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Municipal Solid Waste Combustion: Fuel Testing and Characterization

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MUNICIPAL SOLID WASTE COMBUSTION:
FUEL TESTING AND CHARACTERIZATION

Task 1 Report

May 30, 1990 - October 1, 1990

by

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MASTER

TABLE OF CONTENTS

Page

APPENDICES

TASK 1

MUNICIPAL SOLID WASTE COMBUSTION: FUEL TESTING AND CHARACTERIZATION

OBJECTIVE

The objective of this study is to screen and characterize potential biomass fuels from waste streams. This will be accomplished by determining the types of pollutants produced while burning selected municipal waste, i.e., commercial mixed waste paper residential (curbside) mixed waste paper, and refuse derived fuel (RDF). These materials will be fired alone and in combination with wood (Ponderosa Pine), equal parts by weight. The data from these experiments could be utilized to size pollution control equipment required to meet emission standards.

This document provides detailed descriptions of the testing methods and evaluation procedures used in the combustion testing and characterization project. The fuel samples will be examined thoroughly from the raw form to the exhaust emissions produced during the combustion test of a densified sample. Figure 1 is an overall test schematic identifying tests that will be performed.

QUALITY ASSURANCE

All ASTM Standards referenced in this section can be found in Appendix A. To maintain the credibility of this study, many steps will be taken to ensure quality results. These steps are to include:

Record Keeping. Records of samples, data, and test results will be duplicated and kept in secure locations. Records will be kept up to date and in a consistent format.

Sample Custody and Handling. Samples will be under the control of Oregon State University at all times. Samples sent to a commercial carrier, in accordance with ASTM Standard E954-88, "Packaging and Shipping of Laboratory Samples of Refuse Derived Fuel."

Sample Preparation. Samples will be prepared for analysis in accordance with ASTM Standard E829-88, "Preparing RDF Laboratory Samples for Analysis."

Equipment: Cleaning and Handling. Equipment will be properly maintained in accordance with manufacturer's specifications. All surfaces and components will be inspected before use for cleanliness and operational function.

Standards and Calibration. All testing and equipment use will be performed in accordance with specific standards. Calibration will be performed before use and at required intervals specified by manufacturer.

System Stability. During combustion testing, steady-state conditions will be achieved and maintained before any data collection or sampling occurs. Steady state is achieved when temperatures measured at the outer surface of the combustion change by less than 2% in a 10-minute time interval.

Data Comparison. Several of the tests will be duplicated throughout the study. Data will be compared between duplicate tests for evaluation of repeatability.

Calculations. Calculations will be performed according to specific standards and methodologies. RDF calculations will be performed in accordance with ASTM Standard E791-87, "Calculating RDF Analysis Data from As-Determined to Different Bases."

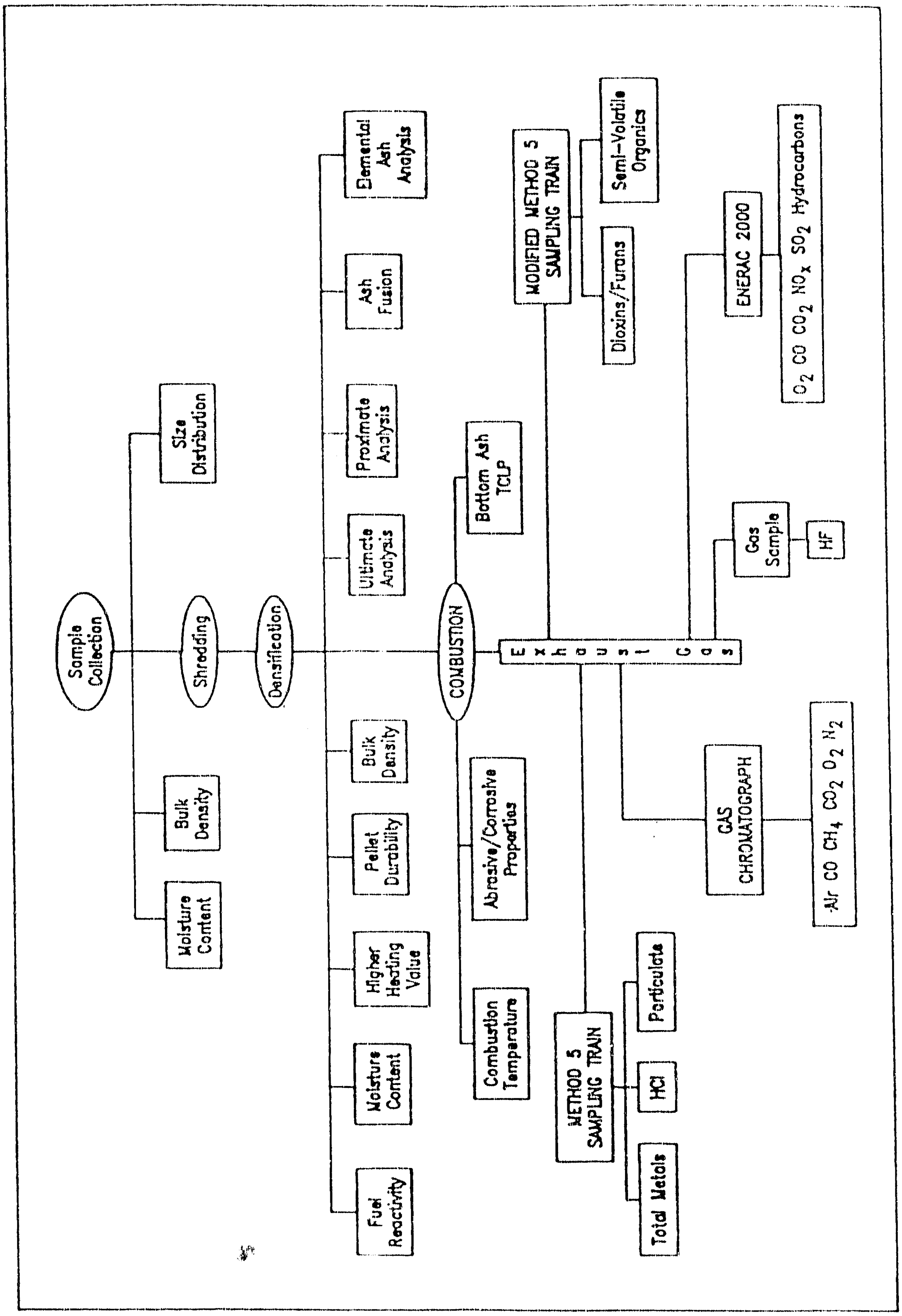

Figure 1: Overall Test Schematic

Technology Transfer. Terms and abbreviations used for presentation and publication will be in accordance with ASTM Standard E856-83, "Definition of Terms and Abbreviations Relating to Physical and Chemical Characteristics of Refuse Derived Fuel," and ASTM Standard E1126-87, "Standard Terminology Relating to Biomass Fuels."

SAMPLING APPROACH - METHODS AND PROCEDURES

Collection

BPA's Technical Support Services Contractor and the Washington State Energy Office Task Force representative will collect RDF and clean mixed waste paper samples from: Tacoma, Seattle, and Olympia, Washington; and Portland, Oregon. Benchmark wood fuel (Ponderosa Pine) will be supplied from Browning Cutstock in Julietta, Idaho. A minimum of 170 pounds of each sample will be collected and handled in airtight containers. The containers will be plastic 5-gallon buckets or the like. Approximately 20 pounds of sample will be required for physical/chemical property analysis, and 150 pounds for combustion analysis. Note that the testing requires 170 pounds of dry sample. The raw sample will be considered dry if it has a wet basis moisture content of 15% or less. If the raw sample has a high moisture content (i.e., wet basis moisture content ≥ 25%), it will be necessary to collect more sample to ensure 170 pounds of dry sample.

Sample Type

This study will look at three types of fuels: refuse-derived fuel, mixed waste paper, and mixed waste paper/woody biomass. The following is an overview of the samples:

1. Mixed Waste Paper (commercial office)
2. Mixed Waste Paper (commercial office)
3. Mixed Waste Paper (curb-side)
4. Mixed Waste Paper (curb-side)

Mixed waste paper samples from a commercial office will be composed primarily of shredded 8½" x 11" sheets of paper of different types. Mixed waste paper samples from curb-side will be composed primarily of magazines, newsprint, and journals.

5. Mixed Waste Paper/Woody Biomass (commercial office)
6. Mixed Waste Paper/Woody Biomass (commercial office)
7. Mixed Waste Paper/Woody Biomass (curb-side)
8. Mixed Waste Paper/Woody Biomass (curb-side)

The woody biomass will be pure Ponderosa Pine pellets produced from finished trimstock lumber. These pellets will also serve as a benchmark for comparison.

9. Tacoma RDF
10. Tacoma RDF
11. Tacoma RDF
12. Tacoma RDF

RDF samples will be collected on a quarterly basis. Samples will undergo the full battery of tests to determine if there is a distinguishable difference in physical/chemical or combustion characteristics due to seasonal variation.

