April 1996 • NREL/TP-430-21127

Retrofit of Waste-To-Energy Facilities Equipped with Electrostatic Precipitators

Volume III: Test Protocol

H. Gregor Rigo
Rigo & Rigo Associates, Inc
Berea, Ohio

A. John Chandler
A.J. Chandler & Associates, Ltd.
Toronto, Ontario

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the U.S. Department of Energy
Managed by the Midwest Research Institute
for the U.S. Department of Energy
Under Contract No. DE-AC36-83CH10093

NREL/TP-430-21127 • UC Category: 1414 • DE96007876

Retrofit of Waste-To-Energy Facilities Equipped with Electrostatic Precipitators

Volume III: Test Protocol

H.Gregor Rigo
Rigo & Rigo Associates, Inc
Berea, Ohio

A. John Chandler
A.J. Chandler & Associates, Ltd.
Toronto, Ontario

NREL Technical Monitor:
Philip Shepherd

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393
A national laboratory of the U.S. Department of Energy
Managed by the Midwest Research Institute
for the U.S. Department of Energy
Under Contract No. DE-AC36-83CH10093

Prepared under Subcontract No. ACK-4-14350-01

April 1996

NOTICE

Available to DOE and DOE contractors from:
Office of Scientific and Technical Information (OSTI)
P.O. Box 62
Oak Ridge, TN 37831
Prices available by calling (423) 576-8401

Available to the public from:
National Technical Information Service (NTIS)
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161
(703) 487-4650

CRTD-Vol. 39

An ASME Research Report

RETROFIT OF WASTE-TO-ENERGY FACILITIES EQUIPPED WITH ELECTROSTATIC PRECIPITATORS

April, 1996

VOLUME III

TEST PROTOCOL

Prepared by
H. Gregor Rigo, Rigo & Rigo Associates, Inc.
A. John Chandler, A.J. Chandler & Associates, Ltd.

Under the direction of
ASME Research Committee on Industrial and Municipal Waste
Electrostatic Precipitator Retrofit Subcommittee
Department of Energy's National Renewable Energy Laboratory

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS
United Engineering Center / 345 East 47th Street / New York, New York 10017

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1. PROJECT DESCRIPTION

1.1. General Overview

The American Society of Mechanical Engineers' [ASME] Center for Research and Technology Development [CRTD] has been awarded a subcontract by the National Renewable Energy Laboratory [NREL] to demonstrate the technical performance and viability of flue gas temperature control in combination with dry acid gas reagent and activated carbon injection at an existing electrostatic precipitator [ESP] equipped municipal waste combustor [MWC]. The objective of this proof-of-concept demonstration test is to economically and reliably meet 40 CFR 60 Subpart Cb Emissions Guidelines for MWC's at existing ESP equipped facilities.

The effort is being directed by a Subcommittee of the ASME Research Committee on Industrial and Municipal Wastes [RCIMW] chaired by Dave Hoecke. Mr. Greg Barthold of ASME/CRTD is the Project Manager. ASME/CRTD contracted with Rigo & Rigo Associates, Inc. in cooperation with A. J. Chandler & Associates, Ltd. to be the Principal Investigator for the project and manage the day-to-day aspects of the program, conduct the testing, reduce and interpret the data and prepare the report.

Testing will be conducted at the 2 by 210 TPD, ESP equipped MWC at the Davis County Resource Recovery Facility in Layton, Utah. The test plan calls for duplicate metals (Cd, Pb and Hg), dioxin and acid gas runs. The parameters to be tested are delineated in Table 1-1.

Nine distinct emissions control conditions (three ESP operating temperatures, three levels of activated carbon addition with the high temperature, low activated carbon addition run replaced by a no acid gas reagent, medium temperature condition) will be tested while the balance of the plant is operated normally. One condition will be replicated to provide a measure of reproducibility and experimental error.

Plant operations, furnace conditions and Continuous Emissions Monitoring System [CEMS] data (CO, O_2 and opacity) will be continuously recorded. A period of baseline operations will also be recorded to establish normal incinerator operating characteristics and enable a demonstration that the facility is operating normally during the proof-of-concept demonstration test.

Each test condition will be established early the night before and testing will commence at dawn the next day. The following emissions will be measured at the stack:

- Front-half particulate matter, metals & mercury,
- Acid gas (HCl),
- Dioxins and Furans (PCDD/F--2,3,7,8 substituted isomers plus homologue totals)
- Combustion gases (CO, NO_x, and SO_2).

The stack test team consists of eight people. Six will take the samples and perform sample recoveries, one will operate the mobile CEM laboratory and another is the field crew leader. QA and plant operations observations will be performed by the Principal Investigator who will be available to assist the test crew on an as-needed basis. Plant staff will take grab samples of ESP residues near the end of each condition's 24-hour run. Combined ash samples will be collected and handled by plant personnel throughout the proof-of-concept demonstration test whenever residues are removed from the site.

The following MWC operating conditions will be met to the greatest practical extent during the test program:

- For a minimum of six hours prior to, and throughout sampling, the tested incinerators will be set to raise 51,400 lb/hr of 500 psig, 500°F steam while the specified ESP temperature (nominally 400, 350 or 300 °F) and targeted acid gas reagent (150 lb/hr of Trona or 110 lb/hr of Sodium Bicarbonate--stochiometric ratio of 1:1) and activated carbon feed rates (0, 15 and 30 lb/hr--0, 200 mg/dsm^3 and 400 mg/dsm^3 to be confirmed) are being achieved.
- Should operations be disrupted prior to or during the testing, the affected runs will be suspended until operations have corrected the problem.
- Aborted tests will be repeated at the end of the scheduled 10-day test program. Provisions have been made for up to two days of additional testing. Conditions for retest will be prioritized to first repeat conditions with the fewest reliable runs.

This Quality Assurance Project Plan (QAPP) has been written to meet EPA level IV standards. It documents:

- project organization and responsibilities,
- quality assurance objectives,
- sampling methodologies,
- analytical methodologies,
- calibration procedures,
- data reduction and validation, and
- internal quality control checks.

Table 1-1 Emissions to be measured using manual methods and CEMS.

Particulate Matter(Method 29)			
Metals(Method 29)			
	ICAP	Cd Pb	
	CVAA	Hg	
Hydrogen Chloride(Method 26A)		HCl, Cl_2	
Trace Organics(Method 23)			
	Dioxins	2,3,7,8-TCDD	Total TCDD
		1,2,3,7,8-PeCDD	Total PeCDD
		1,2,3,4,7,8-HxCDD	
		1,2,3,6,7,8-HxCDD	
		1,2,3,7,8,9-HxCDD	Total HxCDD
		1,2,3,4,6,7,8-HpCDD	Total HpCDD
		1,2,3,4,6,7,8,9-OCDD	
	Furans	2,3,7,8-TCDF	Total TCDF
		1,2,3,7,8-PeCDF	
		2,3,4,7,8-PeCDF	Total PeCDF
		1,2,3,4,7,8-HxCDF	
		1,2,3,7,8,9-HxCDF	
		1,2,3,6,7,8-HxCDF	
		2,3,4,6,7,8-HxCDF	Total HxCDF
		1,2,3,4,6,7,8-HpCDF	
		1,2,3,4,7,8,9-HpCDF	Total HpCDF
		1,2,3,4,6,7,8,9-OCDF	
Sulfur Dioxide (Method 6C)		SO_2	
Oxides of Nitrogen (Method 7E)		NO_x	
Opacity (COMS)			

1.2 Site Selection Criteria

While there is considerable evidence that reducing ESP operating temperature and adding reasonable amounts of acid gas sorbent and activated carbon to incinerator flue gas can theoretically allow existing ESP equipped MWC's to economically meet proposed guidelines, field experience has shown that it is difficult to reliably reduce ESP temperatures using evaporative (water spray) cooling techniques. The problem is the short distance between typical MWC outlets and ESP inlets. Considerable work has been done on this problem, however, and there is good reason to believe that requisite temperatures can be successfully achieved using air or steam atomizers designed to produce a fine (25 μm Sauter mean diameter) cooling spray.

Clean Air Act (Section 129) emissions guidelines existing MWC's are expected to be promulgated before October 31, 1995. So, time is of the essence if this work is to have an opportunity to influence retrofit and closure decisions.

These considerations lead to the following mandatory site selection requirements:

- Close Coupled ESP--this maximizes the likelihood of successful technology transfer
- Single Chamber Massburn type incinerator--particulate carry-over may participate in PCDD/F formation
- Dry injection in use by Sept. 15, 1995--to allow stable operation prior to start of testing
- Existing Permits or a Variance that allow this testing--schedule dictates that protracted regulatory negotiations are not possible

It is preferred that the plant have:

- DCS with PC interface for routine plant data logging
- CEMS for CO, O_2, NO_x, SO_x & Opacity
- APCS and combined residue stream access for sampling

The characteristics of U.S. ESP equipped MWC facilities were reviewed by the Principal Investigator. A number of potential sites were identified and the Principal Investigator contacted those that appeared to meet the mandatory criteria to discern their interest in hosting this proof-of-concept demonstration test.

The Davis County Resource Recovery Facility, Layton, UT, meets the mandatory and preferred criteria. This facility agreed to be the host facility. The selection was presented to and confirmed by the project sponsors and the RCIMW Subcommittee.

1.3 The Davis County Resource Recovery Facility

The Davis County Resource Recovery Facility is a nominal 420 TPD (2 by 210 TPD) MWC that uses a back pressure turbine to generate electricity and export steam to neighboring Hill AFB. The facility has refractory wall Seghers (rocking grate) furnaces and Zurn water-wall waste heat recovery boilers rated to raise 51,344 lb/hr of 500°F, 500 psig steam.

The facility was built with a powdered limestone furnace injection system that is now being used to inject Trona (a natural sodium reagent used for acid gas control and as a cattle feed supplement) between the boiler outlet and economizer. Particulate emissions are controlled by a three-field Environmental Elements Electrostatic Precipitator with a specific collector area of about 600 ft^2/1000 acfm. The facility has a Foxboro DCS with DEC MicroVAX data historian. Compliance monitors include an O_2 diluent corrected CO CEMS and a Continuous Opacity Monitoring System [COMS]. A process NO_x/SO_x monitor is installed on one MWC.

Figure 1-1 is a schematic cross-section of the facility. Table 1-2 presents a heat balance for the facility when burning 4,500 Btu/lb MSW at MCR [maximum continuous rating] conditions. In order to reduce the flue gas temperature to a nominal 300°F, about 9 GPM of water must be atomized between the economizer outlet and ESP inlet. The stochiometric Trona addition rate (based on historic uncontrolled HCl and SO_2 concentrations) is 150 lb/hr. If sodium bicarbonate is used instead, the stochiometric addition rate becomes about 110 lb/hr.

1.4 Statement of Program Objectives

The two objectives of this program are:

- to determine the actual emissions performance level achievable by a combination of ESP inlet temperature control, acid gas reagent injection and activated carbon addition. The target is to meet the emissions guideline requirements.
- to demonstrate that ESP inlet temperature control can be reliably accomplished during the test program and the 2 months immediately following including documenting operating expenses.

1.5 Experimental Design

To accomplish the program objectives, a fractional 4 x 3 factorial test plan with one replicated test condition was developed. Since the purpose of this test is to demonstrate achievement of CAA emission guidelines, the replicate was assigned on engineering grounds to the operating configuration most likely to achieve the program objective.

The order of testing was developed by randomizing a 3 x 3 test matrix that excluded the no acid gas reagent condition. The high temperature, low activated carbon addition test was assigned to the intermediate temperature, no reagent or activated carbon test condition to provide additional uncontrolled baseline data. This test condition is designed to determine what effect acid gas reagent addition alone has on PCDD/F emissions in these facilities.

This is an unbalanced experimental design that makes maximum use of the available test runs. Data reduction is slightly complicated since traditional fractional factorial designs do not include partial replicates and utilize a different pattern. Mathematical tools exist to interpret this data. The selected pattern will enable the fitting of a theoretically based predictive equation to the data so that interpolation to other conditions can be readily performed.

Table 1-3 Test plan matrix showing the day each condition is to be tested.

	ESP OPERATING TEMPERATURE		
	Normal Ops about 400° F	Intermediate 350° F	Minimum 300° F
No AG reagent or AC	-	6	-
AG reagent only	2	9	5
AG reagent + low AC	-	8	10
AG reagent + high AC	7	1,3	4

Figure 1-1 Boiler cross-section for Davis County Incinerator.

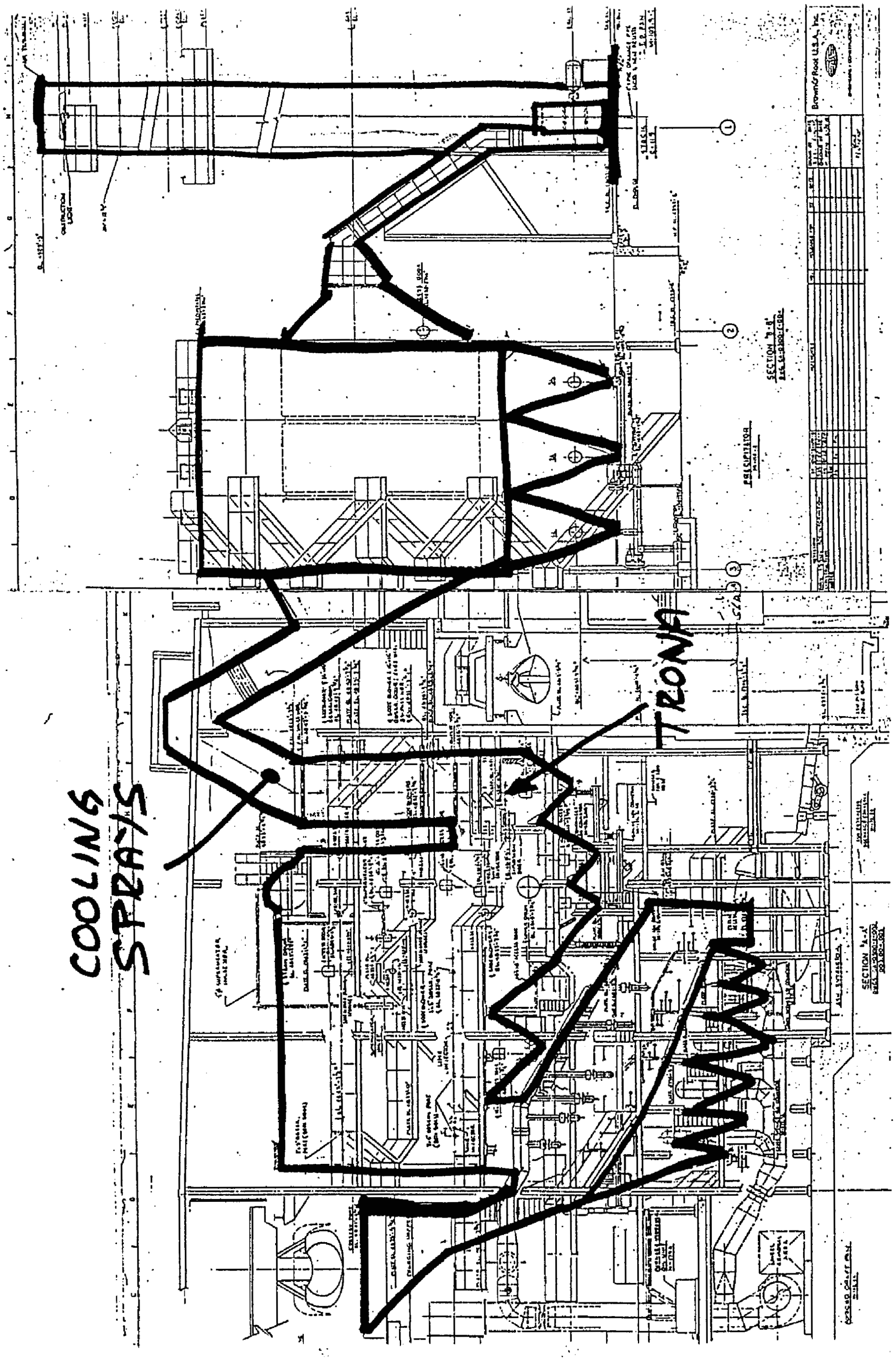


Table 1-2 Boiler heat balance for Davis County Incinerator (4,500 Btu/lb reference fuel).

MODIFIED June 1, 1992	
DAVIS COUNTY CONDITIONS	
Run Date: 11-Sep-95	10:42 AM
FUEL CHARACTERISTICS	
C, % by weight	24.89
H2, % by weight	3.22
N2, % by weight	0.34
S, % by weight	0.13
O2, % by weight	19.38
Cl2, % by weight	0.24
H2O, % by weight	31.80
ASH, % by weight	20.00
HHV, Btu/lb	4,500
Fd, DSCF/MBtu	9,113
Fc, DSCF of CO2/MBtu	1,775
Fo, F ratio	1.08
SYSTEM CHARACTERISTICS	
Main Steam Flow, lb/hr	51,344
S.H. outlet press.. psig	500
S.H. outlet temp.. deg F	500
S.H.outlet enthalpy, Btu/lb	1,229.1
Feedwater press.. psig	600
Feedwater temp.. deg F	300
F.W.inlet enthalpy, Btu/lb	269.6
Drum press.. psig	571
Drum temp.(sat.) deg F	483
Drum sat vapor enth.,Btu/lb	1,203.4
Drum sat liq. enth., Btu/lb	468.0
Blow Down	1.0%
Misc. Steam Leaks & Losses	1.5%
Fraction of Ash to Boiler	10%
Grate ash discharge temp, F	250
UBC in Fly ash	8%
UBC in Bottom Ash	5%
Residue, lb-residue/lb-fuel	21.1%
Avg temperature of residue, F	268
Unburned Comb. loss, %	2.4
UBC in residue , %	5.3
Gas temp lvg econimizer, F	425
Gas temp lvg air heater, F	425
U.F.A. Steam Heater Rise, F	0
Radiation loss, %	3.0
Sensible heat in residue, %	0.2
Unaccounted for loss, %	1.0
Reference Temperature, F	60
Ambient Air Temperture, F	60
Total Excess Air	115%
Fraction air under grate	70%
Excess Air Supplied by Fans, %	102.7
weight flue gas recirculation	0%
General Air leakage-% of Theo.	12.3%
deNOx Carrier air--% of Theo.	0.0%

MOLES/100 lbs FUEL actually burned adjustment for UBC as proportion of heat lost to unburned combustibles	
C =	2.023
H2 =	1.559
S =	0.004
O2 =	0.591
N2 =	0.012
H2O =	1.765
Cl =	0.007
THERO. O2 REQ'D, MOL/100 LBS FUEL	
For: C + O2 = CO2	2.023
For: 2H2 + O2= H2O	0.780
For: S + O2 = SO2	0.004
For: available O2 & Cl	-0.598
Theo. mols O2 to be supplied	2.209
Wet Theo. Air, lb air/lb fuel	3.076
Mols dry air./ mols O2	4.764
Moles Dry air /lb fuel	0.226
Lb. dry air req'd/lb fuel	6.528
Lb. H2O in air/lb fuel	0.085
Lb. Std. Air req'd/lb fuel	6.613
FLUE GAS ANALYSIS	
Moles HCl/ lb fuel	0.00007
Moles CO2/ lb fuel	0.02023
Moles H2O/ lb fuel	0.03789
Moles SO2/ lb fuel	0.00004
Moles N2 / lb fuel	0.17889
Moles O2 / lb fuel	0.02540
Tot. Mols Flue gas/lb fuel	0.26252
FLUE GAS CHARACTERISTICS	
Partial Pressures	
P(CO2)	1.133
P(H2O)	2.122
P(SO2)	0.002
Percent by Volume (Orsat)	
% CO2	9.0
% O2	11.3
PPM SO2	176
PPM HCl	294
Gas weights, lb gas/lb fuel	
Lb. HCl/lb fuel	0.002
Lb. CO2/lb fuel	0.890
Lb. H2O/lb fuel	0.683
Lb. SO2/lb fuel	0.003
Lb. N2/lb fuel	5.011
Lb. O2/lb fuel	0.813
Lb. Dry flu gas/lb fuel burnd	6.719
Lb. Wet flu gas/lb fuel burnd	7.402
Flue gas molecular weight	28.196
H2O in gas, % by weight	9.222

MOLECULAR WEIGHTS		
Hydrochloric Acid (HCl)		36.46
Carbon (C)		12.01
Hydrogen (H2)		2.02
Sulfur (S)		32.06
Oxygen (O2)		32.00
Nitrogen (N2)		28.01
Water (H2O)		18.02
Chlorine (CL2)		70.91
Carbon Dioxide (CO2)		44.01
Sulfur Dioxide (SO2)		64.06
Carbon Monoxide (CO)		28.01
STANDARD AIR COMPOSITION		
O2, % by volume		20.99
N2, % by volume		79.01
H2O, % by weight		1.30
Molecular weight dry air		28.85
ADJUSTMENTS TO HHV FOR DIFFERING CONDITIONS		
Sensible Heat in Fuel	Btu/lb	0.0
Sensible Heat in Air	Btu/lb	0.0
Compression Heat	Btu/lb	8.1
Steam Air Heater Input	Btu/lb	0.0
Effective HHV	Btu/lb	4,508
BOILER EFFICIENCY -- ACTUAL		62.9
-- ADJUSTED TO AS-FIRED HHV		63.1%
HEAT LOSS ANALYSIS		
Dry gas loss, %		13.5
Water from fuel loss, %		16.7
Moist. in air loss, %		0.3
Total losses, %		37.1
BOILER OUTPUTS		
Feed Water Flow		51,863
Blowdown flow, lb/hr		519
High press. h/out-h/in, Btu/lb		959
Blowdown : h/out-h/in, Btu/lb		198
High press. duty, Btu/hour		49,262,514
Blowdown duty, Btu/hour		102,901
Total Boiler Output, Btu/hour		49,365,415
Lb-steam/Lb-fuel		2.95
Fraction of Combustibles Burned		97.67%
BOILER FUEL, AIR, & FLUE GAS FLOW RATES		
Fuel flow rate--tons per day		209
Fuel heat input, Btu/hr		78,435,422
Fuel flow rate. lb/hr		17,399
Total air to boilers, lb/hr		115,051
Flue gas leaving boiler system, lb/hr		128,789
Air leakage, lb/hr		6,568
Thermal DeNox Carrier Air,lb/hr		0
undergrate air flow, lb/hr		75,938
overfire air flow, lb/hr		32,545
Flue gas recirculation, lb/hr		0
Flue gas leaving economizer, lb/hr		128,789
Total residue generation rate, lb/hr		3,675

1.6 Schedule

1.6.1 Overall Project Schedule

The overall project schedule begins with NREL subcontracting with ASME to perform the research described in this Test Protocol and ends with the submission of the final report to the sponsor. The schedule is very aggressive, but is necessary if the results of this research are to be useful.

The following are the key schedule milestone dates for this effort:

- NREL Contract Award -- Aug. 2, 1995
- Order Special Equipment -- Sept. 13, 1995
- Field Testing -- Nov. 15-30, 1995
- Receive last Field Data -- Feb. 16, 1996
- Distribute 1st Draft Report -- March 18, 1996
- Receive Comments -- April 1, 1996
- Distribute Draft Final Report -- April 15, 1996
- Receive Final Comments -- April 22, 1996
- Send Final Report to ASME -- April 29, 1996
- ASME Report Date to NREL -- May 2, 1996

1.6.2 Typical Test Day Schedule

The same test schedule will be followed for each day's testing. After 2 to 3 days of set-up, equipment check-out and site familiarization, the following daily pattern will be followed.

- 6:00 PM -- establish conditions for next day
- 6:00 AM -- set-up for day's runs
- 7:00 AM -- start first PCDD/F run
- 9:00 AM -- start first Acid Gases run
- 10:00 AM -- start first Metals run
- 1:00 PM -- start second PCDD/F run
- 3:00 PM -- start second Acid Gases run
- 4:00 PM -- start second Metals run
- 6:00 PM -- break-down & clean-up, establish tomorrow's operating conditions

This daily field schedule will be adjusted as necessary to accommodate plant break-downs. It is anticipated that some runs will start earlier than scheduled if the stack testing platform and access ports allow simultaneous operation of two trains on cross-traverses.

1.7 Project Organization and Responsibilities

The coordination of this emissions testing program will require a cooperative effort between a number of organizations. It is essential that all participating organizations be aware of their responsibilities and that there are distinct lines of authority linking all organizations and key individuals. Figure 2-1 illustrates the overall program organization.

The chart identifies the primary organizations:

- DOE, the Program Sponsor
- NREL, the Program Administrator
- ASME/CRTD, the Subcontractor and Program Manager
- ASME Research Committee on Industrial and Municipal Waste [RCIMW], EMEWC Subcommittee
- Advisory Board, additional sponsor representatives
- Rigo & Rigo / Chandler; the Principal Investigator
- Davis County Resource Recovery Facility, the Host Facility
- Bovar Concord Environmental, the Testing Subcontractor
- Zenon Environmental, the Analytic Laboratory
- NUS Laboratory, the TCLP Laboratory

As Principal Investigator, Rigo & Rigo will coordinate the work on behalf of ASME/CRTD. They will coordinate the efforts of the field teams and host facility. They will design facility modifications, specify the equipment and assist Davis County RRF implement the necessary spray cooling changes. Rigo & Rigo will coordinate delivery and installation of the activated carbon feed system and acquire the reagent.

Rigo & Rigo will maintain responsibility for the quality of work performed by its personnel and subcontractors (external QA/QC). Additional QA will be provided by the Testing Contractor (internal QA/QC).

Additional on-site oversight will be provided on a random, spot basis by a representative of the RCIWM. The division of responsibilities and QA/QC activities are laid out in Table 1-4.

Figure 1-2 Project Organization Chart.

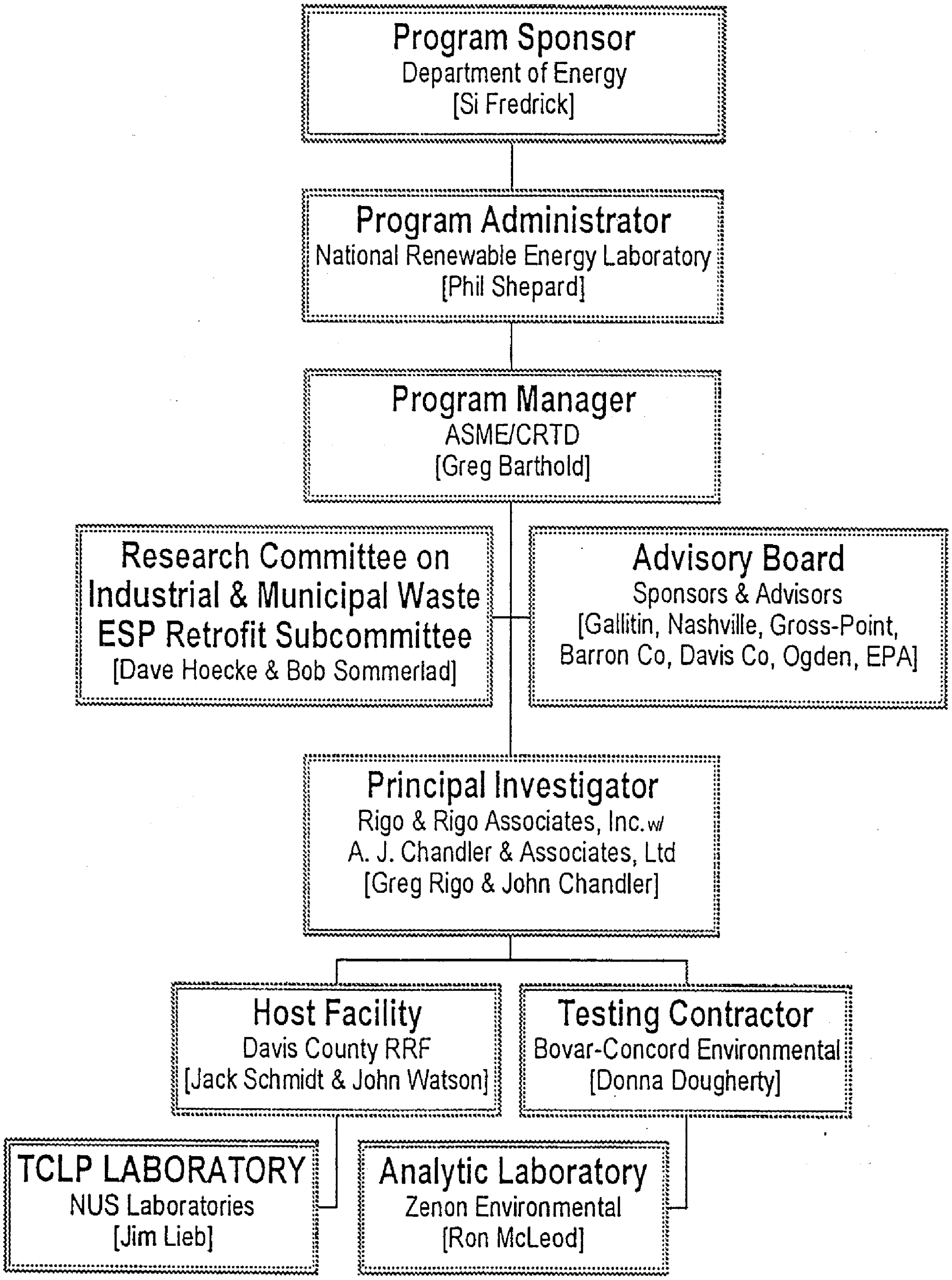


Table 1-4 Comparison of Internal and External QA/QC Responsibility for Selected Subjects

SUBJECT	INTERNAL (TESTING SUBCONTRACTOR) QA/QC RESPONSIBILITY	EXTERNAL (PRINCIPAL INVESTIGATOR) QA/QC RESPONSIBILITY
Test Program	Define program objectives and design test matrix to achieve program objectives.	Assess sampling program and data collection for sufficiency to meet program objectives.
Test Methods	Select methods, detail procedures, and define QC activities and limits.	Review and critique protocols and procedures. Assess protocols for comparability to previous programs.
Calibration of Test Equipment	Verify accuracy of calibration. Document instrument performance.	Observe personnel, equipment, and procedures during equipment calibration. Review documentation of instrument calibration performance. Provide on-site audit checks and document performance.
Sampling Locations	Identify suitable sampling locations and perform necessary modifications.	Check for suitability of location to permit collection of representative samples.
Field Sampling	Provide trained test crew, properly prepared and/or calibrated equipment, and sufficient supply of correct contamination-free reagents.	Observe testing, including leak checks and document any deviations from protocols. Verify calibrations by conducting on-site audits.
CEMS Testing	Document instrument performance and verify accuracy of calibration gases. Provide and follow detailed operating and QC procedures.	Review of documentation on instrument performance and calibration gas analysis. Observe on-site testing and document any deviations from protocol.
Data Acquisition Systems	Establish standard operating procedures, conduct routine QC checks to verify accuracy of program.	Observe operation of system. Document results.
Process Samples		Review sampling sites, sampling equipment, sample handling/preparation protocols, as well as document activities during sampling. Observe plant personnel's efforts for deviations. Witness procedures.
Sample Recovery	Ensure recovery follows defined protocols. Collect reagent blanks and field blanks.	Observe and document recovery operation. Document that correct reagent blanks and field blanks are collected.
Sample Custody	Log samples, prepare chain-of-custody sheets and package samples properly for transportation.	Review sample logging and chain-of-custody documentation. Observe and document sample packaging.
Process and Field Sampling Data	Provide experienced DAS operator(s), reliable hardware, and validated software.	Document accuracy of logged data and verify accuracy of reported and calculated values with technical system audits.
Sample Analysis	Select acceptable methods and detail procedures and changes. Detail laboratory QC including calibrations, control samples, duplicates and matrix spikes.	Review and comment on selected procedures. Review performance and document deviations from selected protocol.
Data Reduction Procedures	Establish standard data reduction procedures. Conduct initial checks on procedures/calculations to verify accuracy.	Review data reduction procedures. Perform audit of procedures/calculations using known data set and document results.

Field sampling activities will be conducted by Testing Contractor personnel experienced with the emissions measurement techniques and QA/QC activities specified for this effort. Each sample train will be operated by a team leader. The team leaders are responsible for operating the sampling trains and ensuring they are operating the trains in accordance with the sampling methodologies. All team leaders are thoroughly trained in the test procedures and have successfully completed similar testing on other test programs. They will report to the Testing Subcontractor's field crew leader on a daily basis to keep him informed of progress. Samples analyses will be performed by a qualified and experienced Analytic Laboratory.

2. QUALITY ASSURANCE OBJECTIVES

The overall objective of the sampling and analysis effort is to provide data that are precise, accurate, comparable, representative and complete. The definitions for these criteria and how compliance with them will be assessed are described below.

2.1 Data Precision and Accuracy and Completeness

The two aspects of data quality of primary concern are precision and accuracy. Precision, as defined in "Guideline and Specifications for Preparing Quality Assurance Project Plans" (U.S. EPA QAMS-005/80), is "a measure of mutual agreement (or variability) among individual measurements of the same property, usually under prescribed similar conditions". Various measures of precision exist depending on these conditions. This term is independent of the error (accuracy) of the analyses and reflects only the degree to which the measurements agree with one another, not the degree to which they agree with the "true" value for the parameter measured.

