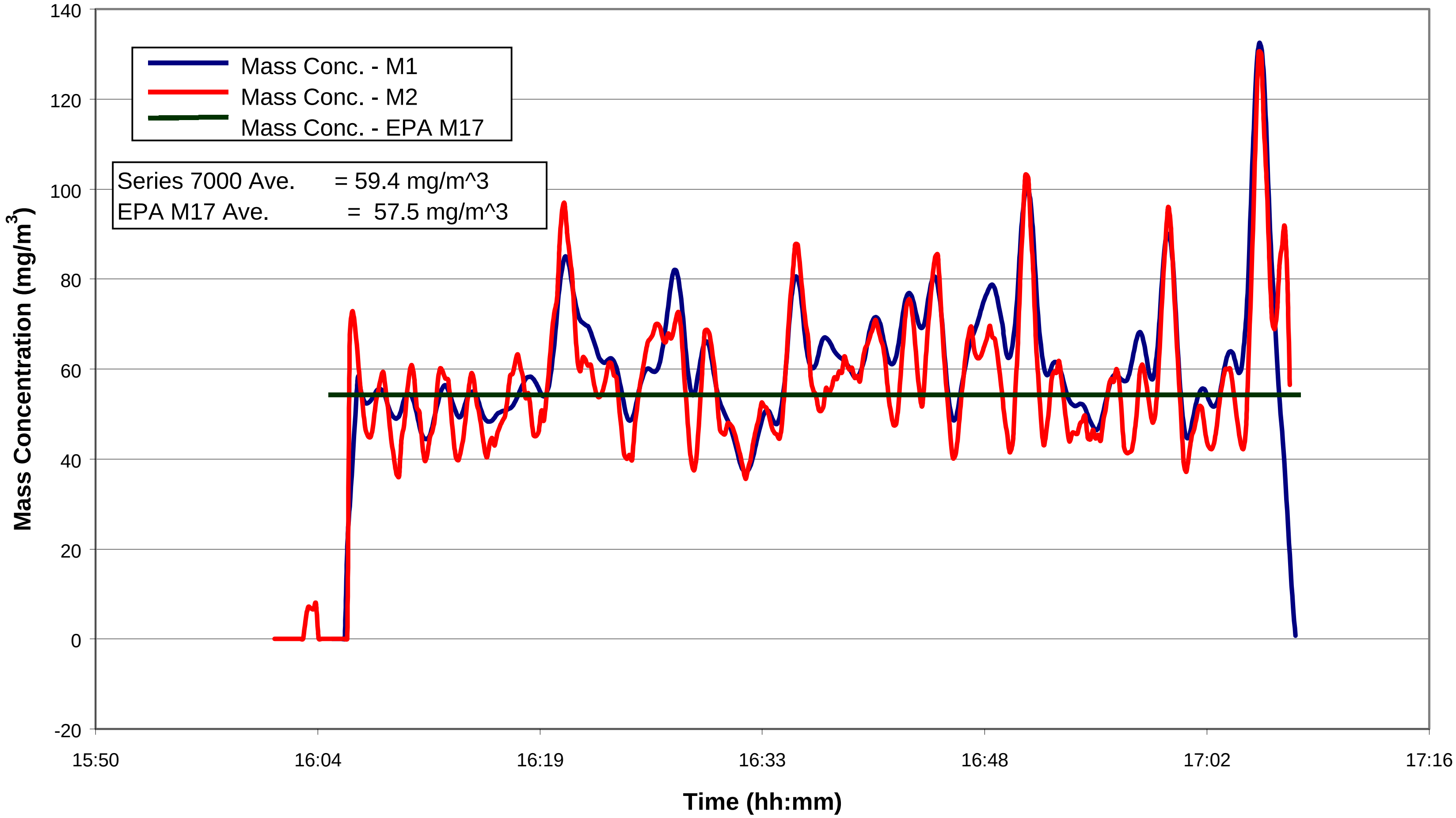


Figure 4

Methods Comparison Study - Cement Plant Data
R&P Series 7000 System M1 & M2 Results
Mass Concentration vs. Time
Run B 7/13/00 09:35 - 10:35

