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Handbook

Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration

Center for Environmental Research Information
Office of Research and Development
U.S. Environmental Protection Agency
Cincinnati, Ohio 45268

Notice

This report has been reviewed by the U.S. Environmental Protection Agency and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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The Handbook was prepared by Midwest Research Institute's (MRI) Environmental Systems Department, with Andrew Trenholm serving as MRI's project manager. Thomas Dux was principal author with assistance from Pamela Gilford. Other authors who contributed sections to this Handbook are F. Bergman, B. Boomer, D. Hooton, and R. Neulicht.

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Chapter 1
Introduction

The Environmental Protection Agency (EPA) has promulgated regulations for hazardous waste incinerators under the Resource Conservation and Recovery Act.[1*] These regulations require the permit applicant to conduct trial burns to demonstrate compliance with the regulatory limits and provide data needed to write the individual permits. Trial burns require a Quality Assurance Project Plan (QAPjP) with quality assurance/quality control (QA/QC) procedures to control and evaluate data quality. Both permit writers and applicants are in need of specific, consistent guidance in preparing QAPjPs and for designing the necessary QA/QC procedures to ensure consistency and adequacy of plans, reports, and overall data quality. Although considerable information is available on sampling and sample analysis for hazardous waste and its incineration, guidance on specific QA/QC methods has not been available previously.

Guidance on the preparation and review of QAPjPs, establishment of quality assurance objectives, design of QA/QC procedures, and assessment of trial burn results are presented in this handbook. In this volume, QA/QC procedures are defined for process monitoring, sampling, and analysis for both the initial trial burn and for later continuing operation of the incineration facility. Pollutant categories discussed are: principal organic hazardous constituents (POHCs), metals, particulates, acid gases, and combustion gases.

This handbook is intended for a diverse audience: engineers, chemists, environmental scientists, facility personnel, and EPA staff at all levels. It has been written with the EPA or state permit writer's information needs in mind, but would be, by extension, of considerable interest to the permit applicant. The handbook assumes the reader understands the technical approach to incineration and is familiar with the basics of most sampling and analysis methods.

Chapter 2 is a background discussion, covering the need for a QAPjP in a trial burn. A standardized format for a trial burn QAPjP has been recommended to unify QA/QC methodologies for hazardous waste incineration and ensure comparability of data across all performance tests. A key concept in the handbook is the use of QC information and the associated QC criteria for acceptance of trial burn data. The QA/QC procedures and associated QA objectives for each critical measurement parameter are identified in this handbook, along with guidance for acceptance limits. The evaluation of trial burn results if QA/QC objectives have not been achieved is discussed in the handbook.

A wide variety of sampling and analytical methods is covered in the handbook. Based upon practical application of the methods, specific QA/QC procedures have been delineated here which are beyond those in available written protocols. Key QC procedures of each method and their associated acceptance criteria are addressed; some minor QC procedures have not been covered.

The QA/QC procedures presented in this handbook should be considered as the minimum necessary for assessing data quality and ensuring attainment of project objectives. For some facilities, regions, or states, these QC procedures may not be sufficient due to the complexity of a given trial burn; in these cases, the handbook guidance should constrain neither the permit applicant nor the regulatory agency.

The primary focus of the handbook is the trial burn itself; however, a discussion of the QA/QC for routine incinerator monitoring and permit compliance is included in a separate chapter. This area has slightly different requirements and objectives from those of the trial burn. The trial burn should be viewed as a short-term project with a defined beginning and end, while compliance monitoring is considered an ongoing process.

If trial burns and routine monitoring are designed using the QA/QC indicated in the handbook and follow the outline and guidance for the development of a QAPjP, the level of precision and accuracy will be documented, and acceptance limits for these parameters will be defined. If the QC information suggested in this handbook is presented as part of the final trial burn report, the subsequent process of reviewing and assessing the results should be easy, effective, and standardized.

*References and a bibliography are listed in Chapter 12.

Chapter 2
QA Project Plans in Hazardous Waste Incineration Trial Burns

The fundamental concepts of quality assurance and quality control as applied to the hazardous waste incineration permitting process are introduced in this chapter. The role of QA objectives in the overall quality assurance project plan (QAPjP) and in the trial burn plan (TBP) is discussed in terms of specific information the permit writer should expect to find in an applicant's documentation. This section covers both the format and content of QA plans required for trial burns. Chapter 11 of this handbook discusses the QA/QC for daily incinerator operation.

Trial burns of hazardous waste incinerators are complex activities requiring operation of the incinerator under rigorously controlled conditions in conjunction with environmental sampling and analysis of constituents in diverse matrices. This complexity is reflected in the permit application and trial burn plans (TBPs) which must cover facility design, theoretical design of the trial burn, incinerator operating conditions (waste streams, temperature, air pollution control equipment, etc.), complex sampling methods (e.g., VOST, SVOST, Orsat), and finally, preparation and analysis of samples ranging from high concentration waste feeds to low concentration stack gas samples. All of the data generated must have a documented, known level for precision and accuracy sufficient to support decisions based upon those data. Often, the key procedures and concepts needed to ensure quality data are vital in presenting the technical design of the incinerator and trial burn.

The QA/QC procedures for a particular trial burn are presented in the Quality Assurance Project Plan (QAPjP). It is designed to document and assess the precision and accuracy of the trial burn data, and to assure the permit reviewer that the data will be of sufficient quality for making regulatory decisions. EPA quality assurance policy stipulates that every monitoring and measurement project must have a written and approved QAPjP.[2] This document should contain, in specific terms, policies, organizational adaptations, overall objectives, functional activities, and tailored QA/QC activities designed to achieve the data quality goals of that particular project or operation. The QAPjP must be prepared by the organization responsible for the project work and approved by the appropriate federal, regional, or state agency.

The QAPjP and TBP should be considered companion documents and should be reviewed at the same time. They may be presented as a single document if that is the applicant's preference. Generally, the TBP covers topics related to the experimental design of the trial burn (e.g., incinerator type, waste feeds, test schedules), sampling design and methods, as well as analytical methods. The QAPjP covers all the QA/QC procedures necessary to fulfill the objectives of the trial burn. In many areas the TBP and QAPjP will overlap, or areas will be repeated in both documents; however, the TBP usually is considered the primary document, and the QAPjP will often refer to subjects already considered in the TBP.

2.1 Structure of QAPjP

2.1.1 Format

The general format and required topics in a QAPjP are outlined by the EPA Quality Assurance Management Staff (QAMS) in *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans*)[2]. The sixteen items that must be considered for inclusion in each QAPjP are outlined in Table 2-1. QAMS states directly, "The sixteen essential elements must be considered and addressed in each QAPjP. If a particular element is not relevant to the project under consideration, a brief explanation of why the element is not relevant must be included."

The permit writer should not accept a QAPjP which does not cover all the elements in the QAMS guidance. Standardizing the format will help unify the QA/QC methodologies for hazardous waste incineration and ensure comparable data quality for all performance tests. Usually, each one of the 16 items is a separate section in the QAPjP. If an item is not relevant to the QAPjP or is covered elsewhere in the accompanying TBP, this may be explained and/or reference may be made to the appropriate section of the QAPjP or TBP.presents

However, the QAMS format should not constrain the applicant if there is a need to cover topics not included in the 16 elements. A slight modification of these 16 elements is presented in Table 2-2 that is more appropriate to incineration trial burns. The only modifications made were the addition of staff qualifi-

Table 2-1. Sixteen Essential Elements of a Quality Assurance Project Plant (QAPjP)

1.	Title page with provision for approval signatures.
2.	Table of contents.
3.	Project description.
4.	Project organization and responsibility.
5.	QA objectives for measurement data in terms of precision, accuracy, completeness, representativeness, and comparability.
6.	Sampling procedures.
7.	Sample custody.
8.	Calibration procedures and frequency.
9.	Analytical procedures.
10.	Data reduction, validation, and reporting.
11.	Internal quality control checks and frequency.
12.	Performance and system audits and frequency.
13.	Preventive maintenance procedures and schedules.
14.	Specific routine procedures to be used to assess data precision, accuracy, and completeness of specific measurement parameters involved.
15.	Corrective action.
16.	Quality assurance reports to management.

From *Interim Guidelines and Specifications for Preparing Quality Assurance Project Plans* (QAMS-005/80).[2]

Table 2-2. Recommended Outline for a Trail Burn Quality Assurance Project Plant (QAPjP)

QAPjP Outline for Hazardous Waste Incinerator Trial Burns

Section 1.0	Title Page (with approval signatures)
Section 2.0	Table of Contents
Section 3.0	Project Description
Section 4.0	Organization of Personnel, Responsibilities, and Qualifications
Section 5.0	Quality Assurance and Quality Control Objectives
Section 6.0	Sampling and Monitoring Procedures
Section 7.0	Sample Handling, Traceability, and Holding Times
Section 8.0	Specific Calibration Procedures and Frequency
Section 9.0	Analytical Procedures
Section 10.0	Specific Internal Quality Control Checks
Section 11.0	Data Reduction, Data Validation, and Data Reporting
Section 12.0	Routine Maintenance Procedures and Schedules
Section 13.0	Assessment Procedures for Accuracy, Precision, and Completeness
Section 14.0	Audit Procedures, Corrective Action, and QA Reporting

cations to the fourth element and the combining of audits, corrective action, and QA reporting into a single section. The sections of a QAPjP and the types of information the permit writer should expect to see in this document are described briefly in the remainder of this chapter. For a more detailed description of the information that belongs in each section of a QAPjP, please refer to the above document (QAMS-005/80).

2.1.2 *Document Control, Title Page, and Table of Contents*

Each page of the QAPjP should have a document control indicator in the top right corner as shown below:

Section No.
Revision No.
Date:
Page ____ of ____

This document control indicator assists the permit writer in finding information, flags changes made during the review process, and enables the permit writer to identify unapproved changes to the QAPjP. Multiple revisions are frequently difficult to track. Revised sections of the QAPjP should be submitted so that the permit writer can update the QAPjP easily and track areas which have been modified. Also, QAPjPs may be photocopied and distributed many times, and the number of pages quickly indicates if a full copy has been received. A document control format is also helpful for the TBP.

The title page and table of contents are self-explanatory. The title page must include approval signatures from the following personnel: (a) the project leader; (b) the project leader's supervisor (if the trial burn is conducted by a subcontractor and not by the facility); (c) the quality assurance coordinator (QAC) for the trial burn; and, (d) the facility-designated signatory (40 CFR 270.11). A revised title page should be submitted with every modification of any section of the QAPjP. Provision should be made for the signatures of the permit writer and the permit writer's quality assurance officer. In approving the TBP and QAPjP, a signed title page should be returned to the applicant indicating approval.

2.1.3 *Project Description*

This section may be redundant since the accompanying TBP should contain a complete project description. However, a short project description is recommended for inclusion along with a diagram of the incinerator indicating sampling points, especially if the QAPjP is a separate document. Sometimes QAPjPs become separated from the TBP and the duplicate information is useful. At a minimum,

reference should be made to the TBP section containing the project synopsis.

2.1.4 *Organization of Personnel, Responsibilities, and Qualifications*

This section of the QAPjP should identify key personnel, their qualifications, and their QA/QC responsibilities. At a minimum, the following personnel must be identified: (a) the facility-designated signatory (40 CFR 270.11); (b) the overall trial burn project manager; (c) the field sampling manager; (d) the analytical manager; and, (e) the QAC. Preferably, a chart or table should be included showing the project organization.

The QAPjP should contain an appendix giving the qualifications, resumes, or curriculum vitae of every individual with key responsibilities. The permit reviewer should examine these qualifications to ascertain that facility and contractor personnel are sufficiently experienced or trained to conduct a trial burn.

A single individual must be designated as QAC. The QAC's function is to conduct or coordinate audits by other personnel of field and laboratory operations to ensure compliance with the TBP and the QAPjP. The QAC should also have the identified responsibility of examining all project records, analysis data, and quality control results, and including a written independent assessment of overall data quality to be submitted with the trial burn report (TBR). This assessment should be in addition to the assessment and conclusions of the primary author of the trial burn report (the project leader). The TBR should include sufficient information to indicate whether the QAC is organizationally independent of the trial burn's technical staff (i.e., not the project leader, field sampling manager, or analysis task manager), and is not directly responsible for any environmental measurements nor accountable to those directly responsible. A designated QAC is essential to an independent assessment of the data quality presented in the trial burn report.

2.1.5 *Quality Assurance and Quality Control Objectives*

QAMS-005/80[2] states, "For each major measurement parameter, including all pollutant measurement systems, list the QA objectives for precision, accuracy, and completeness. These QA objectives should be summarized in a table." These objectives must be based upon the permit writer's decisions. Each measurement must have a defined precision and accuracy objective summarized in a table. If all the QC data meet the objectives, the trial burn results will be judged as having an acceptable quality level, sufficient for making the permitting decision. When QC results are poor and specific criteria have not been established, the acceptance of the data is left to the technical judgment of the permit writer.

Specific QC procedures and associated acceptance criteria are presented in this handbook. These procedures should be summarized and presented in the objectives table. This table should guide the permit writer to all the quality control and associated criteria for each measurement (POHCs, CO, O_2, combustion chamber temperature, spike recovery, etc.). Each associated quality objective must be related to a method for determining that objective. For example, an objective for chloride measurement accuracy stated as 80% to 100% is meaningless, since no basis has been provided to determine this objective. Instead, the objective should be associated with the spike recovery from impingers fortified at the estimated 99% removal level (80% to 120% recovery). Table 2-3 is an example of a QA objective table from a QAPjP.

QAMS-005/80[2] also states that this section should cover the quality objectives of completeness, representativeness, and comparability. Completeness is defined as "the amount of valid data obtained from a measurement system compared to the amount that was expected to be obtained under optimal normal conditions." For the permit to be written, completeness should be 100% in that three valid test runs are needed for each test condition. Acceptable results must be obtained for all three trial burn runs. However, when individual tasks and problems are considered, completeness is not so easily defined. For example, in VOST tube analyses four samples are often collected, and three are analyzed unless there are problems. Although only three or four samples have been analyzed, a valid result for a test run was obtained; the test is complete. The concept of completeness as defined for a QAPjP is probably more pertinent to an entire monitoring project, where a certain amount of data is needed to complete the statistical design.

Representativeness and comparability objectives are generally not quantifiable. Representativeness is defined as "the degree to which data accurately and precisely represent a characteristic of a population, parameter variations at a sampling point, process condition, or an environmental condition," while comparability is defined as "expressing the confidence with which one data set can be compared to another."[2] In stack sampling, a representative sample whose results are comparable to other data sets is ensured primarily through the use of standard EPA methods[3] (e.g., M1, M2, SVOST, VOST). The proper use of a standard stack sampling method ensures a representative sample. If that sample is analyzed using standardized methodology and the results are reported in common units, the results should be comparable to those obtained from other trial burns. In rare situations, a trial burn involves unique POHCs,

Table 2-3. Example Summary Table of Precision and Accuracy Objectives

Parameter	Matrix	QC Procedure	Precision	Accuracy Mean Recovery %
Semivolatile POHC (1,2,3-Trichlorobenzene)	*Stack emissions:*	*Spiked with suitable surrogate compound (use of labeled surrogate is recommended)*	*NA*	
	XAD-2 *Filter* *Water* *Front half rinse* *Back half rinse*	*^{13}C-Hexachlorobenzene* *$^{13}C_6$-1,2,4,5-Tetrachlorobenzene* *For each SVOST component, average over three runs*	*50% RSD*	*50-150*
	Solid waste *Organic liquid wastes*	*As a minimum, one native surrogate will be spiked in each sample.*	*50% RSD*	*50-150*
	Ash	*Average over three runs*	*50% RSD*	*NA*
	Stack emission	*Analysis of spiked blank filter and spiked XAD. Spiked with all POHCs and surrogates*	*NA*	*50-150*
Particulate	*Stack emission*	*Balance calibration with 500 mg weight*	*NA*	*(499.5 - 500.5) (±0.5 mg)*
Chlorine	*Aqueous waste*		*20*	*NA*
	Sludge		*20*	*NA*
	Solid wastes	*Duplicate analysis for 1 run*	*20*	*NA*
	Organic liquid wastes		*20*	*NA*
	Blind knowns			*100 ±10*
Hydrogen Chloride	*NaOH solution/water*	*Chloride standard in water*	*NA*	*100 ± 15*
	NaOH solution/water	*Duplicate analyses for one run*	*30*	*NA*

NA = Not applicable

and standard methodology will not meet the data needs for the regulatory decision. In such a case, the performance of any novel methodology should be determined in advance and documented in the QAPjP. Comparability also refers to the units in which results are reported. The handbook on *Guidance on Setting Permit Conditions and Reporting Trial Burn Results* recommends suitable units for data reporting.[4]

2.1.6 *Sampling and Monitoring Procedures*

Sampling and monitoring procedures are usually described in the accompanying TBP, and there is no need to repeat details already given. However, a table giving all sampling points, sampling frequency, total number of samples plus replicate and field duplicates should be presented in this section. Each sampling activity needs a written procedure. For stack sampling, reference to the EPA method is usually sufficient, but any specific options chosen from those procedures must be given. However, for waste feed and ash sampling, an outline procedure should be presented in the QAPjP. Details of sampling procedures should be discussed in an appendix (see Chapter 4).

The key quality parameters for sampling are: (1) use of standard reference methods; and (2) that sampling procedures and trial burn design call for sufficient POHC mass in the stack gas sample for accurate detection and quantitation at the 99.99% DRE level. The amount of this mass should be included, along with the calibration range of the analytical method used to detect and quantitate the POHC. The mass of POHC in the sample (if DRE is at the 99.99% level) should be within the calibration range and at least 10 times the lowest calibration point to ensure accurate measurement of the DRE. If not, the permit applicant should either change the waste feed rate, the sampling rate, or the analytical method to achieve proper quantitation of the POHC.

For example, the theoretical waste feed input, the stack sampling rate, and 99.99% DRE should be used to calculate a maximum VOST tube concentration (e.g., 100 ng) if the 99.99% DRE is achieved. This should be presented with the calibration range (e.g., 10 to 500 ng) to ensure that a sufficient amount of POHC is present. For SVOST, this presentation should take into account the manner in which the SVOST components are combined; in addition, the POHC and calibration range must be in the same concentration or mass units to be comparable.

2.1.7 *Sample Handling, Custody, and Holding Times*

Each sample should be identified in this section, along with appropriate holding times for each analysis and any associated preservation techniques. All sample handling procedures for the trial burn must be described, including sample labeling, preservation, packing, shipping, laboratory, and field storage procedures. All documentation practices should be described, including field log books, sample analysis request forms, laboratory custody log books, and field

custody forms. Storage of samples for archive purposes must also be covered. Often it is most appropriate to formulate these procedures into a formalized standard operating procedure included as an appendix to the QAPjP. These topics are discussed in more detail in Chapter 3 of this handbook.

2.1.8 *Specific Calibration Procedures and Frequency*

Since the majority of measurements made during a trial burn are performed using standard EPA reference methods, calibration procedures and frequency do not have to be discussed in detail, but should be referenced. This section of the QAPjP should state the source of all standard analytical reference material used in calibration, including chemical standards, gas calibration cylinders, and reference thermometers. The ultimate standards used for the analytical procedure or instrument calibration and the relationship of the calibration scheme to these reference materials should be delineated. For any nonstandard methods (such as facility standard operating procedures), calibration procedure and frequency must be included. Particular attention should be paid to all process monitors and continuous monitors. Calibrations should be summarized in a table. Routine calibration of stack sampling equipment is discussed in Section 3.3. Table 2-4 is an example from a QAPjP.

2.1.9 *Analytical Procedures*

Most of these analytical procedures should follow EPA standard methodology. All samples should be identified in a table, along with the associated analytical procedure. Written procedures in an appendix should describe any analytical procedures unique to that trial burn. All modifications of standard methods must be identified, along with reasons for the changes. Most procedures have allowable options to ensure effective analysis for POHCs. If no options (especially for VOST, SVOST, and metals) have been clearly identified in the QAPjP or TBP, the permit writer should ask the applicant to confirm their absence.

Two items crucial for all POHC analysis are detection limit and POHC quantitation. First of all, if a POHC has not been detected in the stack gas sample, the detection limit should be used for calculation of the DRE. Thus, this determination can be a critical parameter in deciding if the DRE has been achieved. Often, the detection limit will be artificially low if it has been based purely on an instrumental detection limit and does not include method recovery of the POHC and possible interference from stack gas components. However, as long as the 99.99% DRE critical level is above the lower quantitation limit, achievement of DRE based upon the detection limit will not significantly affect a regulatory decision based upon DRE. Actually, if no POHC is detectable in the samples, a more conservative quantitation limit is recommended for DRE calculations as compared to the detection limit.

Secondly, the successful detection and quantitation of the POHC is of particular importance in trial burns. This area requires a great deal of analytical expertise and often involves a choice of options, modifications, or additions to standard analytical methods. This section of the QAPjP should present method performance data for each POHC to demonstrate in advance the effectiveness of the proposed methodologies. These data may be derived from past trial burns (recoveries of isotopically-labeled surrogates of POHCs), from recovery studies of POHC spikes of blank VOST or SVOST components, or, in cases in which the stack gas matrix might present serious interference problems, from a preliminary "mini" trial burn conducted at the incinerator prior to the actual RCRA trial burn. This assures the regulatory agency that the analytical method is capable of providing usable data. Permit reviewers must exercise caution when reviewing the development of alternative analytical methods or alternative sampling approaches. The accuracy of a POHC determination is highly dependent on adequate method development. A qualified chemist should make this determination. Analytical method performance cannot be assumed from theoretical postulates, but must be demonstrated in advance using actual data obtained by the firm conducting the trial burn analysis.

2.1.10 *Specific Internal Quality Control Checks*

For each analysis method, specific internal QC procedures should be detailed in this section of the QAPjP. These procedures should each have an associated quality control objective, as outlined in Section 5 of the QAPjP (Section 2.2.5 of this handbook). For example, if accuracy is to be 80% to 120% for the chloride reference standard, the section under chloride analysis should state the source and concentration of this standard. For SVOST analysis, the instrument check standard, the surrogate spiking levels, the component to be spiked, the type and number of blanks, the spiking levels of the blank SVOST train, and required duplicate analysis of samples should be described in detail.

Some QC procedures have criteria not related to accuracy and precision. Blank analysis is an example. Its objective is to determine the degree of contamination of the measurement system. This objective must be defined by: (a) the type of blank (blank VOST train from field); (b) the frequency of the blank (one per trial burn run); and (c) the acceptance criteria.

Table 2-4. Example Table of Calibration Procedures and Criteria for Sampling Equipment

Parameter	Calibration technique	Reference standard	Acceptance limit[a]	Calibration
1. Probe nozzle	Measure diameter to nearest 0.001 in	Micrometer	Mean of three measurements; difference between high and low ≤ 0.1 mm	Prior to test
2. Gas meter volume	Compare to wet test meter	Wet test meter	Record calibration factor ±5% of factor	Prior to test Posttest
3. Gas meter temperature	Compare to mercury-in-glass thermometer	ASTM Thermometer	±5°F	Prior to test
4. Stack temperature sensor	Compare to mercury-in-glass thermometer	ASTM Thermometer	±1.5°% ±1.5°% mean temp.	Prior to test Posttest
5. Final impinger temperature sensor	Compare to mercury-in-glass thermometer	ASTM Thermometer	±5°F	Prior to test
6. Filter temperature sensor	Compare to mercury-in-glass thermometer	ASTM Thermometer	±5°F	Prior to test
7. Aneroid barometer	Compare to mercury barometer	Mercury column barometer	±2.5 mm	Prior to test
8. S-type pitot tube	NA	Design criteria	Meets RM2 criteria	Prior to test

[a]40 CFR 60, Appendix A.

Occasionally, these items can be summarized in tables or presented more cohesively in the analysis section of the QAPjP (handbook Section 2.2.9). If not, the QC section should at least reference the other section of the QAPjP in which they are presented. Many of the analysis sections of this handbook outline needed QC procedures in addition to those presented in the methods; this chapter of the QAPjP should identify any of those procedures being utilized for a particular trial burn.

2.1.11 Data Reduction, Validation, and Reporting

For each major measurement parameter, a brief description of the following should be included:

* The data reduction scheme for nonroutine methods, including all validation steps and the equations used to calculate the final results.
* Listing of all final experimental data to be reported in the trial burn report.
* Listing of all quality control data to be reported in the trial burn report.

This section of the QAPjP is difficult to define explicitly. Approaches used by past applicants have varied widely. For data reduction schemes in which calculations are specified in the methods, only a summary need be presented with minimal explanation. However, the validation steps in the data reduction process need to be identified. Validation of analysis results can be carried out in many different ways, but the central concept is that QC results must be within the acceptance criteria for a given analysis.

Of particular importance is the use of blank data. Routine correction of any stack gas sample results for blank analysis is generally not recommended, regardless of the type of blank. The purpose of this recommendation is to disallow any routine correction of stack gas results to increase the DRE. If a need does exist for blank correction, the VOST method (0030)[3] and the Hazardous Waste Measurement Guidance Manual[5] give specific procedures for blank correction. Blank corrected emissions data should also be reported without correction for comparison. Any stack gas calculations for DRE, HCl emissions, or metals emissions presented in this section that routinely incorporate blank corrections should be questioned by the permit reviewer.

All reportable test data and QC data must be identified. This will preclude delays during review of the trial burn report (TBR) because of insufficient information. QC data are often neglected in trial burn reports, but they are vital to assessing overall data quality. *Guidance on Setting Permit Conditions and Reporting Trial Burn Results*[4] gives specific reporting requirements and formats that should be used. Section 3.6 of this handbook gives a summary of reportable QC data.

2.1.12 Routine Maintenance Procedures and Schedules

The purpose of this section is to list all critical equipment necessary to maintain permit operating conditions and to demonstrate continuing compliance

to the permit. For each piece of measurement equipment (e.g., a CO monitor, waste feed rate monitor, combustion chamber pressure monitor, etc.), a schedule and maintenance procedure should be outlined. The brief statement "per manufacturer's recommendations" is insufficient. Full procedures must be provided in the permit application or QAPjP.

2.1.13 Assessment Procedures for Accuracy and Precision

The formulae for assessing precision and accuracy are given here. If the number of data points is less than 4, precision should be expressed as:

Range Percent (RP)

$$RP = \left(\frac{X_1 - X_2}{\text{avg. X}}\right) 100 \qquad \text{Eq. 2-1}$$

where X_1 = highest value
X_2 = lowest value

If n ≥4, precision should be expressed as:

Relative Standard Deviation (RSD)

$$RSD = \left(\frac{\text{standard deviation}}{\text{average value}}\right) 100 \qquad \text{Eq. 2-2}$$

Accuracy, if using reference material of known concentration, is usually expressed as:

Accuracy (A)

$$A = \left(\frac{\text{found concentration}}{\text{actual concentration}}\right) 100 \qquad \text{Eq. 2-3}$$

If accuracy is being determined by adding a known amount to a sample (spiking), it is usually expressed as:

Recovery (R);

$$R = \left(\frac{\text{found} - \text{native}}{\text{amount spiked}}\right) 100 \qquad \text{Eq. 2-4}$$

The found level is the amount determined in the spike sample, and the native level is the amount determined in the unspiked sample. For spiked samples, recovery should always be expressed in relation to the amount spiked (a known quantity), not in relation to the amount spiked plus the native level (an unknown quantity, determined by the same analytical system being evaluated for accuracy). Therefore, recovery should *not* be calculated as R = 100[found/(amount spiked + native)].

2.1.14 Audit Procedures, Corrective Action, and QA Reporting

This section of the QAPjP should be divided into two parts, one for trial burn activities and one for routine incinerator operation. This section should cover all QA activities for both topics. For the trial burn, all QAC audits and reports should be identified. A minimum of one audit of overall data quality should be carried out by the applicant and reported in the TBR. Such audits are discussed in greater detail in Section 3.4 of this handbook. All audits, major problems, and significant corrective action need to be reported to QA personnel, project management, and corporate management. The kinds of reports submitted (e.g., audits) and who may receive them (e.g., project leader) should be identified in this section.

2.2 Review of the QAPjP with Trial Burn Plan

The QAPjP should be detailed, specific, and centered on the decisions that the permit writer must make. For the trial burn data to be usable, specific QC procedures must be followed and the related data quality indicators must fall within the prescribed criteria. All of these procedures and accompanying criteria should be clearly identified in the QAPjP and addressed in the TBR.

