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PARTICULATE MATTER CEMS DEMONSTRATION

DuPont Inc.
Experimental Station On-Site Incinerator, Wilmington, DE

VOLUME 1

DRAFT REPORT

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1.0 INTRODUCTION

The U.S. Environmental Protection Agency (EPA) regulates the burning of hazardous waste in incinerators under 40 CFR Part 264/265, Subpart O, and in boilers and industrial furnaces under 40 CFR Part 266, Subpart H. The Agency has proposed revised regulations applicable to these hazardous waste combustion (HWC) devices. This rule is scheduled to be promulgated in 1997. Included in the proposed regulations are draft performance specifications for particulate matter (PM) continuous emissions monitoring systems (CEMS) and requirements for their use. In support of these proposed monitoring requirements, EPA requires the testing of commercially available PM CEMS to ensure that at least one such device can meet the proposed performance specifications and data quality objectives. This testing includes an extended-period durability test.

EPA in the past has relied on opacity monitors as a form of surrogate-PM monitoring to indicate compliance with a PM standard. This approach involved a continuous opacity monitor to demonstrate compliance with a separately-enforceable opacity limit approximately aligned with, or near, the PM emission limit. However, this approach has a serious limitation relative to the proposed HWC rule because of poor correlation between opacity and PM at low PM concentrations near the proposed PM emission limit of 69 mg/dscm (at 7 % O_2). EPA recognizes that there are two inherent problems with the opacity / PM approach: 1) the general concern about the stability of any opacity / PM correlation, which is strongly dependent on particle size distribution and composition, and 2) the specific concern about the insensitivity of opacity monitors typically below PM levels of about 45 mg/dscm (at 7 % O_2). Consequently, opacity monitors would not be sufficient because to maintain compliance with 69 mg/dscm, facilities would generally need to operate near 35 mg/dscm. Thus, emissions would typically be below the detection limits of opacity monitors most of the time. While normal emission levels below the detection limits of CEMS are acceptable, facilities often desire the detection limit to be one-tenth of the emission limit. This gives sufficient warning of how

emissions are changing before the emission limit is approached, and allows the facility, based on CEMS readings, to change operations as necessary to be in compliance.

If possible, EPA desires a quantitative, continuous measure of PM mass concentrations rather than opacity. Based on surveys and preliminary testing, EPA has recently determined that CEMS do exist that do this: beta gauges and light scattering based CEMS. These CEMS rely on calibration / certification of the device by manual gravimetric measurements. Therefore, EPA is proposing use of CEMS based on the availability of these newer technologies and a related Draft PM CEMS Performance Specification for monitoring PM mass concentration. EPA believes that such monitoring is feasible and that opacity monitoring has borderline sensitivity relative to the proposed PM emission limit. The newer technology PM CEMS can give a real-time quantitative measure of low PM concentrations while opacity monitors cannot. From a cost standpoint opacity monitoring is no less expensive than the proposed alternative. Furthermore, EPA believes that PM CEMS are far preferable to the alternative of continuous monitoring for PM-surrogate parameters such as ash feedrate and emission control device performance indicators. This current report documents the initial results from the first months of a planned six-month program demonstrating the performance and reliability of the newer technology CEMS in terms of the proposed performance specifications.

1.1 Program Overview

The CEMS demonstration program is aimed at verifying that at least one, and preferably more, CEMS can meet the proposed performance specifications. The program includes two phases: 1) calibration tests to compare and evaluate results from each of the CEMS with the manual EPA reference method relative to accuracy / precision, and 2) endurance tests over six months to critically examine CEMS performance relative to stability of their calibration relation and the reliability of their continuous operation. The demonstration test has involved installing the CEMS and carrying out testing prescribed in the performance specifications just as if the facility were buying and using the

CEMS for compliance purposes. CEMS performance in all the areas covered by the proposed performance specifications and data quality objectives are being evaluated. In addition, the maintenance record and data availability of each CEMS will continue to be compiled and evaluated.

Six PM CEMS were selected to participate in the demonstration based on proposals received by EPA in response to an announcement and request for proposals that appeared in the Federal Register. The participating CEMS vendors, along with their technologies, are:

- Monitor Labs, representing Verewa - Beta technology;
- Environnement USA, representing Emissions SA (ESA) - Beta technology;
- Durag, Inc.- Light scattering technology;
- Environmental Systems Corporation (ESC) - Light scattering technology;
- Lisle-Metrix Ltd., representing Sigrist - Light scattering technology; and
- Jonas, Inc. - Acoustic energy technology.

Descriptions on each of the CEMS are given in Chapter 3.

The overall scope of the PM CEMS demonstration has included pre-screening measurements for PM, HCl, and particle size distribution; development and laboratory testing of a Modified Method 5 for low PM loading measurements; and field demonstration of the PM CEMS. The main elements are summarized below.

- *Site selection:* The incinerator at the Dupont Experimental Station in Wilmington,

Delaware was selected for the PM CEMS demonstration based on emission level, type of air pollution control system (APCS), and the wide variety of hazardous waste burned.

- *Pre-screening measurements:* Testing has been conducted as part of the facility characterization and permitting campaign following the retrofit of the facility with an electro-dynamic venturi (EDV) system. Some of these results are already available for inclusion in the CEMS demonstration program.

- *Method 5 Modification*: Method 5 was not originally designed in the early 1970's for measuring low PM concentration measurements near or below the 69 mg/dscm level. Results from preliminary demonstration testing that has been carried out by EPA/OSW has revealed that the accuracy / precision of the measurements made with Method 5 is one of the factors limiting exact CEMS calibration at these low PM levels. Therefore, a modified manual method designed to provide improved precision at low PM loadings has been developed, and is being demonstrated and used to calibrate the CEMS. The modified design incorporates a light weight filter holder assembly able to be weighed before and after sampling without disassembly for recovery of the filter. This assembly replaces the conventional filter housing used in Method 5. The proposed Method 5 procedural modification is thus very slight; it merely eliminates the filter recovery step. Nevertheless, this modification has potential to improve its accuracy / precision at low PM levels.

- *Demonstration testing of the CEMS:* The draft data quality objectives require response calibration audits (RCAs) every 1-1/2 years and quarterly checks of calibration error (absolute calibration audits, or ACAs). During the endurance test, RCAs and ACAs are being performed monthly. In addition, the reliability and maintenance requirements of the CEMS are being documented. The elements of the endurance test consist of:

Monthly RCAs (comparison to Reference Method measurements);

Monthly ACAs;

Continuous recording of CEMS data for six months;

Documentation of daily calibration and zero checks;

Documentation of all performed maintenance/adjustments; and

Documentation of all periods of data non-availability.

- *Applicability of Proposed Performance Specifications* : Another important aspect of the demonstration is evaluation of the proposed performance specifications themselves. In particular, all deviations in the demonstration test from the procedural requirements of the performance specifications are being noted. This is important because the performance specifications were drafted with the understanding that revisions in the structure and language may become necessary from discovery during their initial attempted implementation. In these instances, the issues are identified with the rationale for modifying the draft performance specifications being described and justified.

1.2 Description of Facility and Monitors

1.2.1 *General Facility Description*

The site selected for the PM CEMS demonstration is the incinerator at the Dupont

Experimental Station in Wilmington, DE. The rationale for this site's selection is the following:

1) An incinerator was preferred for two general reasons:

- Many incinerators burn a wide variety of waste as their primary feedstream. This has a higher potential, compared to other HW-burning facility types, to produce PM with a wide variation in characteristics (composition, size distribution, shape, and color), representing a worst case challenge for PM CEMS; and

- Incinerators generally have well controlled PM emissions, which allows testing at levels approaching the new proposed emission limits.

2) The particular incinerator facility was chosen for the following reasons:

- Preliminary measurements show that PM emissions generally range from around 8 to 90 mg/dscm (0.003 to 0.04 gr/dscf) at 7% O_2, depending on how the facility is operated.

- The facility is willing to host the demonstration and : 1) allow the necessary CEMS installations to be made; 2) provide ample access, space, and sample location criteria; and 3) vary operating conditions and waste streams as required to perform the calibration of the CEMS.

The incinerator facility has undergone recent equipment upgrades ; the following is a general description of its current design.

A Nichols Monohearth incinerator is used as the primary combustion chamber. Waste is fed to this combustion chamber using three separate means : 1) a ram feeder for solid waste, 2) a

cylindrical chute for batched waste material, and 3) a Trane Thermal liquid waste / No. 2 fuel oil burner. The primary combustor exhausts to a secondary combustion chamber (afterburner) where No. 2 fuel oil is fed using a Trane Thermal burner. This afterburner chamber discharges to a spray dryer where the elevated temperature exhaust gases are used to dry the scrubber liquid in order to remove dissolved and suspended solids previously collected by the wet scrubber system. Some PM is removed by the spray dryer; recycling the scrubber water back into the gas stream serves as another source of PM in addition to the waste feed streams. The exhaust gas from the spray dryer discharges to a cyclone where additional PM is removed from the gas stream. The exhaust gas from the cyclone discharges to a reverse jet gas cooler/condenser which reduces the gas temperature to the dew point. The reverse jet gas cooler/condenser discharges into a variable throat venturi scrubber which is used to remove PM and acid gases. The venturi discharges into a spray absorber in which soda ash neutralized scrubbing solution is used to absorb acid gases. The gas is subcooled in the absorber by use of the cooling tower spray water before exhausting through a chevron-type mist eliminator. After this, the gas is further treated by a set of electro-dynamic venturis (EDVs) which are used to remove fine PM along with the metals that condense as a result of the gas subcooling. The gas then passes through a set of centrifugal droplet separators before being drawn through the induced draft fan and a series of steam heat coils and exhausted out the stack.

1.2.2 *General Description of CEMS Technologies*

Five PM CEMS have produced results of PM emissions concurrent with the MM5 trains. Three of the CEMS use an optical-based technology (Sigrist, Durag, and Environmental Systems Corp.) while two use a beta attenuation-based technology (Verawa and Environment U.S.A.). Both beta monitors and the Sigrist monitor employ an extractive, heated, close-to-isokinetic sampling system to deliver a sample to a particulate-measuring sensor external from the stack. The other two optical systems use an in-situ sampling / measurement approach. A sixth monitor has been installed but has experienced much difficulty in producing acceptable results compatible with the data acquisition system.

Light Scattering CEMS. The light scattering technologies are offered with either in-situ or extractive sampling features. The three techniques being used monitor particle loading by measuring the scattered light in either the forward or backward direction. Various types of light sources (halogen, infrared, and incandescent) are being used to generate a beam with a known wavelength. A light sensor or photometer appropriately positioned in either the forward or backward direction measures the scattered light. In addition to each CEMS being designed with an air-purge system to minimize PM buildup on the optics, each technology utilizes a different approach to adjust and compensate the detector's signal for interferences such as stray light and PM accumulation on its optics. Also each CEMS has an automatic zero and calibration check performed daily. The instruments' response is proportional to the "dry" PM concentration for a given set of PM characteristics (composition, density, size distribution, index of refraction) and provide detection levels near 0.5 to 1.0 mg/dscm. Each individual instrument undergoes a factory calibration to ensure the exact same response for a given set of PM conditions, thus providing interchangeability of individual instruments from the same manufacturer. However, since the instrument response is dependent on PM characteristics, a site specific calibration is generally required to ensure or adjust instrument response. These CEMS produce very frequent signals on a nearly continuous basis. Each of the three CEMS manufacturers has presented evidence to EPA/OSW of worldwide installations numbering >100.

Beta Gauges. Each of the two beta instruments uses a heated sampling line to obtain and deliver a close-to-isokinectic sample which is collected on a filter roll. The sampling flowrate and duration is programmable or adjustable depending on PM loading. After the sampling period is completed, some form of probe purge is performed to entrain any PM deposit onto the filter. The beta transmission through each blank filter is determined before sampling begins. After a batch sample is collected over a few minute period, an automatic filter indexing mechanism moves the filter position to a location between a carbon-14 beta source and a detector. Analysis is performed over a period of about 2 minutes. The difference between the two analysis is representative of the PM collected on the filter. Thus the response of the instrument is relatively independent of the PM characteristics and a site

specific calibration, or adjustment in instrument response, is generally not required. These CEMS produce signals on the order of every 5 to 12 minutes. Each of the two CEMS manufacturers has presented evidence to EPA/OSW of worldwide installations numbering >100.

Acoustic Energy. In this technique shock waves caused by the impact of particles with a probe inserted into the gas flow are used to measure particle loading. The device counts the number of impacts and measures the energy of each impact. This information, coupled with knowledge of the gas velocity, allows calculation of the particle mass and thus concentration. Since the probe inherently distorts the localized flow pattern, changes in flow velocity or particle size distribution will, in principle, alter the instrument's response. Since the instrument response is dependent on PM characteristics, a site specific calibration is expected to be required to ensure or adjust instrument response. This CEMS produces very frequent signals on a nearly continuous basis. This vendor has not yet presented any evidence to EPA/OSW of any installations using this technology in a PM air emission application.

1.3 Program Scope

The overall scope of this program was described in Section 1.1. All testing was made with the unit operating normally. Dupont was responsible for compilation of all incinerator operating data and for delivering that information to EER. The engineer in charge of the Dupont incinerator was Mr. Richard Vickery. EER had overall responsibility for collection and analysis of the PM emission data as well as data reduction and evaluation. Analytical Services, Inc. performed supplemental analysis of the filters using scanning electron microscope and energy-dispersive X-ray methodologies. The overall program was under the direction of Mr. Scott Rauenzahn from the EPA Office of Solid Waste and Mr. Dan Burns of the Department of Energy. Special assistance in the evaluation of the Method 5 modification was provided by Messrs. Tom Logan and Dan Bivens from the EPA Emission Measurement Center.

The primary contacts for each of the participating CEMS vendors are :

- Mr. Richard Hooper of Monitor Labs, representing Verewa;
- Mr. Tony Griguoli of Environment USA, representing Emissions SA;
- Mr. Thomas Kurzawski of Durag, Inc.;
- Mr. Robert Nuspliger of Environmental Systems Corporation;
- Mr. T. J. Medland of Lisle-Metrix Ltd., representing Sigrist; and
- Mr. Ravi Mathur of Jonas, Inc.

The pre-screening phase of the demonstration program was conducted in August 1996 with CEMS installations being completed in September. The initial calibration tests were performed in late September and mid October and RCA tests were performed monthly thereafter. As will be discussed later in this report, a few of the CEMS were not able to produce data due to operational difficulties during periods in October and November. The eight-month demonstration program is scheduled to continue until April 1997, soon after which a final report will be prepared.

2.0 TEST PROGRAM RESULTS

This demonstration program is designed to look at the feasibility of using PM CEMS and development of an approach for verifying their performance. An initial draft performance specification was developed to begin the program. As data are collected and analyzed, they are applied to both as parts of the program. This has led to a progression of modifications in our approach to evaluate the monitors and the performance specifications. Until the program is complete, this state of flux will continue to ensure that the monitors receive a fair evaluation and, if approved, the performance specification is adequate to ensure operation within the regulatory framework. With this in mind, it is important to note that this is a draft interim report and not a final report. As experience is gained, approaches used in this draft interim report will be subject to change.

The current section provides the results from the initial calibration tests performed in September and October along with the November monthly calibration tests in November, December, and January for the PM CEMS demonstration program at the Dupont Experimental Station incinerator. The calibration testing in September / October was intended to establish the initial calibration relation for each CEMS relative to the reference method. Subsequent response calibration audit (RCA) test results from November through January serve a twofold purpose for each CEMS : 1) to determine the acceptability of its RCA data relative to its initial calibration relation, and 2) as additional data to extend its data base in forming an updated master database. As indicated in the introduction, the test program was performed in accordance with the proposed performance specifications for PM CEMS. The calibration tests consisted of conducting simultaneous CEMS and manual Modified Method 5 (MM5) measurements as the reference method under a variety of incinerator operating conditions. Results from the initial and monthly tests are presented in the material that follows, preceded with a summary of the draft performance specification calibration test protocol and facility operations during testing.

2.1 Proposed Performance Specifications Calibration Testing

Draft Performance Specification 11 (DPS 11) has been developed and proposed by EPA to establish the framework for certifying PM CEMS in future regulations governing their formal use on HWC facilities. This specification is to be used for evaluating the acceptability of PM CEMS following their installation and thereafter. Foremost in the DPS 11 is site-specific, rigorous testing of the PM CEMS response in order to initially calibrate and certify its performance. Such initial calibration tests are composed of three main elements : 1) operating the facility across its normal PM emission range and beyond the proposed PM emission limit, 2) conducting PM CEMS and manual gravimetric reference method measurements simultaneously, and 3) performing these tests over fifteen operating conditions. Every 1-½ years thereafter a RCA Test would be conducted to evaluate the adequacy of continuing to apply the initial calibration relation. The range of validity of the response calibration developed in the RCA is restricted to the range of the of PM loadings used to develop the initial calibration relation. If conditions at the facility were to change significantly (i.e., changes in emission controls, feedstreams, or fuel type), then a new RCA test would be required. Since the validity of the response calibration may be affected by significant changes in PM characteristics, such as composition, density, index of refraction, and size distribution, the limitations of the PM CEMS would be evaluated with respect to these possible changes on a site-specific basis.

Because there are no other available means of challenging and certifying the performance of the PM CEMS across its intended range, it becomes necessary to change and control process conditions for developing the appropriate range of PM emission levels. The DPS 11 stipulates that calibration testing be carried out by making simultaneous CEMS and manual reference method (Method 5) measurements at three or more different levels of PM concentrations. Three or more sets of measurements would be obtained at each of these PM concentration levels. The different levels of PM concentration would be obtained by varying the incinerator waste processing conditions as much as the process allows within the normal operating range and permit conditions. This means that, at certain facilities, it would be necessary to vary feed rates for waste, ash level, and/or metals in order to develop a range of PM emission levels over which the calibration is conducted. Alternatively, PM emissions may also be varied by adjusting the performance of one or more of the PM control devices.