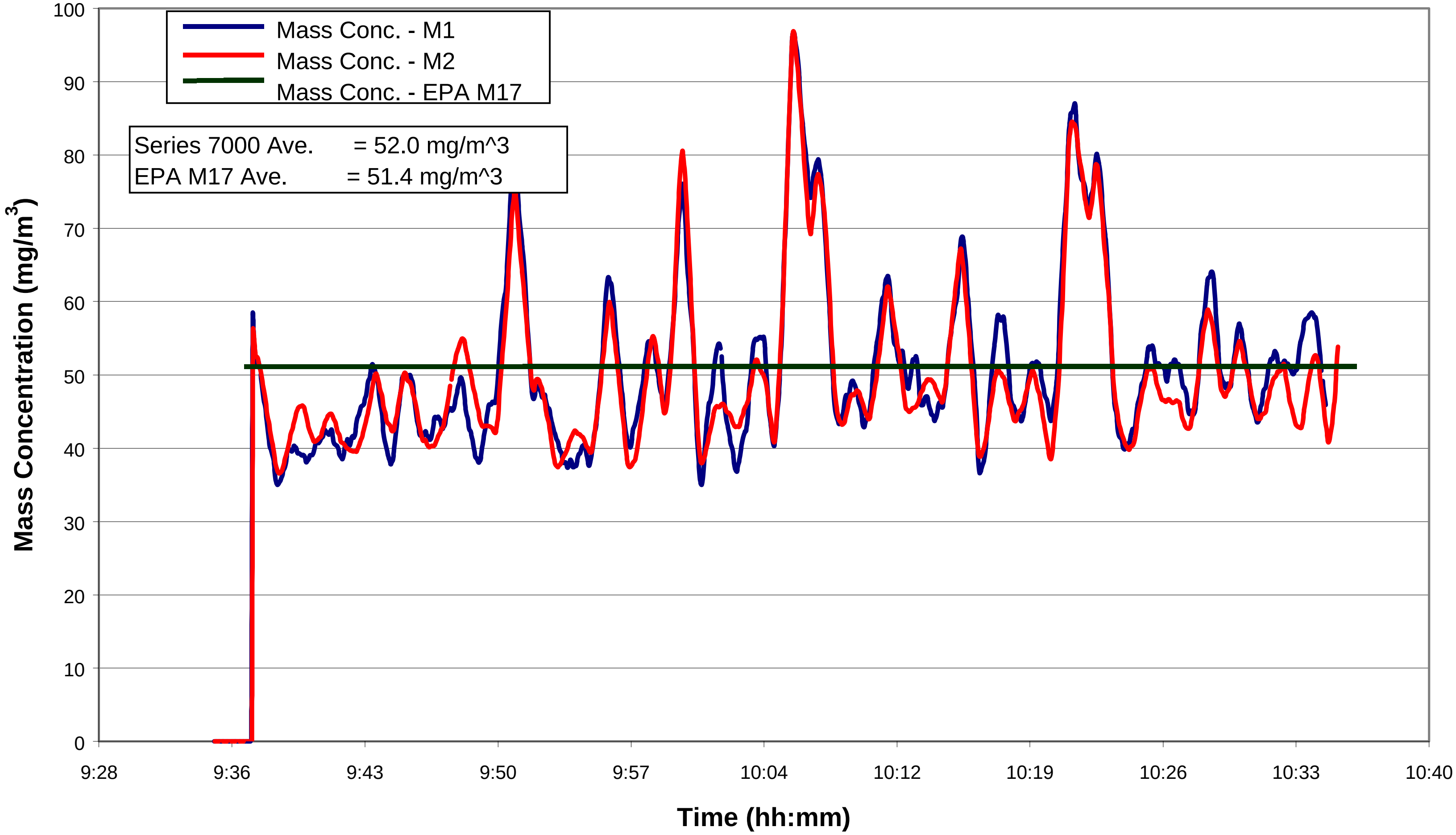


Figure 5

Methods Comparison Study - Cement Plant Data
R&P Series 7000 System M1 & M2 Results
Mass Concentration vs. Time
Run C 7/13/00 12:16 - 13:21