Sampling Methods

Presently, a nationally recognized standard does not exist for sampling wood biomass or municipal solid waste. For this study, the use of a random sampling method is important to obtain information that will be statistically relevant. The following methods are to be used for sampling:

Uniform Fuel Pile. If the RDF samples com from large abandoned fuel piles, they will be obtained by filling containers from five randomly selected sites on the fuel pile. Samples are to be taken both from the surface and from within the pile (12 to 18 inches deep.

Nonuniform Landfill. If the sample collection takes place in a landfill, a rope 36 feet long with a knot every 4 feet will be laid across the refuse material. A 20-pound (approximately) sample will be obtained from beneath each of the eight knots on the rope.

Conveying System. If the RDF samples come from a facility that is operational and currently using the RDF as a fuel, samples will be taken from a moving conveyor belt, auger system, or air separator. The containers will be filled at random times as the material moves on the conveying system.

Commercial Office Waste Stream. Samples collected from commercial office recycle bins will be collected randomly to ensure the collection of a uniform sample. The sample collector is to collect a representative portion of all material types present in the bin.

Curb-Side Recycling Program. Samples collected from residential curb-side recycle bins will be chosen randomly to ensure the collection of a uniform sample. The sample collector is to collect a representative portion of all material types present in the bin.

Sample Identification

Each container will be marked with an identification code. The code consists of letters, numbers, and colors. This code will be used throughout the entire study to ensure that samples will be easily identifiable and not intermixed. The sample coding is as follows:

RDF - refuse derived fuel
MWP - clean mixed waste paper
WPW - clean mixed waste paper with wood samples

00 - month
00 - day
00 - year

T - Tacoma, Washington
S - Seattle, Washington
O - Olympia, Washington
C - commercial office waste stream
R - curb-side recycling program
0 - sequential numbering for duplicate samples

example: MWP 06 26 90 SR 2
Second clean mixed waste paper sample collected from a curb-side recycling program in Seattle, Washington, on June 26, 1990.

SAMPLE HANDLING AND PREPARATION METHODS

After the samples have been collected, the containers will be closed and inspected to ensure an airtight seal. There will be a comment sheet attached to the top of each container for use by sample collection personnel. Any relevant information about the sample (e.g. excessive moisture, pieces too large to be collected) should be noted on this sheet.

Once the containers are sealed, they are to be shipped to:

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Corvallis, OR 97331

Upon arrival, the samples will be catalogued and inspected to ensure a proper sample is available for testing. Within 48 hours of cataloguing and inspection, Oregon State University will begin to analyze the sample. Tests for moisture content, bulk density, and size distribution will be performed on the raw fuel sample. The samples will then be dried, shredded (if necessary), and densified.

The pelletized fuel will be shipped back to Oregon State University for further study. Data collected from testing of pelletized fuel will be used to determine the physical and chemical properties of the sample. Oregon State University will conduct bulk density, moisture content, higher heating value, fuel reactivity, and pellet durability tests. Samples will be sent by Oregon State University to an analytical laboratory for ultimate, proximate, ash fusion temperature, and elemental ash analysis. Figure 2 is a diagram of the tests related to raw fuel and pelletized fuel.

COMBUSTION CHARACTERISTICS

To determine the combustion characteristics of the various fuels, a small-scale combustion test facility will be used. A detailed diagram of the combustion unit is shown in Figure 3.

The combustion testing of the fuel sample will be conducted in three major sections. This will allow for proper use of equipment and personnel. Below is an explanation of the individual sections including a list of the equipment with exhaust emissions analyzed during the test runs.

Test One - Optimization

The first test is to determine the optimum combustion condition for the fuel. The levels of excess air, under fire air, and air temperature will be adjusted to several predetermined amounts during the running of the test. After each new setting has achieved steady-state conditions, data will be collected. Upon completion of the test, the data will be reduced to determine the optimum excess air percentage, under fire air percentage, and air temperature for the combustion process. These values will be based upon the combustion products temperature and the chemical conversion of fuel to products.

Excess Air. The level of excess air will be set at four values. The levels will range from 50% to 200% excess air. The expected levels for testing will be 50%, 100%, 150%, and 200% excess air. The actual levels used will be determined as testing occurs.

Under Fire Air. For each level of excess air, the under fire air level will be set at three values between 30% and 60% of the total air flow. The expected levels for testing will be 30%, 45%, and 60% under fire air. The actual levels used will be determined as testing occurs.