It is recommended that the CEMS be calibrated over PM levels ranging from a minimum normal level to a level twice the emission limit, as this would provide the smallest confidence interval bounds on the calibration relation at the emission limit level. It would also be required to conduct calibration tests at load levels > 50 %.

2.2 Discussion of Outliers

The behavior of results in the data base developed in this program shows variations in some of the reference method results that are not readily explainable. The data produced during these tests show variations between the paired (identical, simultaneously-operated, but differentially-located) sampling trains (1) typically ranging from 2 to 30 %, but (2) occasionally being 35 % or greater.

The first type of variations are considered statistically acceptable since they are within 3 times the reported precision of the reference method. They are explainable on the basis of being within the normal certainty of the method as employed, considering the potential contribution from spatial and temporal variations in the PM profile obtainable from separate traversing with the paired trains. However, the second type (paired data with variations > 35 %) cannot be explained on the basis of the relative uncertainty of the reference method. The term outlier is commonly used to describe an usually high or low value from an individual measurement in the data. In a practical sense, outliers are expected to occur on up to 10 % of the data in any series of individual measurements as a result of a variety of reasons. Due to this frequency and recognition that incorrect conclusions are likely if outliers are included, it is standard practice in statistical analyses of a data base (as in this program) to :

(1) Screen data for outliers,

(2) Eliminate outliers prior to data analysis, and

(3) Identify outliers due to unusual conditions of measurement.

The appearance of outliers in the data base raised the questions of (1) how to approach identifying the outliers, and (2) how should they be treated once identified ? The first question was addressed by looking at the different statistical approaches used to determine if there is statistical significance to the difference in measured values. If there is, then the datum point can be labeled as an outlier. To determine the statistical significance, it was decided that a student -T test approach, as described in EPA's "Quality Assurance Handbook for Air Pollution Measurement Systems - Vol. III Stationary Source Specific Methods EPA 600/4-77-077b), would be used for the type of data base being considered.

Additional approaches for identifying outliers have been utilized during the course of this program with still other approaches under consideration. Concurrent with exploring different means of treating outliers, the overall scope of this program includes consideration for development of data quality criteria beyond the normal reference method criteria. The approaches for treating outliers so far and the new data quality criteria under consideration are discussed below.

Statistical Outliers

Statistical evaluation of the initial calibration data (collected in the September and October tests) was performed to determine the extent of correlation of individual data points with the calibration relation. The standard deviation between each actual data point and the regression line of the calibration relation was determined. This evaluation indicated that the exact same 3 individual data points, fell outside the tolerance limits determined by the regression analysis and could be considered outliers (i.e., with standard deviations > 3) for each of the CEMS. Removal of these standard deviation outliers improved the correlations and was initially justified based on the circumstances in which the different CEMS technologies independently indicated the exact same 3 data points (Conditions designated 3, 6R2, and 8) as outliers. However, this approach for identifying outliers (referred to as *statistical outliers* later in Section 2.4) created controversy because of its weak scientific basis and its poor precedent for future calibrations to be performed by industry presumably with only

one CEMS technology.

Paired Train Outliers

Another means for treating outliers, this one being performed prior to evaluating the correlation between the CEMS / reference method data, was employed during reporting the results obtained in November (Section 2.5). Data were discarded based on the following general approach: (1) if one of the paired trains produced an abnormal result, then both results from that condition were discarded and not just the apparently abnormal point, and (2) if both trains produce results in agreement and within the precision of the method, then both are considered acceptable. This approach, referred to as the paired train approach, was applied *qualitatively* as a basis for disregarding data from Conditions 20, 27, 28, and 30.

Relative Standard Deviation Outliers

More recently, a tentative agreement within the project team was reached in *quantitatively* applying the preceding approach for identifying outliers as follows (1) if the paired reference method data produced from one test condition does not agree within the precision of the reference method, then all the data for that condition has grounds to be suspect and should be thrown out, and (2) if both trains produce results within the reported precision, then both data are considered acceptable. The precision of Method 5 reported from replicate and validation testing in the 1970's for PM levels around 150 mg/dscm (uncorrected for O2) is reported to be (1) linearly related to the PM level, and (2) approximately 10 % when calculated as the relative standard deviation (RSD). A normal statistical approach for identifying outliers in a large data base is to remove data with standard deviations > 3 around a mean or a regression line. Since the paired data sets are from a small data base, this approach for identifying outliers is based on removal of paired train data that does not agree within 3 times the RSD of Method 5, or > 30 % RSD. This means that the paired train results must pass a data quality objective with a RSD < 30 % to be considered acceptable for

inclusion in the calibration data base. The two following equations were used in calculating the RSDs :

Equation 1 : Standard deviation = SD = $(D^2 / M)^{1/2}$

Equation 2 : RSD = $(SD / 2N)^{1/2}$

where : D = Difference in concentration results between the paired trains
M = Mean or average in concentration results between the paired trains
N = Number of samples = 2

Using this approach, the following outliers (referred to as RSD outliers in Section 2.6) were identified in the original data set :

- 2 of the 10 conditions (Nos. 2 and 10R1) in September,
- 1 of the 11 conditions (No.10) in October,
- 1 of the 9 conditions (No. 30) in November,
- 4 of the 9 conditions (Nos. 31, 33, 35, and 39) in December, and
- 2 of the 10 conditions (Nos. 41 and 42) in January.

Another approach for determining the correlation coefficients is also under consideration. This approach would involve developing a statistical means of removing the variation associated with Method 5 from the calibration relation setting process. A potential advantage of this would be that it allows evaluation of the variability associated with the PM CEMS response independent of the relation between the Method 5 and the PM CEMS.

In addition to exploring alternate means of treating outliers, the overall scope of this program

includes consideration for development of new data quality criteria beyond the normal reference method criteria. This consideration would provide protection against other forms of outliers or anomalies which are prone to occur if the reference method is not carefully performed by experienced personnel. An example of this type of problem is when the sampling probe nozzle is brushed against the inner stack wall, artificially increasing the amount of PM collected in the nozzle / probe. Provisions are being considered for establishing new data quality criteria involving sampling train partitioning as an extension and use of Method 5's precision. Since precision in the paired train results is required, it would appear logical to expect comparable precision in terms of the RSD's in, and/or the historical relationship between, two key components (i.e., probe rinse and filter weight gains) forming the end result.

2.3 Facility Operation Summary

The CEMS installations and calibration testing for this demonstration program were conducted in agreement with the DPS 11 protocol. The calibration tests consisted of conducting simultaneous CEMS and manual Modified Method 5 (MM5) measurements under a wide variety of incinerator waste feed stream / air pollution control (APC) conditions.

2.3.1 *Facility Operation During the Initial Calibration Test*

The incinerator process was operated in a manner to maintain the facility at or below their permitted levels and to accommodate the initial calibration test as closely as possible. The calibration testing for this PM CEMS demonstration required an attempt to generate wide variations in PM emission characteristics such as concentration, composition, size distribution, and color. In order to produce these variations, five different types / combinations of fuels and/or wastes were fed to the incinerator over three different EDV power level set points for a total of fifteen test conditions. Table

2-1 presents the matrix of the test conditions. The five types of fuels / waste fed to the primary combustion chamber were :

1) fuel oil only;
2) solids consisting of shredded paper, animal bedding, and office / laboratory waste;
3) Chlorinated solvents;
4) a mixture of chlorinated and non-chlorinated solvents; and
5) paint pigments containing water, resins, and solvents.

The feed stream (fuel and hazardous waste) data from the plant records during testing was collected in order to document the range of plant operation covered during the calibration and any feed stream effects on the performance of the CEMS. The availability of waste influenced the order and accounted for the random sequence of the test conditions.

The APC equipment operations were not deliberately changed except for the EDV power levels. The EDV power levels were adjusted with a programmable logic controller for three set points : 0.3 kilowatts (kW) for the low power condition, 0.6 to 0.7 kW for the mid power condition, and 1.1 kW for the high power conditions. Another key, but not-so-controllable, variable affecting PM emission characteristics is the scrubber water used in the spray dryer operation. Metals, salts, and ash removed by the venturi and EDV are contained in the scrubber water, along with unreacted soda ash (anhydrous sodium carbonate) for pH control, and are continuously fed back into the spray dryer for eventual removal as a dry material in the spray dryer or cyclone. The venturi scrubber pressure drop is not able to be varied, and nor is the PM collection performance of the spray dryer or cyclone.

A summary of the facility operating data for each condition in the September and October testing is presented in Tables 2-2 and 2-3, respectively. Records of the facility operating data during the September testing are included in the Appendix along with particle size distribution test results performed for Dupont. The particle size distribution results show that about 85 % of the PM at the

EDV inlet is < 1 micron, indicating that a smaller particle size distribution (approximately 90 % < 1 micron) would be expected at the EDV outlet and at the stack sampling location.

TABLE 2-1. MATRIX OF RESPONSE CALIBRATION AUDIT CONDITIONS

EDV Power Set Point		
Low	Medium	High
Fuel oil only	Fuel oil only	Fuel oil only
Solids	Solids	Solids
Chlorinated solvents + solids	Chlorinated solvents + solids	Chlorinated solvents + solids
Mixed solvents + solids	Mixed solvents + solids	Solvents mix + solids,
Mixed solvents, solids, paint	Mixed solvents, solids, paint	Mixed solvents, solids, paint

2.3.2 Facility Operation During the October Calibration Test

The facility was operated similarly during the October testing as a wide variety of wastes were fed to the incinerator. No attempt was made to control the waste feed streams for the purpose of the calibration tests, although the EDV power set points were adjusted to the same three levels

as before. A summary of the facility operating conditions for the October tests is contained in Table 2-3.

2.4 CEMS Initial Calibration Test Results

The scope of this subsection is limited to the results produced during the initial calibration testing in September and October; these results form the basis on which the initial calibration relation is established for the CEMS able to operate during this period.

The initial calibration tests consisted of conducting simultaneous CEMS and manual MM5

measurements under a variety of incinerator waste feed stream / air pollution control (APC) conditions. The Method 5 trains were modified by replacing the standard-size filter holder with a smaller unit to improve accuracy and precision. During the fifteen condition initial calibration test series, two MM5 trains traversed the stack while one MM5 train sampled at a single location to simulate the CEMS sampling approach. After fifteen conditions for the initial calibration were completed, only duplicate MM5 trains traversed the stack during the remainder of the monthly calibration testing. Due to a facility outage, two separate testing periods were needed to complete the initial calibration. The field data, recovery, data reduction, and chain-of-custody sheets for the tests can be found in the Appendix.

The sampling times for the traverses with each reference method test (i.e., half of the total sampling time) performed in this program were on the order of 10 to 30 minutes. The response time for the ESA and Verewa Beta monitors was approximately 6 and 12 minutes, respectively. Unaware of the critical need for synchrony with short sampling times and relatively long response times, the starting and stopping of the reference method sampling periods were *not* synchronized with the Beta monitors' sampling periods. As a result of this non-synchrony in sampling times, the calibration results for the two Beta CEMS reported below are based on *semi-representative data*. More discussion on this issue is presented in Section 2.5. Synchronization with the reference method sampling times is not an issue with the light scattering monitors which have response times on the order of 1 second.

Reference Method 5 PM Results. The PM concentration results of the reference method measurements for each train, along with the average values (from the traversing trains), are shown in Tables 2-2 and 2-3 for the September and October tests, respectively. All PM concentration data developed from the reference method were reduced to a dry basis and EPA standard temperature and pressure: 20°C (68°F) and 760 mm Hg (29.92 in. Hg). A nominal value of 1.5 was then universally applied to produce PM concentration values @ 7 % O_2 corrected values, based on a representative stack gas average O_2 content of 11.7 %. The average 7 % O_2 corrected results are presented later in the tables used for the DPS 11 evaluations. The PM emission calibration test results produced from MM5 ranged from 10 to 100 mg/dscm at 7 % O_2. The data are concentrated in the lower / middle part of this range,

which is the normal range of PM emissions for the facility. Most of the 21 runs produced results that agree within 15 % of each other; three conditions produced results with outliers or with variations greater than 20 %. *Review of the paper trail (field data sheets, recovery sheets, and chain of custody) has indicated that the filters were improperly identified.* Most of the weight gain was associated with the filter catch, as there was generally 5 to 25 mg weight gain on the filters and 0.5 to 1.5 mg weight gain from the front-half probe rinses.

CEMS PM Results. The results produced from each of the operating CEMS for each test condition are also presented in Tables 2-2 and 2-3 for the September and October tests, respectively. These were developed from averaging the 1-minute CEMS records collected on the DAS for the corresponding MM5 sampling times, excluding the times during port changes. Data from the ESA and Verewa Beta monitors were offset corresponding to their response times. Discussion on the issue of representative data acquisition from the two Beta CEMS with response times approaching/ exceeding sampling times is presented later.

DPS 11 Calibration Relation. The calculations for the calibration relations were carried out according to the equations and definitions in DPS 11 for the correlation coefficient, confidence interval, and tolerance interval. Briefly, these involve performing a regression analysis on the paired (or set of) CEMS and reference method data with 7 % O_2 corrected values. A linear calibration relation is calculated by performing a linear least squares regression. The CEMS data are taken as the *x* values and the reference method data as the *y* values. The calibration relation, which gives the predicted PM concentration, *y'*, based on the CEMS response *x*, is given by:

$$y' = a*x + b$$

where :

a = slope of the line, and

b = y intercept.

Following this, the 95 % confidence interval for the regression relation is computed, as is a tolerance interval bounding 75 % of the population of the paired data with 95 % confidence; both intervals are calculated at the proposed emission limit level. The equations provided in DPS 11 were put on a spreadsheet, while values for t_f, v_f, and u_n' were manually inserted from Table I in DPS 11. In essence, the confidence interval gives the 95 % confidence on the uncertainty of the PM concentrations calculated from the CEMS response using the regression relation. The tolerance interval bounds the region within which one would expect continued paired data sets to fall, based on the measurement pairs used to perform the calibration. Subsequent measurements comparing the CEMS response to the reference method are considered consistent with the current calibration relation if at least 75 % of them fall within the current tolerance level.

The calculation results of the *complete data set* for the five CEMS are summarized in Tables 2- 4 through 2-8 for the ESA, Verewa, Durag, ESC, and Sigrist monitors, respectively. Each table

presents the 7 % O_2 corrected reference method (*y*) and CEMS (*x*) paired values along with each of the following corresponding spreadsheet-calculated values :

- Predicted *y* plus the confidence interval,
- Predicted *y* minus the confidence interval,
- Predicted *y* plus the tolerance interval,
- Predicted *y* minus the tolerance interval.

The *complete data set* results are graphically presented in Figures 2-1 through 2-5 for the five CEMS in the same respective order as the tables above. Each corresponding figure then illustrates the calibration relation (dashed line), confidence interval (inner pair of solid lines), and tolerance interval (outer pair of solid lines) for the calibration data set. For the complete data set, none of the CEMS meet the correlation coefficient criterion of 0.90, and only the Durag and Sigrist met the 20 % confidence interval and 35 % tolerance intervals. Note that the "complete" data set for the

Verewa and ESA monitors only include results from testing in September, as these two CEMS were not operating during the October testing.

Review of the graphs above clearly show the same 3 outlying points for each CEMS. A statistical evaluation of the complete data set was performed with the results showing that these 3 particular points deviated more than a 3 standard deviations from the calibration relation. Such points are normally considered outliers on a statistical basis, and thus were then deleted from the complete data set on this statistical basis. With these statistical outliers omitted, the DPS 11 calculations were re-performed. The calculation results *without the statistical outliers* are summarized in Tables 2-9 through 2-13, and graphically presented in Figures 2-6 through 2-10 in the same respective order as above. For this data set, all of the CEMS, except the ESA, meet and exceed the correlation coefficient criterion of 0.90 as well as the 20 % confidence interval and 35 % tolerance intervals. (Note that the data acceptance criteria for the ESA and Verewa are not based on the minimum number of 15 data points, and a fundamental difficulty in the testing structure attributes to the non-correlation of the ESA monitor.) Although this statistical outlier approach was attempted in this circumstance, its future use is questionable as alternatative approaches for identifying and treating outliers are being developed and considered.

2.5 PM CEMS November Response Calibration Audit Test Results

After the initial calibration tests in September and October were performed, additional testing with the reference method and the PM CEMS was subsequently performed in November. These additional tests were made to represent the Response Calibration Audit (RCA). The purpose of an RCA is to evaluate the adequacy of continuing to apply the initial calibration relation under subsequent facility operation. The RCA results are compared to the initial calibration relation as the basis of this evaluation. If 75% of the RCA data falls within the initial calibration tolerance intervals, then continued use of the initial calibration relation is considered acceptable to monitor PM emissions until the next RCA is performed. If the 75% threshold is not met, then a new or a different calibration

relation must be developed to monitor PM emissions during subsequent operations.

As an integral part of this PM CEMS demonstration effort, data quality objectives for the manual reference method are being evaluated relative to the (1) the specifications in DPS 11, (2) the intent of the regulation, and (3) the limitations of the monitors. Prior to the start of this effort, certain equipment and procedural modifications to the reference method were proposed for, and then approved to be implemented during this demonstration effort in order to improve the precision of the method at lower PM loadings. Given this agenda, the data produced from the reference method tests has undergone rigorous review and scrutiny. The abnormal results from individual reference method sampling trains were identified and have become the subject of discussion relative to treatment as outliers.