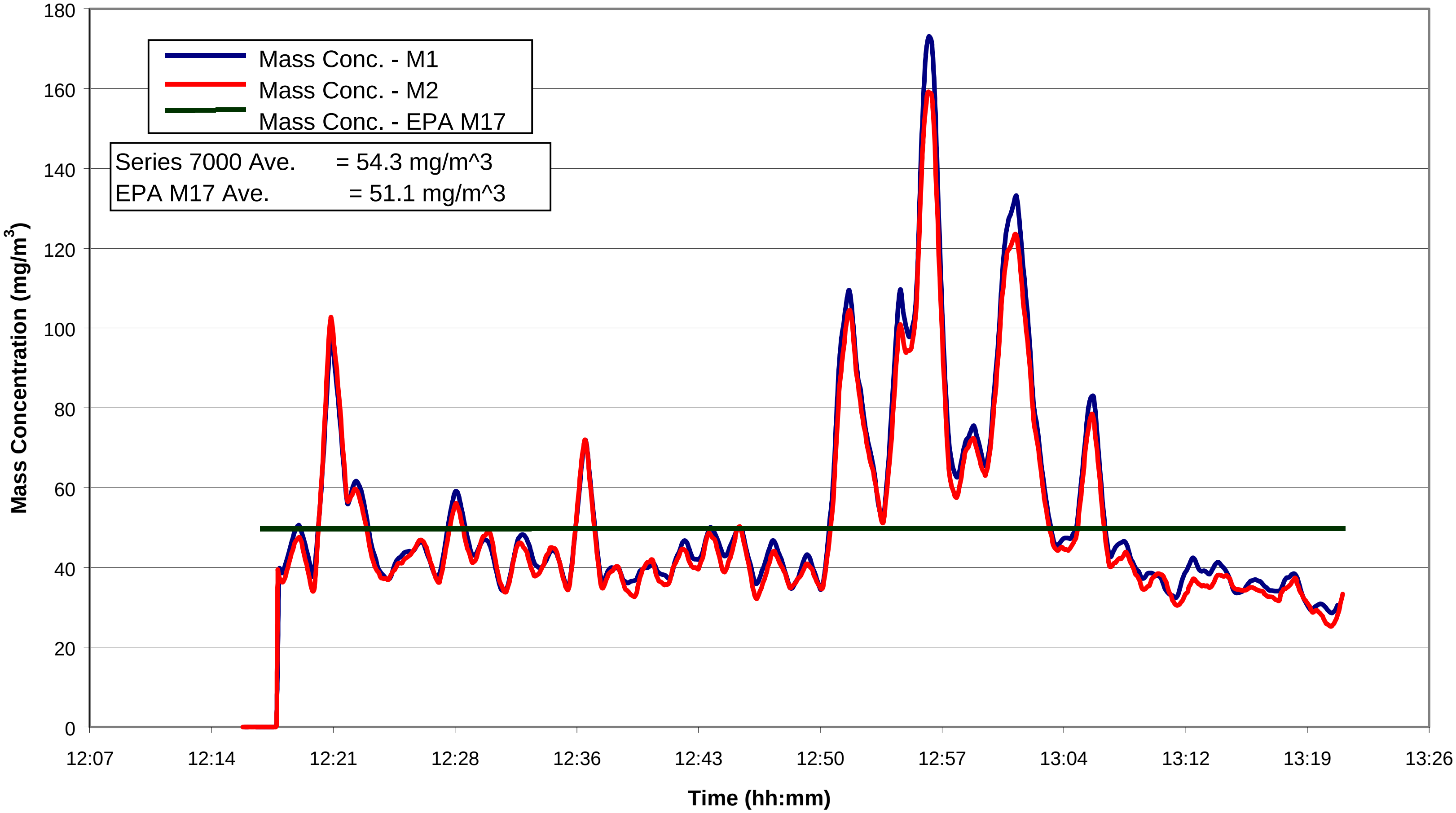


Figure 6

Methods Comparison Study - Cement Plant Data
R&P Series 7000 System M1 & M2 Results
Mass Concentration vs. Time
Run D 7/14/00 09:06 - 10:10