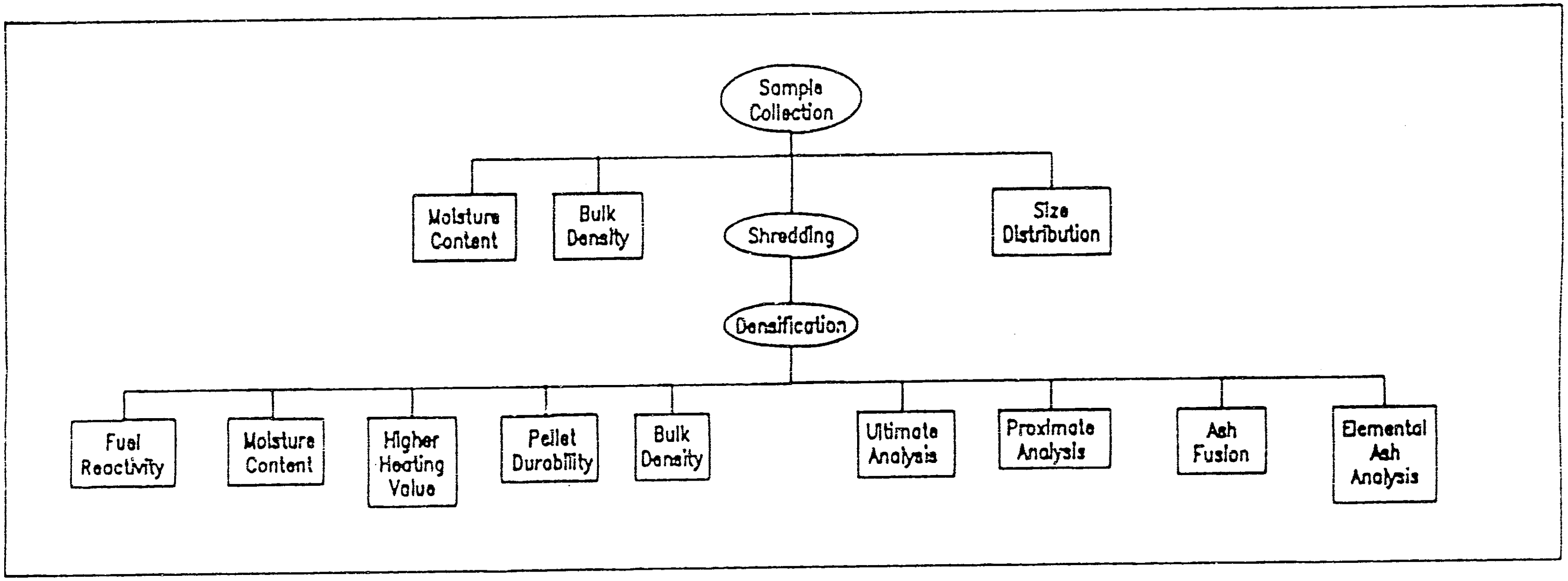

Figure 2: Raw and Pelletized Fuel Tests

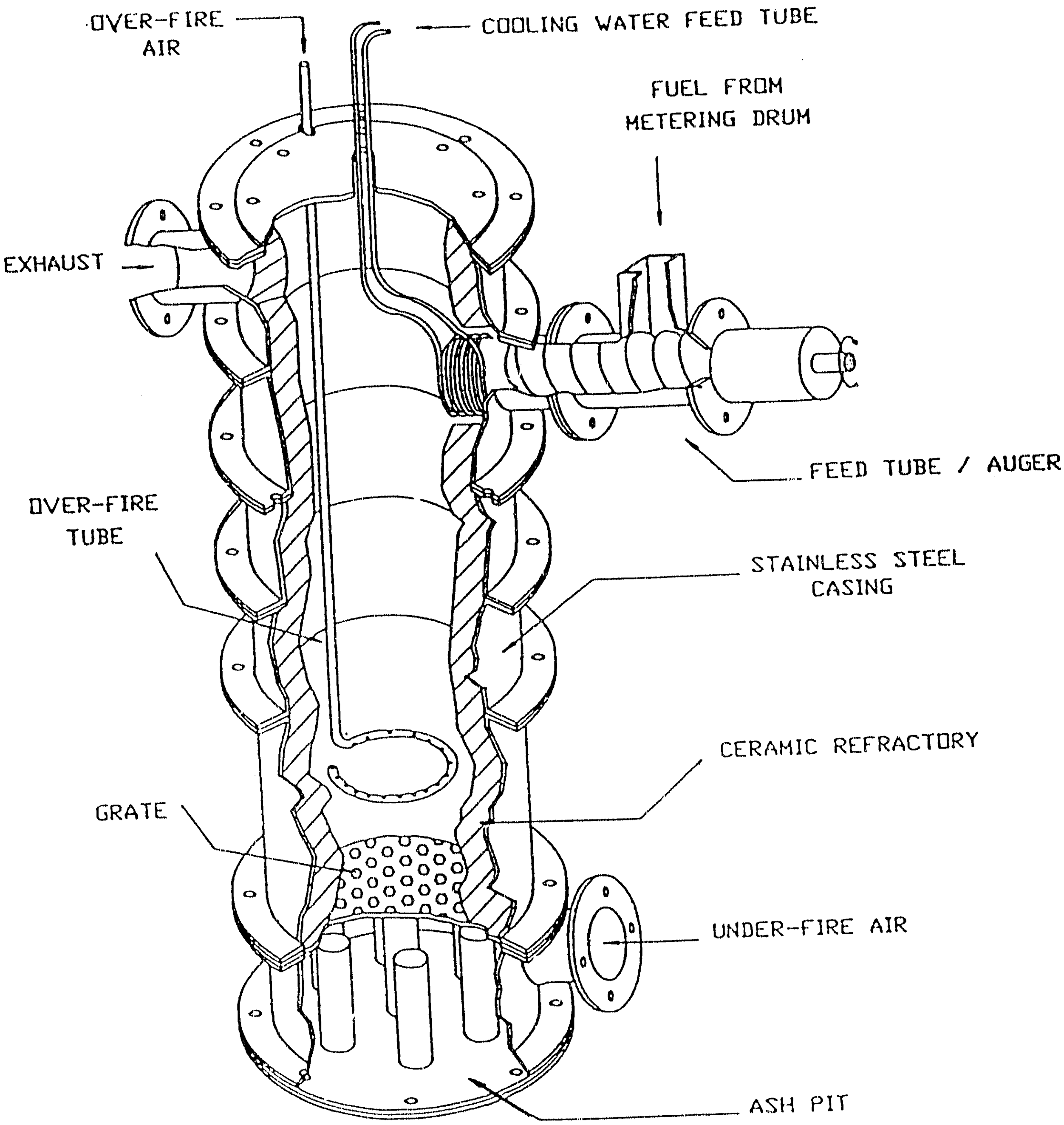

Figure 3: Cutaway View of the Biomass Combustion Unit. Shows Important Components Including: Over Fire Air Tube, Under Fire Air Port, Grate, Ceramic Refractory, Exhaust Port, and Pellet Fuel Feed Mechanism.

Table 1 identifies expected air-level combinations used for testing.

Table 1. Expected Air-Level Combinations

Excess Air (%)	Under Fire (%)
50	30
	45
	60
100	30
	45
	60
150	30
	45
	60
200	30
	45
	60

Air Temperature. The temperature of the air provided for combustion will be ambient for the previous 12 air-level settings. One additional test will be performed at a selected air-level setting with an under fire air temperature elevated to 400°F.

The total number of anticipated optimization test runs for each fuel will be 4 excess air levels times 3 different under fire air levels for a total of 12 tests at ambient air temperature, plus 1 more test at an elevated air temperature for a total number of 13 optimization test runs per fuel.

A schematic of the analysis performed during the optimization test is shown in Figure 4. During the test runs, the following equipment will be used to monitor the combustion process and emissions:

Thermocouples -

- combustion product temperature

Enerac 2000 -

- sulfur dioxide (SO_2)
- carbon monoxide (CO)
- nitrogen oxides (NO_x)
- oxygen (O_2)
- carbon dioxide (CO_2)
- methane (CH_4) (percentages)

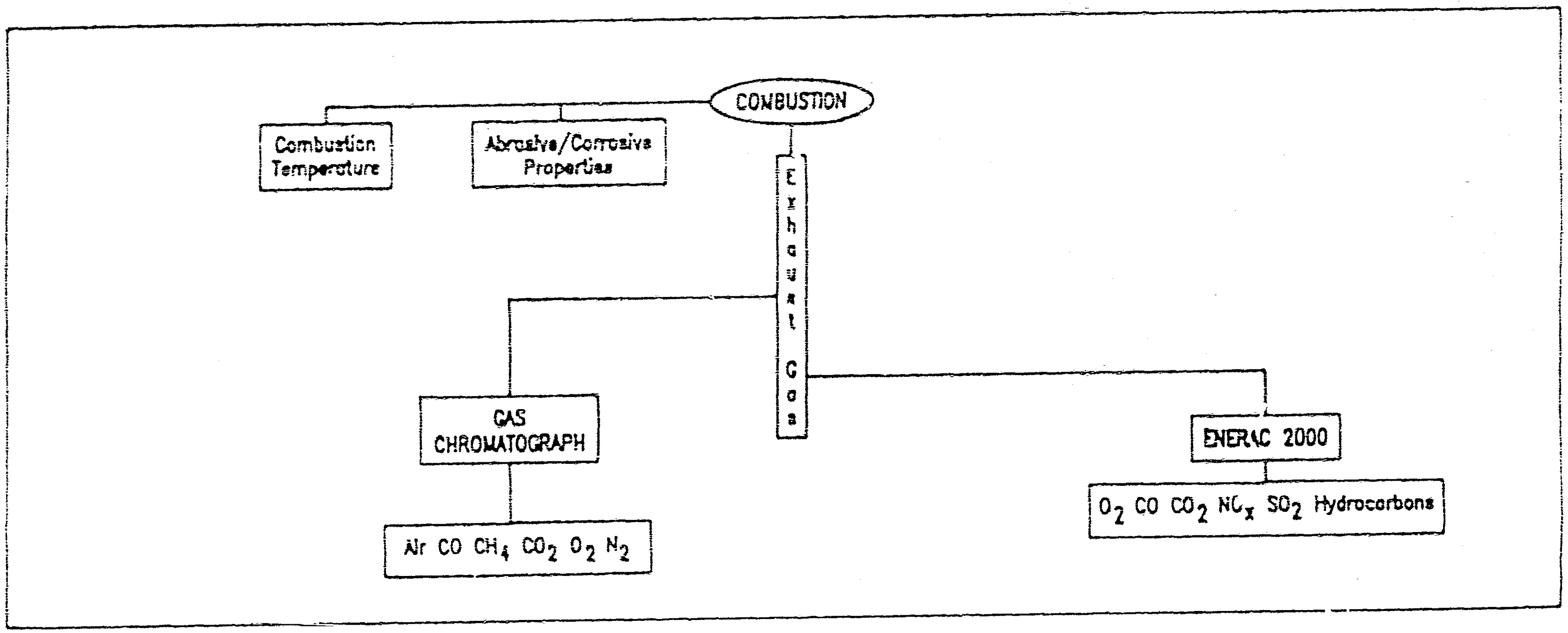

Figure 4: Test One - Combustion Optimization

Gas Chromatograph -

- nitrous oxide (N_2O)
- air
- carbon monoxide (CO)
- carbon dioxide (CO_2)
- oxygen (O_2)
- nitrogen (N_2)
- methane (CH_4) (ppm)

It is expected that this first test will require 80 pounds of pelletized fuel. This amount will allow for unit warm up, the 13 combustion conditions to achieve steady state, and data collection at steady-state conditions.

Test Two - Method 5 Sampling

The second test will examine the particulate, hydrofluoric acid and total heavy metals released from combustion of the fuel sample. This will be performed by stack sampling and bottom ash sampling. The combustion conditions will either be the optimum for the individual sample, or a preselected combustion condition that will be used for all 12 fuel samples to allow direct comparison of all samples. A schematic of the analysis performed during the second test is in Figure 5.

The equipment used and the exhaust emissions analyzed are summarized below:

Method 5 Train -

- particulate
- total heavy metals (Cr, Cd, As, Hg, Ni, Ba, Pb, etc.)
- hydrochloric acid (HCl)

Enerac 2000 -

- sulfur dioxide (SO_2)
- carbon monoxide (CO)
- nitrogen oxides (NO_x)
- oxygen (O_2)
- carbon dioxide (CO_2)
- methane (CH_4) (percentages)

Gas Chromatograph -

- nitrous oxide (N_2O)
- air
- carbon monoxide (CO)
- carbon dioxide (CO_2)
- oxygen (O_2)
- nitrogen (N_2)
- methane (CH_4) (ppm)

Gas Sampling Detector -

- hydrofluoric acid (HF)