The scope of this subsection is limited to a discussion of the results produced from the November response calibration audit (RCA) testing and discussion of the approach developed for the treatment of outliers and its affect on the data quality objectives.

2.5.1 *Treatment of Outliers*

The behavior of the results in the data base thus far has raised the issue of the treatment of outliers. There are two types: one type is when the average of the sampling trains is abnormally high or low as compared to the individual sampling train results and the second type is when the paired train results disagree significantly. Both of these issues were discussed with U.S. EPA Emission Measurement Center personnel. The following discussion covers the current thinking on how outliers should be treated when performing the initial calibration and subsequent RCA.

In the data collected during the calibration tests with ~ 10 sets of (or pairs of differentially-located, simultaneously operated, and identical) reference method sampling trains, typically there were 2 or 3 sets of data with abnormally high or low weight gains on either the filter or probe rinse.

Standard statistical outliers tests such as the one in EPA's Quality Assurance Handbook for Air Pollution Measurement Systems are available for statistically justifying the removal of individual data points. It is EPA's opinion that if one of the two trains produces a statistically "abnormal" result, then both results should be discarded and not just the apparently bad point. If both trains produce results within the precision of the method, then both are considered acceptable.

This approach was then used to discard data retroactively from Condition 20 (performed in October) and from Conditions 27, 28, and 30 (performed in November).

Since one data point was removed from the initial calibration conditions, revised tables and graphs reflecting the DPS 11 statistical evaluation for the initial calibration were redeveloped. The revisions of the Durag, ESC, and Sigrist initial calibrations are :

- shown in Tables 2-14, 2-15, and 2-16 and illustrated in Figures 2-11, 2-12, and 2-13 for the data base *with* the statistical (standard deviation) outliers; and

- shown in Tables 2-17, 2-18, and 2-19 and illustrated in Figures 2-14, 2-15, and 2-16 for the data base *without* the statistical (standard deviation) outliers.

Tables 2-20 and 2-21 presents a summary of each CEMS performance characteristics in terms of the DPS 11 data acceptance criteria, respectively, for the data bases with and without the statistical outliers. These data acceptance criteria consist of the correlation coefficient, confidence interval, tolerance interval, calibration drift, and zero drift. In general, the results presented in the summary tables show that acceptable correlation coefficient, confidence interval, and tolerance interval values are achieved based on the data *without* the statistical outliers, but are not fully achieved *with* the statistical outliers.

2.5.2 *RCA Test Results*

Table 2-22 presents a summary of the incinerator operating conditions, the reference method results, and the corresponding CEMS results. This table reflects that the structure of the November testing was performed similarly to the previous month, meaning :

a) A wide variety of wastes were fed to the incinerator with triplicate test sets performed at the 3 EDV power levels;
b) Two traversing MM5 trains operating simultaneously collected samples for periods of 36 or 48 minutes with results ranging from about 25 to 55 mg/dscm @ 7 % O_2; and
c) Five CEMS produced results during most of the test periods.

An unsuccessful attempt to develop liquid aerosols at the stack sampling location was made over a several-hour period during this testing event for the purpose of evaluating CEMS accuracy and reliability under saturated moisture conditions. This involved a combination of operational changes to decrease the temperature while increasing the moisture content in the exhaust gas stream. Although these operational changes were effective in substantially cooling the exhaust gas stream and raising its moisture content, they were unable to overcome the 35 ^{o}F temperature rise developed by the induced draft fan. If saturated conditions are pursued again in future calibration testing, additional measures to those attempted below will be developed (e.g., water injection downstream of the steam / exhaust gas heat exchanger coils) :

1) Turning off the steam flow to the heat exchanger coils, thereby reducing stack gas temperature from ~ 300 to 200 ^{o}F,
2) Turning off the pump circulating chilled water from the cooling tower to the scrubber water heat exchanger, which allowed
3) Increasing the absorber outlet gas temperature set point from 145 to 170 ^{o}F (i.e., raising the moisture content from about 25 to 50 %), and
4) Checking trend graphs to confirm that all the affected operating conditions had

stabilized.

Depending on the relative progress of each CEMS producing calibration data in this program, the new (RCA) test results are used in multiple ways , including :

- To evaluate the acceptability of the RCA results relative to the initial calibration relation for each of the three light-scattering CEMS (Durag, ESC, and Sigrist) in terms of DPS 11 and the Appendix H - Data Quality Assurance Requirements,
- To add to the initial calibration data base in forming an updated master calibration plot for each of the three light-scattering CEMS.

Acceptability of the November RCA Tests

The following information, along with the accompanying tables and figures, illustrates the DPS 11 approach to evaluate and determine the acceptability of the subsequent November RCA data relative to the initial calibration.

First, a figure is produced showing the calibration relation regression line and the tolerance intervals based on the initial calibration data. Second, the values from the paired sets of data from the subsequent RCA tests are overlaid onto the above figure. Third, the number of points inside and outside the tolerance intervals are separately counted to determine if 75 % of the RCA points fall within the tolerance interval established from the initial calibration. The following material describes and illustrates the evaluation statistical approach outlined above, which is a graph (1) of the regression line (center dashed line) and the tolerance intervals (outer lines) for the initial calibration set, and (2) simple plotting of the subsequent (November) data.

ESA Beta Monitor. No new data are available.

Verewa Beta Monitor . The sample dilution line was inadvertently disconnected during these calibration tests, rendering these results suspect and possibly invalid (see explanation in Section 2.9 and discussion in the summary of this subsection). Therefore, no data are presented in this subsection.

Durag, ESC, and Sigrist Light Scattering Monitors.

Values of the November RCA results are shown overlaid onto the initial calibration graphs, based on the data *with* the statistical outliers, in Figures 2-17, 2-18, and 2-19 to evaluate the acceptability (or consistency / stability) of the initial calibration relation for the Durag, ESC, and Sigrist, respectively. The three figures graphically illustrate the number of new data points that fall on or inside the initial calibration tolerance intervals (outer lines) on their respective graphs for each of these three CEMS, which are:

- 4 of the 6 new data points (67 %) for the Durag, and
- 3 of the 6 new points (50 %) for both the ESC and Sigrist.

Correspondingly, but based on the data *without* the statistical outliers, values of the November RCA results are shown overlaid onto the initial calibration graphs in Figures 2-20, 2-21, and 2-22 to evaluate the acceptability of the initial calibration relation for the same three CEMS, respectively. The three figures graphically illustrate that, for each of the three monitors, 5 of the 6 new data points (83 %) fall within the initial calibration tolerance intervals. Table 2-23 presents the evaluation summary of the PM CEMS November RCA to the initial calibration.

Subsequent measurements (consisting of a minimum of 9 data points) comparing the CEMS response to the reference method are considered consistent if at least 75 % of them fall within the tolerance interval currently established (per Section 5.2.3.1, Appendix to subpart EEE, Part 63 in the

Federal Register - Data Quality Assurance Requirements proposed for PM CEMS at HWCs). This evaluation with only 6 data points still needs to be performed in the appropriate context with a minimum of 9 data points; more data will be available soon to provide this context.

There is ongoing review of the data points falling outside of the tolerance intervals shown above. Review of the filter and probe rinse weight gain data produced from the one of the two RCA data points (Condition 22) falling outside the tolerance levels indicate an inconsistency with the history of data previously collected on PM partitioning within the sampling train. Previously, the weight gain on the filters was typically 2 to 5 times more than those of the probe rinses. In Condition 22, the opposite occurred : the probe rinse weight gains from both sample trains were each about twice the filter weight gains. This abnormality renders the data suspect. Such an abnormality is being considered as a data quality objective in future calibration efforts.

2.5.3 *Cumulative Data Base*

The RCA results for these same three light scattering CEMS were incorporated with the initial calibration data sets forming cumulative databases and plots. Although the DPS 11 data acceptance criteria do not apply to such a database, it is still considered worthwhile to present the results in a DPS 11 format. The cumulative databases and plots *with* the statistical outlier data are shown in Tables 2-24, 2-25, and 2-26 along with Figures 2-23 , 2-24, and 2-25 for the Durag, ESC, and Sigrist, respectively. The cumulative databases and plots *without* the statistical outlier data are shown in Tables 2-27, 2-28, and 2-29 along with Figures 2-26 , 2-27, and 2-28 for the Durag, ESC, and Sigrist, respectively. In both of these cases, the DPS 11 statistical evaluation results show, for each of these three monitors, that the correlation coefficient fall below 0.90, while the confidence and tolerance intervals are maintained with levels near or below 20 % and 35 %, respectively.

Although the November RCA data set is limited in size, it was utilized as an independent set

of results on which an assessment of the DPS 11 data acceptance criteria was performed for the Durag, ESC, and Sigrist. These results are included in Tables 2-20 and 2-21 for the Durag, ESC, and Sigrist.

Jonas Monitor. The initial calibration data for the Jonas acoustic monitor were produced for five conditions. Because it is a limited data set, the DPS 11 statistical evaluation was not performed to assess the performance of the Jonas monitor.

Summary. Tables 2-20 and 2-21 summarize the results of the DPS 11 statistical evaluations applicable for each CEMS. In general terms the results presented in the summary table show that the DPS 11 criteria can be met under certain, but not all, conditions tested so far. This is consistent with their practice and experience in Europe as well as with the proposed provisions in DPS 11.

It is known from more than a decade of experience at numerous installations in Europe that the PM CEMS have sensitivities and limitations relative to their use for compliance monitoring. Despite their sensitivities to PM properties such as particle size and composition, PM CEMS are employed within their limitations and validity by assuring their use under known, reproducible, and tested facility operating conditions. The reliability of the CEMS / PM loading relationships are assured as best as possible through performance based CEMS specifications and suitability testing along with other long term tests run on facilities at normal operating conditions using both CEMS and manual reference methods.

This approach is consistent with the intent of the DPS 11 requirements, which stipulates that a calibration relation is established for a given set of fuel or waste type inputs. If conditions at the facility change (such as changes in fuel / waste types or emission control equipment) that are sufficiently different to significantly alter PM properties (the calibration relation), then another calibration relation needs to be established and appropriately applied.

Although the rationale for selection of this test site was to present a worst-case challenge to

the PM CEMS, there have been several substantive (deliberate and inadvertent) changes with minimal reproducibility in facility operating conditions during the calibration test periods so far. Among the facility conditions that have changed are :

1) No constraints or reproducibility on the wide variety of waste feed streams,
2) Measurable variations in the stack gas conditions in terms of temperature, moisture, diluent concentration, and gas flow rate due to seasonal and normal operational variations, and
3) Variations in equipment operating conditions.

In response to these deliberate and inadvertent changes, the following measures are planned or under consideration, including :

- Further evaluation of the data to evaluate the impact of variations in the stack gas conditions on the CEMS results, and
- Analysis of the remainder of the reference method filters employed in the calibration tests to assess the persistency / diversity in PM properties.

2.6 PM CEMS December / January RCA Test Results

New information and data, available since Section 2.5 was prepared, are presented below in this subsection and consists of :

- A recently developed approach for identifying outliers,
- Revised PM CEMS data,
- Presenting the December and January RCA test data and evaluations,
- Revising accordingly the initial calibration results and former RCA evaluations, and
- Presenting the cumulative data base utilizing data meeting quality objectives.

Relative Standard Deviation Outlier Approach

As discussed in Section 2.2, a new approach for identifying outliers was recently developed based on the relative standard deviation (RSD) of the paired reference method data. This new approach involves calculating the RSD for each paired reference method data utilizing the two equations presented in Section 2.2. Its application means that the paired train data must pass a data quality objective with a RSD < 30 % to be considered acceptable; paired data that do not agree within a RSD > 30 % are identified as outliers and removed from the data set. Calculation of the RSD values for all the reference method data collected during each of the five months of testing (September through January) was performed; data from test conditions with RSD values > 30 % were considered outliers and all data associated with those conditions were discarded.

Revised CEMS Data

Before reporting the December and January RCA test results, it was discovered that there were minor errors in the previous reporting of the PM CEMS data for September, October, and November. These minor reporting errors came from bookkeeping mistakes in transferring the CEMS data from the data logger onto separate electronic spreadsheet files and in averaging the CEMS data for the corresponding reference method sampling times. Most of the changes between the previous and the revised CEMS data are insignificant (i.e., < 3 %) with a minority being 10 to 15 %. The revised CEMS data for the first three months of calibration testing are presented in Table 2-30 incorporating data only from the test conditions with reference method results with RSD values < 30 %.

December and January Calibration Test Results

After the November tests were performed, two other sets of RCA / calibration tests were conducted with the reference method and the PM CEMS in December and January. The tests

conducted in December serve as RCA tests for the Verewa, Durag, ESC, and Sigrist, but are regarded as the second part of the initial calibration test for the ESA since it was out-of-service for the October and November tests. The January tests are treated as an RCA test for all five monitors.

Tables 2-31 and 2-32 present a summary of the December and January tests, respectively, including the incinerator operating conditions, the reference method results, and the corresponding PM CEMS results. The tables reflect that the structure of the December and January tests was performed similarly to previous months, meaning :

- Different wastes were fed to the incinerator,
- Slightly lower stack gas temperatures (~ 290 ^{o}F) and moisture levels (~ 18 - 22 %) were developed relative to the initial calibration conditions of ~ 320 ^{o}F and ~ 28 % moisture,
- Two traversing reference method trains operating simultaneously (except for 5 conditions in January when only one train operated) produced results ranging from about 10 to 50 mg/dscm @ 7 % O_2, and
- Five PM CEMS produced results during most of the test periods.

Revised Initial Calibration Results

Therevised initial calibration results reflecting the application of the RSD outlier approach and the revised PM CEMS data for the ESA, Verewa, Durag, ESC, and Sigrist are presented in Tables 2-33, 2-34, 2-35, 2-36, and 2-37 and graphically illustrated in Figures 2-29, 2-30, 2-31, 2-32, and 2-33, respectively. Based on the revised CEMS data without the RSD outliers, none of the five PM CEMS produced results able to achieve the DPS 11 initial calibration data acceptance criteria except for the Verewa tolerance interval. The correlation coefficients for the revised initial

calibrations ranged from 0.55 to 0.72. A complete summary of the initial calibration results is presented later in this subsection after all the DPS 11 - RCA results are discussed.

RCA Test Results

The RCA test results for the data base with the revised PM CEMS data but without the RSD outliers are presented in Table 2-38 and discussed below for each of the five PM CEMS. Depending on the relative progress of the individual monitors in producing calibration data, the November, December, and January tests serve as either part of the initial calibration and/or a RCA test. These differences will become clear in the following discussion for each monitor. Values of the RCA tests are shown overlaid onto the initial calibration graphs (depicting the revised CEMS data without the RSD outliers) to evaluate the acceptability of the initial calibration relation in PM monitoring for subsequent operating periods. Recall that the RCA data acceptance criterion defines acceptability to be when more than 75 % of the RCA data fall within the initial calibration tolerance interval, which is required to be < 35 % at the proposed emission limit.

ESA Beta Monitor. The January RCA evaluation results are illustrated in Figure 2-34, showing that only 50 % of the data points fall within the ~ 38 % initial calibration tolerance intervals.

Verewa Beta Monitor. The December and January RCA evaluation results are illustrated in Figures 2-35 and 2-36, respectively, showing that 100 % of the data points fall within the ~ 32 % initial calibration tolerance intervals for both months.

Durag Light Scattering Monitor. The November, December, and January RCA evaluation results are illustrated in Figures 2-37, 2-38, and 2-39, respectively. These graphs show that 75 % of the November data, and 100 % of each the December and January data, fall within the ~ 36 % initial calibration tolerance intervals.

ESC Light Scattering Monitor. The November, December, and January RCA evaluation results are illustrated in Figures 2-40, 2-41, and 2-42, respectively. These graphs show that 88 % of the

November data, and 100 % of each the December and January data, fall within the ~ 36 % initial calibration tolerance intervals.

Sigrist Light Scattering Monitor. The November, December, and January RCA evaluation results are illustrated in Figures 2-43, 2-44, and 2-45, respectively. These graphs show that 88 % of the November data, and 100 % of each the December and January data, fall within the ~ 40 % initial calibration tolerance intervals.

Summary of PM CEMS Performance Characteristics

As part of summarizing the effort to date, all the calibration test data are accumulated into a "cumulative data base" for each CEMS. Although the DPS 11 data acceptance criteria are not applicable to a cumulative set of data, it is still considered valuable and sensible to tabulate and illustrate these results in a DPS 11 initial calibration format. The cumulative data bases and corresponding plots (with the revised CEMS data but without the RSD outliers) are presented in Tables 2-39, 2-40, 2-41, 2-42, and 2-43 and graphically illustrated in Figures 2-46, 2-47, 2-48, 2-49, and 2-50, for the ESA, Verewa, Durag, ESC, and Sigrist, respectively. Review of the cumulative data base by itself shows in general that (1) much of the test data lies close to the linear regression line and within the confidence interval boundaries, and (2) a minority of data reside close to or outside of the tolerance interval boundaries.