Quality control procedures, such as control sample analyses and replicate analyses, represent the primary mechanism for evaluating measurement data variability or precision. Control sample analyses are used to define repeatability, replicate analyses are used to define analytical replicability, and results for replicate samples may be used to define the total variability (replicability) of the sampling/analytical system as a whole. QC objectives for laboratory control samples (prepared QC standards) and duplicates are outlined in Table 2-1.

Table 2-1 Analytical Objectives for Laboratory Quality Control Samples (Guidelines)

PARAMETER	PRECISION[a] (% Difference)	ACCURACY[b] (%)
Dioxins & Furans: Trace Organic train	< 50	50 - 120
Gravimetric Analysis	1% of the total particulate[c] weight or 0.6 mg, whichever is greater	± 0.5 mg[d]
Metals Aqueous (impinger solutions) Solids (filters and fly ash)	 < 20 < 20	 85 - 115 70 - 130
Acid Gases (HCl) Aqueous (impinger solutions)	 < 20	 90 - 100

a) Expressed as the percent difference between replicate measurements of similar laboratory control samples (i.e., prepared QC standards and duplicates/replicate analysis).

b) Expressed as the measured versus the expected value of laboratory control samples.

c) Constant weight procedure for Method 5.

d) Measured using a 0.5 mg Class S weight.

The QA/QC objectives for precision, accuracy and completeness established for each major compound measured are considered guidelines. For a measurement system, if all QC data meets these objectives, the test results are judged as having acceptable quality. When specific QC criteria are not met, the data will be flagged and the acceptance left to the technical judgment of the data user and the regulatory agency.

Precision estimates must be considered not only by their absolute value (% difference) but also by the concentration measured. Lower sample concentrations (at or near the detection limit) may yield lower precision estimates while higher sample concentration typically yield higher precision values.

For the manual train samples in this program, precision of the measurement data will be based on duplicate analyses of the same pollutant in a sample (analytical replicability) where feasible. It will be expressed as the percent difference (% D) between the two measurements.

$$\% D = \frac{|A_1 - A_2|}{(A_1 + A_2)/2} x\ 100$$

where:

% D = percent difference between duplicate results
A_1 and A_2 = results of first (1) and second (2) analysis
$|A_1 - A_2|$ = absolute difference between duplicate analyses, A_1 and A_2

For continuous emission monitoring, the precision of the measurement data will be based on repeated analyses of control samples (i.e., calibration gases) (repeatability). The variability will be expressed in terms of the coefficient of variation (CV) for the repeat analyses where:

$$CV\% = \frac{s}{x} x\ 100$$

where:

s = standard deviation of the measurements
x = mean of the measurements

The CV is in units of percent since it is the ratio of the standard deviation of the mean to the mean times 100 (relative standard deviation).

Standard deviation is defined as follows. For a sample, the standard deviation 's' is the positive square root of the sample variance.

$$s = \sqrt{\sum_{i=1}^{N} \frac{(X_i - \overline{X})^2}{n - 1}}$$

For a finite population, the standard deviation, s is:

$$\sigma = \sqrt{\sum_{i=1}^{N} \frac{(X_i - \mu)^2}{N}}$$

where:

m is the true arithmetic mean of the population, and
N is the number of values in the population.

Completeness is defined as the measure of the amount of valid data obtained from a measurement system compared to the amount that was expected to fully evaluate and understand the system under prescribed test conditions, usually expressed as a percentage.

Completeness, expressed as a percentage, is defined as:

$$\frac{\text{data obtained over test period}}{\text{total data expected over test period}} \times 100$$

The field objective is to obtain 100 percent of the scheduled samples. As a secondary objective, at least one valid laboratory result must be obtained for each type of test and run condition.

Representativeness expresses the degree to which the data accurately and precisely represent a characteristic of a process condition or an environmental condition.

Table 2-2 is an outline of the QA objectives for laboratory measurements (i.e., analysis of field samples) while Table 2-3 is a summary of the QA objectives for the field measurements.

Table 2-2 QA Objectives for Precision, Accuracy and Completeness for Analysis of Field Samples

PARAMETER	PRECISION[a] (%)	ACCURACY[b] (%)	COMPLETENESS[c] (%)
Dioxins & Furans (EPA Method 23)			
Trace Organic train	NA[d]	50 - 120	90
Metals (EPA Method 29)			
Metals, Particulate	NA[d]	80 - 120	90
Aqueous (impinger solutions)	< 20	80 - 120	90
Solids (ash)	< 20	50 - 130	90
Acid Gases (HCl) (EPA Method 26A)			
Aqueous (impinger solutions)	< 20	80 - 120	90

[a] Expressed as the average percent difference between replicate field sample analytical results.

[b] Expressed as the observed versus the expected value of matrix spike and matrix spike duplicate samples. For trace organic analysis, surrogate standards will be used to monitor for accuracy.

[c] Expressed as the percentage of analyses deemed valid over all planned analyses of this type.

[d] Replicate stack gas samples will not be taken.

NA - not acceptable.

The QA/QC objectives for precision, accuracy and completeness established for each major compound measured are considered guidelines. For a measurement system, if all QC data meets these objectives, the test results are judged as having acceptable quality.

Data that fails to meet the guidelines will be inspected for errors and a case-by-case determination made of representativeness. Based on the findings, the data may be retained for interpretation or rejected as not meeting QA/QC criteria. When specific QC criteria are not met, the data will be flagged and the acceptance left to the technical judgment of the data user.

Table 2-3 QA Objectives for Precision, Accuracy, and Completeness for Sampling Measurements (Guidelines)

MEASUREMENT	PRECISION (RSD) (%)	ACCURACY[a] (%)	COMPLETENESS (%)
Continuous Methods			
Oxides of nitrogen	± 20	15	95
Sulfur dioxide (UV)	± 20	15	95
Manual Methods			
Particulate Matter	12	ND[b]	90
Metals, HCl	± 15[c]	± 15[c]	90
Gas temperature (type K thermocouple)	ND	± 3[d]	95
Dioxins	± 50[c]	± 50[c]	90

RSD - Relative Standard Deviation of replicate analysis of calibration gases.

[a] Relative accuracy will not be determined during this test program.

[b] Not determinable within limits of method precision.

[c] Analytical phase only.

[d] Relative accuracy compared to NBS-traceable thermometer.

2.2 Method Comparability and Data Representativeness

Comparability is a measure of the confidence with which one data set can be compared to another. The following measures will be taken to ensure the comparability and representativeness of the data.

- establish test conditions far enough ahead of testing for unit stabilization
- record and analyze process data to demonstrate that the intended conditions have been achieved
- use of Reference Methods whenever possible;
- standardized written sampling and analysis procedures;

- standardized handling and shipping procedures used for all collected samples;
- standardized analytical procedures and experienced personnel used throughout the program; and
- report results in consistent units.

2.3 Steps to Take if an Objective is not Met

The test matrix calls for duplicate testing at 10 conditions. Nine conditions are unique; one condition is a replicate to provide an indication of reproducibly and accuracy.

During testing, any number of field extengencies can occur which could prevent completing all the runs scheduled for a given test condition. In such an event, as much testing as can be practically completed during the remainder of the day will be accomplished. The next scheduled test condition will be then established per the matrix and the new condition tested the next day.

At the end of the scheduled 10 days of testing, conditions with incomplete data will be repeated, in the original order. A whole day's test schedule conducted for each repeated test.

Two days have been reserved to allow for equipment failures or the need to repeat a test. In the event that more than two days are needed to complete the test matrix, the completeness will be examined. If at least one of each scheduled type of test has been successfully completed, the test condition will not be repeated. If additional test days are still required to complete the matrix, they will only be conducted if they involve medium or low ESP operating temperature and low or high activated carbon addition. That is, under no circumstance will field testing be considered complete unless there is at least one valid run for each parameter for the conditions scheduled to be tested on days 1, 3, 4, 8, and 10.

In the event that samples are lost during shipment to the analytic laboratory or destroyed during recovery, the impact of missing the data on project completion will be judged. If at least one valid run remains for each test condition and type of analysis remains, no further action will be taken. In the event that the loss or damage results in no valid measurement for a parameter on test days 1, 3, 4, 8 or 10, remobilization and retesting will be conducted as deemed necessary by Program Administrator and Program Sponsor.

3. SAMPLING AND ANALYTIC PROCEDURES

3.1 Preliminary Activities

Activities (and the responsible party in parentheses) for the mobilization phase of the testing at Davis County RRF will include:

1. design, installation, start-up and run-in of the spray-atomization and activated carbon addition systems (Principal Investigator);
2. preparation, precleaning, and proofing of manual stack sampling trains and sample containers (Testing Subcontractor);
3. quality checks of chemicals, reagents, filters, and XAD-2 sorbent (Testing Subcontractor and Analytic Laboratory);
4. calibration of all sampling and monitoring equipment (Testing Subcontractor);
5. development (and review) of data acquisition, data reduction and summary procedures (Testing Subcontractor);
6. development of external QA field data sheets (external QA/QC team);
7. review of equipment calibration logs (external QA/QC team); and
8. review of proposed field and laboratory procedures (external QA/QC team).

3.1.1 Preparation, Precleaning and Proofing of Manual Stack Sampling Trains and Sample Containers

The Contractor will ensure that all of the components of the equipment to be used meet the requirements specified in the Reference Methods.

All components used for the manual stack sampling as well as sample containers will undergo preparation, precleaning, and proofing (Dioxin & Furan train only) following the procedures outlined in the appropriate sampling protocols. Cleaning and proofing of the trains will be performed at Analytic Laboratory.

All glassware for organics trains including probe liner and laboratory use will be scrupulously cleaned according to the following procedure:

a) Soak in hot soapy water for one hour and scrub with brush.
b) Rinse with hot tap water at least five times.
c) Minimum four hour soak in chromate.
d) Rinse with copious quantities of tap water.
e) Rinse three times with reagent grade acetone.

f) Rinse three times with distilled in glass hexane.

g) Rinse three times with distilled in glass dichloromethane.

h) Air dry.

The trace organics sampling train components (i.e., glassware, filters, resin) and sample containers proofing involves analyzing proofing samples obtained by recovering the cleaned components per the Reference Method 23 procedures. Since there are not proofing requirements in Method 23 and the Principal Investigator's experience indicates that such proofing is required, the proofing samples will be analyzed following the procedures employed by the USEPA and Environment Canada in their joint effort at the Mid-Connecticut Resource Recovery Facility. That is, the proofing samples from these items will be analyzed for PCBs (by GC/ECD) and PAHs (by GC/ECD or HPLC). The maximum contamination level is < 50 ng/train total PCBs. Proof samples will be screened for PAHs for background contamination of PAHs. Confirmation analysis by HRGC/HRMS will be conducted if contamination is indicated. PCB's and PAH's have been selected as proofing surrogates because experience shows that trains free of these materials are also PCDD/F free. Also, PCB and PAH analyses are much less expensive, so they are suitable for routine Quality Assurance Activities.

All glassware and sample containers for the particulate and metals train will be cleaned according to the following procedure (Method 29):

a) Rinse with hot tap water and then wash in hot soapy water

b) Rinse three times with tap water

c) Rinse with DI water

d) Soak in 10% (v/v) nitric acid solution for 4 hours

e) Rinse three times with DI water,

f) Rinse a final time with acetone

g) Air dry.

3.1.2 Quality Checks of Chemicals, Reagents, Filters and Sorbents

The quality of the chemicals, reagents, filters, and sorbents used for the sampling and analytical procedures will be checked by the Contractor to assure that these items are below the acceptable contamination level of the target analytes. In most of the cases, the quality control checks will involve analysis of the chemicals and reagents for the target analytes using the same analytical methodologies and with the same analytical detection limits applied to the actual samples.

XAD-2 resin and filters will be cleaned according to EPA Method 23 involving a water rinse, and successive soxhlet extractions with water, methanol and dichloromethane. The resin is dried with a stream of an organic free gas such as ultrapure nitrogen. Liquid nitrogen is often an excellent source for this purpose. Alternatively, the excess solvent may be removed by vacuum drying at ambient temperature. These materials will also be proofed and analyzed prior to use in the program.

Reagents and chemicals will conform to the requirements specified in the appropriate sampling protocols. American Chemical Society (ACS) pesticide grade Chemicals and Type I Reagent water will be used for all metal and acid gas sampling trains and analysis. Pesticide grade solvents and HPLC grade water will be used for trace organic sampling train preparation and sample analysis. Filters will conform to Method 29 purity requirements of <1.3 mg/in^2 of any metal of interest.

CEMS calibration gases will all meet 40 CFR 60 Appendix F CGA Audit Standards and be NIST traceable.

3.1.3 Review of Equipment Calibration Procedures and Logs

The calibration procedures to be used by the Host Facility, the Testing Subcontractor and the Analytic Laboratory will be reviewed. All calibration logs will be received, reviewed, and initialed by an external QA/QC team member to indicate acceptability, prior to testing.

Calibration of field sampling equipment must be performed prior to the field sampling effort. Calibration procedures must be consistent with procedures outlined in the EPA publication "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods" (EPA, 1977). Table 3-1 lists the recommended calibration procedures and acceptance limits for items to be calibrated.

Table 3-1 Equipment Calibration Details

ITEM	CALIBRATED PARAMETER	RECOMMENDED TO CALIBRATE AGAINST/USING	RECOMMENDED ACCEPTANCE LIMITS	FREQUENCY
Probe Nozzle	Internal diameter	Vernier caliper - to nearest 0.025 mm	for n = 4 measurements high-low < 0.1 mm	once daily
Pitots and Manometers	Pitot coefficient, Dp vs standard Dp	Wind tunnel or equivalent (normally 1000 to 5000 ft./min)	(coefficient typically 0.8-1.2)	within 6 months of testing
Temperature Sensors (Thermocouple)	°C or °F measured vs actual (theoretical) (use boiling H_2O boiling oil and ice water)	Output plotted vs published Tables and/or NBS (ASTM D363)	±1.5% over the range	within 6 months of testing
Barometer • Aneroid • Mercury	Pa, measured vs actual Pa, measured vs actual	Calibrated mercury barometer Secondary standard traceable to NBS (ASTM D363)	±50 pa (±0.015 in Hg)	before testing
Analytical Balance	Grams, milligrams	Class S weights (10 mg - 5g)	Within ±0.1%	weekly
Triple Beam or Digital Balance	Grams	Class S weights (100, 500, 1000 g)	±0.1 g (the ~ readability) or ±1%	weekly
Dry Gas Meter	Meter flow	Calibrated wet-test meter or bell-prover positive displacement system	±1% over the working range factor of 0.95 - 1.05	within 6 months of testing
Orifice	Orifice constant	Wet test meter	Not applicable	once during program
Cylinder Gases	ppm or %	Traceable to standard gases	Analytic Laboratory and supplier analysis within 2%	low, medium, high
Continuous Monitors	Linearity	Multipoint calibration - zero, low, medium, high done in laboratory	Linearity > 0.995	before and after test program
	System bias check	Introduce calibration gas at outlet of sampling probe then directly to the analyzer daily	±5% of span	daily before and after test
	Reproducibility	Inject span gas through the sampling system at least 3 times, once during program	±20% RSD	once during program

Reference method calibration procedures will be used. The ensures that,

- all critical measurement parameters, including all critical pollutant measurement systems, reference the applicable standard operating procedures or provide a written description of the calibration procedures to be used;
- the frequency of calibration is stated; and
- the calibration standards to be used and their source(s) including traceability procedures are stated.

The calibration procedures used will be reviewed for conformance with Reference Method requirements and good practice. All calibration logs will be received, reviewed, and initialed by the external QA/QC team to indicate acceptability, prior to testing.

Calibration of field sampling equipment must be performed prior to the field sampling effort. Calibration procedures must be consistent with procedures outlined in the EPA publication "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume III, Stationary Source Specific Methods" (EPA, 1977) and the Reference Methods. Table 3-4 details the recommended calibration procedures and acceptance limits for various items to be calibrated.

Plant instrumentation will be calibrated in accordance with facility procedures. Any instrumentation scheduled for calibration within a month of the end of testing will be calibrated prior to the start of the test period.

3.1.4 Preliminary Site Work

Before conducting formal emission testing, preliminary tests will be conducted to:

- establish sampling conditions, and
- identify any adverse conditions at the sampling locations or in gas flow and develop approved work arounds.

The following duct and flue gas parameters will be confirmed:

- inside diameter,
- moisture content--measured for each of the three temperature conditions,
- static pressure,
- velocity pressure profiles--measured for each of the three temperature conditions,
- temperature profiles-- measured for each of the three temperature conditions, and

- combustion gas composition--measured for each of the three temperature conditions, special attention will be paid to the CO_2 contribution of the sodium acid gas reagent as sodium bicarbonate and sodium sesquicarbonate "calcine" and evolve CO_2.

Because new conditions will be tested each day, expected moistures will be used for the first run and moistures will be verified at the end of that run. The most recent measured moistures will be used in subsequent testing.

Velocity pressure and temperature profiles will be measured across the sampling ports of each duct to determine if there is a flow distribution across the duct.

3.2 Sampling Procedures

This section outlines the sampling protocols, pretest QA/QC and on-site QA/QC activities to be performed during the test program. Emphasis has been placed on sampling and QA/QC protocols for manual and continuous stack emission measurement.

The protocols described in this section ensure that representative samples of the flue gases to be monitored are collected and that sample integrity is maintained. The use of these sampling procedures will significantly reduce, if not eliminate, the possibility of sample contamination from external sources. Sample handling (e.g., collection techniques, preservation and transportation) and stringent documentation requirements (e.g., sample identification, and chain of custody) are key factors in this program.

The protocols to be used for manual sampling and continuous monitoring during testing include:

- EPA Method 29 Determination of Multiple Metals Emissions from Stationary Sources (40 CFR 266, Appendix IX, Section 3.1) including the determination of front-half particulate matter. The laboratory recovery may be modified for mercury recovery from an aliquot from the acidified hydrogen peroxide impingers by adding potassium permanganate to neutralize the excess peroxide which appears to cause a low bias of Method 29 compared to Method 101A for some sources.
- EPA Method 23 - Determination of Polychlorinated Dibenzo-p-dioxins and Polychlorinated Dibenzofurans from Stationary Sources. (40 CFR 60, Appendix A)
- EPA Method 26A - Determination of Hydrogen Chloride from Stationary Sources. (40 CFR 60 Appendix A)
- US EPA Method 6C and 7E Continuous Emission Monitoring Approved CEMS procedures for NO_x (Chemiluminescence) and SO_2 (non-dispersive ultra violet-NDUV). (40 CFR 60 Appendix B)
- Davis County Resource Recovery Facility, Ash Sampling Protocol, Revision 2, for combined ash and ESP residue grab samples. (Copy attached)

The sample procedures applicable to all manual sampling trains to be used in this program are discussed in terms of the daily sequence as follows:

1. The sampling trains will be prepared and assembled in the on-site laboratory using the procedures described in the QAPP and will be retrieved from the laboratory with all openings sealed.
2. All pretest, port change, and post-test leak-checks will be observed by a member of the external QA/QC team. The pretest leak-check will be conducted on a heated sample train at the nozzle; if the leak rate is found to be unacceptable (>0.02 ft^3/min at 15" Hg or 4% of the normal sampling rate, whichever is less) the source of the leak must be identified and fixed. Further leak checks will be performed until the leak check acceptability criterion is satisfied or if leak excessive (2-3 ft^3 or greater) train will be replaced. Care should be taken not to contaminate the sample train while the nozzle is open.
3. Prior to sampling, the heated sampling train components will be warmed up and stabilized at the proper temperatures for sampling.
4. The external QA/QC team members will review the sampling parameters (delta H and isokinetic input data) prior to the test and during testing to assure that the sampling will be conducted isokinetically.
5. Sampling will commence upon notification by the Principal Investigator that the facility is ready for test.
6. Additional leak-checks will be performed on the sampling trains before and after a move to another sampling port. Leak-checks must be performed before and after any change in sample train components.
7. The sampling train will be broken down into transportable components. The components of each section will be sealed at the end of the test and transported to the cleanup area. All sampling trains will be recovered by designated clean-up personnel.
8. Sample recovery and packing will be spot checked by a member of the external QA/QC team. The designated cleanup personnel will recover the samples, record sample information in the sample log book, and label sample containers.
9. Field blank trains (organic train) will be prepared in a manner identical to actual sampling trains. They will be assembled and left for a period of time equal to an actual sampling run. The field blanks will be recovered and analyzed using the same procedures as the field samples. Reagent and filter blanks will be collected as outlined in each of the sampling protocols.

Sampling train summary sheets and data sheets will be completed for each sampling train. A daily operator's log will be kept for each test. Davis County RRF DCS and CEMS data will be logged throughout testing. Copies of the data, the daily operator's log and a special log book developed to record events related to the spray cooling system will be obtained.

3.3 Sample Recovery and Sample Custody

Sample train preparation and recovery procedures will ensure that:

- no external contamination is present in the sample train and containers;
- the sample is quantitatively removed from the sample train into the designated containers;
- the sample integrity is maintained until analysis; and
- because of the possibility of higher concentration PCDD/F runs contaminating a sampling train for subsequent runs with lower expected PCDD/F concentrations after train proofing, recovered glass ware from normal temperature and runs without activated carbon addition will not be reused for medium and low temperature, activated carbon runs.

Sample custody procedures and preparation of samples for shipment will be spot checked by an external QA/QC team member to document that the Contractor followed the procedures described in these sections. The team member will initial sample recovery sheets to document that the appropriate sample recovery and sample train clean-up procedures were followed.

Tables 3-2 to 3-4 provide an outline of key highlights for each of the manual stack sampling protocols.

A Method 29 sampling train will be used for the collection of particulate material, metals and mercury. The sample train is operated as a Method 5 train with modifications to the impinger configuration to enhance the collection of the mercury.

The QA/QC activities (and the responsible party in parentheses) for the mobilization phase of the emission tests at Davis County Resource Recovery Facility include:

1. preparation, precleaning, and proofing of manual stack sampling trains and sample containers (Testing Contractor);
2. quality checks of chemicals, reagents, filters, and XAD-2 sorbent (Testing Contractor);
3. calibration of all sampling and monitoring equipment (Testing Contractor);
4. calibration of plant instrumentation (Host Facility)
5. development (and review) of data acquisition, data reduction and summary procedures (Principal Investigator);
6. development of external QA field data sheets (external QA/QC team);
7. review of equipment calibration logs (external QA/QC team); and
8. review of proposed field and laboratory procedures (external QA/QC team).

Table 3-2 Summary of Method 29 Particulate Material, Metals and Mercury

TRAIN CONFIGURATION	
Nozzle	Quartz
Probe Liner	Quartz
Filter	Quartz fiber filter without organic binders and background metal content of < 1.3 mg/m^2
Impinger Solutions	1. Empty 2. HNO_3/H_2O_2 (100 mLs) 3. HNO_3/H_2O_2 (100 mLs) 4. Empty 5. $KMnO_4/H_2SO_4$ (100 mLs) 6. $KMnO_4/H_2SO_4$ (100 mLs) 7. Silica Gel (200 - 300 g)

SAMPLE RECOVERY COMPONENTS

CONTAINER	CONTENTS	ANALYSIS REQUIRED
1	Filter	Particulate, Metals and Hg
2	Acetone Front Half Rinse (100 mL)	Particulate and Metals
3	Probe Rinse 0.1 N HNO_3 (Front Half Rinse) (100mL)	Metals and Hg
4	Back Half Filter, Impinger Contents (1,2,3) and Nitric Acid Rinses (100 mL)	Metals and Hg
5A	Impinger 4 content and 100 mL HNO_3 rinse Impinger Contents (5,6) and 100 mL	Mercury
5B	$KMnO_4$ rinses HCl (25 mL) rinse of Impingers 5 & 6 in	Mercury
5C	200 mL of DI water	Mercury

SAMPLE STORAGE CONTAINERS

- 1000 mL or 500 mL glass amber (wide mouth) sample containers with Teflon lined caps liquid samples and blanks
- petri dish for filter

Table 3-2 Summary of Method 29 Particulate Material, Metals and Mercury (Continued)

SAMPLE ANALYSES SCHEME

PARAMETER	METHOD	COMBINED LAB SAMPLE
Particulate Material Determination	Gravimetric	Containers 1 and 2
Metal Analysis	ICAP	Containers 1, 2, and 3
Cd, Pb		
Hg	Cold Vapor AA	Containers 1, 2 and 3 Container 4 Containers 5A, 5B & 5C

BLANKS

Reagent Blanks Collected in the Field and Held for Possible Analysis:

Acetone	100 mLs
0.1 N HNO_3	200 mLs
5% HNO_3/10% H_2O_2	200 mLs
Acidified $KMnO_4$	300 mLs
8 N HCl/DI Water	50 mLs
Filter Blank	50 mLs

Blank Train:

Taken through all the steps from preparation to recovery without actual sampling. Four blank trains will be collected and analyzed during the test program.

3.3.1 Sample Identification, Custody and Tracking Procedures

To ensure that all samples required for each test are collected or recovered, a comprehensive sample list will be prepared for each run. Once a sample is recovered or collected and identified, it will be logged into the QA/QC Master Sample List. With this system in place, the QA team will be able to identify any errors or deficiencies and correct them immediately. Information to be documented in the log will include:

1. the test number;
2. the test date;
3. field codes;
4. a brief sample description;

5. the initials of the individuals logging-in shipping and receiving the sample;
6. the name of analytical laboratory performing the analysis; and
7. status of sample (i.e., analyzed or archived).

Table 3-3 Summary of EPA Method 23 PCDD/F

TRAIN CONFIGURATION		
Probe	Glass with Nickel plated stainless steel nozzle	
Filter	Glass fiber filter without organic binders	
Resin	Amberlite XAD-2	
Impinger Solutions	1. empty - short stemmed	
	2. R.O. Water	(100 mLs)
	2. R.O.Water	(100 mLs)
	3. Empty	
	4. Silica Gel	(200 - 300 g)

SAMPLE RECOVERY COMPONENTS		
CONTAINER	CONTENTS	ANALYSIS REQUIRED
1	Filter	Trace Organics
2	Acetone Rinse (3x); DCM Rinse (3x) Front Half, Back Half and Condenser Coil	Trace Organics
3	Toluene Rinse (3x) Front Half, Back Half and Condenser Coil	Trace Organics
4	Amberlite XAD-2	Trace Organics
5	Impinger Contents and R.O water rinses (3x)	Trace Organics

SAMPLE STORAGE CONTAINERS
- 1000 mL or 500 mL glass amber (wide mouth) sample containers with Teflon lined caps - Glass petri dishes for filters - clean aluminum foil to wrap XAD-2 trap and filled storage containers

SAMPLE ANALYSIS SCHEME		
	METHOD	COMBINED LAB SAMPLE
	GC/MS High Resolution	One sample analysis per train (Containers 1, 2, 3, 4, 5 and 6)

Table 3-3 Summary of EPA Method 23 PCDD/F (CONTINUED)

BLANK TRAIN

Blank Train: Taken through all the steps from preparation to recovery with leak check volume ambient conditions sampling. Four blank trains will be collected and analyzed during the test program.
Field Blanks: Combined acetone/hexane, combined water/glycol, XAD-2 trap, glass fiber filter. Samples collected and archived; analyzed if necessary.
Field Spiking: Spiking of the resin cartridge will take place at Analytic Laboratory prior to sampling and will include the following 5 labeled compounds:

$^{37}Cl_4$-2,3,7,8-TCDD
$^{13}C_{12}$-1,2,3,4,5,7,8-HpCDF
$^{13}C_{12}$-2,3,4,7,8-PCDF
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF

Reference method calibration procedures will be used. The ensures that:

- all critical measurement parameters, including all critical pollutant measurement systems, reference the applicable standard operating procedures or provide a written description of the calibration procedures to be used;
- the frequency of calibration is stated; and
- the calibration standards to be used and their source(s) including traceability procedures are stated.

Table 3-5 Summary of EPA Method 26 Hydrogen Chloride (HCl)

<table>
<tr><th colspan="6">TRAIN CONFIGURATION</th></tr>
<tr><td colspan="2">Probe Liner</td><td colspan="4">Glass</td></tr>
<tr><td colspan="2">Filter</td><td colspan="4">25 mm Teflon, glass mat or Pallflex filter</td></tr>
<tr><td colspan="2">Impinger Solutions</td><td colspan="4">1. 0.1 N H_2SO_4 (15 mL)
2. 0.1 N H_2SO_4 (15 mL)
3 0.1 N NaOH (15 mL)
4. 0.1 N NaOH (15 mL)
5. Silica Gel or Drying Tube (200 - 300 g)</td></tr>
<tr><th colspan="6">SAMPLE RECOVERY COMPONENTS</th></tr>
<tr><td>CONTAINER</td><td colspan="3">CONTENTS</td><td colspan="2">ANALYSIS REQUIRED</td></tr>
<tr><td>1</td><td colspan="3">Impinger 1& 2 and DI Water</td><td colspan="2">HCl</td></tr>
<tr><td>2</td><td colspan="3">Rinsings
Impinger 3 & 4 and DI Water Rinsings and sodium thiosulfate</td><td colspan="2">Cl_2</td></tr>
<tr><th colspan="6">SAMPLE STORAGE CONTAINERS</th></tr>
<tr><td colspan="6">- 100 or 250 mL HDPE sample container with Teflon lined screw lids</td></tr>
<tr><td colspan="6">SAMPLE ANALYSES SCHEME</td></tr>
<tr><td colspan="2">PARAMETER</td><td colspan="2">METHOD</td><td colspan="2">COMBINED LAB SAMPLE</td></tr>
<tr><td colspan="2">HCl
CL_2</td><td colspan="2">Ion Chromatography
Ion Chromatography</td><td colspan="2">Container 1
Container 2</td></tr>
<tr><th colspan="6">BLANKS</th></tr>
<tr><td colspan="6">Reagent Blanks Collected in the Field and analyzed:
0.1 N H_2SO_4 diluted with DI water 30 mL + DI water
0.1 N NaOH diluted with DI Water 30 mL + DI water</td></tr>
</table>

3.3.2 Method 29 Train for Particulate, Metals & Mercury Analysis

The acidified $KMnO_4$ solutions will be prepared fresh daily and stored at 4°C in a glass amber bottle. The $KMnO_4$ impingers will be wrapped in aluminum foil. Additional acidified potassium permanganate solution will be added to the $KMnO_4$ impingers (or the actual impingers will be replaced with impingers containing fresh $KMnO_4$) during a test if oxidation occurs (indicated by a color change).

Stock $KMnO_4$ solutions and sulfuric acid solutions will be provided fresh weekly. The $KMnO_4$ will not be acidified until the test day.

This sampling train consists of nickel plated stainless steel nozzle attached to a heated Teflon line. A thermocouple and S-type pitot tube are attached to the probe for measurement of gas temperature and velocity. Sample gas is drawn through the nozzle and probe and then through a heated quartz (QR 100) filter. Particulate matter collected on the filter and in the probe will be weighed and analyzed for the metals of interest. The impingers will be weighed before and after the test run to permit gravimetric moisture determination.

Leak checks on the assembled train will be performed before and after each sampling run and during port changes. In the event that any portion of the train is disassembled and reassembled (i.e., filter change), leak-checks will be performed prior to disassembling the train and resuming sampling. All leak-checks and leakage rates will be documented on the relevant field test data sheet.

Preparatory activities for this train include equipment calibration and filter weighing, standard to Method 29. An additional preparation for this train's glassware and associated sample containers is the precleaning as outlined in Section 3.1.1.

Recovery procedures for the sample train will be:

1. Remove the sampling train to the recovery site.
2. Note the condition of the train (i.e., filter condition, impinger contents color, silica gel color, etc.).
3. Disassemble the filter housing and transfer the filter to its original petri dish. Seal the container with Teflon tape and label it with the appropriate sample information
4. Weigh all impingers for gravimetric moisture determination.
5. Brush-rinse the front half of the train (nozzle, probe, front half filter housing, and cyclone, if applicable) with acetone into precleaned containers
6. Repeat the front half rinsing of the train with 0.1 N nitric acid into a precleaned container
7. Empty the contents of impingers 1, 2, 3 and 4 into a clean polyethylene sample bottle. Rinse the impingers back half of filter housing, filter support and connecting glassware with 0.1 N HNO_3 into the precleaned container.
8. Empty the contents of impingers 5 and 6 (acidified $KMnO_4$) into a clean glass amber sample bottle. Rinse the impingers with acidified $KMnO_4$ and add the rinsings to the glass amber sample bottle containing the impinger solutions. Remove any residue with 8 N HCl solution.
9. Weigh silica gel impinger.
10. At this point, check all containers to ensure they are sealed, labeled, and all liquid levels are marked. Log all samples onto the chain-of-custody record.

The samples recovered from this train will be identified as follows:

- TS1 = filter,
- TS2 = acetone probe and front half rinsings,
- TS3 = 0.1 N nitric acid probe and front half rinsings,
- TS4 = DI water and HNO_3 impinger solutions and impingers 1, 2, 3 and 4 nitric acid rinsings,
- TS5 = $KMnO_4$ impinger solutions and impingers 5 and 6 rinsings, and

A blank train will be used for field blank sample analysis. The field blank will consist of assembling and loading the particulate material and metals train and performing the sample recovery procedures. The samples from the blank train will be analyzed. One blank train will be collected with each set of three tests. Reagent blanks will be collected in the field once during the field test but they will not be analyzed unless warranted.

3.3.3 Method 23 Train for PCDD/F Analysis

The Modified Method 5 (MM5) sampling train outlined in the EPA Method 23 will be used for the collection of polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans (PCDD/F), and for trace organics.