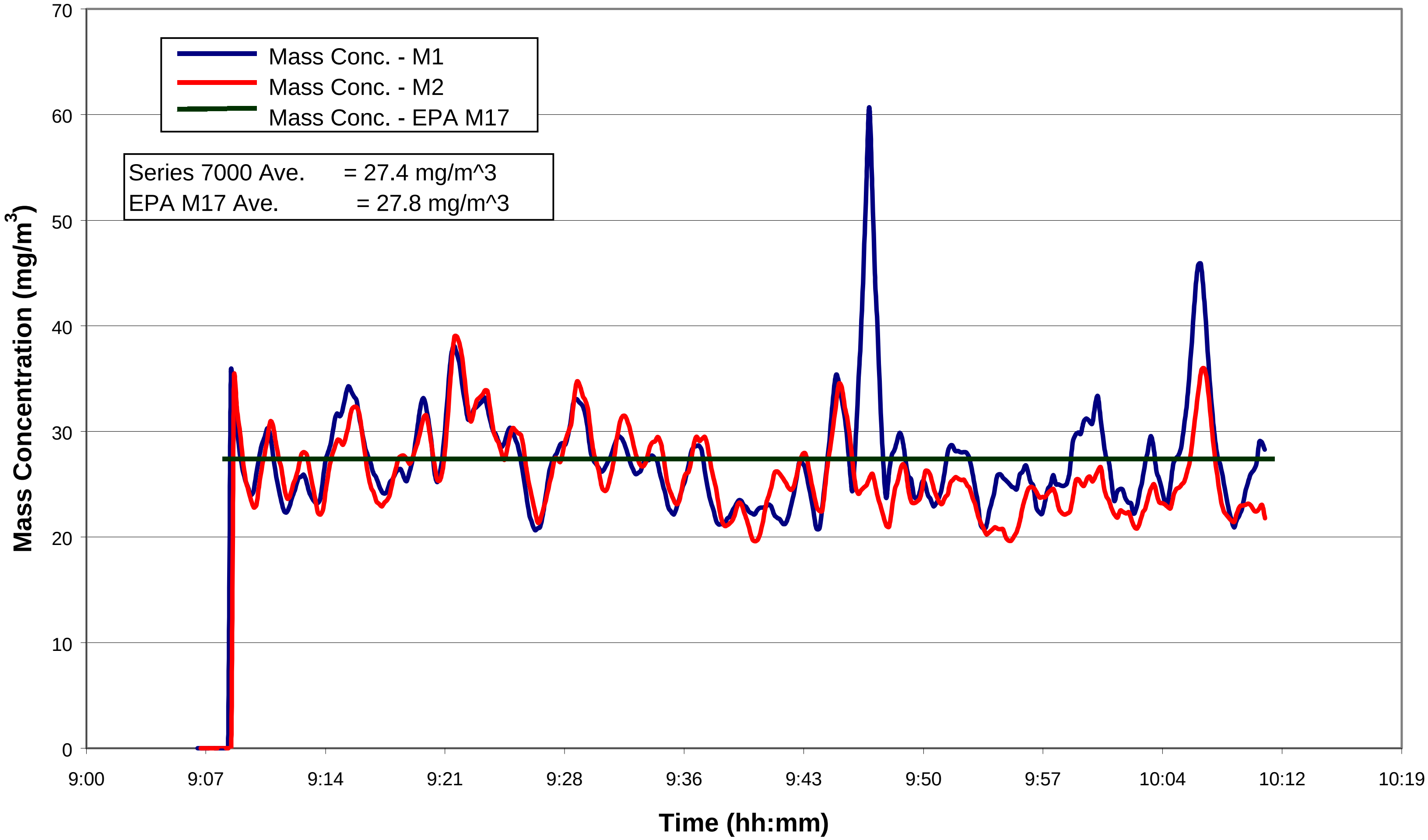


Figure 7

Methods Comparison Study - Cement Plant Data
R&P Series 7000 System M1 & M2 Results
Mass Concentration vs. Time
Run E 7/13/00 11:45 - 12:15