Perhaps additional insight and understanding is available by reviewing Table 2- 44 which summarizes the DPS 11 data acceptance criteria results from all the tests, including those from the initial calibration, the monthly RCA tests, and the cumulative data base. Note that the correlation coefficient values (1) for the initial calibration results and the cumulative data set (in the range of 0.5 to 0.7), but are mostly above 0.9 for the RCA test results. Again, it is recognized that the RCA test results are *not intended to be independently evaluated similarly* as the initial calibration test (not to calculate the data acceptance criteria based on the RCA data, but rather *evaluate them relative to* the

initial calibration tolerance intervals). However, the trend noted above is interesting in that the initial calibration results show both data with a reasonably close fit to, and data skewed from, the regression line, resulting in relatively *low correlation coefficients with high confidence / tolerance intervals*. Meanwhile, the RCAs show most data consistently close to the regression line resulting in *high correlation coefficients with low confidence / tolerance intervals*. Since the initial calibration and RCA tests were performed and structured similarly, the divergence in these trends raises the question of why the marked difference in the results ? This could be explained by either a fundamental difference between the two tests or there could be a fundamental flaw / problem with some or all of the initial calibration data. Despite the fact that the initial calibration should serve as the foundation of these and future CEMS calibration efforts, nonetheless, it was the initial attempt of the test team to collect / integrate all the necessary data. Further efforts to sort all this information and data is ongoing, and will be presented in the next version of the report along with the addition of the February RCA results.

2.7 Scanning Electron Microscope Results

Each of the filters utilized in the September and October calibration tests were analyzed by a scanning electron microscope (SEM) to provide a general assay or survey of the collected PM material. Results from the SEM analysis showed that the material covering the filter was predominately NaCl. Other metals or minerals found on the filters in relatively large amounts were Fe, S, and Al. Analysis of blank filters showed the composition to be (in descending order) Si, Al, Ca, O, and Mg.

Following SEM analysis, a photomicrograph was taken of a select portion of each filter which appeared to represent most of the particles collected by the filter. The photographs reveal a variety of shapes (discrete spheres and cubes, along with flakes and other irregular forms) and sizes (from sub-micron to > 100 micron) of PM.

In addition, Energy-Dispersive X-ray (EDX) was performed on the various particles on each

filter. Results from the EDX analysis showed that there were at least 12 other metals and minerals found and identified composing the wide variety of PM collected on the filters, including K, Zn, Pb, Si, Cu, P, Ba, I, Ag, Cr, Ti, and Ni.

In summary, these analyses clearly show that the PM covering the filter consisted of a layer of NaCl with an additional number of at least 15 different elements exhibiting an assortment of physical shapes, sizes, and, to a lesser extent, colors. The SEM data demonstrate that, even in upset conditions, the PM characteristics are not likely to differ enough to bias the PM results over the range of the CEMS' calibrations.

2.8 Presentation of DPS 11 Issues

One important aspect in this demonstration program is the evaluation of the DPS 11 requirements themselves. These performance specifications were drafted with the understanding that some revisions in the structure or language would likely become necessary based on discovery in the initial attempt to implement DPS 11, including some new issues not yet recognized. The purpose of the following material is to raise these issues for consideration and subsequent revision / resolution, and are based on the experience developed thus far in the demonstration program. The key issues discussed below are :

- Identification and treatment of outliers,
- Management of PM emission levels during initial calibration tests, and
- Beta CEMS response time and reference method sampling time relationship.

Outlier Provisions / Allowances. Other EPA performance specifications for evaluating the acceptability of CEMS contain explicit provisions and allowances for disregarding data in performing relative accuracy test audits (RATAs). Performance Specifications 2 and 3 (for CO / O_2, and NOx /

SO_2, respectively) stipulates that a facility must perform and report a minimum of 9 sets of test results, may perform up to 12 test sets, and is allowed to reject up to 3 sets as long as they are reported. The rationale and practice for selecting / rejecting data is based on how well the individual sets of results agree with the RATA correlation requirements. No explanation or justification is required for discarding data set. The methodology, established over 10 years ago, allows for a fixed number of inadvertent problems and inaccuracies to be tolerated.

There are no provisions / allowances for identifying or treating outliers in DPS 11 at this time. If not performed carefully with experienced personnel, there are numerous errors and inadvertent problems that are possible and not necessarily documented in performing the manual Method 5 procedures. EPA has recognized that Method 5 may pose accuracy / precision limitations that could hinder exact calibration of the CEMS at these low PM concentrations and has authorized its modification for these tests, potentially improving its accuracy / precision. Provisions for identifying and treating outliers under consideration include: 1) establishing a protocol based on the precision (relative standard deviation) of Method 5 using paired trains for identifying outliers, 2) developing a statistical approach that incorporates the variation in Method 5 into the calibration relation setting process, 3) allowing a certain number of test sets to be disregarded, and 4) developing new data quality criteria beyond the normal Method 5 criteria.

Management of PM Emissions During Initial Calibration Tests. This issue primarily centers around the control and management of PM emission levels during initial calibrations; it deals with *the novel concept and practice* of varying the generation, as well as the removal, of PM for developing / maintaining test conditions over the appropriate emission range for CEMS calibrations. Relative to these issues, the language in item 7.3 of DPS 11 is somewhat vague in defining: 1) the number of replicate test sets to be carried out, 2) the number of different levels of PM concentrations to be obtained, 3) the criteria for establishing different levels of PM concentrations, and 4) the PM emission range over which the initial calibration is performed. These statements appear vague because there is

a wide range of facility characteristics which defy a single universally-applicable approach, as reflected below.

Concerning 1) and 2) above, this item currently reads "three (or more) different levels" of PM concentration... and "three (or more) sets of measurements shall be obtained at each level"... for "a total of at least 15 measurements..." This statement reflects the intent to achieve the complete range of normal operations and of PM emissions for at least 15 measurements during the initial calibration tests to establish the calibration relation.

Concerning points 3) and 4) above, the current language only "*...recommends...*" achieving PM levels "...roughly twice the emission limit..." and does not provide any specific guidance on the five levels of PM concentrations required in the calibration. Again, this reflects the intent to achieve the widest range of PM emissions over the expected range of future operations. It is conceivable that some facilities may not be able to achieve levels twice the emission limit due to the nature of their emission control system. Testing should cover the following five PM concentration ranges : < 20, 20 to 40, 40 to 60, 60 to 80, and 80 to 100% of the expected range of PM emissions during future operations. It is advantageous for EPA and industry from a statistical standpoint to perform the calibrations across a range extending to twice the emission limit, when practically possible, for

achieving suitable confidence and tolerance intervals at the midpoint of the range -- the emission limit.

Beta CEMS Response Time and Reference Method Sampling Time Relationship. This issue only pertains to calibrating the Beta monitors (or any other CEMS technology). These monitors have a relatively long response time (5 to 15 minutes) and produce new readings at intervals corresponding to their response times; this presents a potential difficulty in relation to reference method traverse sampling times of a similar period. As explained below, this is a non-issue with the light scattering CEMS which make measurements with short response times of one to three seconds. Short response time provides a large number of CEMS measurements to be made and averaged for comparison with

the time-integrated reference method results.

The sampling times for the traverses with each reference method test (i.e., half of the total sampling time) performed in the early stages of this program were on the order of 10 to 30 minutes. The response time for the ESA and Verewa Beta monitors was approximately 6 and 12 minutes, respectively. Unaware of the critical need for synchrony, the starting and stopping of the reference method sampling periods were *not* synchronized with the Beta monitors' sampling periods. As a result of this non-synchrony in sampling time relationship, the calibration results initially reported for the September tests were based on *semi-representative data* for the two Beta CEMS. This limitation in the initial testing structure may have had an *adverse affect* on the initially reported Beta CEMS calibration results and may be partially responsible for the reduced level of correlation in the reported results for September.

Corrective measures to resolve this issue were made, and included :

1) Considering the Beta CEMS respective response times, and evaluating their relation with the reference method results on corresponding time periods; and

2) Increasing the modified reference method sampling time while reducing the two Beta monitors response time to 5 or 6 minutes.

2.9 CEMS Reliability and Endurance

Beyond their accuracy / precision, EPA is also interested in assuring that the performance of the CEMS is suitable for continuous, reliable, and virtually automatic operation, and thus have arranged an eight-month demonstration program. The monitors are designed to be self-operating / self-calibrating, and have additional means for further calibrations and linearity checks performed manually. Most are reliable enough that they are only checked by off-site personnel every two weeks.

Information presented in this section provides an account of their calibrations along with any service adjustments, alterations, or any interruptions in producing data for whatever reason for each CEMS. This endurance-related information is presented in ascending order of the service required to maintain the CEMS during the first five months (September - January) of the program and is summarized in Table 2- 45.

2.9.1 Environmental Systems Corp. (ESC) - Light scattering monitor

This monitor has worked reliably well without any adjustment, alterations, or interruptions in data availability. It has maintained its instrument calibration consistently except for the end of January in which the span value was adjusted to the set point. The monitor is able to restart itself after a facility outage.

2.9.2 Durag - Light scattering monitor

This monitor has worked well with the rare exception of the shutter for the optics closing twice early in the program. For the times this very minor occurrence has happened, it has been suspected to be caused by a power interruption or by vibration. It has maintained its instrument calibration consistently. In early January a commercially-available automatic reset feature for the optics shutter was installed along with a heated purge air line to provide protection against flue gas condensation under winter ambient conditions. Also at this time a third-party (TUV) approved linearity test kit with five points was manually used to demonstrate linearity in the instrument response. The unit is also designed to restart itself after a facility outage.

2.9.3 Sigrist - Light scattering monitor

This monitor has also worked reliably well. Data availability was interrupted only during facility outages when the unit turned itself off as a protection against the probe heater overworking

itself. The site-specific correction factor was adjusted in the middle of October to more closely align the readings with the reference method results and changing the range of its scale by tenfold to units of mg/m^3. The unit has passed a 3-point linearity check performed manually each month.

2.9.4 Verewa - Beta monitor

This monitor worked reliably well until the first part of October. At this time the unit quit producing data due to a problem with a pin in the linkage of the solenoid that disengages the filter paper from the detector assembly. During its attempted repair before the October calibration test, one of the two Geiger counters imploded a lens. Replacement parts (actuator arm and Geiger counter) were installed, a change in data linking with the DAS was made (i.e., the range was changed from 0 - 50 mg/m^3 to 0 - 100 mg/m^3), and the response time was reduced to 5-minutes prior to December's calibration testing.

2.9.5 Emissions SA - Beta monitor

This monitor worked reliably well also until the first part of October, then the unit quit producing data apparently due to failure of the venturi (sample flow control) transducer. Miscommunication between EER and the manufacturer / representative was the main reason for the unit being off-line until repairs were made in early December. The response time was reduced to 5-minutes in December and then changed to 6-minutes in January. It has maintained its instrument calibration consistently.

2.9.6 Jonas - Acoustic monitor

This prototype monitor had experienced difficulty despite several changes in equipment setup and data logger programming links. However, after modification the monitoring system (controller

and probe) was reinstalled and able to produce data compatible with the DAS during several of the calibration test conditions in September, October, and November. Immediately following November's calibration testing, the probe was removed for further servicing through the end of the month. It was later re-installed and then removed again for more servicing in December through late January.

2.10 Summary

Initial milestones of a CEMS demonstration program aimed at verifying that available CEMS can meet the proposed performance specifications have been completed. Over forty sets of measurements with five commercially-available PM CEMS and the PM reference method have been performed and reported above. Testing consistent with DPS 11 was performed on a HWC incinerator burning a wide variety of waste streams and while operating an APC device under three different power (collection performance) levels. The principal program objectives included :

- Establishing the calibration relation for the CEMS relative to the reference method,
- Evaluating the DPS 11 data acceptance criteria for the correlation coefficient, the confidence interval, and the tolerance interval of each CEMS,
- Evaluating the applicability and practicality of the structure and terms within DPS 11, and
- Assessing the reliability and endurance of the CEMS.

The scope of the report covers the first five months of operation with calibration testing conducted on five separate monthly occasions. Modifications to the reference method in an attempt for improving its accuracy / precision were employed during the calibration tests. The three light scattering CEMS technologies (Durag, ESC, and Sigrist) produced results for all five test periods and functioned reliably with only very minor equipment adjustments and servicing. The two Beta technology CEMS produced results for most of the testing except for equipment problems experienced in the second month (for the Verewa) and the second and third month for the ESA.

Results of the modified reference method ranged from 10 to 100 mg/dscm @ 7 % O_2. Results from each of the CEMS were recorded on a common data logger and then compiled for the corresponding reference method sampling periods. The individual sets of results were evaluated using the procedures and calculations in DPS 11 to determine the data quality acceptance criteria for the correlation coefficient, the confidence interval, and the tolerance interval. For the complete data set with outliers, none of the CEMS meet all the data quality acceptance criteria for the initial calibration. Identification and treatment of outliers has dramatically improved the correlation with the reference method results. One of the subsequent monthly tests show correlation coefficients over 0.99 for each of the three light scattering monitors; the balance of the other monthly results yield an average correlation coefficient around 0.90 and normally fall within the acceptable tolerance intervals for the initial calibration.

Each of the filters with collected PM from the September and October tests underwent analysis by scanning electron microscope and energy-dispersive X-ray and were photomicrographed. Results from these determinations clearly showed that the collected PM consisting of NaCl with at least 15 other metals/ minerals exhibiting an assortment of physical shapes, sizes, and, to a lesser extent, colors.

The structure and terms of DPS 11 appear practical and applicable with only a few issues under consideration based on the experience and data of the initial five months. The critical issues deals with identifying and treating outliers and developing new data quality criteria beyond the normal Method 5 criteria.

2.11 Conclusion

One conclusion from this report can be made at this time with the understanding that it is drawn from a limited data base. The *apparent* conclusion follows :

Viability of PM CEMS as HWC Regulatory Tool. The wide variety of wastes fed (to a incinerator with

common types of APC technologies for HWCs) during these calibration tests produced PM consisting of sodium chloride with at least 15 different metals/minerals exhibiting an assortment of physical shapes and sizes along with a few different colors. Despite this heterogeneity of PM characteristics, most of the CEMS were able to meet the DPS 11 data acceptance criteria with certain outliers deleted. Implications from these limited results indicate that the PM emission characteristics at this facility may be close-to-representative of many, but not all, HWC incinerators equipped with high pressure drop venturis and packed-bed or spray-tower scrubbers employing sodium-based neutralization (such as soda ash or sodium hydroxide). This APC configuration (venturi, packed-bed or spray tower with sodium neutralization) is common in the HWC incinerator industry, and is known to produce PM consisting of sodium chloride with other metals/minerals. Consequently, the apparent acceptability of the PM CEMS technologies at this facility (with a deliberate worst-case variety of waste feed streams) offers promise that this acceptability may be extrapolated to many other incinerators in the industry similarly equipped.

The reference method results presented in this report on based on use of a subtle yet significant modification to Method 5. Experience has shown that the largest source of error in Method 5 at low PM concentrations comes from inaccuracies produced from unnecessary filter handling performed (1) after the pre-test weighing during assembly into the filter holder, and (2) before the post-test weighing during disassembly and recovery. An improvement, or modification, to Method 5 was made by simply scaling down the filter and filter holder to such a size (47 mm) and mass (~ 30 mg) that the entire filter / filter holder assembly could be weighed by a micro-balance. This prevents, and eliminates inaccuracies produced during, filter handling in steps (1) and (2) above. An account of this evaluation is included in the Appendix.

Editor's Note: Insert the Figures found in the document "pmcems4.fig" here.

Editor's Note: Insert the Tables found in the document "pmcems4.tbl" here.

3.0 TEST PROGRAM PROTOCOL

In order in achieve the project goals, a number of measurements at different periods were performed of the flue gas for the facility. In addition, six ports along with the necessary utilities and data acquisition system were installed to support and accommodate this PM CEMS demonstration test program. The following sections discuss details of the sampling locations, the modified reference test methods performed for this program, and each of the CEMS.

Although the tests were conducted with the facility operating under normal conditions, coordination / communication with facility personnel occurred regularly. As discussed in the preceding section, the facility was operated in a manner to maintain the facility within permitted conditions and to achieve the range of PM emissions that are an integral part of the calibration testing protocol. The matrix of plant operating conditions over which the CEMS calibration were performed were obtained by varying EDV power level set points as well as waste feed stream composition. Figure 3-1 presents a schematic of the principal components of the incinerator facility to help provide an integrated picture on the overall scope of this novel form of this testing.