One of the inherent difficulties with a QAPjP is that it forces an arbitrary distinction between QA/QC procedures and the technical design and procedures of the project itself. To avoid this, many people integrate the TBP and the QAPjP. However, the problem with this approach is that QC and the associated data assessment parameters (and criteria) get lost in the technical discussion of the project. The QAPjP does not have to repeat details which are given in the TBP; however, if the details are in the TBP appendices or the analytical methods, *all* QA/QC objectives and procedures at least must be *summarized* in the QAPjP.

The regulatory agency needs the QAPjP as a basis for justifying acceptance or rejection of the trial burn. The QAPjP should be considered as similar to a contract. The permit reviewer in approving the QAPjP is stating, "If all QA/QC procedures are followed and meet the appropriate acceptance criteria, then the trial burn data will be judged a sufficient base for making the permitting decision." An unclear QAPjP can contribute to many difficulties in reviewing test reports and possibly the rejection of a test as inadequate. Previously agreed upon objectives (via a QAPjP) serve as a useful vehicle for supporting acceptance or rejection of trial burn results.

Chapter 3
General Topics

Overview discussions of selected general topics that should be covered in the QAPjP are provided in this chapter. The topics are not specific to any particular method. They are relevant to the overall data quality and conduct of a trial burn.

3.1 Sample Handling and Custody

Chain of custody (COC) is not required for trial burns; however, the permit applicant may choose to use COC procedures. A description of COC requirements can be found in SW-846 (Section 1.3)[3] and the National Enforcement Investigations Center (NEIC) Policy and Procedures.[6] Strict sample custody is currently all that is required. Procedures for sample custody should be outlined in Section 7 of the QAPjP or in a standard operating procedure appended to the QAPjP. At the minimum, these procedures should contain the following elements:

- A master record containing a list of all samples taken, time and date of sampling, description of sample, unique identifier for each sample, and sample preservation and sample storage conditions before shipment.
- For each sampling event, a sample data form should be presented, including one for stack samples, waste feed samples, scrubber water samples, etc. At the minimum, each form should indicate: (a) the individual taking the sample; (b) the date and time of sample collection; (c) sampling technique; (d) compositing technique; (e) sample container; (f) sample identifier; (g) sample location; (h) sampling equipment; and (i) any sample preservation or storage before shipment.
- Each sample shipment should be accompanied by a sample inventory form which should indicate: (a) every sample shipped (by identifier); (b) sample packaging; (c) date of shipment; (d) carrier; and (e) any sample preservation such as packing in ice. Upon receipt, the following should be recorded on the same form: (a) all samples received; (b) their condition upon receipt; (c) if shipped with ice, temperature of samples upon receipt; (d) person receiving samples; and (e) storage conditions upon receipt.

Examples of the above forms and all records should be presented in the QAPjP. Every sample collection form, sample shipping inventory, and the master records should be available to the permit writer. As part of the review of the trial burn report (TBR), the permit writer may spot check these records to ensure that samples have been handled properly, taken at the correct time and in the correct manner, assigned a unique identifier, received intact by the laboratory, and that all sample preservation was appropriate. If samples are not traceable or not properly handled, explicit justification for data acceptance from the permit applicant is required.

3.2 Holding Times

Most analytes have a finite stability in a sample matrix. Holding time is the maximum allowable time between sample collection, sample preparation, and sample analysis; after the holding time has expired, a significant probability of lowered analyte concentration in the sample exists. Holding times are dependent upon the analyte sample matrix and sample preservation techniques such as storage temperature and chemical methods to stabilize the analytes (e.g., pH adjustment).

Since a lower analyte concentration is the expected result of exceeded holding times, from the regulatory perspective (attainment of DRE), waste feed holding times are not as critical as those for stack gas, ash, and air pollution control samples (if waste feeds are biased low, this will lower the DRE). VOST samples must be kept at or below 5°C and analyzed within 14 days after collection; SVOST samples must be stored at the 5°C temperature, extracted within 14 days, and analyzed within 40 days after extraction. These traditional holding times are not based on experimental data for the individual analyte in each matrix, but on information about general classes of compounds and the most common analytical matrices. Particularly reactive or labile compounds may require a more stringent holding time or a different preservation technique.

General guidance on holding times for incineration samples is given in Table 3-1, and SW-846 holding times are contained in Table 3-2. All holding times should be summarized and reported in the TBR. Whenever intended holding times are extended in the QAPjP or actual holdings times after the trial burn, justification based upon actual sample data should be requested from the permit applicant.

Bag samples or grab samples of stack gas or gaseous waste feed samples are a very special case. An analyte in the gaseous state is potentially more reactive and labile as well as difficult to contain. Therefore, if bag samples or grab samples of a gaseous media are taken, the permit writer should require holding times as short as is logistically feasible.

3.3 Routine Calibration of Stack Sampling Equipment

The quality of stack sampling cannot be evaluated by a performance audit. The QA/QC results therefore must be managed by controlling the sampling procedures and the calibration of stack sampling equipment. The stack sampling components requiring calibration consist of dry gas meters, rotameters, pitot tubes, vacuum gauges, manometers, barometers, and temperature-indicating devices.

Many testing organizations have found it desirable to establish a routine calibration for these components before trial burns. In all cases, the calibration is best performed after every field test and after repairs have been made on any components. These calibrations then serve effectively as pretest calibrations for the tests to follow.

All calibrations must be documented. Copies of the documents should be included in the TBR. The calibration documentation should include as a minimum: (a) the device being calibrated; (b) identification (ID) number; (c) reference device; (d) date reference device last calibrated; (e) ID of reference device; (f) date calibration performed; (g) by whom calibration was performed; (h) description of reference device; and (i) total volume sampled (when applicable).

The calibration documents should be included in the TBR to enable a permit writer to determine if proper procedures were employed. A document of certification performed by an outside organization without a description of the procedures used and the organization's qualifications is insufficient.

Procedures specified in the *Quality Assurance Handbook for Air Pollution Measurement Systems*[8] and amendments to the methods published in the *Federal Register* provide the calibration procedures.

Dry gas meters used in sampling trains may be calibrated using either a wet test meter, a secondary standard dry gas meter, or an orifice. The procedures are reported in detail in 50 FR 01164 (01/09/85) and for critical orifices in 52 FR 09657 (03/26/87), and 52 FR 22888 (06/16/87). Reviewers of the TBR should check calibration for procedural errors. For example, volume measurement devices may be operated outside of the range and/or for an insufficient time period. One or more complete revolutions of wet and dry gas meters are required and at least three calibration runs should be made at each setting or rate.

Rotameters used to set a sampling rate such as used in Method 3 and VOST do not need to be calibrated but may use the manufacturer's calibration curves. This allowance is permitted because total gas sample volume is measured by the dry gas meter.

Assurance of the calibration of pitot tubes consists of visual inspection before and after a test. If the pitot tube is part of an assembly, it must either meet the noninterference standards outlined in EPA Method 2 or be calibrated against a reference pitot tube following the procedure specified in EPA Method 2.

The procedures to be followed for calibrating gauges, manometers, barometers, and temperature-indicating devices are specified in the procedures. In most cases, calibration should be performed after every test and documented. Documentation is not simply a statement that a device was calibrated following recommended procedures. The documentation of the calibration process is used to facilitate location of any procedural errors which may have been introduced into the system. In those cases in which an item is a subcomponent of a system (e.g., vacuum gauge on a meter console), the item should at least be listed on the system check record. Barometer calibration records should indicate the reference source and any altitude correction that may have been applied. In calibrating temperature-indicating devices, any indirect reading systems should be calibrated using the entire device, i.e., sensor, umbilical cord, and read-out system.

The criteria and methods discussed in this section were summarized in Table 2-4.

3.4 Internal Auditing

Internal audits are conducted by the applicant or the applicant's contractors. External audits are conducted by agency personnel or agency contractors.

Firms conducting trial burns should have a QA program run by a Quality Assurance Coordinator (QAC). This program may include:

Table 3-1. General Recommendations for Containers, Preservation, and Holding Times

Measurement	Matrix	Containers[a]	Preservative	Maximum holding time before extraction (days)	Holding time for extraction to analysis (days)	Maximum holding time from sampling time to analysis (days)
Semivolatile POHCs	XAD-2	Standard cartridge	Chill with ice	14	40	-
	Stack gas filter	Standard petri dish	Chill with ice	14	40	-
	Waste feeds	G, Teflon-lined cap	Chill with ice	14	40	-
	Ash	G, Teflon-lined cap	Chill with ice	14	40	-
Volatile POHCs	Tenax or charcoal	VOST Cartridge	Chill with ice[b]	NA	NA	14
	Liquid wastes	VOA vial[c] (no headspace)	Chill with ice	NA	NA	14
	Solid wastes	G, Teflon-lined cap	Chill with ice	NA	NA	14
Chlorine	Liquid wastes	G	None	NA	NA	30
	Solid wastes	G	None	NA	NA	30
Hydrogen chloride	NaOH solution and condensate	G or P	None	NA	NA	30
Stack gas particulate	Quartz filter	Standard petri dish	None	NA	NA	NA
Orsat (O_2, CO, CO_2)	Gaseous	Integrated bag	None	NA	NA	4 h

NA = not applicable.
[a] Polyethylene (P) or amber glass (G).
[b] Must be placed on ice immediately following collection.
[c] 50 mL amber, screw-capped vial; cap is lined with a teflon-backed silicon rubber septum.

Table 3-2.[a] SW-846 Holding Times for Water Samples

40 CFR Section 136.3, Table 11--Required Containers, Preservation Techniques, and Holding Times (taken from *Test Methods for Evaluating Solid Waste* (SW-846), except where noted with an (*))

Parameter No./name	Container[b]	Preservation	Maximum holding time
INORGANIC TESTS:			
1. Acidity	P,G	Cool, 4°C	14 days
2. Alkalinity	P,G	Cool, 4°C	14 days
3. Ammonia	P,G	Cool, 4°C, H_2SO_4 pH < 2	28 days
4. Bromide	P,G	None required	28 days
5. Cyanide, total and amenable to chlorination	P,G	Cool, 4°C, NaOH to pH > 12, 0.6 ascorbic acid	14 days
6. Hydrogen ion (pH)	P,G	None required	Analyze immediately
7. Sulfide	P,G	Cool, 4°C, add zinc acetate plus sodium hydroxide to pH ≥ 9	7 days
METALS:			
1. Chromium VI	P,G	Cool, 4°C	24 hours
2. Mercury	P,G	HNO_3 to pH <2	28 days
3. Metals, except chromium and mercury	P,G	HNO_3 to pH <2	6 months
ORGANICS:			
1. Purgeable halocarbons	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$	14 days
2. Purgeable aromatic	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$, HCl to pH 2	14 days * 7 day unpreserved
3. Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4°C, 0.008% $Na_2S_2O_3$, adjust pH to 4-5	14 days
4. Phenol	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$,	7 days until extraction
5. Benzidines	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$,	7 days until extraction
6. Phthalate esters	G, Teflon-lined septum	Cool, 4°C	7 days until extraction 40 days after extraction
7. Nitrosamines	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$, store in dark	40 days after extraction
8. PCBs	G, Teflon-lined cap	Cool, 4°C	40 days after extraction
9. Polynuclear aromatic hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$, store in dark	40 days after extraction
10. Chlorinated hydrocarbons	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$	40 days after extraction
11. TCDD (dioxin)	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$	6 months prior to extraction
12. TCDF (dibenzofuran)	G, Teflon-lined cap	Cool, 4°C, 0.008% $Na_2S_2O_3$	6 months prior to extraction
PESTICIDE TESTS:			
1. Pesticides	G, Teflon-lined cap	Cool, 4°C, pH 5-9	40 days after extraction

[a]Adapted from "Removal Program Sampling QA/QC Plan - Interim Guidance," Emergency Response Division, EPA, OERR, OSWER, OSWER Directive 9360.4-01, February 2, 1989.
[b]Polyethylene (P) or glass (G).

- System audits of field and/or laboratory operations to ensure that the procedures specified in the TBP and QAPjP are followed.
- Instrument calibration check samples.
- Blind spikes of blank SVOST trains with POHC and surrogate POHC. (A "blind spike" means that the amount spiked is known only to the QAC.) This is used to independently verify the accuracy of the sample extraction and analysis.
- Submission of blind calibration check standard for each instrumental analysis as an independent verification of calibration accuracy.
- Submission of blind spikes of the POHC waste feed for analysis and determination of spike recovery.
- Submission of EPA and/or NIST reference samples for metals and target analytes.
- Audits of the field records, raw analysis data, and other project records to determine if the trial burn was conducted as specified in the TBP and the QAPjP. This audit entails the tracing of one run's data and verification of selected analysis results and is referred to in Section 2.1.14 of this handbook.
- Overall assessment of data quality based upon reported QC data.

The level of effort described above is not required for every trial burn. However, all these audits are suggested in cases in which the trial burn data are likely to be challenged, or when the trial burn is highly complex. These checks are made independently of the analysis team, and thus are relatively free of any bias, as well as carrying more weight in validating sample results. All internal audits identified in the QAPjP should be reported in the TBR.

For all trial burns, the QAC should do an audit of data quality, inspecting field records, raw analysis data, and project records as well as assessing overall data quality based on reported QC data. The QAC should inspect all the data for at least one run and ensure traceability from field records through analysis records to final results (DRE, particulate, chloride, etc.). In this audit, the performance of the experimental work must be compared with the TBP and QAPjP for compliance. Selected data should be independently recalculated and verified by the QAC. In addition to this audit, all QC data should be examined and compared to the criteria for data acceptance given in the QAPjP. All data which do not meet the QC criteria must be discussed in the TBR in terms of acceptance of sample results, given the failure to meet the criteria. A brief summary of the audit results and data quality assessment should be included as an appendix to the TBR. This summary must be prepared by the QAC, not the project leader or TBR author.

The purpose of the QAC audit and quality assessment is to provide an independent review of the trial burn results and supporting documentation before submission to the regulatory agency. This internal audit should ensure that the data are usable, which will save time during permit application review. Data quality problems and possible incomplete or missing sections of the TBR should be addressed by the applicant before the TBR is submitted. The EPA requires a similar review and narrative summary in other programs for acceptance of experimental results. Following this audit sequence should also relieve the permit writer of some of the burdensome review of the field and analysis records, and allow more time for engineering and regulatory assessment of the trial burn results.

3.5 Use of External Audits

3.5.1 *Types of Audits*

External audits can be a powerful tool in controlling and assessing the quality of an environmental data collection program. Four basic types of external audits that may apply to a trial burn are:

- *Field audit.* Conducted on-site during the trial burn. Consists of observation of all sampling and analysis activities conducted during the trial burn.

- *Laboratory system audit.* Conducted at the laboratory doing the analysis. Consists of observing the analysis of trial burn samples and inspecting analysis and project records. This audit is difficult to accomplish if analysis is performed at more than one location.

- *Performance audit.* This audit is an external check of the accuracy of the measurement system. It consists of supplying a sample for analysis whose concentration is known only to the regulatory agency. Analysis results are compared to the actual concentration for an accuracy determination. One common example is the VOST audit cylinders.

- *Referee analysis audit.* This audit is also an external check of accuracy. Trial burn samples (waste feeds, impingers for chloride, etc.) are sent to a referee laboratory (contracted by the regulatory agency) for analysis. Results from the referee analysis are compared to the results in the TBR for a determination of accuracy or precision.

3.5.2 *Audits Recommended for All Trial Burns*

A field audit is recommended for every trial burn. The audit usually includes observation by the permit writers or their representatives and use of a VOST audit cylinder. QA/QC in field sampling is considerably more subjective than the QA/QC in analysis. Chemical analysis can be designed to include many indicators of data quality; however, the quality of field sampling is more dependent upon the skills of the field sampling crew. The permit writer who observes the trial burn can be assured that sampling was conducted according to plan, and that all sampling or incinerator problems are resolved with his or her concurrence. Ideally, two individuals should be present, one on the stack to observe the critical stack sampling continuously and the other to observe waste feed sampling, air pollution control equipment sampling, ash sampling, incinerator operation, and the operation of continuous monitoring systems.

Field audits should be conducted by individuals with an intimate and thorough knowledge of sampling methodology. Auditing procedures are discussed in many documents; however, *Trial Burn Observation Guide* (Reference 1), is a good source for specific guidance on auditing hazardous waste incineration trial burns.

If any of the POHCs is volatile, the field audit should include an analysis of a VOST audit cylinder. VOST audit cylinders and field audits have been effectively used for many years and constitute accepted practice. VOST audit cylinders can be used for both VOST and gas bag sampling. (Use of VOST audit cylinders is required for all trial burns except where Method 0010[3]

Table 3-3. Available Audit Cylinders[a]

Analytes	Concentration range[b]
Group I	
Carbon tetrachloride	7 - 90 ppb
Chloroform	90 - 430 ppb
Perchloroethylene	430 - 10,000 ppb
Vinyl chloride	
Benzene	
Group II	
Trichloroethylene	7 - 90 ppb
1,2-Dichloroethane	90 - 430 ppb
1,2-Dibromoethane	
F-12	
F-11	
Bromomethane	
Methyl ethyl ketone	
1,1,1-Trichloroethane	
Acetonitrile	
Group III	
Vinylidene chloride	7 - 90 ppb
F-113	90 - 430 ppb
F-114	
Acetone	
1,4-Dioxane	
Toluene	
Chlorobenzene	
Group IV	
Acrylonitrile	7 - 90 ppb
1,3-Butadiene	430 - 10,000 ppb
Ethylene oxide	
Methylene chloride	
Propylene oxide	
Ortho-xylene	

[a]From SW-846, Method 0030; cylinders can be obtained from:

Audit Cylinder Gas Coordinator (MD-77B)
Quality Assurance Division
Environmental Monitoring Systems Laboratory
Research Triangle Park, NC 27711

[b]Analytes are in nitrogen. Concentration based on volume (v/v).

is the only sampling method.) Cylinders available in 1986 and their source are shown in Table 3-3. To be an effective audit, the cylinder should be brought to the trial burn by the field auditor and the field sampling crew should conduct the sampling. The audit cylinder seal should be broken by an authorized person, and the cylinder should be sampled in the presence of the auditor before the trial burn begins or immediately afterwards. Four samples should be taken. Only three must be analyzed; the fourth serves as a backup. If the fourth sample is analyzed, results of all four analyses should be reported. The cylinder should not be left with the sampling crew; it should remain in the possession of the auditors and be returned by them following the trial burn. Accuracy criteria for VOST audits are ±50% of actual concentration (see Section 7.3 and Method 0030[3]).

3.5.3 *Audits Recommended in Special Circumstances*

Most trial burns are conducted by contractors of the incineration facility. This lends a degree of independence to the analysis of the samples. However, in some cases the facility is large enough to have the necessary resources to conduct all determinations internally. In this case, performance audits, laboratory system audits, and referee analysis audits are suggested.

At the minimum, performance audits should consist of:

- Analysis of a calibration standard containing each POHC at the final expected sample concentration of the 99.99% DRE level.
- Analysis of a standard reference solution of chloride.
- Analysis of a synthetic waste sample at a POHC concentration similar to the waste used during the trial burn. For trial burns using synthetic waste streams or a spiking solution for waste feeds making a synthetic waste sample in these situations is not overly difficult.
- Analysis of the VOST audit cylinder.

At a minimum, the laboratory system auditor should observe and examine:

- Sample preparation and analysis for samples from VOST, SVOST, chloride, waste feed, air pollution control devices, and ash.
- Analysis and balance calibration records for particulates.
- Analysis staff credentials.

Referee audits should consist of:

- Analysis of waste feed for POHCs.
- Analysis of impingers for chloride.

3.5.4 *Documentation of Audits and Objectives of the Audits*

All audit objectives should be set out in detail in advance by the regulatory agency. Preferably, they should be outlined in the letter indicating acceptance of the TBP and QAPjP and providing a schedule for all audits. The facility should be informed that acceptance of the trial burn results is dependent on receiving a positive assessment from all field and laboratory auditors. All performance audits and referee

audits should show an accuracy within predetermined acceptance criteria.

Scheduling and discussing the audits in advance is important. Sometimes there is limited room for field auditors in the incinerator control room or on the stack. A performance audit or referee analysis audit without accompanying acceptance criteria is of limited use. The acceptance criteria should be agreed to by both the regulatory agency and the permit applicant. Without acceptance criteria, the validity of performance audit results is left to technical judgment and is open to interpretation. Since sample analysis is often conducted over 40 to 50 days, laboratory system audits need to be scheduled so that a complete preparation and analysis cycle can be observed.

Finally, audits must be reported. All field and laboratory audits must be reported as soon as possible, preferably within 2 weeks of completion. These audit reports should be appended to the TBR, and any noted problems or deficiencies should be addressed by the applicant. Performance audit results should be reported in the TBR. The accuracy indicators for performance audit samples (e.g., audit cylinders) should be calculated by the permit writer and the results reported to the applicant. The permit applicant should respond to any difficulties following receipt of the audit results.

3.6 Reporting QA/QC Results

This section of the handbook gives a general summary of the QC information needed for the major measurement areas. QA/QC information from the trial burn that will be reported should be outlined in the QAPjP. All field records, all calibration data (analytical and field), all precision and accuracy determinations associated with QA objectives (e.g., surrogates, spikes, duplicates, standard reference material), all internal audits, and the data quality assessment report from the QAC should be included in the TBR.

Precision and accuracy determinations should be clearly presented with all results calculated. For example, if duplicates are analyzed to determine precision by range percent (RP), the individual determinations plus the calculated RP should be presented. Any value which falls outside the data quality objectives should be flagged in the data tables and discussed in the text (or a footnote) in terms of how the apparent problem affects overall sample results.

In general the following QA/QC information is desirable.

Sample traceability:

- Master record or inventory giving all samples and identifiers.

Holding times:

- For analysis of volatile organics in waste feed, fuel or ash, and air pollution control device (APCD) samples, the number of days between sampling and analysis should be presented either in a separate table or be incorporated into the sample results table.

- For analysis of semivolatiles in waste feed, fuel, ash, and APCD samples (both GC/MS and non-GC/MS analyses), the number of days between sampling and extraction, as well as the number of days between extraction and analysis should be reported.

- Any sample analysis that exceeded holding times should be specifically mentioned in the text. Technical justification for use of the data must be offered before sample results obtained after holding times have expired can be considered for acceptance. However, exceeding holding times must be avoided and usually results in rejection of the sample data.

Waste/fuel/APCD sampling:

- All field records showing sampling method, dates, times, sampling equipment, field sampling personnel, sample preservation, sample identification number, and compositing techniques.

Stack gas sampling:

- All field records required in the methods.

- All calibration records for pretest and posttest calibration.

- All calibration records for calibration equipment.

Analysis:

- All initial calibration results (e.g., source and purity of standards, calibration standards and responses for calibration curve, calculation of response factors, calculation of linearity, average response factors, standard deviations). The forms in SW-846 Chapter 14 may be used. Tables or graphs contained in output from analytical data systems may be sufficient.

- All continuing calibration results (e.g., daily calibration, calculation of percent difference from initial calibration). Again, tables or graphs

contained in output from analytical data systems are sufficient. Balance calibrations should be reported for particulate determinations.

- All accuracy determinations (e.g., calibration check standards, interference check standards, spikes, analyses of reference materials, analysis of performance audit samples, analyses of spiked sampling trains, and surrogate analyses). All accuracy values such as percent recovery should be calculated. Summary averages are sometimes needed, particularly for surrogate recoveries, yet the individual values should be reported also. Comparisons or averages of heterogeneous matrix types should be avoided. For example, surrogate or spike recoveries for aqueous waste should be compared only to recoveries for similar aqueous waste, not to a liquid organic waste.

- All precision determinations (e.g., replicate analyses, replicate sample preparation and analyses). Again, comparison should be made only between similar matrix types.

- All blank determinations. At a minimum, this should include all field blanks and at least one method blank per analysis. Volatile organic analyses should include a method blank determination for each day.

Quality control assessment:

- Each measurement of precision and accuracy and each instrument calibration which does not meet criteria established in the method or QAPjP should be discussed in terms of its effect upon sample results.

- The quality control assessment should be made by the author of the TBR, included in the main text of the TBR, and discussed or elaborated upon by the QAC in the QAC report.

Quality assurance coordinator report:

- All internal system audits and audits of field records, analysis records, and other project records should be summarized and reported with an assessment of the overall data quality found during the audits. This assessment of data quality should refer to or include any quality assessments conducted by other project personnel and reported in the TBR.

- Results of all samples submitted for analysis by the QAC should be reported, along with associated precision and accuracy results.

3.7 Evaluating Trial Burn QA/QC Results

3.7.1 Use of Data Quality Indicators and Acceptance Criteria

Quality assurance objectives, QA/QC procedures, and the acceptance criteria for these parameters must be clearly identified in the QAPjP. Assessing the data quality is relatively simple if: (a) agreement exists on these points; (b) all QC data are reported; and (c) the TBR contains the independent assessment done by the QAC.

All measurement systems will have an agreed upon level of precision and accuracy as well as accompanying QC procedures to indicate achievement of this level. The QAC must see that all QC procedures have been completed and have met criteria. Cases in which the criteria have not been met or procedures have not been completed will be noted by the QAC, and data should not be accepted unless the applicant provides an adequate technical justification for use of the data. The permit writer will need to spot check critical QC areas to ensure that the QAC review was valid and then accept or reject the rationale for accepting any results outside the QC criteria.

When QA objectives are based upon regulatory decisions and agreed upon in advance, a judgment on data quality does not have to be made at the TBR stage of the project if the QC data meet the acceptance criteria. A decision on data quality is a major benefit of using QA objectives; however, it is dependent upon rigorous planning, and it cannot be added after the data have been acquired.

3.7.2 Checklist for Reviewing RCRA Trial Burn Reports

A checklist for reviewing RCRA TBRs has recently been developed (Reference 2). This checklist has six basic functions:

- Foster consistency in TBR review.
- Evaluate the completeness of the TBR.
- Evaluate the validity of the TBR in relation to regulatory statutes and policy.
- Compare the actual trial burn to the planned activities.
- Ensure that QC results have met the associated objectives and criteria.
- Provide written documentation of the TBR review.

The checklist serves as a supporting document for regulatory decisions based upon trial burn data. The

various sections of the checklist concerning sampling, engineering, regulatory policy, analytical methods, and quality control would best be completed by experts in each related field. The final decision maker then needs only to review the checklist to find the critical problem areas and any data of questionable quality. It is suggested that the checklist be given to the permit applicant before the TBR is written to ensure that all necessary information will be included in the report. The applicant's QAC may fill out the pertinent sections of the checklist (sampling, analysis, and QA/QC) to ensure that the TBR is complete and that any questionable data areas have been addressed.

This checklist can serve as a guide to "auditing" the trial burn results and isolating key information for later agency management review. However, some areas in the checklist concerning QA/QC cover topics which are not pertinent to all trial burns. The key documents to be reviewed are the TBP and the QAPjP.

The analysis and QA/QC portions of the checklist assume that the permit writer has full access to all the raw data supporting the trial burn results (field data, analysis data, etc.). Sometimes these data can come from multiple laboratories or be intermixed with another project's records. Since supplying the raw data is a burden, this need should be conveyed to the applicant in advance. One option for the reviewer is to read the TBR, decide which trial burn run is the most critical (if possible), and thoroughly review the records for only that run. However, the logistics of obtaining all raw data from a single run can still present problems.

Sometimes the TBR and associated raw data are reviewed by a team of technical experts (e.g., chemists, engineers, sampling personnel). One problem with a team review of a TBR is closing the loop on the decision process. An analytical or sampling expert may raise serious questions concerning data quality and relay concerns to the permit writer. However, the process should not end here. Any serious problems raised during a trial burn review should be presented along with an assessment of its impact upon overall acceptance of the results for permitting purposes. The concerns of the individual experts should be relayed to the applicant for justification of data acceptance given the quality problems. The applicant response should be forwarded to the initial expert reviewer who should respond as to the appropriateness of the justification. This whole process should be documented in writing in support of the permitting decision.

3.7.3 Review of TBR--Decision-Based Criteria

The data presented in the TBR must be of sufficient quality to be the basis for regulatory decisions and must contain the necessary information for outlining the permit operating conditions. There are three main performance-based regulatory questions:

- Was the 99.99% DRE achieved?
- Were the hydrogen chloride emissions < 4 lb/h or were 99% of potential chloride emissions removed?
- Were the particulate emissions less than 0.08 grains/dscf?