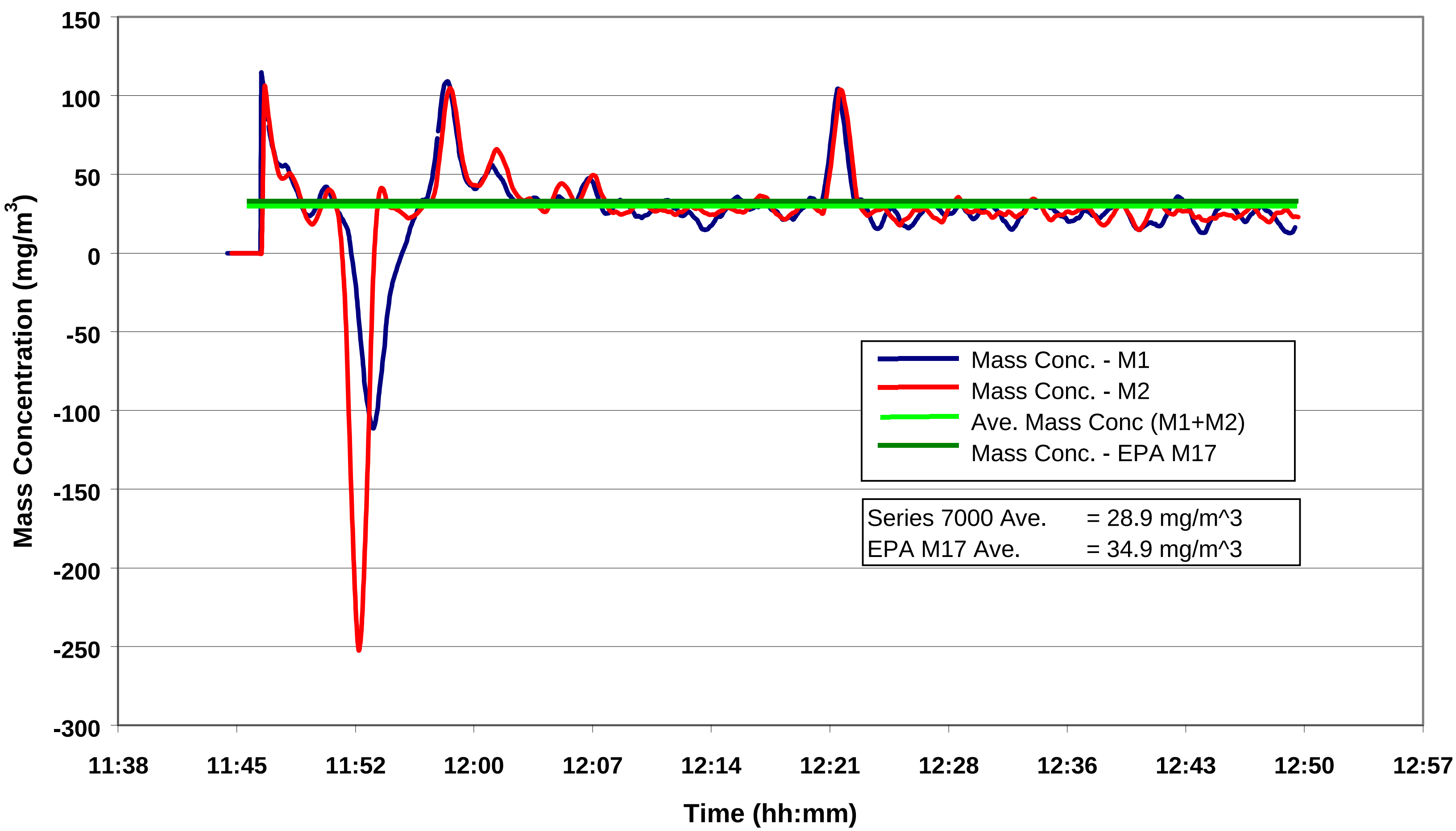