The flue gas sampling utilized Modified Method 5 for PM as the reference method. The reference method measurements were conducted on the stack using the two sampling ports already installed and located 90° apart. Traversing measurements were made using duplicate trains. The current port locations on the stack are easily accessible from the relatively large platform surrounding the stack. The ports were configured for performing compliance tests and meet all necessary EPA Method 1 criteria for upstream and downstream disturbances. The stack is round with a four foot inner diameter. The sampling platform is located about 90 feet above ground level. The nearest flow disturbance is five diameters upstream and two diameters downstream of the sampling location. A schematic of the stack configuration with the location of the Method 5 ports and the respective levels for each of the CEMS is shown in Figure 3-2. Figure 3-3 shows the

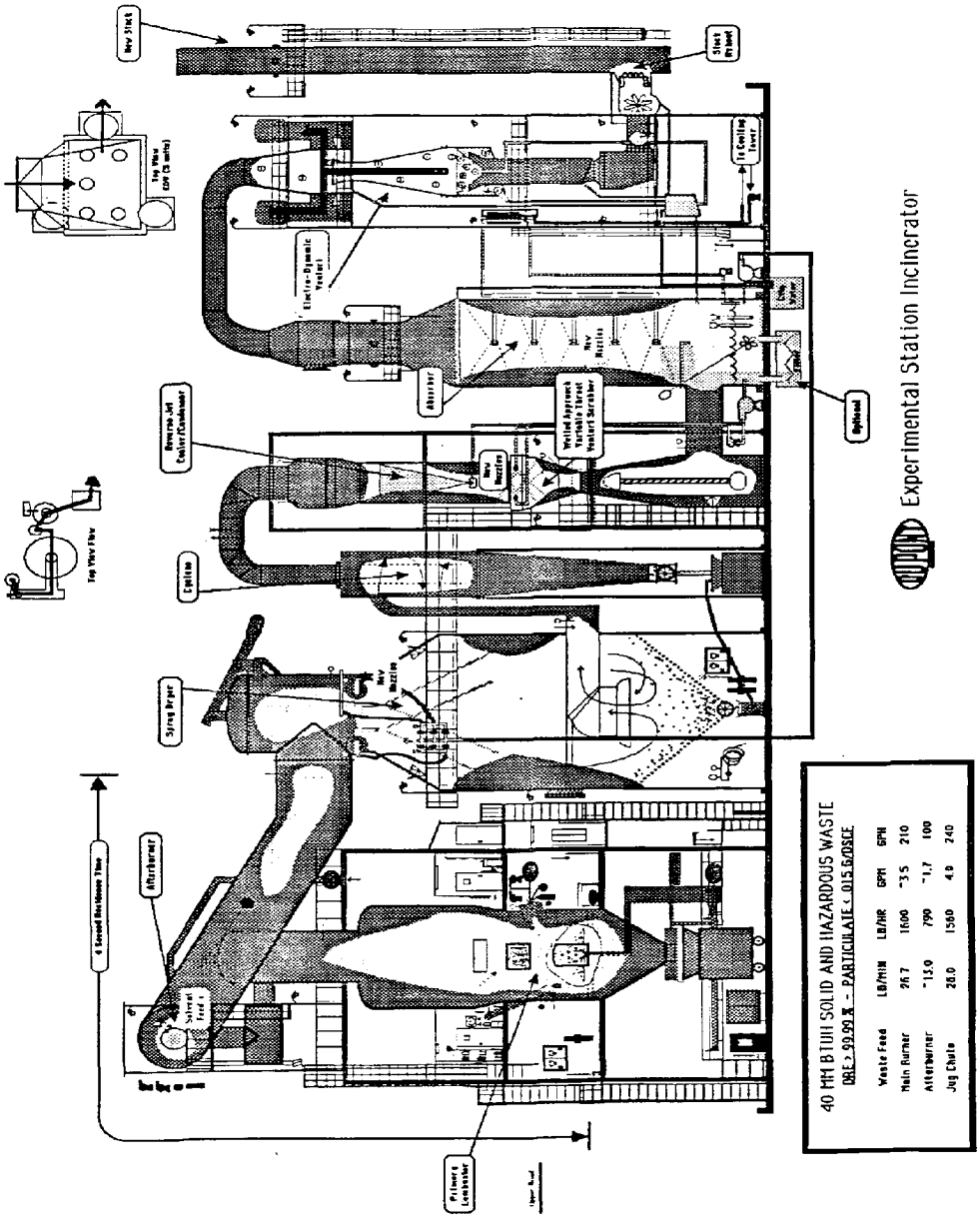


Figure 3-1. DuPont Incineration Schematic.

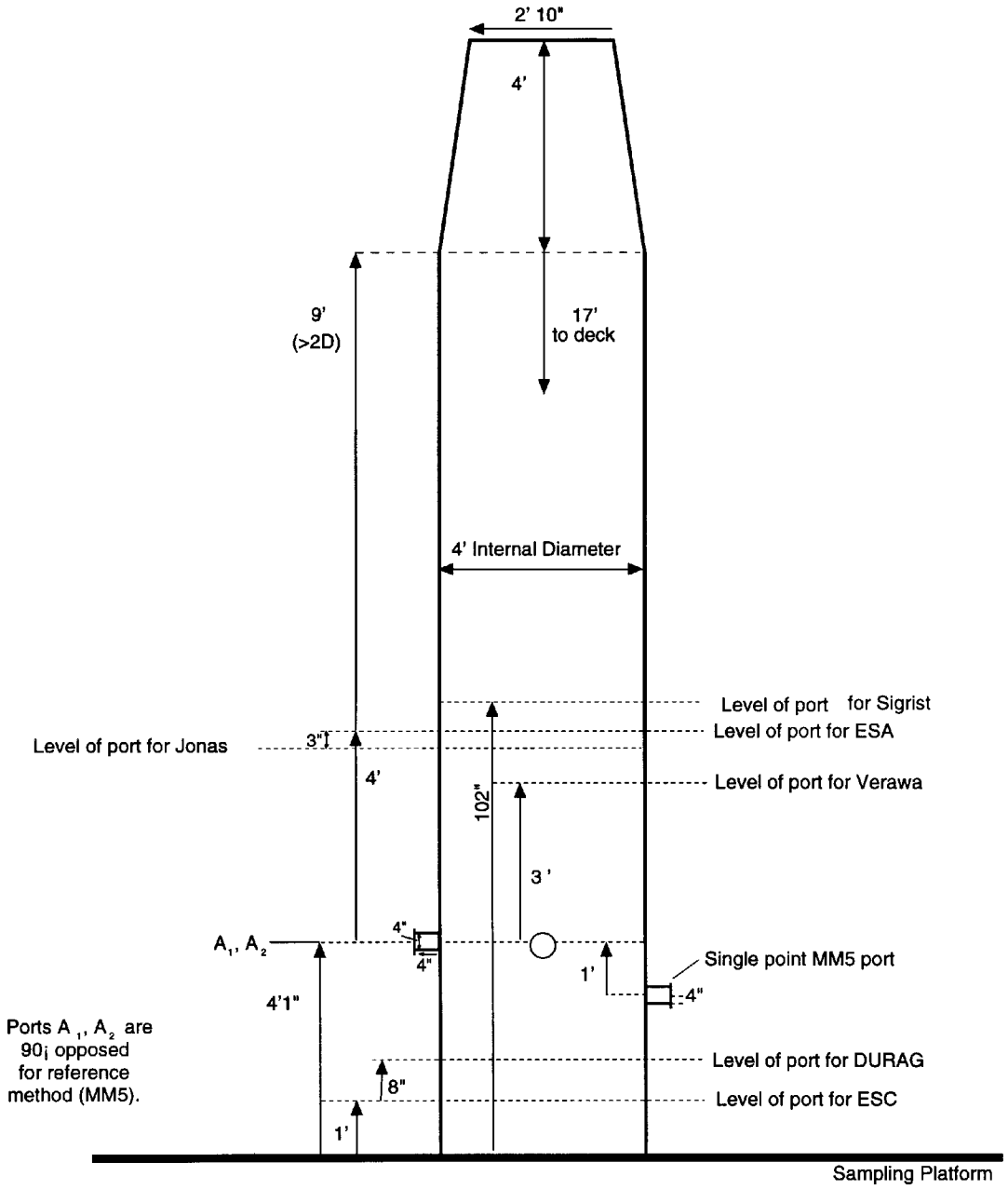
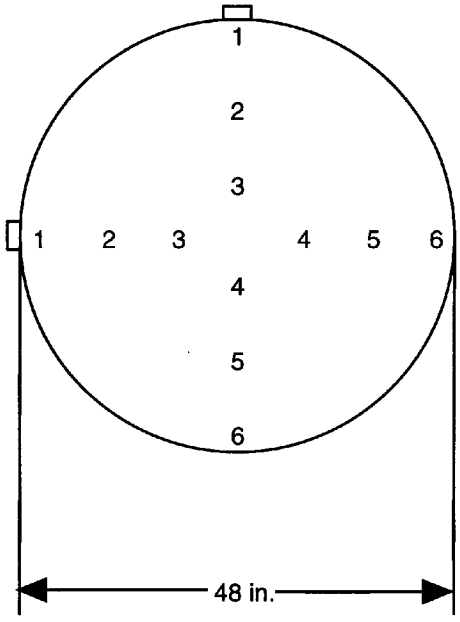


Figure 3-2. Stack schematic.



Point	Distance from wall (in.)
1	2.11
2	7.00
3	14.20
4	33.80
5	41.00
6	45.90

All measurements in inches.

Figure 3-3. Sampling port configuration and traverse points for slip stream at DuPont.

traverse points that were used for the Modified Method 5 measurements. The port lengths, insulation thickness, and actual stack dimensions were measured on-site and the appropriate adjustments to the traverse points were implemented. Flue gas conditions at this sampling location were determined to be as follows:

Temperature:	300-330	°F (with steam reheat)
Static pressure:	+0.2	inches of water
Flow Rate:	15,000	dscfm
Velocity:	35	ft/sec
Moisture:	22-28	%
PM Loading:	10 - 100	mg/dscm at 7% O_2

3.1 Reference Method and CEMS Sampling Locations

The reference method measurements with the traversing trains were made using two pre-existing 90^0 - opposed ports while a third port was used for the single point reference method sampling. The CEMS were located on the stack platform at ports specially installed for each CEMS. The CEMS ports were located around the stack at various, nearby levels (within 3 feet) above the plane of the reference method location. They were arranged around the stack such that no CEMS measures directly downstream of another CEMS or the reference method trains. Figures 3-4 and 3-5 are helpful in illustrating the staggered arrangements of the sampling port locations for the reference methods and the CEMS.

3.2 Reference Method Sampling Procedures

In order to achieve acceptable data from this test program, detection limits need to be

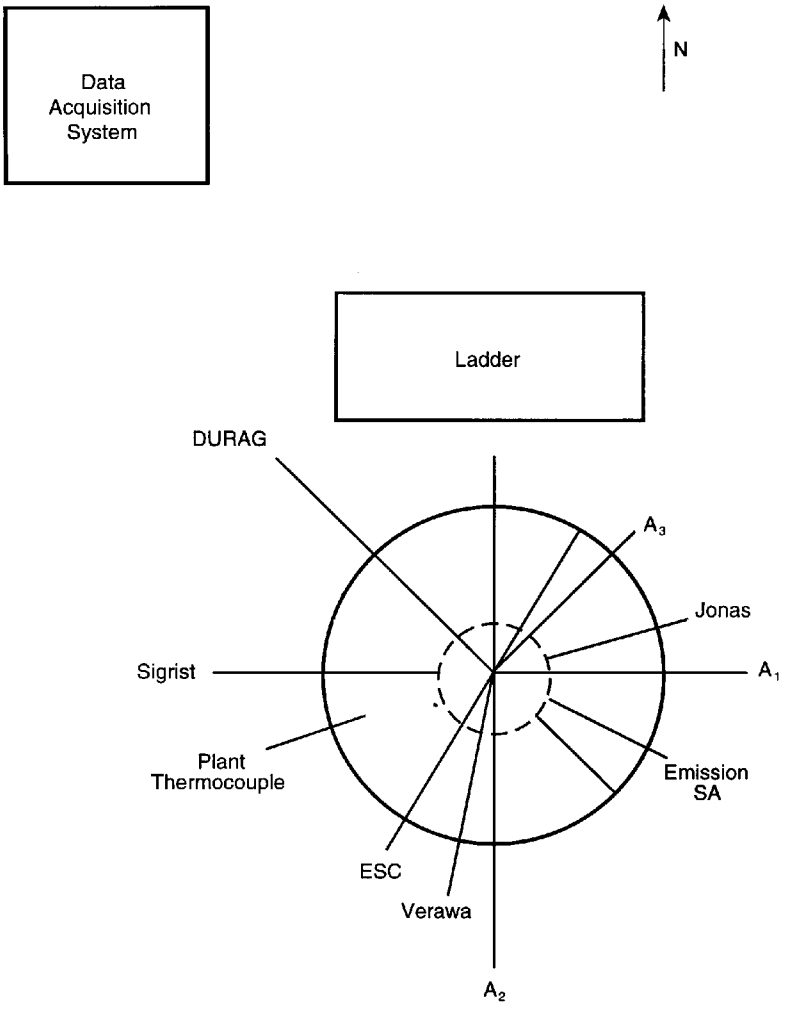


Figure 3-4. Plan view showing location of CEMS' sampling axes.

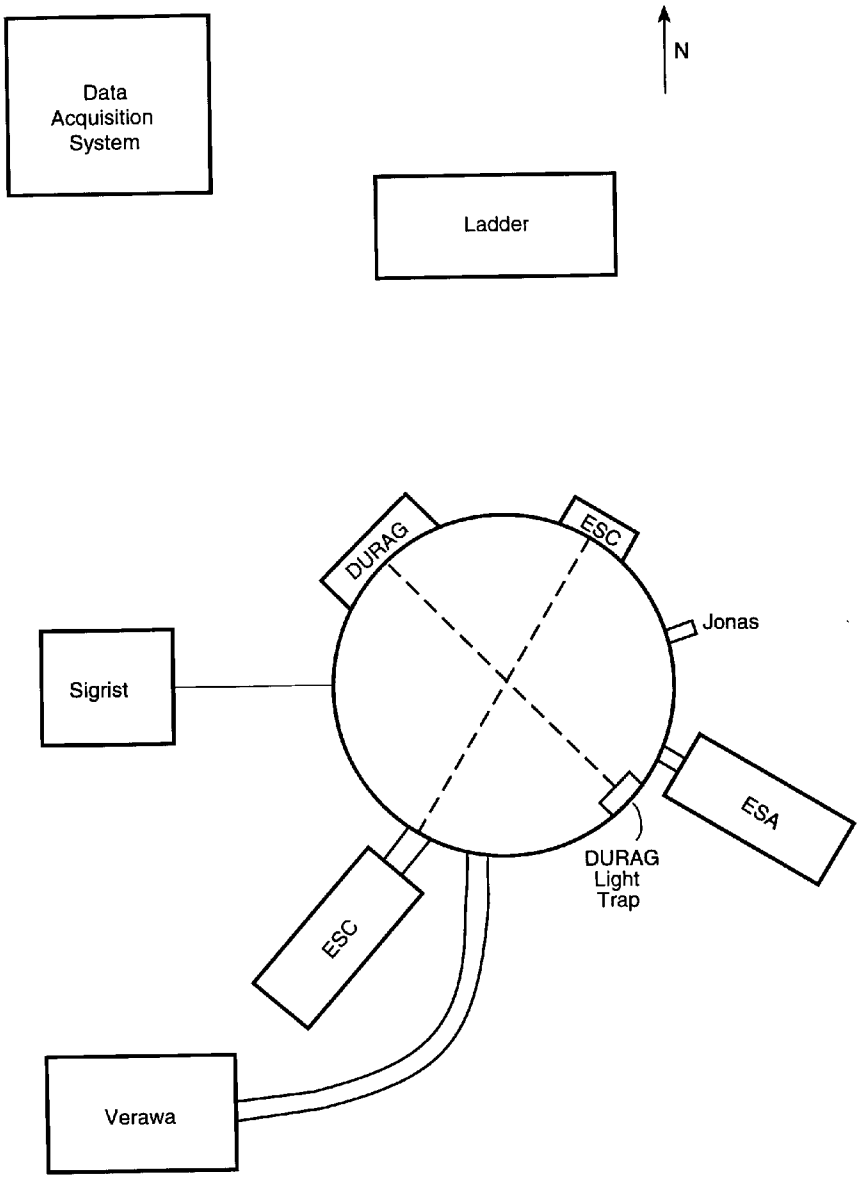


Figure 3-5. Plan view showing locations of all the monitors.

established and achieved. For flue gas measurements, the detection limit is a function of the analytical detection limit and the total sample collected. Depending on PM concentrations, the MM5 sampling trains were operated for 18 to 60 minutes, depending on the PM loading. Measurements were made during various process and APC conditions to vary the PM loadings over the different operating conditions. Details of the sample trains, sampling procedures, recovery procedures follow.

3.2.1 *Sample Train Description and Sampling Procedures*

EPA Methods 1, 2 - Traverse Point Determination, Stack Gas Temperature, Velocity, and Volumetric Flow Rate

EPA Method 1 was used to determine the sample and velocity traverse points for velocity measurements and isokinetic sampling. With EPA Method 1, the duct or stack cross-section is divided into equal areas. A traverse point is located in the centroid of each of the resulting areas.

The minimum number of equal areas and traverse points depends on the duct diameter and length in equivalent diameters directly upstream and downstream of the sample location. Schematic layouts of the sample locations and traverse points are shown in Figure 3-3.

EPA Method 2 was used to determine the stack gas temperature, velocity, and volumetric flow rate. The velocity of the stack gas was determined from the density of the gas and the measurement of the average velocity head. A stainless steel sheathed Type-K thermocouple (TC) was used to measure stack temperature, while a stainless steel Type-S pitot, and an incline manometer of applicable sensitivity is used to measure stack gas velocity. To minimize the mutual interference, the TC and pitot are assembled according to the method specifications. Pre-test and post-test leak checks were conducted to ensure the accuracy of the velocity measurements.

EPA Methods 3A and 4 - Stack Gas Analysis and Moisture Content Determination

EPA Method 3 was used to determine the stack gas oxygen ($O_{2)}$ and carbon dioxide ($CO_{2)}$ concentrations and the dry molecular weight. A stack gas sample was collected from the MM5 sample train and examined using an Fyrite analyzer to determine carbon dioxide and oxygen content. The dry molecular weight of the stack gas was calculated using the measured O_2 and CO_2 levels, assuming the remainder of the stack gas composition is nitrogen. Low levels (ppm range) of CO, SO^2, NOx, hydrocarbons, and other compounds are not significant factors in the molecular weight determination. The molecular weight and excess O_2 levels are used in velocity, isokinetic sampling rate, and pollutant emission rate calculations.

EPA Method 4 was used to determine the moisture content of the stack gas for a pre-test determination. Moisture was determined from all MM5 sampling trains during the calibration tests..

EPA Method 5 - Determination of Particulate Emissions from Stationary Sources

As directed by the Code of Federal Regulations, Method 5 applies specifically to the gravimetric determination of the emission rate of particulate matter from stationary sources. For this to be achieved, the location of the sampling points must be determined (Method 1) and the volumetric flow rate (Method 2) calculated. To calculate the volumetric flow rate, the values for carbon dioxide and oxygen contents (Method 3), and moisture content (Method 4) must be determined, per the methods discussed in the previous section.