If the data associated with these decisions do not meet the criteria established for precision and accuracy, sample results should not be automatically rejected. For example, if the observed DRE is 99.9996%, well above the regulatory minimum, then minor problems with accuracy or precision can be considered moot. Precision and accuracy data can in some cases be used to define a confidence window around reported values, which can then support the regulatory decision. The same can be said concerning particulate and hydrogen chloride emissions.

However, even though potential precision and accuracy problems appear minor when the regulatory objectives have been achieved with large margins for error (e.g., 99.9996% DRE), if precision and accuracy are not measured and quality control procedures are not followed, the data quality is unknown. In these cases, the permit writer cannot judge whether the data are acceptable. The only recourse remaining is to assess the impact of the missing QC data. For example, if no spike sample was used for the back impinger of a chloride determination, but levels were very low compared to the front impingers, then this missing information is not critical. However, if surrogates were not spiked into the SVOST components and no POHCs were spiked into a blank train for recovery determinations, then there is no indication of the accuracy of the complete sample preparation and analysis. Data critical to the DRE decision is then of completely unknown accuracy. In this case, if no POHCs are detected in stack samples there is no evidence to indicate they would have been detected if the POHCs had been present in the stack samples. QA/QC criteria need to be applied carefully. Data that do not meet the criteria should not be accepted unless the applicant provides adequate technical justification for use of the data.

Chapter 4

QC Procedures for Sampling Waste, Ash, Fuel, and Air Pollution Control Device (APCD) Effluent

The QA/QC procedures that pertain to sampling of waste, ash, fuel, and APCD effluent are covered in this chapter. with emphasis on the establishment of written procedures and documentation as well as ensuring that they are performed.

4.1 General

The QA/QC aspects of field sampling operations are much more subjective than the QA/QC aspects of analysis. The wide diversity of waste feeds, POHCs, incinerators, APCD, and trial burn experimental design precludes the establishment of firm QA/QC procedures applicable in all situations. Although some guidance on sampling design is presented in this chapter, the major QA/QC activities associated with sampling are to establish written procedures and to document that those procedures have been followed.

The basic objective of hazardous waste incineration sampling is to obtain a representative sample, i.e., one that exhibits the average properties of the media being sampled. This sample must be collected over a period of time that is sufficient to represent the time-dependent variability inherent in the relatively continuous process of incineration. The achievement of this objective is dependent upon design and implementation. Proper design of the sampling operation includes sampling points, number of samples, sampling equipment, size of sample, and sampling technique. Implementation of the sampling design relies on following written procedures, documenting that procedures have been performed, and observation in the field to verify that procedures were followed.

The specific QA/QC elements of which to be aware in sampling are:

- Sampling design must produce a sample which is representative.
- Sampling design must be translated into written procedures.
- Sampling activities must be thoroughly documented.

4.2 Sampling Design--Representative Samples

Some key concepts that need to be considered in three areas while sampling any media are presented in Chapter 9 of the publication "Test Methods for Evaluating Solid Waste."[3] These concepts are interrelated and are presented below with some examples of how they should be applied in incineration sampling to ensure samples which are representative. Specific guidance on sampling intervals, number of samples, etc., is also available.[5,8,9]

4.2.1 Waste/Media Considerations

(1) Physical State--The physical state of each type of media to be sampled must be described. For example, is the waste a liquid? Is the ash solid or a solid/water slurry? What is the temperature of the scrubber water? Is the waste homogeneous or heterogeneous? Is it stratified into layers? The physical state of the media being sampled determines both the sampling technique and the sample container.

(2) Composition--The composition of the media to be sampled should be given. For example, one waste stream may be fiberboard drums containing toluene-soaked rags, with 2 to 3 lb of toluene per drum. A second waste stream may be an organic liquid waste which is 25% tetrachloroethylene and 75% methanol. Sample composition is used to determine the amount of sample necessary to produce a sufficient sample size to exceed the detection limit of the analyte.

(3) Volume/Mass--The total volume/mass of the material to be sampled needs to be given and any change of volume/mass with time. The total volume/mass is needed to judge whether a sample point is appropriate (given the specific incinerator process) and whether the sample size is adequate.

4.2.2 *Site/Location Considerations*

(1) Accessibility--Places where the waste can be accessed should be given (sampling ports, etc.). Where can samples be taken? How hard is it to reach the sampling point? Does that area have sufficient electric power for sampling equipment? From a conceptual standpoint, waste feeds should be sampled as close to the introduction of waste to the incinerator as possible. For example, if a spiking liquid is being added to an organic or aqueous waste, it would be preferable to sample the mixed spiked waste instead of just sampling the spiking fluid. However, this is often impractical, especially when the waste and spiking liquid might not be completely mixed, or in the case of containerized waste, when time considerations on the day of the trial burn may make this impractical.

(2) Generation/Handling--The generation of the waste APCD effluent, etc., and how it is handled should be described. For example, ash in a rotary kiln might take a significant amount of time to reach the sampling point; thus, ash sampled during or immediately after stack sampling may be more representative of the ash generated before the trial burn. Sometimes, the generation and handling of solid waste feeds may present the most difficult sampling problem.

(3) Time Events--Any time-dependent characteristics of the waste should be detailed. Are there any timed events in the relatively continuous operation of the incinerator? For example, the barrel feed rate creates a discrete timed event every time a barrel is introduced into the incinerator. For liquid feeds, given a steady waste feed rate, every time a new tank truck is brought on line a timed event occurs. All possible timed events and time-dependent phenomena need to be outlined in the TBP or QAPjP.

4.2.3 *Sampling Equipment and Sample Storage*

(1) Sample Change--Sampling equipment and storage containers must introduce little or no change in samples. Samples for the analysis of volatile components require special containers and sampling techniques to ensure the integrity of the volatile analytes. For samples containing particularly labile analytes, cold temperatures must be maintained from the moment of sampling.

(2) Sample Properties--The sampling equipment and containers must be able to withstand effects of the physical and chemical properties of the sample itself. Samples may be very hot or corrosive and may melt or dissolve the sample container. Wide-mouthed sampling containers may be needed for samples which are very viscous or heterogeneous (e.g., sludge to prevent spillage or possible segregation by particle size).

All sampling strategies must be justified in the TBP, covering all topics discussed above. The permit applicant should outline all sampling strategies and offer a clear justification of the design. A clear delineation of the reasoning behind the experimental design is invaluable in creating a defensible sampling strategy.

Trial burns are conducted in triplicate runs, and the regulatory decisions and operating parameters are based upon the average values for each run. This requires a general sampling design consisting of systematic random grab samples taken throughout the run and composited into a single sample per run for analysis. The literature regarding sampling of hazardous waste incinerators[5,8,9] contains basic guidelines for ensuring a representative sample.

Sampling design should include: number of samples, duration of sampling, and a sample composition scheme, if necessary. A sampling scheme should reflect the degree of variability of that particular waste stream. Continuous waste feeds, such as liquid organic waste, slurries, and solid waste on conveyors, should be treated differently from APCD effluent and ash or containerized waste.

4.3 Standard Operating Procedures (SOP) for Sampling Activities

The majority of TBPs rely on the ASTM procedures for sampling or on the procedures given in *Sampling and Analysis Methods for Hazardous Waste Combustion*.[8] These procedures are too general for use on a trial burn; a specific set of instructions or a SOP should be developed.

Taking an exarnple, a certain TBP states that liquid organic waste would be pumped from a trailer tank and sampled from a port immediately following the waste feed pump but before the flow rate meter using the tap sampling Method S004 from the above book. This citation is all that was given. Method S004 states that: (a) a sample collection line will be used; (b) the sample vessel and collection line will be rinsed with the liquid waste; and (c) a 2 L sample will be taken. However, in reality, there was no need for a separate sampling line; the sample vessels were clean and did not need to be rinsed (rinsing containers with sample sounds appropriate, but is generally not recommended when the substance is a known hazardous waste). Containers can be purchased precleaned. Only a 100 mL sample was needed.

In the field, the first sample taken had multiple phases, since the pump had been used for aqueous waste before the trial burn. The multiple phases were due to residual waste in the sampling tap; the sampler had not been told to flush the lines of the sampling tap with waste. The sampler did not have a copy of

the cited Method S004. The multiple phases were noted by an observer, not the sampler. After ~ 3 L of liquid had run through the tap, the waste stream was clear. The first sample was discarded and then the flush time for the tap was made long enough to allow at least three to five full sampling line volumes of liquid to flow before collection of the sample.

Samples were taken at the appropriate times, but since all field information had been recorded on the sample label, there was no field sampling notebook or field sampling forms. Thus the only record of the date, time, and sampler was on the sampling container which was discarded after analysis. There was no record of the sampling technique, the compositing technique, the flush time, the original sample which had been discarded, or the resulting corrective action. When the field data were presented with the TBR, there was no record of any of the field sampling other than the stack sampling.

An example of a sampling form with instructions is presented in Figure 4-1. All sampling should have a short SOP and form or data recording instructions. If not presented in the TBP, the permit reviewer should request that the information be provided. Samplers should have written instructions for all sampling activities.

4.4 Summary

The primary QA/QC requirements for the sampling of waste, ash, fuel and APCD are good planning, fully written procedures, and documented field activities. Thorough planning must be evidenced in the TBP by a complete description of various media and their properties, sampling location and necessary equipment, along with justification of each sampling method as tailored to each type of media. Sampling design must have been translated into comprehensive written instructions and later supported by information and data recorded in the field.

Facility: Frank's Hazardous Waste Incinerator
Type of Sample: Liquid Organic Waste
Reference Sampling Method: Tap, S004 [Sampling and Analysis Methods for Hazardous Waste Combustion (NTIS PB84-155845)].
Sampler:_____
Date of Sampling:_____
Run Number:_____
Run Description:_____
Sample Identification Number:_____

Equipment: one gallon wide-mouth compositing jar and two 1 L sample jars with Teflon-lined polycarbonate tops; one 500 mL graduated beaker; one funnel; one pail and two 1 gal jugs for waste.

Instructions

(1) Before the trial burn run starts, clear sampling line (2 in ID x 2 ft) by opening the tap and collecting not less than 1 L of waste. Examine waste to assure the liquid is homogeneous (e.g., free from water, solids, sludge etc.). If not, contact field sampling crew chief before trial burn starts.
(2) At the beginning of the trial burn and every 15 min (±5 min), open the tap, rinse about 1/2 L into the bucket, close tap. Visually inspect waste to ensure that it is homogeneous. If not contact crew chief.
(3) Open tap slowly, fill beaker to 300 mL mark. Place sample in compositing jar. Seal jar.
(4) Record the time, and any comments. Dump waste in bucket into the waste jug.
(5) Repeat Steps 1-4 every 15 min for the 2 h run. This will result in eight grab samples and 2.4 L of sample at the end of the run.
(6) Mix the final sample by inverting the sealed jar at least 20 times.
(7) Pour the sample into each 1 L sample jar.
(8) Following the traceability procedures, label the jar, seal the jar and fill out the necessary chain of custody forms.
(9) Deliver the sample to the field sample custodian for packaging and shipment.

Grab No.	Time of Grab	Comments
1	_____	_____
2	_____	_____
3	_____	_____
4	_____	_____
5	_____	_____
6	_____	_____
7	_____	_____
8	_____	_____
9	_____	_____
10	_____	_____

USE BACK OF FORM FOR ANY ADDITIONAL INFORMATION

Figure 4-1. Example sampling instructions and field record form.

Chapter 5

QC Procedures for Analysis of Waste, Ash, Fuel, and Air Pollution Control Device (APCD) Effluent

Sample analysis QA/QC procedures for waste, ash, fuel, and APCD effluent are covered in this chapter. The concepts of precision, accuracy, detection limits, spiking, and calibration are presented and discussed as appropriate. Stack gas sample analysis is discussed in Chapter 7. Some general analysis topics are discussed in Chapter 8. If the permit writer is not familiar with these analyses, review of these areas of the TBP, QAPjP, or TBR should be done by qualified personnel.

5.1 Analysis of Waste Samples for Heating Value, Ash, Viscosity, and Chlorine

5.1.1 Sample Matrix

ASTM methods are followed almost universally for these analyses. These methods are often specific to a particular matrix, such as chlorine in petroleum products (ASTM D808), or chlorine in organic compounds (ASTM E442). The permit applicant must provide the full title of each procedure, which will give the appropriate matrix for a given method. The applicant must justify the use of a procedure if it appears that the matrix might be incompatible.

For example, the accuracy of chloride analysis is dependent upon choosing the appropriate analysis procedure for a given sample chloride level. For samples with high levels of chloride, sample preparation/digestion followed by titration or silver chloride precipitation is often the method of choice; while for low level samples, ion chromatography is the preferred analysis method.

5.1.2 Precision Determination

Since field samples are large compared to the amount needed for each analysis and the analyses are relatively inexpensive, multiple determinations for demonstration of precision present little difficulty. Because most of these samples are analyzed by subcontractors, a sample can be split in the field and shipped as two samples to the laboratory. At a minimum, one test run's sample should be split, prepared, and analyzed in duplicate for all parameters. Recommended precision criteria are given in Table 5-1.

5.1.3 Accuracy Determination

The recommended procedure for accuracy determination for trial burn analyses is to use reference materials with known values for ash, total chlorine, heating value, and viscosity. These samples are submitted for analysis without being distinguished from field samples and provide an independent check for any systematic bias and support data validation of the laboratory.

Reference materials are relatively easy to procure or prepare and can be chosen to match the relative physical properties of samples. For example, if the liquid organic waste feed is primarily 5% tetrachloroethylene in a waste oil, then a solution of 5% tetrachloroethylene in white oil (chlorine-free oil) can be submitted as a reference standard. For higher heating value samples, a compound of known heating value can be submitted (such as hexane), or the National Institute of Standards and Technology (NIST) provides reference material of a known heat of combustion. For ash, obtaining a reference material that mimics the field sample composition can be difficult (e.g., 5% ash in organic liquids). Zinc oxide can be blended with a solid or liquid sample or a fuel oil and used as a spike. At least one unspiked sample and two samples spiked at different levels should be submitted to the laboratory for analysis.

5.1.4 Summary of QC Procedures

A summary of the QC procedures discussed above is presented in Table 5-1. These parameters are loosely based upon the precision and accuracy values given in the most commonly used ASTM methods. The permit reviewer is encouraged to check the acceptance criteria given in the QAPjP versus the precision and accuracy values given in the methods.

Each quality parameter must be reported in the TBR, and acceptance of sample results must be justified by the applicant if the QC procedures were not followed or the criteria were not met. In cases in which preci-

Table 5-1. Summary of QA/QC Procedures for Heating Value, Ash, Viscosity, and Chlorine Analysis

Quality parameter	Method of determination	Frequency	Target criteria
Method selection	Check method to ensure if it is appropriate to sample matrix and has an acceptable method detection limit	During QAPjP review	Choice must be justified if method appears inappropriate
Precision	Duplicate preparation and analysis of at least one run's samples	Once per test	10% range
Accuracy	Analysis of a reference material	Once per test	90%-110% of stated reference value
Accuracy--optional	Spike of sample at 2 times sample level	Once per test	90%-110% of spiked value

sion and accuracy are poor, acceptance of the data can be decided based upon the way the information is to be utilized. For example, if chloride precision is poor, yet chloride levels are close to the detection limit and the emission limit of not more than 4 lb/h has been met, then poor precision will not affect the regulatory decision.

Most of these analyses are relatively inexpensive. The preferred option is to repeat the analysis if the precision and accuracy are not sufficient to make the permitting decisions. However, the samples must not be biologically or chemically active and must be stored to prevent evaporation.

5.2 Analysis for Principal Organic Hazardous Constituents (POHCs)

5.2.1 General

POHC concentrations in samples collected from an incinerator trial burn are highly variable. Waste feeds may have POHC concentrations in the range of 0.1% to 30%, while ash or APCD samples can have very low concentrations (1 ppm). The waste feed analysis is the most critical; however, ash and APCD analyses are sometimes used to justify delisting the waste to allow its disposal as a nonhazardous material.

Since the analysis system used for stack gas samples is designed to detect low concentrations of POHCs, it can be applied to the analysis of POHCs in ash and APCD. For a volatile POHC, similar surrogates, calibration curve, and analysis conditions can often be used as for VOST. For semivolatile POHCs, solid samples can be extracted in a manner identical to that used for the SVOST XAD/filter (Soxhlet extraction), and the aqueous samples can be extracted like the SVOST condensate (liquid extraction). The surrogates, calibration curve, and analysis conditions will be the same as for SVOST. Please refer to Sections 7.3 and 7.4 of this handbook for criteria.

Detection limits for ash and APCD samples may be important if decisions regarding disposal are based on the amount of POHCs found in the sample. The QAPjP should make specific mention of the method chosen for determining the detection limit, and the TBR should give the results of that determination. Sections 7.3 and 7.4 give guidance on detection limits. Also, at least one sample of each matrix type should be prepared and analyzed in duplicate for a precision determination and spiked (at 5 times the detection limit) for an accuracy determination.

POHC levels in waste feed samples are often so high that using the same analytical system as for stack gas samples is impractical. The precision and accuracy of gas chromatography with detectors such as flame ionization, thermal conductivity, electron capture, or flame photometry may be more precise and accurate than GC/MS. The permit writer may accept non-specific detectors coupled to a gas chromatograph if the waste feed matrix is relatively simple (such as a completely synthetic waste or a single component waste from an industrial process).it

The specific QC elements to include in waste feed determinations are:

- Calibration of the analytical system.
- Determination of accuracy using calibration check standards, spiked samples, and surrogates.
- Determination of precision by multiple analysis of samples.

This section covers QC elements that are not specifically addressed in the SW-846 methods.

5.2.2 Calibration for Waste Feed Analysis

Waste feed composition should be very well characterized before the permitting process begins. The calibration range of the analytical system should bracket all expected concentrations of the POHC with a minimum of five standard concentrations. Samples with concentrations greater than the highest standard should be diluted into the calibration range and reanalyzed. Samples lower than the lowest calibration level

should be concentrated and reanalyzed. If this is not feasible, the calibration range should be extended with the inclusion of lower or higher concentration standards. The calibration range, concentration of calibration standards, and the expected sample concentration should be presented in the TBP or the QAPjP.

Criteria for both initial and daily GC/MS calibration for POHCs are given in Sections 7.3 and 7.4. Calibration criteria for other analysis methods are given in Section 8.4. The essential point for calibration, irrespective of the analysis method, is a successful calibration before and after sample analysis. The initial calibration curve must pass the criteria before any sample analysis. At the end of each analysis period, an end-of-day calibration standard must be analyzed and must pass the continuing calibration criteria. Every group of samples must be bracketed by two successful continuing calibrations--one preceding sample analysis and one following. If the calibration check following sample analysis does not meet the criteria, it should be repeated; if it fails the second time, analysis problems should be investigated and corrected and the samples following the last successful calibration should be reanalyzed. All initial and continuing calibration results must be reported in the TBR.

5.2.3 *Accuracy Determination for Waste Feeds*

Calibration--A five-point calibration curve is usually prepared from a single stock solution of the reference material (SW-846, Method 8270).[3] As a check on the validity of the calibration and the identity of the reference material, a calibration check standard should be analyzed. This calibration check standard must: (a) contain all the POHCs and surrogates used; (b) be at the expected concentration level of the POHCs in the waste samples; and, (c) be analyzed after each preparation of calibration standards and before sample analysis.

Standards should be prepared from EPA standard reference material obtained from the EPA repository (QA Branch, EMSL-Cincinnati, USEPA, Cincinnati, Ohio 45268). Preparation of the check standard from material of documented purity should be done by the QAC or by personnel not responsible for the preparation of the calibration standards. This independent preparation should reveal any systematic bias that may be present. If EPA reference material is not available, the laboratory must characterize a standard material for this use. Characterization entails a qualitative identification of the chosen calibration standard and a quantitative determination of standard purity.

The calibration check standard should be within the same accuracy window as that used for continuing calibration (e.g., GC/MS 70% to 130%). If the criterion has not been met, the analytical problem should be corrected before sample analysis begins. The results for all calibration check standards should be presented with the appropriate calibration curve results in the TBR.

Surrogates--All GC/MS methods must incorporate analysis of isotopically labeled surrogates. These surrogates should be added to the sample at the beginning of sample preparation at a concentration equal to the estimated POHC level. If surrogate POHCs are not available, other isotopically labeled surrogates chemically similar to the POHC can be substituted; however, the selection must be justified in the QAPjP. For non-GC/MS methods, in which isotopes cannot be distinguished from native compounds, a compound chemically similar to the POHC can be chosen as a surrogate. Surrogate recovery of each sample should be within the 50% to 130% range of the amount spiked and must be reported in the TBR. For POHC analysis of waste feeds, a low recovery means the calculated DRE could be lower than the actual. However, a recovery higher than 130% should not be accepted and could mean that the calculated DRE is higher than the actual.

Spikes--For analysis methods that do not employ GC/MS, accuracy is determined through use of a waste feed sample spiked with the POHCs. In addition, sometimes the cost of surrogates does not allow spiking the samples at the beginning of sample preparation; thus, the recovery of surrogates is not indicative of total method accuracy. A minimum of one sample from a run should be split and a portion spiked with each POHC at a level of not more than twice the expected POHC concentration. Samples should be spiked just before sample preparation. Spike recoveries must be reported in the TBR; the accuracy criterion is 50% to 130% of the amount spiked. As with surrogates, a low bias is less critical than a high bias.

5.2.4 *Precision Determinations for Waste Feed*

For analyses using surrogates, precision can be determined from surrogate recoveries. The relative standard deviation (RSD) of surrogate recovery from all three test runs should be < 35%. Surrogate recovery results should not be compared across sample matrices (e.g., aqueous sample results should not be mixed with liquid organic sample data).

Precision data must be calculated also and presented in the TBR. Precision is determined by duplicate preparation and analysis of a sample from each matrix. If problems with precision are anticipated, all waste feed samples should be prepared and analyzed in duplicate and the average result used in the DRE calculation. The percent range should be less than 35%. If the precision determination shows a wide variability between duplicate sample results, a few

samples should be reanalyzed to determine if the precision problem is related to sample preparation or analysis. If the problem is sample preparation, the method should be modified and all samples should be reprepared and reanalyzed. If the problem is sample analysis, the analysis system should be modified and all samples should be reanalyzed. If this subsequent analysis shows that precision problems are not systematic, the average POHC concentration should be used for DRE calculation. If precision is a systematic problem, the lower of the two values could be used in the DRE calculation. All precision data must be calculated and reported in the TBR.

5.2.5 *Blanks for Waste Feed Analyses*

Method blanks must be analyzed to demonstrate that the sample preparation and analysis system is free from any significant positive bias. Method blanks must be reported in the TBR and must be below 5% of the sample POHC levels measured for the sample extracts. If the blank value is above these levels, it is recommended that the sample preparation and analysis system be examined and corrected. Sample results should not be corrected for blank values.

5.2.6 *Summary of QC Procedures for Waste Feed Analyses*

A summary of QC procedures for waste feed analysis is presented in Table 5-2. Each quality parameter must be reported in the TBR. If the QC procedure was not followed or the criteria have not been met, sample results should not be accepted unless the applicant provides an adequate technical justification for the inclusion of the data. The QC procedures related to calibration and calibration accuracy must be completed and must be within the criteria before sample analysis begins.

For surrogate and POHC spike recovery results, the 50% to 130% range is the suggested limit. High recovery would significantly affect the regulatory decision. (Sample results would be biased high, and the calculated DRE would be higher than actual.) However, if individual recoveries are lower than 50%, trial burn results should not be accepted unless the applicant supplies an adequate technical justification for the use of the data. Sample results should be corrected for low surrogate recovery. Guidance on using surrogate recoveries for correction of environmental data should be published in the *Federal Register* by the end of 1989.

Results that lack sufficient precision are of great concern because POHC waste feed concentration is a critical parameter. If precision is poor, the laboratory should attempt to identify and correct the problem. If this is not possible, all samples should be prepared and/or analyzed in duplicate.

5.3 Analysis for Metals in Waste, Ash, and APCD Samples

Metals analysis of waste samples is used in two ways for regulatory decisions. One is for a metals removal efficiency calculation; in this case, a high bias to sample results will result in a removal efficiency that is better than actual. The other use is for a risk assessment calculation, assuming all metals in the waste stream are vented to the atmosphere. In this case, a low bias will have an unfavorable effect on the regulatory decision. The acceptance criteria for these analyses are determined by the permit writer's use of the data.

For these determinations, the specific QC elements to be aware of are:

- Calibration of the analytical system.
- Determination of accuracy or matrix effects using calibration check standards and spiked samples.
- Determination of precision by multiple analysis of samples.

This section covers QC elements that must be addressed outside the scope of the SW-846[4] methods. The general requirements of the SW-846 inorganic methods are discussed in Section 8.4.

5.3.1 *Sample Matrix*

Waste feed ash and APCD samples can present some unique problems in metals analysis. These matrices can vary in composition from virtually 100% organic material to aqueous solutions. Ten inorganic analytes are of primary interest: arsenic, beryllium, cadmium, chromium, antimony, barium, lead, mercury, silver, and thallium. These samples may be prepared by a variety of methods (e.g., microwave digestion, chemical digestion, dissolution) and analyzed by multiple methods [e.g., graphite furnace atomic absorption (GFAA), cold vapor atomic absorption (CVAA), inductively coupled plasma (ICP)]. The TBP and QAPjP should justify the selection of all sample preparation and analysis methods. Particular attention should be paid to the selection of the sample preparation method in terms of achieving complete digestion and optimal analyte recovery as well as the choice of an appropriate analysis method for the necessary detection limit.

5.3.2 *Calibration*

The calibration method is often dependent upon the type of instrumentation used for analysis. For example, some inductively coupled plasma spectrometers as designed require only a blank and one standard for calibration, while some atomic absorption spectrophotometers need multiple standards to

Table 5-2. Summary of QA/QC Procedures for Principal Organic Hazardous Constituent Determination in Waste Feed Samples

Quality parameter	Method of determination	Frequency	Target criteria
Method selection	Ash and air pollution control device samples should be analyzed by the same methods as stack gas samples	During QAPjP review	See Sections 7.3 and 7.4 for QC procedures and criteria
Calibration	Initial analysis of five standards at different levels	At least once	See Sections 7.3, 7.4, or 8.4
	Sample analysis must be bracketed by calibration standards	All samples	NA
	Continuing calibration	Before and after sample analysis	See Sections 7.3, 7.4, or 8.4 for appropriate criteria
Accuracy--calibration	Analysis of calibration check standard	After each preparation of standards and initial calibration	Must be within continuing calibration criteria
Accuracy--surrogates	Isotopically labeled POHC spiked at the expected POHC level before sample preparation	Every sample	50%-130% recovery
Accuracy--spikes	One sample from each matrix spiked with POHC at 2 times the expected level	One per sample matrix	50-130% recovery
Precision--surrogates	Same as for surrogate accuracy--surrogates	One per test condition	< 35% RSD of recovery
Precision--POHC	Duplicate preparation and analysis of one sample from each matrix	One per sample matrix	< 35% range
Blanks	Method blank carried through all sample preparation steps	One per sample batch	< 5% of sample levels

calibrate the instrument. The applicant should know the general levels of metals in waste feed samples because the waste feed should have been very well characterized before the beginning of the planning process. The calibration range of the analytical system should bracket all expected concentrations of metals in the waste. Any samples with concentrations greater than the highest level should be diluted into the calibration range and reanalyzed or the calibration range should be extended. For samples below the lowest calibration standard, if possible, the calibration range should be extended or the samples should be concentrated.

Criteria for initial and continuing calibration are given in Section 8.5 and summarized in Table 8-7. The initial calibration curve (which includes all calibration standards) must pass the criteria before sample analysis. At the end of each analysis period, a calibration standard should be analyzed and must pass the continuing calibration criteria. Every sample must be bracketed by two successful calibrations--one full calibration preceding sample analysis and one midrange calibration standard following each group of samples. If the calibration standard following sample analysis does not meet the criteria, it should be repeated. If it fails the second time, the analysis problem should be rectified and the samples that were analyzed after the last successful calibration should be reanalyzed. All initial and continuing calibration results must be reported in the TBR.

The instruments used in inorganic metals analysis have a tendency to drift at both the high and low ends of the calibration range. Therefore, all continuing calibrations must also be accompanied by the analysis of a reagent blank. The acceptance of this blank is somewhat subjective, depending upon the sample results and whether the drift is positive or negative. Calibration blank results should be reported in the TBR, and any drift greater than 50% of the lowest standard should be noted and explained.