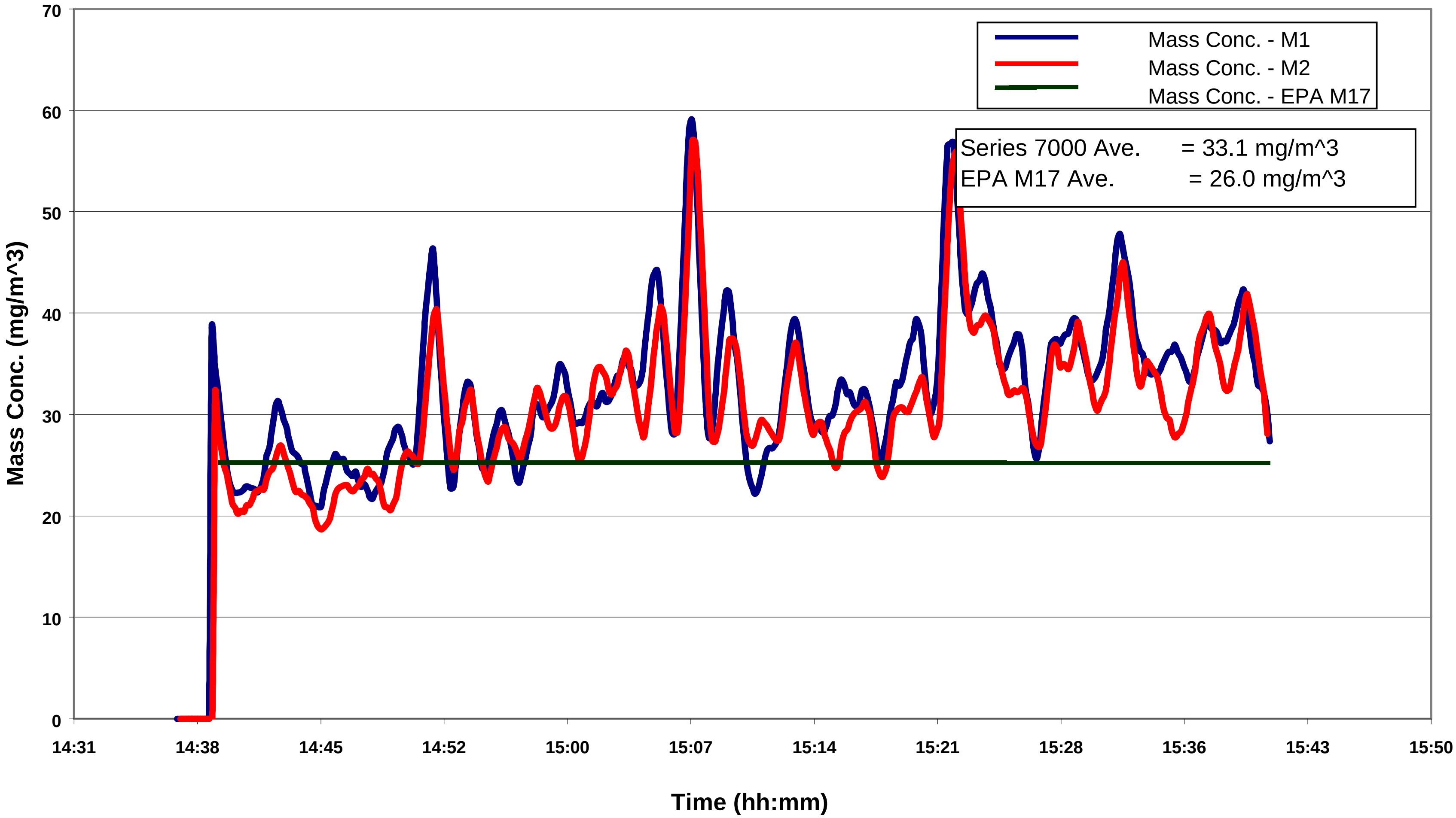