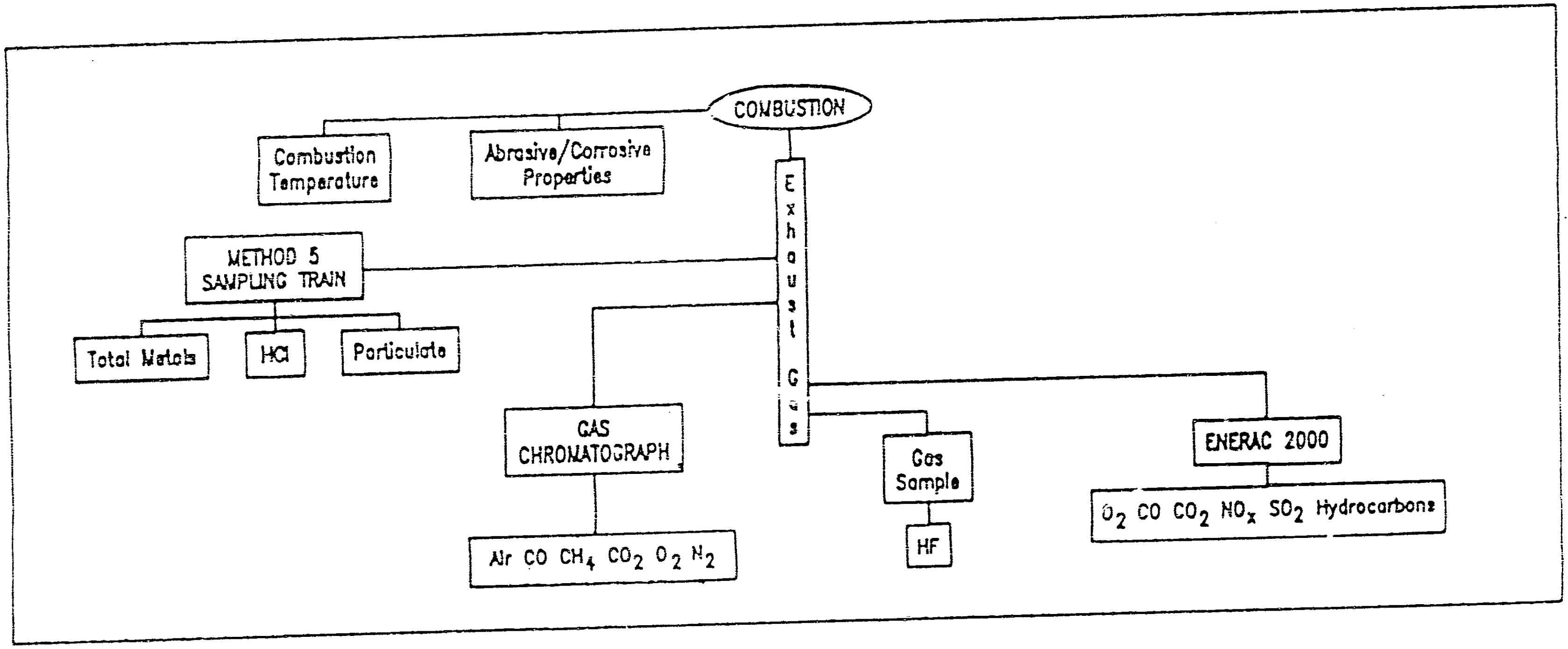

Figure 5: Test Two - Method 5 Sampling

Thermocouples

- combustion product temperature

It is expected that this test will require 35 pounds of pelletized fuel. This will allow for unit warm up, uncontaminated bottom ash sampling, and stack sampling to be completed.

Test Three - Modified Method 5 Sampling

The third test will examine the amount of dioxins/furans, semi-volatile organics, particulate, and hydrochloric acid present in the exhaust emissions from combustion of the fuel sample. These will be determined by stack sampling. The combustion conditions will either be the optimum for the individual sample, or a preselected combustion condition that will be used for all 12 fuel samples to allow direct comparison of all samples. A schematic of the analysis performed during the third test is shown in Figure 6. The equipment used and the exhaust emissions analyzed are summarized below:

Modified Method 5 Train -

- semi-volatile organics
- dioxins, furans
- Polycyclic Aromatic Hydrocarbons (PAH)

Enerac 2000 -

- sulfur dioxide (SO_2)
- carbon monoxide (CO)
- nitrogen oxides (NO_x)
- oxygen (O_2)
- carbon dioxide (CO_2)
- methane (CH_4) (percentages)

Gas Chromatograph -

- nitrous oxide (N_2O)
- air
- carbon monoxide (CO)
- carbon dioxide (CO_2)
- oxygen (O_2)
- nitrogen (N_2)
- methane (CH_4) (ppm)

Bottom Ash Trap -

- bottom ash TCLP

Thermocouples -

- combustion product temperature

It is expected that this test will require 35 pounds of pelletized fuel. This will allow for steady state, stack sampling, and proper sample collection of dioxins and furans

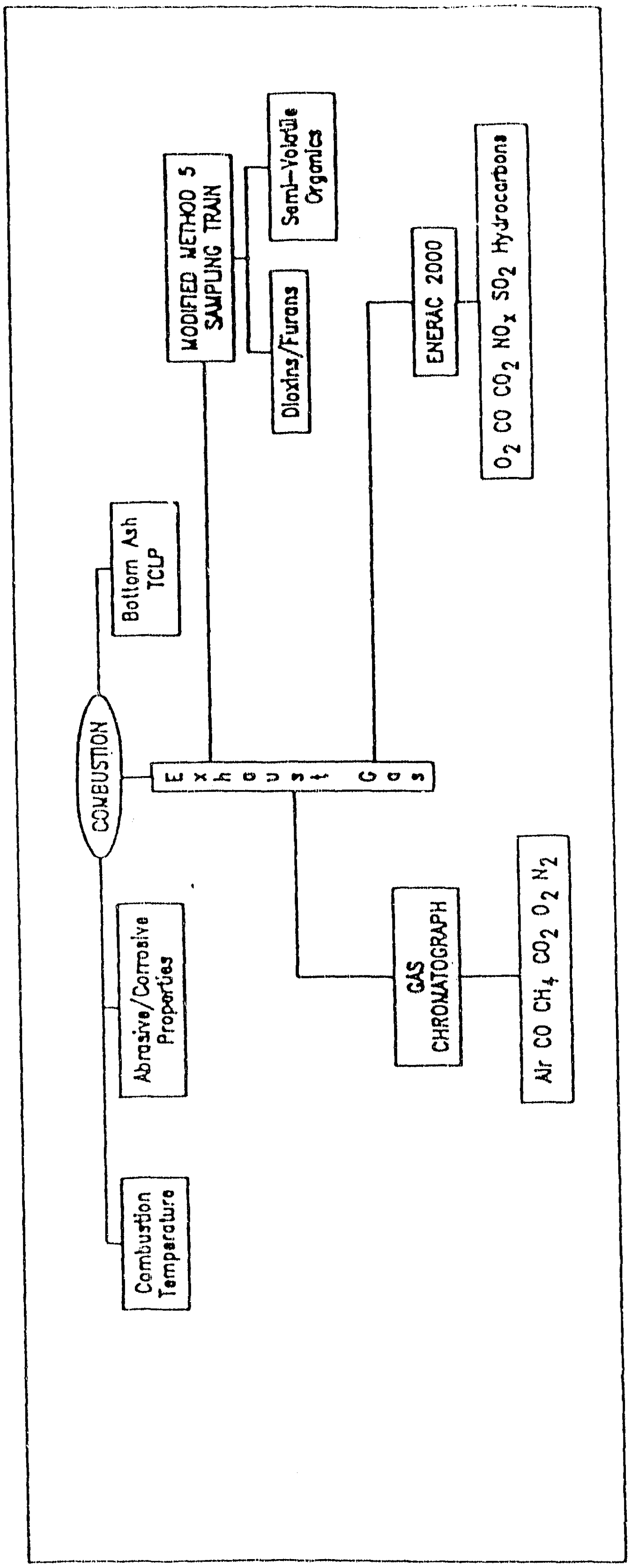

Figure 6: Test Three - Modified Method Five Sampling

DATA COLLECTION

Data for temperature, and all continuous monitoring of flue gases will be collected by use of a data acquisition unit. An IBM-compatible computer in conjunction with Keithley 500 data acquisition software/hardware will automatically collect and reduce the data from thermocouples and combustion analyzers.

Data from the gas chromatograph will be collected by use of an integrator. The integrator will be calibrated to indicate the percentage of each chemical species scanned for in the exhaust gas sample.

Data from the stack sampling trains will be obtained with the assistance of technicians from the Environmental Engineering Laboratory at OSU. The control unit for each train has temperature monitors and flow meters that will be used to calculate the amount of stack sample collected.

Visual data collection will be performed by engineering students at OSU. This data will be used for qualitative analyses.

CHARACTERIZATION AND TESTING - METHODS AND PROTOCOLS

Oregon State University has the lead responsibility for all tests. Several tests involve extensive procedures and will be performed by experienced personnel in commercial analytical laboratories.

The following is a list of tests that will be conducted during the study. They are grouped with respect to the substance that is to be tested. Included is the method/protocol that will be used, and also a brief explanation. All ASTM Standards referenced in this section are in Appendix B.

Raw Fuel

Moisture Content. This test will be conducted by OSU in accordance with ASTM Standard E790-87, "Residual Moisture in a Refuse-Derived Fuel Analysis Sample." This method covers the determination of total weight basis moisture in the analysis sample of particulate wood fuel. It is used for calculating other analytical results to a dry basis.

Bulk Density. This test will be conducted by OSU in accordance with ASTM E873-82, "Bulk Density of Densified Particulate Biomass Fuels." The results will be used to determine the difference in bulk density between the unpelletized and pelletized fuel.

Size Distribution. This test will be conducted by OSU in accordance with ASTM Standard E828-81, "Designating the Size of RDF-3 from its Sieve Analysis." This test will look at the physical shape of the raw fuel. The composition (i.e., plastic, wood, etc.) will also be noted at this time.

Pelletized Fuel

Ultimate Analysis. This analysis will be performed by an analytical laboratory in accordance with ASTM Standard E870-82, "Standard Test Methods for Analysis of Wood Fuels," and relevant ASTM Standards. The ultimate analysis is the determination of carbon and hydrogen in the fuel, as found in the gaseous products of its complete combustion, the determination of sulfur, nitrogen, and ash in the fuel as a whole, and the calculation of oxygen by difference.