5.3.3 Accuracy Determination

Calibration--Virtually all SW-846 methods[3] require some initial check on calibration accuracy using a second standard different from the one used for calibration, which is called a "calibration check standard." It should be analyzed following calibration and prior to sample analysis. This calibration check standard must fall within 90 to 110% of the actual concentration. This range is fairly wide for the analysis of a pure standard; results outside this range are thus unacceptable. Any problem must be solved before sample analysis proceeds.

Spikes--A minimum of one sample from each matrix should be split and a portion spiked with each metal. Effort should be exerted to achieve a spike level of not more than three times the expected sample level or five times the detection limit, whichever is greater. Samples should be spiked at the beginning of sample preparation. Spike results must be reported in the TBR, and the accuracy target range is 70% to 130% of the amount spiked.

5.3.4 *Precision*

Precision is determined by preparation and analysis of duplicate samples from each matrix. If precision is expected to be a problem, all samples should be prepared and analyzed in duplicate and the average result be used for calculations. The percent range should be less than 35% if the sample result is greater than the lowest calibration standard. If the precision determination shows a wide variability in sample results, a few samples should be reanalyzed. If these precision results are good, the problem is related to sample analysis. All samples should be reanalyzed if sample analysis appears to be at fault. If the precision results still are not improved, the problem probably is related to sample preparation. If the problem appears to be sample preparation, it should be modified and all samples should be reprepared and analyzed. If this subsequent work shows that the precision problems are a relatively isolated occurrence, the average should be used for all calculations. However, if precision appears to be a systematic problem, the value leading to the most conservative regulatory decision can be used in subsequent calculations. All precision data must be calculated and reported in the TBR.

5.3.5 *Method Blanks*

For metals determinations, method blanks are critical experimental design elements of the trial burn. Method blanks are samples consisting of the reagents used in sample preparation. These blanks are processed exactly like the environmental samples. One method blank should be introduced per batch of samples. Method blanks are routinely used in inorganic analysis to identify contamination problems occurring during sample preparation and to correct for any systematic low inorganic levels found in the reagents used in sample preparation and analysis. However, these corrections may be inappropriately applied. For data to be method blank-corrected, the blank result must be statistically different from the sample result, and the blank result must be indicative of the "average" level of contamination.[5] An ordinary single blank determination does not give enough information for determining if these criteria have been met. Thus, sample results should be reported without correction, and if blank correction is justified, results should be reported with and without the correction. If correction is desired, multiple blanks should be analyzed, the average value used, plus the blank values should be shown to be statistically different from sample values.

The permit writer should be aware that contamination in trace metals analysis can be a severe problem. If metals analysis is a critical decision area and the levels in the samples are very low in comparison with the SW-846[3] detection limit, the permit applicant must present a statistical design for the method blanks. Method blanks must be used to interpret sample results in trace metals analysis, but multiple blanks (rather than a single blank per sample batch) must be analyzed to properly characterize the extent of the system contamination. Method blanks must be reported in the TBR. If the blank value is above the detection limit, the detection limit should be changed to 1.5 times the blank level.

5.3.6 *Detection Limit Determination*

Many times metals are not detected in the samples at all; thus the permit reviewer must decide whether metals emissions are a problem. The QAPjP should identify a method for determining the detection limit of each analyte. The TBR must give the results of this detection limit determination. If this subject is not addressed in the TBP, the permit writer should request that the applicant supply the information. All detection limits must be corrected for the sample weight/volume and dilutions/concentration used in sample preparation.

5.3.7 *Summary of QC Procedures for Metals Determination*

A summary of the QC procedures for metals determination is presented in Table 5-3. Each quality parameter must be reported in the TBR, and acceptance of sample results must be justified by the applicant if the QC procedure was not done or the criteria were not met. The QC procedures related to calibration and calibration accuracy must be completed and must be within the criteria before sample analysis occurs. Deviations from the criteria after the trial burn should not be accepted.

As stated previously, a high spike recovery in waste sample results is not acceptable if the data are to be used in an emission efficiency calculation; a low spike recovery should not be accepted when the permitting decision assumes all metals are being discharged to the atmosphere, ash, or APCD. The permit reviewer should consult the guidance document which addresses the measurement of metals[10] and another document which addresses the necessary permitting decisions regarding metals.[11]

Table 5-3. Summary of QA/QC Procedures for Metals Determination in Waste Feed Ash and APCD Samples

Quality parameter	Method of determination	Frequency	Target criteria
Method selection	Review by expert in inorganic analysis	During review	Choices must be justified by applicant
Calibration	Initial analysis of standards at different concentration levels	At least once before sample analysis	Instrument-dependent. Suggest that linear correlation coefficient of standard data > 0.995
	Continuing midrange calibration standard	Before and after sample analysis	80%-120% of expected value for GFAA and CVAA, 90%-110% of expected value for ICP
Accuracy--calibration	Analysis of calibration check standard	After every initial calibration	90%-110% of theoretical value
Accuracy--spikes	One sample from a run spiked with analytes at 3 times the detection limit or 2 times the sample level	One per sample matrix	70%-130% recovery
Precision	One sample prepared and analyzed in duplicate	One per sample matrix	Range < 35% if sample result above lowest standard
Blank	Method blank carried through all sample preparation and analysis steps	One per sample batch	Below detection limit
Detection limit determination	Method is variable; must be given in QAPP	One for each non-detected analyte per sample matrix	NA

Chapter 6
QC Procedures for Stack Sampling

Methods that are used for stack sampling are introduced and described in this chapter. All aspects of QA/QC for EPA Methods 1 through 8, 6A and 6B, 7A and 7D, 9, 10, 13A and 13B, 17, and 18 (40 CFR 60, App. A) are provided in the "Quality Assurance Handbook for Air Pollution Measurement Systems".[7] This chapter covers conditions in a trial burn which may affect the quality of the test data. Internal QA/QC items such as repairs, maintenance, spares, etc., will not be addressed. QA/QC procedures for the analysis of stack samples are given in Chapter 7 of this handbook.This chapter introduces and describes

6.1 EPA Methods 1 and 2 (40 CFR 60, App. A): Location and Velocity

The QA/QC procedures required for sample site selection and velocity traverses consist of ensuring that the required operations have been properly carried out and that the equipment has been calibrated. These operations cannot be checked by a performance audit, but must be controlled by strict adherence to the specified procedures. Questions which should be addressed and answered according to the methods include: (1) Does the sampling site meet criteria? (2) Were flow angles measured for cyclonic flow? (3) Have the proper number of sampling points been selected? (4) Are all points at least 1/2 inch from the wall? (5) Are the ports properly located?

Numerous modifications of EPA methods are published in the *Federal Register*. Only the latest version of a method should be accepted for a trial burn. These are available in the *Code of Federal Regulations* from the Office of the Federal Register. For instance, if a gauge other than an inclined manometer is used, the gauge must be checked against an inclined manometer. If a Method 5 probe is used for the initial velocity traverse, the pitot assembly must either meet the noninterference criteria specified under Method 5 or have been calibrated.

To ensure good quality data, one must perform quality control checks and independent audits of the measurement process; document these checks and audits by recording the results, as appropriate; and use materials, instruments, and measurement procedures that can be traced to an appropriate standard of reference.

Working calibration standards should be traceable to primary standards. Two recommended primary standards for establishing traceability are:

1. Calibrating the pitot tubes against a standard pitot tube with a known coefficient obtained from the National Institute of Standards and Technology (NIST) or against the design specification in the method which has previously been shown to give acceptable coefficients.

2. Comparing the stack temperature sensor to an American Society for Testing and Materials (ASTM) reference thermometer.

Calibration data on field equipment should contain at least the information provided in Figure 6-1.

6.2 EPA Methods 3 and 3A: Gas Analysis for Carbon Dioxide, Oxygen and Excess Air, and Dry Molecular Weight (40 CFR 60, App. A)

QC procedures for gas analysis are included in the method, so that quality assurance consists of ensuring that the procedure has been accurately followed and documented. The review should determine that the proper method was used, that the required leak checks were performed, and that the sampling rate was constant ($\pm$ 10%). A performance audit should be conducted with a cylinder gas of known concentration.

If Method 3A is to be used, the analyzers must be tested prior to the trial burn. Documentation should be available showing that the units have been checked for interference response (Method 3A, 6.2), analyzer calibration error, and sampling system bias (Method 3A, 6.3), in addition to the calibration concentration verification required (Method 3A, 6.1). An audit should be performed either following Method 3 or using a separate audit gas cylinder.

Data must be routinely obtained by repeat measurements of standard reference samples, or primary, secondary, and/or working standards. Working

Date_____ Completed by_____

Pitot Tube Type

Identification No.:_____ Date_____

Dimension specifications checked?*

Calibration required?

Date_____ C_p_____

Identification of calibration reference_____

Temperature Sensor

Identification No.:_____

Calibrated?*

Was a pretest temperature correction used?

If yes, temperature correction_____ °C (F°)

Identification of reference sensor_____

Barometer

Was the pretest field barometer reading correct?*

Identification of reference barometer_____

Differential Pressure Gauge

Was pretest calibration acceptable?*

* Most significant items/parameters to be checked.

Figure 6-1. Pretest sampling checks.

calibration standards should be traceable to primary standards.

When absorption type gas analyzers are used, operator techniques and analyzer operations can be checked by sampling certified mixtures of bottled gas containing 2% to 4% O_2 mixed with 14% to 18% CO_2, and 2% to 4% CO, with the balance being N_2. Bottled gases used for audit purposes should be traceable to NIST standards.

6.3 EPA Methods 4 and 5: Moisture and Particulates (40 CFR 60, App. A)

Method 4 is used to determine water vapor and contains guidance in setting the isokinetic sampling rate. A preliminary measurement is made using the Method 4 sampling train. Measurements required during a trial burn are normally taken simultaneously with measurement of particulates in the Method 5 train by analyzing the moisture in the desiccant impingers of the sampling train. The QA/QC procedures used in conjunction with the Method 5 train will ensure obtaining moisture data of the quality required in a trial burn.

Specific details of procedures that will provide sufficient QA/QC are available in the method description. The citation of Reference Method 5 in the TBP as the procedure to be followed is acceptable. However, this statement must be modified to include specific details of areas in which optional procedures have been chosen. For example, the probe may be quartz instead of Pyrex; the probe may be air- or water-cooled; or space limitation may re-quire the use of a flexible line between the probe and the sample box.

In other words, the desired approach in preparing a TBP is to provide the detail necessary to avoid any misunderstanding between the organizations involved in the test and to document fully any options which have been exercised. This allows a permit writer to assess and approve or reject any proposed options prior to the test. In addition, the information provided will assist a reviewer in evaluating the quality of the test results. These requirements can be satisfied by the inclusion of a specific written procedure in the TBP.

Calibration of Method 5 apparatus is one of the most important functions in maintaining data quality. These

calibration procedures are rather straightforward with two exceptions: the dry gas meter and the pitot tube.

The Method 5 (M5) procedure calls for calibration of the dry gas meter using a wet test meter (M5, Section 5.3); for an alternate to calibration, use a standard dry gas meter (M5, Section 7.1) or critical orifices (M5, Section 7.2). Method procedures require a specific unit of measurement for calibration. Deviation is not recommended, as an erroneous calibration may result.

Full documentation of the calibration procedure should be included in the TBR. This document should include the method used, the standard device identification, the date the reference device was last calibrated or certified, and the organization calibrating or certifying.

The pitot tube specifications provided in Method 2, Section 2.1, should be followed strictly to prevent gas flow interference. Type 2 pitot tube assemblies that fail to meet any of the specifications of M5 Figures 2-6 through 2-8 should be calibrated according to Method 2, Sections 4.1.2 through 4.1.5. These steps of the calibration procedure should be fully documented and reported.

Providing complete documentation of all calibration procedures should not prove to be a burden since most firms which routinely do stack testing will already have these documents on file. The documents need only to be copied and added to other supporting data, usually as an appendix. Intent to supply all calibration documentation in the final report should be stated clearly in the TBP.

In addition to documentation of calibration procedures, documentation of all procedures should be required in the final report, including filter weighing (before and after sampling to establish constant weight), moisture recovery, the particulate field sampling sheet as shown in the "QA Handbook for Air Pollution Measurement,"[7] and documentation of the isokinetic calculations. Sample calculations should be included in sufficient detail to permit the reviewer to check all calculations. Calibration records for the balances used for filter and moisture collection weights should be included in the TBR.

Inclusion of the simple statement in the TBP, "Copies of all data will be included in the final report," should be sufficient to assure submittal of calibration data with the TBP. However, to avoid misunderstanding, an itemization of the data and procedural descriptions that will be included in the final report should be listed in the TBP.

6.4 Hydrogen Chloride

Sampling of chloride requires employing what is essentially a Method 5 or Method 6 sampling train. The draft method describes method-required QC and includes brief calibration procedures. Since the train configurations are the same for Methods 5 and 6, these two reference methods provide thorough calibration instructions. The discussion of Method 5 in this handbook should be used for QC on the M5 version, and appropriate QC should be employed when the midget impinger version is used.

The field blank consists of 100 mL of absorbing solution placed into blank train impingers, which is recovered and transferred to storage bottles, labeled, and returned to the laboratory for analysis. At least one field blank should be collected at the end of the test period.

6.5 Volatile Organic Sampling Train (VOST)--Method 0030

The most recent method description is available in SW-846[3] (0030). The testing organization should describe its train and procedure in considerable detail, giving all chosen options in the method plus any deviations to the method. Discussion should include a description of the sorbent tubes, the method for cleaning and preparation of tubes, the method used for storing and shipping the tubes, and the method used for checking tube background. The TBP should contain a statement that a new Teflon sample line will be used for the trial burn and the sampling train will use greaseless fittings and connectors.

A clear statement of the number of pairs of sorbent tubes that will be collected during each run should be a part of TBP. A basic run consists of at least three pairs of sorbent tubes, each tube run until not more than a 20-L sample has been obtained. A fourth pair is often collected in case one pair is broken or lost during analysis. The actual sampling time should add up to a total of at least 1 hour; however, 2 hours is optimal (exclusive of the time for tube changes and leak checks). Other options should be fully explained and justified in the TBP. One pair of field blanks should be collected for each run (one pair of blanks for each six pairs of samples). In addition, one laboratory blank pair and one shipping blank pair should be analyzed for each test series.

The sample collected should be large enough to establish compliance, and the front and back tube must be analyzed separately. Samples are considered valid (no breakthrough) if the back trap contains no more than 30% of the quantity collected on the front trap. This criterion does not apply when the quantity of sample is less than 75 ng on the back trap (see Section 7.3 on VOST analysis).

The VOST method (0030) does not contain a section on calibration of apparatus. These procedures,[12] included in Appendix A of this handbook, are recommended for VOST calibration.

6.6 Bag Sampling

The collection of gas samples to determine volatile organics using a Tedlar bag is listed only as a backup technique for VOST. This alternative is seldom used because of: (a) a lack of data on the stability of organics in Teflon bags; (b) no ability to concentrate analytes; (c) poor storage characteristics for many analytes; (d) difficulties involved in shipping the bags; and (e) the high probability of leaks in the bag. The procedure followed is similar to that for an integrated bag sample under Method 18. A more appropriate and detailed procedure is being developed for inclusion in SW-846.

General QA procedures are provided in Method 3. These consist of leak-checking the bag and the sample line. In addition, the ratemeter (rotameter) should be accurate enough to permit setting a sampling rate which allows sampling for the entire run without overfilling the bag.

QA procedures which are specific to this method consist of efforts to demonstrate the absence of cross contamination and the rate of decay of the POHC of interest. New bags should be used. A field blank filled from a tank of high purity air or nitrogen should be collected daily, and a minimum of two trip blanks should be processed every week. Analysis in the field is preferred; however, an alternate overnight delivery of samples by air or surface vehicle to the analysis location followed by immediate analysis will likely be acceptable. Holding times should be kept as brief as possible. Stability in bags must be demonstrated before use.

6.7 Semi-Vost (SVOST)--Method 0010

The QA/QC for this method consists of verifying that the test organization understands the correct procedure and is following that procedure, particularly in critical areas. Calibration of critical components is the same as specified in Method 5. With Method 0010, the probe liner must be glass or quartz and the filter support must be either glass, quartz, or Teflon®.

The temperature of the gas entering the sorbent trap must be monitored, preferably every 5 minutes, and its temperature must be held to 20°C, or lower, but above 0°C.

In Method 0010, procedures are specified for the cleanup of the XAD-2 resin including a maximum 4-week holding time. The trial burn plan should address the resin cleanup required, and the trial burn report should specify the date the resin was cleaned. The report should also contain the results of the residual methylene chloride test and the residual extractable organics test on that resin. Alternatively, a certificate of purity and date of preparation from the resin supplier stating that the resin meets or exceeds the purity specified for Method 0010 is acceptable.

To assist the reviewer, the trial burn test plan should contain a complete description of the sampling train assembly and a detailed diagram (not a generalized block diagram). A complete description of the wash and brush procedure should also be included in the TBP. The entire train should be considered as containing the sample, and all interior surfaces should be considered in the recovery procedure.

All components ahead of the filter should be brushed, and all components should be solvent-rinsed. All particulates and liquids are considered part of the sample. Handling of these components after sampling should also be addressed in the TBP.

The TBP must show the calculations that will be used to determine the required sample volume, which must generally exceed 3 dscm (with compounds that exhibit relatively high volatility, lower volumes could be appropriate), and indicate the lower detection limit. Sampling points should be clearly defined. Minimal statements such as "all sampling will comply with the method requirements" are insufficient.

6.8 Determination of Multiple Trace Metal Emissions--Draft Method

The sampling train for trace metal collection (draft method from U.S. EPA, AREAL, Source Methods Standardization Branch, Research Triangle Park, NC 27711) is similar to a Method 5 train with five impingers. Reference should be made to Method 5 in this handbook for QA procedures referring to train preparation, calibration, and documentation.

The target level of each metal should be stated, and the lower detection limit (LDL) for each should be provided by the specific analytical laboratory handling the sample. Calculations should be provided to demonstrate that the proposed sample volume will meet the program requirements. Typical LDL are reported in the draft method. This subject is also discussed in Section 7.6 of this document concerning analysis of the sampling train components.

A glass or Pyrex probe and filter frit are required, and their use should be stated in the TBP. The recommended filter is quartz and must have a metal blank low enough to allow quantitation of the analytes at expected concentrations. Information on the actual levels should be provided in the TBP.

The draft method for trace metals outlines a specific cleaning procedure for the train components. The TBP should address this subject to demonstrate that the test organization is aware of the requirements. These requirements include the use of surgical gloves

and acid-washed nylon brushes for sample recovery. If zinc is an analyte, surgical gloves should be checked, since some use a zinc-containing dust. As in all procedures using a train, field blanks and a train blank should be collected. Blanks of all reagents should be collected in the field at the end of the test period and every time a new reagent lot is opened or the supply container is changed. Reagent blanks do not require analysis unless the train blank shows high levels of contamination. Full documentation and reporting of all operations and procedures, including all raw data, should be part of the TBR.

Chapter 7
QC Procedures for the Analysis of Stack Samples

This chapter of the handbook gives general background information on analyses to be used for stack gas samples. Topics concerning precision, accuracy, detection limits, and calibration are defined and discussed. If the permit writer is not familiar with these analyses, review of these sections of the TBP, QAPjP, and TBR should be done by qualified personnel.

7.1 Gas Analysis for Carbon Dioxide, Oxygen, and Dry Molecular Weight; Methods for Moisture and Particulates

Gas analysis may be performed following EPA Method 3 (Orsat) for excess air or emission rate correction factor, Fyrite for dry molecular weight determination, or instrumentally following EPA Method 3A under specified conditions. Information on analytical procedure, equipment identification, leak check performance, and calculations should be reported on data sheets.

QA/QC for gas analysis is enhanced by the analysis of performance samples. A common practice is to use ambient air as an audit sample. In this case, triplicate analysis of air samples should show 20.8 ± 0.5% for oxygen. In most atmospheric samples, the carbon dioxide content is too low to be measured using either the Orsat or Fyrite. Therefore, certified gases should be obtained from specialty gas manufacturers. Pressurized canisters containing CO_2, O_2, and CO in nitrogen are available.

For CO_2, analyses should agree within 0.3% when CO_2 is > 4.0% and by 0.2% when CO_2 is ≤4.0%. For O_2, analyses should agree within 0.3% when O_2 is < 15% or by 0.2% when O_2 is > 15%. For CO, analyses should agree within 0.3%.

When gas analysis is performed using EPA Method 3A, QA/QC consists of determining the following: that the system was evaluated according to the procedure, that the method was operating properly, and that performance samples have been analyzed. Before analysis begins, the instrument should be evaluated for calibration errors, sampling system bias, and calibration drift and an interference check performed. The applicant should provide this information in the TBR.

The average stack concentration of O_2. and CO_2 cannot be less than 20% of the span value, and the minimum detection limit should be less than 2% of span. Calibration should be performed using three calibration gases; a high-level gas at 80% to 100% of span, a medium-level gas at 50% to 60% of span, and a low-level gas at 0% to 10% of span.

An audit should be performed using EPA audit cylinders, but a suitable alternative would be to perform a Method 3 analysis on samples obtained at the inlet to the CO and O_2 analyzers. Agreement in either case should be within ±5%.

Moisture is determined using either EPA Method 4 or 5. Use of the Method 5 sampling train to collect HCl does not interfere with the simultaneous determination of water content. Neither method is valid if the stack gas contains water droplets because the heated probe vaporizes the water, which is then condensed in the train and measured as moisture. Method 4 is normally employed only as a pretest procedure to assist in determining the proper isokinetic sampling rate. As such, the method needs only to be approximated. For either Method 4 or Method 5, QA/QC consists of determining the moisture collected in the impingers and should be determined to the nearest 0.5 mL using either volume or gravimetric procedures. A graduated cylinder with subdivisions no greater than 2 mL or a laboratory balance capable of weighing to the nearest 0.5 g or less is suitable.

Particulates are determined gravimetrically by collection on a filter, drying, and weighing. The filters should be dried to a constant weight, which is defined as two successive weighings at a 6-hour interval showing a weight change of less than 0.5 mg.

Before and after each set of filter weighings, the balance should be checked by weighing a check weight of approximately the same weight as the filter assembly being weighed. If the check weight disagrees by more than ±0.5 mg, the weighing should be repeated.

Analytical procedures should be fully documented. Copies of the documents should be provided in the TBR. Filters should be identified with a unique number, traceable from field to analysis records.

7.2 Hydrogen Chloride

7.2.1 General

Analysis of HCl can be done by many techniques (e.g., silver chloride precipitation, titration, or colorimetry); however, the current guidance[10] indicates that ion chromatography by ASTM Method D-4327 or EPA Method 300.0 is preferred. The QC procedures described in this section are tailored to the ion chromatography method, although the general principles are applicable to other methods. The precision and accuracy of all the methods are similar. The ion chromatography method is free of some of the interferences of the other methodologies that can lead to a positive bias in the chloride results.

Usually in chloride analysis there are two or more impinger samples from each run. The early impingers usually contain at least 80% of the chloride and are the more critical samples in making the regulatory decision. If a chloride sample is lost during shipment, and the lost sample is from the front impingers, the data for that run are unusable. If the back impinger samples are lost, and the back impingers from the other two runs show relatively low chloride levels, the average distribution for front- to-back impingers can be used to estimate the concentration of the lost impinger, and the data may still be usable for regulatory purposes.

The specific QA/QC elements of which to be aware for this determination are:

- Calibration of the analytical system.
- Accuracy using calibration check standards and spiked samples.
- Precision by multiple analysis of samples.
- Detection limit.

7.2.2 Calibration

Qualitative Concerns--For most chromatography procedures, qualitative identification is based upon the retention time of the analyte or its retention time relative to an internal standard. However, for ion chromatography, the chloride ion will exhibit a changing retention time with different concentration levels. In some cases, the influence of the sample matrix can cause a shift in retention. Four acceptable ways to ensure the identity of the chloride component in the chromatogram are:

- Internal Standard--An internal standard, such as sulfate, can be added to all the standards and samples, and retention time measured relative to the retention time of the sulfate ion. (The peak is considered chloride if the relative retention time [RRT] of the peak is within three standard deviations of the average RRT observed during initial calibration.) Most stack gas samples will contain some sulfate (sulfuric acid is added to the first impinger in the draft sampling method), and in many cases sulfate will have to be added only to the standard solutions.
- Average Retention Time--The average retention time of the calibration standards is computed. All peaks within three standard deviations of that time are considered to be chloride.
- Retention Time Range--The retention time range of the standard (high to low concentration) is used; any peak within the range of the chloride retention time seen in the standards is considered chloride. For this method sample concentrations *must* be bracketed by standard concentrations.
- Spike Confirmation--All samples are first analyzed by one of the above three techniques for identification of the chloride ion. Each sample is then spiked with chloride at a level twice the approximate sample level. The chromatogram of the spike must exhibit a single peak in the retention time window for confirmation of the chloride ion. If two peaks are observed in the spike sample chromatogram, no chloride is present.

Irrespective of which one of the first three methods is followed, the spike confirmation technique should be used for any sample in which identity criteria are suspect because of interference peaks (poor separation of chloride from other stack gas components) or any samples in which the identification is marginal. Qualitative concerns must be addressed in the TBP or QAPjP. They are not covered in the ASTM method; therefore merely citing the standard methodology does not address qualitative identification.

Quantitation--The chloride levels in the waste and the theoretical efficiency of the air pollution control device are known parameters. Thus, the expected concentration range for the chloride levels in the impingers should be determined in advance, The calibration range for the instrument should consist of at least four standards that bracket the expected sample levels and are presented in the TBP or QAPjP. Sometimes two calibration curves are used, one for high-level samples and one for low-level samples. Any sample with a concentration greater than the highest

standard should be diluted into the calibration range. The linearity criterion for acceptance of the standard curve is that a plot of the standard response versus standard concentration must yield a linear correlation coefficient greater than 0.995. If this criterion cannot be met, sample analysis should not be carried out until linearity can be demonstrated over the entire calibration range.

Calibration of the analytical system should be checked on a regular basis. A calibration standard close to the expected chloride concentration in the front impinger should be analyzed after every 10 samples and at the end of the analysis period. The concentration of this standard determined from the calibration curve must be within 10% of the theoretical value. Every group of 10 samples must be bracketed by two successful calibrations--one preceding sample analysis and one following. If the calibration check following sample analysis does not meet the criteria, it should be repeated; if it fails a second time, the analysis system should be regenerated and the samples following the last successful calibration should be reanalyzed.

All initial and continuing calibration results must be reported in the TBR.

7.2.3 *Accuracy Determination*

Calibration--A five-point calibration curve is usually prepared from a single stock solution of the reference material. This means that all stack sample results are traceable to that one weighing. As a check on the validity of the calibration and the identity of the reference material, a calibration check standard should be analyzed. This calibration check standard must be at the chloride concentration level expected in the front impinger and must be analyzed after each initial calibration curve and before sample analysis. This standard should be prepared from a stock solution obtained from a different source than the calibration standards. The stock solution concentration should be certified by the manufacturer.

The calibration check standard should be within the same accuracy window as that used for continuing calibration, i.e., 90% to 110% of the expected concentration. If this criterion cannot be achieved, the analytical problem should be identified and rectified before sample analyses are begun. The results for all calibration check standards with the appropriate calibration curve results should be presented in the TBR.

Spikes--A minimum of one front and one back impinger sample from each run should be spiked with chloride at a level of not more than 3 times the theoretical sample level. The samples should be spiked at the beginning of sample preparation. Accuracy results must be reported in the TBR, and the accuracy criterion is 85% to 115% of the amount spiked.

7.2.4 *Precision*

Precision must be determined by duplicate preparation and analysis of a front and back impinger sample from at least one run. Given the relatively inexpensive nature of this analysis, duplicate chloride determinations for all samples are highly recommended. Experience has shown that an incinerator operator is more likely to be denied a permit based upon chloride (and particulate) emissions than upon DRE determination. Precision is calculated as percent range and must be less than 25%. If the sample results are within 5 times the detection limit, the RPD should be below 50%.

All precision data must be calculated and reported in the TBR.

7.2.5 *Detection Limit Determination and Method Blanks*

Ordinarily, all impinger samples will contain chloride. Since chloride is virtually ubiquitous, most method blanks also will contain some chloride. Sample results should not be corrected for levels of chloride in the blanks. Usually, blank values are very low in comparison with sample results.