The sample train consists of a heat-traced probe with a nickel-plated, stainless steel nozzle, and attached thermocouple and pitot tube. The glass probe will be maintained at a temperature of 120°C ±14°C. After the probe, the gas passes through a heated glass fiber filter. Downstream of the heated filter, the sample gas passes through a water-cooled module, then through a sorbent module containing approximately 30 to 40 g of XAD-2 resin (pack trap). The XAD module, which is kept at a temperature below 20°C, is followed by a series of four impingers. The XAD inlet temperature will be monitored to ensure that the temperature of the flue gas sample entering the module is maintained below 20°C. The first impinger is connected to the outlet of the XAD module, and is modified with a short term stem so that the sample gas does not bubble through the collected condensate.

The first impinger will be empty and the second and third impingers will contain 100 mL of HPLC grade water, the fourth will be empty and the fifth will contain a known weight of silica gel. The impingers, condenser and XAD-2 resin module will be weighed prior to assembling the sampling train to permit gravimetric moisture determination. All connections within the train will be glass or Teflon; no sealant greases will be used. The impingers are followed by a pump, dry gas meter, and a calibrated orifice meter.

Prior to sampling, all gas-contacting components of the train will be washed with alconox and water and thoroughly rinsed with solvents. All trace organic train components and sample containers will be proof rinsed, the rinses analyzed, and components and glassware deemed free of contamination prior to use.

Sampling will be isokinetic (100 ± 10 percent) with readings of flue gas parameters recorded at every sampling point through the traverse. In the event that isokinetic sampling cannot be maintained due to a high pressure drop through the sampling train, the train will be shut down and the problem remedied. In the event that steady operation is not maintained, or that there are atypical fluctuations in monitored gas parameters, the testing will be stopped until these conditions are stabilized. Steady operation of each unit will be the responsibility of facility personnel.

Each point will be sampled to allow collection of sufficient cumulative flue gas volume to perform necessary analyses (about 2-4 m^3). The largest practical sample volumes time permits will be collected during the second run for conditions 1, 3, 4, 8 and 10.

Sampling will be conducted while traversing the Method 23 train across each of the ports at locations which satisfy the criteria delineated in the Method. At each test point within the stack, all necessary sampling train parameters will be measured. During sampling, the XAD cartridge will be wrapped in foil to shield the resin from sunlight.

Leak-checks on the sampling train will be performed before and after each sampling run and during each port change. In the event that any portion of the train is disassembled and reassembled (i.e., due to filter or resin changes), leak-checks will be performed. The sample train leak-checks and leakage rate (where applicable) will be documented on the field test data sheet for each respective run.

Following completion of each test run, the trains will be transported to a recovery area on-site, recovered and the analytic samples secured for transportation to Analytic Laboratory. The recovery procedure for the trace semi-volatile train will be:

1. At the end of sampling, remove the probe from the stack and cap nozzle. Allow to cool briefly.
2. Conduct a leak-check to ensure a leakage rate of < 0.02 ft^3/m.
3. Remove the sampling train to the recovery site.
4. Note the condition of the train (i.e., filter condition, impinger contents color, silica gel color, etc.).
5. Weigh the XAD-2 trap and impingers for gravimetric moisture determination.
6. Disconnect the sampling probe from the train and seal all open end with clean aluminum foil. Store all train components in a clean and cool (4°C) area until shipment to Analytic Laboratory.

The following recovery procedures will be performed:

1. Disassemble the filter housing and transfer the filter with the exposed side up to precleaned foil with hexane rinsed tweezers. Brush any loose particulate from the filter holder onto the filter. Fold the filter in half (particulate cake inside fold), crimp the foil to close the edges and place in a Petri dish.
2. Quantitatively recover the material in the nozzle and probe line, front half of the filter holder and any connecting glassware, first by brushing then rinsing each three times with acetone and then by rinsing three times with methylene chloride (Dichloromethane - DCM). The acetone and methylene chloride rinsing will be placed in a precleaned amber glass sample container and sealed with Teflon-lined lids, mark liquid levels.
3. Repeat the rinsings described in 2 (probe liner, nozzle and front half filter holder) using toluene as the rinse solvent. Collect the rinses in a precleaned amber glass sample container (with Teflon lids) and mark liquid levels.
4. Remove resin trap from the connecting glassware and seal the open ends with precleaned aluminum foil. Transfer the XAD-2 resin into a glass extraction thimble if resin trap is to be cleaned and proofed for subsequent tests.
5. Rinse the back half of the filter holder, the condenser coil empty resin trap and connecting glassware, sequentially three times each with acetone and methylene chloride. Collect rinsings.
6. Repeat the rinsings described in 5 (back half filter holder, condenser coil empty resin trap and connecting glassware) using toluene as the rinsing solvent. Collect the rinses.
7. Transfer the impinger contents from the first three impingers into a precleaned glass-amber sample container and seal with a Teflon-lined lid.
8. Rinse the first three impingers and connecting glassware three times each with acetone and methyelene chloride. Collect rinsings in the precleaned glass-amber sample jar containing the back half acetone/methylene chloride rinse.
9. Repeat rinsings described in 8 (impingers and connecting glassware) three times each with toluene. Add rinsings to the sample jar containing the toluene rinses of the back half filter holder, condenser coil and empty resin trap, then seal with Teflon-lined lid. Mark liquid level.
10. Remove and recycle the silica gel from the fourth impinger.

All recovered samples will be stored in a refrigerator at 4°C immediately following sample recovery. The samples will be identified as follows:

1. TS1 = filter
2. TS2 = acetone/methylene chloride front half and back half rinsings

3. TS3 = toluene front half and back half rinsings
4. TS4 = XAD-2 resin
5. TS5 = impinger solutions (i.e., impinger contents)

Four blank Method 23 sampling train will be used. The blank trains will be treated at the sampling site in the same manner as the test trains, except that the only gas drawn through the blank train will be ambient air equivalent in volume to the sampling train leak check volumes. The purpose of these blank trains is to provide background concentrations of trace organic compounds.

3.3.4 Method 26 Sampling Train for HCl

The train consists of a heated glass probe and filter followed by a three way stop clock and 30 mL midget-impingers. The first two impingers will contain 15 mLs of 0.1 N H_2SO_4 while the third and fourth impingers will contain 15 mLs of 0.1 N NaOH. A final impinger containing silica gel will be placed after the fourth impinger to protect the dry gas meter and pump.

The train will be leak checked by plugging the probe inlet and turning on the sample pump to pull a vacuum of 10 inches of Hg. The needle valve will be turned off and the vacuum should remain stable for 30 seconds.

The sampling system will be leak checked at the completion of the run.

The recovery procedures for this train will be:

1. Weigh the impingers and silica gel
2. Quantitatively transfer the contents of impingers 1, 2 and 3 and label the sample container.
3. Rinse the impingers and connecting glassware with DI water.
4. Seal and label the container then mark the liquid level.
5. Remove and recycle the silica gel.

3.3.5 CEMS for Combustion Gases and Criteria Pollutants.

The concentration of the following combustion gases will be monitored on a continuous basis using the monitors described in Table 3-7:

- carbon monoxide (CO),
- oxygen (O_2)
- sulfur dioxide (SO_2), and
- nitrogen oxides (NO_x).

A sample of the flue gases will be drawn from stainless steel tube, filtered to remove particulate material then transferred by a Teflon line to the gas conditioning unit and individual analyzers. The gas conditioning unit and analyzers will be located in the testing subcontractor's mobile CEMS Laboratory.

The Teflon sample line will be heated to at least 160°C or at least 5°C above the dew point of the flue gases whichever is greater.

Prior to the start of testing, several preliminary assessments and calibrations will be made. These activities include:

1. During the preliminary tests, the sampling probe will be traversed across the CEM sampling location for stratification. Acceptable stratification is when all points are within 10% of the average. If unacceptable stratification is present, a sampling probe with sufficient multiple sampling orifices will be used.
2. System bias checks will be conducted prior to the tests. This will involve a three-point calibration of the instruments through the complete collection system by directing calibration gas to a point of entry immediately after the sampling probe and to the analyzers directly.
3. Reproducibility check will be conducted. This will involve conducting replicate (at least 3) analysis of calibration gas.
4. Instrument linearity checks will be done prior to going on-site and after test program complete. Calibrations will be at three points plus a zero with a resultant R = 0.995 deemed acceptable.

A sample recovery check (system bias check) will be conducted prior to testing and daily during testing program with 90% recovery. Calibration gases will be introduced:

1. at the sample probe inlet upstream of the sample transport pump,
2. directly to the analyzers.

The differences in readings will be interpreted to be losses in the transport or conditioning system.

A calibration (zero, mid-point and span check) of each CEM will be conducted prior to each test period and at the completion of each test. The individuals performing the calibrations are required to complete calibration data sheets which contain the following information:

1. test number and sampling location,
2. date and time,
3. operator,

4. instrument serial number, model, etc.,
5. span gas concentration and cylinder reference number,
6. instrument settings (range, attenuation, zero, span), and
7. instrument response.

Table 3-6 Combustion Gas Analyzer Specifications

ANALYZER	MODEL	PRINCIPLE	RANGE OF OPERATION
Nitrogen Oxides	TECO Mode 10A	Chemiluminescent	0-5000
Sulfur Dioxide	Western Research 721AT2	NDUV	0-500 + 0-5000

If a monitor must be recalibrated during a test, the new calibration information must be documented. Calibration data sheets will be initialed by the individual performing the calibration and by the on-site external QA/QC.

3.3.6 ESP Ash, Acid Gas Reagent and Activated Carbon Sampling and Processing

Composite samples of ESP residue, acid gas reagent and activated carbon will be collected near the end of each condition's run.

Grab samples of ESP residue will be taken from the fly ash screw conveyor that connects the bottom of the baghouse hoppers to the ash bunker. Incremental grab samples of the Trona and activated carbon being used during any test will be obtained throughout the day and composited in a new 5 liter plastic bucket. The solid samples will be archived in a 1 liter wide mouth glass jar fitted with a Teflon lined lid. Sample labels (pre-gummed paper labels taped over) for moisture resistance will be prepared by the Testing Contractor. Each label will contain the following information:

1. date when sample was taken;
2. sample code;
3. run number;
4. sampling location;
5. sample description;

6. sample destination;
7. name of individual collecting or recovering sample; and
8. comments.

At the present time, no analyses are planned for the ESP ash samples which will be archived.

In addition, Davis County RRF is scheduled to collect combined ash samples during the anticipated test period. If they do so, representative combined ash samples will be analyzed for TCLP metals. One combined residue subsample, selected at random, will be analyzed for trace organics.

3.3.7 Process Data Acquisition

Basic system operating data will be continuously recorded in the Davis County RRF Data Historian which is an integral part of the Provox Operating System. The operating data collected will be provided to the Principal Investigator as an Excel file. This data will be summarized as run maximums, minimums and averages. Run time characteristics will be compared to baseline operating characteristics to verify that the facility was in normal operating condition when the testing was conducted. Operating data will be provided:

1. at least one week prior to start of testing;
2. throughout the test period, and
3. throughout the two month period immediately following testing.

Continuously recorded process parameters for the tested incinerator are:

1. Gas temperatures at:
    a) lower furnace control thermocouple
    b) furnace throat
    c) boiler top temperature
    d) boiler inlet and outlet
    e) economizer outlet
    f) conditioning section inlet and outlet
    g) ESP inlet
    h) stack
2. Boiler steam characteristics: temperature, flow and pressure
3. Boiler feed water characteristics: flow and temperature
4. Spray water characteristics: flow, temperature & pressure
5. Atomizing air pressure & flow

6. Incinerator draft
7. Opacity, other CEMS (CO) and PEMS (NO_x & SO_x) data
8. Stoker operating characteristics
9. Acid Gas Reagent feed rate
10. Activated Carbon feed rate

3.3.8 Sample Chain of Custody and Shipment

Shipping of samples to the Analytic Laboratory will be performed in such a manner that the integrity and identity of the sample will be maintained. A chain-of-custody form will be completed by the individual shipping the sample to document sample transfer in the field and from sampling personnel to the laboratory. The original copy will accompany the samples and a copy retained by the Testing Contractor.

The Principal Investigator will review all forms to ensure that they have been completed correctly and accurately. Any omissions or errors will be identified, corrected and a revised copy forwarded to the appropriate laboratory.

Test Contractor personnel will coordinate the packing and shipment of all samples. They will maintain the Master Sample List. The assigned person will verify that all samples are properly sealed, liquid levels marked, labels firmly fixed to the container and that samples are stored properly to maintain its integrity. The Principal Investigator will verify and retain copies of all shipping documents.

Upon receipt at the laboratory, the form will be cross-checked by the laboratory personnel with the samples received to ensure all samples listed on the form have been received and their integrity maintained (i.e., no cross-contamination, leakage or breakage occurred). The bottom of the form will be signed and copies forwarded to the Principal Investigator and Testing Contractor.

3.4. ANALYTIC PROCEDURES

The analytical procedures and instrumental methods to be used on the samples collected during the testing program are summarized in Table 3-7. A brief outline of analytical and QC procedures are provided. The Analytic Laboratory will be responsible for analyzing all train samples. TCLP analyses of combined residue samples will be performed by the Utah Certified Laboratory that routinely performs the Host Facility's TCLP analyses.

3.4.1 Trace Metals (Method 29)

The analytical procedures for measuring the trace metals in samples collected by the Method 29 train samples are based on analyzing the metals formed upon dissolution of the metals in the impinger reagent and digestion of the metals associated with the particulate fraction. The sample preparation scheme by acid digestion (using HF and HNO_3) for the train components is illustrated in Table 3-8.

After a sample has been digested, it is aspirated into the plasma discharge of the Inductively Coupled Argon Plasma (ICAP) unit are atomization and electronic excitation occur and radiation is emitted. The energy of the radiation is indicative of a specific element and the intensity of the radiation is directly proportional to the amount of analyte present. ICAP methods are relatively free of matrix problems but do suffer from spectral interferences when a very low concentration of one element is being measured in the presence of a high concentration of another.

Inductively-coupled argon plasma emission spectroscopy (ICAP) analysis of the sample extracts will be performed for all metals except mercury. Mercury will be determined by cold vapor atomic absorption.

Table 3-7 Analytical Methodologies for Stack Samples

COMPONENT	METHOD	REFERENCE
Particulate Material	Gravimetric	Method 5
Metals	Inductively Coupled Plasma Atomic Evaluation Spectroscopy (ICAP): Cd, Pb	Method 29 & SW-846 6010
Mercury	Cold Vapor Atomic Absorption (CVAA)	Method 29 & SW-846 7470
Hydrogen Chloride	Ion Chromatography (IC)	EPA Method 26
Dioxins and Furans	High resolution gas chromatography/high resolution mass spectrometry (high resolution GC/MS)	EPA Method 23 & SW-846 8290

Table 3-8 Inorganic Sample Preparation Methods (Train Samples)

1. Desiccate and weigh the **filter**

2. Reduce and weigh **(acetone probe rinse)**
   a) Transfer to a tarred Teflon bomb and evaporate to dryness
   b) Cool to ambient temperature in a desiccator and weigh the "particulate catch"

3. Place the solids sample into the bomb (along with the particulate catch), add 5 mL aqua, and digest with gentle heating to 60°C
   a) Dilute to volume and analyze portions for mercury (CVAA) and metals (ICAP).
   b) Record analytes as total weight

4. **Nitric acid impinger solutions and rinsings**
   a) Combine all portions and obtain volume by weight
   b) Split 50 mL for mercury analysis taking the remaining sample volume for other metals as described below.
   c) Acidify to pH 2 with HNO_3
   d) Reduce volume to about 35 mL
   e) Add 7 mL aqua regia and permangate and microwave for 10 min or digest for 2 hr at 95°C
   f) Dilute to volume (50 mL)
   g) Analyze for trace metals

5. **Acidified $KMnO_4$ impinger solutions and rinsings**
   a) Determine volume by weight
   b) Remove an aliquot for mercury analysis as outlined below
   c) Add 3.0 mL concentrated sulfuric and 1.5 concentrated nitric acid to a 50 mL sample
   d) Heat for 2.0 hours on a water batch at 95°C maintaining excess permanganate oxidant
   e) Cool to room temperature
   f) Add 1.0 mL of 20% hydroxylamine hydrochloride solution (or more with the solution is colorless)
   g) Dilute the sample with 50 mL of 5% H_2SO_4/2.5 % HNO_3 and analyze by CVAA.

Analysis of mercury by cold vapor atomic absorption involves reduction of the oxidized forms of mercury in the sample followed by purging of the mercury into the absorption cell.

At least one duplicate and one spiked sample will be analyzed with every 20 samples to verify precision of the method and one QC sample (mid point of calibration curve) with every 10 samples. Matrix spike samples (one of each with every 10 samples) will be performed to document the effect of the sample matrix on the analysis. Duplicate sample analyses (one with every 10 samples) will be performed to determine analytical precision and method blanks will serve to assess the degree of background contamination.

Separate analytic results will be reported for front-half, back-half and potassium permanganate impinger catches. Analytic results will be reported in accordance with ASTM D 4210-83; that is, results less than 3 blank standard deviations (instrument noise) will be reported as BDL and those between the BDL value and the LQL (laboratory quantification limit or 10 blank standard deviations) will be reported as EMC (estimated maximum concentration or Tentative).

3.4.2 Trace Organic Compounds

The analysis of trace organic compounds by GC/MS a highly specialized procedure involving a complex series of extraction and clean-up procedures. The approach in analysis of the organic compounds involves the use of selected ion monitoring (SIM) GG/MS. EPA Method 23 (High resolution GC/MS) specifically will be used for PCDD and PCDF analysis.

One analysis per train will be performed. The filter section and resin will be extracted separately and combined prior to clean-up. Based on laboratory experience, the following modifications are proposed:

a) toluene is substituted for benzene as a solvent; and

b) for solvent exchange into hydrocarbon solvent, toluene replaces hexane.

This protocol for analysis of the trace organic samples contains analytical criteria for confirmation of PCDD/F, quantification procedures, and QA/QC requirements for analytical data, which are described below.

To monitor the extraction, clean-up, and analysis of trace organic samples, labeled surrogates will be added to field samples, field and laboratory blanks, and matrix spikes prior to extraction. One set of labeled surrogates will be added in all the Soxhlet extraction steps. A second set of the labeled surrogates will be added to impinger samples from the Method 23 train during extraction.

According to the EPA protocol, recoveries for surrogate compounds should typically be in the range from 60 to 90%. Since these surrogates can be used to adjust the results for native PCDD's and PCDF's, low recoveries do not invalidate the data, but do result in higher than desired detection limits.

The surrogates are shown below, and target recoveries for these are 70 to 130% with the precision of blind duplicates analysis as ± 50%.

Dioxins and Furans

2,3,7,8-TCDD-$^{13}C_{12}$
1,2,3,7,8-PeCDD-$^{13}C_{12}$
1,2,3,6,7,8-HxCDD-$^{13}C_{12}$
1,2,3,4,6,7,8-HpCDD-$^{13}C_{12}$
OCDD-$^{13}C_{12}$

The following internal standards will be used:

PCDD/PCDF - 1,2,3,4-TCDD-$^{13}C_{12}$ and 1,2,3,4,7,8-HxCDD-$^{13}C_{12}$

Field spiking of the XAD-resin prior to sampling will be performed at Analytic Laboratory. Each resin cartridge will be spiked with:

$^{37}Cl_4$-2,3,7,8-TCDD
$^{13}C_{12}$-1,2,3,4,5,7,8-HpCDF

A criterion for validating analytical data will be demonstration that the extraction and clean-up systems are free of contamination. Method blanks and matrix blanks will be analyzed with every other extraction to demonstrate contamination below the target minimum limits of detection.

Corrective action for excessive contamination (concentration above minimum detectable levels) found in the laboratory blanks will be based on discussions with the Principal Investigator on a case-by-case basis. The corrective action may include blank correcting all analytical results.

The following analytical criteria will be used for confirmation of the target trace organic compounds.

1. GC/MS retention time of specific trace organic isomers available;
2. GC/MS retention time window of respective trace organic series of isomers based on standard mixtures;
3. chlorine isotope ratios of molecular ions of trace organic isomers with ± 15% of the values determined from the external standards;
4. responses of trace organic masses greater than 2.5 times the signal-to-noise ratio;
5. a five point calibration (RRF) must have a standard deviation of 25% or less to be valid; and

Corrective action for discrepancies in the confirmation criteria will require reanalysis of the samples. If the criteria are not met after reanalysis, the confirmation of specific isomers will not be considered valid.

Once the trace organic compounds have been identified and confirmed by the procedures described above, quantitation of the compounds will be made by comparison of the response factors of the sample analytes to the response factors of unknown amounts of native trace organic compound external standards.

3.4.3 Halogen (HCl) Analysis Procedures

HCl will be determined using ion chromatography. Aqueous impinger solutions will be injected into a stream of 4-hydroxybenzoic acid elutent prior to entering a separation column where the anions present are separated based on their relative affinities for the strong base anion exchangers. The separated anions are measured on a conductivity detector and identified based on their retention time relative to known standards. Quantification is based on peak area using electronic integration. Calibration curves will be composed of a blank and a minimum of three standards. Duplicates QC samples and check standards will be run with every group of ten samples.

3.4.4 Particulate Emissions

Particulate samples (front-half acetone rinse and the filter) collected from the particulate/metals train will undergo gravimetric determination prior to metals analysis. The gravimetric analysis will follow the procedures outlined in Method 5. The gravimetric analysis requires measuring the weight gain on the particulate filter and the residue left over in the acetone rinse of the front-half train components. The gravimetric analysis requires desiccation of the samples prior to weight determination. Samples are weighed to a constant weight of ± 0.5 mg. When gravimetric determinations are completed, the samples will be forwarded to the inorganic laboratory for metals analysis.

4. APPROACH TO QA/QC

The overall objective of the sampling and analysis effort is to provide data that are precise, accurate, comparable, representative and complete. The definitions for these criteria and how compliance with them will be assessed are described below.

The two aspects of data quality of primary concern are precision and accuracy. Precision, as defined in "Guideline and Specifications for Preparing Quality Assurance Project Plans" (U.S. EPA QAMS-005/80), is "a measure of mutual agreement (or variability) among individual measurements of the same property, usually under prescribed similar conditions". Various measures of precision exist depending on these conditions. This term is independent of the error (accuracy) of the analyses and reflects only the degree to which the measurements agree with one another, not the degree to which they agree with the "true" value for the parameter measured.

Quality control procedures, such as control sample analyses and replicate analyses, represent the primary mechanism for evaluating measurement data variability or precision. Control sample analyses are used to define repeatability, replicate analyses are used to define analytical replicability, and results for replicate samples may be used to define the total variability (replicability) of the sampling/analytical system as a whole. QC objectives for laboratory control samples (prepared QC standards) and duplicates are outlined in Table 4-1.

The QA/QC objectives for precision, accuracy and completeness established for each major compound measured are considered guidelines. For a measurement system, if all QC data meets these objectives, the test results are judged as having acceptable quality. When specific QC criteria are not met, the data will be flagged and the acceptance left to the technical judgment of the data user.

The QA/QC objectives for precision, accuracy and completeness established for each major compound measured are considered guidelines. For a measurement system, if all QC data meets these objectives, the test results are judged as having acceptable quality. When specific QC criteria are not met, the data will be flagged and the acceptance left to the technical judgment of the data user and the regulatory agency.

Table 4-1 Analytical Objectives for Laboratory Quality Control Samples (Guidelines)

PARAMETER	PRECISION[a] (% Difference)	ACCURACY[b] (%)
Trace Organics:		
Trace Organic train	< 50	50 - 120
Solids (ash and filters)	< 50	50 - 120
Gravimetric Analysis	1% of the total particulate[c] weight or 0.6 mg, whichever is greater	± 0.5 mg[c]
Metals		
Aqueous (impinger solutions)	< 20	85 - 115
Solids (filters and fly ash)	< 20	70 - 130
Acid Gas Anions (HCl)		
Aqueous (impinger solutions)	< 20	90 - 100

a) Expressed as the percent difference between replicate measurements of similar laboratory control samples (i.e., prepared QC standards and duplicates/replicate analysis).

b) Expressed as the measured versus the expected value of laboratory control samples.

c) Constant weight procedure for Method 5.

Table 4-2 QA Objectives for Precision, Accuracy, and Completeness for Sampling Measurements (Guidelines)

MEASUREMENT	PRECISION (RSD) (%)	ACCURACY[a] (%)	COMPLETENESS (%)
Continuous Methods			
Oxides of nitrogen (Chemiluminescence)	± 20	15	95
Sulfur dioxide (UV)	± 20	15	95

RSD - Relative Standard Deviation of replicate analysis of calibration gases.

4.1 CALCULATION OF RESULTS

All process parameters will be monitored by the plant DCS during each test run. This data will be provided to the testing team for inclusion in their report.

Additionally, CEMS measurements taken during the tests by the plant's system will be acquired for data collection and reduction. CEMS data to be acquired from this system will include:

Opacity Monitor:	measures opacity in the stack
Carbon Monoxide Monitor:	measure concentration in the stack
Oxygen Monitor:	measures concentration in the stack

Data from the Testing Subcontractor CEMS will be reduced after each run and submitted for review by the Principal Investigator and the QA/QC team. This will allow the determination of the level of success that was achieved the previous day with respect to the selected objectives (i.e., isokinetics checked daily by external QA/QC).

Data processing involves reexpressing the data retrieved during the test runs into a more meaningful form, e.g., producing suitable averages (15 minute, 1 hour and run averages corresponding to each manual test from the 15 minute averages). During this procedure and upon examination of the results, any problems anomalous results will be noted and recorded on the data sheets.

All data collected by the data acquisition system and by hand will be stored and standardized to reference conditions using spreadsheets in a micro-computer program. Data analysis will be done using bench-marked statistical analysis programs. For this effort, SPSS-PC^{+} has been chosen.

Standardized forms will be used for field data collection. The data collected will be reviewed in the field by at least one field crew member. Errors and deviations will be noted in the field book. The field book will also be reviewed by the QA/QC team member each night and any serious problems will be documented in the daily on-site QA/QC reports and the final QA/QC report. Isokinetics will be done daily and checked by QA/QC.

Analytical results will be reduced to concentration units as specified by the analytical procedure, using the corresponding equations provided by the analytical procedures. The analytical data will be reviewed, summarized and filed. The data sheets will also be reviewed by a member of the sampling team and any discrepancies will be documented as annotations on the data sheets.

At Analytic Laboratory, all instruments collect and store the analytical data generated in micro or mini computers. The raw and calculated data are retained both electronically and as a hard copy. Data from some instruments (i.e., ICAP, GC/MS), directly transfer the calculated results to the Laboratory Information Management System (LIMS). Some data (i.e., particulate catches) are manually entered into the LIMS at a terminal. Transcriptions of GC/MS data to the LIMS computers are performed by one analyst and verified by a second analyst.

All analytical data is reviewed by Analytic Laboratory's scientist in-charge and the project manager. Analytic Laboratory LIMS contains limit values for all routine tests. Review and sign off are required when limits are exceeded.

Analytic Laboratory will provide an electronic copy of the analytical data as well as a hard copy report.

All data from the manual sampling trains will be input to the field computer system and processed daily. Laboratory data will be included in the data base as they become available following the test program. The moisture results from manual trains will be used to correct any wet measurements to dry basis.

Data validation is a systematic procedure of reviewing data against a set of established criteria to provide a level of assurance of its validity prior to its intended use. The data will be coded either valid or invalid depending on the adherence to quality control criteria.

Field sampling data will first be validated by the Field Team Leader and external QA/QC based on their judgment of the representativeness of the sample, maintenance and cleanliness of sampling equipment, and adherence to approved, written sample collection procedures. The technical staff and the external QA/QC team will also validate the data on a daily basis on-site based on the following additional criteria:

- process conditions during sampling or testing;
- adherence to the control limits; and
- acceptable external performance evaluation and technical systems audit results.

Data summary sheets will be created using computer spreadsheets, thus ensuring easy modification of format to suit subsequent reporting requirements. Summary sheets will be filled out at the end of the test, presenting all pertinent test parameter results for both manual field sampling and computer monitored instrumentation. The summary sheets will present, but not be limited to, the following data:

- critical process parameters;
- flue gas analysis for the continuous monitoring equipment;
- parameters associated with process sampling, including sample weight and sampling duration; and
- parameters associated with the manual sampling trains, including sampling irregularities or sample recovery problems, maximum leak check rate, total sample volume, moisture, flue gas flow and temperature and isokineticity.

The stack test report will include:

- Sampling locations description
- Sampling equipment description
- Outline of test procedure for each tested contaminant (flow measurement, stack temperature measurement, stack gas composition, sampling equipment preparation, sampling methodology, sample handling, sample recovery, sample analysis, and sampling and analytical QA/QC activities)
- Uncorrected and corrected to 7% O_2 sample volumes and quantitation of the organics and metal captured by the sampling trains
- Uncorrected and corrected CEMS data generated by the Testing Contractor
- Instrument calibration records, procedures and frequencies
- Sampling and analytical QA/QC records - summarize by contaminant including a discussion of the significance of any deviation
- Presentation of Chain-of-Custody records
- Presentation of all other activities of the implemented QAPP
- Comment on Factors that should be considered when interpreting the test results

4.2 INTERNAL QUALITY CONTROL

This section describes the internal quality control methods which will be implemented by Testing Subcontractor and the Principal Investigator during testing. All internal quality assurance and quality control procedures will be strictly adhered to during this test program to ensure the production of useful and valid data throughout the course of the project.

The acceptance criteria, control limits, and corrective action that will be followed are summarized in Table 4-3.

All values which fall outside the QC limits will be noted. The following guidelines will be used:

1. All recovery data will be evaluated to determine if the QC limits are appropriate and if a problem may exist even though the limits are being achieved (e.g., one compound that is consistently barely within the lower limit).
2. All recovery data which are outside the established limits will be evaluated. This evaluation will include an independent check of the calculation.
3. Corrective action will be performed if any of the following are observed:
    a) all recovery values in any one analysis are outside the established limits;
    b) over 50 percent of the values for a given sample set are outside limits; or
    c) one compound is outside the limits in over 50 percent of the samples.

Table 4-3 Summary of Acceptance Criteria, Control Limits, and Corrective Action

Criteria	Control Limits[a,b,c]	Corrective Action
Manual Sampling		
Flow Alignment	Avg. cyclone check resultant angle within 10°	------
Isokineticity	100 ± 10%	------
Final Leak Rate (after each port)	<0.02 acfm or 4% of sampling rate, whichever is less	None, invalidate run
Dry Gas Meter Calibration	Post average factor (Y) agree ± 5% of pre-factor	Adjust sample volumes using the Y that gives smallest volume
Individual Correction factors (Y_i)	Agree within 2% of average factor	Redo correction factor
Average Correction Factor	1.00 ± 5%	Adjust the dry gas meter and recalibrate
Analytical Balance (top loader)	0.1 g of NBS Class S Weights	Repair balance and recalibrate
Barometric Pressure	Within 2.5 mm Hg of a mercury-in-glass barometer	Recalibrate
CEM Measurements		
Linearity Multipoint Calibration	R > 0.995	Adjust instrument, redo multipoint
Daily Drift (zero and span)	a) ± 5% of span b) ± 5% to <20% of span c) > 20% of span d) 2 days with drift greater than 10% indicates the need for instrument maintenance	Data not adjusted Adjust assuming linear drift Reject data Perform maintenance
Sampling System Bias Check	±10% of span except SO_2 ±15% of span	Check heat tracing and sample conditioner and/or clean sample line and/or sample conditioner

Table 4-3 Summary of Acceptance Criteria, Control Limits, and Corrective Action (Cont'd)

Criteria	Control Limits [a,b,c]	Corrective Action
Stratification check	Vertical traverse with each point with 10% of average of all points	Use point of average concentration
Line Leak Check	Vacuum 20" - let stand 15 mm, must not drop below 3" to be acceptable - alternatively Vacuum at highest level during sampling 0-100 cc rotameter @ pump outlet leak < 1% flow or < 50 cc/min (lesser)	Locate and repair leak, recheck leak on negative side of system during test period reject data. Leak on positive side. Review data and judgment made by external QA/QC
Manifold Leak Check	No visible flow through rotameter at a vacuum of 25" Hg	Locate and repair leak, recheck.
Trace Metal Analytical Results		
Instrument Calibration Standard Check (every 10 samples)	± 10% of true value	Recalibrate
Instrument Calibration Blank Check (every 10 samples)	± 3 times the standard deviation of the mean blank value	Identify and correct problem, recalibrate and reanalyze previous 10 samples
Instrument Interference Check (before and after every analytical run or at least once every four hours)	± 20% of true value	Reverify interelement and background correction factors
Duplicate (every 10 samples)	± 20% relative percent difference	Reanalyze
Duplicate Matrix Spike Recovery (every 10 samples)	± 20% of true value	Reanalyze
Trace Organic Analytical Results		
Internal Standard recoveries	100 ± 30%	Save residue and re-extract and reanalyze
Surrogate Recoveries	100 ± 30%	No action
Verification of Identification 1) Ratio of Quantitation Ion to Confirmation Ions	Within 15% of value, determined during analysis of standard compounds	Reconsider peak identification

Table 4-3 Summary of Acceptance Criteria, Control Limits, and Corrective Action (cont'd)

Criteria	Control Limits[a,b,c]	Corrective Action
2) Retention Time	Within 3 seconds of the corresponding or nearest ^{13}C internal standard or surrogate standard (with reference to continuing calibration)	Reconsider peak identification
3) Signal to Noise Ratio	Greater than 2.5	Reconsider peak identification
Sample Glassware Proofing	<50 ng/train PCB	Reclean glassware
Duplicates	Percent difference < 50%	Reanalyze
<u>Anion Analytical Results</u>		
Duplicates (every 10 samples)	Percent difference <10%	Reanalyze
Internal Audit Sample	Relative error ± 0% of audit	Reanalyze
Linearity of Calibration Curve	$R > 0.995$	Redo calibration
<u>Weighing</u>		
Scales	Precision and accuracy within 10%	Repair and/or recalibrate scale

[a] Relative error (%) derived from audit analyses, where:

$$\text{Percent Error} = \frac{\text{Measured Value} - \text{Theoretical Value}}{\text{Theoretical Value}} \times 100$$

[b] Percent difference for duplicate analyses, where:

$$\text{Percent Error} = \frac{\text{First Value} - \text{Second Value}}{0.5\,(\text{First} + \text{Second Values})} \times 100$$

[c] Control limits are established based on previous test programs conducted by the USEPA

The following general pretest QC criteria must be satisfied for the manual sampling methods:

1. All sampling equipment will have to pass through a visual and operational check prior to and after shipment to ensure clean and operable parts. At no time will equipment that fails to pass this check be used in the field.
2. Only a magnahelic gauge (calibrated against an oil-filled manometer gauge) or an oil-filled manometer gauge that has been properly leveled and zeroed (no drift allowed) will be used to measure the pressure across the S-type pitot tube.
3. A run will be considered acceptable if the proper number and location of sampling traverse points have been sampled (Method 1).
4. The temperature measurement system must be capable of measuring the ambient temperature prior to each traverse to within ± 2°C of the average measured ambient temperature.
5. The number and location of the sampling traverse points will be checked before taking measurements.
6. All sampling data and calculations will be recorded in ink on preformatted data sheets.
7. Any unusual occurrences will be noted during each run on the appropriate data form.
8. The Field Crew Chief will review all calibration (i.e., calibration data) and sampling data forms daily during testing. Data that is incomplete or inaccurate will not be considered acceptable.
9. Flue gas measurements will be recorded in ink on preformatted data forms at least once every three minutes.
10. Only tapered edge sampling nozzles and S-type pitot tubes that have passed a visual and caliper inspection will be used for sampling.
11. Each leg of the S-type pitot tube must achieve an acceptable leak check. No change in the differential pressure gauge reading should occur.
12. The entire sampling train must meet a leakage rate of less than or equal to 0.02 ft^3/m or 4% of the average sampling rate (whichever is less) before and after any move from one sampling port to another during a run or if a component change takes place.
13. The S-type pitot tube and the sampling nozzle must be maintained at 90° to the flow during sampling.
14. The filter compartment must be maintained at 120°C ± 14°C during sampling.
15. Readings of the dry gas meter, delta P, delta H, temperature, and pump vacuum must be made at least twice during sampling at each traverse point.
16. Isokinetic sampling rates must be maintained to within ± 10 percent of the duct velocity, otherwise, the run will be considered invalid.