With EPA Method 5, a gas sample is withdrawn isokinetically from the stationary source and passed through a heated glass fiber filter. The filter collects any solid particulate matter contained in the effluent gas stream while allowing any uncombined water vapor to pass through for collection in the impinger train containing a known volume of water. The mass of the particulate is then determined by desiccating the filter and associated probe rinse. For this study, the recovery of the filter was modified to accommodate a new light-weight filter housing. The housing is designed such that the filter and the front half of the filter housing is one integral piece that can be tared as a single unit. The moisture content was determined by measuring the amount of water collected in the impingers. The

volumetric flow rate of the gas stream was determined by the velocity and temperature traverse. These values were then used to calculate the particulate mass concentration. Figure 3-6 gives a schematic of the modified Method 5 sampling train.

The largest area of significant error in Method 5 testing at low PM concentrations comes from inaccuracies produced from *unnecessary filter handling after pre-weighing and before final weighing*. In the original Method 5 procedure, 1) filters were pre-weighed and then handled during assembly into the filter holder; 2) following sampling, filters were handled during recovery from the filter assembly, desiccated, and then weighed. As a result of this procedure it was common for small filter pieces / fibers to be inadvertently removed / lost (after pre-taring) during filter handling in assembly and/or in recovery (before final weighing). The problem with this approach stems from filter handling after pre-weighing; it was further compounded from further handling before final weighing.

For this PM CEM program the standard Method 5 filter and its holding assembly was replaced with a smaller (47 mm) filter and smaller holder to minimize inadvertent loss of small filter pieces in its handling during assembly and recovery. The new filter holder allows the filter to be assembled, and then pre-weighed in the low-weight assembly; following sampling, the assembly was desiccated and then weighed before disassembly - - without the filter being directly handled during pre-test and post-test activities. This approach eliminates filter handling after pre-weighing and before final weighing and, thereby, simplifies as well as improves the method.

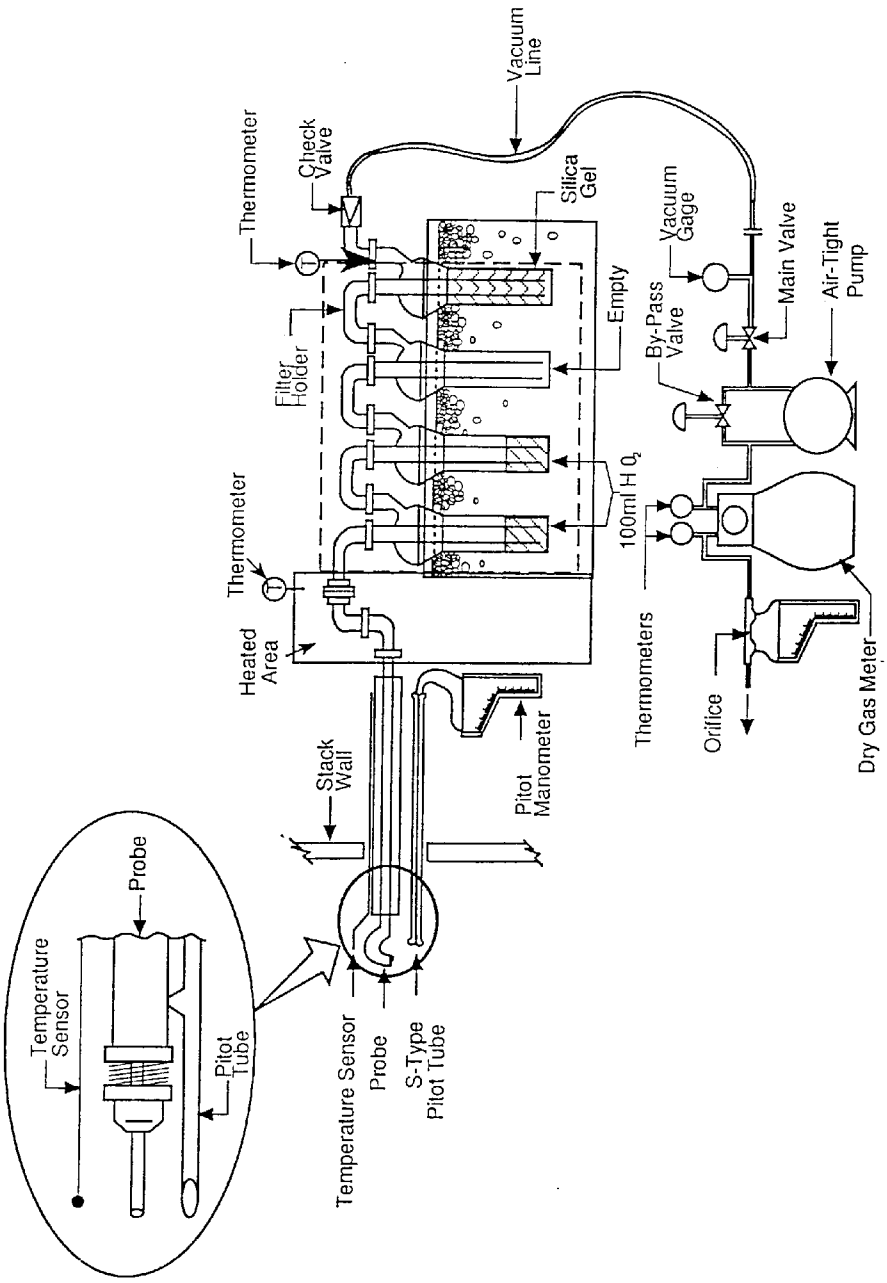


Figure 3-6. EPA Method 5 sampling train schematic.

Filter assembly were properly marked with non-reactive ink and tared; and the filters used for sampling were immediately removed and carefully transferred to a desiccator. After allowing the filter to cool and a successful post-test leak check, the filter holder was removed from the sample box and immediately the exposed ends of the probe, glass "L," and filter holder were covered with Teflon tape. The filter holder was taken to the recovery area; the probe and impingers were recovered on the stack platform. The filter was recovered by loosening the rings of the holder and separating the filter halves. The fronthalf of the filter housing and the filter disassemble as one unit and were placed directly into a desiccator to continue cooling and allow the weight to stabilize. The average weight of these units was approximately 30 grams, allowing the pre-taring and final weighings to be performed on a micro balance with a resolution of ±0.1 mg.

Each of the four impingers were individually weighed to the nearest 0.5g. before and after sampling to determine stack moisture concentrations.

Sample train fronthalf recovery was accomplished using a damp cloth or paper towel to remove any accumulated particulate from the exteriors of the nozzle and the probe. Then, the probe and nozzle were rinsed three times using acetone and a small brush. The rinsate was placed in a small glass container labeled with the run and sample train number.

Analysis of the samples for particulate catch was accomplished using an a microbalance with a capability of 0.1 mg resolution. The filter and fronthalf rinse were weighed after being desiccated for several hours. The acetone rinses were evaporated, desiccated and weighed separately. The samples were evaporated at $20^{o} \pm 6^{o}$ C ($68^{o} \pm 10^{o}$ F). The samples were weighed until three successive weighings were achieved that agreed to ± 0.5 mg. Prior to analysis the balance was calibrated using Class S weights that are traceable to a National Institute of Standards and Technology (NIST) standard.

3.2.2 *Calibration Procedures*

All equipment used in this test program was maintained and calibrated using approved procedures and EPA, American Standards Testing Material (ASTM), and/or National Institute of Standards and Technology (NIST) traceable reference equipment, where applicable. Calibrations were routinely performed on all key equipment so that required pre-test calibrations were performed prior to mobilization. During equipment preparation, the calibration records were reviewed to ensure that specified calibrations were up-to-date. The applicable equipment was also checked in the field to assure that handling and use did not affect the calibrations. Following the test program, the equipment was again routinely calibrated in order to verify continuous calibration status throughout the on-site testing. If at any time during testing the operator has reason to believe a piece of equipment may no longer be in calibration due to unusual change in readings or possible damage, a recalibration was performed to verify accuracy. Equipment which required calibration included meter boxes, thermocouples, nozzles, and pitot tubes. Reference calibration procedures were followed when available, and the results properly documented and retained in a calibration log book. A discussion of the techniques used to calibrate this equipment is presented below.

Type-S Pitot Tube Calibration

The EPA has specified guidelines concerning the construction and geometry of an acceptable Type-S pitot tube. If the specified design and construction guidelines are met, a pitot tube coefficient of 0.84 can be used. Information related to the design and construction of the Type-S pitot tube is presented in detail in Section 3.1.1 of EPA Document 700/4-77/027b. Only Type-S pitot tubes meeting the required EPA specifications were used during this project. Pitot tubes were inspected and documented as meeting EPA specifications prior to the field sampling.

Sampling Nozzle Calibration

EPA Method 5 prescribes the use of stainless steel buttonhook nozzles for isokinetic particulate sampling. However, for this study glass nozzles will be used. Calculation of the isokinetic sampling

rate requires that the cross-sectional area of sampling nozzle be accurately and precisely known. All nozzles used for Methods 5 sampling were thoroughly cleaned, visually inspected, and calibrated according to the procedure outlined in Section 3.4.2 of EPA Document 600/4-77-027b.

Temperature Measuring Device Calibration

Accurate temperature measurements are required during emission sampling. Bimetallic stem thermometers and thermocouple temperature sensors were calibrated using the procedure described in Section 3.4.2 of EPA Document 600/4-77-027b. Each temperature sensor was calibrated at a minimum of three points over the anticipated range of use against an NIST-traceable mercury-in-glass thermometer. All sensors were calibrated prior to field sampling.

Dry Gas Meter Calibration

Dry gas meters (DGMs) were used in the Method 5 trains to monitor the sampling gas flowrate and to measure the sample gas volume. All dry gas meters were calibrated (documented correction factor) just prior to the departure of the equipment to the field. A post-test calibration check was performed as soon as possible after the equipment was returned to EER's shop. Pre- and post-test calibrations agreed within 5%.

Dry gas meters were calibrated using the calibration system. Prior to calibration, a positive pressure leak-check of the system was performed using the procedure outlined in Sections 3.3.2 of EPA Document 600/4-77-27b. The system was placed under approximately 10 inches of water pressure and a gauge oil manometer was used to determine if a pressure decrease can be detected over a one-minute period. If leaks were detected, they were eliminated before actual calibrations were performed.

After the sampling console was assembled and leak-checked, the pump was allowed to run for 15 minutes. This allows the pump and dry gas meter to warm up. The valve was then adjusted to

obtain the desired flow rate. For the pre-test calibrations, data were collected at orifice manometer settings (Δ H) of 0.5, 1.0, 1.5, 2.0, 3.0, and 4.0 inches of H_2O. Gas volumes of 5 ft^3 were used for the two lower orifice settings and volumes of 10 ft^3 for the higher settings. The individual gas meter correction factors (Y_i) were calculated for each orifice setting and averaged. The method requires that each of the individual correction factors must fall within 2% of the average correction factor or the meter must be cleaned, adjusted, and recelebrated. For the post-test calibration, the meter was calibrated three times at the average orifice setting and highest vacuum used during the actual test.

Analytical Balance Calibration

Analytical balances were calibrated over the expected range of use with standard weights (NIST Class S). Measured values must agree within ± 0.1 mg for the probe rinse and filter weights, and 1.0 mg for moisture, respectively. The balances were calibrated prior to the field measurement program.

Field checks of balance accuracy were made daily using a set of quality control weights which have previously been weighed side-by-side with the NIST traceable weights.

3.2.3 Data Reduction, Validation, and Reporting

Manual methods operations data were input onto computer spreadsheets each day following receipt from testing. Results of samples weighings were input onto the computer system as soon as they were available. Data was reduced and analyzed using hand-held calculator programs, computer spreadsheets, and other computer programs. The actual equations and nomenclature are shown on the calculator program data sheets and on the spreadsheets. This feature enabled operator and analyst familiarity with the programmed computations, gave facilities separate spot-checking of computed results by hand, and eliminated the need to show equations separately in the text.

Standardized run data forms were used for each method. All run sheets were reviewed daily by the Field Manager for evaluation of progress, completeness, and problems. Standardized computer spreadsheets were used to reduce and analyze field data. At the end of each test day, test data was input onto these spreadsheets. Lab analytical results were not available at the end of each test day. However, results were input as they become available. A standard data set, which had been verified by hand, was used to demonstrate the accuracy of the spreadsheet calculations before the test program.

For each test condition, the field data was reduced manually at the end of each test. An isokinetic ratio was then estimated at the end of each condition using an average or typical moisture value. The estimated moisture value, estimated isokinetic ratio, and all intermediate calculations were noted on the run sheet. Upon entry into the computer spreadsheet program, both the data and the program were validated by checking the estimated isokinetic ratio against the manually determined value.

Spreadsheet calculations for the various runs observed the following guidelines:

1. Isokinetic calculations for each train were conducted using the input run data from that specific run rather than from the average or other values from previous runs. Stack gas moisture content was determined using the condensed water measured in that train;

2. Stack temperature, moisture content, velocity, and flow rate values for each sampling train were average values from all of the combined applicable runs for that test condition. The exception to this rule would be the exclusion of any data from a single run which may deviate more than 20% from the average of the data from the other runs. In addition, this exception may occur if there were questionable data for a specific run due to operator error, process failure, equipment failure, or other circumstances;

3. In the case of questionable data due to operator error, the average results of the other runs was used to correct the results of this run where applicable. For example, if the velocity readings for a specific run are thought to be erroneous due to moisture condensation in the pitot lines, the average velocity measurements from the other simultaneous runs at that location would have been used to determine isokinetic rate for that run; and

4. There may be other cases of questionable data, such as measured moisture content, which exceeds the saturation value under the existing stack pressure and temperature conditions. These values would have been corrected for actual stack pressure using the equation below:

$$C_{H2O,Ps} = \left(\frac{C_{H2O,29.92}}{29.92} \right) * Ps$$

$$C_{t,adj} = C_{t,meas} * \frac{II}{100}$$

where: $C_{H2O,Ps}$ = Moisture content at stack pressure

$C_{H2O,29.92}$ = Moisture content measured

Ps = Stack static pressure

The accepted range for the isokinetic rate is 90 to 110%. All the isokinetic rates were within the acceptable range.

If sampling occurs outside the 90-110% isokinetic sampling range in the remaining tests, the concentration and mass emission rate would be corrected according to the sampling rate. From Shigehara, the calculated concentration C_t may be biased proportionally to the degree of sampling

rate deviation from the isokinetic rate. Since the mass emission rate (m_s) is calculated from C_t (using the concentration method), then m_s is equally biased. The actual values for $_tC$ and $_sm$ would be between the measured values and the adjusted values as follows:

$$m_{s,adj} = m_{s,meas} * \frac{I}{100}$$

When the sampling rate is outside the 90-110% range, then the actual C_t and m_s for that run would be approximated by taking the average of the measured values and the adjusted values:

$$m_s = \frac{m_{s,meas} + m_{s,adj}}{2}$$

Upon daily completion of testing, the Field Manager was responsible for preparation of a data summary which included:

$$C_t = \frac{C_{t,meas} + C_{t,adj}}{2}$$

- Raw data sheets;
- Calculation of isokinetic ratio for each run;
- Traverse start and stop times for each run;
- Calculation of sample volume for each run;
- Calculation of stack gas flow rate; and
- Problems encountered during sampling and/or deviations from standard procedure.

The daily data summary was submitted to the QA Coordinator. The final section of this report includes a separate QA/QC section which summarizes any audit results from manual sampling procedures, as well as QC data collected throughout the duration of the program. The EER QA/QC Officer has reviewed the manual methods QC data and provided data quality input for this report.

3.2.4 *Sample Tracking, Shipping, Storage, and Custody Procedures*

The execution of this program included the acquisition and compilation of field data and the physical collection, handling, storage, shipping, and analysis of various types of field samples. Both acquired data and physical samples required rigorous documentation and safeguarding to maintain data and sample integrity and to ensure against loss of valuable test results. Field data, such as computer files, operator logs, and data sheets, was filled out and checked for completeness, and then copied and stored or maintained in systematic fashion. In addition, physical samples were promptly labeled and tracked. Physical samples were handled, stored, and/or shipped using methods and observing procedure, according to the specific methodologies. These steps are critical for samples since the number of physical samples was large and many of the samples were shipped or changed hands between operations in order to conduct sample analysis. *However, there were lapses in filter tracking during the initial test in September as filter numbers were not recorded accurately on the field data sheets for Conditions 2, 11 - Rerun, 10 - Rerun, and 3. Corrective action was taken by developing new and additional field recovery and test summary forms to provide redundancy in filter tracking.*

The Field Manager was responsible for proper data and sample logging and custody. Run sheets, data sheets, files, and sample tracking forms were completed by each of the respective team members responsible for data acquisition, equipment operation, sample recovery, and manual data logging, except as noted above. The Test Team Leader checked off the completion of logging, documentation, and storage tasks lists on a daily basis. The sample recovery specialist was responsible for signing sample custody forms and transferring samples.

3.3 CEMS Sampling and Analysis

The CEMS sampling locations were arranged around the stack at the platform location as shown in Figures 3-2, 3-4, and 3-5. All of the CEMS were downstream of the reference method location. Ports as required for each CEMS were installed at the locations indicated in the figures. The CEMS probes for the ESA, Verawa, Sigrist, and Jonas extended 20 inches into the stack (the same distance as the single-point MM5 train). The six CEMS participating in the demonstration are described below. Additional vendor provided information with more detailed descriptions of the

CEMS are contained in the Appendix. In the following sections, the CEMS are briefly described with their performance specifications summarized. Table 3-1 profiles each CEMS sampling and analysis characteristics.