In the rare instance in which no chloride is detected in the impingers, a detection limit must be determined. The method of determining the detection limit should be reported along with the sample results. All detection limits must be adjusted for any sample dilution and the total contents of the impinger. If the blank value is higher than the detection limit, the detection limit should be set at 1.5 times the blank level.

7.2.6 *Summary of QC Procedures*

A summary of the QA/QC procedures for chloride determination is presented in Table 7-1. Each parameter must be reported in the TBR and acceptance of sample results must be justified by the applicant if the QA/QC procedure was omitted or if the criteria were not met. The QA/QC procedures related to calibration and calibration accuracy must be completed and must be within the criteria before sample analysis begins. Deviations from the criteria after the trial burn should not be accepted.

In the case of poor accuracy, low recovery could indicate that the calculated emission rate was lower than the actual, while high recovery could indicate that the calculated rate was higher than the actual. Any accuracy difficulties connected to the back impingers should not be considered a problem unless the chloride distribution between the front and back impingers indicates that the back impinger contains a

Table 7-1. Summary of QA/QC for Chloride Determination

Quality parameter	Method of determination	Frequency	Criteria
Calibration--qualitative	Relative retention time	Every calibration curve	±3 standard deviations of average
	Average retention time	Every calibration curve	Within retention time window of standards
Calibration--quantitative	Initial calibration with a minimum of four standards	At least once before sample analysis	Linear correlation coefficient < 0.995
	Continuing calibration	Every 10 samples and at end of day	90%-110% of theoretical concentration
Accuracy--calibration	Certified reference solution	After every initial calibration before sample analysis	90%-110% of theoretical concentration
Accuracy--spikes	One front and one back impinger spiked at no more than 3 times native level	Once per test	85%-115% recovery
Precision	One duplicate preparation of both a front and back impinger	Once per test	±25% range; if less than 5 times detection limit ±50% range
Detection limit	Method must be reported in TBR	Only if a sample is reported beneath limit	NA
Blank	One method blank carried through sample preparation and analysis	One per test	Less than 5% of sample levels

significant amount of the chloride collected and must be considered in the regulatory decision.

If precision is poor, the laboratory should reprepare and reanalyze the samples. Chloride determinations are not expensive in light of the importance of the chloride data to the regulatory decision. Sample preparation usually entails only dilution. If subsequent work indicates a systematic problem with precision, contamination problems in the analytical laboratory, or a matrix effect from other stack gas components, could be indicated. If precision is poor, the highest value for the samples can be used (instead of the average). This high chloride value would provide a conservative estimate of whether chloride levels are in compliance with regulations.

7.3 Volatile Organic Sampling Train (VOST)--Method 0030/5040

7.3.1 General

The primary method for collection of volatile principal organic hazardous constituents (POHCs) from the stack gas effluents of hazardous waste incinerators is the Volatile Organic Sampling Train (VOST), as described in Method 0030 of SW-846. The analysis method for VOST is described in the "Protocol for Analysis of Sorbent Cartridges from Volatile Organic Sampling Train" as described in Method 5040 and Method 8240 of SW-846.[3] According to EPA guidance, VOST is preferred over integrated bag sampling.

Volatile POHCs, generally with boiling points between 30° and 100°C, are collected from a gaseous effluent source at rates typically from 0.5 to 1.0 L/min and trapped on a pair of traps comprised of Tenax (front trap) and Tenax/charcoal (back trap). A maximum of 20 L of sample is run through each pair of traps, and up to six pairs of sorbent traps may be used to complete a test run.

The analytical method for VOST is based on the quantitative thermal desorption of volatile POHCs from the Tenax and Tenax/charcoal traps and analysis by purge-and-trap GC/MS.

The specific QA/QC elements of which the permit writer should be aware are:

- Sample handling/blank results.
- Calibration of the GC/MS.
- Method performance at the 99.99% DRE level.
- Accuracy and precision determinations.
- Breakthrough ratios of POHCs on trap pairs.
- Detection limit determination.

7.3.2 Method Performance

The primary concern of the permit applicant and writer is whether an analytical system is available that can be used to reliably identify and quantify the sampled POHCs at the expected stack concentration where the 99.99% DRE is achieved. The QAPjP should present all estimated POHC concentrations in both the Tenax and Tenax/charcoal trap at the DRE critical level (concentration at 99.99% DRE) plus the calibration

range of the GC/MS. The concentration of the POHCs at 99.99% DRE should be at least one order of magnitude greater than the concentration of the lowest standard. Highly efficient incinerators might be able to achieve DREs significantly better than 99.99%. In such cases, the 99.99% level would be at the high end of the calibration curve. If the concentration is not at least one order of magnitude greater than the lowest standard concentration, the permit reviewer should request that the applicant reevaluate the sampling strategy and calibration to ensure proper mass of POHCs in the samples and reliable identification and quantitation.

VOST analysis is not always a simple undertaking. The permit applicant should demonstrate in the TBP the analytical methodology that will be used for the POHCs. Four ways are available to demonstrate performance.

1. Presenting surrogate POHC recoveries from past trial burns.

2. Presenting POHC recoveries from two VOST cartridges spiked with POHCs, prepared and analyzed in advance specifically for this trial burn.

3. Performing an analysis of a VOST audit cylinder containing the POHCs of interest.

4. Conducting a miniature trial burn in advance and presenting the results of surrogate POHC analysis. (This advance burn is especially helpful if other stack gas components are expected to significantly interfere with the sample analysis.)

Given the time and money expended on a trial burn, successful analysis of the sample should be supported by performance data, not left to theoretical performance. If these data are not presented in the TBP, the permit reviewer should request performance results from the applicant or a justification of why they are not needed. Average recoveries of the POHCs or surrogate POHCs should be between 50% to 150%. If they are not, the permit writer should request justification of the experimental design.

7.3.3 Sample Handling

The quantitation of a particular volatile POHC depends on the level of interference and the presence of detectable levels of volatile POHCs in the blanks. Interference arises primarily from background contamination of sorbent traps before or after sample collection, usually from exposure to solvent vapors during preparation or from ambient air at hazardous waste incinerator sites.

Because of this potential for contamination, numerous field blanks must be analyzed with the field samples to demonstrate that background levels and sensitivity are acceptable and/or to identify the source of any contamination.

Three types of blanks should be reported with the VOST sample results: field blanks, trip blanks, and laboratory or system blanks.

- Field blanks are VOST traps taken to the field and uncapped during changeovers to simulate exposure to ambient conditions. A minimum of one pair of field blanks is required with each six pairs of traps collected.

- Trip blanks are VOST traps transported to and from the field and included with each shipment of samples back to the laboratory. These blanks are intended to demonstrate that no cross-contamination of samples has occurred during storage and shipment.

- Laboratory blanks are VOST traps that are not sent to the field but remain in the laboratory. They are analyzed daily after high-level samples or if high levels of contaminants are found in the field or trip blanks.

All blanks must be identified in the QAPjP. However, VOST blank trap results should not be used routinely to correct trial burn results. Blanks should be used to correct results only if they are found to be statistically different from the samples as outlined in the method (0030) and the two guidance manuals.[5,9] For all cases where a blank correction is used, both corrected and uncorrected emission data should be presented.

Improper handling of samples may affect the analyses either by giving the samples a high bias, which would lower DRE results, or in extreme cases increasing the method detection limit so that it falls above the concentration levels required for meeting DRE regulations.

7.3.4 Calibration

Calibration criteria for VOST trap analysis are listed in Method 5040 and in Method 8240 "Gas Chromatography/Mass Spectrometry for Volatile Organics."[3] The primary objective of calibration for VOST addresses the POHCs and POHC surrogates.

Stock standard solutions should be prepared from EPA-supplied standard materials or purchased as certified solutions. If EPA reference material is not available, all POHC standard materials should be characterized for identity and purity. The source and purity of all POHC standards should be reported in the TBR.

Fresh stock standards should be prepared weekly for volatile POHCs with boiling points of < 35°C; all

other standards should have been prepared no earlier than 30 days prior to analysis.

A minimum of three concentration levels for each analyte of interest is required for calibration. Each calibration standard should be analyzed on both a Tenax and a Tenax/charcoal cartridge; response factors for both traps are used for determining quality control acceptance and for quantitation of sample results. To ensure adequate sensitivity of the analytical system, the calibration range should bracket the 99.99% DRE POHC concentration level. The expected POHC concentration in both the Tenax and Tenax/charcoal traps (at 99.99% DRE) must be presented in the QAPjP and must be shown to be at least 10 times the level of the lowest calibration standard. Some applicants know their incinerator is capable of achieving a much better DRE than required. In these cases, the 99.99% level might be above the calibration range. A decision of this type represents some risk to the permit applicant. Should incinerator performance not be significantly better than required to meet DRE, analysis results will be out of calibration range. Sometimes the calibration range can be extended by immediately analyzing a higher concentration standard, but results outside the calibration range are unacceptable and generally rejected.

Quantitation is performed for all standard data using the internal standard method for determining relative response factors (RRF). If the RRF value over the working range is a constant (< 20% RSD), the average RRF may be used to calculate concentration of POHCs in samples; alternatively, the results can be used to plot a calibration curve of response ratios (area standard/area internal standard) vs. RRF. Some TBP and QAPjP give a criterion of ±25% for the average RRF and do not allow the optional calibration method. The working calibration curve or RRF must be verified each working day, or every 12 hours of operation, by the analysis of a continuing calibration standard. The continuing calibration check is valid if the RRF falls within ±25% of the initial calibration data. If this check does not meet the criterion, the standard should be reanalyzed. If the second check does not meet the criterion, the acceptance of sample results from the last successful check must be justified. All initial and continuing calibration checks must be reported in the TBR.

Internal standard responses and retention times must also be monitored during data acquisition. The internal standard retention time should not change by more than 30 seconds from the last calibration check. The internal standard areas in samples must be within 65% to 135% of the area observed in the last continuing calibration standard analysis. If either of these parameters changes during sample analysis, a calibration standard check should be performed. For samples in which a low internal standard area occurs, the fourth VOST trap pair may be analyzed once the analysis difficulty has been corrected.

7.3.5 *Precision and Accuracy Determination*

To establish the precision and accuracy of the analysis, triplicate Tenax and Tenax/charcoal traps must be spiked with each POHC and surrogate POHC and analyzed immediately following the initial calibration and before sample analysis. The spiking level must be at the expected POHC mass if 99.99% DRE has been achieved. The spiking standard must be prepared from stock standards separate from those used for calibration and, preferably, prepared by different personnel to avoid any systematic bias. Recovery for each POHC and surrogate POHC should be within 75% to 125% of spiked value. A low POHC recovery may indicate an artificially high calculated DRE; however, a high bias may indicate that the calculated DRE may be artificially low. The relative standard deviation associated with each analyte should be less than 25%.

The average recovery from this determination should be used as an acceptance criteria for sample results. The surrogate recovery in each sample must be within three standard deviations of the average recovery obtained from the initial precision and accuracy determination. If Tenax and Tenax/charcoal traps give equivalent recoveries, the overall average and standard deviation for both traps may be used.

In addition to the precision and accuracy determinations, an EPA performance audit must be completed during a trial burn as a check on the entire VOST system (see Section 3.5). An EPA audit cylinder is sampled during the trial burn by the same person on multiple traps at the same time, and using the same analytical procedure as for the regular VOST trial burn samples. Generally, four pairs of traps are taken and three are analyzed, with one pair saved as a backup. All analyzed pairs should be reported. The criteria for acceptability of the EPA audit cylinder is 50% to 150% of the audit value. A recovery above the limit is sometimes less of a problem (where DRE is concerned) than a low recovery (DRE could be artificially high).

7.3.6 *Detection Limit Determination*

For each POHC, a detection limit (DL) must be determined. The DL is a critical parameter since POHCs are not detected in many trial burns and the DRE is based upon the DL. The method of determining the DL can vary from laboratory to laboratory. However, if the 99.99% DRE level is within the calibration range, the DL is not critical in determining achievement of the performance standard. The method for DL determination must be described in the QAPjP. If this subject has not been addressed, the permit writer should request that the

applicant supply this information. Guidance is being developed for detection limit determination in hazardous waste incineration.

7.3.7 *Breakthrough Ratios of POHC*

The front and back VOST traps should be analyzed separately to determine POHC breakthrough to the charcoal adsorbent. The analysis of the Tenax/charcoal trap should indicate less than 30% of the POHC collected on the front Tenax trap. Breakthrough of the POHC to the charcoal trap above this level may cause loss of desorption efficiency and result in a negative bias in the DRE calculations. This criterion does not apply when less than 75 ng is detected on the back trap.

7.3.8 *VOST Condensate Analysis*

The condensate from the sampling train also has to be analyzed by purge and trap GC/MS, SW-846 Method 8240.[3] The QC procedures consist of spiking with the surrogate POHCs. The accuracy is calculated by the recovery of the POHC, which should be between 50% and 150%, and precision is calculated as the relative standard deviation of the surrogate recovery from trial burn samples and should be less than 35%. If the sample is sufficient, the precision can be determined by duplicate analysis of one run's condensate sample and calculated as the percent range of the POHC levels found in both analyses. A method for the determination of detection limit of the POHC in the condensate needs to be identified in the TBP or QAPjP and the results of the determination reported in the TBR.

7.3.9 *Summary of QA/QC Procedures*

A summary of QA/QC procedures for the VOST method is presented in Table 7-2. Each quality parameter must be reported in the TBR, and sample results must be justified by the applicant if the QA/QC procedure has not been performed or the criteria were not met. QA/QC procedures related to calibration and the precision and accuracy determinations must be complete and must be within the established criteria before sample analysis is initiated.

In assessing the QA/QC results for acceptance of sample data, precision and accuracy problems are not as critical if the calculated DRE is much larger than 99.99%. For example, a surrogate recovery below the criterion is not as critical for a DRE of 99.9999% as it is if the DRE is only 99.99%. Sample results should be corrected for low surrogate recovery.

Both segments of a VOST trap pair must be analyzed, preferably separately. However, sometimes a single segment of the pair is lost due to breakage. In this case, one of the backup VOST pairs should be analyzed and used in the DRE calculation. Also, since the compounds quantitated in the VOST analysis are by nature highly volatile, the time between sample collection and analysis for all samples should be reported in the same table with VOST results. The recommended holding time is generally 14 days.

7.4 Semivolatile Organic Sampling Train (SVOST)--Method 0010

7.4.1 *General*

The primary method for SVOST is 0010 (SW-846).[3] There are three matrices from the SVOST train: (a) the XAD resin and filter, each prepared separately by Soxhlet extraction; (b) the aqueous condensate and impingers, each prepared by solvent extraction; and (c) the organic solvent rinses of the probe and train components, each prepared by solvent extraction. Usually, these matrices are analyzed by GC/MS Method 8270,[3] using isotopically labeled analogs (surrogates) of the POHCs or compounds chemically similar to the POHCs. This section covers QA/QC elements outside the scope of Method 8270 that need to be addressed. Discussion focuses on the POHCs and the concentration of final sample extracts at the 99.99% DRE level. Analysis methods which are not GC/MS are discussed briefly in Section 7.4.8.

The specific QA/QC elements of which to be aware are:

- Demonstration of method performance at the 99.99% DRE level before the trial burn.
- Calibration of the GC/MS.
- Determination of accuracy using calibration check standards, spiked samples, and surrogates.
- Determination of precision by multiple analysis of samples.
- Determination of the detection limit.

7.4.2 *Method Performance*

The primary concern of the applicant and permit writer is whether an analytical system is available that can be used to reliably identify and quantify the POHCs in the SVOST fractions. All estimated POHC concentrations in the SVOST fractions at the critical DRE level (concentration at 99.99% DRE) and the calibration range of the GC/MS should be presented in the QAPjP. If possible, the concentration of the POHC in the SVOST fractions should fall in the middle of the calibration curve, but at least 10 times above the concentration of the lowest standard. If not, the permit reviewer should request that the applicant reevaluate the sampling strategy, sample preparation methods, and calibration to ensure proper mass of POHC in the samples for reliable identification and quantitation.

Table 7-2. Summary of QA/QC Procedures for VOST

Quality parameter	Method of determination	Frequency	Criteria
Demonstrated ability to do analyses	1. Historial data for surrogates, or 2. Spiked trap recovery of POHC, or 3. Surrogate results from anothr incinerator trial burn, or 4. VOST audit cylinder analysis	Before trial burn	50%-150% recovery
Blanks--sample integrity and field contamination	Field blanks, 1 pair of traps	1 pair per 6 samples	Less than lowest standard
Blanks--verify no cross-contamination in storage and shipment	Trip blanks--1 pair of traps	1 pair with each shipment container	Less than lowest standard
Blanks--verify no laboratory contamination and system control	Lab blanks--1 pair of traps	Daily, before analysis of samples and in between high-level samples	Less than lowest standard
Initial calibration of GC/MS	3 to 5 standards bracketing DRE level	Prior to sample analysis	Variability of average RRF ≤ 20% RSD
Continuing calibration	Midlevel standard	Prior to sample analysis, then every 12 h, or after sample set	RRF within ±25% of initial calibration (RRF)
Consistency in chromatography	Monitor internal standard; retention time and area	Every sample, standard, and blank	Retention time within ±30 sec of last calibration check Area is within 65% to 135% from last daily calibration check
Precision and accuracy	Replicate analysis of 3 traps spiked with a standard independent of calibration standards at the expected level of 99.99% DRE	Demonstrated prior to sample analysis	75%-125% recovery; ±25% RSD
Continuing accuracy check	Spike each sample with surrogate POHC	Every sample	Within 3 standard deviations of the initial accuracy found during the precision and accuracy determination
Verification of VOST system accuracy	Analysis of samples from EPA audit cylinder	Required with each trial burn	Within 50%-150% of certified concentration
Detection limit	Open to choice by applicant	At least once for each POHC if limit is used in DRE calculation	NA
Breakthrough determination	Separate analysis of front and back traps	Every pair	Tenax/charcoal trap must have less than 30% of POHC amount on Tenax trap (does not apply if there is less than 75 ng POHC on back trap)
VOST condensate: precision and accuracy	Surrogate POHCs spiked	All trial burn condensate samples	Recovery between 50%-150%; relative standard deviation of all recoveries <35%

SVOST analysis is not a sample preparation procedure that can be oversimplified or streamlined. It involves multiple manipulations prior to a relatively complex analysis. No single analytical technique is applicable because POHCs exhibit diverse chemical properties. Method 0010 allows the selection of an appropriate extraction method and solvents to optimize the recovery of POHCs. In the TBP, the permit applicant should document the performance of the analytical methodology for the POHCs. This can be accomplished in three ways:

- Presenting surrogate POHC recoveries from past trial burns, or
- Presenting POHC recoveries from a train spiked with POHCs, prepared and analyzed in advance specifically for this trial burn, or
- Conducting a miniature trial burn in advance and presenting the results of surrogate POHC analysis. (This advance burn is a particularly useful option if other stack gas components are expected to significantly interfere with sample analysis.)

Given the time and money expended on a trial burn, successful analysis of the sample should be supported by performance data, not left to theoretical performance. If these data are not presented, the

permit reviewer should request performance results or a justification of why they are not needed. Average recoveries of the POHC or surrogate POHCs should range from 50% to 150%. If they do not meet these criteria, the permit reviewer should request justification of the experimental design.

7.4.3 Calibration

The primary calibration objectives for SVOST analysis concern the POHCs and the surrogate POHCs. Method 8270 is designed for a broad spectrum of compounds, but the trial burn itself focuses on a limited number of compounds (approximately one to three). Method 8270 requires a five-point calibration curve for each analyte, and the relative standard deviation (RSD) of the average RRF must be < 30%. A continuing calibration standard (CCS) must be analyzed every 12 hours and at the end of each analysis day. The RRF for the CCS must be within 30% of the average RRF.

The criteria for both initial and continuing calibration are critical parameters and need to be calculated and evaluated before sample analysis. However, in addition to monitoring the CCS analysis, the POHCs should be included in the CCS and meet the same calibration criteria. The POHCs are the critical analytes upon which the primary regulatory decisions are based. Sample analysis should not proceed until the analytical problem has been rectified and the criteria met. All reported sample results must be bracketed by two successful CCS analyses. If samples are analyzed and the end-of-day (or 12 hour) CCS analysis does not meet the criteria, the CCS should be reinjected before any corrective action is taken. If the CCS still fails to meet the criteria, all samples analyzed since the last acceptable CCS should be reanalyzed and the initial analysis data rejected. Sample results should not be reported from a GC/MS system that does not meet the calibration criteria. All initial and continuing calibration data for the POHCs and surrogates must be included in the TBR.

7.4.4 Accuracy Determination

7.4.4.1 Calibration

The five-point calibration curve is usually prepared from a single stock solution of the reference material. This means that all stack sample results are traceable to that one standard preparation. A calibration check standard should be analyzed to validate the calibration and the identity of the reference material. The calibration check standard (a) must contain all the POHCs and surrogates; (b) should be at the concentration level of the POHCs at the DRE critical point; (c) should be analyzed after each preparation of standards and each calibration curve before sample analysis; and (d) should be prepared from EPA reference solutions or prepared from EPA standard reference material obtained from the EPA repository (QA Branch, EMSL-Cincinnati, USEPA, Cincinnati, Ohio 45268). The preparation of the standard should be done by personnel not responsible for the preparation of the calibration standards. Independent preparation should eliminate any systematic bias.

If EPA reference material or certified neat standards are not available, the laboratory must characterize the standard material. Characterization should entail a qualitative identification of the standard and a quantitative determination of standard purity.

Since GC/MS calibration has a window of 30% relative standard deviation, the calibration check standard must be within 70% to 130% of its theoretical concentration. If this criterion has not been met, corrective action should be taken to resolve the analytical problems before any sample analyses are initiated. The results for all calibration check standards should be presented with the appropriate calibration curve results in the TBR.

7.4.4.2 Surrogates

SVOST Method 0010 specifies that all elements of the sampling train should be spiked with surrogates of the POHCs and processed separately to yield three final samples for analysis: combined XAD and filter, impingers, and solvent rinses. Although Method 0010 states that all surrogates should be spiked at approximately 10 times the MDL, for trial burns surrogates must be spiked at a level not more than 2 times the DRE critical level because the DRE level is the concentration of regulatory concern and that level should be well within the calibrated concentration range of the instrument. If surrogate POHCs are not available, other surrogates may be chosen; however, the selection must be *justified*. The recovery of the surrogates in each sample must be within 50% to 150% of the amount spiked and must be reported.

Method 0010 specifies that all elements of the sampling train are to be processed separately to yield three final extracts for analysis. Train components should **not** be combined prior to sample preparation (e.g., XAD-2 resin combined with the particulate filter and the back half rinse; front half rinse and condensate combined) and after sample preparation to yield a single extract for analysis.

7.4.4.3 Spikes

At a minimum, a blank of each SVOST component (e.g., unused XAD/filter or deionized water for condensate) should be spiked with each POHC and surrogate POHC at a level not more than two times the amount of the DRE critical level. If the SVOST components are to be combined, the guidance discussed above for surrogates also applies. The

required accuracy is 50% to 150% of the amount spiked and results must be reported in the TBR.

7.4.5 Precision

Each SVOST component is completely used up in sample preparation, so replicates are not available for determining precision. Since each SVOST component must be spiked with the surrogate POHC, however, precision can be determined from comparison of surrogate recoveries from the different runs. The RPD of surrogate recovery from each component should be ±50%. If there are more than three determinations (a complex trial burn with multiple test conditions), the RSD can be used and should be less than 35%. Surrogate results should not be averaged across the SVOST components (e.g., XAD results should not be mixed with condensate results). However, when train components are combined, the surrogate recoveries are indicative of the extraction method (e.g., Soxhlet or liquid/liquid) and are not related to the recovery from the individual components.

Precision of the analysis can only be determined by duplicate analysis of the extracts from one run. The SVOST components from the run with the highest level of POHC should be chosen for reanalysis. The percent range should be less than 50%. If the POHC concentration falls beneath the lowest standard in the calibration curve, the RPD should be less than 100%.

7.4.6 Blanks

Blanks are useful in locating problem areas in the sampling and analysis program, but should not be used to routinely correct sample data. There are three major kinds of blanks: (a) SVOST trains shipped to the field and returned (trip blanks); (b) SVOST trains hooked up to sampling apparatus on the stack but never used for stack gas sampling (field blanks); and (c) blank XAD/filters and deionized water analyzed by the laboratory and never shipped to the field (analytical method blanks).

The analytical method blanks demonstrate that the detection limit claimed for the analysis is valid given the background concentration of the POHC in the laboratory. Sometimes detection limits used for DRE calculations are based upon analysis of standard solutions and do not include any possible background contamination from the laboratory preparation. All blanks must be reported in the TBR, and values should be less than twice the estimated detection limit determined for the sample extracts. If the method blank value is above this level, it is recommended that 1.5 times the level of POHC in the method blank should be used as the detection limit.

Significant background contamination at the incinerator could artificially lower a DRE by increasing the POHC levels determined in the stack gas. If this problem is expected, the applicant should present a statistical design for the number and kinds of blank SVOST and how they will be used for correcting the DRE. At a minimum, each run should contain at least one trip blank and one field blank, plus one method blank per sample batch. If sample data are corrected for blank results, both the uncorrected and corrected results must be reported.

7.4.7 Detection Limit Determination

For each POHC the detection limit (DL) must be determined. The DL is a critical parameter because many times no POHCs are found and thus the DRE is based upon the DL. The method of determining the DL can vary from laboratory to laboratory. The method used must be described in the QAPjP and the determination presented in the TBR. However, if the 99.99% DRE level is above the lowest calibration standard, the DL is not critical for assessing achievement of the performance standard. Guidance is being developed for detection limit determinations in hazardous waste incineration. Detection limits used in DRE calculations **must** be determined on the actual sample matrix – not an ideal sample without interferences.

7.4.8 SVOST – Analysis by Other Methods

Other methods that may be used for trial burn analysis are described in this section.

7.4.8.1 Background

Not all trial burns require the sensitivity and the specificity of GC/MS analysis, and some POHCs (e.g., formaldehyde) are not amenable to GC/MS. Other techniques, such as GC with flame ionization detection (GC/FID) or electron capture detection (GC/ECD), may give a much more precise and accurate analysis when compared to GC/MS. Often the increase in precision is by a factor of 2 or 3. GC/MS analysis is very expensive, and it generates large amounts of data that must be reduced and evaluated by personnel with a very high skill level. Since GC/FID and GC/ECD analysis is less complex, problem samples may be more easily and more cost-effectively reanalyzed.

From the perspective of the permit applicant, GC/MS provides more assurance against a mistaken identification of POHC in the stack gas samples due to more specificity in the analysis. It also assures the permit applicant that the POHC is being quantitated and not some other stack gas component. However, if the 99.99% DRE level is within the analytical system's calibration range, demonstration of a lower DRE is a moot point. GC/MS also has one other distinct advantage, which is the use of surrogates to determine analytical accuracy for each stack gas sample. This advantage is not available with any other technique.

Some researchers use compounds chemically related to the POHC for a surrogate, but these compounds are not considered as reliable as the use of isotopically labeled surrogates.

7.4.8.2 QA/QC

Situations exist in which GC/MS cannot be used because the POHC has a low volatility, is unstable, or is highly reactive. In these cases other chromatographic techniques such as high pressure liquid chromatography or ion chromatography should be used. However, all the QA/QC elements for GC/MS delineated below must be followed:

- Demonstration of method performance before trial burn is conducted.
- Calibration curve bracketing concentration at 99.99% DRE.
- Independent calibration check standards, analyzed before samples and passing criteria.
- Spikes of blank SVOST components for accuracy.
- Duplicate analysis for precision.
- Detection limit determination.

Some of the key elements of the design for any determination of POHC in stack gas samples using a technique other than GC/MS are highlighted below.