For the trace organic sampling, the following additional QC criteria specific to the sampling method will be used:

1. Only proofed glassware and prepared sorbent traps that have been kept closed with ground glass caps or precleaned foil will be used for the sampling trains.
2. Only solvent extracted filters that have been stored in precleaned glass petri dishes sealed with Teflon tape will be used for the sampling trains.
3. Only pre-extracted XAD-2 resin will be used in the sorbent traps.
4. The flue gas entering the sorbent trap must be maintained and recorded at or below 20°C during sampling.
5. At least one field blank must be collected for every 3 runs to evaluate any background contamination. Runs are not blank corrected. The acceptance criteria for contamination levels in the blanks is at or below the detection limit of the analytical method used for a particular species of interest.

Continuous monitoring for SO_2, CO and, NO_x will be performed using the various instruments. Quality control procedures for all instruments will be identical. The primary control check for precision of the continuous monitors will be analysis of control standards. The control standards, which will be certified (± 2% accuracy) by the gas manufacturer, will be introduced at the probe and then directly into the analyzer. The acceptance criteria for the control standard determination will be agreement within ± 10 percent of the overall (running) mean for previous analyses. Results of the control sample analyses for all parameters will be tabulated in a bound laboratory notebook.

Prior to set up on-site, a four-point (zero plus three upscale) calibration will be performed on each instrument to provide a linearity check. The acceptance criteria for the linearity check will be a correlation coefficient, $r < 0.9950$ for all the Testing Contractor's continuous monitors with a linear response; Host Facility CEMS will meet Appendix F criteria. In addition, reproducibility checks and zero/span drift checks will be conducted.

After sampling each day, zero and span gases will be introduced into the instruments to check for drift. No adjustments to the zero and span settings will be permitted during testing.

The following corrective action will be taken if a drift is noted:

± 5% of span	data not drift corrected
± 5% to < 20% of span	adjust data assuming a linear drift.
> 20% of span	reject data.

After two consecutive days with a drift greater than ± 10%, the instruments will be serviced and/or repaired.

The CEM sample lines and pumps will also be leak-checked (on negative side of system) before and after each test day. Leaks will be eliminated prior to the start of sampling and any leaks detected at the conclusion of testing will be reported. This will be performed by pressurizing the system to 15" Hg. Sealing the system and monitoring pressure drop over 15 min.

All CEM calibration data will be recorded and logged by the Testing Contractor and reviewed by the auditor.

All analyses for this program will be performed using accepted laboratory procedures in accordance with the specified analytical protocols. Gas standards used for quantitation will be certified standards (± 2 percent accuracy). Adherence to prescribed QC procedures will ensure data of consistent and measurable quality. Analytical quality control will focus on the use of control standards to provide a measure of analytical precision and accuracy. Also, specific acceptance criteria are defined for various analytical operations, including calibrations, control standard analyses, drift checks, blanks, etc.

The following general QC procedures will be incorporated into the analytical effort:

1. The on-site Testing Contractor's team leader will review all data and QC data on a daily basis for completeness and acceptability.
2. A master logbook will be maintained.
3. Analytical QC data will be tabulated using the appropriate charts and forms on a daily basis.
4. Copies of the QC data tabulation will be submitted to the external QA/QC team following the test.
5. All hard copy raw data (i.e., chromatograms, computer printouts, etc.) will be maintained in organized files.

Specific analytical QC procedures for each of the instrumental analyses and the analyses of samples collected by manual methods are discussed below.

The analysis of samples for trace metals will involve sample digestion followed by ICAP analysis (Pb and Cd) or CV AA (mercury). The analytical quality control for the trace metals analysis will include the following:

1. Instrument calibration standard analyzed with every 10 samples will be within 10% of the true value.
2. Instrument calibration blank check sample analyzed with every 10 samples will be within three times the standard deviation of the mean blank value.
3. Instrument interference check sample for ICAP analysis will be analyzed before and after each analytical run or at least once every four hours. The value(s) found for the interference check sample will be within ± 20% of the true value.

4. Duplicate sample analysis will be performed with every 20 samples, and valid results will be required to have a relative percent difference of less than ± 20%.
5. Duplicate matrix spike recovery samples will be analyzed with every 20 samples, and the results will be within 20% of the true value.

Analysis of samples for anions will involve ion chromatography. The analytical quality control for analysis will include the following:

1. Calibration check sample analyzed with every 20 samples or after an eluent change will be within 10% of the true value.
2. Blank check samples (analyzed at the beginning and end of each analytical run) must be below the detection limit.
3. Duplicates of 10% of the field samples will be analyzed, and valid results are required to have a relative percent difference of less than ± 10%.
4. A matrix spike sample will be analyzed with every 20 samples to confirm the identity of the anion. The results of the matrix spike sample must be within 10% of the true value.

The analysis of samples for trace organic compounds will involve complex sample extraction and cleanup, followed by HRGC/HRMS analysis. The analytical quality control for the trace organic analysis will include the following:

1. Surrogate standard recoveries must be reported with all field data.
2. The verification of a trace organic target compound requires that the ratio of the quantitation ion to the confirmation ions be within 20% of their values determined during analysis of the external quantitation standard.
3. The verification of individual isomers requires a HRGC retention time within three seconds of the corresponding or nearest 13°C internal standard or surrogate (with reference to continuing calibration).
4. The signal-to-noise ratio for any individual isomer must be > 2.5.
5. The results from duplicate analyses must have a percent difference < 50%.

The analysis of samples for mercury will employ cold vapor atomic absorption spectroscopy. The analytical quality control procedures for mercury analysis will include the following:

1. Instrument blank check samples will be analyzed before and after each analytical run, and the results will be within 3 times the standard deviation of the blank sample.
2. Instrument calibration check samples will be analyzed with every 15 samples and must be within 10% of the true value.
3. Duplicate sample analysis will be performed with every 10 samples, and the results must have a relative percent difference of less than ± 20%.

4. Matrix spike duplicate samples will be analyzed with every 10 samples, and the results must be within 20% of the true value.

All data and/or calculations for flow rates, moisture contents, isokinetic rates, and pollutant concentrations made using computer programs will be validated by independent checks. In addition, all calculations performed by hand will be spot checked for accuracy and completeness.

In general, all measurement data will be validated based on the following criteria:

1. On completion of testing, the field crew chiefs will be responsible for preparation of a complete data summary including calculation results and raw data sheets.
2. During testing, the field test crews will prepare daily summaries and submit them to the on-site Principal Investigator.

The field crew chiefs will be responsible for providing the Principal Investigator with a summary of all QC data collected. The test program reports will include separate QA/QC sections which summarize any audit results, as well as the QC data collected throughout the duration of the program. QC reports will address the following:

1. summary of activities and general program status;
2. summary of any corrective action activities;
3. status of any unresolved problems;
4. assessment and summary of data completeness; and
5. summary of any significant QA/QC problems and recommended and/or implemented solutions not included above.

4.3 DATA QUALITY INDICATORS

A quality assurance audit is an independent assessment of a measurement system. It typically includes a performance evaluation using apparatus and/or standards that are different from those used in the measurement system. It also may include an evaluation of the potential of the system to produce data of adequate quality to satisfy the objectives of the measurement efforts. The independent, objective nature of the audit requires that the auditor be functionally independent of the sampling/analytical team.

During a given testing period, the QA/QC team and Principal Investigator will be on-site to perform independent performance and system audits. The QA/QC personnel will:

- Observe procedures and techniques being used in the various measurement efforts, including field sampling and laboratory operations.
- Check and verify records of calibration.
- Assess the effectiveness of and adherence to the prescribed QC procedures.

- Review document control procedures.
- Identify and correct any weakness in the sampling/analytical methods.

The QA/QC personnel will use the methods and procedures described in tables 4-5 and 4-6 as appropriate.

Generally, the role of the QA/QC team will be to observe and document the overall performance of each of the various sampling and analytical systems. Meter box audits will be conducted. Based on the audit results, the QA/QC team may, as necessary, recommend corrective action at the project level, through the on-site. The systems audits will be used to determine compliance with this QA/QC plan and to assess the overall quality of data collected during the measurement program.

Generally, the role of the QA/QC team will be to observe and document the overall performance of each of the various sampling and analytical systems. Meter box audits will be conducted. Based on the audit results, the QA/QC team may, as necessary, recommend corrective action at the project level, through the on-site. The systems audits will be used to determine compliance with this QA/QC plan and to assess the overall quality of data collected during the measurement program.

Table 4-5 QA Coordinator and Field Supervisor Pre-Test QA/QC Activities

1. Prepare (in conjunction with the project manager) the Quality Assurance Project Plan.
2. Ensure that proper and complete equipment calibration has been performed, (manual trains, continuous analyzers and calibration gas).
3. Ensure that all sampling equipment (train components and sample containers) are properly cleaned and proven for appropriate sample collection and analysis.
4. Ensure that reagent and chemical quality checks are performed.
5. Review, standardize and ensure completeness of all field data sheets (sampling data sheets).
6. Develop a chain of custody protocol for all samples and ensure that there is a numbering scheme for all stack and process samples.
7. Review all test procedures at the initiation of the program.

TECHNICAL SYSTEMS AUDITS A systems audit is an on-site qualitative review of the various aspects of a total sampling and/or analytical system to assess its overall effectiveness. It represents an objective evaluation of each system with respect to its strengths, weaknesses, and potential problem areas. The audit provides an evaluation of the adequacy of the overall measurement system(s) to provide data of known quality that are sufficient, in terms of quantity and quality, to meet the program objectives.

The objective of the system audit is to evaluate all components of a critical measurement system to determine their proper selection and use; these components include all on-site facilities, equipment, systems, record keeping, data validation, operation, maintenance, calibration procedures, reporting requirements, and field and laboratory quality control procedures.

Table 4-6 Tasks Performed by On-Site QC Coordinator and Principal Investigator on a Typical Test Day.

1. Meet with Host Facility personnel to confirm that the test condition and stable operation have been achieved.
2. Ensure that proper and complete CEMS calibrations (and system checks) have been performed, documented and meet pre-test QC criterion.
3. Observe operation of manual trains and ensure that manual train operators complete a QC checklist.
4. Audit data entry - review data to ensure all data has been entered correctly and completely.
5. Flag errors or omissions.
6. Review manual train data for inconsistencies, errors and omissions.
7. Review sample recovery, mark liquid levels and ensure all samples are properly labeled, sealed and stored until shipping. Ensure that all Chain of Custody forms are filled out completely and accurately.
8. Ensure appropriate field bias blanks, blank trains and reagent blanks are collected and shipped with the samples.
9. Ensure that the sampling glassware are appropriately cleaned prior to usage.
10. Maintain a QC and project log book.
11. Challenge the various measurement systems with audit standards.
12. Conduct meter box audits.
13. Prepare summary reports describing the on-site QA/QC activities.
14. Review daily CEMS QC procedures.
15. On-site preparation and review of the manual gas sampling procedures (including all leak checks) during the tests to assess compliance with stated sampling protocol.
16. Review sample handling, transport, and chain-of-custody procedures during the tests to assess compliance with stated protocol.
17. Review QAPP with test team.
18. Inspect communication equipment and review procedures with test team and QA team.
19. Review manual sampling equipment calibration records and inspect equipment.
20. Inspect sample recovery area and equipment and observe recovery procedures used to recover field samples and blanks.
21. Spot check recovery of manual train samples (field blanks and actual).
22. Review raw field data sheets for completeness and data reduction for accuracy.

The specific QC procedures developed will be followed to ensure the continuous production of useful and valid data throughout the course of this test program. These QC checks and procedures represent an integral part of the overall sampling and analytical scheme, and adherence to them will be the basis for the systems audit.

In addition to general QC procedures, specific QC protocols for each sampling method will be incorporated into the sampling scheme. These method-specific procedures and the technical systems audit data forms are provided in the Appendix of this QAPP. These forms will be used by the external QA/QC team to conduct on-site technical systems audits during the course of the test program.

The systems audits will consist of observations and documentation of all aspects of the on-site sampling and analytical activities. Checklists that delineate the critical aspects of each methodology would be used by the auditor and will serve to document all observations. In addition, the systems audit will emphasize review of all record keeping and data handling systems associated with:

1. calibration of both instruments and apparatus;
2. data forms and notebooks;
3. data review and validation;
4. data storage and filing;
5. sample logging;
6. field laboratory custody;
7. documentation of quality control data (control charts, etc.);
8. documentation of field maintenance activities; and
9. malfunction reporting procedures.

PERFORMANCE EVALUATION AUDITS While the systems audit is a qualitative evaluation, the performance audit represents a quantitative assessment of the measurement data quality. Properly designed, it provides a direct, point-in-time evaluation of the accuracy of the various measurement systems. This is accomplished by challenging the measurement systems with accepted reference standards for the parameters of interest.

General Approach for Manual Sampling Methods. For the manual sampling methods, the performance audits for sample collection will be conducted prior to, at the midpoint of, and upon completion of the test program. They will also be conducted in the event of any equipment changes. Corrective action will be taken in cases where the results of an audit are not within the stated audit value range.

To check sample collection, the dry gas meters will be audited with a critical orifice meter. The results should be within 5% of the audit value. The temperature sensors will be checked with an ASTM mercury-in-glass thermometer, and should be within 1.5% of the absolute measured temperature. The data for both audits will be recorded on the form provided in the appendix.

A digital micrometer will be used to verify the measurement and reported value of the nozzles internal diameter. At least three measurements will be taken from each nozzle and the difference between the high and low measurements should not exceed 0.01 mm (0.004 in). The nozzles will also be visually inspected to ensure that they are tapered with sharp edges.

General approach for data quality. Audits of data quality will be conducted using data quality indicators which require the detailed review of: (1) the recording and transfer of raw data; (2) data calculations; (3) the documentation of procedures; and (4) the selection and discussion of appropriate data quality indicators.

Some of the data quality indicators to be used are:

1. comparison of the measured volumetric flow rates from the different sampling locations;
2. comparison of the control system's instrumentation temperature readings with the manual methods readings;
3. comparisons of the relative concentrations of the emissions at the different sampling locations; and
4. comparisons of these results with those from previous field test results from this site (i.e., are there any similarities).

All noted deviations from this test protocol will be noted in the field logs of the Testing Contractor, the Principal Investigator and the Testing Contractor's QA personnel. The steps taken to correct the deficiency, measures taken to prevent a recurrence and an assessment of any impact it may have on the result will be included.

In the event that material deviations from this sampling protocol become unavoidable due to field extengencies, the Program Manager shall be promptly notified by telephone with telefax confirmation. Testing shall be suspended for a period of not more than 2 hours to the Program Manager an opportunity to suggest alternatives and confer with the Subcommittee Chairman and Sponsor.

APPENDIX A

DESCRIPTION OF FINAL REPORT

APPENDIX A
DESCRIPTION OF FINAL REPORT

Sections of the final report outlined in Table A-1 will be written as early in the project process as they can. Once the data has been received, standardized, reduced, analyzed and interpreted, the complete report will be edited into a smooth, integrated whole. The report will conform to the NREL Style Guide.

Given the target audience for this report, US MWC plant owners and operators, conventional US usage and units will be employed in the text. Components fabricated out of standard US components which have no exact metric equivalents (e.g., 1.5 inch Schedule 40 pipe) will be described in nominal units. However, metric units are generally preferred and will provided in tables and in the text to the extent that readability is not overly impaired. This will maximize the long term utility of the results and facilitate technology transfer to other countries and industries.

As the field results are received from the Testing Contractor, data tables will be set up. All emissions test results will be reported in USEPA standard reference conditions (dry, 68°F, 29.8" Hg, and 7% O_2). The tables will be completed as results are received from the Analytic Laboratory. Criteria and Section 129 pollutants will be expressed in appropriate regulatory units: Particulates, lead, cadmium and mercury in mg/dsm^3; Dioxins and Furans in ng/dsm^3; Hydrogen chloride, Sulfur Dioxide and Oxides of Nitrogen in PPM. All other measurements will be expressed in conventional engineering units (i.e., diluent Oxygen in percent, gas temperatures in plant standard °F, spray water flow in gallons per minute, etc.).

A master data spreadsheet will be utilized to make sure that the same numeric results are used throughout the analysis and report. This becomes particularly important if a field or laboratory error is uncovered and corrected. When the mistake is corrected in one place, this approach ensures that it is corrected everywhere.

Summary statistics will be generated in spreadsheets and detailed analysis and exploration of the data will be done in commercially available statistical analysis packages (e.g. SPSS\PC+ and SYSTAT) that have been checked against benchmark problems.

It is anticipated that the blank train results will provide a reasonable estimate of method precision. Repeated condition analyses (the daily pairs) and condition replicate (the pair when the condition is repeated) should provide a reasonable estimate of control method performance uncertainty. Emission limitations for each test condition will be statistically derived from the average performance measured for each condition and accounting for the sources of variability listed above (method precision and performance uncertainty). These emission limitations will be compared to the promulgated 40 CFR 60, Subpart Cb Emission Guidelines. If the Emissions Guidelines have not yet been promulgated when the report is written, the values in the most current draft will be employed.

The results of the Phase I effort will be analyzed by focusing on two criteria:

1. Were the Emissions Guidelines values achieved?
2. Was the spray cooling system reliable and practical?

The need for the work outlined in Phase II of the contract will be determined by the ability of the Phase I modifications (e.g., spray cooling, acid gas reagent injection and activated carbon addition) to achieve the Emissions Guidelines. If adequate dioxin control is not achieved, further work is clearly indicated. In addition, if compliance with all standards except dioxin standards can be achieved without activated carbon addition, then the dioxin killer/inhibitor approach should be investigated as an alternative.

The need for Phase III to demonstrate sensible heat cooling depends on the spray cooling system reliability. Sensible heat coolers are comparatively expensive devices that can require extensive facility modifications. Consequently, if the spray cooling system is reliable, it is unlikely that a facility owner would elect to make the investment. On the other hand, the spray cooling system may only be reliable when extraordinary preventative maintenance efforts are employed. Under this circumstance, sensible heat cooling may be economically attractive. A demonstration is indicated since spray dryer adsorber experience indicates that both flue gas moisture content and APCS operating temperature affect system performance. Even though MWC's probably have sufficient inherent flue gas moisture to effectuate the separation reactions, the validity of this assumption needs to be tested. Phase III will be recommended if the spray cooling system proves unreliable or requires excessive maintenance.

Figure A-1. Final Report Outline.

VOL. I -- REPORT

1. **EXECUTIVE SUMMARY**

2. **INTRODUCTION**

3. **DESCRIPTION OF TEST BED**
   - 3.1. HOST FACILITY DESCRIPTION
   - 3.2. SPRAY COOLING SYSTEM DESIGN
   - 3.3. DRY REAGENT INJECTION SYSTEM DESIGN

4. **QUALITY ASSURANCE PROJECT PLAN SYNOPSIS**
   - 4.1. PLANNED TEST MATRIX & ACTUAL SCHEDULE
   - 4.2. STACK GAS TEST PROCEDURES
   - 4.3. RESIDUE SAMPLING & TCLP ANALYSIS PROCEDURES
   - 4.4. QA/QC (EPA LEVEL IV) PROCEDURES

5. **DATA REDUCTION METHODS & ANALYTIC PROCEDURES**
   - 5.1. DATA STANDARDIZATION
   - 5.2. OUTLIER IDENTIFICATION & MANAGEMENT
   - 5.3. BDL HANDLING
   - 5.4. DETERMINING THE SIGNIFICANCE OF CHANGES IN EMISSIONS BETWEEN TEST CONDITIONS
   - 5.5. ESTIMATING METHOD PRECISION, CONDITION UNCERTAINTY AND STATISTICAL EMISSIONS LIMITATIONS
   - 5.6 DEMONSTRATING MWC CONDITION SIMILARITY BETWEEN TESTS

6. **RESULTS & DISCUSSION**
   - 6.1. OBSERVED EMISSIONS CONTROL PERFORMANCE
     - 6.1.1. PCDD/F AIR EMISSIONS REDUCTIONS
     - 6.1.2. MERCURY AIR EMISSIONS REDUCTIONS
     - 6.1.3. ACID GAS AIR EMISSIONS REDUCTIONS
   - 6.2. SYSTEM OPERATING CHARACTERISTICS
   - 6.3. QUALITY ASSURANCE FINDINGS

7. **CONCLUSIONS & RECOMMENDATIONS**
   - 7.1. DEMONSTRATED EMISSIONS CONTROL CHARACTERISTICS
   - 7.2. SYSTEM OPERATING CHARACTERISTICS -- LESSONS LEARNED
   - 7.3. DESIGN CONSIDERATIONS & CRITERIA
   - 7.4 RECOMMENDATION REGARDING THE NEED FOR PHASES II AND III

APPENDIX

A) BUDGETARY COST ESTIMATE FOR A GENERIC 400 T/D ESP EQUIPPED WTE FACILITY

B) HOST FACILITY COMBINED RESIDUE SAMPLING PROGRAM

C) USEPA REFERENCE METHODS FOR PCDD/F (23), METALS (29) & HCl (26)

VOL. II -- FIELD AND LABORATORY REPORTS

1. EMISSIONS STACK TEST REPORT

2. TCLP COMBINED RESIDUE ANALYSES

3. REAGENT CHARACTERISTICS

3. FACILITY OPERATING DATA

4. SPRAY SYSTEM EVENT LOG

APPENDIX B

HOST FACILITY COMBINED RESIDUE SAMPLING PROGRAM

COMBINED ASH RESIDUE CHARACTERIZATION AND QUALITY ASSURANCE PLAN

Davis County Solid Waste Management
and Energy Recovery Special District
Layton, Utah

Revision No. 2
August 1995

H. Gregor Rigo

Recommended for Use
Rigo & Rigo Associates, Inc.

Approved for Use
Plant Manager

REVISION HISTORY

0 Original Protocol (May, 1994)

1 General Revision to incorporate draft EPA Guidance (May, 1995)

2 Clarified laboratory sample size and replaced draft Appendix F with final EPA Guidance (August, 1995)

TABLE OF CONTENTS

LIST OF APPENDICES

Rev 2

INTRODUCTION AND PURPOSE

Municipal solid waste [MSW] is a highly variable material consisting of many waste components and elements. In the combustion process, the organics and metals break down and combine with oxygen and other elements in the waste and air to form new compounds. Some of the resulting materials accumulate in the combined ash residues leaving the facility. These residues may or may not exhibit the characteristics of hazardous wastes. Prudent environmental practice and regulatory compliance require that the toxicity characteristics of these residues be correctly characterized so that they can be managed in an environmentally protective and legally correct manner. It is also very important since improper characterization can result in either environmental degradation or extra expense to the facility.

The highly variable (heterogeneous) nature of combined ash residues means that correct characterization of incinerator residues is a difficult and exacting process. Accurate characterization begins with obtaining representative samples of the combined ash residues leaving the facility. It continues through preparation of representative laboratory subsamples. The laboratory procedures must be accurate and follow the prescribed regulatory methods and the final data reduction must correctly compare the laboratory results to regulatory standards to correctly characterize the incinerator residues.

Following the Combined Ash residue Characterization and Quality Assurance Plan provides assurance to staff, management and the public that the residues leaving the facility for disposal are properly characterized. This way, they can be properly managed.

Your enthusiastic and intelligent participation in this program is essential to the future of the Facility. When you effect your signature to quality control and assurance documents, it is the District's assurance that the procedures designed to produce accurate results have been followed.

Please direct any questions regarding your responsibilities or liability to the Plant Manager.

This QA plan is a living document. As you find ways to improve the procedures, bring them to the Plant Manager for formal consideration and incorporation in the next revision.

FACILITY RESIDUE HANDLING

The Davis County Energy Recovery and Special Service District Incinerator facility in Layton, Utah uses up to 140,000 tons of MSW per year to produce district heating steam for Hill Air Force Base and electricity for Utah Power & Light. After utilization, approximately 37,000 tons per year of combined incinerator ash and air pollution control system [APCS] residue remain for disposal.

The combined ash is accumulated in a segmented concrete ash storage bin. This bin is also called a bunker or pit. It has four separate segments.

Bottom ash is extruded from water filled ram dischargers at the end of the grate onto vibratory conveyors. As the ash moves the short distance to the bin, boiler ash is deposited on top of the bottom ash. APCS residue is moved from the hoppers to the bin in closed screw conveyors. The APCS residue is moistened prior to being discharged into the divided bin opposite the bottom ash from the same boiler.

In the segmented bin, combined residues are mixed as they are moved from the first and third segments (A and C) to the central bin (B). Several times a 12 hour shift, the residue is transferred to the larger end bin (D) for storage until it is loaded into covered dump trucks.

Residues are out-loaded to covered dump trucks 6 to 12 hours per day, 3 to 6 days per week. Out-loading, like between bin transfer and mixing, is accomplished using a clam shell grapple. Residue is dug out of out-loading bin D and discharged into the dump trucks through a load-out hopper. The truck pulls forward, is covered and leaves the fully enclosed ash via the facility truck scale. After weighing, the truck goes to the landfill and discharges the combined ash at the bottom of the working face.

REGULATORY REQUIREMENTS

The Resource Recovery and Conservation Act and implementing regulations (40 CFR 262.11) require that a person who generates solid waste determine if that waste is a hazardous waste as defined in 40 CFR 261.20. The waste is to be managed in accordance with that determination.

For municipal solid waste combustors (incinerators), EPA had historically held that the residues derived from burning MSW were exempt from the characterization requirement. On

May 2, 1994, however, the Supreme Court held in City of Chicago v. EDF that EPA's determination that incinerator residues were exempt from RCRA management requirements was outside their legal authority and incinerators had to characterize their residue streams. Importantly, the court did not find that incinerator ash was hazardous, rather that it must be managed in accordance with its RCRA characteristics.

In response to this ruling, EPA issued guidance concerning the Sampling and Analysis of Municipal Refuse Incinerator Ash (EPA\530-R-95-036, June 1995) that provides some advice on the design of sampling plans beyond that contained in SW-846. The guidance specifies that the 90 percent (one sided) statistical confidence level upper confidence limit for the sample increments is compared to the regulatory thresholds and that good statistical practice be followed in making the comparison.

REV. 2

The point at which the in-plant residue stream became subject to RCRA classification (i.e., the point at which they should be sampled) was clarified by the February 3, 1995 (60 FR 6666) publication of "EPA policy interpretation of point at which RCRA Section 3001(i) jurisdiction begins for municipal waste combustion ash at waste-to-energy facilities" and distribution of the March 22, 1995 joint memorandum from the Assistant Administrators for the Office of Solid Waste and Emergency Response [OSWER] and Office for Enforcement and Compliance Assurance [OECA] to the Regional Administrators entitled "Revised implementation strategy for City of Chicago v. EDF municipal waste combustion (MWC) Ash Supreme Court Decision". These documents make it clear that the residue becomes subject to RCRA sampling requirements when it leaves the combustion building and that the 14 samples suggested by the sampling guidance be taken on sequential residue removal days.

These guidance documents necessitate that the Davis County Incinerator combined ash residue sampling and testing protocol be updated to sample the combined ash stream as it leaves the facility. Basically, historic residue sampling was conducted for 7 continuous calendar days rather than 7 continuous ash hauling days and the sample increments were taken from all ash storage bins, rather than the final bin from which contains the fully mixed combined ash that is removed from the incineration building.

This sampling and analysis protocol revision modifies the point of increment collection to conform with EPA's current guidance. It also modifies the periodic random sampling plan to conform to the intent of the regulation. Enhanced QA/QC procedures such as in-plant determination of the TCLP Extraction Fluid to use are included between sampling campaigns.

RESIDUE SAMPLING AND TESTING PROTOCOL

Representative combined ash samples generated at the Davis County Incinerator has consistently tested RCRA non-hazardous under the TCLP protocol[1]. The sampling and testing protocol includes full characterization and re-characterization four times annually. The month in which to perform each quarter's sampling is selected at random and tabulated in the attachments for the year. Sampling is to begin in the middle of selected month. The actual start date shall accommodate scheduled plant maintenance outages and planned vacations.

During the characterization, combined ash is sampled as it is withdrawn from bin D for removal to the landfill. Daily sampling is separated into "morning" and "afternoon" hauling periods by equally dividing the number of hours residue hauling is expected to occur in half. Sample increments are taken every hour--on a random, sequential basis--and composited to create two samples per residue hauling day. This is a periodic random sampling plan as described in SW-846.

After seven sequential residue hauling days have been sampled, each composite sample is reduced to pass a 9 mesh (3/4 inch) screen, thoroughly mixed and extract a nominal 1,000 g laboratory samples from each composite sample using a trier sampler made from 2", schedule 40 pipe. Then, 4 of the laboratory samples are analyzed for all 8 TCLP metals and the remaining 10 are analyzed for lead and cadmium, the only metals consistently found above method detection limits.

REV. 2

One randomly selected sample a year is subjected to ZHE (zero head space) extraction to reconfirm that the organics are all at least a factor of 10 below the regulatory threshold.

Laboratory results are compared to the regulatory thresholds provided in 40 CFR 261.24 using the methods outlined in SECTION NINE of SW-846. As long as the 90 percent statistical confidence level upper confidence level [UCL] for the data average is less than the regulatory threshold, the combined residue is RCRA non-hazardous[2].

---

[1] USEPA, Test Methods for Evaluating Solid Waste, SW-846, Third Edition, November 1986 (with 1994 revisions), Method 1311 (Revision 0, July 1992).

[2] ibid and USEPA, Sampling and Analysis of Municipal Refuse Incinerator Ash, EPA530-R-94-020, May 1994.

Results are to be reported to the Plant Manager as quickly as practicable. Necessary documentation includes the sampling log, Chain of Custody forms, Laboratory QA/QC documentation and statistical data reduction and interpretation. The results shall be accompanied by a certification statement signed by the individual(s) in responsible charge of sampling and data interpretation that the results are representative, correct and accurate to the best of their knowledge. All deviations from this protocol and referenced EPA procedures are to be documented and the impact each deviation has on the results is to be determined. If the cause of the deviation was an error, steps to prevent recurrence shall be noted. If the cause is a change in facility operation, this protocol should be revised as appropriate to keep this living document accurate and representative. A determination shall be made to the Plant Manager regarding the regulatory status of the facilities combined ash residue based on the sampling program.

COMBINED ASH SAMPLING

Combined ash is sampled from bin D in the segmented ash bin as it is ready to leave the facility. This residue is representative of the materials deposited in the sanitary landfill for ultimate disposal. The periodic random sampling procedure is as follows:

- Acquire and label 14, clean 5 gallon plastic pails with covers. Put these pails at a convenient location in the ash handling area making sure that they are kept covered and any fugitive dusts in the enclosed space is not allowed to accumulate in such a way that the dust will become commingled with the sample increments when the lid is opened or closed.