Proximate Analysis. This analysis will be performed by an analytical laboratory in accordance with ASTM Standard E870-82, "Standard Test Methods for Analysis of Wood Fuels," and relevant ASTM Standards. The proximate analysis is an assay of the moisture, ash, volatile matter, and fixed carbon as determined by prescribed test methods.

Ash Fusion Temperature. This test will be performed by an analytical laboratory in accordance with ASTM Standard E953-88, "Standard Test Method for Fusibility of Refuse-Derived Fuel (RDF) Ash." This method covers the observation of the temperatures at which triangular pyramids (cones) prepared from RDF ash attain and pass through certain stages of fusing and flow when heated at a specific rate in controlled, mildly reducing, and oxidizing atmospheres.

Elemental Ash Analysis. This analysis will be performed by an analytical laboratory in accordance with ASTM Standard D3682-87, "Major and Minor Elements in Coal and Coke Ash by Atomic Absorption." The sample to be analyzed is ashed under standard conditions and ignited to constant weight. The ash is fused with lithium tetraborate ($Li_2B_4O_7$) followed by a final dissolution of the melt in dilute hydrochloric acid (HCl). The solution is analyzed by atomic absorption/emission for silicon dioxide (SiO_2), aluminum oxide (Al_2O_3), iron oxide (Fe_2O_3), calcium oxide (CaO), magnesium oxide (MgO), sodium oxide (Na_2O), potassium oxide (K_2O), titanium dioxide (TiO_2), and manganese dioxide (MnO_2).

Moisture Content. This test will be performed by OSU in accordance with ASTM Standard E790-87, "Residual Moisture in a Refuse-Derived Fuel Analysis Sample." This method covers the determination of total weight basis moisture in the analysis sample of particulate wood fuel. It is used for calculating other analytical results to a dry basis.

Higher Heating Value. This test will be performed by OSU in accordance with ASTM Standard E711-87, "Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter," using a Parr Model 1261 Bomb Calorimeter. Calorific value is determined in this method by burning a weighed analysis sample in an oxygen bomb calorimeter under controlled conditions. the calorific value is computed from temperature observations made before and after combustion, taking proper allowance for thermometer and thermochemical corrections.

Fuel Reactivity. This test will be performed by OSU. Reactivity of fuel is defined as the time rate of mass loss of the fuel for a given set of combustion conditions. This test will be performed with induction furnace balances where variables of temperature, composition, and mass loss can be controlled and measured accurately.

Pellet Durability. This test will be performed by OSU in accordance with ASTM Standard E1288-89, "The Durability of Biomass Pellets." Fuel pellet durability is a measure of a pellet's propensity to produce fines while under physical agitation. Testing of pellets requires the use of a tumbler of specific design, weighing apparatus accurate to 0.1 gram, and standard Tyler sieves.

Bulk Density. This test will be performed by OSU in accordance with ASTM Standard E873-82, "Bulk Density of Densified Particulate Biomass Fuels." The results will be used to determine the difference in bulk density between the unpelletized and pelletized fuel. Additionally, ASTM Standard E1037-84, "Measuring Particle Size Distribution of RDF-5," will be used to determine the size of the pelletized fuel.

Bottom Ash Trap

Bottom Ash TCLP. This test will be performed by an analytical laboratory in accordance with EPA Method 1311. Appendix C contains the appropriate EPA documents. The Toxicity Characteristic Leaching Procedure (TCLP) is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes. The leachate obtained from the TCLP is analyzed for the presence of the 52 constituents at regulatory levels.

Combustion Unit

Combustion Temperature. This test will be performed by Oregon State University. The temperature of the combustion chamber and exhaust gases will be measured with ceramic insulated type-K and type-R thermocouples.

Abrasive/Corrosive Properties. This test will be performed by OSU. Abrasive and corrosive properties are to be visually determined by inspection of the grate and refractory surfaces after combustion. This will be a qualitative analysis. Thickness of deposition and coloration will be noted.

Exhaust Gases

Method 5 (M5) Sampling Train

Total Metals. This test will be performed by OSU in conjunction with an analytical laboratory in accordance with an EPA draft document, "Methodology for the Determination of Metals Emissions in Exhaust Gases from Hazardous Waste Incineration and Similar Combustion Processes." Appendix D contains this draft document and schematics of the preparation and analysis methods. This method is applicable for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorous (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) emissions from hazardous waste incinerators and similar combustion processes. This method also may be used for determination of particulate emissions following additional procedures. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing a solution of dilute nitric acid in hydrogen peroxide in two impingers, and acidic potassium permangante solution in two (or one) impingers. The concentration of metals present is performed by Inductively Coupled Plasma (ICP) Spectroscopy or by Atomic Absorption Spectroscopy (AAS).

Particulate. This test will be performed by OSU in accordance with EPA Stack Sampling Methods. Appendix E contains the appropriate EPA documents. The amount of particulate collected in the sampling train will be determined by using EPA Method 5 calculations and procedures.

Hydrochloric Acid. This test will be performed by OSU simultaneously with EPA Method 23, in accordance with EPA Method 26, "Determination of Hydrogen Chloride Emissions from Stationary Sources." Appendix G contains the appropriate EPA document. An exhaust gas sample is extracted by a MM5 stack sampling train with impingers filled with dilute sulfuric acid. In the dilute acid, the HCl gas is dissolved and forms chloride (Cl^-) ions. The Cl^- is analyzed by ion chromatography.

Modified Method 5 (MM5) Sampling Train

Dioxins/Furans. This test will be performed by OSU in conjunction with an analytical laboratory in accordance with EPA Method 23, "Determination of Polychlorinated Dibenzo-p-Dioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs) from Stationary Sources." Appendix F contains the appropriate EPA document. 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 PCDDs and PCDFs are extracted from the sample, separated by high resolution gas chromatography, and measured by high resolution mass spectrometry.

Gas Chromatograph

CH_4, O_2, CO, CO_2, N_2, N_2O. This test will be performed by OSU. A sample will be withdrawn from the stack with an automated sampling valve. The sample will be injected into a gas chromatograph and the concentration of oxygen, carbon dioxide, carbon monoxide, methane, nitrogen, and nitrous oxide will be determined. This automated process will run continuously during a combustion test run.

Gas Sampling Detector

Hydrofluoric Acid. This test will be performed by OSU. A sample will be withdrawn from the stack with a hand-operated bellows pump. A disposable detection tube inserted into the pump will determine the concentration of hydrofluoric acid present in exhaust gases.

Continuous Monitoring

O_2, CO_2, CO, NO_x, SO_2, CH_4. This test will be performed by OSU. An exhaust emission analyzer (ENERAC 2000) will be used to continuously monitor the concentration of oxygen, carbon monoxide, carbon dioxide, nitrogen oxides, sulfur dioxide, and unburned hydrocarbons present in exhaust gases.

APPENDIX A

QUALITY CONTROL:

ASTM STANDARDS

Designation: E 791 – 90

Standard Test Method for Calculating Refuse-Derived Fuel Analysis Data from As-Determined to Different Bases[1]

NOTE—Significance and Use Section was added editorially and the designation date was changed June 1, 1990.

1. Scope

1.1 This test method gives equations to enable analytical data from the application of RDF analyses procedures to be expressed on various different bases in common use. Such bases are: as-received; dry; dry, ash-free; and others (see 2.1.12).

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Terminology

2.1 *Descriptions of Terms Specific to This Standard:*

2.1.1 *ash*—inorganic residue remaining after ignition of combustible substances, determined by definite prescribed methods. Ash may not be identical, in composition or quantity, with the inorganic substances present in the material before ignition.

2.1.2 *as-determined basis*—experimental data obtained from the analysis sample of RDF. These data represent the numerical values obtained for a particular moisture or ash content, or both, in the sample at the time of measurement.

2.1.3 *air drying*—a process of partial drying of RDF to bring its moisture content near to equilibrium with the atmosphere in which further reduction, division, and characterization of the sample are to take place. In order to bring about this equilibrium, the RDF is usually subjected to drying under controlled temperature conditions ranging from 30 to 40°C.

2.1.4 *air dry loss*—the decrease in mass presumed to be moisture of a sample due to air drying.

2.1.5 *as-received basis*—experimental data calculated to the moisture condition of the sample as it arrived in the laboratory and before any laboratory processing or conditioning. The total moisture value that is calculated from the air dry loss and residual moisture value is used to convert data from the dry basis to the as-received basis (see *dry ash-free basis*).

2.1.6 *dry ash-free basis*—the experimental data calculated to a theoretical base of no moisture or ash associated with the sample. Numerical values (air-dry loss, residual moisture values, and ash content) are used for converting the as-determined data to a moisture and ash-free basis.

2.1.7 *dry basis*—the experimental data calculated to a theoretical base of no moisture associated with the sample. The numerical value (residual moisture value) is used for converting the as-determined data to a dry basis.

2.1.8 *fixed carbon*—the ash-free carbonous material that remains after volatile matter is driven off during the proximate analysis of a dry sample.

2.1.9 *gross calorific value* (gross heat of combustion at constant volume) Q_v (gross)—the heat produced by combustion of a unit quantity of solid fuel, at constant volume, in an oxygen bomb calorimeter under specified conditions such that all water in the products remains in liquid form.