- Sample results should be calculated using an internal standard technique. The lack of an internal standard must be justified in the TBP or QAPjP.
- If possible, a compound chemically similar to the POHC should be identified and spiked into all samples. The same guidance given for isotopically labeled surrogates would apply to this compound. The lack of a chemical surrogate must be justified in the TBP or QAPjP.
- If possible and given the desired detection limit, some consideration should be given to dividing the condensate, impingers, and solvent rinse samples for one run with one portion spiked with POHC at twice the DRE critical level and the other analyzed unspiked. This measures accuracy as recovery. However, the XAD and filter should not be split; in that case the final extract should be analyzed and then spiked at twice the DRE critical level and reanalyzed. The recovery should be 50% to 150%. Good recovery demonstrates a lack of significant interference from other stack gas components for the XAD resin samples.
- The impingers and solvent rinse samples for one run should be divided, prepared, and analyzed in duplicate. Precision as RPD can then be measured.
- The identity of the POHC must be confirmed by the use of relative retention times (RRT) compared to the internal standard. The RRT window should be set daily using the RRT of the daily calibration standard and three times the standard deviation of the RRTs of the calibration curve standards. If questionable identification occurs due to matrix interference of a peak that otherwise meets the retention time criteria, the sample should be spiked at the same level and reanalyzed. If two peaks are observed, the tentatively identified peak should not be considered to be the POHC. The use of capillary GC reduces the possibility of false positives and certainly second column confirmation should be given some consideration to confirm compound identification.

7.4.9 Summary of QC Procedures

A summary of QA/QC procedures discussed in this section is presented in Table 7-3. Each quality parameter must be reported in the TBR. If the QA/QC procedure was not followed or the criteria not met, sample results should not be accepted unless the applicant provides an adequate technical justification for the use of the data. The QA/QC procedures related to method performance, calibration, and calibration accuracy must be completed and must be within the criteria before sample analysis begins.

For surrogate and POHC spike recovery results, the 50% to 150% level is acceptable. If recovery is above 150%, sample results could be biased high and the calculated DRE would be lower than the actual efficiency. Sample results should be corrected for low surrogate recovery. If individual recoveries are lower than 50%, results should be rejected.

7.5 Metals Determination

7.5.1 General

EPA methods for sampling and analysis of metal emissions are Method 12 for lead, Method 101A for mercury, Methods 103 and 104 for beryllium, and Method 108 for arsenic. For the past 2 years, a method has been under development for sampling and analysis of multiple metal analytes.[13] At this writing, the draft method can be applied to 16 analytes. It has become the most commonly used procedure for metals because few incinerators process waste containing only one metal analyte. **NOTE:** At this time no valid procedure for stack gas determination of chromium in the hexavalent state is

Table 7-3. Summary of QA/QC Procedures for SVOST

Quality parameter	Method of determination	Frequency	Criteria
Method performance--accuracy	1. Historical data for surrogates, or 2. Blank SVOST spiked with POHC, or 3. Miniature trial burn surrogate results	Before trial burn	50%-150% recovery
Calibration	Five-level calibration curve; DRE critical level at least 10 times higher than lowest standard; continuing calibration standard	At least once; at beginning of day; continuing calibration once every 12 h and at end of day	< 30% RSD[a] of average RRF[b] within 30% of average RRF from calibration
Accuracy--calibration	Analysis of calibration check	After every initial calibration	70%-130% of theoretical value
Accuracy-surrogates	Isotopically-labeled POHC spiked at not more than two times DRE critical level	Every SVOST component	50%-150% recovery
Accuracy--spikes	POHC and surrogate POHC spiked not more than two times the DRE level into each SVOST component of a blank train	One per trial burn	50%-150% recovery
Precision--surrogates	Same as for accuracy-surrogates pool results for each SVOST component	Every SVOST component	< 40% RPD[c] of surrogate recovery. If more than three determinations RSD < 35%
Precision--POHC	Duplicate analysis of all SVOST components from the run with the highest POHC level	One per trial burn	±50% range if POHC concentration is above lowest calibration standard; ±100% all other cases
Blanks	Method blank for each SVOST component	One per batch of samples	Blank value < 2 DL. If greater, DL is changed to 1.5 x blank level
	For Methods Other Than GC/MS		
Identification	Internal standard RRT[d] window	Internal standard in every sample	±3 SD of RRT from initial calibration survey
Quantitation	Internal standard RRF	Internal standard in every sample	NA
Chemical surrogate--accuracy	Chemically related to POHC	Spiked into every sample	50%-150% recovery
Sample spikes--accuracy	Spilt impinger and rinsate samples. Spike one with POHC at two times DRE critical level	At least one run	50%-150% recovery
XAD spike--accuracy	Analyze XAD extract then spike at two times ~~DRE~~ critical level	At least one run	80-120% reovery

[a]RSD = relative standard deviation.
[b]RRF = relative response factor.
[c]RPD = relative percent difference.
[d]RRT = relative retention time.

available. Discussion in this section focuses on the draft method.

One of the biggest difficulties associated with the permitting process for metals is the lack of a clearly defined decision level based upon the metals data. Unlike DRE or particulate emissions, metals emissions do not have a clear cut-off point for decision-making based upon stack gas concentration. The draft document, "Guidance on Metals and Hydrogen Chloride Controls for Hazardous Waste Incinerators,"[11] contains the procedures for determining whether metals emission rates determined with a risk-based assessment model must be used in reviewing the permit application and deciding if emission testing for metal analytes is necessary.

If testing is required, a target analyte list should be developed, based upon the expected waste composition. A stack gas target concentration for regulatory decision-making should be set for each analyte based upon the maximum acceptable emission rate determined from risk assessment modeling. The draft metals procedure should be modified (according to the guidance given in the method) to produce a theoretical method detection limit at least 10 times lower than the target regulatory limit. Determination of the regulatory concentration limit and necessary method modifications should be discussed in the TBP or QAPP.

A metals emission determination without a clear definition of the analytes of concern and their critical concentration levels can result in a data set of limited use. For example, metals determinations in the low concentration ranges can be subject to severe problems with contamination, precision, and accuracy. If a low concentration determination is needed, ultrapure reagents and determination of blank train reagent levels in advance of the trial burn are suggested. Metals analysis techniques are chosen with regard to the expected analyte concentration range. For example, if arsenic is a concern only at higher levels, inductively coupled plasma would be chosen for analysis; however, a low level arsenic determination is usually carried out by graphite furnace atomic absorption.

The QAPP or TBP should contain a discussion answering the following questions:

- Why is metals determination necessary?
- What are the target analytes?
- What are the stack gas concentrations of concern?
- What modification to the existing methods will be needed to quantitate the analytes at the concentrations of interest?

The following parameters should be clearly delineated:

- Target analytes.
- Stack gas concentrations.
- Final expected concentration range in each sampling train fraction before and after sample preparation.
- Calibration range of the analysis system to bracket the expected sample concentrations.

The specific QA/QC elements suggested for these analyses are:

- Clear definition of the need for metals analysis, the metal analytes of interest, and the regulatory concentration limits.
- Determination of accuracy using calibration check standards, reference materials, and spiked samples.
- Determination of precision by multiple preparation and analysis of samples.
- Determination of the detection limit.

7.5.2 Method Performance

Two primary concerns exist regarding metals method performance. First, the analytical system must be capable of reliably identifying and quantifying the metals in the sampling train fractions. Second, since stack sampling and analysis for metals is not as routine as that for VOST and SVOST, the organization conducting the measurements should be requested to demonstrate their ability in this area. The draft multiple metals protocol allows the selection and modification of various sample preparation and analysis steps to optimize the measurements system. In the TBP the permit applicant should demonstrate the performance of the analytical methodology for the metals. This capability can be accomplished in two ways:

- Presenting QA/QC results from past trial burns for analysis of similar metals at similar concentrations.
- Conducting a miniature trial burn in advance and presenting the QA/QC and emission results.

This demonstration of the ability to carry out the measurements is burdensome but it ensures some possibility of obtaining reliable data. This demonstration is particularly critical with low levels of metals and the determination of chromium in the hexavalent state.

7.5.3 Calibration

Calibration procedures are dependent upon the type of instrumentation used for analysis. The expected concentrations for the various sampling train fractions must be presented along with the selected analytical methods and the calibration range. The calibration range of the analytical system should bracket all expected concentrations of the metals. Samples with concentrations greater than the highest standard level should be diluted into the calibration range and reanalyzed.

Criteria for both initial and continuing calibration are given in Section 8.4. The essential points for calibration, irrespective of the analysis method, are before and after sample analysis. The initial calibration curve

must pass the criteria before any samples are run. At the end of each analysis period, a calibration standard should be analyzed and pass the continuing calibration criteria. Thus, every sample must be bracketed by two successful calibrations; one full calibration curve preceding sample analysis and one midrange calibration standard following sample analysis. If the calibration check following sample analysis does not meet these criteria, it should be repeated; if it fails the second time, the analysis system should be recalibrated and the samples following the last successful calibration should be reanalyzed. All initial and continuing calibration results must be reported in the TBR in the exact order in which they were analyzed.

The instruments used in metals analysis have a tendency to drift at both the high and low levels of the calibration range. Thus, all continuing calibrations must be accompanied by results of analysis of a reagent blank (all reagents contained in standard solutions). The acceptance of this blank is somewhat subjective, depending upon the sample results and whether the drift is positive or negative. The reagent blank should be reported in the TBR and any drift greater than 50% of the lowest standard should be commented upon.

7.5.4 Accuracy Determination

Calibration: Virtually all of the SW-846 methods require some initial check on the accuracy of calibration using a second standard, different from that used for calibration. This sample should be analyzed immediately following calibration and must fall within 90% to 110% of the actual concentration. This is a fairly wide range for the analysis of a pure standard; results outside this range are unacceptable. Sample analysis should not proceed until a result within this range is achieved.

Reference material. Spiked samples of all sampling train fractions are usually not possible since most fractions cannot be split for spiking purposes. This is particularly true for the filters. However, the National Institute of Standards and Technology provides standard reference material for the analysis of metals on filter media. The available metals and their concentration levels are given in Table 7-4. If these metals are target analytes, a minimum of two filters in the appropriate concentration range (twice the target regulatory levels) must be analyzed. Precision can be determined from duplicate analyses. Recoveries should be within 75% to 125% of the reference value, and results must be reported in the TBR.

Spikes: At least two complete blank sampling train components consisting of all reagents from each impinger should be spiked with each appropriate metal analyte. Efforts should be exerted to identify a spiking concentration which will give a spike level of not more than twice the expected sample level or five times the detection limit, whichever is greater. The samples should be spiked at the beginning of sample preparation. The duplicate spiked blank train results will be used for determining precision.

For mercury analysis, an aliquot is taken for analysis from each fraction (nitric and permanganate impingers) except for the filter/probe rinse fraction. The aliquot should be large enough to allow a split and then a spike of the actual sample without significantly reducing the total volume of the original impinger samples. For one sampling train, a portion of the aliquot from each sampling train fraction (including the postdigestion filter/probe rinsate) must be spiked for each metal analyte. Effort should be exerted to identify a spiking concentration level which will give a spike of not more than 3 times the expected sample level or five times the detection limit, whichever is greater.

The accuracy target range is 70% to 130% of the amount spiked. Results should be reported in the TBR.

Post Sample Preparation Spike: For all analytes except mercury, one sample preparation from each sampling train component (e.g., one condensate, one nitric impinger sample) should be analyzed and then spiked at about two times the sample level. The target recovery of the amount spiked into the sample should be within 70% to 130%. If the recovery is not within this range, the sample should be diluted (at least 1:5) and reanalyzed. If the value is higher than the undiluted result, the diluted sample should be spiked and, again, the target recovery should be within 70% to 130%. The diluted sample result should be reported.

If recovery is still poor, the dilution process should be continued either until the recovery is within the limits or until further dilution will approach the detection limit. If the diluted sample result shows little or no change from the undiluted sample, this is indicative of a matrix effect which cannot be easily rectified by dilution; the results from the undiluted sample should be reported with a discussion of the affect of these findings upon sample results.

7.5.5 Precision

Precision is determined from duplicate preparation and analysis of the standard reference filters and the spiked blank trains. The target for precision should be less than 35% range. For mercury, all the components from one stack gas sampling train should be analyzed in duplicate and must meet the same criteria. Precision data must be calculated and reported in the TBR.

Table 7-4. Standard Reference Material (SRM)--Metals on Filter Media*

SRM	Type	Unit size	Material certified	Quantity certified (µg/filter) I	II	III	IV
2676c	Metals on filter media	Set of 12	Cadmium	0.954	2.83	10.09	(< 0.01)
			Lead	7.47	14.92	29.81	(< 0.01)
			Manganese	2.11	9.92	19.85	(< 0.01)
			Zinc	9.99	49.68	99.28	(< 0.01)
2677	Beryllium and arsenic on filter media	2 sets of 4	Beryllium	0.052	0.256	1.03	< 0.001
			Arsenic	0.103	1.07	10.5	<0.002

Note: 1. These SRM's consist of potentially hazardous materials deposited on filters to be used to determine the levels of these materials in industrial atmospheres.
2. Values in parentheses are not certified but are given for information only.
*These can be obtained from the National Institute of Standards and Technology (NIST), Gaithersburg, Maryland 20899, Phone: 301-975-6776.

7.5.6 *Method Blanks*

Blanks can become critical experimental design elements of the trial burn when detection limits are pushed to very low levels. Three major kinds of blanks are: (a) sampling train reagents shipped to the field and returned (trip blanks); (b) sampling trains hooked up to sampling apparatus on the stack but never used for stack gas sampling (field blanks); and (c) reagent blanks of the filters and impinger solutions analyzed by the laboratory but never shipped to the field (analytical method blanks).

Many detection limits are based upon the analysis of standard solutions and do not include any possible background contamination from the laboratory preparation. Method blanks must be analyzed to demonstrate that the detection limit claimed for the analysis is valid, given the background concentration of the metals in the laboratory. Method blanks must be reported in the TBR and must not be more than twice the estimated detection limit. If the blank value is above this criterion 1.5 times the level of analyte in the blank should be used as the detection limit.

If the permit applicant expects significant background contamination at the incinerator which could result in an artificially high metals determination, this topic should be discussed in detail in the QAPjP. The applicant should present a statistical design for the number and kinds of blanks and how they will be used to correct the sampling results. At a minimum, each run should consist of at least one trip blank and one field blank (including probe rinses), plus one method blank per sample batch. Guidance in these areas is given in Reference 5.

All blank determinations must be reported in appropriate units along with the associated samples. All values that are blank corrected must be flagged as corrected, and all subsequent results from those values must also be flagged. Final results must be presented both with and without the blank correction.

7.5.7 *Detection Limit Determination*

A detection limit (DL) must be determined for each analyte. The DL is a critical parameter since metals are not detected for many trial burns and the regulatory decision is then based upon the DL. The method of determining the DL can vary from laboratory to laboratory, but must be described in the QAPjP. If this subject has not been addressed, the permit reviewer should request that the applicant supply the information. The results of the DL determination must be presented in the TBR. Guidance is being developed for detection limit determinations in hazardous waste incineration.

7.5.8 *Summary of QC Procedures*

QC procedures for metals determination are summarized in Table 7-5. Each quality parameter must be reported in the TBR. If the QC procedure was not completed or the criteria were not met, sample results should not be accepted unless the applicant provides an adequate technical justification for use of the data. The QC procedures related to calibration and calibration accuracy in particular must be entirely documented and must be within the criteria before sample analysis begins.

A high bias demonstrated in the accuracy determination indicates that metals emissions are probably lower than presented. A low bias in the spiked blank train samples is indicative of a loss of analyte in the preparation and analysis procedures. This will mean the regulatory decision is based upon stack gas emission values that are lower than actual. In all cases, any blank corrections applied to the data should be examined in detail, and their use must be clearly justified by the applicant.

Table 7-5. Summary of QA/QC Procedures for Metals Determination in Stack Gas Samples

Quality parameter	Method of determination	Frequency	Target criteria
Method selection	Use guidance documents to determine overall data quality objectives	Once	NA
Method performance	Past trial burns or a "mini burn" at the subject facility	Once	QC results for overall precision and accuracy of spiked samples within criteria given below for spiked blank trains
Calibration	Initial analysis of standards at multiple levels	At least once	Method-dependent. Suggest linear correlation coefficient of standard data: < 0.995
	Continuing mid-range calibration standard	At least before and after sample analysis	80% to 120% of expected value for GFAA; 90% to 110% for ICP
	Continuing calibration blank	With continuing calibration standard	Subject to interpretation
Accuracy--calibration	Analysis of a calibration check standard	A every initial calibration	90% to 110% of theoretical value
Accuracy--filters	Analysis of NIST standard reference filters	Twice	75% to 125% of reference value
Accuracy--spikes	Analysis of a full blank sampling train spiked at approximately twice the expected concentration or five times the detction limit	Twice	70% to 130% recovery
Accuracy--spike (mercury only)	Spike one portion of a mercury aliquot from each matrix at ~ 2 times the expected level or 5 times the detection limit	Once	70% to 130% of recovery or reference value
Accuracy--postpreparation spike	Spike at ~ 2 times the level in sample	Once per sample component	Recovery of spike 70% to 130%
Precision--mercury	Duplicate analysis of one sample from each matrix	Once	25% RPD
Blanks	Trip blanks Field blanks Method blanks	One each per trial burn	Evaluated on case by case basis
Detection limit	Must be presented in TBP or QAPjP	Once for each analyte and each method analysis	NA

If precision on spiked blank train samples is poor, the precision problem could be in the sample preparation stage or just the result of an outlier in one of the spiked train samples. The two spiked blank train results should be closely examined to determine if the precision problem was caused by contamination. Since each fraction of the train is spiked, the results for the spiked blank train can be compared as the sum of all components. If this comparison shows generally good agreement (< 35% range), a precision problem in only one fraction could be considered of minimal concern. Assessment of the effect of the precision problem should be based upon the relative importance of that fraction in the particular analyte determination. Results from the three test runs should all be examined to see whether a lack of agreement exists between the runs or whether the precision problem is just with the two spiked blank trains.

Chapter 8
QC Procedures for General SW-846 Analytical Methods

Key QC procedures which are specified in SW-846[3] Methods 8240, 9270, 7000, and 6010 and general chromatography (HPLC or GC) are addressed in this chapter. The purpose of this chapter is to present the key QC procedures with guidance on data validation, allowing data users to gain a level of understanding of the QC. The various methods are complex and designed for technical experts; however, the key QC procedures all share common elements and can be relatively easily evaluated to detect common problems. If the person evaluating the trial burn data is not familiar with these analyses, review of these data should be done by qualified personnel.

8.1 Volatile Organic GC/MS Analysis

8.1.1 General

Chapter 5 covers QC procedures for POHC analysis of waste and stack gas samples. Most of these samples are analyzed by GC/MS using SW-846 Method 8240. Often a TBP will indicate that waste and stack gas samples will be analyzed for the Appendix VIII compounds amenable to GC/MS. This section will cover QC procedures for Method 8240 and offer some guidance on areas that should be considered in assessing trial burn results using analysis records with the "Checklist for Reviewing RCRA TBR."[14] If a thorough review and validation of the non-POHC analytes is needed, Reference 7 contains very good guidance for validating and accepting analytical data from GC/MS. POHC analysis is the primary focus of concern in this handbook, while the full Appendix VIII analysis is secondary.

8.1.2 Surrogate Standards

Surrogates identified in Method 8240 are added to all sample standards and blanks. Method 8240 recommends toluene-d_8, 4-bromofluorobenzene (BFB), and 1,2-dichloroethane. Surrogate recovery is dependent on the matrix. Sample surrogate recovery should be within 75% to 125%. Data that fall outside these limits should be flagged and evaluated for possible effect on trial burn results. When recovery is low, surrogates should be used to correct sample data.

8.1.3 Calibration

The GC/MS must be tuned to the criteria given in Table 8-1 for Method 8240 using BFB. Instrument calibration should not proceed until these criteria have been met. In reviewing analysis records, the BFB tuning should be checked. If the tuning does not meet criteria (see Table 3-1), all sample results for that analysis day are suspect and should not be accepted unless the applicant provides an adequate technical justification for the use of the data. If the tuning problem is severe, the absence of a given analyte should also be questioned.

Table 8-1. BFB Key Ions and Ion Abundance Criteria (Method 8240 Criteria)

Mass	Ion abundance criteria
50	15% to 40% of mass 95
75	30% to 60% of mass 95
95	base peak, 100% relative abundance
96	5% to 9% of mass 95
173	> 2% of mass 174
174	< 50% of mass 95
175	5% to 9% of mass 174
176	< 95% < 101% of mass 174
177	5% to 9% of mass 176

Before sample analysis begins, a five-point calibration curve must be analyzed; the average RRFs for each analyte must exhibit a relative standard deviation < 30%. Every day or every 12 hours, a continuing calibration standard containing all analytes must be analyzed. The RRF for specific calibration check compounds in the daily standard must be within 25% of the initial calibration average RRF; if not, then analysis should not proceed. The other analytes should also be within the 25% calibration criteria; however, Method 8240 does allow some deviation based upon technical judgment. Nevertheless, the POHCs should meet the calibration criteria in all cases.

8.1.4 Analyte Identification

Analyte identification is done by comparison of relative retention time (RRT) and GC/MS spectra; these areas can be checked if the analysis records are submitted with the TBR. The RRT of the sample analyte must be within 0.006 RRT units of the daily standard. If the RRT deviates significantly, the identification should be considered suspect. Computer identification by mass spectra should be confirmed by a mass spectrometrist. For critical analytes such as POHCs, the analysis records must clearly document the rationale if a component that appears to meet the RRT criteria for POHC identification is rejected because of mass spectral data. In general, detected ions greater than 10% relative intensity in a sample should match the ions in the standard spectra to within ±20% agreement.

8.1.5 Quality Control Requirements

Method blanks (reagent water) should be analyzed initially to demonstrate that the system is contaminant-free, and after high-level samples have been run, to demonstrate no cross-contamination with the next sample.

Duplicate spikes of each matrix type (e.g., scrubber water, waste feed) should be performed with all target compounds to obtain accuracy and precision data. Accuracy as recovery should be within 50% to 150% of the amount spiked. Precision as percent range should be within 25%.

Internal standard areas should be recorded and monitored by the analyst. The criterion is specified by Method 8240 as -50% to +100% agreement with the last daily calibration check. A change in the internal standard area could indicate either a problem with the GC/MS or with that particular sample. A drop or rise in the area over several samples would be more indicative of a GC/MS system problem. Whatever the cause, reanalysis of this sample (if possible) is recommended.

A QC check standard should be analyzed to verify the accuracy of the calibration. The QC check sample should be a standard solution, prepared independently from the standard solutions used for calibration. This check standard can be purchased with a certified concentration or obtained from EPA (QA Branch, EMSL-Cincinnati, USEPA, Cincinnati, Ohio 45268). Agreement should be within ±30% of the certified value.

8.2 Semivolatile Organic GC/MS Analysis

8.2.1 General

QC procedures for POHC analysis of waste and stack gas samples were covered in Chapter 5 and Section 7.3. GC/MS using SW-846[3] Method 8270 is the preferred method for these samples. Often the TBP indicates that waste and stack gas samples will be analyzed for the Appendix VIII compounds amenable to GC/MS analysis. This section will cover the QC procedures for Method 8270 and give some guidance for areas that should be covered when assessing trial burn results. If a thorough review and validation is needed, very good guides exist for validating and accepting analytical data from GC/MS.[15,16] These handbooks view the POHC analysis as the primary concern, while the full Appendix VIII analysis is secondary.

8.2.2 Surrogates

If the full range of analytes are to be analyzed, the surrogates identified in Method 8270 (see Table 8-2) must be spiked into all samples. (Please refer to Section 7.4 for a discussion on surrogate spiking in SVOST components.) Generally, surrogate recovery below 50% is considered suspect and should be closely reviewed. Surrogate recovery limits for soil, sediment, and water samples are listed in the table; however, these limits are not applicable to all samples seen in a trial burn. Many samples, such as the relatively clean water in the impingers and the XAD resin, will give better than 50% recovery. Recovery may be influenced by the solvent used in sample preparation; if this solvent is optimized for POHC extraction some of these surrogates may exhibit poor recovery. Some laboratories use historical data to supply surrogate recovery limits; however, surrogate data from different matrices, solvents, and extraction methods often are combined, yielding wide boundaries of limited value in judging data acceptance. If the QAPjP presents historically-defined limits, the sample matrix, extraction, and solvent and extraction method used to derive the acceptable criteria should be identified.

Table 8-2. Surrogate and Spike Recovery Limits

Surrogate compound	Low/medium water (%)	Low/medium soil/sediment (%)
Nitrobenzene-d_5	35-114	23-120
2-Fluorobiphenyl	43-116	30-115
p-Terphenyl-d_{14}	33-141	18-137
Phenol-d_6	10-94	24-113
2-Fluorophenol	21-100	25-121
2,4,6-Tribromophenol	10-123	19-122

From SW-846, Method 8270.

All surrogates should be identified in the QAPjP along with their acceptance criteria. Surrogate recoveries should be reported in the TBR. Any values outside the criteria given in the QAPjP must be flagged and should not be accepted unless the applicant provides an adequate technical justification for the use of the data. Guidance is available on accepting, qualifying, or

rejecting sample data based upon the surrogate recoveries.[15,16] When recovery is low, surrogates should be used to correct sample data.

8.2.3 Calibration

The GC/MS must be tuned using decafluorotriphenylphosphine (DFTPP) to the criteria given in Table 8-3. Instrument calibration should not proceed until these criteria have been met. Some slight deviations are allowable within the expanded criteria in Table 8-3; however, these instances should be documented and explained in the TBR. In reviewing analysis records, DFTPP tuning should be checked. If the tuning does not meet either criterion, then all sample results for that analysis day should be considered suspect.

Table 8-3. Decafluorotriphenylphosphine (DFTPP) Key Ions and Ion Abundance Criteria (Method 8270 Criteria[a])

Mass	Ion abundance criteria
51	30%-60% of mass 198
68	< 2% of mass 69
70	< 2% of mass 69
127	40%-60% of mass 198
197	< 1% of mass 198
198	Base peak, 100% relative abundance
199	5%-9% of mass 198
275	10%-30% of mass 198
365	> 1% of mass 198
441	Present but less than mass 443
442	> 40% of mass 198
443	17%-23% of mass 442
	Expanded DFTPP Criteria[b]
51	22.0%-75.0% of m/z 198
68	Less than 2.0% of m/z 69
70	Less than 2.0% of m/z 69
127	30.0%-75.0% of m/z 198
197	Less than 1.0% of m/z 198
198	Base peak, 100% relative abundance
199	5.0%-9.0% of m/z 198
275	7.0%-37.0% of m/z 198
365	Greater than 0.75% of m/z 198
441	Present but less than m/z 443
442	Greater than 30.0% of m/z 198
443	17.0%-23.0% of m/z 442

[a] Eichelberger, J. W., L. E. Harris, and W. L. Budde, "Reference Compound to Calibrate Ion Abundance Measurement in Gas Chromatography-Mass Spectrometry," *Analytical Chemistry*, 47, 995 (1975).

[b] Laboratory Data Validation Functional Guidelines for Evaluating Organic Analysis, U.S. EPA Hazardous Site Evaluation Division, February 1, 1988.

Before sample analysis, a five-point calibration curve must be analyzed. The average RRFs for each analyte must exhibit a relative standard deviation of < 30%. However, the calibration check compounds (CCC) and POHCs presented in Table 8-4 should be within this criterion before commencing analysis. Every day, or every 12 hours, a continuing calibration standard containing all analytes must be analyzed. The RRF for the CCC and POHCs in the daily standard should be within 30% of the daily standard; if not, analysis should not proceed. Also, every day the GC/MS should be checked before sample analysis and every 12 hours with the system performance check compounds (SPCC) (*N*-nitroso-di-*n*-propylamine, hexachlorocyclopentadiene, 2,4-dinitrophenol, and 4-nitrophenol). These compounds should exhibit a minimum RRF commensurate with the method before any sample analysis is initiated.

Table 8-4. Calibration Check Compounds

Base/neutral fraction	Acid fraction
Acenaphthene	4-Chloro-3-methylphenol
1,4-Dichlorobenzene	2,4-Dichlorophenol
Hexachlorobutadiene	2-Nitrophenol
N-Nitroso-di-*n*-phenylamine	Phenol
Di-*n*-octylphthalate	Pentachlorophenol
Fluoranthene	2,4,6-Trichlorophenol
Benzo[*a*]pyrene	

From SW-846, Method 8270.

The SPCC and CCC criteria exist to ensure that the GC/MS system is capable of detecting and quantifying the large range of analytes necessary. If the criteria have not been met, this information should be reported in the TBR and discussed in relation to sample data. However, since POHCs are the critical analytes, POHCs should meet all calibration criteria daily (see Section 7.4.3). The use of all SPCCs and CCCs noted in Method 8270 may not be required when analysis is conducted to quantitate a few very specific POHCs. The use of fewer SPCCs and CCCs should be discussed and justified in the TBP or the QAPjP.