- Select a convenient day to begin sampling within month identified for the quarter in Appendix A for the current year when experienced and qualified personnel will be available to complete the sampling program without missing a residue hauling day. Check with the residue hauling contractor and determine how long he intends to remove ash each day. Divide the expected residue removal time in half to form two sampling periods each day.

- Once each hour, stop the grapple as it is traversing from the out-loading bin D to the discharge hopper at a safe location to remove a sample. Knock off any loose dirt from the sampling shovel and rinse it in a bucket of water filled from the source used to quench the ash.

- Because the clam shell closing action will cause fine material to sift and roll from the center of the residue pile as the grapple closes, use the cleaned shovel to remove the top 4 to 6 inches of the residue from the center of the grapple. Put this potentially non-representative material to the side of the grab. Then, extract a shovel full of residue from the center of the cleared area. Be careful to take as representative a sample as possible. Include oversized and bulky items. In the event the sampling area is blocked by a large item (i.e., a water heater or muffler), uncover another adjacent area from which to take the sample.

- Put the shovel full of incremental sample into the correctly labeled container and cover.

- Repeat the previous step until all hourly increments have been accumulated.

- After all the periodic samples scheduled for accumulation have been put in the container, the 5 gallon bucket contains the morning or afternoon subsample for that sampling day.

- Continue sampling until a total of 14 subsamples, two per day, have been accumulated. Since the facility out-loads combined ash residue 3 to 6 days per week, this will require sampling 8 or 16 calendar days in a row.

SAMPLE PREPARATION

Once a subsample has been obtained, it should be kept covered until prepared for shipment to the analytic laboratory. Preparation consists of reducing the sample to pass a No. 9 (3/8 inch) screen, thoroughly mixing and extracting representative laboratory samples.

- Open the sample container.
- Either:
  - Pass all the samples through a 3/8" jaw crusher, or
  - Alternately:
    - Pass the sample over a No. 9 sieve or screen made up out of ½ inch hardware cloth. Accumulate the fines on a sheet of heavy gage plastic. Set aside the underflow, this material passed the sieve.

  - Using a sledge hammer or other suitable device, reduce the nonmetallic oversized material so that it will fit into the jaw crusher. Accumulate all fines and add them to the material that originally passed the screen.

  - Irreducible metallic items are either described, weighed and discarded, *or* reduced using shears and saws to a nominal 3/8 inch top size. If discarded, describe and record the weight of material separated.

  - Pass the remainder of the material through the jaw crusher. The jaws should be set to produce a 3/8 inch top size.

- Recombine the fines, sheared metallics and crushed material. Mix on a sheet of plastic and then split using a nominal 2 inch splitter until the sample size is reduced to about 2 gallons.

- Rinse out the 5 gallon sampling container and put the split into it. Put the 5 gallon sample container into a rotary cement mixer and thoroughly mix the subsample for a minimum of 5 minutes.

- Stop the mixer and extract about 1 kg (1 quart) of mixed residue using a sampling thief made out of an appropriate length of nominal 1½ inch, schedule 10 pipe split along the centerline. The thief should be slid along the bottom of the 5 gallon container and lifted straight up to obtain a representative sample. Alternatively, after rinsing, the splitter can be used repeatedly until an appropriately sized laboratory sample is obtained. It is prudent to prepare at least one archived sample in case of damage in transit or additional material is needed for confirmatory analyses.

- Put the laboratory sample into a clean, borosilicate or Polyethylene bottle with a Teflon lined cap. Attach an appropriate label identifying the sample, sample date, sampler and person preparing the laboratory sample.

- Once a practical shipment (usually all 14 samples) are prepared, arrange to ship the samples to the laboratory. Notify the laboratory that the samples have been sent and ask to be notified upon receipt.

LABORATORY ANALYSIS

- Request the laboratory to perform TCLP extractions on all samples. Each leachate should be analyzed for lead and cadmium. Identify the 4 samples selected using the random selection program (Appendix A) for complete TCLP metals analysis. One sample a year is to be subjected to zero head space extraction (ZHE) and organics analysis. This sample is designated on the sample selection program by quarter and sample number.

- Most combined ash samples require Extraction Fluid No. 1. Direct the laboratory to confirm any determination that Extraction Fluid No. 2 should be used by performing two additional determinations. Use the extraction fluid identified by at least two of the three determinations.

- Request the laboratory to retain all TCLP extracts until the 4 complete samples for each quarter have been analyzed.

- If any of the 4 samples exhibit a TCLP metal concentration in excess of one third of the regulatory limit (other than lead or cadmium), assume that the data are lognormally distributed and request that the balance of the extracts be analyzed for that metal if the UCL calculated using the 4 results exceeds three quarters of the regulatory threshold.[3]

- Require the Utah certified laboratory to provide a statement that the TCLP extraction was performed in strict accordance with Method 1311 and the analytic protocols in SW-846. The analytic report must be accompanied by laboratory QA/QC documentation including blanks, calibrations, and matrix spikes, the completed Chain of Custody Form and any other materials required by the most recent edition of SW-846.

---

[3] SW-846 requires that the laboratory quantitation limit be no more than 10 percent of the regulatory threshold. Consequently, for a lognormally distributed population, as long as the largest value is 34.5 percent of the regulatory threshold, the maximum UCL for a sample of 4 is the regulatory threshold because the geometric mean is the average of the natural logs of the detection limit and 34.5 percent of the regulatory threshold; the geometric standard deviation is the difference between the natural logs of the detection limit and 34.5 percent of the regulatory threshold.

INITIAL QUALITY CONTROL DATA SCREENING

- Upon receipt of the laboratory results, enter the following information into a spreadsheet along with the extraction fluid and final extract pH. Look at the data for any obviously high or low results that might be typographical errors. If there is no data entry error, review the laboratory QA/QC report to make sure that the data has been properly transcribed from the back-up sheets to the laboratory summary report.

- Review the laboratory QA/QC reports for any notations that might indicate there is a problem with the analysis (interferences or sample compromised during laboratory processing).

- Prepare a plot of TCLP metal concentration versus pH for each metal. Put pH on the horizontal scale and concentration on the vertical scale. The vertical scale should be logarithmic. The data should fall in a relatively narrow band. The data range should be comparable to that shown in Figure 6.4[4] for lead and Figure 6.3 for cadmium (see attachments). If the results are outside these ranges, or other ranges developed for the plant data, then something has changed, either in the plant or at the laboratory. Investigate and find out what caused the change and include the finding in the summary report.

- Combined ash residue usually requires Extraction Fluid No. 1. Due to statistical change alone, one or two of the 14 quarterly samples may indicate Extraction Fluid No. 2 should be used. If more than this number require Extraction Fluid No. 2, then it is imperative to find out why. At a minimum, submit the archived duplicate samples to another Utah certified laboratory for Extraction Fluid determination. If the original findings are confirmed, investigate what occurred in the facility to cause the change. If the findings are not confirmed, audit the original laboratory to determine what caused the finding.

COMPARISON TO REGULATORY THRESHOLDS

Determination of regulatory status is done in accordance with SW-846 and EPA guidance on sampling and analysis of incinerator residues. These are provided in Appendix B along with a

---

[4] The International Ash Working Group, An International Perspective on Characterization and Management of Residues from Municipal Solid Waste Incineration, Summary Report, December 1994.

paper[5] that consolidates the statistics and provides a conservative, upper bound estimate of the upper confidence limit.

Begin the analysis by assembling all the TCLP results into a spreadsheet. Record the sample identification, sampling date and time period, weight of total sample, weight and description of any rejected materials, final pH of the extraction fluid and the leachate concentrations. Add to the notes any deviations from accepted standards identified in the laboratory QA/QC report.

If the summary sheet identifies a result as not detected, record the detection limit as a negative number and display the result in () notation. If the instrument scan sheet provides a positive value (that is, a result that does not meet laboratory detection or quantitation limit standards) record the measured value and flag the value as tentative [T] in the next column per ASTM convention instead of recording the detection limit; add the detection limit notes at the bottom of the page. Use the tentative value in preference to half the detection limit in any subsequent mathematical procedures that require uncensored data.

Beginning with metals with 14 analytic results, the determination is made on a metal-by-metal basis as follows:

- Find the largest value. If this is less than the regulatory threshold, STOP. The material is RCRA non-hazardous for that constituent.
- Find the fourth largest value. If this is less than the regulatory threshold, STOP. The material is RCRA non-hazardous for that constituent.
- Determine the type of data distribution using the methods in SW-846 and the Rigo paper. Compute the upper confidence limit [UCL] following the procedure. Make sure that appropriate corrections are used if there are any censored results (Below Detection Limits values). Compare the UCL to the regulatory threshold. If the UCL is below the regulatory threshold, the combined ash is RCRA non-hazardous.

---

[5] Rigo, H. G., Interpreting TCLP Results -- a Simplified Approach, Solid Waste Management, Thermal Treatment & Waste-to-Energy Conference, AWMA, April 17-21, 1995 and Docket Comments submitted on EPA530-R-94-020.

- For metals with less than 14 samples analyzed, if the largest value of each of the 4 increments submitted for analysis of all RCRA metals is less than a third of the regulatory threshold, the maximum possible UCL is the regulatory threshold. The combined ash is RCRA non-hazardous for these metals. The UCL should be calculated using both normal and lognormal distribution assumptions and the higher value compared to the regulatory standard. In the event that all four results are below detection limits [BDL], then the combined ash residue is declared RCRA non-hazardous for that material[6].

If the value is above the regulatory threshold, then the material needs to be handled in an appropriate manner. The plant manager must be notified immediately and steps taken to either isolate the combined ash for future disposition or dispose of it in a RCRA compliant manner.

ROUTINE QUALITY ASSURANCE PROCEDURES

Providing assurance that the combined ash stream maintains its characteristics between quarterly sampling campaigns is important. Experience with combined ash streams indicates that changes manifest themselves as:

- Significant increases or decreases in the relative weight of combined ash residue generated per ton of MSW burned (the MSW composition may have changed), or

- The type of extraction fluid indicates has changed from Extraction Fluid No. 1 to No. 2.

To detect either of these two changes, the following routine QA/QC procedures are to be followed:

- Establish 3-sigma control limits for normal residue generation by dividing the amount of residue removed each week by the amount of MSW combusted. The average is the center of the distribution and 99 percent of the time a week's generation is expected to reside within 3 standard deviations (sigma) of the mean.

---

[6] If all results are BDL, the best that can be done is to substitute half the detection limit and calculate the mean, standard deviation and UCL. If the detection limit [DL] is the same for each sample, then the standard deviation will always calculate out to be zero; the UCL is then, by definition, equal to half the detection limit. Since SW-846 requires a maximum detection limit equal to 10 percent of the regulatory threshold, it is impossible for half the DL to exceed the regulatory threshold.

- At the beginning of each week, calculate the relative residue generation and add it to the ongoing plot. If it is within the 3-sigma bounds, the plant is operating normally and no change in generation rate is indicated.

- Paying attention to trends can yield important information. If 6 weeks in a row increase or decrease, or remain on one side of the average, then something small may have changed and investigation is warranted to prevent a control limit exceedance. This is known as an out-of-control situation. Identifying statistical out-of-control situations is very important. It provides a means of identifying when something has changed in the facility. Out-of-control does not mean that there is necessarily a problem or regulatory violation. Rather, it means that the cause of a difference can be identified and corrected, if necessary, before a violation occurs.

- Two or three times a week, take a single subsample increment exactly as if a full sampling program is being conducted. Pass the subsample increment over a No. 9 sieve (3/8 inch screen--a piece of 1/2 inch hardware cloth is satisfactory) and mix the fines. Note that this sample of fines is biased. Samples prepared in this manner are not suitable for determining the toxicity characteristics of the waste stream since they are not representative. They do not include a proportionate amount of +3/8 inch material. These are suitable for QC purposes since the pH for the fines where basic elements concentrate should govern the final pH for representative samples that include prorated portions of the comparatively inert large material as well.

- Extract 5 grams (within 0.1 grams) and put it in a 500 ml beaker with 96.5 ml of reagent (distilled, deionized) water and stir vigorously for 5 minutes. Record the pH.

- If the pH is greater than 5, add 3.5 ml of 1N HCl[7], stir briefly, cover with a watch glass and heat to 50°C and hold at 50°C for 10 minutes. Remove from the heat and let the solution cool to room temperature. Record the pH.

- Develop control charts to track the water extract and final (HCl extract) pH of the QC subsample increment determinations. Resample and analyze two additional samples if a change in Extraction Fluid is indicated. Like ash quantity, investigate the cause of any trends.

---

[7] Dilute 9.35 ml of 39% reagent grade HCl with reagent water to 100 ml to make a 1N HCl solution.

If an out-of-control situation persists for more than two samplings, prepare a representative sample and perform a TCLP extraction and lead and cadmium analyses. Compare these results to those determined during the last quarterly characterization. If the results are less than the highest values found during the quarterly characterization, conclude that the change is not material. If the previously established bound is exceeded, move up the next quarterly sampling to establish the RCRA classification of the changed waste stream.

APPENDIX C

USEPA REFERENCE METHODS FOR PCDD/F (23), METALS (29), & HCl (26)

METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) from stationary sources.

1.2 Principle. A sample is withdrawn from the gas stream isokinetically and collected in the sample probe, on a glass fiber filter, and on a packed column of adsorbent material. The sample cannot be separated into a particle vapor fraction. The PCDD's and PCDF's are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

2. Apparatus

2.1 Sampling. A schematic of the sampling train used in this method is shown in Figure 23-1. Sealing greases may not be used in assembling the train. The train is identical to that described in section 2.1 of Method 5 of this appendix with the following additions:

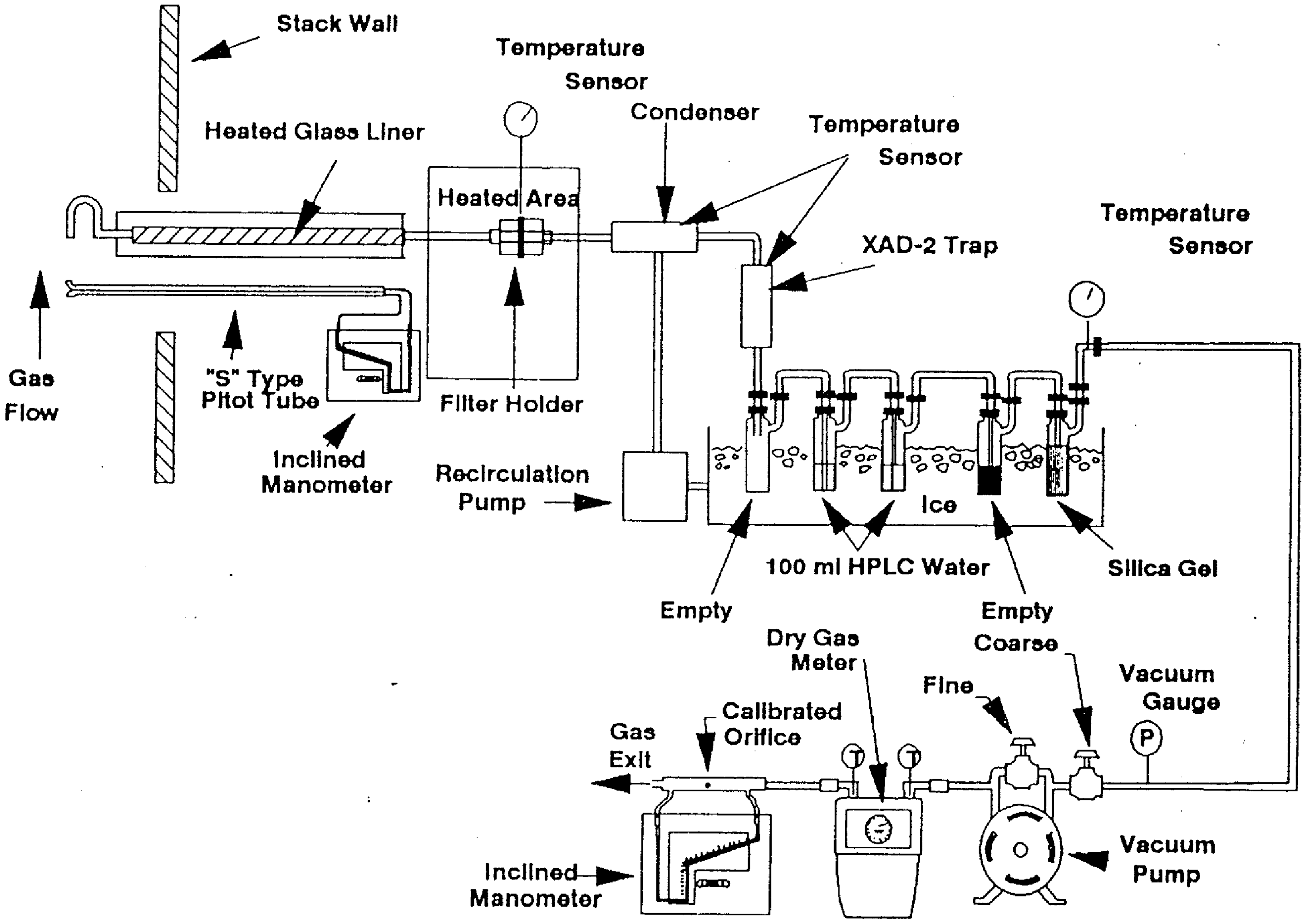


Figure 23.1 Sampling train

2.1.1 Nozzle. The nozzle shall be made of nickel, nickel-plated stainless steel, quartz, or borosilicate glass.

2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE ($^1/_2$ in. OD with $^1/_8$in. wall) with connecting fittings that are capable of forming leak-free, vacuum-tight connections without using sealing greases. The line shall be as short as possible and must be maintained at 120 °C.

2.1.1 Filter Support. Teflon or Teflon-coated wire.

2.1.2 Condenser. Glass, coil type with compatible fittings. A schematic diagram is shown in Figure 23-2.

2.1.3 Water Bath. Thermostatically controlled to maintain the gas temperature exiting the condenser at <20 °C (68 °F).

2.1.4 Adsorbent Module. Glass container to hold the solid adsorbent. A shematic diagram is shown in Figure 23-2. Other physical configurations of the resin trap/condenser assembly are acceptable. The connecting fittings shall form leak-free, vacuum tight seals. No sealant greases shall be used in the sampling train. A coarse glass frit is included to retain the adsorbent.

2.2 Sample Recovery.

2.2.1 Fitting Caps. Ground glass, Teflon tape, or aluminum foil (Section 2.2.6) to cap off the sample exposed sections of the train.

2.2.2 Wash Bottles. Teflon, 500-ml.

2.2.3 Probe-Liner Probe-Nozzle, and Filter-Holder Brushes. Inert bristle brushes with precleaned stainless steel or Teflon handles. The probe brush shall have extensions of stainless steel or Teflon, at least as long as the probe. The brushes shall be properly sized and shaped to brush out the nozzle, probe liner, and transfer line, if used.

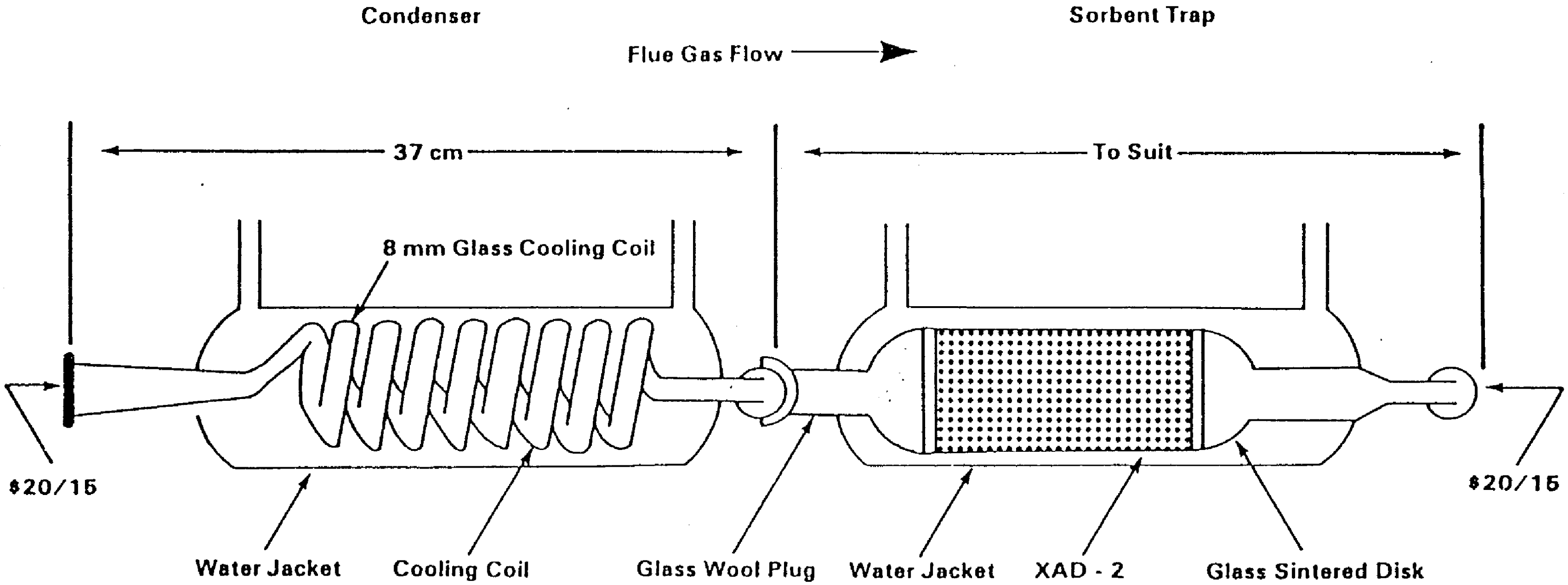


Figure 23.2. Condenser and adsorbent trap

2.2.4 Filter Storage Container. Sealed filter holder, wide-mouth amber glass jar with Teflon-lined cap, or glass petri dish.

2.2.5 Balance. Triple beam.

2.2.6 Aluminum Foil. Heavy duty, hexane-rinsed.

2.2.7 Metal Storage Container. Air tight container to store silica gel.

2.2.8 Graduated Cylinder. Glass, 250-ml with 2-ml graduation.

2.2.9 Glass Sample Storage Container. Amber glass bottle for sample glassware washes, 500- or 1000-ml, with leak free Teflon-lined caps.

2.3 Analysis.

2.3.1 Sample Container. 125- and 250-ml flint glass bottles with Teflon-lined caps.

2.3.2 Test Tube. Glass.

2.3.3 Soxhlet Extraction Apparatus. Capable of holding 43 x 123 mm extraction thimbles.

2.3.4 Extraction Thimble. Glass, precleaned cellulosic, or glass fiber.

2.3.5 Pasteur Pipettes. For preparing liquid chromatographic columns.

2.3.6 Reacti-vials. Amber glass, 2-ml, silanized prior to use.

2.3.7 Rotary Evaporator. Buchi/Brinkman RF-121 or equivalent.

2.3.8 Nitrogen Evaporative Concentrator. N-Evap Analytical Evaporator Model III or equivalent.

2.3.9 Separatory Funnels. Glass, 2-liter.

2.3.10 Gas Chromatograph. Consisting of the following components:

2.3.10.1 Oven. Capable of maintaining the separation column at the proper operating temperature ± °C and performing programmed increases in temperature at rates of at least 40 °C/min.

2.3.10.2 Temperature Gauge. To monitor column oven, detector, and exhaust temperatures ±1 °C.

2.3.10.3 Flow System. Gas metering system to measure sample, fuel, combustion gas, and carrier gas flows.

2.3.10.4 Capillary Columns. A fused silica column, 60×0.25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m×0.25 mm ID coated with DB-225. Other column systems may be used provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

2.3.11 Mass Spectrometer. Capable of routine operation at a resolution of 1:10000 with a stability of ±5 ppm.

2.3.12 Data System. Compatible with the mass spectrometer and capable of monitoring at least five groups of 25 ions.

2.3.13 Analytical Balance. To measure within 0.1 mg.

3. Reagents

3.1 Sampling.

3.1.1 Filters. Glass fiber filters, without organic binder, exhibiting at least 99.95 percent efficiency (<0.05 percent penetration) on 0.3-micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D 2986-71 (Reapproved 1978) (incorporated by reference—see §60.17).

3.1.1.1 Precleaning. All filters shall be cleaned before their initial use. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into a Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the silica gel bed and top with the cleaned glass wool. Charge the Soxhlet with toluene and reflux for 16 hours. After extraction, allow the Soxhlet to cool, remove the filters, and dry them under a clean N_2 stream. Store the filters in a glass petri dish sealed with Teflon tape.

3.1.2 Adsorbent Resin. Amberlite XAD-2 resin. Thoroughly cleaned before initial use.

3.1.2.1 Cleaning Procedure. This procedure may be carried out in a giant Soxhlet extractor. An all-glass filter thimble containing an extra-course frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and a stainless steel ring because it floats on methylene chloride. This process involves sequential extraction in the following order.

Solvent	Procedure
Water	Initial rinse: Place resin in a beaker, rinse once with water, and discard. Fill with water a second time, let stand overnight, and discard.
Water	Extract with water for 8 hours.
Methanol	Extract for 22 hours.
Methylene Chloride	Extract for 22 hours.
Toluene	Extract for 22 hours.

3.1.2.2 Drying.

3.1.2.2.1 Drying Column. Pyrex pipe, 10.2 cm ID by 0.6 m long, with suitable retainers.

3.1.2.2.2 Procedure. The adsorbent must be dried with clean inert gas. Liquid nitrogen from a standard commercial liquid nitrogen cylinder has proven to be a reliable source of large volumes of gas free from organic contaminants. Connect the liquid nitrogen cylinder to the column by a length of cleaned copper tubing, 0.95 cm ID, coiled to pass through a heat source. A convenient heat source is a water-bath heated from a steam line. The final nitrogen temperature should only be warm to the touch and not over 40 °C. Continue flowing nitrogen through the adsorbent until all the residual solvent is removed. The flow rate should be sufficient to gently agitate the particles but not so excessive as the cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual toluene.

3.1.2.3.1 Extraction. Weigh 1.0 g sample of dried resin into a small vial, add 3 ml of toluene, cap the vial, and shake it well.

3.1.2.3.2 Analysis. Inject a 2 µl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft×1/8 in stainless steel containing 10 percent OV-101 on 100/120 Supelcoport.

Carrier Gas: Helium at a rate of 30 ml/min.

Detector: Flame ionization detector operated at a sensitivity of 4×10^{-11} A/mV.

Injection Port Temperature: 250 °C.

Detector Temperature: 305 °C.

Oven Temperature: 30 °C for 4 min; programmed to rise at 40 °C/min until it reaches 250 °C; return to 30 °C after 17 minutes.

Compare the results of the analysis to the results from the reference solution. Prepare the reference solution by injection 2.5 µl of methylene chloride into 100 ml of toluene. This corresponds to 100 µg

0013-9211/93/$0+$1.00

of methylene chloride per g of adsorbent. The maximum acceptable concentration is 1000 μg/g of adsorbent. If the adsorbent exceeds this level, drying must be continued until the excess methylene chloride is removed.

3.1.2.4 Storage. The adsorbent must be used within 4 weeks of cleaning. After cleaning, it may be stored in a wide mouth amber glass container with a Teflon-lined cap or placed in one of the glass adsorbent modules tightly sealed with glass stoppers. If precleaned adsorbent is purchased in sealed containers, it must be used within 4 weeks after the seal is broken.

3.1.3 Glass Wool. Cleaned by sequential immersion in three aliquots of methylene chloride, dried in a 110 °C oven, and stored in a methylene chloride-washed glass jar with a Teflon-lined screw cap.

3.1.4 Water. Deionized distilled and stored in a methylene chloride-rinsed glass container with a Teflon-lined screw cap.

3.1.5 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, dry at 175 °C (350 °F) for two hours. New silica gel may be used as received. Alternately other types of desiccants (equivalent or better) may be used, subject to the approval of the Administrator.

3.1.6 Chromic Acid Cleaning Solution. Dissolve 20 g of sodium dichromate in 15 ml of water, and then carefully add 400 ml of concentrated sulfuric acid.

3.2 Sample Recovery.

3.2.2 Acetone. Pesticide quality.

3.2.2 Methylene Chloride. Pesticide qualtity.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. ACS grade, 2-percent (weight/volume) in water.

3.3.2 Sodium Sulfate. Granulated, reagent grade. Purify prior to use by rinsing with methylene chloride and oven drying. Store the cleaned material in a glass container with a Teflon-lined screw cap.

3.3.3 Sulfuric Acid. Reagent grade.

3.3.4 Sodium Hydroxide. 1.0 N. Weigh 40 g of sodium hydroxide into a 1-liter volumetric flask. Dilute to 1 liter with water.

3.3.5 Hexane. Pesticide grade.

3.3.6 Methylene Chloride. Pesticide grade.

3.3.7 Benzene. Pesticide Grade.

3.3.8 Ethyl Acetate.

3.3.9 Methanol. Pesticide Grade.

3.3.10 Toluene. Pesticide Grade.

3.3.11 Nonane. Pesticide Grade.

3.3.12 Cyclohexane. Pesticide Grade.

3.3.13 Basic Alumina. Activity grade 1, 100-200 mesh. Prior to use, activate the alumina by heating for 16 hours at 130 °C before use. Store in a desiccator. Pre-activated alumina may be purchased from a supplier and may be used as received.

3.3.14 Silica Gel. Bio-Sil A, 100-200 mesh. Prior to use, activate the silica gel by heating for at least 30 minutes at 180 °C. After cooling, rinse the silica gel sequentially with methanol and methylene chloride. Heat the rinsed silica gel at 50 °C for 10 minutes, then increase the temperature gradually to 180 °C over 25 minutes and maintain it at this temperature for 90 minutes. Cool at room temperature and store in a glass container with a Teflon-lined screw cap.

3.3.15 Silica Gel Impregnated with Sulfuric Acid. Combine 100 g of silica gel with 44 g of concentrated sulfuric acid in a screw capped glass bottle and agitate thoroughly. Disperse the solids with a stirring rod until a uniform mixture is obtained. Store the mixture in a glass container with a Teflon-lined screw cap.

3.3.16 Silica Gel Impregnated with Sodium Hydroxide. Combine 39 g of 1 N sodium hydroxide with 100 g of silica gel in a screw capped glass bottle and agitate thoroughly. Disperse solids with a stirring rod until a uniform mixture is obtained. Store the mixture in glass container with a Teflon-lined screw cap.

3.3.17 Carbon/Celite. Combine 10.7 g of AX-21 carbon with 124 g of Celite 545 in a 250-ml glass bottle with a Teflon-lined screw cap. Agitate the mixture thoroughly until a uniform mixture is obtained. Store in the glass container.

3.3.18 Nitrogen. Ultra high purity.

3.3.19 Hydrogen. Ultra high purity.

3.3.20 Internal Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Internal Standards" in 10 ml of nonane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of nonane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDD's and PCDF's at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of nonane.

4. Procedure

4.1 Sampling. The complexity of this method is such that, in order to obtain reliable results, testers should be trained and experienced with the test procedures.

4.1.1 Pretest Preparation.

4.1.1.1 Cleaning Glassware. All glass components of the train upstream of and including the adsorbent module, shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." Special care shall be devoted to the removal of residual silicone grease sealants on ground glass connections of used glassware. Any residue shall be removed by soaking the glassware for several hours in a chromic acid cleaning solution prior to cleaning as described above.

4.1.1.2 Adsorbent Trap. The traps must be loaded in a clean area to avoid contamination. They may not be loaded in the field. Fill a trap with 20 to 40 g of XAD-2. Follow the XAD-2 with glass wool and tightly cap both ends of the trap. Add 100 μl of the surrogate standard solution (section 3.3.21) to each trap.

4.1.1.3 Sample Train. It is suggested that all components be maintained according to the procedure described in APTD-0576.

4.1.1.4 Silica Gel. Weigh several 200 to 300 g portions of silica gel in an air tight container to the nearest 0.5 g. Record the total weight of the silica gel plus container, on each container. As an alternative, the silica gel may be weighed directly in its impinger or sampling holder just prior to sampling.

4.1.1.5 Filter. Check each filter against light for irregularities and flaws or pinhole leaks. Pack the filters flat in a clean glass container.

4.1.2 Preliminary Determinations. Same as section 4.1.2 of Method 5.

4.1.3 Preparation of Collection Train.

4.1.3.1 During preparation and assembly of the sampling train, keep all train openings where contamination can enter, sealed until just prior to assembly or until sampling is about to begin.

[Part 60, Appendix A, Method 23]

NOTE: Do not use sealant grease in assembling the train.

4.1.3.2 Place approximately 100 ml of water in the second and third impingers, leave the first and fourth impingers empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fifth impinger.

4.1.3.3 Place the silica gel container in a clean place for later use in the sample recovery. Alternatively, the weight of the silica gel plus impinger may be determined to the nearest 0.5 g and recorded.

4.1.3.4 Assemble the train as shown in Figure 23-1.

4.1.3.5 Turn on the adsorbent module and condenser coil recirculating pump and begin monitoring the adsorbent module gas entry temperature. Ensure proper sorbent temperature gas entry temperature before proceeding and before sampling is initiated. It is extremely important that the XAD-2 adsorbent resin temperature never exceed 50 °C because thermal decomposition will occur. During testing, the XAD-2 temperature must not exceed 20 °C for efficient capture of the PCDD's and PCDF's.