NOTE 1—The conditions are: initial oxygen pressure of 20 to 40 atm (2 to 4 MPa), initial and final temperatures between 68 and 95°F (20 and 35°C).

NOTE 2—The gross calorific value is closely related to the internal energy of combustion for the same reaction at constant standard temperature and pressure (Δu comb.). It is of opposite sign and differs by a small amount due to energy effects resulting from compression, temperature differences, and solution effects that vary with combustion conditions. Because of the variation of conditions allowed in Note 1, the definition of gross calorific value does not lead to a unique value for any given fuel. However, the specified conditions limit the possible value to a narrow range for which approximate limits can be calculated for a given fuel.

2.1.10 *higher heating value*—synonym for *gross calorific value*.

2.1.11 *proximate analysis*—the determination, by prescribed methods, of moisture, volatile matter, fixed carbon (by difference), and ash. Unless otherwise specified, the term proximate analysis does not include determinations of chemical elements or any determinations other than those named.

2.1.12 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*:[2]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous separation.

RDF-3—Combustible waste fraction reduced to particle

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[1] This test method is under the jurisdiction of ASTM Committee D-34 on Resource Recovery and is the direct responsibility of Subcommittee D34.13 on Waste Derived Fuels.

Current edition approved June 1, 1990. Published August 1990. Originally published as E 791 – 81. Last previous edition E 791 – 87.

[2] *Thesaurus on Resource Recovery Terminology*, *ASTM STP 832*, ASTM, 1983, p. 72.

TABLE 1 Conversion Chart

NOTE— To convert any of analyses values for the parameters listed in 4.1 from one basis to another, multiply the given value by the value shown in the appropriate column.

To convert from Multiply by	Conversion Factor As-Determined (ad)	 As-Received (ar)	 Dry (d)	 Dry, Ash-Free (daf)
As-determined (ad)	. . .	$\frac{100 - M_{ar}}{100 - M_{ad}}$	$\frac{100}{100 - M_{ad}}$	$\frac{100}{100 - (M_{ad} - A_{ad})}$
As-received (ar)	$\frac{100 - M_{ad}}{100 - M_{ar}}$	. . .	$\frac{100}{100 - M_{ar}}$	$\frac{100}{100 - (M_{ar} - A_{ar})}$
Dry (d)	$\frac{100 - M_{ad}}{100}$	$\frac{100 - M_{ar}}{100}$	. . .	$\frac{100}{100 - A_d}$
Dry, ash-free (daf)	$\frac{100 - (M_{ad} - A_{ad})}{100}$	$\frac{100 - (M_{ar} - A_{ar})}{100}$	$\frac{100 - A_d}{100}$	. . .

sizes, 95 % passing 2 in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

2.1.13 *residual moisture*—the moisture content remaining in an RDF sample after it has been milled down to an analysis sample. Prior to milling, the RDF sample should have been subjected to either a total moisture determination (single stage), or an air drying procedure.

2.1.14 *total moisture*—the weight loss resulting from drying a sample to constant weight in an oven usually maintained between 103 and 107°C.

2.1.15 *ultimate analysis*—the determination of the percentages of carbon, hydrogen, sulfur, nitrogen, chlorine, ash, and oxygen in a dry sample. The percentage of oxygen may be obtained by calculating the difference between 100 % and the other determined elemental analyses.

2.1.16 *volatile matter*—those products, exclusive of moisture, given off by a material as gas or vapor, determined by definite prescribed methods which may vary according to the nature of the material.

2.2 *Symbols:*

2.2.1 The symbols used in this test method are as follows:

M = moisture, weight %,
M_{ar} = moisture as-received (total moisture), weight %,
M_{ad} = moisture as-determined (residual moisture, weight %,
ADL = air-dry loss, weight %,
P = any analysis parameter listed in 4.1, weight % (except gross calorific value in Btu/lb),
H = hydroxygen, weight %,
O = oxygen, weight %, and
A = ash, weight %.

2.2.2 Subscripts used in this test method are as follows:

$_{ad}$ = as-determined,
$_{ar}$ = as-received,
$_{d}$ = dry, and
$_{daf}$ = dry, ash-free (equivalent to moisture and ash-free, maf).

3. Significance and Use

3.1 This test method is available to producers and users of RDF to use in converting laboratory data from one basis to another.

TABLE 2 Procedures for Converting As-Determined Values to Other Bases

Parameter	As-Determined	As Received H_{ar} and O_{ar} include H and O in M_{ar}	 H_{ar} and O_{ar} do not include H and O in M_{ar}	Dry Basis	Dry, Ash-Free Basis
P (ash, carbon, nitrogen, sulfur, chlorine)	no corrections (see standard method)	$P_{ar} = P_{ad} \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)$	. . .	$P_d = P_{ad} \times \left(\frac{100}{100 - M_{ad}}\right)$	$P_{daf} = P_{ad} \times \left(\frac{100}{100 - M_{ad} - A_{ad}}\right)$
H (hydrogen)	no corrections (see standard method)	$H_{ar} = \left[(H_{ad} - 0.1119\ M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)\right] + 0.1119\ M_{ar}$	$H_{ar} = (H_{ad} - 0.1119\ M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)$	$H_d = (H_{ad} - 0.1119\ M_{ad}) \times \left(\frac{100}{100 - M_{ad}}\right)$	$H_{daf} = (H_{ad} - 0.1119\ M_{ad}) \times \left(\frac{100}{100 - M_{ad} - A_{ad}}\right)$
O (oxygen)	$O_{ad} = 100 - (A_{ad} + C_{ad} + H_{ad} + N_{ad} + S_{ad} + Cl_{ad})$	$O_{ar} = \left[(O_{ad} - 0.8881\ M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)\right] + 0.8881\ M_{ar}$	$O_{ar} = (O_{ad} - 0.8881\ M_{ad}) \times \left(\frac{100\text{ b}- M_{ar}}{100 - M_{ad}}\right)$	$O_d = (O_{ad} - 0.8881\ M_{ad}) \times \left(\frac{100}{100 - M_{ad}}\right)$ or $O_d = 100 - (A_d + C_d + H_d + N_d + S_d + Cl_d)$	$O_{daf} = (O_{ad} - 0.8881\ M_{ad}) \times \left(\frac{100}{100 - M_{ad} - A_{ad}}\right)$

TABLE 3 Standard Reporting Form Analyses Data of RDF

	As-Determined	As-Received		Dry Basis	Dry, Ash-Free Basis
		H_{ar} and O_{ar} include H and O in sample M_{ar}	H_{ar} and O_{ar} do not include H and O in sample M_{ar}		
Air dry loss, %	18.69	. . .	. . .	. . .	. . .
Residual moisture (M_{ad}), %	2.15	. . .	. . .	. . .	. . .
Total moisture (M_{ar}), %	. . .	20.44	20.44	. . .	. . .
Ash, %	20.68	16.82	16.82	21.14	. . .
Volatile matter, %	62.29	50.65	50.65	63.66	80.73
Fixed carbon, %	14.88	12.09	12.09	15.20	19.27
Total, proximate	100.00	100.00	100.00	100.00	100.00
Total, moisture, %	. . .	. . .	20.44	. . .	. . .
Ash, %	20.68	16.82	16.82	21.14	. . .
Carbon, %	39.66	32.25	32.25	40.53	51.40
Hydrogen, %	5.12	6.25	3.97	4.99	6.32
Nitrogen, %0.60	0.60	0.49	0.49	0.61	0.78
Chlorine, %	0.30	0.24	0.24	0.31	0.39
Sulfur, %0.15	0.15	0.12	0.12	0.15	0.19
Oxygen, %	33.49	43.83	25.68	32.28	40.93
Total, ultimate	100.00	100.00	100.00	100.00	100.00
Gross heating value, Btu/lb	6868	5584	5584	7019	8900
Chloride, water soluble, %	0.19	0.15	0.15	0.19	0.25

4. Applicable Parameters

4.1 The calculation procedures defined in 6.1.3, 6.2.2, and 6.3.2 are applicable to the following analysis parameters when expressed as a weight percent (except gross calorific value as Btu/lb).

4.1.1 Ash,

4.1.2 Carbon,

4.1.3 Chloride, water-soluble,

4.1.4 Chlorine, total,

4.1.5 Calorific value (gross),

4.1.6 Fixed carbon,

4.1.7 Nitrogen,

4.1.8 Sulfur, and

4.1.9 Volatile matter.

5. Sampling

5.1 Sampling techniques are not directly applicable to this test method. However, sampling procedures are identified in the respective methods of analyses.

6. Methods for Calculating Data

6.1 Converting from the as-determined analysis sample basis to the as-received basis:

6.1.1 *Moisture:*

$$M_{ar} = [M_{ad} \times (100 - ADL)/100] + ADL$$

6.1.2 *Hydrogen and Oxygen*—Inasmuch as hydrogen and oxygen values may be reported on the basis of containing or not containing the hydrogen and oxygen in water (moisture) associated with the sample, alternate conversion procedures are defined as follows:

6.1.2.1 Hydrogen and oxygen reported include hydrogen and oxygen in water:

$$H_{ar} = \left[(H_{ad} - 0.1119\ M_{ad}) \times \frac{100 - M_{ar}}{100 - M_{ad}}\right] + 0.119\ M_{ar}$$

$$O_{ar} = \left[(O_{ad} - 0.8881\ M_{ad}) \times \frac{100 - M_{ar}}{100 - M_{ar}}\right] + 0.881\ M_{ar}$$

where:

0.1119 = ratio of the weight of hydrogen in water to the molecular weight of water, and

0.8881 = ratio of the weight of oxygen in water to the molecular weight of water.