8.2.4 Analyte Identification

Analyte identification is done by RRT and GC/MS spectra comparison, and these areas may be checked by the permit writer if the analysis records are submitted with the TBR. The analyte identification requirement discussed previously in Section 8.1.4 applies also to semivolatile analyses.

8.3 Gas Chromatography (GC), High Performance Liquid Chromatography (HPLC), Ion Chromatography (IC)

8.3.1 General

These analysis techniques are grouped together because they share two fundamental characteristics. First, they depend upon chromatography to separate the analytes of interest from other sample components. Second, these separate analytes are

quantitated by a relatively simple detector. SW-846 Method 8000 covers the basic QC principles used for GC; these principles are highlighted in this section. The primary QC concepts of which to be aware are:

- Calibration criteria.
- Retention time criteria.

General QA/QC procedures for these analysis techniques are summarized in Table 8-5.

8.3.2 Calibration

All chromatographic systems are initially calibrated with standards at varying concentrations. The initial calibration serves three purposes: (a) demonstration of linearity over the concentration range; (b) delineation of retention time windows for qualitative identification of analytes in samples; and (c) establishment of the calibration constants for use in the calculation of sample results.

Calibration systems follow either the external standard method or the internal standard method. The external standard method uses the ratio of the response (peak area or peak height) of a standard compound relative to its concentration or mass on the column to calculate a response factor (RF). The internal standard method uses an internal standard (a compound chemically similar to the analytes of interest) added at a fixed concentration to every standard and sample. The relative response factor (RRF) is calculated from the ratio of the response of an analyte to the response of the internal standard related to the ratio of the concentrations of the internal standard and the analyte.

The internal standard method is the method of choice. It compensates for physical variance in sample introduction, such as injection size, solvent effects, and leaking septums. Also, its retention time markers provide a more precise identification of target compounds. However, without a selective detector such as the mass spectrometer, occasionally other sample components interfere with the quantitation of internal standards. In these cases, the permit applicant should provide technical justification in the TBP or QAPjP for using an HPLC, GC, or IC procedure without an internal standard, or the data should not be accepted.

All initial and continuing calibration data should be reported. All quality control results (e.g., linearity data) should be calculated, and all data falling outside criteria should be flagged and explained. If calibration criteria were not met, sample results should not be accepted unless the applicant provides an adequate technical justification for use of the data.

8.3.2.1 Initial Calibration

Each analysis type, including stack gas samples, waste feed analysis, and scrubber water analysis, should be discussed in the TBP or QAPjP, along with the expected concentrations of analytes in the waste, the predicted final concentration in samples for analysis, and the calibration range. The calibration range of the instrument should bracket expected concentrations. A minimum of three different concentration levels (preferably five) in the standards as well as a reagent blank should be used to span the calibration range. The reagent blank should contain all the reagents in the standards and no analyte should be detected at a concentration greater than one-fifth the lowest calibration standard. Sample results higher than 120% of the high calibration standard should be diluted into the calibration range. All expected critical regulatory concentrations (e.g., DRE) should be at least 10 times the concentration of the lowest standard to ensure reliable detection and quantitation.

Initial calibration can be used to demonstrate the linearity of the analytical system in two ways. First, the relative standard deviation of the RRF for any analyte calculated from all standards analyzed for initial calibration must be less than 20%. Sample results are calculated from the average RF or RRF. Alternatively, a plot of the response (or response relative to the internal standard) vs. the concentration of the compound in the standard must yield a linear correlation coefficient greater than 0.995. Sample results in this case should be calculated using the linear regression equation that fits the calibration data.

Most calibrations for trial burn analysis are linear by nature. However, some calibration systems are non-linear. For these systems, an acceptance criterion for initial calibration must be established. This criterion could be the correlation coefficient for a polynomial fit of the standard data, or it could be the relative error of values for the calibration standards calculated from the mathematical fit of the standard data. The key issue is that a criterion for initial calibration must be established.

The accuracy of this calibration should be verified by a calibration check standard that includes all analytes. This standard should be prepared independently of calibration standards and, ideally, from EPA reference solutions. The observed concentrations of these standards should fall within 75% to 125% of the expected values. If any calibration criteria have not been met, the problem should be rectified before sample analysis progresses. If automated equipment is being used, samples should be reanalyzed if the subsequent data analysis shows that initial calibration did not pass criteria.

Table 8-5. Summary of QA/QC Procedures for GC/HPLC and IC Determinations

Quality parameter	Method of determination	Frequency	Target criteria
Analysis type	Recommend internal standard	Added to every standard and sample	NA
Calibration-initial	Must bracket expected sample concentrations	Each matrix type	NA
	Minimum of three standards Generation of RRF or RF	At least once	Correlation coefficient for linear plot < 0.995. Relative standard deviation for average < 20%.
	Blank	Once following calibration	One-fifth of lowest standard response
Calibration-initial-accuracy	Calibration check standard	Once following calibration	85% to 115% of expected concentration
Calibration-continuing	Continuing calibration standard	Beginning and end of analysis period and once every 10 samples	85% to 115% of expected concentration
	Continuing calibration blank	Beginning and end of analysis period and once every 10 samples	One-fifth of lowest standard
Qualitative identification	Retention time	Every sample	Must be within three standard deviations of average calibration relative retention time
Sample validation	Internal standard area	Every sample	Must be within 75% to 125% of area in last calibration standard

8.3.2.2 Daily or Continuing Calibration

Once the linearity of the measurement system has been verified, calibration standards should be analyzed regularly to verify that the system stays in calibration. A standard should be analyzed at the beginning and end of each analysis period and after every 10 samples. The observed concentration of each analyte in this check standard should be within 75% to 125% of the theoretical concentration. The calibration level for continuing calibration should be chosen to meet either the decision level of the analysis (e.g., sample concentration when 99.99% DRE was achieved) or the level which best tests the accuracy of the measurement system (e.g., high level standard for GC/ECD analysis). All samples must be bracketed by two successful calibrations, one before sample analysis and one after. If the continuing calibration criteria have not been met, the analytical problem should be rectified and all samples since the last acceptable calibration should be reanalyzed. Sample results obtained from an analytical system in which daily calibration was not done or did not meet criteria should not be accepted unless the applicant supplies an adequate technical justification for use of the data.

A reagent blank should also be analyzed at the same frequency as the continuing calibration standard as a check on any possible contamination in the analytical system. In general, no analyte concentration greater than one-fifth the lowest calibration standard should be detected in the blank.

8.3.3 Qualitative Identification

GC, HPLC, and IC generally rely upon detectors which are not specific enough to positively identify analytes. The retention of the analyte on the chromatographic column or its retention relative to an internal standard provide some identification. Although this method is inferior to the specific identification provided by the mass spectrometer, identification by retention time can be sufficient for incineration analyses. These methodologies have a greater possibility of obtaining an incorrect positive identification, and for cases in which interference with chromatographic peaks may occur, the amount of a POHC can be overestimated.

Initial calibration data should be used to calculate the average retention time (or relative retention time for internal standard methods). All peaks within three standard deviations of this average are identified as the analyte. Every continuing calibration standard must be within the current retention time window; however, the absolute retention time can be updated when a continuing calibration standard is analyzed. In chromatographic systems for which there is very little measurable difference in retention times, three other options exist:

- Use of ±5% of the average retention time.
- Inclusion of all the continuing calibration standards analyzed during the project to provide more variability in the retention time and thus a larger retention time window.

- Use of a spike confirmation technique. All samples are first analyzed using one of the other techniques for identification of the analytes, then each sample is spiked with the analyte at a level twice the approximate sample level. The spike chromatogram must exhibit one peak in the retention time window for confirmation of analyte identity. If two peaks are observed in the spike sample chromatogram, no analyte is present.

Irrespective of which method is used for identification, the spike confirmation technique should be used for any sample in which identity criteria are suspect due to interference peaks (poor separation of analytes from other sample components) or for samples in which the identification is marginal. The topic of qualitative identification must be addressed in the QAPjP.

8.3.4 Sample Validation

For analysis using an internal standard, an additional quality control check is available. The internal standard area for each sample should be 75% to 125% of the area observed in the last continuing calibration standard. If this criterion has not been met, the sample should be reanalyzed. If still not met, the problem should be investigated and any acceptance of sample results should be accompanied by technical justification by the applicant.

8.4 Metals Determinations

8.4.1 General

Atomic spectroscopy is used for metals detection and quantitation. SW-846 Methods 7000 and 6010 discuss the basic QC principles involved. These principles are outlined and amplified in this section. The most important QC procedures of which to be aware are:

- Calibration of the analytical system.
- Determination of accuracy or matrix effects using calibration check standards and spiked samples.
- Determination of precision by multiple analysis of samples.

8.4.2 Initial Calibration

All atomic spectroscopy instruments are calibrated daily with standards at varying concentrations. The calibration serves two purposes: (a) demonstrating linearity over the concentration range; and (b) establishing the calibration constants used in the calculation of sample results.

As discussed in previous sections, the TBP or QAPjP should present all analysis types, including stack gas samples, waste feed analysis, and scrubber water analysis, along with the expected analyte concentrations in the waste, the final concentration predicted in samples for analysis, and the calibration range. The calibration range of the instrument should bracket those expected concentrations. All expected regulatory critical concentrations (e.g., DRE) must be at least twice the concentration of the lowest standard to ensure reliable detection and quantitation. In general, a minimum of three different concentration levels in the standards plus a reagent blank should be used to span the calibration range. Some spectrometers are designed to require only a blank and one standard for calibration. Sample results higher than the high calibration standard should be diluted into the calibration range. The reagent blank should contain all the reagents in the standards; no analyte should be detected at a concentration greater than one-half of the lowest calibration standard. For inductively coupled plasma (ICP) analysis, a reagent blank analysis should follow the initial calibration.

Initial calibration must demonstrate the linearity of the analytical system for all analytes. A plot of the response (absorbance units) vs. the concentration of the compound in the standard must yield a linear correlation coefficient greater than 0.995. Sample results should be calculated using the linear regression equation that fits the calibration data. For instruments using only two concentration levels, the correlation coefficient cannot be calculated.

Accuracy of initial calibration: For all analyses, the accuracy of the calibration should be checked by the analysis of a calibration check standard obtained from another source and prepared independently of those used for instrument calibration. This check standard should be analyzed following the calibration curve and before sample analysis. This check standard should give an observed concentration within 90% to 110% of its expected value.

For ICP analysis, Method 6010 requires that the highest standard be reanalyzed immediately following initial calibration; the observed concentration must be within 95% to 105% of its expected value. Next, the above calibration check standard should be analyzed and should be within 90% to 110%. Following this standard, analyze an interference check standard; the observed concentration must be within 80% to 120% of the expected value. The interference check standard should be designed to mimic the interfering analytes found in the sample matrix type and can contain elements such as Al, Ca, Fe, Na, Zn, Ba, Ca, Mg, Mn, Cr, Cu, and Ni. A quick ICP survey of one

sample from each matrix type will assist in choosing the appropriate analytes.

If any calibration criteria have not been met, the problem should be rectified before sample analysis proceeds. If automated equipment is being used, samples should be reanalyzed if subsequent data review shows initial calibration does not fall within criteria.

8.4.3 *Daily or Continuing Calibration*

Once linearity of the measurement system has been verified, a calibration standard should be reanalyzed on a regular basis to verify that the system maintains its calibration. A standard should be analyzed at the beginning and end of each analysis period and after every 10 samples. The observed concentration of each analyte in this standard must be within 80% to 120% for GFAA and CVAA, and 90% to 110% for ICP of the theoretical concentration. The concentration for continuing calibration should be around the middle of the calibrated concentration range. All samples must be bracketed by two successful calibration checks, one before sample analysis and one after. If the continuing calibration criteria have not been met, the analytical problem should be identified and rectified, and all samples since the last acceptable calibration check should be reanalyzed.

A reagent blank should also be analyzed at the same frequency as the continuing calibration standard. No concentration greater than one-half the lowest calibration standard should be detected in the analyte blank. For ICP analysis the reagent blank value must be within three standard deviations of the average values for the blanks analyzed during initial calibration. If blank values do not fall within these criteria, the state of the instrument should be investigated. Low level samples analyzed since the last acceptable blank analysis should be reanalyzed if necessary.

8.4.4 *Summary of QC Procedures*

A summary of the QC procedures for metals discussed in the previous sections is presented in Table 8-6. Each quality parameter involving initial and continuing calibration should be calculated and reported in the TBR, and acceptance of sample results should be justified by the applicant. If QC procedures have not been carried out or the criteria have not been met, sample results should be rejected unless sufficient technical justification has been provided by the applicant. The QC parameters should be calculated and available for review along with the raw data supporting the analyses.

Table 8-6. Summary of QA/QC Procedures for Metals Determinations

Quality parameter	Method of determination	Frequency	Target criteria
Calibration-initial	Must bracket expected sample concentrations	Each matrix type	NA
	Minimum of three standards generating a standard curve[a]	At least once	Correlation coefficient of linear plot > 0.995
	Blank	At least once	Must be beneath one-fifth of lowest standard
Calibration-initial-accuracy	Analysis of a calibration check standard	At least once	90% to 110% of expected value
	For ICP, reanalysis of high level standard	At least once	95% to 105% of expected value
	For ICP, analysis of interference standard	At least once	80% to 120% of expected value
Calibration-continuing	Analysis of a middle level standard	Every 10 samples	90% to 110% of expected value for ICP; 80% to 120% of expected value for GFAA and CVAA
Calibration-continuing	Analysis of a calibration blank	Every 10 samples	Less than one-half of the lowest calibration level or (ICP only) within three standard deviations of average blank

[a]Some ICP spectrometers by design require only a blank and one standard for calibration.

Chapter 9

Specific Quality Control Procedures for Continuous Emission Monitors

The instrumental analyzers used for continuous monitoring of emissions are the focus of this chapter, with emphasis on carbon monoxide and oxygen measurements. Guidance is presented on quality assurance objectives and specific quality control procedures important to the decision-making process.

Instrumental analyzers are used to continuously monitor the concentrations of carbon monoxide in incinerator emissions. In some cases, analyzers are also used to measure oxygen. Many types of analyzers are available commercially from different manufacturers. However, the basic quality objectives are essentially the same for the different types of monitors. Calibration procedures used for each instrument will vary, and specific procedures typically are specified by the manufacturer.

The QA/QC procedures associated with the trial burn include:

- Conducting an initial performance test.
- Conducting calibration checks during the trial burn.
- Obtaining complete data records.

9.1 Carbon Monoxide Monitors

9.1.1 Initial Performance Test

Soon after installation of a Continuous Emission Monitoring System (CEMS), the acceptability of the system should be evaluated by conducting a performance specification test. This test is performed upon installation to determine if the CEMS is capable of providing adequate data. The draft procedures for conducting the performance test and the criteria for determining if the CEMS performance is acceptable are available in Appendix A of Reference 10.

The performance specification test on the CEMS must be conducted and passed before the trial burn is conducted. The performance specification test criteria are summarized in Table 9-1. Each of these criteria is discussed in detail in the Performance Specifications.[10] They are discussed only briefly here.

Table 9-1. Carbon Monoxide Performance Test Criteria

Criterion	Acceptable limit
1. CEMS measurement location	Representative sample obtained
2. Calibration drift (precision)	≤ 5% full scale measurement
3. Calibration error (accuracy)	≤ 5% full scale measurement
4. Response time	≤ 1.5 min
5. Relative accuracy	≤ the greater of: 20 ppm or 10% of reference method value, whichever is greater

The location of the CEMS sampling point is important to ensure obtaining a representative sample. Recommendations for acceptable sampling locations are contained in the Performance Specifications. The primary consideration is that a representative sample be obtained. However, the location should also be accessible to allow for routine maintenance.

Both the calibration error and calibration drift of the instrument must be checked. Both specifications are presented as a percentage of the instrument's full-scale measurement range span values. For example, the acceptable calibration drift is ≤5% full scale; for an instrument with a 100-ppm full-scale range, the acceptable drift is ≤5 ppm. For an instrument with a 2,000-ppm full-scale range, the acceptable drift is ≤ 100 ppm. The instrument span range chosen will determine the absolute level (ppm) of calibration error that is considered acceptable. Consequently, the span value chosen for the CEMS is important and should be consistent with the monitoring objectives. Recommended span values are presented in the Performance Specifications.

The calibration error should be checked at low, mid, and high levels of the instrument range to ensure that the instrument is capable of accurately measuring over the entire range; typically this check is conducted only once during the performance specification test. The calibration drift test is

conducted over a one-week period to evaluate the precision of the measurement. A calibration check is conducted every 24 hours using the same standard, and the difference between daily measurements is evaluated. Calibration drift is calculated and used in evaluating whether the CEMS is capable of maintaining calibration over an extended period.

The response time test simply measures the lag time required for the CEMS to respond to a change in concentration level. Excessive response lag times are not desirable since the objective of continuous monitoring is to be able to obtain real time data to use in process control.

A relative accuracy test using a reference method (RM) is the only independent measure of the accuracy of the CEMS data. An RM is used to measure the CO concentration, and the results of the RM measurements are compared to the CEMS data. The criterion for acceptance is that the CEMS data not deviate by more than 20 ppm or 10% of the RM results,* whichever is greater (i.e., at levels greater than 200 ppm, a variation of 10% is allowed).

In conducting the CEMS performance test, the entire system must be evaluated in its normal operation state. For example, the sampling line, sample conditioning system, and analyzer should all be checked, not just the analyzer. However, conducting the tests using the entire sampling line and/or conditioning system may not be practical because of the amount of calibration gas which may then be required to purge the system. In such cases, the integrity of the sampling line may be checked at the beginning of the performance test by some other means, such as a leak test (e.g., plugging the sampling line and seeing if a vacuum can be generated). Also, any problem within the sampling line or conditioning system will be identified, since the CEMS will then fail the test of comparison to the RM values.

If the CEMS fails the performance test, then corrective action should be taken and the parts of the test that the monitor failed should be repeated. If major modifications are made to the system, the entire performance test may need to be repeated; judgment must be used in determining what parts of the test must be repeated. For example, if the sample flow rate has been increased to reduce response time, no effect on calibration is likely. In this case, only the response time test need be repeated. On the other hand, if the primary electronic circuit boards have been replaced and the instrument recalibrated to reduce calibration drift, the calibration error should also be rechecked and the relative accuracy test repeated.

*Refer to Performance Specifications[10] for actual calculation of variance.

9.1.2 Calibration

The CEMS is first calibrated according to the manufacturer's instructions prior to the initial performance test. After the initial performance test, calibration must be checked on a routine basis, and if the calibration has drifted outside allowable limits, adjustments must be made.

The recommended calibration check is to challenge the monitor with both a low-level standard (0 to 20% of full scale) and a high-level standard (80% to 100% of full scale). Although two standards are preferable, a single high-level standard is sometimes substituted. During the trial burn, calibration checks should be conducted daily to confirm that the instrument remains calibrated.

9.1.3 Data Records

Calibration records sufficient to evaluate performance are required. The data recording system for use during normal operation should also be used for the performance test and trial burn. When both data loggers and chart recorders are used, the recorded values from each device should be compared during calibration to ensure their consistency.

Typically, either a data logger or a chart recorder, or both, are used to record real-time CEMS data. Sometimes, an integrator is used to average the data as it is collected, and the time-weighted average (e.g., hourly) is recorded. Minimum data requirements include recording a value every minute by recording the measured value or updating the rolling average (e.g., a 1-minute rolling hourly average). When multiple data recorders are used, one recording medium must be chosen as the source of the official record. The designated device should be used as the data source throughout the trial burn.

During the trial burn, the minimum and maximum values obtained also are of interest, and the recording system should be capable of storing these values. If a real-time chart recorder is used, the minimum and maximum values can be obtained from the chart recorder. If a data logger is used, the data logger should be capable of storing the minimum and maximum values (before averaging).

If a data logger system is used and the data logger is programmed to calculate a CO concentration normalized to a standard oxygen level (e.g., 7% O_2), provisions should be made during the performance test and routine calibrations so that adequate and sufficient data will be obtained to be able to evaluate

the calibration results. Two approaches can be used. The first approach is to use calibration gases which include a known oxygen concentration (such as 7% oxygen); the measured normalized value can then be checked against the calculated normalized value of the standard gas mixture. The other approach is to ensure that the data logger system is capable of also providing the uncorrected (not normalized) CO data so that these data can be evaluated against the calibration standard.

Calibration records should be maintained so that the calibration history is available for review. Calibration records should include:

a. Calibration values on the data logger and/or chart record.

b. Calibration standards (e.g., cylinder gas identification and manufacturer's certified value, gas filter cell identification, and certified value).

c. Documentation of values obtained during calibration checks.

d. Calibration log book (including a record of the date and time of any calibration adjustments made or changes in the standards used).

A maintenance log book identifying all routine and nonroutine maintenance on the CEMS should also be kept and cross-referenced to the calibration log book when maintenance procedures require subsequent recalibration.

9.1.4 *Quality Assurance Objectives and Assessment*

The quality assurance objectives for a CO CEMS and the means for assessing data quality are summarized in Table 9-2. Accuracy and precision objectives are presented as a percent of the full-scale range of the instrument. Some judgment should be used in determining whether the calibration accuracy and precision values are sufficient. For example, if the instrument's full-scale range is 100 ppm, then the calibration error should be ≤ 5 ppm (5% of 100 ppm). If a calibration check indicates a calibration drift of 8 ppm, there is no need for concern if the facility is operating consistently at a CO level of 20 ppm and the regulatory CO standard is 100 ppm. However, a trend in calibration drift or an excessive daily drift should be corrected. Proper calibration records must be maintained so that the data can be evaluated.

9.2 Oxygen Monitors

9.2.1 *Introduction*

An oxygen monitor may be used in conjunction with a CO monitor as a diluent monitor; i.e., to obtain the data necessary to adjust the measured CO concentration to a reference concentration (such as 7% oxygen). Consequently, the same quality control procedures that are used for CO monitors apply to oxygen monitors. These are:

- Initial performance test.
- Calibration checks during the trial burn.
- Complete data records.

9.2.2 *Initial Performance Test*

The initial performance test for oxygen monitors is conducted in conjunction with the performance test for CO monitors, using the same approach. The specification procedures for oxygen monitors are summarized in Table 9-3

When the oxygen monitor is used as a diluent monitor, the sampling location of the oxygen monitor should be adjacent to the sampling location of the CO monitor so that the same portion of gas flow is measured.

For the relative accuracy test, the performance of the combined CO/O_2 system can be evaluated in lieu of separate evaluations. In other words, the relative accuracy criterion can be evaluated using the CO concentration normalized for O_2 and comparing it to the acceptable limit for CO monitors rather than evaluating the measured CO and O_2 separately.

9.2.3 *Calibration*

The oxygen monitor should be calibrated according to the manufacturer's instructions prior to conducting the initial performance test. The calibration must be checked on a routine basis; and if the calibration has drifted outside allowable limits, adjustments must be made. The recommended calibration check procedure is to challenge the monitor with a low-level standard (0% to 20% of full scale) and a high-level standard (80% to 100% of full scale) at routine intervals. Although use of two standards is preferable, a single high-level standard is sometimes used.

During the trial burn, calibration checks should be conducted daily to confirm that instrument calibration has not drifted.

9.2.4 *Data Records*

The requirements for data records for oxygen monitors are the same as for CO monitors (see Section 9.1.3).

9.2.5 *Quality Assurance Objectives and Assessment of Results*

The quality assurance objectives for oxygen monitors are summarized in Table 9-4. Assessment results are similar to those for CO monitors as discussed in Section 9.1.4.

Table 9-2. Quality Assurance Objectives for CO Monitors

Quality parameter	Method of determination	Frequency	Criteria
Accuracy	• Multipoint calibration • Relative accuracy test	Performance test prior to TB Performance test prior to TB	≤ 5% FS[a] ≤ 20 ppm or 10% of RM[b] value (whichever is greater)
Precision	• Calibration checks	Performance test prior to TB Daily check during TB	≤ 5% FS ≤ 5% FS
Documentation	• Data records	Ongoing	• Complete calibration records for performance specification test • Calibration records for daily checks • Complete data records for trial burn 1-min reading maximum/minimum values

[a]FS = full scale.
[b]RM = reference method.

Table 9-3. Oxygen Performance Test Criteria

Criterion	Acceptable limit
1. CEMS measurement location	Adjacent to CO monitor (if to be used as diluent monitor)
2. Calibration drift (precision)	≤ 0.5% O_2
3. Calibration error (accuracy)	≤ 0.5% O_2
4. Response time	≤ 1.5 min
5. Relative accuracy	≤ 1.0% O_2 or 20% of reference method value, whichever is greater

Table 9-4. Quality Assurance Objectives for Oxygen Monitors

Quality parameter	Method of determination	Frequency	Criteria
Accuracy	• Multipoint calibration • Relative accuracy test	Performance test prior to TB Performance test prior to TB	≤0.5% O_2 ≤ 1% O_2 or 20% of RM[a] value (whichever is greater)[b]
Precision	• Calibration checks	Performance test prior to TB Daily check during TB	≤0.5% O_2 ≤0.5% O_2
Documentation	• Data records	Ongoing	• Complete calibration records for PST[c] • Calibration records for daily checks • Complete data records for trial burn: (a) 1-min readings (b) maximum and minimum values

[a]RM = reference method.
[b]Performance test criteria for O_2 may be omitted if performance is evaluated using normalized CO measurement.
[c]Performance specification test.

Chapter 10
Specific Quality Control Procedures for Process Monitors

Guidance in establishing quality control procedures for process monitors is offered in this chapter. Although instrument types and parameters vary widely across facilities, the general topics of calibration and operational checks, data records, and quality assurance objectives must be addressed in every trial burn plan. The discussion in this chapter, therefore, focuses on general guidance, not specific parameters and instruments.

10.1 Introduction

A variety of process operating parameters are monitored during trial burns to provide the data necessary for developing permit limits. Some of these parameters are applicable to all trial burns; others are specific to a given incineration facility. Many of the parameters can be monitored with a wide variety of instrument types; e.g., many instruments are available to monitor waste feed rates. Some of the quality control procedures needed for the trial burn are similar to those discussed in Chapter 11 for continuing operations.

10.2 General QC Procedures

This section covers calibration and operational checks, data records, and quality assurance objectives.

10.2.1 Calibration and Operational Checks

Prior to a trial burn, all process monitors and instruments used to record process data should be calibrated, if appropriate, and checked for proper operation. Calibration procedures vary widely, not only with the type of instrument, but also among manufacturers. Instrumentation should, however, be calibrated according to manufacturer's recommended procedures and meet manufacturer's specifications. Many instruments are received from the manufacturer already calibrated. In that case, written records should be available showing the procedures and results of that calibration.

Prior to the trial burn, all process monitors should be checked under the incinerator operating conditions expected during the trial burn. The automatic waste feed cutoff system should be included in these checks. These checks should include visual inspection to ascertain that the instruments are functioning and that values obtained for the parameters are within range. Other possible checks include comparison of readings from redundant units (e.g., thermocouples), back-up instruments (e.g., CO monitors), or alternative methods. For example, the reading from an installed flow meter may be checked against the change in a feed tank level for an approximate comparison. Instruments that are subject to drift on a short-term basis should be recalibrated throughout the test period either before each test run or on a daily basis.

10.2.2 Data Records

Adequate data records should be maintained for all process monitors to evaluate their functioning and performance. These records should document the procedures and results of calibrations and operational checks, as well as the specifications the monitors must meet. The data records should reflect the units and format specified in the TBP. A log book with records of all routine and nonroutine maintenance should also be kept. Maintenance records should be cross-referenced to the associated calibrations and operational checks.

10.2.3 Quality Assurance Objectives

The QA objectives for process monitors are affected by the actual capabilities of each monitor as well as by the method of determining the objective. For example, a calculation of DRE is based not only on analysis results (e.g., constituent concentration) and sampling criteria (e.g., sample volume), but also on the waste feed rates that may be obtained from process monitors.

Actual QA objectives for monitored parameters will vary depending on the type of instruments used and the individual capabilities of the specific manufactured unit. Instrument manufacturers may state specifications as follows: temperature (thermocouples), ±0.5%-0.75% accuracy; gas velocity measurements, ±3% precision; and mass flow meters, ±0.4% accuracy. Such values may be of limited usefulness to the permit writer in selecting data quality objectives.

For example, the specification may not be valid for the instrument as installed for the specific application, no alternative method may exist for verifying the specification, or the specification may exceed needed accuracy. For a thermocouple reading of 2000°F, a ±2.5% accuracy may be adequate (i.e., ±50°F).