Table 3.1 Summary of PM/CEMS Charateristics.

	Analysis						Sampling		
MFG	**Type**	**Detection Limit**	**Range(s)**	**Location**	**Response Time**	**Unique Features**	**Isokinetic**	**Rate**	**Heated Probe**
ESC	Back-scattering @ 180° with Infrared LED Light source	0.5 mg/am^3	0-100 mg/am3 0-500 mg/am3 0-2,000 mg/am3 0-10,000 mg/am3	In-Situ	~ 1 sec.	Second reference detector for self-compensation	Not; In Situ Probe	NA	No
DURAG	Back-scattering @ 120° with Halogen light sources	0.5 mg/m^3	0-1 mg/m^3 0-50 mg/m^3 0-100 mg/m^3	In Situ	~ 1 sec.	Purge air optics cleaning; 2 light sources and 1 trap	Not; In Situ No Probe	NA	No
Sigrist	Forward-scattering @15° with Incandescent light source	0.003 mg/m^3	0-0.1 mg/m^3 0-1000 mg/m^3 DL of 10 on 0-1000 mg/m^3	External	~ 5 sec.	Purge air optics cleaning; Double-beam compensation split by oscillating mirror	Semi-ISO	1 am^3/min; large sample extracted with 35 l pm sub-sample analyzed	170°C
ESA	Beta attenuation; blank & sample analysis	0.1 mg/m^3	2-4000 mg/m^3	External	~ 6 min.	Real-time gas velocity and temperature; Close-off valve for probe cleaning with back-flushing	ISO-pitot and TC venturi for sample flow rate control; eductor instead of pump	~ 0.05 am^3/min	170/180°C (340-360°F)
Verawa (Monitor Labs)	Beta Attenuation blank & sample analysis; dual source/detectors	0.1 mg/Nm^3	10-2,000 mg/Nm^3	External	12.3 min. total: 10 min. sampling, 20 sec. tape transport	Dual light sources and detectors	Semi-ISO with dilution; rotary vane; compressor-cooler; mass flow meter for sampling flow rate control	~ 0.05 am^3/min	170/180°C
Jonas	Acoustic	To Be Determined	To be Determined	External	~ 1 sec.	Design technology	Not; in-situ	NA	No

Note: All monitors have internal zero and span calibrations performed automatically.
NA = Not Applicable

3.3.1 *Verewa F-904-KD Beta Gauge Monitor*

The Verewa F-904-KD continuous particulate monitor extracts a sample from the stack under close-to-isokinetic conditions at a nominal design point. Isokinetic sampling is not actively maintained as stack flow changes. The stack sample is diluted for this application since moisture / acid gas dew points are feasible and /or for high dust loadings >200 mg/dscm . The sample passes through a heated probe and sample line and is collected on a filter. The sampled gas is dried by cooling and the flow rate measured, thus allowing reporting on a dscm basis. A filter tape mechanism allows long duration operation and positions the filter spot in either a "measurement" or "sample" location. In the "measurement" location, the attenuation of beta particles from a carbon-14 source is measured. Each filter spot location used for sampling is measured before and after sampling: the difference between these two measurements is representative of the PM mass sampled. The attenuation of the beta particles is virtually independent of the composition / properties of the PM, thus a site-specific calibration is not generally required. The F-904-KD uses a dual source/detector arrangement to allow measurement of the previous sample while acquiring the current sample. Sampling and analysis is thus almost continuous. Zero and span calibration checks are carried out at programmable intervals. The zero check is performed by measuring the same location on the filter tape twice, in succession, without collecting a sample. The span calibration is checked using a radiation attenuator inserted into the measurement beam. In this application, it takes ten minutes for sample collection on the filter, two minutes for filter analysis, and about twenty seconds for filter tape transport time. Using the dual source/detector configuration, measurements are thus reported every 12.3 minutes. These times are programmable, however, so different sample and reporting times can be obtained depending on the sample loading.

3.3.2 *Emissions SA 5M Beta Gauge Monitor*

The Emissions SA Beta 5M uses a heated sampling probe with real-time pitot and thermocouple measurements to obtain an isokinetic sample that is maintained automatically. These features are suitable for applications where moisture / acid gas dew points are approached and/or where larger particles (>5 microns) prevail. The sample is collected on a filter, which, at the end of the sampling period, is moved using a continuous filter tape mechanism to a measurement location between a carbon 14 beta particle source and a detector. The beta transmission through each blank filter is determined before sampling begins. The sampling duration is programmable and determines the mass concentration detection limit. At high PM loadings it must be kept small enough to prevent sampling excessive amounts of PM, and is usually set at two minutes for typical applications. Analysis takes six minutes, and thus a measurement is made every eight minutes. At the end of each sampling period, the probe nozzle is temporarily closed, opened, and closed again in order to re-entrain any PM deposited in the probe. It is equipped with a programmable logic controller which monitors and diagnoses key sampling and analysis operations. The instrument is relatively insensitive to variations in PM composition and properties, thus a site-specific calibration is not generally required, although certification tests are performed.

3.3.3 *Durag DR-300 Light Scattering Monitor*

The Durag model D-R 300-40 light scattering monitor measures the back scattered light at approximately 120° by the PM. The light beam is generated by a halogen lamp (400-700 nm) modulated at 1.2 kHz., and the sample volume is located in a region 80 to 280 mm (centered at 150 mm) from the wall. Both the light source and the detector are located in a single unit, thus requiring only one point of access to the duct. The D-R 300-40 is designed to carry out automatic zero and span checks, and provides automatic compensation for dirt on the optics even though the optics are protected by an air purge system. Stray light from surface reflections of the transmitted beam is minimized through the use of a light trap mounted on the opposite side of the duct. The D-R 300-40 is normally located directly on the duct wall, thus making an in-situ measurement. For applications where moisture / acid gas dew points are approached, a hot bypass system is available but not provided for this demonstration.

3.3.4 *ESC P5A Light Scattering Monitor*

Environmental Systems Corp. model P5A light scattering instrument monitors the back scattered light (180°) from an infrared light emitting diode (LED). The instrument has a roughly constant response to particles in the 0.1 to 10 micron range and a measurement range of 1 to 10,000 mg/dscm. The probe volume is located 4.5 inches from the end of a probe containing both the transmitting and receiving optics that is inserted into the flow through a standard flange. The probe is purged with its own blower supplied air to keep the optics clean. Only one point of access to the stack is required; measurement is accomplished in-situ without an extractive probe. The instrument automatically carries out zero and span calibrations, and is continuously compensated for any changes in the LED intensity due to aging or temperature changes via a second reference detector. A site specific calibration is recommended to maximize accuracy.

3.3.5 *Sigrist KTNR Light Scattering Monitor*

The Sigrist model KTNR is an extractive sampling light scattering monitor suitable for applications where moisture / acid gas dew points are approached. This device extracts a heated slipstream (1 m^3/min) from the stack, a small portion of which is sampled (35 liters / min) and passes through a scattered light photometer. The entire sample, including the bypass portion of the slipstream, is then returned to the duct. The sample rate is set up to be close-to-isokinetic at a normal stack flow, but isokinetic sampling is not actively maintained. Rather, a constant sample rate is maintained. The photometer measures the forward light scattered at 15° from a incandescent bulb emitting over the range 360 to 2800 nm. A double beam compensation measuring method is used in which the light path is split and the intensity of the reference path adjusted by an attenuator to equal the intensity of the measurement path. The amount of adjustment necessary is reflected in the output signal. This approach makes the output signal independent of fluctuations or aging in the optical and electronic components, including the buildup of dirt on the optics. Drift of the calibration and zero point is absent. Periodic cleaning and checks with optical filters supplied with the instrument are carried out on a typical six to 12 month basis. Measuring ranges run from 0 to 0.1 mg/dscm to 0 to 1000

mg/dscm. It is recommended that a site specific calibration be performed to improve accuracy.

3.3.6 *Jonas, Inc.*

The Jonas Consulting Acoustic Energy PM monitor uses shock waves caused by the impact of particles with a probe inserted into the flow to measure particle loading. The device counts the number of impacts and also measures the energy of each impact. This information, coupled with knowledge of the flow velocity, allows calculation of the particle mass. Since the probe distorts the flow, changes in flow velocity and particle size distribution will, in principle, change the instrument response.

3.3.7 *CEMS Data Acquisition System*

All the data from the CEMS instruments are collected and stored on a dedicated data acquisition system (DAS) manufactured by Environmental Systems Corp. This system includes a data logger with a personal computer and a modem for automatic downloading of data. The DAS is housed in an air-conditioned and weather-proofed cabinet located on the stack sampling platform, as shown in Figures 3-4 and 3-5. The data logger samples each CEMS signal output (typically 4 to 20 milliamp) once per second, and calculates one minute averages based on these samples. The one-minute averages are further used to produce 10- and 60-minute rolling averages. Additional channels are available for other inputs such as stack gas temperature, O_2, and gas flowrate.

3.4 Scanning Electron Microscope Analytical Procedure

Each filter from the September and October tests was assigned a sequential laboratory number. A wedge shaped sample was cut from the filter and mounted on an aluminum planchet using silver paint. Each sample was analyzed using a JEOL JSM 840A Scanning Electron Microscope (SEM). The filters were scanned using Backscattered ED Electron Microscopy (BEM). A compositional image is selectively obtained using a paired semiconductor element conductor in the

BEM. This form of microscopy is very useful for surveying sample surfaces prior to X-ray analysis.

A photo micrograph was taken of a selective portion of each sample which appeared to represent most of the particles collected on the filter. These photos were taken using BEM. Particles with elements of high atomic numbers produce bright images in the photomicrograph.

Energy-Dispersive X-ray (EDX) analysis was performed on the various particle types found on each sample. Electrons produced during EDX analysis emit unique and characteristic patterns of x-rays. Under analytical conditions, the number of x-rays emitted by each element reflects its concentration.

3.5 Process Data Acquisition

Process data from the September tests has been received from Dupont and is included in the Appendix.

4.0 QUALITY ASSURANCE/QUALITY CONTROL

Quality Assurance Program

Quality assurance is an integrated system of activities which involves planning, quality control, quality assessment, reporting, and quality improvement to ensure that the test program meets standards of quality with a stated level of confidence. Quality assurance encompasses the organization within which quality control activities are performed. The QC activities which accompany testing, lab analysis and other procedures provide control of data and quantify the quality of data so that it meets the needs of the users as stated in the quality assurance objectives.

Generally, EER's QA procedures follow the guidelines in the "Quality Assurance Handbook for Air Pollution Measurement Systems," Volumes I through III. These procedures outline pre-test preparation and calibrations of sampling equipment, post-test sample handling, and post-test calibrations. Standardized, written procedures, calculator programs, and spreadsheets are used for test planning, pre-surveys, equipment checklists, preliminary calculations, data and sample collection, sample tracking, sample and data analysis, and reporting.

Test procedures were based on applicable EPA test methods. However, slight modifications of the standard Method 5 filter holder assembly and filter recovery procedure were made to improve quality of the data. For each key measurement area, there were specific QC activities and checks to ensure that written procedures were followed during all preparation, validation, sampling, and recovery activities. There are also criteria to quantify and judge the performance of the measurements and corrective action procedures for correcting deficiencies.

Quality Assurance Approach

The EPA has defined Categories I through IV to define the content of QA plans according to the goals of the program with which the QA plan is associated (Preparation Aids for the Development of RREL Quality Assurance Project Plans, U.S. EPA, Risk Reduction Engineering Laboratory, Cincinnati, OH, 1989). The four categories are defined as follows:

Category	Description
I	Projects for support of enforcement, compliance, or litigation. This level of QA is the highest possible for legal challenge. The cost of the QA program for this type of project is typically 20-30% of the total cost.
II	Projects for producing results used to complement (or in combination with) other projects of similar scope for rule making, regulation making, or policy making. Data quality indicators (DQIs) for completeness, representativeness, and comparability may not be easily defined. The cost of the QA program for this type of project is typically 10-30% of the total cost.
III	Projects for producing results used for engineering, technology development, feasibility studies, or preliminary assessments. QA requirements are more broadly defined, although definitive documentation of QC activities and results is still required for reports.
IV	Projects for producing results used in assessing suppositions, feasibility studies, or fundamental investigations.

The purpose of this test program was to generate data to evaluate: (1) the acceptability of commercially-available PM CEMS towards the Draft Performance Specification 11, (2) the applicability of those draft performance specifications, and (3) the acceptability of modifying Method 5 for measuring low PM emission levels. Category II QA/QC was implemented during this test

program. Phase I required an abbreviated form of the QA/QC required in a Category II program since fewer samples were collected than are required to calculate the necessary DQIs.

QA/QC Organization

The QA/QC structure for this test project is shown in Figure 4-1. The Test Program Investigator was Mr. Steve Schliesser of EER. EER's Quality Assurance Officer is Mr. Jerry Cole, and EER Project QA Coordinator was Mr. Steve Schliesser. Mr. Schliesser had overall responsibility for all project QA. The QA Coordinator's activities consisted of test plan review, on-site performance and system audits, analytical system and performance audits, and reporting of all QA/QC activities and data. The efforts of the QA coordinator were designed to assure that the specific goals for precision, accuracy, and completeness were achieved.

4.1 Quality Assurance Objectives

Quality assurance objectives are goals for test data accuracy, precision, and completeness. Accuracy is the degree of agreement of a measurement (or average of measurements) with an accepted reference or true value. Precision is a measure of mutual agreement of replicate measurements. Completeness is a measure of the amount of valid data compared to the amount that was expected to be obtained under correct operating conditions. QA objectives should be defined for all of the critical measurements of the test program. The objectives should be based on the limitations and requirements of the test methods, where available. The quality assurance objectives

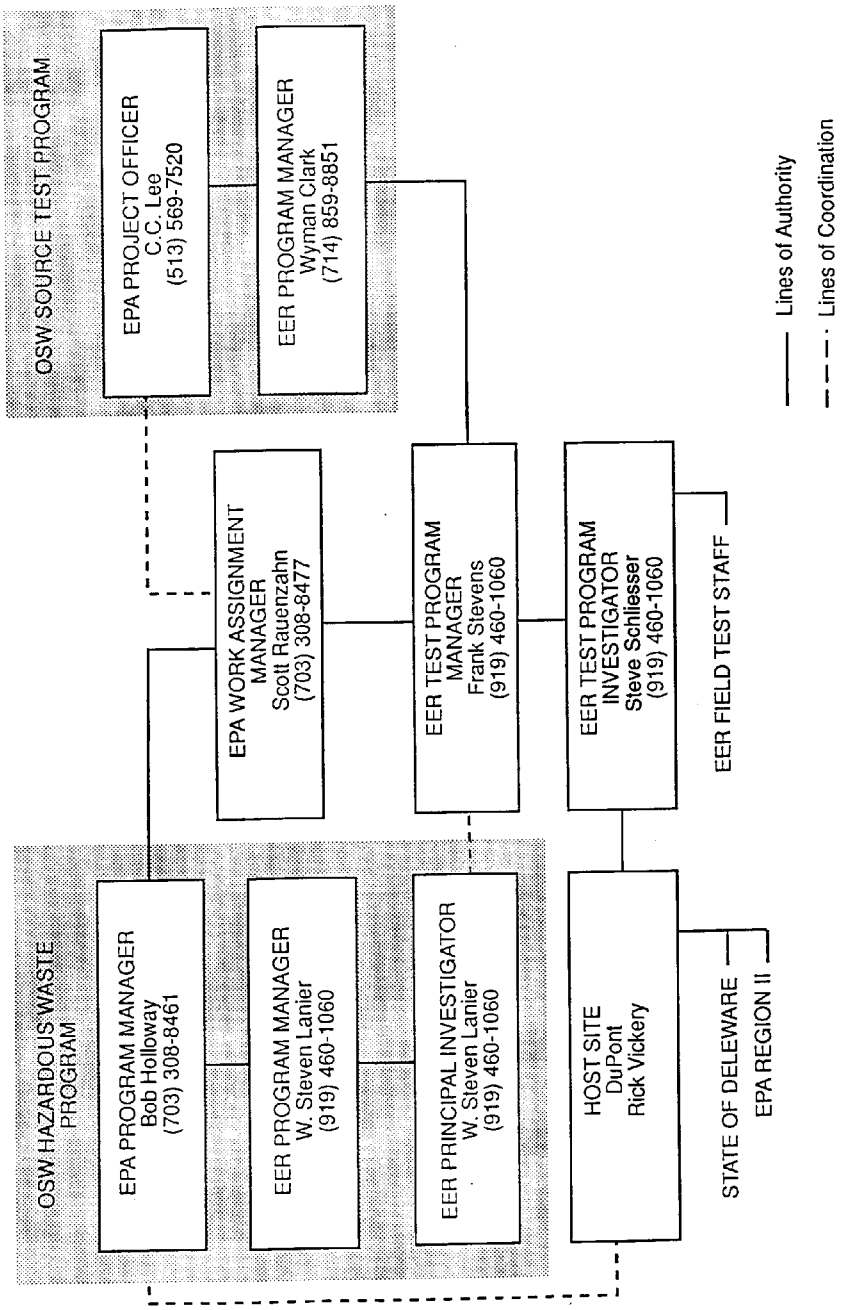


Figure 4-1. Project orgainization for DuPont PM Demonstration.

for the particulate matter are: completeness of 100%; precision of a constant weighing ± 1%; and accuracy of ±6%.