6.1.2.2 Hydrogen and oxygen reported do not include hydrogen and oxygen in water:

$$H_{ar} = (H_{ad} - 0.1119\ M_{ad}) \times \frac{100 - M_{ar}}{100 - M_{ad}}$$

$$O_{ar} = (O_{ad} - 0.881\ M_{ad}) \times \frac{100 - M_{ar}}{100 - M_{ad}}$$

6.1.3 *Other Parameters*—The following equation is applicable to all parameters, *P*, listed in 4.1:

$$P_{ar} = P_{ad} \times \frac{100 - M_{ar}}{100 - M_{ad}}$$

6.2 Converting from the as-determined analysis sample basis to the dry basis:

6.2.1 *Hydrogen and Oxygen:*

$$H_d = (H_{ad} - 0.1119\ M_{ad}) \times \frac{100}{100 - M_{ad}}$$

$$O_d = (O_{ad} - 0.881\ M_{ad}) \times \frac{100}{100 - M_{ad}}$$

6.2.2 *Other Parameters*—The following equation is applicable to all parameters, *P*, listed in 4.1:

$$P_d = P_{ad} \times 100/(100 - M_{ad})$$

6.3 Converting from the as-determined analysis sample basis to the dry, ash-free basis (see Note 4).

6.3.1 *Hydrogen and Oxygen:*

$$H_{daf} = (H_{ad} - 0.1119\ M_{ad}) \times \frac{100}{100 - M_{ad} - A_{ad}}$$

$$O_{daf} = (O_{ad} - 0.8881\ M_{ad}) \times \frac{100}{100 - M_{ad} - A_{ad}}$$

6.3.2 *Other Parameters*—The following equation is applicable to all parameters, *P*, listed in 4.1:

$$P_{daf} = P_{ad} \times \frac{100}{100 - M_{ad} - A_{ad}}$$

Note 3—It may not always be practical to report some parameters on a dry, ash-free basis due to oxidation of constituents as well as some elements being retained in the ash. The data calculated are to a theoretical base of no moisture or ash present in the sample.

7. Conversion Chart

7.1 To convert any of the analysis values for the parameters listed in 4.1 from one basis to another, multiply the given value by the value shown in the appropriate column in Table 1.

7.2 Hydrogen and oxygen on the as-determined basis include hydrogen and oxygen in free water (moisture) associated with the analysis sample. However, hydrogen and oxygen values reported on other moisture-containing bases may be reported either as containing or not containing the hydrogen and oxygen in water (moisture) reported on that basis. Conversion procedures are shown in Table 2.

8. Sample Calculations

8.1 An example of analysis data tabulated for a hypothetical RDF on various bases is shown in Table 3.

9. Reporting of Results

9.1 Report the results of the proximate and ultimate analysis based on the example shown in Table 3.

9.2 To avoid ambiguity and to provide a means for conversion of data to other than the reported basis, it is essential that an appropriate moisture and ash content be given in the data report.

9.3 If hydrogen or oxygen data, or both, are reported on an as-received basis (or any other moisture basis), a footnote or some other means shall be employed in the report to indicate whether the values reported do or do not include hydrogen and oxygen in the moisture associated with the sample.

Designation: E 829 – 88

Standard Test Method for Preparing RDF Laboratory Samples for Analysis[1]

1. Scope

1.1 This test method covers the preparation of RDF laboratory samples for analysis, the laboratory samples having been previously obtained from representative RDF samples.

1.2 The test method given may also be used for other RDF types but additional sample preparation steps may be necessary prior to the application of this method.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific hazard statements are given in Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[3]

E 791 Method for Calculating Refuse-Derived Fuel Analysis Data from As-Determined to Different Bases[3]

3. Definitions

3.1 *air-drying*—a process of partially drying RDF to bring its moisture content to near equilibrium with the ambient atmosphere in which further reduction, division, and characterization of the sample are to take place. In order to bring about this equilibrium, the RDF is usually subjected to drying under controlled temperature conditions ranging from 30 to 40°C.

3.2 *analysis sample*—final subsample prepared from the air-dried laboratory sample but reduced by passing through a mill with a 0.5-mm (0.02-in.) size or smaller final screen.

3.3 *bias*—a constant or systematic error in the test results. The error is a persistent positive or negative deviation from the accepted reference value.

3.4 *gross sample*—a sample representing one lot and composed of a number of increments on which neither reduction nor division has been performed.

3.5 *laboratory sample*—a representative portion of the gross sample received by the laboratory for further analysis.

3.6 *lot*—a large designated quantity (greater than the quantity of the final sample) of RDF that can be represented by a properly selected gross sample.

3.7 *precision*—a term used to indicate the capability of a person, an instrument, or a method to obtain reproducible results; specifically, a measure of the random error as expressed by the variance, the standard error, or a multiple of the standard error.

3.8 *refuse-derived fuel*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared defined as follows in *ASTM STP 832*:[4]

RDF-1—wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—combustible waste fraction processed to particle sizes, 95 % weight passing 2-in.^{2} screening.

RDF-4—combustible waste fraction processed into powder form, 95 % weight passing 10-mesh screening.

RDF-5—combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

3.9 *representative sample*—a sample collected in such a manner that it has characteristics equivalent to the lot sample.

3.10 *sample division*—the process of extracting a smaller sample from a sample so that the representative properties of the larger sample are retained. During this process it is assumed that no change in particle size or other characteristics occurs.

3.11 *sample preparation*—the process that includes drying, size reduction, division, and mixing of a laboratory sample for the purpose of obtaining an unbiased analysis sample.

3.12 *sample reduction*—the process whereby sample particle size is reduced without change in sample weight.

3.13 *significant loss*—any loss that introduces a bias in final results that is of appreciable importance to concerned parties.

4. Summary of Test Method

4.1 Sample moisture is reduced by air-drying to allow the mechanical reduction of the sample without significant change to the sample's fuel properties. The final sample is in

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

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[2] *Annual Book of ASTM Standards*, Vol 15.05.

[3] *Annual Book of ASTM Standards*, Vol 11.04.

[4] *Thesaurus on Resource Recovery Terminology*, *ASTM STP 832*, ASTM, 1983.

a form suitable for further analysis.

5. Significance and Use

5.1 Using this procedure a sample of RDF can be converted into a physical form suitable for laboratory fuel analysis.

5.2 As indicated in Method E 791, air-dry moisture, which is determined by this procedure, is essential to the calculation of other laboratory results on an as-received basis. The air-dry moisture value is used in conjunction with the results of the residual moisture determination in Test Method E 790 to calculate total sample moisture.

6. Apparatus

6.1 *Air-Drying:*

6.1.1 *Drying Oven*—A large chamber mechanical draft oven capable of maintaining a controlled temperature in the range from 25 to 40°C. Air changes should be at the rate of 1 to 4 changes per minute. Air flow should be baffled to prevent samples from being blown out of the sample containers.

6.1.2 *Drying Pan*—A noncorroding pan or mesh basket to be used for holding the sample during air-drying operations.

6.1.3 *Balance* (Laboratory Sample)—A balance of sufficient capacity to weigh the sample and container with a sensitivity of 0.5 g.

6.2 *Sample Reduction:*

6.2.1 *Mill*—A mill operating on the principle of cutting or shearing action shall be used for sample particle size reduction. It shall have the capability to regulate the particle size of the final product by means of either interchangeable screens or mill adjustments. The mill shall be enclosed and should generate a minimum amount of heat during the milling process to minimize the potential for loss of moisture. The final product shall pass through a 0.5-mm or smaller screen into a receiver integral with the mill. Access should be provided so that the mill can be quickly and easily cleaned between samples.

6.3 *Analysis Sample Containers*—Heavy, vapor impervious bags, properly sealed; or noncorroding cans, glass jars, or plastic bottles with airtight sealing covers may be used to store RDF samples for analysis. Containers shall be checked for suitability by measuring weight loss or gain of the sample and container stored for 1 week under ambient laboratory conditions. The weight loss or gain should be less than 0.5 % of the sample weight stored in the container.

6.4 *Drying Oven*—A drying oven of either the mechanical or natural circulation type which is capable of constant uniform temperature within the specimen chamber regulated at 107 ± 3°C.

6.5 *Shredder*—A laboratory shredder capable of shredding or cutting larger particle sizes of solid waste. The final product shall pass through a 2-in. or smaller screen into a receiver integral with the shredder.

NOTE 1—A garden-type shrubbery shredder equipped with a screen and bag for collection of shredded samples is satisfactory.

7. Hazards

7.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while shredding RDF samples; conducting tests under a negative pressure hood when possible; and washing hands before eating or smoking.