Thus, QA objectives must be based upon the instrument's capabilities, the ability to measure tolerance values, and the decisions that will be based upon the measurement.

Chapter 11

QA/QC Associated with Permit Compliance and Daily Operation

In this final chapter of the handbook the RCRA permitting program is outlined in terms of achieving and maintaining acceptable performance. Also, procedures for corrective action and record keeping requirements are described.

The RCRA permitting program defines the acceptable performance of a permitted incinerator in terms of specific operating limits that are continuously monitored by facility operators. Since these operating limits are the primary indicators of incinerator performance, monitoring procedures and instrumentation must function reliably on a continuing basis. Permits should be very specific in identifying requirements for the continuous monitoring, testing, calibration, and record-keeping activities that are associated with the demonstration of compliance. Each permit-limited condition has associated monitoring/testing/calibration procedures and record-keeping systems.

Major categories of permit-limited conditions include:

- Waste feed limits.
- Gaseous emission limits.
- Other key operating parameters for the combustion chambers and air pollution control equipment.

The measurements associated with waste feeds, for example, contribute to the performance of the automatic waste feed shutoff system, which is an essential safeguard in case an incinerator's operations deviate from allowable conditions.

Adequate documentation of continuous monitoring requirements in the permit provides three major benefits:

1. Establishes in advance the minimum requirements for measurement quality.
2. Provides specific criteria to facility owners/operators.
3. Establishes enforceable specifications for EPA/state control agency staff who conduct subsequent compliance inspections.

The types of specifications that a permit writer should consider for inclusion in RCRA incinerator permits are discussed in the following sections. These specifications are not a substitute for a thorough preliminary review effort to evaluate the adequacy of each proposed key monitoring instrument. Such a review should occur early in the permit review process and address such key issues as:

- Appropriate technique and equipment type.
- Adequate operating range, response time, precision, and accuracy.
- Proper location of sensor.
- Adequate readouts/data recording.

11.1 Routine Procedures for Monitoring and Testing/Calibration

11.1.1 Waste Feed Limitations

Permits will typically limit the waste feed in terms of allowable feed rates and allowable waste feed characteristics. Both types of limits may be used to calculate loading rate limits for such parameters as chloride, metals, ash, and heat input.

11.1.1.1 Feed Rate Monitoring

Waste feed rates for gases, liquids, sludges, and solids typically are determined by such diverse devices as differential pressure meters, velocity meters, mass flow meters, volumetric methods, level or stationary weight indicators, and conveyor weighing systems.

At least semiannually, the calibration of feed rate monitoring devices should be checked and, if warranted, recalibrated. Applicable calibration methods, depending on the device, may include:

- Using standard weights or other known weights/flows.
- Comparing readings with duplicate or alternative devices.
- Using manufacturer's methods.
- Returning the instrument to the manufacturer for recalibration.

A more limited form of "calibration" is a zero adjustment having a negligible impact on full-scale readings. The specified calibration method should be applicable to the allowable range of feed rates specified in the permit.

Deviations from a semiannual calibration may be appropriate in two cases. First, if a waste feed is abrasive or is otherwise potentially damaging to the feed rate sensing device, recalibration should be required on a more frequent basis. Second, if a device is very reliable but is also very difficult to calibrate in situ (e.g., some mass flow meters), a less frequent calibration (e.g., factory calibration) may be appropriate. In such cases, alternating the use of two instruments may be an option.

The permit writer should clearly identify the required calibration method and frequency in the permit. The calibration method should be specified as thoroughly as possible.

11.1.1.2 Waste Feed Characteristics

The permit should specify the frequency of reanalysis, the parameters to be determined, and the documentation requirements associated with continuing waste characterization. As a minimum, the typical frequency requirement is annual reanalysis and additional reanalysis whenever waste characteristics may have changed (e.g., as a result of process modifications). Some facilities may be required to analyze waste feeds for selected parameters on a batch basis.

Depending on the issues associated with a particular incinerator, waste characterization may include:

- Appendix VIII constituents.
- Compounds prohibited in the feed (PCBs, etc.).
- Chloride and ash content.
- Viscosity.
- Heating value.
- Other characteristics as applicable.

Documentation of the waste characterization should include, at a minimum:

- Date sample was obtained.
- Sampling method used to obtain a representative sample.
- Laboratory performing each analysis.
- Sample preparation and analysis methods.
- Date analyses were performed.
- Results (value and units).
- Analytical QC results and assessment of data quality.
- Signature of generator representative.

Additional requirements associated with the waste analysis plan (in the permit application) may also apply and should be summarized or referenced within the permit. If practical, waste analysis and associated QC should be similar to that used in the trial burn.

11.1.1.3 Calculation of Compliance--

If some permit limits are expressed as loading rates (e.g., total chloride input, total heat input), a calculation is needed to demonstrate compliance with these limits. The calculation may involve the multiplication of a concentration or similar value (mg/L, Btu/lb) and a flow rate (ton/h, gal/min, etc.) with appropriate conversion factors to yield a loading rate (lb/h of chloride, MBtu/h, etc.).

Permits should require periodic calculations of compliance with these categories of operating limits. Calculations may be continuous, based on automatic computerized calculations using computerized analysis results, or less frequent based on manual calculations. Calculations must be performed at least once a week by selecting an operating point that represents approximately the highest waste feed rate of the week. Continuous calculations should be displayed on computer log sheets with other monitored parameters. Manual calculations should be recorded in operators' log files, and within a special file as part of the records inventory.

11.1.2 Continuous Emission Monitor Systems (CEMS) for Carbon Monoxide and Oxygen

The initial performance test discussed in Chapter 9 is used to evaluate the performance of the CEMS when first installed. A QC program is required to ensure that the CEMS continues to operate properly and that

reliable results continue to be obtained. The primary components of a QC program for CEMS are:

- Routine calibration checks.
- Preventive maintenance program.
- Performance tests.
- Record keeping.

The routine QC procedures are summarized in Table 11-1.

11.1.2.1 Calibration Checks

The routine calibration check is the primary QC procedure for ensuring accurate data on an ongoing basis. Manufacturer's procedures should be followed. The check should be made daily unless performance data indicate less frequent calibration is sufficient. The recommended calibration check is to challenge the monitor daily with a low-level standard (0% to 20% full scale) and a high-level standard (80% to 100% full scale). Although it is preferable to use two standards, a single mid-level or high-level standard is sometimes substituted. Corrective action consists of adjusting the calibration when it has drifted outside the allowable limit. When the CEMS includes a diluent monitor for normalizing the CO data, a combined CO/O_2 standard may be used to evaluate the monitor calibration on a normalized CO concentration basis.

11.1.2.2 Record Keeping

Record-keeping requirements should include: (a) all calibration and calibration check records; (b) maintenance records; and (c) data records.

The results of the daily calibration checks should be recorded automatically by the chart recorder or data logger system as part of the normal data recording system. A calibration log book should be maintained and should include:

1. Chronological record of any calibration/ adjustments.
2. Records of the calibration standards, including a unique identifier for each standard and the manufacturer's certified value.
3. Records showing when calibration standards have been replaced.
4. Cross references to any maintenance log book, if calibration problems require maintenance or if maintenance requires recalibration.

A maintenance log of the monitoring system will help identify recurring problems so that a preventive maintenance program can be initiated or modified to address those problems.

Data records sufficient to show compliance with permit conditions must be maintained. Normally, this includes chart records or data logger records showing ppm of CO. Depending upon the permit limits, the CO data may be 1-minute rolling hourly averages or some other permit-limited condition. Normalization to 7% oxygen also may be required.

11.1.2.3 Preventive Maintenance Program

A proper QC program for a CEMS will include preventive maintenance. The preventive maintenance program will be based on manufacturers' recommendations and will include such items as:

1. Checking the integrity of probe and sample line and backflushing as necessary.
2. Checking and maintaining the sample conditioning system; e.g., cleaning or replacing filters.
3. Cleaning optical lens (in situ monitors).
4. Checking operation of recorders and data loggers (e.g., replacing pens, ink, charts, etc.).

The preventive maintenance program should be established by the facility operator and should identify daily, weekly, monthly, and annual maintenance activities. A maintenance log for the CEMS should be maintained.

11.1.2.4 Performance Tests

Performance tests of the monitoring system can be repeated as necessary. Repetition of the relative accuracy test is recommended every 2 years to verify monitoring system performance. If the relative accuracy acceptance criterion is no longer achieved, then the cause of the problem must be determined, corrective action taken, and the performance test repeated. Repetition of the complete performance test or portions of it may be necessary at other times if problems are encountered and if the corrective action taken requires that the monitoring performance be reevaluated. For example, when the fuel cell for an in situ oxygen monitor is replaced, a multipoint calibration should be conducted and the relative accuracy should be checked against a reference method (e.g., Orsat analysis).

11.1.3 Other Monitored Parameters

Proper continuing operation of each monitoring instrument associated with a permit-limited operating condition is a crucial portion of the RCRA incineration program. However, the approach used for continuing

Table 11-1. QA/QC for Routine Operation--CO and O_2 Monitors

Activity	Frequency	Acceptance criterion	Corrective action
• Calibration check	Daily	CO ≤ 0.5% FS[a] O_2 ≤ 0.5% O_2	Adjust calibration
• Record keeping	Daily	• Record calibration results • Record calibration adjustments • Record changes in calibrated standards • Record maintenance activities • Record emissions data per permit requirements	NA
• Maintenance	Daily	Establish preventive maintenance program	
• Performance test Relative accuracy	Every 2 years; more frequently if instrument calibration/repairs warrant	CO ≤ 20 ppm or ≤ 10% RM[b] (whichever is greater) O_2 ≤ 1% O_2 or ≤ 20% RM (whichever is greater)	Replace/repair equipment then retest

[a]Full scale.
[b]Reference method.

calibration checks is not as straightforward for all monitoring instruments as it is for the CO and oxygen monitors. This variety derives from the many designs of monitors and incinerators.

Three examples demonstrate the types of issues facing the permit writer when addressing instrument calibration procedures:

- Thermocouples (used for most of the critical temperature monitoring requirements) are typically compared with duplicate units in situ. Nonfunctioning or suspect malfunctioning units are replaced. Calibration is not an applicable term for thermocouples. The permit writer should require duplicate thermocouples and establish minimum replacement criteria (e.g., when duplicate thermocouples vary by more than 50°F). This ensures the precision of the temperature measurement and keeps the temperature range similar to that in the trial burn.

- An annubar (used to measure gas flow) is typically calibrated in a wind tunnel prior to installation. Indirect monitoring of changes in the calibration factor may be accomplished by using a calibrated pitot tube to obtain an independent measure of velocity. The independent measure is compared to velocity measured by the annubar. Recalibration would require removal of the unit for a repeat test in a wind tunnel.

- Magnehelics (used to measure pressure) may be checked by temporarily replacing the unit with an alternative unit for a calibration check. One example is the use of an inclined manometer connected, if possible, to parallel pressure taps. Malfunctioning units may be adjusted or replaced.

The permit writer should make calibration evaluations on a case-by-case basis. Calibration requirements should include the calibration method, the minimum frequency, an allowable range of variation, and documentation requirements for calibration and maintenance.

11.1.4 Automatic Waste Feed Shutoff System

RCRA requires that incinerators be equipped with a system that automatically stops the flow of waste feed into the incinerator whenever certain key operating conditions (e.g., temperature, combustion gas velocity) deviate from allowable levels. The automatic waste feed shutoff system (AWFSO) includes: sensing devices for each key condition; transmitters that send the signals from sensing devices to a receiver; a receiver/signal processor that evaluates the signals and sends a shutoff signal when limits are exceeded; and a shutoff device that effectively shuts down the flow of waste materials going into the incinerator. The AWFSO must operate properly on a continuous basis.

The permit writer should specify the following in the permit:

- Required frequency of testing the AWFSO.
- Format of the test.
- Any special operating considerations.

RCRA regulations [40 CFR 264.347(c)] require a weekly test (or a monthly test if the applicant provides justification). Testing less frequently than once a week should be allowed only in special cases. Records of required periodic tests must be maintained.

The permit writer should specify the format of the test in terms of the parameters that trigger the AWFSO system. Some complex incineration facilities may have

more than a dozen parameters that can trigger automatic waste shutoff. The permit writer should specify how all triggering parameters are to be included in the AWFSO tests on a periodic basis. Options may include testing at least one parameter a week on a rotating basis, or weekly testing that includes all triggering parameters over a month's time. Records must be maintained to document compliance with shutoff limits and any specified time restrictions associated with the excursions that trigger the system.

For some systems, permit writers may consider restrictions in the testing of the AWFSO in response to the potential for the release of uncontrolled emissions as a result of such tests. Testing for selected parameters may be appropriate while the facility is operating with nonhazardous feed material. Simulated shutoff conditions may be appropriate for some portion of the AWFSO testing plan instead of creating actual shutoff conditions. Examples include: (1) the use of a high CO standard gas to trigger a shutoff; or (2) overriding actual readings with keyed-in computer override values to trigger a shutoff.

11.2 Record Keeping

Incineration facilities are required to maintain detailed records to document compliance with permit conditions. These records are important for compliance inspections conducted by EPA and state agency staff. The required records can be reviewed by inspectors to demonstrate recent and past operations at the facility. Permit writers should be very specific in each permit in defining the following:

- Which records must be maintained?
- What is the content and format of the records?
- What is the frequency of inputs to each type of record (continuous, weekly, etc.)?
- How are the records stored for ease of access?

In general, documentation maintained by the facility includes:

- Records associated with continuously monitored operating parameters (e.g., strip charts, computerized logs, operator logs).
- Records associated with waste characterization.
- Records associated with the characterization and handling of by-product wastes.
- Records associated with daily (and additional) inspections performed by facility staff.
- Calibration and maintenance logs.
- Automatic waste feed shutoff system records (documentation of shutoff incidents and system tests).
- Records of facility-specific issues (e.g., emergency vent stack openings, waste acceptance, blending, etc.).

The content and format of each record should be defined in the permit in sufficient detail to ensure that all needed information will be available to inspectors. For example, records of calibrations should document date, calibration method, initial reading, and final reading. Specific requirements for strip charts may include: (a) minimum chart speed, (b) minimum labeling of date and time (e.g., minimum daily manual labeling by the operator), and (c) use of different ink colors when the same strip chart is used for more than one parameter. The permit should clearly identify the minimum frequency of inputs to records. Examples include an update each minute of a calculated 60-minute rolling average for CO concentration and semiannual calibration records of a flow meter.

Ideally, all records should be stored for ease of access for inspections. A permit writer can assist the inspectors by permit requirements such as the following:

- All records maintained in one central location.
- A daily master log (filed by month) that cross-references all permit-required activities completed during each day.
- Separate detailed files maintained for each type of required activity (e.g., waste characterization, operating strip charts, calibration of instruments, etc.). Files to be cross-referenced with the daily master log.

Chapter 12
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Appendix A
VOST Calibration

Note: These procedures are taken from Reference 12 and are presented to give added detail on sampling train component calibration not presented in Method 0030.

1.0 Calibration of Apparatus Used in VOST

Calibration of the apparatus is one of the most important functions in maintaining data quality. All calibrations should be recorded on standardized forms and retained in a calibration log book.

1.1 Metering System

1.1.1 Wet Test Meter

The wet test meter is used to calibrate the dry test meter; it also must be calibrated and have the proper capacity. The wet test meter should have a capacity of at least 3 L/min. No upper limit is placed on the capacity; however, a wet test meter dial should make at least one complete revolution at the specified flow rate for each of the three independent calibrations.

Wet test meters are calibrated by the manufacturer to an accuracy of ±0.5%. Calibration of the wet test meter must be checked initially upon receipt and yearly thereafter.

The following liquid positive displacement technique can be used to verify and adjust, if necessary, the accuracy of the wet test meter to ±1%.

1. Level the wet test meter by adjusting the legs until the bubble on the level located on the top of the meter is centered.

2. Adjust the water volume in the meter so that the pointer in the water level gauge just touches the meniscus.

3. Adjust the water manometer to zero by moving the scale or by adding water to the manometer.

4. A description of the set up of the apparatus can be found in Figure 2-1 of Section 3.5.2 of reference 12.

   a. Fill the rigid-wall 5-gal jug with distilled water to below the air inlet tube. Put water in the impinger, or saturate and allow both to equilibrate to room temperature (about 24 h) before use.

   b. Start water siphoning through the system, and collect the water in a 1-gal container, located in place of the volumetric flask.

5. Check operation of the meter as follows:

   a. If the manometer reading is < 10 mm (0.4 in) H_2O, the meter is in proper working condition. Continue to step 6.

   b. If the manometer reading is > 10 mm (0.4 in) H_2O, the wet test meter is defective or the saturator has too much pressure drop. If the wet test meter is defective, return it to the manufacturer for repair unless the defect(s) (e.g., bad connections or joints) can be found and corrected.

6. Continue the operation until the 1-gal container is almost full. Plug the inlet to the saturator. If no leak exists, the flow of liquid to the gallon container should stop. If the flow continues, correct for leaks. Turn the siphon system off by closing the valve, and unplug the inlet to the saturator.

7. Read the initial volume (V_i) from the wet test meter dial, and record on the wet test meter calibration log.

8. Place a clean, dry volumetric flask (Class A) under the siphon tube, open the pinch clamp, and fill the volumetric flask to the mark. The volumetric flask must be large enough to allow at least one complete revolution of the wet test meter with not more than two fillings of the volumetric flask.

9. Start the flow of water and record the maximum wet test meter manometer reading during the test after a constant flow of liquid is obtained.

10. Carefully fill the volumetric flask, and shut off the liquid flow at the 2-L mark. Record the final volume on the wet test meter.

11. Steps 7 through 10 must be performed three times.

The air volume can be compared directly with the liquid displacement volume for two reasons. First, the water temperature in the wet test meter and reservoir has been equilibrated to the ambient temperature. Second, the pressure in the wet test meter will equilibrate with the water reservoir after the water flow is shut off. Any temperature or pressure difference would be less than measurement error and would not affect the final calculations.

The error should not exceed ±1%. Should this error magnitude be exceeded, check all connections within the test apparatus for leaks, and gravimetrically check the volume of the standard flask. Repeat the calibration procedure. If the tolerance level is not met, adjust the liquid level within the meter (see the manufacturer's manual) until the specifications are met.

1.1.2 Sample Meter System

The sample meter system--consisting of the drying tube, needle valve, pump, rotameter, and dry gas meter--is calibrated by stringent laboratory methods before it is used in the field. The initial calibration is then rechecked after each field test series. This recheck requires less effort than the initial calibration. When a recheck indicates that the calibration factor has changed, the tester must again perform the complete laboratory procedure to obtain the new calibration factor. After the meter is recalibrated, the metered sample volume is multiplied by the calibration factor (initial or recalibrated) that yields the lower gas volume for each test run.

Initial calibration. The metering system should be calibrated when first purchased and at any time the posttest check yields a calibration factor that does not agree within 5% of the pretest calibration factor. A calibrated wet test meter (properly sized, with ±1% accuracy) should be used to calibrate the metering system.

The metering system should be calibrated in the following manner before its initial use in the field:

1. Leak check the metering system (drying tube, needle valve, pump, rotameter, and dry gas meter) as follows:

   a. Temporarily attach a suitable rotameter (e.g., an airflow range of 0 to 40 cm^3/min) to the outlet of the dry gas meter, and place a vacuum gauge at the inlet to the drying tube.

   b. Plug the drying tube inlet. Pull a vacuum of at least 250 mm (10 in) Hg.

   c. Note the flow rate as indicated by the rotameter.

   d. A leak of < 0.02 L/min must be recorded or leaks must be eliminated.

   e. Carefully release the vacuum gauge before turning off pump.

2. Assemble the apparatus, as shown in Figure 2-3 in Reference 9 of Section 3.5.2, with the wet test meter replacing the drying tube and impingers; that is, connect the outlet of the wet test meter to the inlet side of the needle valve and the inlet side of the wet test meter to a saturator which is open to the atmosphere. **Note:** Do not use a drying tube.

3. Run the pump for 15 min with the flow rate set at 1 L/min to allow the pump to warm up and to permit the interior surface of the wet test meter to become wet.

4. Collect the information required in the forms shown in Reference 9 of Section 3.5.2, Figures 2-4A (English units) or 2-4B (metric units), using sample volumes equivalent to at least five revolutions of the dry test meter. Three independent runs must be made.

5. Calculate Y_i for each of the three runs using Equation 1. Record the values on the form (Figures 2-4A or 2-4B, Reference 9 of Section 3.5.2).

$$Y_i = \frac{V_w P_m + \frac{D_m}{13.6}(t_d + 460)}{V_d P_m (t_w + 460)} \qquad \text{(Eq. 1)}$$

where

Y_i = ratio for each run of volumes measured by the wet test meter and the dry gas meter; dimensionless calibration factor,

V_w = volume measured by wet test meter, m^3 (ft^3),

P_m = barometric pressure at the meters, mm (in) Hg,

D_m = pressure drop across the wet test meter, mm (in) H_2O,

t_d = average temperature of dry gas meter, °C (°F),

V_d = volume measured by the dry gas meter, m^3 (ft^3), and

t_w = temperature of wet test meter, °C (°F)

6. Adjust and recalibrate or reject the dry gas meter if one or more values of Y_i fall outside the interval Y ±0.002Y, where Y is the average for three runs. Otherwise, the Y (calibration factor) is acceptable and will be used for future checks and subsequent test runs. The completed form should be forwarded to the supervisor for approval, and then filed in the calibration log book.

An alternative method of calibrating the metering system is to substitute a dry gas meter that has been properly prepared as a calibration standard for the wet test meter. This procedure should be used only after obtaining approval of the Administrator.

Posttest calibration check. After each field test series, conduct a calibration check as in Subsection 1.2, with the following exceptions:

1. The leak check is not conducted because a leak may have been corrected that was present during testing.

2. Three or more revolutions of the dry gas meter may be used.

3. Only two independent runs need be made.

4. If a temperature-compensating dry gas meter was used, the calibration temperature for the dry gas meter must be within ±6°C (10.8°F) of the average meter temperature observed during the field test series.

When a lower meter calibration factor is obtained as a result of an uncorrected leak, the tester should correct the leak and then determine the calibration factor for the leakless system. If the new calibration factor changes the compliance status of the facility in comparison to the lower factor, either include this information in the report or consult with the administrator for reporting procedures. If the calibration factor does not deviate by more than 5% from the initial calibration factor Y (determined in Subsection 1.2), then the dry gas meter volumes obtained during the test series are acceptable. If the calibration factor does deviate by more than 5%, recalibrate the metering system as in Subsection 1.2. For the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

1.2 Thermometers

The thermometers used to measure the temperature of gas leaving the first cartridge should be initially compared with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications:

1. Place both the mercury-in-glass and the dial type or an equivalent thermometer in an ice bath. Compare the readings after the bath stabilizes.

2. Allow both thermometers to come to room temperature. Compare readings after both are stabilized.

3. The dial type or equivalent thermometer is acceptable if values agree within ±1°C (2°F) at both points. If the difference is greater than ±1°C (2°F), either adjust or recalibrate the thermometer until the above criteria are met, or reject it.

4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer with that of the meter thermometer at room temperature. If the values are not within ±2°C (4°F) of each other, replace or recalibrate the meter thermometer.

The thermometer(s) on the dry gas meter inlet used to measure the metered sample gas temperature should be compared initially with a mercury-in-glass thermometer that meets ASTM E-1 No. 63C or 63F specifications:

1. Place the dial type or an equivalent thermometer and the mercury-in-glass thermometer in a hot water bath, 40° to 50°C(104° to 122°F). Compare the readings after the bath has stabilized.

2. Allow both thermometers to come to room temperature. Compare readings after the thermometers have stabilized.

3. The dial type or equivalent thermometer is acceptable if values agree within 3°C (5.4°F) at both points (steps 1 and 2 above) or if the temperature differentials at both points are within ±3°C (5.4°C), and the temperature differential is taped to the thermometer and recorded on the meter calibration form (Figures 2-4A or 2-4B, Reference 9 of Section 3.5.2).

4. Prior to each field trip, compare the temperature reading of the mercury-in-glass thermometer at room temperature with that of the thermometer that is part of the meter system. If the values or the corrected values are not within ±6°C (10.8°F) of each other, replace or recalibrate the meter thermometer.

1.3 Rotameter

The Reference Method does not require that the tester calibrate the rotameter. The rotameter should be cleaned and maintained according to the manufacturer's instructions. For this reason, the calibration curve and/or rotameter markings should be checked upon receipt and then routinely checked with the posttest meter system check. The rotameter may be calibrated as follows:

1. Determine that the rotameter has been cleaned as specified by the manufacturer and is not damaged.

2. Use the manufacturer's calibration curve and/or markings on the rotameter for the initial calibration. Calibrate the rotameter as described in the meter system calibration of Subsection 1.2, and record the data on the calibration form (Figures 2-4A or 2-4B, Reference 9 of Section 3.5.2).

3. Use the rotameter for testing if the pretest calculated calibration is within 1.0 ±0.05 L/min. If the calibration point is not within ±5%, however, determine a new flow rate setting, and recalibrate the system until the proper setting is determined.

4. Check the rotameter calibration with each posttest meter system check. If the rotameter check is within ±10% of the 1-L/min setting, the rotameter can be acceptable with proper maintenance. If the check is not within ±10% of the flow setting, however, disassemble and clean the rotameter and perform a full recalibration.

1.4 Barometer

The field barometer should be adjusted initially and before each test series to agree within ±2.5 mm (0.1 in) Hg with a mercury-in-glass barometer or with the pressure value reported from a nearby National Weather Service Station and corrected for elevation. The tester should be aware that the pressure readings are normally corrected to sea level. The uncorrected readings should be obtained. The correction for the elevation difference between the weather station and the sampling point should be applied at a rate of -2.5 mm Hg/30 m (-0.1 in Hg/100 ft) elevation increase, or vice versa for elevation decrease.

The calibration checks should be recorded on the pretest sampling form (Figure 2-5, Reference 9 of Section 3.5.2).

Appendix B
Acronym List

APCD	Air Pollution control device
APCE	Air pollution control equipment
AREAL	Atmospheric Research & Exposure Assessment Laboratory
ASTM	American Society of Testing and Materials
AWFSO	Automatic waste feed shutoff
CCS	Calibration check standard
CO	Carbon monoxide
COC	Chain of custody
CEMS	Continuous emission monitoring system
CVAA	Cold vapor atomic absorption--for metals
DL	Detection limits
DE	Destruction efficiency
DRE	Destruction and removal efficiency
dscf	Dry standard cubic feet
EICP	Extracted ion current plots
GC/MS	Gas chromatography/mass spectrometry
GFAA	Graphite furnace atomic absorption--for metals
HWERL	EPA's Hazardous Waste Engineering Research Laboratory. Now known as Risk Reduction Engineering Laboratory (RREL)
IDL	Instrument detection level
LDL	Lower level of detection
LOQ	Limit of quantitation
M1, M2, M5	Designation of specific EPA sampling and analysis methodologies
MDL	Method detection limits
NBS	National Bureau of Standards
NIST	National Institute for Standards and Technology (formerly the National Bureau of Standards)

PCC	Primary combustion chamber
POHCs	Principal organic hazardous constituents
POM	Polycyclic organic matter
QAC	Quality assurance coordinator
QAMS	Quality assurance management staff
QAP	Quality assurance plan
QAPjP	Quality assurance project plan
QAPP	Quality assurance program plan
QA/QC	Quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RIC	Reconstructed ion chromatograms
RIS	Recovery internal standards
RF	Response factor: ratio of the response of an analyte (peak height or area) to its concentration or mass injected into a chromatography system
RM	Reference method
RPD	Relative percent difference
RRF	Relative response factor: ratio of the response of an analyte (peak height or area) to the response of an internal standard related to the ratio of the concentrations of the internal standard and analyte
RRT	Relative retention time: ratio of the chromatographic retention time of an analyte to the retention time of an internal standard
RSD	Relative standard deviation
SCC	Secondary combustion chamber
SIM	Selected ion monitoring
SOP	Standard operating procedure
SVOST	Semivolatile organic sampling train (same as Method 0010 in SW-846)
SW-846	EPA methods publication (see reference 3)
TBP	Trial Burn Plan
TBR	Trial Burn Report
VOST	Volatile organic sampling train (same as Method 0030 in SW-846)
XAD-2	Resin used in SVOST tube