Some of the data validation will not be complete until after the testing phase has ended. In this case, it may not be possible to take corrective action to meet the quality assurance objectives (for example, if the analytical laboratory irrecoverably contaminates or loses a sample). Daily records of completeness were maintained by the EER QA Coordinator for each test method. These daily records are based on the validity of each run.

Calculation of Quality Assurance Objectives

The quality assurance objectives for precision, accuracy, and completeness will support the integrity of the data generated for each source test. Precision will be a measure of mutual agreement among individual measurements of the same property. Precision will be generally determined for each of the key measurements through either the percentage agreement between duplicate measurements or by determining the relative percent standard deviation for three or more replicate measurements. For duplicate measurements, precision will be indicated as a percentage based on the ratio of the difference between the two values and the average of the two values expressed as the relative percent difference.

When three or more replicate measurements are available, then the relative standard deviation (RSD) from the mean of all the replicate values will be used to indicate precision, calculated using the equations below:

$$\overline{X} = \frac{1}{n}\sum_{i=1}^{n} X_i \qquad RSD = \frac{S}{\overline{X}} * 100$$

$$S^2 = \frac{1}{n-1}\sum_{i=1}^{n}\left(X_i - \overline{X}\right)^2$$

where: RSD = relative standard deviation

S = standard deviation of the measurements, x

$\overline{X}$= mean of the measurements, x

n = number of replicate measurements

Accuracy, defined as the percent difference between a measurement and a reference or standard value, will be calculated by the following equation:

$$A\ (\%) = \frac{X - X_R}{X_R} * 100$$

where: A = accuracy

X = measurement

XR = reference or standard value

Completeness will be a measure of the amount of valid data obtained compared to the amount which was expected to be obtained. Completeness will be calculated by the following equation:

$$C\ (\%)\ =\ \left(\frac{D_v}{D_p}\right)\ *\ 100$$

where: C =Completeness

Dv=Quantity of valid data

Dp=Quantity of expected data

4.2 Reference Method QC

The quality assurance (QA) objectives provide a standard of quality for the various measurements to be made in this program. These objectives include criteria for precision, accuracy, and completeness. In order to quantify how well the measurements have satisfied these objectives, comprehensive internal QA/QC activities were implemented. The efforts of the internal QA coordinator are designed to assure that the specific goals for precision, accuracy, and completeness are achieved. The specific system of internal quality control (QC) procedures to establish the performance of the measurement systems is presented in this section. This system of internal checks is an integral part of the emissions characterization program.

For each key measurement area, there were specific QC activities and checks, which ensure that written procedures are followed during all preparation, validation, sampling, and recovery activities. There are also criteria used to quantify and judge the performance of the measurements and corrective action procedures for correcting deficiencies, if necessary.

Quality control is the overall system of activities whose purpose is to provide a quality product or service: for example, the routine application of procedures for obtaining prescribed standards of

performance in the monitoring and measurement process. Quality assurance, on the other hand, is a system of activities whose purpose is to provide assurance that the QC system is adequate to ensure that the program goals will be achieved and that it is being implemented effectively. The program quality control system includes these features:

- Calibration procedures and schedules;
- Specific checklists and procedures for pre-test, test operation, and post-test activities for each measurement system;
- Standard pre-programmed calculation routines using hand-held calculators and computer spreadsheets;
- Blanks, spikes, duplicates, QC audit samples, and other analytical quality control procedures for each measurement system; and
- Organization and documentation of all calibration records, run sheets, data sheets, process logs, calculation sheets and spreadsheet files and printouts.

QA audits were conducted In order to ensure that the above QC activities were effectively implemented. The following sub-sections discuss QC activities ensuring data validity.

Quality control samples are used to determine QA objectives and to provide data which supports the generated data. Quality control samples include field blanks, matrix spikes, matrix spike duplicates, and laboratory control spikes.

4.2.1 *Quality Control Procedures*

This program involved sampling and analysis of a number of different process streams. These streams included the air pollution control device (APCD) inlet and APCD outlet flue gas, APCD collected transport stream. This section describes the QA/QC activities and criteria accomplished during the sampling, as well as the analytical phases of this test program.

4.2.2 *QC for Flue Gas Sampling and Analysis*

The following section discusses the QA/QC activities utilized for this program's flue gas sampling and analytical procedure.

EPA Method 1, 2, and 4 - Sample point determination, flue gas velocity, and moisture content

Sampling: The S-type pitot tube was visually inspected before sampling. Both legs of the pitot tube were leak checked before and after sampling. Proper orientation of the S-type pitot tube was maintained while making measurements. The roll and pitch axis of the S-type pitot tube is maintained at 90°F to the flow. The oil manometer was leveled and zeroed before each run. The pitot tube/manometer umbilical lines were inspected before and after sampling for moisture condensate. Cyclonic or turbulent flow checks was performed prior to testing the source. An average velocity pressure reading were recorded at each point instead of recording extreme high or low values. Reported duct dimensions were checked by measurements to determine cross-sectional duct area. If a negative gas static pressure was present, checks were made for air in leakage at ports resulting in possible flow and temperature errors (leaks were sealed if found). The stack gas temperature measuring system was checked by observing ambient temperatures prior to placement in the stack. Duplicate readings of temperature and differential pressure were taken at each traverse point and agreed to within ±1.6% and ±6%, respectively. The balance zero was checked, and rezeroed if necessary, before each weighing. Pre-test liquid volumes of impinger solutions were recorded as a check on tare weights. The balance was leveled and placed in a clean, motionless environment for weighing. The indicating silica gel was fresh for each run and periodically inspected and replaced during runs if necessary. The silica gel impinger gas temperature was maintained below 68°F. The dry gas meter is fully calibrated every month using an EPA-approved intermediate standard. Pre-test, port change, and post-test leak checks are completed (must be less than 0.02 cfm or 4% of the average sample

rate). The gas meter was read to the thousandth of a cubic foot for the initial and final readings. The meter thermocouples were compared with ambient prior to the test run as a check on operation. Readings of the dry gas meter, meter orifice pressure (ΔH) and meter temperatures were taken at every sampling point.

Accurate barometric pressures were recorded at least once a day. Post-test dry gas meter checks were completed to verify the accuracy of the meter full calibration constant (Y).

Analysis: Prior to daily use, the balance was be calibrated with NIST-traceable weights. The impingers were weighed to the nearest 0.5 g.

EPA Draft Method 5

Sampling: All sampling equipment was thoroughly checked to ensure clean and operable components. The oil manometer or Magnehelic gauge used to measure pressure across the S-type pitot tube were leveled and zeroed. The pitot tubes and connecting tubing were leak checked. The temperature measurement system was visually checked for damage and operability by measuring the ambient temperature prior to each traverse. All train components were sealed with Teflon tape before train was leaked checked.

During Test: Duplicate readings of temperature and differential pressure were taken at each traverse point. Isokinecity were maintained at each traverse point. The sample train was leak-checked between port changes.

The probe and filter temperature were maintained at 248 (± 25)°F. The impinger out was maintained at < 68°F. Any unusual occurrences were noted during each run on the appropriate data form.

Post-test: The Field Team Leader reviewed sampling data sheets daily during testing. Each train operator recorded final gas meter readings; performed a final leak-check at the highest observed vacuum; ensured that the Field Task Manager had the data sheets; and transported samples to recovery area. The recovery train uses specified procedures, and all equipment used for recovery was cleaned accordingly.

Analysis: Method 5 QC samples collected in the field included a field train blank and field acetone blanks. Sample results were corrected for field reagent blanks only as described in Method 5. The field train blank results are reported with the sample results.

Analysis of particulate in Method 5 samples were conducted by a microbalance with resolution of ± 0.1 mg. The balance was calibrated prior to analysis using NIST-traceable Class S weights. The calibration was checked using one of the Class S weights every 10 sample weighings. Table 4-1 lists the QA/QC criteria for the stack gas sampling procedure.

4.3 Field Data Reduction

Data gathered during this program falls into the following categories:

1. Manual methods sampling operations data and sample analysis data; and
2. Process data.

Manual methods operations data were input onto computer spreadsheets each day following receipt from testing. Results of samples analysis were input onto the computer system upon receipt from analytical labs. Process data consisted of logs and continuously monitored data. Data was reduced and analyzed using hand-held calculator programs, computer spreadsheets, and other computer programs. The actual equations and nomenclature are shown on the calculator program data sheets

and on the spreadsheets. This feature enables operator and analyst familiarity with the programmed computations, gives facilities separate spot-checking of computed results by hand, and eliminates the need to show equations separately in the text.

4.3.1 *Manual Methods Data Reduction*

Standardized run data forms were used for each method. All run sheets were reviewed daily by the Field Manager for evaluation of progress, completeness, and problems. Standardized computer spreadsheets were used to reduce and analyze field data. At the end of each test day, test data was input onto these spreadsheets. Lab analytical results were not available at the end of each test day. However, results were input as they became available. A standard data set, which has been verified by hand, was used to demonstrate the accuracy of the spreadsheet calculations before and after the test program at each site.

TABLE 4-1. SUMMARY OF QA/QC FOR STACK GAS EXAMPLES

STACK GAS PARAMETER	QUALITY PARAMETER	METHOD OF DETERMINATION	FREQUENCY	CRITERIA
Gas Flow	Pitot tube angle & dimensions	Measurements with vernier micrometer and angle indicator	Post-test	Specifications in EPA Method 2
	Barometer	Calibrated against lab Hg-in-glass barometer	Pre-test	Within 0.1 in. Hg
	Stack thermocouple	Calibrated against ASTM Hg-in-glass thermometer	Pre- and post-test	Within 1.5% as deg. R
Isokinetic sampling trains	Dry gas meter	Calibrated against a reference test meter	Pre- and post-test	Y within 0;05 of pre-test Y; delta H@ within 0.15 of pre-test
	Probe nozzle	Measurements with vernier micrometer to 0.001 in.	Post-test	Maximum difference in any two dimensions within 0.004 inches
	Dry gas meter thermocouples	Calibrated against ASTM Hg-in-glass thermometer	Post-test	Within 5°F
	Trip balance	Calibrated against 10 LM weights	Post-test	Within 0.5 g
Particulate matter	Electronic balance	Calibrated against Class S weights	Post-test	Within 1.0 mg
	Constant filter weight	Documentation	Each sample	Difference of no more than 0.5 or 1 % of total weight
	Accuracy	Documentation of train component and analytical calibrations	N/A	N/A
	Precision	Not possible to assess	N/A	N/A
	Blanks	One filter and reagent blank carried through sample prep & analysis	One per test	Reagent blank less than 0.01 mg/g; filter less than 5 mg or 2% of sample weight

For each manual method, the field data was reduced manually at the end of each test. An isokinetic ratio was then estimated at the end of each day using an average or typical moisture value. The estimated moisture value, estimated isokinetic ratio, and all intermediate calculations were noted on the run sheet. Upon entry into the computer spreadsheet program, both the data and the program were validated by checking the estimated isokinetic ratio against the manually determined value. Verification of the spreadsheet program was conducted using a standard data set which has been manually calculated.

Spreadsheet calculations for the various runs observed the following guidelines:

1. Isokinetic calculations for each train were conducted using the input run data from that specific run rather than from the average or other values from previous runs. Stack gas moisture content was determined using the condensed water measured in that train;

2. Stack temperature, moisture content, velocity, and flow rate values for each of the inlet and outlet locations were average values from all of the combined applicable runs for that test condition. The exception to this rule would be the exclusion of any data from a single run which may deviate more than 20% from the average of the data from the other runs. (This exception may occur if one particular sample port location is unavoidably in a location which does not meet EPA Method 1 criteria and has less than ideal flow conditions.) In addition, this exception may occur if there is questionable data for a specific run due to operator error, process failure, equipment failure, or other circumstances;

3. In the case of questionable data due to operator error, the average results of the other runs were used to correct the results of this run where applicable. For example, if the velocity readings for a specific run are thought to be erroneous due to moisture condensation in the pitot lines, the average velocity measurements from the other simultaneous runs at that location were used to determine isokinetic rate for that run;

and

4. There may be other cases of questionable data, such as measured moisture content, which exceeds the saturation value under the existing stack pressure and temperature conditions. These values will be corrected for actual stack pressure using the equation below:

$$C_{H2O,Ps} = \left(\frac{C_{H2O,29.92}}{29.92} \right) * Ps$$

where:

$C_{H2O,Ps}$	=	Moisture content at stack pressure
$C_{H2O,29.92}$	=	Moisture content measured
Ps	=	Stack static pressure

The accepted range for the isokinetic rate is 90 to 110%. A sample rate below the isokinetic rate can result in a greater proportionate capture of large particles relative to gas volume collected. Some of the large particles, due to their momentum, may enter the nozzle even though gas streamlines curve around the nozzle. On the other hand, a sample rate above the isokinetic rate may result in a smaller proportionate capture of large particles relative to the gas collected. Both the particulate concentration and mass emission rate may be erroneously high in the case of a low sampling rate, or low in the case of a high sampling rate.

If sampling occurs outside the 90-110% isokinetic sampling range, the concentration and mass emission rate is corrected according to the sampling rate. From Shigehara, the culate concentration C_t may be biased proportionally to the degree of sampling rate deviation from the isokinetic rate. Since the mass emission rate (m_s) is calculated from C_t (using the concentration method), then m_s is equally biased. The actual values for C_t and m_s is between the measured values and the adjusted values as

follows:

$$m_{s,adj} = m_{s,meas} * \frac{I}{100}$$

When the sampling rate is outside the 90-110% range, then the actual C_t and m_s for that run is approximated by taking the average of the measured values and the adjusted values:

$$m_s = \frac{m_{s,meas} + m_{s,adj}}{2}$$

Upon daily completion of testing, the Field Manager was responsible for preparation of a data summary which will include:

$$C_{t,adj} = C_{t,meas} * \frac{II}{100}$$

- Raw data sheets; $C_t = \frac{C_{t,meas} + C_{t,adj}}{2}$
- Calculation of isokinetic ratio for each run;
- Traverse start and stop times for each run;
- Calculation of sample volume for each run;
- Calculation of stack gas flow rate; and
- Problems encountered during sampling and/or deviations from standard procedure.

The daily data summary was submitted to the QA Coordinator. The final project report includes a separate QA/QC section which summarizes any audit results from manual sampling procedures, as well as, QC data collected throughout the duration of the program. The EER QA/QC Officer reviewed the manual methods QC data and provided data quality input for the final report.

4.3.2 *Data Validation*

Data validation is a systematic procedure of reviewing data against a set of established criteria to provide a level of assurance of its validity prior to intended use. Data was validated internally by QC personnel. All measurement data was validated based upon process conditions during sampling or testing, acceptable sample collection/testing procedures as outlined in Section 3, consistency with expected and/or other results, adherence to prescribed QC procedures, and the specific acceptance criteria. The data was coded as valid or invalid based on its adherence to these criteria. Data validation was conducted at several critical stages of data reduction:

- Field checks of raw and reduced field data by the Field Manager and Crew Leaders;
- Analytical laboratory QC Checks by a lab QA Supervisor;
- Spot checks of reduced raw data by the Project QA Coordinator;
- Review of summary tables for consistency with reduced raw data by the Project QA Coordinator;
- Draft final report review by the QA Manager, Program Manager, Principal Investigator and Project Manager; and
- Final report review by the Program Manager, Principal Investigator, and Project Manager.

Data validation consists of verification of calculation methodology, consistency of raw, reduced and summarized data tables, comparison of expected results, and consistency of results among multiple measurements at the same location.

Field data was initially validated by the EER Field Manager and the internal QC Coordinator based on their judgement of the representativeness of the sample, maintenance and cleanliness of sampling equipment, and the adherence to the sample collection procedures defined in Section 3. They also validated the data on a daily basis based on :

- Process conditions during sampling;
- Adherence to acceptance criteria; and

- Acceptable external performance evaluation and technical system audit results conducted by the external audit team.

When the data set is complete, the EER field QA Officer performed an overall review of the data. This review considered:

- The previously listed criteria; and
- The reasonableness and consistency of the data based on a knowledge of the site characteristics and the specific location of the samples.

The review also contained an evaluation of the data in terms of meeting the quality assurance objectives of the program discussed in Section 4 of this plan. The QC criteria for data validation contains consistency, duplicate sample calibration, tests for outliers, transmittal error, and uncertainty analysis.

Outliers were identified by comparison with other measurements in a set of observations using the standard student T-Test procedures for outliers. This test flagged specific data points as potential outliers; however, it didl not automatically disqualify any data. Corrective action was initiated immediately to determine the outlier cause. If possible, the associated sample was reanalyzed. The acceptance rejection of the data was in a uniform and consistent manner based on the established validation criteria. Data was rejected only if a validated and documentable reason is identified.

Validation of spreadsheet calculations used for data reduction was conducted by entering a QA data set which has been verified by hand. This was done at the beginning and end of the test program.

Data flags were added to all tables to identify special handling procedures or unusual data results. These flags included:

- Quantities including analytical results which are at or below method minimum detection limits;

- Any results where contamination is suspected;
- Any average results which exclude any individual test run results;
- Any test data which was corrected for moisture content or isokinetic sampling rate;
- Any CEM data where drift exceeded acceptance criteria;
- Calculation of polychlorinated dibenzo-p-dioxins/polychlorinated dibenzo furans (PCDD/PCDF) results using confirmation analysis; and
- Other special data handling procedures or qualifications.

4.4 CEMS Data Aquisition/Reduction

The CEM data is transferred by modem from the site CEM's data aquisition system to the EER office. The data is stored in a holding directory and later printed as an Excel file.

CEM data taken during the field reference method test is averaged. The data average is an average of the time the manual method sampling was conducted, minus the period of time needed for port changes.