4.1.4 Leak-Check Procedure. Same as Method 5, section 4.1.4.

4.1.5 Sample Train Operation. Same as Method 5, section 4.1.5.

4.2 Sample Recovery. Proper cleanup procedure begins as soon as the probe is removed from the stack at the end of the sampling period. Seal the nozzle end of the sampling probe with Teflon tape or aluminum foil.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe. Remove the probe from the train and close off both ends with aluminum foil. Seal off the inlet to the train with Teflon tape, a ground glass cap, or aluminum foil.

Transfer the probe and impinger assembly to the cleanup area. This area shall be clean and enclosed so that the chances of losing or contaminating the sample are minimized. Smoking, which could contaminate the sample, shall not be allowed in the cleanup area.

Inspect the train prior to and during disassembly and note any abnormal conditions, e.g., broken filters, colored impinger liquid, etc. Treat the samples as follows:

4.2.1 Container No. 1. Either seal the filter holder or carefully remove the filter from the filter holder and place it in its identified container. Use a pair of cleaned tweezers to handle the filter. If it is necessary to fold the filter, do so such that the particulate cake is inside the fold. Carefully transfer to the container any particulate matter and filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and a sharp-edged blade. Seal the container.

4.2.2 Adsorbent Module. Remove the module from the train, tightly cap both ends, label it, cover with aluminum foil, and store it on ice for transport to the laboratory.

4.2.3 Container No. 2. Quantitatively recover material deposited in the nozzle, probe transfer lines, the front half of the filter holder, and the cyclone, if used, first, by brushing while rinsing three times each with acetone and then, by rinsing the probe three times with methylene chloride. Collect all the rinses in Container No. 2.

Rinse the back half of the filter holder three times with acetone. Rinse the connecting line between the filter and the condenser three times with acetone. Soak the connecting line with three separate portions of methylene chloride for 5 minutes each. If using a separate condenser and adsorbent trap, rinse the condenser in the same manner as the connecting line. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.4 Container No. 3. Repeat the methylene chloride-rinsing described in Section 4.2.3 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.5 Impinger Water. Measure the liquid in the first three impingers to within ±1 ml by using a graduated cylinder or by weighing it to within ±0.5 g by using a balance. Record the volume or weight of liquid present. This information is required to calculate the moisture content of the effluent gas.

Discard the liquid after measuring and recording the volume or weight.

4.2.7 Silica Gel. Note the color of the indicating silica gel to determine if it has been completely spent and make a mention of its condition. Transfer the silica gel from the fifth impinger to its original container and seal.

5. *Analysis*

All glassware shall be cleaned as described in section 3A of the "Manual of Analytical Methods for the Analysis of Pesticides in Human and Environmental Samples." All samples must be extracted within 30 days of collection and analyzed within 45 days of extraction.

5.1 Sample Extraction.

5.1.1 Extraction System. Place an extraction thimble (section 2.3.4), 1 g of silica gel, and a plug of glass wool into the Soxhlet apparatus, charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Remove the extraction thimble from the extraction system and place it in a glass beaker to catch the solvent rinses.

5.1.2 Container No. 1 (Filter). Transfer the contents directly to the glass thimble of the extraction system and extract them simultaneously with the XAD-2 resin.

5.1.3 Adsorbent Cartridge. Suspend the adsorbent module directly over the extraction thimble in the beaker (See section 5.1.1). The glass frit of the module should be in the up position. Using a Teflon squeeze bottle containing toluene, flush the XAD-2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module catching the rinsings in the beaker containing the thimble. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. Add the XAD-2 glass wool plug into the thimble.

5.1.4 Container No. 2 (Acetone and Methylene Chloride). Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus, at a temperature of less than 37 °C. Rinse the sample container three times with small portions of methylene chloride and add these to the concentrated solution and concentrate further to near dryness. This residue contains particulate matter removed in the rinse of the train probe and nozzle. Add the concentrate to the filter and the XAD-2 resin in the Soxhlet apparatus described in section 5.1.1.

5.1.5 Extraction. Add 100 μl of the internal standard solution (Section 3.3.20) to the extraction thimble containing the contents of the adsorbent cartridge, the contents of Container No. 1, and the concentrate from section 5.1.4. Cover the contents of the extraction thimble with

[Part 60, Appendix A, Method 23]

the cleaned glass wool plug to prevent the XAD-2 resin from floating into the solvent reservoir of the extractor. Place the thimble in the extractor, and add the toluene contained in the beaker to the solvent reservoir. Pour additional toluene to fill the reservoir approximately 2/3 full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle three times per hour. Extract the sample for 16 hours. After extraction, allow the Soxhlet to cool. Transfer the toluene extract and three 10-ml rinses to the rotary evaporator. Concentrate the extract to approximately 10 ml. At this point the analyst may choose to split the sample in half. If so, split the sample, store one half for future use, and analyze the other according to the procedures in sections 5.2 and 5.3. In either case, use a nitrogen evaporative concentrator to reduce the volume of the sample being analyzed to near dryness. Dissolve the residue in 5 ml of hexane.

5.1.6 Container No. 3 (Toluene Rinse). Add 100 μl of the Internal Standard solution (section 3.3.2) to the contents of the container. Concentrate the sample to a volume of about 1-5 ml using the rotary evaporator apparatus at a temperature of less than 37 °C. Rinse the sample container apparatus at a temperature of less than 37 °C. Rinse the sample container three times with small portions of toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract separately according to the procedures in sections 5.2 and 5.3, but concentrate the solution in a rotary evaporator apparatus rather than a nitrogen evaporative concentrator.

5.2 Sample Cleanup and Fractionation.

5.2.1 Silica Gel Column. Pack one end of a glass column, 20 mm x 230 mm, with glass wool. Add in sequence, 1 g silica gel, 2 g of sodium hydroxide impregnated silica gel, 1 g silica gel, 4 g of acid-modified silica gel, and 1 g of silica gel. Wash the column with 30 ml of hexane and discard it. Add the sample extract, dissolved in 5 ml of hexane to the column with two additional 5-ml rinses. Elute the column with an additional 90 ml of hexane and retain the entire eluate. Concentrate this solution to a volume of about 1 ml using the nitrogen evaporative concentrator (section 2.3.7).

5.2.2 Basic Alumina Column. Shorten a 25-ml disposable Pasteur pipette to about 16 ml. Pack the lower section with glass wool and 12 g of basic alumina. Transfer the concentrated extract from the silica gel column to the top of the basic alumina column and elute the column sequentially with 120 ml of 0.5 percent methylene chloride in hexane followed by 120 ml of 35 percent methylene chloride in hexane. Discard the first 120 ml of eluate. Collect the second 120 ml of eluate and concentrate it to about 0.5 ml using the nitrogen evaporative concentrator.

5.2.3 AX-21 Carbon/Celite 545 Column. Remove the botton 0.5 in. from the tip of a 9-ml disposable Pasteur pipette. Insert a glass fiber filter disk in the top of the pipette 2.5 cm from the constriction. Add sufficient carbon/celite mixture to form a 2 cm column. Top with a glass wool plug. In some cases AX-21 carbon fines may wash through the glass wool plug and enter the sample. This may be prevented by adding a celite plug to the exit end of the column. Rinse the column in sequence with 2 ml of 50 percent benzene in ethyl acetate, 1 ml of 50 percent methylene chloride in cyclohexane, and 2 ml of hexane. Discard these rinses. Transfer the concentrate in 1 ml of hexane from the basic alumina column to the carbon/celite column along with 1 ml of hexane rinse. Elute the column sequentially with 2 ml of 50 percent methylene chloride in hexane and 2 ml of 50 percent benzene in ethyl acetate and discard these eluates. Invert the column and elute in the reverse direction with 13 ml of toluene. Collect this eluate. Concentrate the eluate in a rotary evaporator at 50 °C to about 1 ml. Transfer the concentrate to a Reacti-vial using a toluene rinse and concentrate to a volume of 200 μl using a stream of N_2. Store extracts at room temperature, shielded from light, until the analysis is performed.

5.3 Analysis. Analyze the sample with a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. Immediately prior to analysis, add a 20 μl aliquot of the Recovery Standard solution from Table 1 to each sample. A 2 μl aliquot of the extract is injected into the GC. Sample extracts are first analyzed using the DB-5 capillary column to determine the concentration of each isomer of PCDD's and PCDF's (tetra- through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then analyze another aliquot of the sample in a separate run, using the DB-225 column to measure the 2,3,7,8 tetra-chloro dibenzofuran isomer. Other column systems may be used, provided that the user is able to demonstrate using calibration and performance checks that the column system is able to meet the specifications of section 6.1.2.2.

5.3.1 Gas Chromatograph Operating Conditions.

5.3.1.1 Injector. Configured for capillary column, splitless, 250°C..

5.3.1.2 Carrier Gas. Helium, 1-2 ml/min.

5.3.1.3 Oven. Initially at 150°C. Raise by at least 40°C/min to 190°C and then at 3°C/min up to 300°C.

5.3.2 High Resolution Mass Spectrometer.

5.3.2.1 Resolution. 10000 m/e.

5.3.2.2 Ionization Mode. Electron impact.

5.3.2.3 Source Temperature 250°C.

5.3.2.4 Monitoring Mode. Selected ion monitoring. A list of the various ions to be monitored is summarized in Table 3.

5.3.2.5 Identification Criteria. The following identification criteria shall be used for the characterization of polychlorinated dibenzodioxins and dibenzofurans.

1. The integrated ion-abundance ratio (M/M+2 or M+2/M+4) shall be within 15 percent of the theoretical value. The acceptable ion-abundance ratio ranges for the identification of chlorine-containing compounds are given in Table 4.

2. The retention time for the analytes must be within 3 seconds of the corresponding ^{13}C-labeled internal standard, surrogate or alternate standard.

3. The monitored ions, shown in Table 3 for a given analyte, shall reach their maximum within 2 seconds of each other.

4. The identification of specific isomers that do not have corresponding ^{13}C-labeled standards is done by comparison of the relative retention time (RRT) of the analyte to the nearest internal standard retention time with reference (i.e., within 0.005 RRT units) to the comparable RRT's found in the continuing calibration.

5. The signal to noise ratio for all monitored ions must be greater than 2.5.

[Part 60, Appendix A, Method 23]

6. The confirmation of 2, 3, 7, 8-TCDD and 2, 3, 7, 8-TCDF shall satisfy all of the above identification criteria.

7. For the identification of PCDF's, no signal may be found in the corresponding PCDPE channels.

5.3.2.6 Quantification. The peak areas for the two ions monitored for each analyte are summed to yield the total response for each analyte. Each internal standard is used to quantify the indigenous PCDD's or PCDF's in its homologous series. For example, the $^{13}C_{12}$-2,3,7,8-tetra chlorinated dibenzodioxin is used to calculate the concentrations of all other tetra chlorinated isomers. Recoveries of the tetra- and penta- internal standards are calculated using the $^{13}C_{12}$-1,2,3,4-TCDD. Recoveries of the hexa- through octa- internal standards are calculated using $^{13}C_{12}$-1,2,3,7,8,9-HxCDD. Recoveries of the surrogate standards are calculated using the corresponding homolog from the internal standard.

6. Calibration

Same as Method 5 with the following additions.

6.1 GC/MS System.

6.1.1 Initial Calibration. Calibrate the GC/MS system using the set of five standards shown in Table 2. The relative standard deviation for the mean response factor from each of the unlabeled analytes (Table 2) and of the internal, surrogate, and alternate standards shall be less than or equal to the values in Table 5. The signal to noise ratio for the GC signal present in every selected ion current profile shall be greater than or equal to 2.5. The ion abundance ratios shall be within the control limits in Table 4.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject on μl of solution Number 3 from Table 2. Calculate the relative response factor (RRF) for each compound and compare each RRF to the corresponding mean RRF obtained during the initial calibration. The analyzer performance is acceptable if the measured RRF's for the labeled and unlabeled compounds for the daily run are within the limits of the mean values shown in Table 5. In addition, the ion-abundance ratios shall be within the allowable control limits shown in Table 4.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDD's and PCDF's that documents resolution between 2,3,7,8-TCDD and other TCDD isomers. Resolution is defined as a valley between peaks that is less than 25 percent of the lower of the two peaks. Identify and record the retention time windows for each homologous series.

Perform a similar resolution check on the confirmation column to document the resolution between 2,3,7,8 TCDF and other TCDF isomers.

6.2 Lock Channels. Set mass spectrometer lock channels as specified in Table 3. Monitor the quality control check channels specified in Table 3 to verify instrument stability during the analysis.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 μl of the surrogate standards in Table 1 to the absorbent cartridge of each train before collecting the field samples.

7.2 Internal Standard Percent Recoveries. A group of nine carbon labeled PCDD's and PCDF's representing, the tetra-through octachlorinated homologues, is added to every sample prior to extraction. The role of the internal standards is to quantify the native PCDD's and PCDF's present in the sample as well as to determine the overall method efficiency. Recoveries of the internal standards must be between 40 to 130 percent for the tetra-through hexachlorinated compounds while the range is 25 to 130 percent for the higher hepta- and octachlorinated homologues.

7.3 Surrogate Recoveries. The five surrogate compounds in Table 2 are added to the resin in the adsorbent sampling cartridge before the sample is collected. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. They are not used to measure native PCDD's and PCDF's. All recoveries shall be between 70 and 130 percent. Poor recoveries for all the surrogates may be an indication of breakthrough in the sampling train. If the recovery of all standards is below 70 percent, the sampling runs must be repeated. As an alternative, the sampling runs do not have to be repeated if the final results are divided by the fraction of surrogate recovery. Poor recoveries of isolated surrogate compounds should not be grounds for rejecting an entire set of the samples.

7.4 Toluene QA Rinse. Report the results of the toluene QA rinse separately from the total sample catch. Do not add it to the total sample.

8. Quality Assurance

8.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, an audit sample must be analyzed, subject to availability.

8.2 Audit Procedure. Analyze an audit sample with each set of compliance samples. The audit sample contains tetra through octa isomers of PCDD and PCDF. Concurrently, analyze the audit sample and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for the compliance samples and the EPA audit sample.

8.3 Audit Sample Availability. Audit samples will be supplied only to enforcement agencies for compliance tests. The availability of audit samples may be obtained by writing: Source Test Audit Coordinator (MD-77B), Quality Assurance Division, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC 27711, or by calling the Source Test Audit Coordinator (STAC) at (919) 541-7834. The request for the audit sample must be made at least 30 days prior to the scheduled compliance sample analysis.

8.4 Audit Results. Calculate the audit sample concentration according to the calculation procedure described in the audit instructions included with the audit sample. Fill in the audit sample concentration and the analyst's name on the audit response form included with the audit instructions. Send one copy to the EPA Regional Office or the appropriate enforcement agency and a second copy to the STAC. The EPA Regional office or the appropriate enforcement agency will report the results of the audit to the laboratory being audited. Include this response with the results of the compliance samples in relevant reports to the EPA Regional Office or the appropriate enforcement agency.

9. Calculations

Same as Method 5, section 6 with the following additions.

9.1 Nomenclature.

A_{ai}=Integrated ion current of the noise at the retention time of the analyte.

A^{*}_{ci}=Integrated ion current of the two ions characteristic of the internal standard i in the calibration standard.

A_{cij}=Integrated ion current of the two ions characteristic of compound i in the jth calibration standard.

A^*_{cij}=Integrated ion current of the two ions characteristic of the internal standard i in the jth calibration standard.

A_{csi}=Integrated ion current of the two ions characteristic of surrogate compound i in the calibration standard.

A_i=Integrated ion current of the two ions characteristic of compound i in the sample.

A^*_i=Integrated ion current of the two ions characteristic of internal standard i in the sample.

A_{rs}=Integrated ion current of the two ions characteristic of the recovery standard.

A_{si}=Integrated ion current of the two ions characteristic of surrogate compound i in the sample.

C_i=Concentration of PCDD or PCDF i in the sample, pg/ M^3.

C_T=Total concentration of PCDD's or PCDF's in the sample, pg/ M^3.

m_{ci}=Mass of compound i in the calibration standard injected into the analyzer, pg.

m_{rs}=Mass of recovery standard in the calibration standard injected into the analyzer, pg.

m_{si}=Mass of surrogate compound i in the calibration standard, pg.

RRF_i=Relative response factor.

RRF_{rs}=Recovery standard response factor.

RRF_s=Surrogate compound response factor.

9.2 Average Relative Response Factor.

$$RRF_i = \frac{1}{n} \sum_{j=1}^{n} \frac{A_{cij}\, m^*_{ci}}{A^*_{cij}\, m_{ci}} \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDD's and PCDF's.

$$C_i = \frac{m_i^*\, A_i}{A_i^*\, RRF_i\, V_{mstd}} \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = \frac{A_{ci}^* m_{rs}}{A_{rs}\, m_{ci}^*} \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R^*).

$$R^* = \frac{A_i^*\, m_{rs}}{A_{rs}\, RF_{rs}\, m_i^*} \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRF_s = \frac{A_{ci}^*\, m_s}{A_{cis}\, m_{ci}^*} \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = \frac{A_s\, m_i^*}{A_i^*\, RRF_s\, m_s} \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Minimum Detectable Limit (MDL).

$$MDL = \frac{2.5\, A_{si}\, m_i^*}{A_{ci}^*\, RRF_i} \qquad \text{Eq. 23-7}$$

9.9 Total Concentration of PCDD's and PCDF's in the Sample.

$$C_{Tr} = \sum_{i=1}^{n} C_i \qquad \text{Eq. 23-8}$$

Any PCDD's or PCDF's that are reported as nondetected (below the MDL) shall be counted as zero for the purpose of calculating the total concentration of PCDD's and PCDF's in the sample.

10. Bibliography

1. American Society of Mechanical Engineers. Sampling for the Determination of Chlorinated Organic Compounds in Stack Emissions. Prepared for U.S. Department of Energy and U.S. Environmental Protection Agency. Washington DC. December 1984. 25 p.

2. American Society of Mechanical Engineers. Analytical Procedures to Assay Stack Effluent Samples and Residual Combustion Products for Polychlorinated Dibenzo-p-Dioxins (PCDD) and Polychlorinated Dibenzofurans (PCDF). Prepared for the U.S. Department of Energy and U.S. Environmental Protection Agency. Washington, DC. December 1984. 23 p.

3. Thompson, J. R. (ed.). Analysis of Pesticide Residues in Human and Environmental Samples. U.S. Environmental Protection Agency. Research Triangle Park, NC. 1974.

4. Triangle Laboratories. Case Study: Analysis of Samples for the Presence of Tetra Through Octachloro-p-Dibenzodioxins and Dibenzofurans. Research Triangle Park, NC. 1988. 26 p.

5. U.S. Environmental Protection Agency. Method 8290-The Analysis of Polychlorinated Dibenzo-p-dioxin and Polychlorinated Dibenzofurans by High-Resolution Gas Chromotography/High-Resolution Mass Spectrometry. In: Test Methods for Evaluating Solid Waste. Washington, DC. SW-846.

TABLE 1—COMPOSITION OF THE SAMPLE FORTIFICATION AND RECOVERY STANDARDS SOLUTIONS

Analyte	Concentration (pg/µl)
Internal Standards:	
$^{13}C_{12}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100
$^{13}C_{12}$-OCDD	100
$^{13}C_{12}$-2,3,7,8-TCDF	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100
Surrogate Standards:	
$^{37}Cl_4$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	100
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	100
Recovery Standards:	
$^{13}C_{12}$-1,2,3,4-TCDD	500
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	500

TABLE 2—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS

Compound	Concentrations (pg/µL)				
	Solution No.				
	1	2	3	4	5
Alternate Standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
Recovery Standards:					
$^{13}C_{12}$-1,2,3,4-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8,9-HxCDD	100	100	100	100	100

[Part 60, Appendix A, Method 23]

0013-9211/93/$0+$1.00

TABLE 3—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDD'S AND PCDF'S

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
2	292.9825	LOCK	C_7F_{11}	PFK
	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl^{37}O$	TCDF
	315.9419	M	${}^{13}C_{12}H_4{}^{35}Cl_4O$	TCDF (S)
	317.9389	M+2	${}^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	TCDF (S)
	319.8965	M	$C_{12}H_4{}^{35}ClO_2$	TCDD
	321.8936	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD
	327.8847	M	$C_{12}H_4{}^{37}Cl_4O_2$	TCDD (S)
	330.9792	QC	C_7F_{13}	PFK
	331.9368	M	${}^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	${}^{13}C_{12}H_4{}^{35}Cl\ {}^{37}ClO_2$	TCDD (S)
	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2\ O$	PeCDF
	351.9000	M+2	${}^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	${}^{13}C_{12}H_3{}^{35}Cl^{3537}Cl_2\ O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_{3}37ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2\ O_2$	PeCDD
	367.8949	M+2	${}^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	${}^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2\ O_{T22}$	PeCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
3	373.8208	M+2	$C_{12}H_2\ 35Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2\ {}^{35}Cl_4{}^{37}Cl_2\ O$	HxCDF
	383.8639	M	${}^{13}C_{12}H_2\ {}^{35}Cl_6O$	HxCDF (S)
	385.8610	M+2	${}^{13}C_{12}H_2\ {}^{35}Cl_5{}^{37}ClO$	HxCDF (S)
	389.8157	M+2	$C_{12}H_2\ {}^{35}Cl_5{}^{37}ClO_2$	HxCDD
	391.8127	M+4	$C_{12}H_2\ {}^{35}Cl_4{}^{37}Cl_2\ O_2$	HxCDD
	392.9760	LOCK	C_9F_{15}	PFK
	401.8559	M+2	${}^{13}C_{12}H_2\ {}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	${}^{13}C_{12}H_2\ {}^{35}Cl_4{}^{37}Cl_2\ O$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2\ {}^{35}Cl_6{}^{37}Cl_2\ O$	OCDPE
	430.9729	QC	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2\ O$	HpCDF
	417.8253	M	${}^{13}C_{12}H^{35}Cl_7O$	HpCDF (S)
	419.8220	M+2	${}^{13}C_{12}H^{35}Cl_6{}^{37}ClO$	HpCDF (S)
	423.7766	M+2	$C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD
	425.7737	M+4	$C_{12}H^{35}Cl_5{}^{37}Cl_2\ O_2$	HpCDD
	435.8169	M+2	${}^{13}C_{12}H^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	${}^{13}C_{12}H^{35}Cl_5{}^{37}Cl_2\ O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H^{35}Cl_7{}^{37}Cl_2\ O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2\ O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2\ O_2$	OCDD
	469.7779	M+2	${}^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	${}^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2\ O_2$	OCDD (S)
	513.6775	M+4	$C_{12}{}^{35}Cl_8{}^{37}Cl_2\ O_2$	DCDPE
	442.9728	QC	$C_{10}F_{17}$	PFK

(a) The following nuclidic masses were used:
H = 1.007825
C = 12.000000
${}^{13}C$ = 13.003355
F = 18.9984
O = 15.994915
${}^{35}Cl$ = 34.968853
${}^{37}Cl$ = 36.965903
S = Labeled Standard
QC = Ion selected for monitoring instrument stability during the GC/MS analysis.

TABLE 4—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDD'S AND PCDF'S

No. of chlorine atoms	Ion type	Theoretical ratio	Control limits	
			Lower	Upper
4	M/M+2	0.77	0.65	0.89
5	M+2/M+4	1.55	1.32	1.78
6	M+2/M+4	1.24	1.05	1.43
6[a]	M/M+2	0.51	0.43	0.59
7[b]	M/M+2	0.44	0.37	0.51
7	M+2/M+4	1.04	0.88	1.20
8	M+2/M+4	0.89	0.76	1.02

[a] Used only for ^{13}C-HxCDF.

[b] Used only for ^{13}C-HpCDF.

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Unlabeled Analytes:		
2,3,7,8-TCDD	25	25
2,3,7,8-TCDF	25	25
1,2,3,7,8-PeCDD	25	25
1,2,3,7,8-PeCDF	25	25
2,3,4,7,8-PeCDF	25	25
1,2,4,5,7,8-HxCDD	25	25
1,2,3,6,7,8-HxCDD	25	25
1,2,3,7,8,9-HxCDD	25	25
1,2,3,4,7,8-HxCDF	25	25
1,2,3,6,7,8-HxCDF	25	25
1,2,3,7,8,9-HxCDF	25	25
2,3,4,6,7,8-HxCDF	25	25
1,2,3,4,6,7,8-HpCDD	25	25
1,2,3,4,6,7,8-HpCDF	25	25
OCDD	25	25
OCDF	30	30
Internal Standards:		
$^{13}C_{12}$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-1,2,3,7,8-PeCDD	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	30	30
$^{13}C_{12}$-OCDD	30	30
$^{13}C_{12}$-2,3,7,8-TCDF	30	30
$^{13}C_{12}$-1,2,3,7,8-PeCDF	30	30
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	30	30
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	30	30
Surrogate Standards:		
$^{37}Cl_4$-2,3,7,8-TCDD	25	25
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	25
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	25
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	25

TABLE 5—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS—Contd.

Compound	Relative response factors	
	Initial calibration RSD	Daily calibration % difference
Alternate Standard:		
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

METHOD 24—DETERMINATION OF VOLATILE MATTER CONTENT, WATER CONTENT, DENSITY, VOLUME SOLIDS, AND WEIGHT SOLIDS OF SURFACE COATINGS

Applicability and Principle

1.1 Applicability. This method applies to the determination of volatile matter content, water content, density, volume solids, and weight solids of paint, varnish, lacquer, or related surface coatings.

1.2 Principle. Standard methods are used to determine the volatile matter content, water content, density, volume solids, and weight solids of the paint, varnish, lacquer, or related surface coatings.

2. *Applicable Standard Methods*

Use the apparatus, reagents, and procedures specified in the standard methods below:

2.1 ASTM D1475-60 (Reapproved 1980), Standard Test Method for Density of Paint, Varnish, Lacquer, and Related Products (incorporated by reference—see §60.17).

2.2 ASTM D2369-81, Standard Test Method for Volatile Content of Coatings (incorporated by reference—see §60.17).

2.3 ASTM D3792-79, Standard Test Method for Water Content of Water-Reducible Paints by Direct Injection into a Gas Chromatograph (incorporated by reference—see §60.17).

2.4 ASTM D4017-81, Standard Test Method for Water in Paints and Paint Materials by the Karl Fischer Titration Method (incorporated by reference—see §60.17).

2.5 ASTM D4457-85 Standard Test Method for Determination of Dichloromethane and 1,1,1-Trichloroethane in Paints and Coatings by Direct Injection into a Gas Chromatograph (incorporated by reference—see §60.17).

3. *Procedure*

3.1 Multicomponent Coatings. Multicomponent coatings are coatings that are packaged in two or more parts, which are combined before application. Upon combination a coreactant from one part of the coating chemically reacts, at ambient conditions, with a coreactant from another part of the coating. To determine the total volatile content, water content, and density of multicomponent coatings, follow the procedures in section 3.7. For all other coatings analyze as follows:

3.2 Volatile Matter Content. Use the procedure in ASTM D2369-81 (incorporated by reference—see §60.17) to determine the volatile matter content (may include water) of the coating. Record the following information:

W_1=Weight of dish and sample before heating, g.

W_2 =Weight of dish and sample after heating, g.

W_3=Sample weight, g.

Run analyses in pairs (duplicate sets) for each coating until the criterion in Section 4.3 is met. Calculate the weight fraction of the volatile matter (W_v) for each analysis as follows:

$$W_v = \frac{W_1 - W_2}{W_3} \qquad \text{Eq. 24-1}$$

Record the arithmetic average (W_v).

3.3 Water Content. For waterborne (water reducible) coatings only, determine the weight fraction of water (W_w) using either "Standard Content Method Test for Water of Water-Reducible Paints by Direct Injection into a Gas Chromatograph" or "Standard Test Method for Water in Paint and Paint Materials by Karl Fischer Method." (These two methods are incorporated by reference—see §60.17). A waterborne coating is any coating which contains

~~5.1.2 Begin sampling by purging the sample lines and cooling coil with at least four volumes of waste. Collect the purged material in a separate container and dispose of it properly.~~

~~5.1.3 After purging, stop the sample flow and transfer the Teflon sampling tube to a sample container. Sample at a flow rate such that the temperature of the waste is <10°C (<50°F). Fill the sample container halfway (±5 percent) and cap it within 5 seconds. Store immediately in a cooler and cover with ice.~~

~~5.1.4 Alternative sampling techniques may be used upon the approval of the Administrator.~~

~~5.2 Analysis.~~

~~5.2.1 Allow one hour for the headspace vials to equilibrate at the temperature specified in the regulation. Allow the FID to warm up until a stable baseline is achieved on the detector.~~

~~5.2.2 Check the calibration of the FID daily using the procedures in Section 6.1.2.~~

~~5.2.3 Follow the manufacturer's recommended procedures for the normal operation of the headspace sampler and FID.~~

~~5.2.4 Use the procedures in Sections 7.4 and 7.5 to calculate the vapor phase organic vapor pressure in the samples.~~

~~5.2.5 Monitor the output of the detector to make certain that the results are being properly recorded.~~

~~6. Operational Checks and Calibration~~

~~Maintain a record of performance of each item.~~

~~6.1 Use the procedures in Section 6.1.1 to calibrate the headspace analyzer and FID and check for linearity before the system is first placed in operation, after any shutdown longer than 6 months, and after any modification of the system.~~

~~6.1.1 Calibration and Linearity. Use the procedures in Section 6.2.1 of Method 18 of Part 60, Appendix A, to prepare the standards and calibrate the flowmeters, using propane as the standard gas. Fill the calibration standard vials halfway (±5 percent) with deionized water. Purge and fill the airspace with calibration standard. Prepare a minimum of three calibration standards in triplicate at concentrations that will bracket the applicable cutoff. For a cutoff of 5.2 kPa, prepare nominal concentrations of 30,000, 50,000, and 70,000 ppm as propane. For a cutoff of 27.6 kPa, prepare nominal concentrations of 200,000, 300,000, and 400,000 ppm as propane.~~

~~6.1.1.1 Use the procedures in Section 5.2.3 to measure the FID response of each standard. Use a linear regression analysis to calculate the values for the slope (k) and the y-intercept (b). Use the procedures in Sections 7.2 and 7.3 to test the calibration and the linearity.~~

~~6.1.2 Daily FID Calibration Check. Check the calibration at the beginning and at the end of the daily runs by using the following procedures. Prepare two calibration standards at the nominal cutoff concentration using the procedures in Section 6.1.1. Place one at the beginning and one at the end of the daily run. Measure the FID response of the daily calibration standard and use the values for k and b from the most recent calibration to calculate the concentration of the daily standard. Use an equation similar to 25E-2 to calculate the percent difference between the daily standard and C_s. If the difference is within 5 percent, then the previous values for k and b may be used. Otherwise, use the procedures in Section 6.1.1 to recalibrate the FID.~~

~~7. Calculations~~

~~7.1 Nomenclature.~~

~~A = Measurement of the area under the response curve, counts.~~
~~b = y-intercept of the linear regression line.~~
~~C_a = Measured vapor phase organic concentration of sample, ppm as propane.~~
~~C_{ma} = Average measured vapor phase organic concentration of standard, ppm as propane.~~
~~C_m = Measured vapor phase organic concentration of standard, ppm as propane.~~
~~C_s = Calculated standard concentration, ppm as propane.~~
~~k = Slope of the linear regression line.~~
~~P_{bar} = Atmospheric pressure at analysis conditions, mm Hg (in. Hg).~~
~~P^* = Organic vapor pressure in the sample, kPa (psi).~~
~~$\beta = 1.333 \times 10^{-7}$ kPa/[(mm Hg)(ppm)], (4.91×10^{-7} psi/[(in. Hg)(ppm)])~~

~~7.2 Linearity. Use the following equation to calculate the measured standard concentration for each standard vial.~~

$$C_m = kA + b \qquad \text{Eq. 25E-1}$$

~~7.2.1 Calculate the average measured standard concentration (C_{ma}) for each set of triplicate standards and use the following equation to calculate the percent difference (PD) between C_{ma} and C_s.~~

$$PD = \frac{C_s - C_{ma}}{C_s} \times 100 \qquad \text{Eq. 25E-2}$$

~~The instrument linearity is acceptable if the percent difference is within five for each standard.~~

~~7.3 Relative Standard Deviation (RSD). Use the following equation to calculate the RSD for each triplicate set of standards.~~

$$RSD = \frac{100}{C_{ma}} \sqrt{\frac{\sum (C_m - C_{ma})^2}{2}} \qquad \text{Eq. 25E-3}$$

~~The calibration is acceptable if the RSD is within five for each standard concentration.~~

~~7.4 Concentration of organics in the headspace. Use the following equation to calculate the concentration of vapor phase organics in each sample.~~

$$C_a = kA + b \qquad \text{Eq. 25E-4}$$

~~7.5 Vapor Pressure of Organics in the Headspace Sample. Use the following equation to calculate the vapor pressure of organics in the sample.~~

$$P^* = \beta P_{bar} C_a \qquad \text{Eq. 25E-5}$$

* * * * *

~~[Method 25E added at 59 FR 62923, Dec. 6, 1994]~~

METHOD 26—DETERMINATION OF HYDROGEN CHLORIDE EMISSIONS FROM STATIONARY SOURCES

1. Applicability, Principle, Interferences, Precision, Bias, and Stability

1.1 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) [hydrogen chloride (HCl), hydrogen bromide (HBr), and hy-

[Part 60, Appendix A, Method 26]

drogen fluoride (HF)] and halogens (X_2) [chlorine (Cl_2) and bromine (Br_2)] from stationary sources. Sources, such as those controlled by wet scrubbers, that emit acid particulate matter must be sampled using Method 26A.