Figure 8

Methods Comparison Study - Cement Plant Data
R&P Series 7000 System M1 & M2 Results
Mass Concentration vs. Time
Run F July 2000 - 14:37 -15:40



Tables

Table 1
Summary of Results

Run	Date	Start Time (hh:mm)	End Time (hh:mm)	Series 7000 Systems Mass Concentration (mg/m^3)		Method 17 Manual Trains Mass Concentration (mg/m^3)	
				M1[1]	M2[1]	M17-1[2]	M17-2[2]
A	7/12/00	16:04	17:06	61.9	56.9	70.6	44.5
B	7/13/00	9:35	10:35	52.6	51.5	54.8	48.0
C	7/13/00	12:16	13:21	55.9	52.7	57.2	45.0
D	7/14/00	9:06	10:10	28.2	26.5	30.8	24.9
E	7/14/00	11:45	12:50	28.8	29.0	40.6	29.3
F	7/14/00	14:37	15:40	33.1	33.4	32.9	19.1

[1] M1 is Series 7000 System 1; M2 is Series 7000 System 2

[2] M17-1 is Method 17 Train 1; M17-2 is Method 17 Train 2

Table 2

Variance of Series 7000 Method With Respect to Method 17

Run	Series 7000 Systems Mass Concentration (mg/m^3)		Series 7000 Systems Average Mass Concentration (mg/m^3)	Mass Conc. Δ%	Method 17 Manual Trains Mass Concentration (mg/m^3)		Method 17 Manual Trains Average Mass Concentration (mg/m^3)	Mass Conc. Δ%	d_i	d_i^2
	M1	**M2**	**(M1+M2)/2**		**M17-1**	**M17-2**	**(M17-1+M17-2)/2**			
A	61.9	56.9	**59.4**	8.5%	70.6	44.5	**57.5**	45.3%	1.88	3.52
B	52.6	51.5	**52.0**	2.1%	54.8	48.0	**51.4**	13.3%	0.68	0.46
C	55.9	52.7	**54.3**	5.8%	57.2	45.0	**51.1**	24.0%	3.22	10.37
D	28.2	26.5	**27.4**	6.2%	30.8	24.9	**27.8**	21.1%	-0.45	0.21
E	28.8	29.0	**28.9**	-0.6%	40.6	29.3	**34.9**	32.4%	-6.03	36.36
F	33.1	33.4	**33.2**	-0.7%	32.9	19.1	**26.0**	53.0%	7.25	52.58
		averages =	42.6	3.5%		averages =	41.5	31.5%	Σd_i^2 =	**103.50**

Variance (s^2) = (Σd_i^2)/2n = 8.6

where: d_i = difference between Series 7000 average concentration and Method 17 average concentration

Table 3
Comparison of Variance of Series 7000 and Method 17 Results
(F Test)

Run	Series 7000 Systems Mass Concentration (mg/m^3)				Method 17 Trains Mass Concentration (mg/m^3)			
	M1	**M2**	d_i	d_i^2	**M17-1**	**M17-2**	d_i	d_i^2
A	**61.9**	**56.9**	**5.0**	**25.4**	**70.6**	**44.5**	**26.1**	**680.2**
B	**52.6**	**51.5**	**1.1**	**1.2**	**54.8**	**48.0**	**6.8**	**46.8**
C	**55.9**	**52.7**	**3.1**	**9.8**	**57.2**	**45.0**	**12.3**	**150.1**
D	**28.2**	**26.5**	**1.7**	**2.9**	**30.8**	**24.9**	**5.9**	**34.5**
E	**28.8**	**29.0**	**-0.2**	**0.0**	**40.6**	**29.3**	**11.3**	**128.1**
F	**33.1**	**33.4**	**-0.2**	**0.0**	**32.9**	**19.1**	**13.8**	**189.6**

F Test: ($F = S_p^2 / S_v^2$)

where: Critical Value of F is 1

S_p^2 is Variance of Series 7000 Method = $(\Sigma d_i^2)/2n$; d_i's are differences between Series 7000 method values

S_v^2 is Variance of Method 17 = $(\Sigma d_i^2)/2n$; d_i's are differences between Method 17 values

$S_p^2 = (\Sigma d_i^2)/2n =$ 3.28

$S_v^2 = (\Sigma d_i^2)/2n =$ 102.44

$F = S_p^2 / S_v^2 =$ 0.03

Table 4
Bias Analysis (Determination of "t-Statistic")

Run	Series 7000 Systems Mass Concentration (mg/m^3)		Ave. Series 7000 Mass Concentration (mg/m^3)	Method 17 Trains Mass Concentration (mg/m^3)		Ave. Method 17 Mass Concentration (mg/m^3)	d_i	$d_i - d_m$	$(d_i - d_m)^2$
	M1	M2	$(M_{1i} + M_{2i})/2$	M17-1	M17-2	$(M17\text{-}1_{1i} + M17\text{-}2_{2i})/2$			
A	61.9	56.9	59.4	70.6	44.5	57.5	-1.9	1.7	3.0
B	52.6	51.5	52.0	54.8	48.0	51.4	-0.7	0.6	0.4
C	55.9	52.7	54.3	57.2	45.0	51.1	-3.2	3.0	8.7
D	28.2	26.5	27.4	30.8	24.9	27.8	0.5	-0.4	0.2
E	28.8	29.0	28.9	40.6	29.3	34.9	6.0	-5.5	30.6
F	33.1	33.4	33.2	32.9	19.1	26.0	-7.3	6.7	44.2
								$\Sigma(d_i - d_m)^2 =$	87.0

Bias = Mean of differences (d_m) between Series 7000 Method and Method 17 = **-1.1**

Standard Deviation of the differences (SD_d) = SQRT ($\Sigma(d_i - d_m)^2/(n-1)$) = **4.2**

t-Statistic (t) = $d_m/(SD_d/SQRT(n))$ = **-0.640**