[Note: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.]

[1.1 revised at 59 FR 19308, April 22, 1994]

1.2 Principle. An integrated sample is extracted from the source and passed through a prepurged heated probe and filter into dilute sulfuric acid and dilute sodium hydroxide solutions which collect the gaseous hydrogen halides and halogens, respectively. The filter collects other particulate matter including halide salts. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-), and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added in excess to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC).

[1.2 revised at 59 FR 19308, April 22, 1994]

1.3 Interferences. Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and a hydrohalous acid upon dissolution in water. However, the use of acidic rather than neutral or basic solutions for collection of the hydrogen halides greatly reduces the dissolution of any halogens passing through this solution. The simultaneous presence of HBr and CL_2may cause a positive bias in the HCL result with a corresponding negative bias in the Cl_2result as well as affecting the HBr/Br_2split. High concentrations of nitrogen oxides (NO_X) may produce sufficient nitrate (NO_3^-) to interfere with measurements of very low Br^-levels.

[1.3 revised at 59 FR 19308, April 22, 1994]

1.4 Precision and Bias. The within-laboratory relative standard deviations are 6.2 and 3.2 percent at HCl concentrations of 3.9 and 15.3 ppm, respectively. The method does not exhibit a bias to Cl_2 when sampling at concentrations less than 50 ppm.

1.5 Sample Stability. The collected Cl^- samples can be stored for up to 4 weeks.

[1.5 revised at 59 FR 19308, April 22, 1994]

1.6 Detection Limit. The analytical detection limit for $Cl^-$is 0.1 μg/ml. Detection limits for the other analyses should be similar.

[1.6 revised at 59 FR 19308, April 22, 1994]

2. Apparatus

2.1 Sampling. The sampling train is shown in Figure 26-1, and component parts are discussed below.

2.1.1 Probe. Borosilicate glass, approximately 3/8-in. (9-mm) I.D. with a heating system to prevent moisture condensation. A Teflon-glass filter in a mat configuration shall be installed behind the probe to remove particulate matter from the gas stream (see section 2.1.5). A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result.

2.1.2 Three-way Stopcock. A borosilicate glass three-way stopcock with a heating system to prevent moisture condensation. The heated stopcock should connect directly to the outlet of the heated filter and the inlet of the first impinger. The heating system shall be capable of preventing condensation up to the inlet of the first impinger. Silicone grease may be used, if necessary, to prevent leakage.

0013-9211/94/$0+$1.00

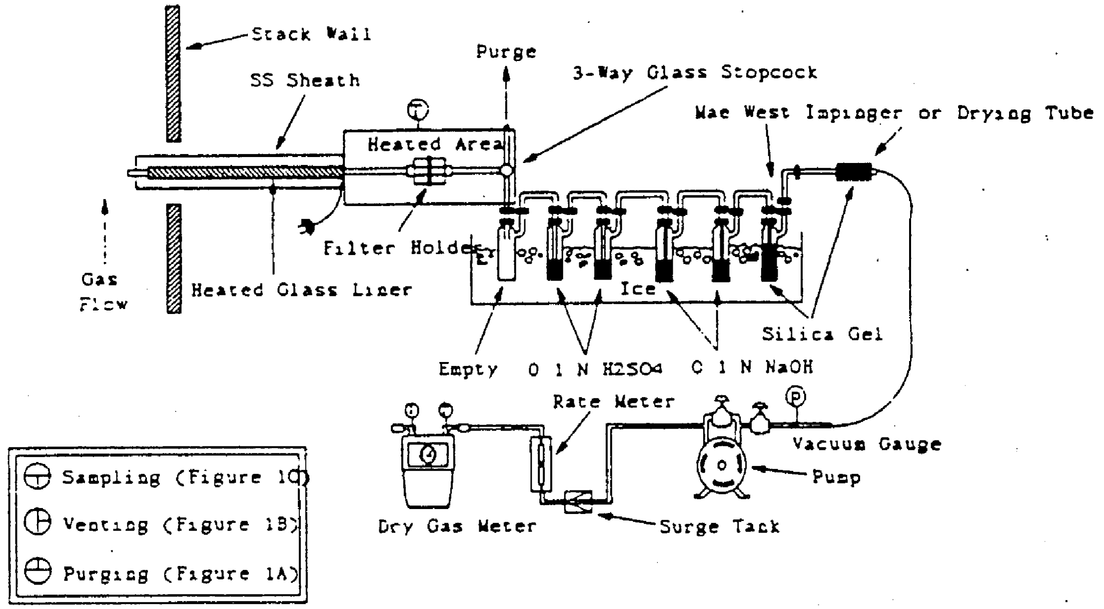


Figure 26-1 Sampling train

[Figure 26-1 revised at 59 FR 19308, April 22, 1994]

2.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakage. For sampling at high moisture sources or for sampling times greater than 1 hour, a midget impinger with a shortened stem (such that the gas sample does not bubble through the collected condensate) should be used in front of the first impinger.

2.1.4 Drying Tube or Impinger. Tube or impinger, of Mae West design, filled with 6- to 16-mesh indicating type silica gel, or equivalent, to dry the gas sample and to protect the dry gas meter and pump. If the silica gel has been used previously, dry at 175 °C (350 °F) for 2 hours. New silica gel may be used as received. Alternatively, other types of desiccants (equivalent or better) may be used.

When the stack gas temperature exceeds 210°C (410°F) and the HCl concentration is greater than 20 ppm, a quartz-fiber filter may be used.

[2.1.5 revised at 59 FR 19308, April 22, 1994]

2.1.6 Filter Holder and Support. The filter holder should be made of Teflon or quartz. The filter support shall be made of Teflon. All-Teflon filter holders are availabe from Savillex Corp., 5325 Hwy. 101, Minnetonka, MN 55345.

2.1.7 Sample Line. Leak-free, with compatible fittings to connect the last impinger to the needle valve.

2.1.8 Rate Meter. Rotameter, or equivalent, capable of measuring flow rate to within 2 percent of the selected flow rate of 2 liters/min.

2.1.9 Purge Pump, Purge Line, Drying Tube, Needle Valve, and Rate Meter. Pump capable of purging the sampling probe at 2 liters/min, with drying tube, filled with silica gel or equivalent, to protect pump, and a rate meter capable of measuring 0 to 5 liters/min.

2.1.10 Stopcock Grease, Valve, Pump, Volume Meter, Barometer, and Vacuum Gauge. Same as in Method 6, Sections 2.1.4, 2.1.7, 2.1.8, 2.1.10, 2.1.11, and 2.1.12.

2.1.11 Temperature Measuring Devices. Temperature measuring device to monitor the temperature of the probe and a thermometer or other temperature of the sampling system from the outlet of the probe to the inlet of the first impinger.

2.1.12 Ice Water Bath. To minimize loss of absorbing solution.

2.2 Sample Recovery.

2.2.1 Wash Bottles. Polyethylene or glass, 500-ml or larger, two.

2.2.2 Storage Bottles. 100- or 250-ml, high-density polyethylene bottles with Teflon® screw cap liners to store impinger samples.

[2.2.2 amended at 59 FR 19308, April 22, 1994]

2.3 Sample Preparation and Analysis. The materials required for volumetric dilution and chromatographic analysis of samples are described below.

2.3.1 Volumetric Flasks. Class A, 100-ml size.

2.3.2 Volumetric Pipets. Class A, assortment. To dilute samples into the calibration range of the instrument.

2.3.3 Ion Chromatograph. Suppressed or nonsuppressed, with a conductivity detector and electronic integrator operating in the peak area mode. Other detectors, strip chart recorders, and peak height measurements may be used.

3. *Reagents*

Unless otherwise indicated, all reagents must conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society (ACS reagent grade). When such specifications are not available, the best available grade shall be used.

3.1. Sampling.

3.1.1 Water. Deionized, distilled water that conforms to ASTM Specification D 1193-77, Type 3.

3.1.2 Acidic Absorbing solution, 0.1 N Sulfuric Acid (H_2SO_4). To prepare 100 ml of the absorbing solution for the front impinger pair, slowly add 0.28 ml of concentrated H_2SO_4 to about 90 ml of water while stirring, and adjust the final volume to 100 ml using additional water. Shake well to mix the solution.

[3.1.2 amended at 59 FR 19308, April 22, 1994]

3.1.3. Alkaline Absorbing Solution, 0.1 N Sodium Hydroxide (NaOH). To prepare 100 ml of the scrubber solution for the back pair of impingers, dissolve 0.40 g of solid NaOH in about 90 ml of water, and adjust the final solution volume to 100 ml using additional water. Shake well to mix the solution.

[3.1.3 amended at 59 FR 19308, April 22, 1994]

3.1.4 Sodium Thiosulfate ($Na_2S_2O_3 \cdot 5 H_2O$)

[3.1.4 added at 59 FR 19308, April 22, 1994]

3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Absorbing Solution Blanks. A separate blank solution of each absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of each absorbing solution to approximately the same final volume as the field samples using the blank sample of rinse water.

[3.2.2 revised at 59 FR 19308, April 22, 1994]

3.2.3 Halide Salt Stock Standard Solutions. Prepare concentrated stock solutions from reagent grade sodium chloride (NaCl), sodium bromide (NaBr), and sodium fluoride (NaF). Each must be dried at 110°C for two or more hours and then cooled to room temperature in a desiccator immediately before weighing. Accurately weigh 1.6 to 1.7 g of the dried NaCl to within 0.1 mg, dissolve in water, and dilute to 1 liter. Calculate the exact Cl^- concentration using Equation 26-1.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44 \quad Eq.\ 26\text{-}1$$

In a similar manner, accurately weigh and solubilize 1.2 to 1.3 g of dried NaBr and 2.2 to 2.3 g of NaF to make 1-liter solutions. Use Equations 26-2 and 26-3 to calculate the Br^- and F^- concentrations.

$$\mu g\ Br^-/ml = g\ of\ NaBr \times 10^3 \times 79.904/102.90 \quad Eq.\ 26\text{-}2$$

$$\mu g\ F^-/ml = g\ of\ NaF \times 10^3 \times 18.998/41.99 \quad Eq.\ 26\text{-}3$$

Alternately, solutions containing a nominal certified concentration of 1000 mg/l NaCl are commercially available as convenient stock solutions from which standards can be made by appropriate volumetric dilution. Refrigerate the stock standard solutions and store no longer than one month.

[3.2.3 revised at 59 FR 19308, April 22, 1994]

3.2.4 Chromatographic Eluent. Effective eluents for nonsuppressed IC using a resin- or silica-based weak ion exchange column are a 4 mM potassium hydrogen phthalate solution, adjusted to pH 4.0 using a saturated sodium borate solution, and a 4 mM 4-hydroxy benzoate solution, adjusted to pH 8.6 using 1 N NaOH. An effective eluent for suppressed ion chromatography is a solution containing 3 mM sodium bicarbonate and 2.4 mM sodium carbonate. Other dilute solutions buffered to a similar pH and containing no interfering ions may be used. When using suppressed ion chromatography, if the "water dip" resulting from sample injection interferes with the chloride peak, use a 2 mM NaOH/2.4 mM sodium bicarbonate eluent.

4. *Procedure*

4.1 Sampling.

4.1.1 Preparation of Collection Train. Prepare the sampling train as follows: Pour 15 ml of the acidic absorbing solution into each one of the first pair of impingers, and 15 ml of the alkaline absorbing solution into each one of the second pair of impingers. Connect the impingers in series with the knockout impinger first, if used, followed by the two impingers containing the acidic absorbing solution and the two impingers containing the alkaline absorbing solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or impinger at the end of the impinger train.

[4.1.1 revised at 59 FR 19308, April 22, 1994]

4.1.2 Adjust the probe temperature and the temperature of the filter and the stopcock, i.e., the heated area in Figure 26-1 to a temperature sufficient to prevent water condensation. This temperature should be at least 20° C above the source temperature, but not greater than 20° C. The temperature should be monitored throughout a sampling run to ensure that the desired temperature is maintained.

0013-9211/94/$0+$1.00

4.1.3 Leak-Check Procedure. A leak-check prior to the sampling run is optional; however, a leak-check after the sampling run is mandatory. The leak-check procedure is as follows: Temporarily attach a suitable (e.g., 0-40 cc/min) rotameter to the cutlet of the dry gas meter and place a vacuum gauge at or near the probe inlet, pull a vacuum of at least 250 mm Hg (10 in. Hg), and note the flow rate as indicated by the rotameter. A leakage rate not in excess of 2 percent of the average sampling rate is acceptable. (*NOTE:*Carefully release the probe inlet plug before turning off the pump.) It is suggested (not mandatory) that the pump be leak-checked separately, either prior to or after the sampling run. If done prior to the sampling run, the pump leak-check shall precede the leak-check of the sampling train described immediately above; if done after the sampling run, the pump leak-check shall follow the train leak-check. To leak-check the pump, proceed as follows; Disconnect the drying tube from the probe-impinger assembly. Place a vacuum gauge at the inlet to either the drying tube or pump, pull a vacuum of 250 mm (10 in.) Hg. plug or pinch off the outlet of the flowmeter, and then turn off the pump. The vacuum should remain stable for at least 30 sec. Other leak-check procedured may be used, subject to the approval of the Administrator, U.S. Environmental Protection Agency.

4.1.4 Purge Procedure. Immediately before sampling, connect the purge line to the stopcock, and turn the stopcock to permit the purge pump to purge the probe (see Figure 1A of Figure 26-1). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes before sampling.

4.1.5 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train (see Figure 1C of Figure 26-1). Adjust the sampling rate to 2 liters/min, as indicated by the rate meter, and maintain this rate to within 10 percent during the entire sampling run. Take readings of the dry gas meter volume and temperature, rate meter, and vacuum gauge at least once every 5 minutes during the run. A sampling time of 1 hour is recommended. Shorter sampling times may introduce a significant negative bias in the HCl concentration. At the conclusion of the sampling run, remove the train from the stack, cool, and perform a leak-check as described in section 4.1.2.

4.2 Sample Recovery. Disconnect the impingers after sampling. Quantitatively transfer the contents of the acid impingers and the knockout impinger, if used, to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. Repeat this procedure for the alkaline impingers and connecting glassware using a separate storage bottle. Add 25 mg sodium thiosulfate per the product of ppm of halogen anticipated to be in the stack gas times the dscm stack gas sampled. [Note: This amount of sodium thiosulfate includes a safety factor of approximately 5 to assure complete reaction with the hypohalous acid to form a second Cl⁻ ion in the alkaline solution.] Save portions of the absorbing reagents (0.1 N H_2SO_4 and 0.1 N NaOH) equivalent to the amount used in the sampling train (these are the absorbing solution blanks described in Section 3.2.2); dilute to the approximate volume of the corresponding samples using rinse water directly from the wash bottle being used. Add the same amount of sodium thiosulfate solution to the 0.1 N NaOH absorbing solution blank. Also, save a portion of the rinse water used to rinse the sampling train. Place each in a separate, prelabeled storage bottle. The sample storage bottles should be sealed, shaken to mix, and labeled. Mark the fluid level.

[4.2 revised at 59 FR 19308, April 22, 1994]

4.3 Sample Preparation for Analysis. Note the liquid levels in the storage bottles and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Quantitatively transfer the sample solutions to 100-ml volumetric flasks, and dilute to 100 ml with water.

[4.3 revised at 59 FR 19308, April 22, 1994]

4.4 Sample Analysis.

4.4.1 The IC conditions will depend upon analytical column type and whether suppressed or nonsuppressed IC is used. An example chromatogram from a nonsuppressed system using a 150-mm Hamilton PRP-X100 anion column, a 2 ml/min flow rate of a 4 mM 4-hydroxy benzoate solution adjusted to a pH of 8.6 using 1 N NaOH, a 50 μl sample loop, and a conductivity detector set on 1.0 μS full scale is shown in Figure 26-2.

4.4.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^-, Br^-, or F^- appears in the chromatogram. If any of these ions are present, repeat the load/injection procedure until they are no longer present. Analysis of the acid and alkaline absorbing solution samples requires separate standard calibration curves; prepare each according to Section 5.2. Ensure adequate baseline separation of the analyses.

[4.4.2 revised at 59 FR 19308, April 22, 1994]

4.4.3 Between injections of the appropriate series of calibration standards, inject in duplicate the reagent blanks, quality control sample, and the field samples. Measure the areas or heights of the Cl^-, Br^-, and F^- peaks. Use the mean response of the duplicate injections to determine the concentrations of the field samples and reagent blanks using the linear calibration curve. The values from duplicate injections should agree within 5 percent of their mean for the analysis to be valid. Dilute any sample and the blank with equal volumes of water if the concentration exceeds that of the highest standard.

[4.4.3 revised at 59 FR 19308, April 22, 1994]

4.5 Audit Analysis. An audit sample must be analyzed, subject to availability.

[Part 60, Appendix A, Method 26]

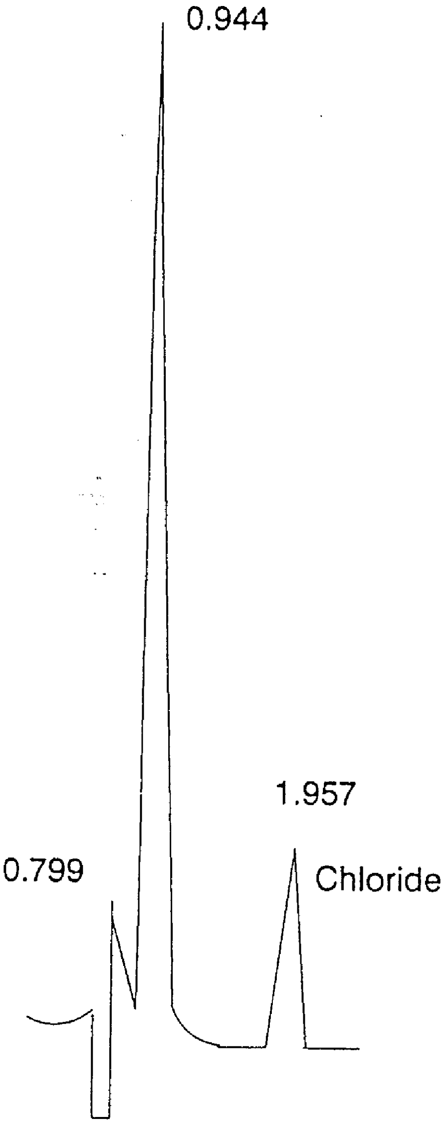


Figure 26-2. Example Chromatogram

5. Calibration

5.1 Dry Gas Metering System, Thermometers, Rate Meter, and Barometer. Same as in Method 6, sections 5.1, 5.2, 5.3, and 5.4.

5.2 Ion Chromatograph. To prepare the calibration standards, dilute given amounts (1.0 ml or greater) of the stock standard solutions to convenient volumes, using 0.1 N H_2SO_2 or 0.1 N NaOH, as appropriate. Prepare at least four calibration standards for each absorbing reagent containing the appropriate stock solutions such that they are within the linear range of the field samples. Using one of the standards in each series, ensure adequate baseline separation for the peaks of interest. Inject the appropriate series of calibration standards, starting with the lowest concentration standard first both before and after injection of the quality control check sample, reagent blanks, and field samples. This allows compensation for any instrument drift occurring during sample analysis.

Determine the peak areas, or heights, for the standards and plot individual values versus halide ion concentrations in μg/ml. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

[5.2 revised at 59 FR 19308, April 22, 1994]

6. Quality Assurance

6.1 Applicability. When the method is used to analyze samples to demonstrate compliance with a source emission regulation, a set of two audit samples must be analyzed.

6.2 Audit Procedure. The audit sample are chloride solutions. Concurrently analyze the two audit samples and a set of compliance samples in the same manner to evaluate the technique of the analyst and the standards preparation. The same analyst, analytical reagents, and analytical system shall be used both for compliance samples and the EPA audit samples. If this condition is met, auditing the subsequent compliance analyses for the same enforcement agency within 30 days is not required. An audit sample set may not be used to validate different sets of compliance samples under the jurisdiction of different enforcement agencies, unless prior arrangements are made with both enforcement agencies.

6.3 Audit Sample Availability. The audit samples may be obtained by writing or calling the EPA Regional Office or the appropriate enforcement agency. The request for the audit samples must be made at least 30 days prior to the scheduled compliance sample analyses.

6.4 Audit Results.

6.4.1 Calculate the concentrations in mg/dscm using the specified sample volume in the audit instructions.

NOTE Indication of acceptable results may be obtained immediately by reporting the audit results in mg/dscm and compliance results in total μg HCl/sample to the responsible enforcement agency. Include the results of both audit samples, their identification numbers, and the analyst's name with the results of the compliance determination samples in appropriate reports to the EPA Regional Office or the appropriate enforcement agency. Include this information with subsequent analyses for the same enforcement agency during the 30-day period.

6.4.2 The concentrations of the audit samples obtained by the analyst shall agree within 10 percent of the actual concentrations. If the 10 percent specification is not met, reanalyze the compliance samples and audit samples, and include initial and reanalysis values in the test report.

6.4.3 Failure to meet the 10 percent specification may require retests until the audit problems are resolved. However, if the audit results do not affect the compliance or noncompliance status of the affected facility, the Administrator may waive the reanalysis requirement, further audits, or retests and accept the results of the compliance test. While steps are being taken to resolve audit analysis problems, the Administrator may also choose to use the data to determine the compliance or noncompliance status of the affected facility.

7. Calculations

Retain at least one extra decimal figure beyond those contained in the available data in intermediate calculations, and round off only the final answer appropriately.

7.1 Sample Volume, Dry Basis, Corrected to Standard Conditions. Calculate the sample volume using Eq. 6-1 of Method 6.

7.2 Total μg HCl, HBr, or HF Per Sample.

$m_{HX}=K\ V_s\ (S_{X^-}-B_{X^-})$ Eq. 26-4

where:

B_{X^-}=Mass concentration of applicable absorbing solution blank, μg halide ion (Cl^-, Br^-, F^-)/ml, not to exceed 1 μg/ml which is 10 times the published analytical detection limit of 0.1 μg/ml.

m_{HX}=Mass of HCl, HBr, or HF in sample, μg.

S_{X^-}=Analysis of sample, μg halide ion (Cl^-, Br^-, F^-)/ml.

0013-9211/94/$0+$1.00

V_s=Volume of filtered and diluted sample, ml.

K_{HCl}=1.028 (μg HCl/μg-mole)/(μg Cl^-/μg-mole).

K_{HBr}=1.013 (μg HBr/μg-mole)/(μg Br^-/μg-mole).

K_{HF}=1.053 (μg HF/μg-mole)/(μg F^-/μg-mole).

[7.2 revised at 59 FR 19308, April 22, 1994]

7.3 Concentration of HCl in the Flue Gas.

$$C=\frac{K_m}{V_{m(std)}} \qquad \text{Eq. 26-3}$$

where:

C = Concentration of HCl, dry basis, mg/dscm.

K = 10^{-3} mg/μg.

m = Mass of HCl in sample, μg.

$V_{m(std)}$ = Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

7.3 Total μg Cl_2 or Br_2 Per Sample.

$m_{X2}=V_s\ (S_{X^-}-B_{X^-})$ Eq. 26-5

where:

m_{X2}=Mass of Cl_2 or Br_2 in sample, μg.

[The second 7.3 added at 59 FR 19308, April 22, 1994]

7.4 Concentration of Hydrogen Halide or Halogen in Flue Gas.

$C=K\ m_{HX,X2}/V_{m(std)}$ Eq. 26-6

where:

C=Concentration of hydrogen halide (HX) or halogen (X_2), dry basis, mg/dscm.

$V_{m(std)}$= Dry gas volume measured by the dry gas meter, corrected to standard conditions, dscm.

K=10^{-3} mg/μg.

[7.4 added at 59 FR 19308, April 22, 1994]

8. Bibliography

1. Steinsberger, S.C. and J.H. Margeson. "Laboratory and Field Evaluation of a Methodology for Determination of Hydrogen Chloride Emissions from Municipal and Hazardous Waste Incinerators," U.S. Environmental Protection Agency, Office of Research and Development, Report No. 600/3-89/064, April 1989. Available from the National Technical Information Service, Springfield, VA 22161 as PB89220586/AS.

2. State of California, Air Resources Board. Method 421. "Determination of Hydrochloric Acid Emissions from Stationary Sources." March 18, 1987.

3. Cheney, J.L. and C.R. Fortune. Improvements in the Methodology for Measuring Hydrochloric Acid in Combustion Source Emission. J. Environ. Sci. Health. A*19*(3): 337-350. 1984

4. Stern, D. A., B. M. Myatt, J. F. Lachowski, and K. T. McGregor. Speciation of Halogen and Hydrogen Halide Compounds in Gaseous Emissions. In: Incineration and Treatment of Hazardous Waste: Proceedings of the 9th Annual Research Symposium, Cincinnati, Ohio, May 2-4, 1983. Publication No. 600/9-84-015. July 1984. Available from National Technical Information Service, Springfield, VA 22161 as PB84-234525.

[4. added at 59 FR 19308, April 22, 1994]

5. Holm, R. D. and S. A. Barksdale. Analysis of Anions in Combustion Products. In: Ion Chromatographic Analysis of Environmental Pollutants. E. Sawicki, J. D. Mulik, and E. Wittgenstein (eds.). Ann Arbor, Michigan, Ann Arbor Science Publishers. 1978. pp. 99-110.

[5. added at 59 FR 19308, April 22, 1994]

[Method 26 amended at 57 FR 24550, June 10, 1992; revised at 59 FR 19308, April 22, 1994]

~~METHOD 26A— DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES—ISOKINETIC METHOD~~

~~1. Applicability, Principle, Interferences, Precision, Bias, and Stability~~

~~1.1 Applicability. This method is applicable for determining emissions of hydrogen halides (HX) [hydrogen chloride (HCl), hydrogen bromide (HBr), and hydrogen fluoride (HF)] and halogens (X_2) [chlorine (Cl_2) and bromine (Br_2)] from stationary sources. This method collects the emission sample isokinetically and is therefore particularly suited for sampling at sources, such as those controlled by wet scrubbers, emitting acid particulate matter (e.g., hydrogen halides dissolved in water droplets). [Note: Mention of trade names or specific products does not constitute endorsement by the Environmental Protection Agency.]~~

~~1.2 Principle. Gaseous and particulate pollutants are withdrawn isokinetically from the source and collected in an optional cyclone, on a filter, and in absorbing solutions. The cyclone collects any liquid droplets and is not necessary if the source emissions do not contain them; however, it is preferable to include the cyclone in the sampling train to protect the filter from any moisture present. The filter collects other particulate matter including halide salts. Acidic and alkaline absorbing solutions collect the gaseous hydrogen halides and halogens, respectively. Following sampling of emissions containing liquid droplets, any halides/halogens dissolved in the liquid in the cyclone and on the filter are vaporized to gas and collected in the impingers by pulling conditioned ambient air through the sampling train. The hydrogen halides are solubilized in the acidic solution and form chloride (Cl^-), bromide (Br^-) and fluoride (F^-) ions. The halogens have a very low solubility in the acidic solution and pass through to the alkaline solution where they are hydrolyzed to form a proton (H^+), the halide ion, and the hypohalous acid (HClO or HBrO). Sodium thiosulfate is added to the alkaline solution to assure reaction with the hypohalous acid to form a second halide ion such that 2 halide ions are formed for each molecule of halogen gas. The halide ions in the separate solutions are measured by ion chromatography (IC). If desired, the particulate matter recovered from the filter and the probe is analyzed following the procedures in Method 5. [Note: If the tester intends to use this sampling arrangement to sample concurrently for particulate matter, the alternative Teflon^R probe liner, cyclone, and filter holder should not be used. The Teflon^R filter support must be used. The tester must also meet the probe and filter temperature requirements of both sampling trains.]~~

~~1.3 Interferences. Volatile materials, such as chlorine dioxide (ClO_2) and ammonium chloride (NH_4Cl), which produce halide ions upon dissolution during sampling are potential interferents. Interferents for the halide measurements are the halogen gases which disproportionate to a hydrogen halide and an hypohalous acid upon dissolution in water.~~

May 25, 1994

DRAFT: DO NOT QUOTE OR CITE.

40 CFR Part 60, Appendix B

METHOD 29:

Determination of Metals Emissions from Stationary Sources

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn) emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

1.1.1 Hg emissions can be measured, alternatively, using EPA Method 101A of Appendix B, 40 CFR Part 61. Method 101-A measures only Hg but it can be of special interest to sources which need to measure both Hg and Mn emissions.

1.2 Principle. A stack sample is withdrawn isokinetically from the source, particulate emissions are collected in the probe and on a heated filter, and gaseous emissions are then collected in an aqueous acidic solution of hydrogen peroxide (analyzed for all metals including Hg) and an aqueous acidic solution of potassium permanganate (analyzed only for Hg). The recovered samples are digested, and appropriate fractions are analyzed for Hg by cold vapor atomic absorption spectroscopy (CVAAS) and for Sb, As, Ba, Be, Cd, Cr, Co, Cu, Pb, Mn, Ni, P, Se, Ag, Tl, and Zn by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Cd, Co, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analysis of all listed metals if the resulting in-stack method detection limits meet the goal of the testing program.

2. Range, Detection Limits, Precision, and Interferences

2.1 Range. For the analysis described and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per ml (ng/ml) to micrograms per ml (μg/ml) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 μg/ml As, Cr, or Pb should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 μg/ml of Cd should be diluted to that level before analysis.

2.2 Analytical Detection Limits.

Note: See Section 2.3 for the description of in-stack detection limits.

2.2.1 ICAP analytical detection limits for the sample solutions (based on <u>SW-846</u>, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

2.2.2 The analytical detection limits for analysis by direct aspiration AAS (based on <u>SW-846</u>, Method 7000 series) are approximately as follow: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

2.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the <u>digestion</u> of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2ng/ml, depending upon the type of CVAAS analytical instrument used.

2.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

2.3 In-stack Detection Limits.

2.3.1 For test planning purposes in-stack detection limits can be developed by using the following information: (1) the procedures described in this method, (2) the analytical detection limits described in Section 2.2, (3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3. The resultant in-stack method detection limits for the above set of conditions are presented in Table 29-1 and were calculated by using Eq. 29-1.

$$A \times B/C = D \qquad \text{Eq. 29-1}$$

where:

A = Analytical detection limit, µg/ml.
B = Liquid volume of digested sample prior to aliquotting for analysis, ml.
C = Stack sample gas volume, dsm^3.
D = In-stack detection limit, $\mu g/m^3$.

METAL	Front-half: Probe & Filter	Back-half: Impingers 1-3	Back-half: Impingers (4-6)[a]	Total Train:
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Cobalt	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.06**	0.3**	0.2**	0.56**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

[a] Mercury analysis only.
* Detection limit when analyzed by GFAAS, (_.__)
** Detection limit when analyzed by CVAAS, estimated for Back-Half and Total Train. See Sections 2.2 and 5.4.3.

Note: Actual Method in-stack detection limits may vary from these values, as described in Section 2.3.3.

Table 29-1. In-stack method detection limits ($\mu g/m^3$) for the front-half, the back-half, and the total sampling train using ICAP and AAS.

2.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

2.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29-1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of Hg only, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

2.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased to four hours and 5 m^3 are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29-1.

2.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

2.3.3.3 When both of the modifications described in Sections 2.3.3.1 and 2.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

2.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test performed at a sewage sludge incinerator were found to be as follows:
Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent),
Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent),
Pb (11.6 percent), P (14.6 percent), Se (15.3 percent),
Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

2.5 Interferences. Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Refer to Method 6010 of Citation 1 of the Bibliography or the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

3. Apparatus

3.1 Sampling. A schematic of the sampling train is shown in Figure 29-1. It has general similarities to the Method 5 train.

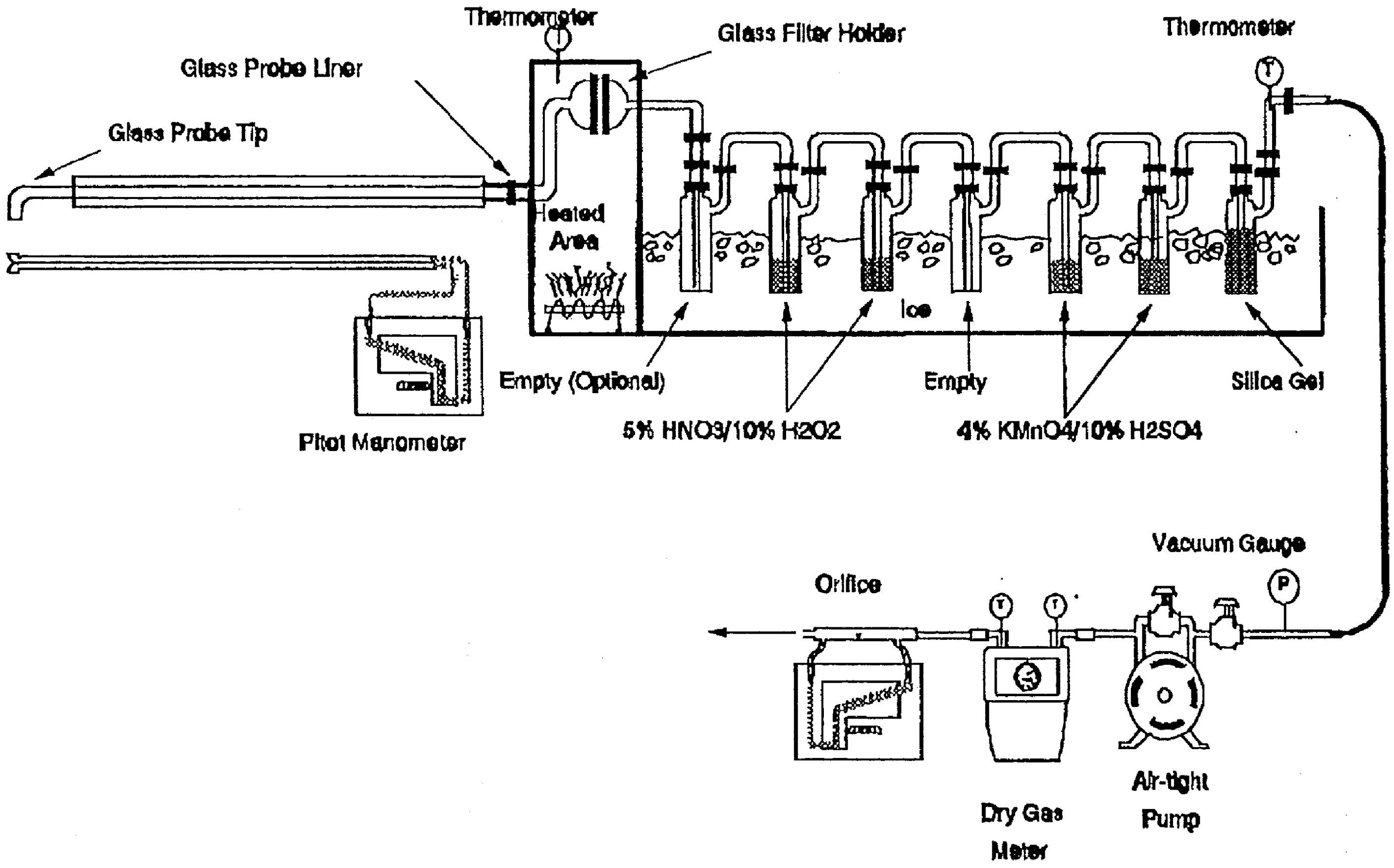


Figure 29-1. Sampling train.

3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If desired, a single glass piece consisting of a combined probe tip and probe liner may be used.

3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.

3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first HNO_3/H_2O_2 impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second HNO_3/H_2O_2 impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, Section 2.1.7. The fourth (empty) impinger and the fifth and sixth (both acidified $KMnO_4$) impingers are the same as the first impinger in Method 5. Place a thermometer capable of measuring to within 1°C (2°F) at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.

3.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

3.2.2 Sample Storage Containers. Use glass bottles (see the **<u>Precaution:</u>** in Section 4.3.2 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified $KMnO_4$-containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

3.2.3 Graduated Cylinder. Glass or equivalent.

3.2.4 Funnel. Glass or equivalent.

3.2.5 Labels. For identifying samples.

3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.3 Sample Preparation and Analysis.

3.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample dilutions.

3.3.2 Graduated Cylinders. For preparation of reagents.

3.3.3 Parr^R Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

3.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

3.3.6 Filter Funnels. For holding filter paper.

3.3.7 Disposable Pasteur Pipets and Bulbs.

3.3.8 Volumetric Pipets.

3.3.9 Analytical Balance. Accurate to within 0.1 mg.

3.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

3.3.11 Hot Plates.

3.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Bibliography Citation 1 Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl).

3.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10°C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Citation 2 of the Bibliography. See **Note No. 2:** Section 5.4.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.02 μg/ml were obtained.

3.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Citation 1 of the Bibliography.

4. Reagents

4.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

4.2 Sampling Reagents.

4.2.1 Sample Filters. Without organic binders. The filters shall contain less than 1.3 $\mu g/in.^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide (SO_2) or sulfur trioxide (SO_3) shall be as described in Section 3.1.1 of Method 5.

4.2.2 Water. To conform to ASTM Specification D1193-77, Type II (incorporated by reference). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

4.2.3 Nitric Acid (HNO_3). Concentrated. Baker Instra-analyzed or equivalent.

4.2.4 Hydrochloric Acid (HCL). Concentrated. Baker Instra-analyzed or equivalent.

4.2.5 Hydrogen Peroxide (H_2O_2), 30 Percent (V/V).

4.2.6 Potassium Permanganate ($KMnO_4$).

4.2.7 Sulfuric Acid (H_2SO_4). Concentrated.

4.2.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

4.3 Pretest Preparation of Sampling Reagents.

4.3.1 HNO_3/H_2O_2 Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H_2O_2. Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.3.2 Acidic $KMnO_4$ Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent H_2SO_4

(V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of the potassium permanganate with the acid, there could be pressure buildup in the solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.3.3 HNO_3, 0.1 N. Add with stirring 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.3.4 HCl, 8 N. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

4.4 Glassware Cleaning Reagents.

4.4.1 HNO_3, Concentrated. Fisher ACS grade or equivalent.

4.4.2 Water. To conform to ASTM Specifications D1193-77, Type II.

4.4.3 HNO_3, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.5 Sample Digestion and Analysis Reagents.

The metals standards, except Hg, may also be made from solid chemicals as described in Citation 3 of the Bibliography. Refer to Citations 1, 2, or 5 of the Bibliography for additional information on Hg standards. The 1000 µg/ml Hg stock solution standard may be made according to Section 6.2.5 of Method 101A.

4.5.1 HCL, Concentrated.

4.5.2 Hydrofluoric Acid (HF), Concentrated.

4.5.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

4.5.4 HNO_3, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.5.5 HNO_3, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.5.6 Water. To conform to ASTM Specifications D1193-77, Type II.

4.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Citation 2 of the Bibliography for preparation.

4.5.8 Stannous Chloride. See Citation 2 of the Bibliography for preparation.

4.5.9 $KMnO_4$, 5 Percent (W/V). See Citation 2 of the Bibliography for preparation.

4.5.10 H_2SO_4, Concentrated.

4.5.11 Potassium Persulfate, 5 Percent (W/V). See Citation 2 of the Bibliography for preparation.

4.5.12 Nickel Nitrate, $Ni(N0_3)_2 \cdot 6H_20$.

4.5.13 Lanthanum Oxide, La_20_3.

4.5.14 Hg Standard (AAS Grade), 1000 µg/ml.

4.5.15 Pb Standard (AAS Grade), 1000 µg/ml.

4.5.16 As Standard (AAS Grade), 1000 µg/ml.

4.5.17 Cd Standard (AAS Grade), 1000 µg/ml.

4.5.18 Cr Standard (AAS Grade), 1000 µg/ml.

4.5.19 Sb Standard (AAS Grade), 1000 µg/ml.

4.5.20 Ba Standard (AAS Grade), 1000 µg/ml.
4.5.21 Be Standard (AAS Grade), 1000 µg/ml.
4.5.22 Co Standard (AAS Grade), 1000 µg/ml.
4.5.23 Cu Standard (AAS Grade), 1000 µg/ml.
4.5.24 Mn Standard (AAS Grade), 1000 µg/ml.
4.5.25 Ni Standard (AAS Grade), 1000 µg/ml.
4.5.26 P Standard (AAS Grade), 1000 µg/ml.
4.5.27 Se Standard (AAS Grade), 1000 µg/ml.
4.5.28 Ag Standard (AAS Grade), 1000 µg/ml.
4.5.29 Tl Standard (AAS Grade), 1000 µg/ml.
4.5.30 Zn Standard (AAS Grade), 1000 µg/ml.
4.5.31 Al Standard (AAS Grade), 1000 µg/ml.
4.5.32 Fe Standard (AAS Grade), 1000 µg/ml.

4.5.33 Hg Standards and Quality Control Samples. Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily: add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.

4.5.34 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Co, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO_3. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO_3. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.5.36 Matrix Modifiers.

4.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(NO_3)_2 \cdot 6H_20$ in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

4.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

4.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of La_20_3 in 10 ml of concentrated $HN0_3$, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

4.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

5. Procedure

5.1 Sampling. The complexity of this method is such that, to obtain reliable results, both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinse three times with water, rinse a final time with acetone, and allow to air dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train.

5.1.3.1 Set up the sampling train as shown in Figure 29-1. Follow the same general procedures given in Method 5,
Section 4.1.3, except place 100 ml of the HNO_3/H_2O_2 solution (Section 4.3.1 of this method) in each of the second and third impingers as shown in Figure 29-1. Place 100 ml of the acidic $KMnO_4$ absorbing solution (Section 4.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29-1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

5.1.3.2 The following options are available to the tester based on the source specific sampling requirements and conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml. If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29-1 are not required.

5.1.3.3 Because of possible sample contamination problems, use Teflon tape or other non-contaminating material instead of silicone grease to ensure leak-free sampling train connections.

Precaution: Exercise extreme care to prevent contamination within the train. Prevent the acidic $KMnO_4$ from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic H_2O_2 from mixing with the acidic $KMnO_4$.

5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. When sampling for Hg, use a procedure analagous to that described in Section 7.1.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 Sample Recovery.

5.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed,

non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

5.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

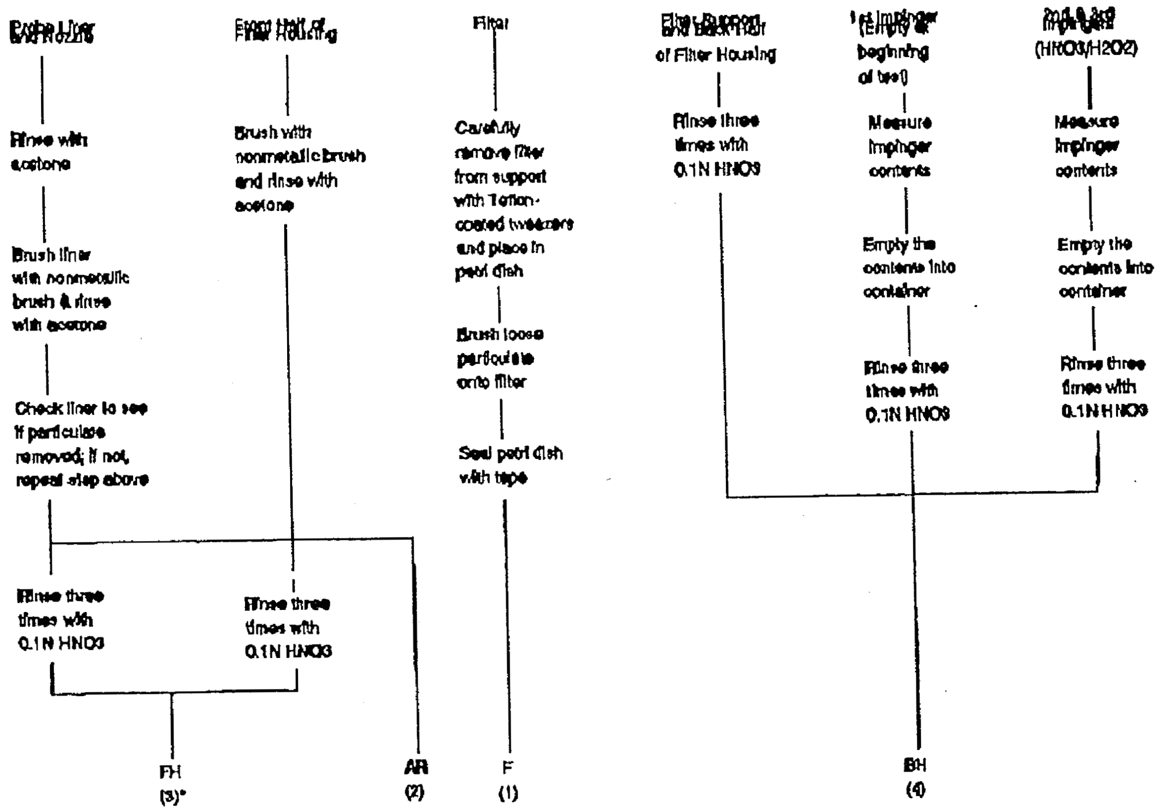
5.2.3 Alternatively, the folowing procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

5.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29-2a and 29-2b):

5.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

5.2.6 Container No. 2 (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surgfaces gets in the sample. The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

5.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.



* Number in parentheses indicates container number

Figure 29-2a. Sample recovery scheme.

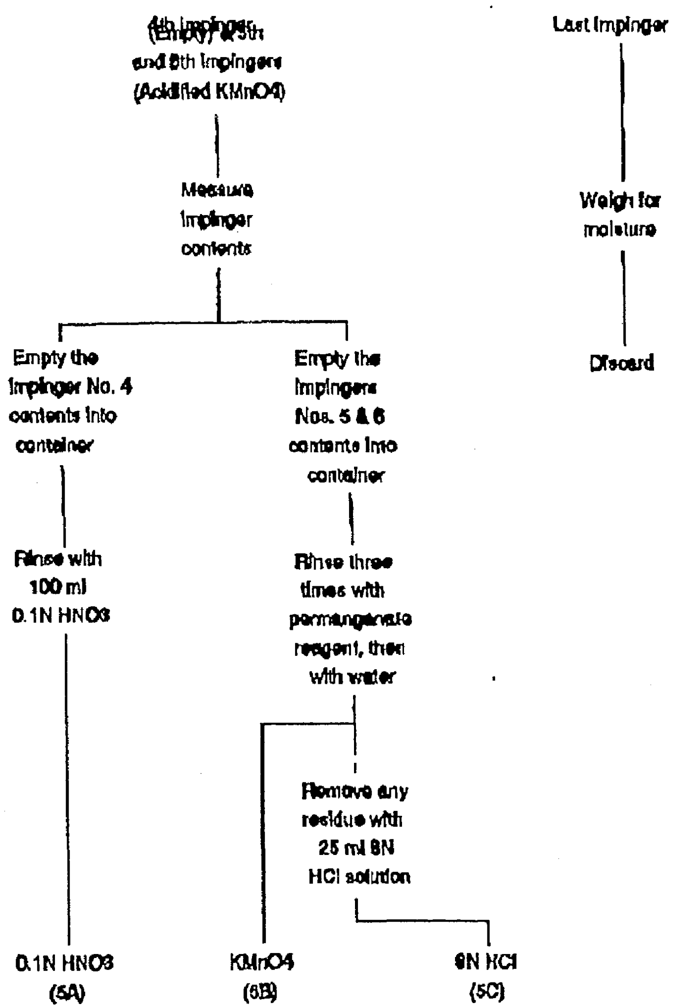


Figure 29-2b. Sample recovery scheme.

5.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

5.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents. 5.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N HNO_3, and place the wash into a sample storage container.

<u>NOTE</u>: The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.

Perform the rinses as applicable and generally as described in Method 12, Section 5.2.2. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

5.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used, HNO_3/H_2O_2 Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO_3 using the procedure as applicable in Method 12, Section 5.2.4.

<u>NOTE</u>: The use of exactly 100 ml of 0.1 N HNO_3 rinse is necessary for the subsequent blank correction procedures.

Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

5.2.9 Container Nos. 5A (0.1 N HNO_3), 5B ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8 N HCl rinse and dilution).

5.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N HNO_3 and place this rinse in Container No. 5A.

5.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this acidic $KMnO_4$ solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified $KMnO_4$ solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the **Precaution:** in Section 4.3.2.

NOTE: Due to the potential reaction of $KMnO_4$ with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70-72 hole drilled in the container cap and Teflon liner has been used successfully.

5.2.9.3 If no visible deposits remain after the water rinse, no further rinse is necessary. However, if deposits remain on the impinger surfaces, wash them with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport.

5.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

5.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

5.2.12 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

5.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

5.2.14 Container No. 9 (5 Percent HNO_3/10 Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent HNO_3/10 Percent H_2O_2 solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

5.2.15 Container No. 10 (Acidified $KMnO_4$ Blank). At least once during each field test, place 100 ml of the acidified $KMnO_4$ solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in Section 5.2.9.2. Read the **Precaution:** in Section 4.3.2. and read the **NOTE** in Section 5.2.9.2.

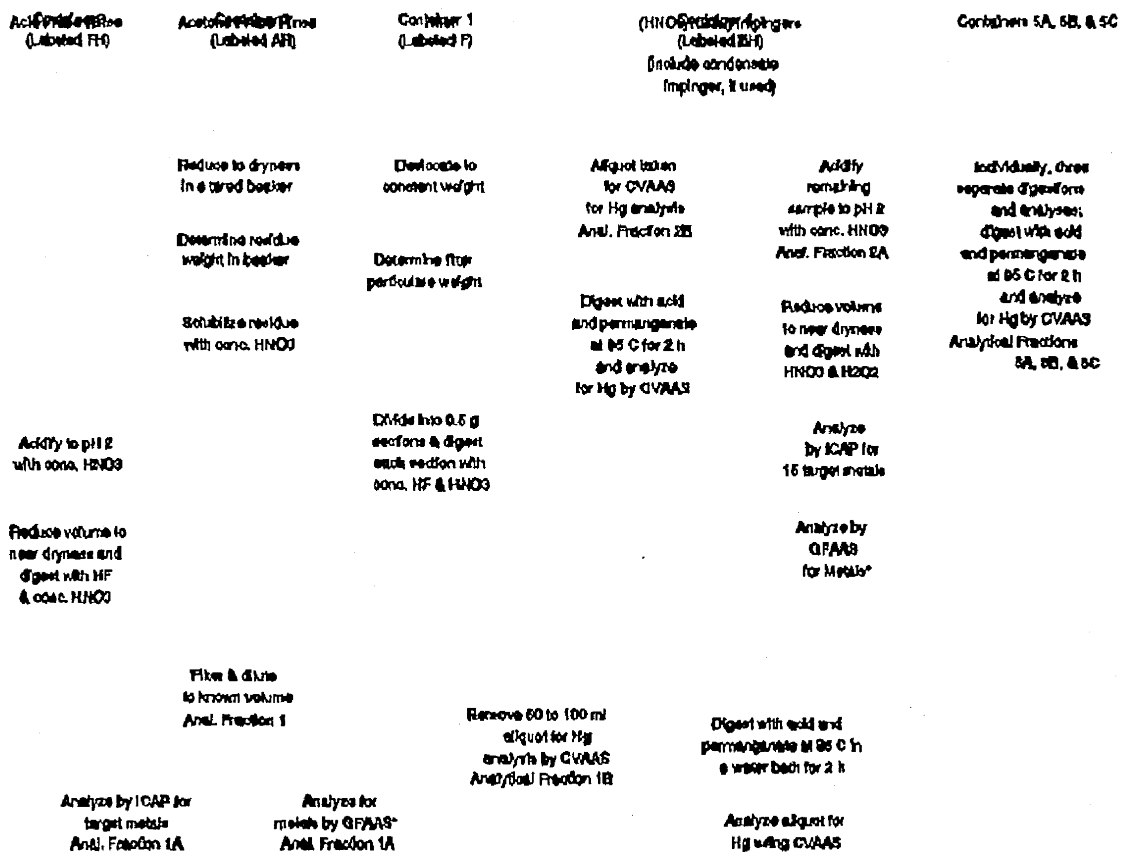
5.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

5.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

5.3 Sample Preparation. Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29-3.

5.3.1 Container No. 1 (Sample Filter).

5.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in Section 4.3 of Method 5. 5.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr^{R} Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel.



*Analyze by AAS for metals found at less than 2 ug/ml in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

Figure 29-3. Sample preparation and analysis scheme.

For conventional heating, heat the Parr^R Bombs at 140°C (285°F) for 6 hours. Then cool the samples to room temperature, and combine with the acid digested probe rinse as required in Section 5.3.3.

5.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in Section 5.3.1.2 and then combine the digestate with the digested filter sample.

5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3. Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated HNO_3 to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr^R Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3, 4 ml of concentrated HF, and then continuing to follow the procedures described in Section 5.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1.2. The resultant combined sample is referred to as "Sample Fraction 1". Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is "Analytical Fraction 1". Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as "Analytical Fraction 1B". Label the remaining 250-ml portion as "Analytical Fraction 1A". Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample to within 0.5 ml and label it "Sample Fraction 2". Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot "Analytical Fraction 2B". Label the remaining portion of Container No. 4 as "Sample Fraction 2A". Sample Fraction 2A defines the volume of Analytical Fraction 2A prior to digestion. All of Sample Fraction 2A is digested to produce "Analytical Fraction 2A". Analytical Fraction 2A defines the volume of Sample Fraction 2A after its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watchglass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 5.3.4.1 or 5.3.4.2.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3, and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 and heat for 6 minutes total <u>heating</u> time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in Section 5.3.1. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

<u>NOTE</u>: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.

5.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be Analytical Fraction 3A. To remove any brown MnO_2 precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized <u>vented</u> container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

5.4 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated ; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29-3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP or AAS analysis as described in Sections 5.4.1 and 5.4.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in Section 5.4.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and HNO_3/H_2O_2 impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the $H_2SO_4/KMnO_4$ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in Section 5.4.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

5.4.1 ICAP Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in Section 7.3.1. Recommended wavelengths for analysis are as follows:

Element	Wavelength (nm)	
Aluminum		308.215
Antimony		206.833
Arsenic		193.696
Barium	455.403	
Beryllium		313.042
Cadmium		226.502
Chromium		267.716
Cobalt	228.616	
Copper		324.754
Iron		259.940
Lead		220.353
Manganese		257.610
Nickel	231.604	
Phosphorous		214.914
Selenium		196.026
Silver	328.068	
Thallium		190.864
Zinc		213.856

These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb.

NOTE: When analyzing samples in a HF matrix, an alumina torch should be used; since all front-half samples will contain HF, use an alumina torch.

5.4.2 AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29-2 to determine

Table 29-2. Applicable techniques, methods and minimization of interference for *AAS analysis.*

Metal	Technique	SW-846 Method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 ul of phosphorus acid to 1 ml of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternate	Background correction required
				Fe, Co, and Cr	Matrix matching or nitrous-oxide/ acetylene flame
				Nonlinear response	Sample dilution or use 352.3 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization
				Adsorption & scatter	Background correction is required and Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Adsorption & scatter	Background correction is required
				AgCl insoluble	Avoid hydrochloric acid unless silver is in solution as a chloride complex
					Sample and standards monitored for aspiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required Verify that losses are not occurring for volatization by spiked samples or standard addition; Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu, & P	Strontium removes Cu and phosphate
				Contamination	Great care taken to avoid contamination

Metal	Technique	SW-846 Method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/ml Pb Ni, Cu, or acid	Use secondary wavelenthe of 231.1 nm; match sample & standards' acid concentration or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic volatilization	Spiked samples and add nickel nitrate solution to digestates prior to analysis
				Aluminum	Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium	High hollow cathode current and narrow band set
				Barium ionization	2 ml of KCl per 100 ml of sample
Be	Aspiration	7090	234.9	500 ppm Al	Add 0.1% fluoride
				High Mg and Si	Use method of standard additions
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects
Cd	Aspiration	7130	228.8	Absorption and light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above	As above
				Excess chloride	Ammonium phosphate used as a matrix modifier
				Pipet tips	Use cadmium-free tips
Cr	Aspiration	7190	357.9	Alkali metal	KCl ionization suppressant in samples and standards--Consult mfgs' literature
Cr	Furnace	719			

which techniques and procedures to apply for each target metal. Use Table 29-2, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

5.4.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F, or, optionally using **NOTE No. 2** at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. Dilute the aliquot to 100 ml with water. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see **NOTE No. 1** at end of this Section). The total amount of Hg in the aliquot shall be less than 1 µg and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of SW-846 Method 7470 or Method 303F. (See **NOTE No. 2** at the end of this Section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the "0.15 HNO_3 percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

NOTE No. 1: When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29-1, select a 10 ml aliquot for digestion and analysis as described.

NOTE No. 2: Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIMS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps: (1), Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this Section 5.4.3.: (The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

6. Calibration

Maintain a laboratory log of all calibrations.

6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leak-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures.

6.3 Atomic Absorption Spectrometer - Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in Section 4.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in SW-846

Method 7470 or in Standard Methods for Water and Wastewater Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

7. Quality Control

7.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in Sections 5.2.11 through 5.2.17, respectively.

7.1.1 Digest and analyze one of the filters from Container No. 12 per Section 5.3.1, 100 ml from Container No. 7 per Section 5.3.2, and 100 ml from Container No. 8A per Section 5.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

7.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per Section 5.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

7.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

7.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in Section 5.3.5, except do not dilute the 133 ml. Analyze this blank for Hg within 48 hr of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the actual volumes of the other analytical blanks when calculating their mass values.

7.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the blank for Analytical Fraction 3B by the same procedure as described in Section 5.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

7.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per Section 5.4.1 and/or Section 5.4.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per Section 5.4.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

7.2 Quality Control Samples. Analyze the following quality control samples.

7.2.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010 in SW-846. For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

7.2.2 Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

7.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent, analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Method 303F.

8. Calculations

8.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

8.2 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

8.3 Stack Gas Velocity. Using the data from this test and Equation 2-9 of Method 2, calculate the average stack gas velocity.

8.4 Metals (Except Hg) in Source Sample.

8.4.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_{a1} F_d V_{soln,1} \qquad \text{Eq. 29-1}$$

where:

M_{fh} = Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), µg.

C_{a1} = Concentration of metal in Analytical Fraction 1A as read from the standard curve, µg/ml.

F_d = Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range, $F_d = 5$).

$V_{soln,1}$ = Total volume of digested sample solution (Analytical Fraction 1), ml.

NOTE: If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29-1 through 29-3 to reflect this approach.

8.4.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh} = C_{a2} F_a V_a \qquad \text{Eq. 29-2}$$

where:

M_{bh} = Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2), µg.

C_{a2} = Concentration of metal in Analytical Fraction 2A as read from the standard curve, (µg/ml).

F_a = Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (see Section 5.3.4.)

V_a = Total volume of digested sample solution (Analytical Fraction 2A), ml (see Section 5.3.4.1 or 5.3.4.2, as applicable).

8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \qquad \text{Eq. 29-3}$$

where:

M_t = Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_{fhb} = Blank correction value for mass of metal detected in front-half field reagent blank, µg.

M_{bhb} = Blank correction value for mass of metal detected in back-half field reagent blank, µg.

NOTE: If the measured blank value for the front half (m_{fhb}) is in the range 0.0 to "A" µg [where "A" µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in in.^{2} of the sample filter], use m_{fhb} to correct the emission sample value (m_{fh}); if m_{fhb} exceeds "A" µg, use the greater of I or II:

I. "A" µg.
II. the lesser of (a) m_{fhb}, or (b) 5 percent of m_{fh}.

If the measured blank value for the back-half (m_{bhb}) is in the range 0.0 to 1 µg, use m_{bhb} to correct the emission sample value (m_{bh}); if m_{bhb} exceeds 1 µg, use the greater of I or II:

I. 1 µg.
II. the lesser of (a) m_{bhb}, or (b) 5 percent of m_{bh}.

8.5 Hg in Source Sample.

8.5.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount of Hg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29-4:

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}} (V_{soln,1}) \qquad \text{Eq. 29-4}$$

where:

Hg_{fh} = Total mass of Hg collected in the front- half of the sampling train (Sample Fraction 1), µg.

Q_{fh} = Quantity of Hg, µg, <u>TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis .</u> **<u>NOTE</u>**: For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to Section 5.4.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{fh}.

$V_{soln,1}$ = Total volume of Analytical Fraction 1, ml.

V_{f1B} = Volume of aliquot of Analytical Fraction 1B analyzed, ml. **<u>Note</u>**: For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in Section 5.4.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to Section 5.4.3 and analyzed, V_{f1B} would be 0.02 ml.

8.5.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

8.5.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29-5:

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} (V_{soln,2}) \qquad \text{Eq. 29-5}$$

where:

Hg_{bh2} = Total mass of Hg collected in Sample Fraction 2, µg.

Q_{bh2} = Quantity of Hg, µg, <u>TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis .</u> **<u>NOTE</u>**: For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to
Section 5.4.3 and its NOTES Nos. 1 and 2), then
calculate and use the total amount of Hg in the 10
ml aliquot for Q_{bh2}.

$V_{soln,2}$ = Total volume of Sample Fraction 2, ml.

V_{f2B} = Volume of Analytical Fraction 2B analyzed, ml. **Note**: For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in Section 5.4.3 to bring it into the proper analytical range, and then 5 ml of that 10-ml was analyzed, V_{f2B} would be 0.5 ml.

8.5.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29-6:

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}} \left(V_{soln,3(A,B,C,)}\right) \qquad \text{Eq. 29-6}$$

where:

$Hg_{bh3(A,B,C)}$ = Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, µg.
$Q_{bh3(A,B,C)}$ = Quantity of Hg, µg, TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, or 3C selected for digestion and analysis , (see previous notes in Sections 8.5.1 and 8.5.2 describing the quantity "Q" and calculate similarly).
$V_{f3(A,B,C)}$ = Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in Sections 8.5.1 and 8.5.2, describing the quantity "V" and calculate similarly).
$V_{soln,3(A,B,C)}$ = Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

8.5.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29-7:

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3A} + Hg_{bh3B} + Hg_{bh3C} \qquad \text{Eq. 29-7}$$

where:

Hg_{bh} = Total mass of Hg collected in the back-half of the sampling train, µg.

8.5.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29-8:

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \qquad \text{Eq. 29-8}$$

where:

Hg_t = Total mass of Hg collected in the sampling train, µg.
Hg_{fhb} = Blank correction value for mass of Hg detected in front-half field reagent blank, µg.
Hg_{bhb} = Blank correction value for mass of Hg detected in back-half field reagent blanks, µg.

Note: If the total of the measured blank values ($Hg_{fhb} + Hg_{bhb}$) is in the range of 0.0 to 0.6 µg, then use the total to correct the sample value ($Hg_{fh} + Hg_{bh}$); if it exceeds 0.6 µg, use the greater of I. or II:

I. 0.6 µg.
II. the lesser of (a) ($Hg_{fhb} + Hg_{bhb}$), or (b) 5 percent of the sample value ($Hg_{fh} + Hg_{bh}$).

8.6 Individual Metal Concentrations in Stack Gas. Calculate the concentration of each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29-9:

where:

C_s = Concentration of a metal in the stack gas, mg/dscm.

$$C_s = \frac{K_4 \ M_t}{V_{m(std)}} \qquad \text{Eq. 29-9}$$

K_4 = 10^{-3} mg/µg.
M_t = Total mass of that metal collected in the sampling train, µg; (substitute Hg_t for M_t for the Hg calculation).
$V_{m(std)}$ = Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

8.7 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively.

9. Bibliography

1. Method 303F in Standard Methods for the Examination of Water Wastewater, 15th Edition, 1980. Available from the American Public Health Association, 1015 18th Street N.W., Washington, D.C. 20036.

2. EPA Methods 6010, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, Test Methods for Evaluating Solid Waste: Physical/Chemical Methods. SW-846, Third Edition. September 1988. Office of Solid Waste and Emergency Response, U. S. Environmental Protection Agency, Washington, D.C. 20460.

3. EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1991.

5. EPA Method 101A, Code of Federal Regulations, Title 40, Part 61, Appendix B, July 1, 1991.

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

1. AGENCY USE ONLY (Leave blank)

2. REPORT DATE
April 1996

3. REPORT TYPE AND DATES COVERED
Subcontract Report

4. TITLE AND SUBTITLE
Retrofit of Waste-to-Energy Facilities Equipped with Electrostatic Precipitators
Volume 3: Test Protocol

5. FUNDING NUMBERS
(C)
(TA)WM51.1010

6. AUTHOR(S)
H. Gregor Rigo, Rigo & Rigo Associates, Inc.
A. John Chandler, A.J. Chandler & Associates, Ltd.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Rigo & Rigo Associates, Inc., Berea, Ohio
A.J. Chandler & Associates Ltd., Toronto, Ontario

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401-3393

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
TP-430-21127
DE 96007876

11. SUPPLEMENTARY NOTES

NREL Technical Monitor: Phil Shepherd

12a. DISTRIBUTION/AVAILABILITY STATEMENT

National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

12b. DISTRIBUTION CODE

UC Category: 1414

13. ABSTRACT (Maximum 200 words)

Many municipal waste combustion facilities are equipped with electrostatic precipitators (ESPs); few have acid gas control systems. A retrofit technology using water spray temperature reduction combined with dry acid gas control reagent and powdered activatedcarbon (PAC) injection was tested. 2000 mg/dsm^3 @ 7%O_2 (150 ib/hr) of trona (a natural sodium sesquicarbonate ore) injected through a rapid dispersion lance successfully controlled more than 50% of the acid gases. This should let facilities under 250 TPD meet the small plant guidelines for acid gas control. Various levels of PAC were injected along with the trona. 300 mg/dsm^3 @ 7% O_2 of PAC provides a comfortable margin between the emissions limitations achieved and both large and small plant regulatory guidelines for tetra-through octa-chlorinated dibenzo-p-dioxins and dibenzofurans and mercury, when ESP is operated below 350°F. Bi-fluid nozzles were used to spray finely atomized water between the economizer outlet and ESP inlet to maintain temperatures in the desired 300-350°F range. Particulate and metals emissios limitations were met by this 400 ft^2/1000acft^2 specific collector area (SCA)m 3-field ESP. Both the water sprays and PAC improved ESP performance. The proof-of-concept demonstration was successful.

14. SUBJECT TERMS

Municipal waste combustion, electrostatic precipitators, water spray, powdered activated carbon injection

15. NUMBER OF PAGES

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT

18. SECURITY CLASSIFICATION OF THIS PAGE

19. SECURITY CLASSIFICATION OF ABSTRACT

20. LIMITATION OF ABSTRACT