7.2 Laboratory sample handling and reduction shall be performed by trained personnel. If all precautions regarding sample preparations are not followed, the error in the preparation may bias some or all of the analyses performed on the sample.

7.2.1 All preparation steps shall be done rapidly and in as few operations as possible, since moisture loss depends on several factors other than total moisture content, such as time required for milling, atmospheric temperature and humidity, and the type of laboratory sample reduction equipment.

7.2.2 At all times RDF samples should be protected from moisture change due to exposure to rain, snow, and sun, or contact with absorbent materials.

7.2.3 Samples should be transported to the laboratory and analyzed as soon as possible. If any sample-handling step involved an extended time period, the sample and container should be weighed before and after the process to determine any weight gain or loss. This weight gain or loss shall be included in the calculation of moisture content.

7.2.4 Force-feeding of the sample through the mill can overload the motor. An overload can cause rapid heating of the rotor and mill chamber with possible loss of residual moisture.

8. Sampling[5]

8.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative sample from the RDF lot to be characterized.

8.2 The sampling method for this procedure should be based on agreement between the involved parties.

8.3 For this procedure the laboratory sample size will normally not exceed 2 kg with some variation possible depending on the laboratory equipment available.

8.3.1 Due to the heterogeneous nature of RDF, dividing a laboratory sample to a very small size analyses sample may result in nonrepresentative results. Since milling operations mix the sample as well as reduce particle size, laboratory samples should not be divided before the initial preparation steps have been completed.

9. Procedure

9.1 Weigh the entire laboratory sample into a tared air-drying pan. Sample depth in the drying pan shall be no greater than 100 mm (4 in.) and any lumps of sample should be broken up. Use more than one pan if necessary. If a very fine mesh-type drying pan is used, size the mesh such that the sample will not be lost.

9.2 Air-dry the sample at 10 to 15°C above ambient, but not greater than 40°C until the weight loss is less than 0.1 % of the sample weight per hour. Samples can normally be allowed to air-dry for a set time period such as overnight or

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[5] ASTM Subcommittee E38.01 is currently in the process of developing a procedure for sampling RDF. The chairman of E38.01 should be contacted for details.

24 h. To speed the drying stage the sample may be carefully stirred avoiding loss of sample.

NOTE 2—The air discharge of the forced draft air-drying oven should be filtered prior to discharge to minimize laboratory contamination by air-entrained RDF dust.

9.3 Separate and weigh the millables and nonmillables for classification and use, or analysis, if necessary. Calculate the millables and nonmillables as described in 10.2.

9.4 Dry a representative portion of the air-dried millable fraction at 107 ± 3°C to constant weight as follows:

9.4.1 Heat a clean, empty drying pan at a minimum temperature of 107 ± 3°C for at least 1 h. When cool, transfer to a desiccator and tare weigh to an accuracy of 0.5 g.

9.4.2 Place the laboratory sample of RDF in the drying pan(s). A maximum sample depth of 50 to 100 mm is recommended. Weigh the pan and sample to an accuracy of 0.5 g. More than one drying pan may be necessary.

NOTE 3—If a mesh-type pan is used, place a clean sheet of aluminum foil under the pan to check for any sample fall through. If any occurs, a smaller-mesh drying pan is required.

9.4.3 Place the pan and sample in the drying oven at 170 ± 3°C for a minimum of 1 h.

NOTE 4—Observe the sample periodically to make certain that the sample does not decompose or ignite at this temperature.

9.4.4 After an appropriate drying time, remove the pan and sample from the oven and place in a desiccator to cool. When cool, weigh the sample and pan to the nearest 0.5 g.

9.4.5 Place the sample and pan in the oven for an additional 1 h at 107 ± 3°C.

9.4.6 Remove the sample and pan and place in the desiccator to cool. When cool, weigh the sample and pan to the nearest 0.5 g. If the sample weight loss was less than 0.1 %/h of the original sample weight, the determination is complete; if not, repeat 9.4.5 and 9.4.6.

NOTE 5—At this point the dried sample can be used for further analysis if desired.

9.4.7 Calculate the moisture of the nonmilled millable fraction of the laboratory sample as described in 10.3.

9.5 Reduce the air-dried sample to a smaller particle size by using a cutting- or shearing-type shredder or mill. The final product should pass through a 0.5-mm or smaller screen. Depending on the specific RDF product, this step may involve more than one stage or reduction, that is, passing the sample through a shredder or mill with larger size screens first and then milling to pass the final screen. Even though the sample has been air dried, minimum atmospheric exposure is recommended and the milling process should be conducted to avoid significant moisture change. If necessary, the milled sample should be well mixed by either manual or mechanical means to ensure thorough intermix of heavy fines and milled fluff.

9.6 The mixed, air-dried, finely ground laboratory sample can then be further subdivided to an analysis-size sample (Note 6). Retain a minimum of 50 g as the analysis sample. Any division method used shall ensure that the retained analysis sample is representative of the original laboratory sample.

NOTE 6—If it is possible to riffle the product, a small laboratory riffle can be used to divide the sample. If it is not possible to riffle the sample, use some other valid method to divide the sample.

9.7 Keep the analysis sample in a labeled sample container having a moixture-tight seal.

9.8 Determine the residual moixture of the analysis sample as described in Test Method E 790.

10. Calculation

10.1 Calculate the air-dry moisture as follows:

$$ADL = [(G - L)/G] \times 100$$

where:

ADL = air-dry loss, %,
G = weight of the laboratory sample before air-drying, and
L = weight of the laboratory sample after air-drying.

10.2 Calculate the millables and the nonmillables of the air-dried sample as follows:

$$M = [W_{M}/(W_{M} + W_{NM})] \times 100$$

where:

M = millables, %,
W_M = weight of the millables in the air-dried sample,
NM = nonmillables, %, and
W_{NM} = weight of the nonmillables in the air-dried sample.

10.3 Calculate the moisture in the nonmilled millable fraction of the air-dried fraction of the laboratory sample as follows:

$$MAD = [(W_{bd} - W_{ad})/W_{bd}] \times 100$$

where:

MAD = moisture of nonmilled millable fraction of the air-dried sample, %,
W_{bd} = weight of the nonmilled millable fraction of the air-dried sample before drying at 107 ± 3°C, and
W_{ad} = weight of the nonmilled millable fraction of the air-dried sample after drying at 107 ± 3°C.

NOTE 7—Moisture loss or gain during particle-size reduction (shredding/milling) can be determined by comparing the moisture of the nonmilled millable fraction of the air-dried sample with the residual moisture-content value and used accordingly.

NOTE 8—Nonmillables usually are noncombustible and can be used in contributing to the ash value or noncombustible-value portion of the sample.

11. Precision and Bias

11.1 The standard deviations of the individual determinations, in percent absolute, are:

Typical Average Value	Within Laboratory	Between Laboratories
16	1.8	2.9

11.1.1 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

11.2 *Bias*—Due to the variability in what is considered to be "in equilibrium with ambient conditions" it is not possible to describe any measure of bias regarding this test method.

Designation: E 856 – 83 (Reapproved 1988)

Standard Definitions of Terms and Abbreviations Relating to Physical and Chemical Characteristics of Refuse Derived Fuel[1]

accuracy—generally, a term used to indicate the reliability of a measurement, or an observation. Specifically, a measure of closeness of agreement between a test result and a recognized standard value. For example, the difference between the observed and a standard value for the sulfur content of a sample of refuse-derived fuel. This difference includes both random and systematic errors.

air-drying—a process of partial drying of refuse-derived fuel (RDF) to bring its moisture content near to equilibrium with the atmosphere in which further reduction, division, and characterization of the sample are to take place. In order to bring about this equilibrium, the RDF is usually subjected to drying under controlled temperature conditions ranging from 30 to 40°C.

air-dry loss—the decrease in sample mass due to air-drying. This decrease is presumed to be moisture.

analysis sample—final subsample prepared from the air-dried laboratory sample but reduced by passing through a mill with a 0.5-mm (0.02-in.) size or smaller final screen.

as-determined basis—analytical data obtained from the analysis sample after conditioning and preparation in accordance with Method E 829. As-determined basis data represent the numerical values obtained at the particular moisture and ash level in the sample at the time of analysis.

ash—the residue remaining after ignition of refuse-derived fuel determined by definite prescribed methods. The ash may not be identical in composition or quantity with the inorganic substances present in the refuse-derived fuel before ignition.

as-received basis—the test data calculated to the moisture condition of the sample as it arrived in the laboratory and before any laboratory processing or conditioning.

bias—a systematic error that is consistently negative or consistently positive. The mean of errors resulting from a series of observations which does not tend toward zero.

calorific value—the energy of combustion of a unit quantity of refuse-derived fuel. It may be expressed in kilojoules per kilogram (kJ/kg), British thermal units per pound (Btu/lb), or calories per gram (cal/g) (obsolete).

combustible—that portion of the refuse-derived fuel sample which is consumed upon ignition exclusive of the moisture present in the sample.

d-RDF—abbreviation for densified refuse-derived fuel.

dry, ash-free—the test data calculated to a theoretical base of no moisture or ash associated with the sample.

dry basis—the test data calculated to a theoretical base of no moisture associated with the sample.

duplicate analysis—paired determinations on the same sample performed by one analyst at essentially the same time.

gross calorific value—the energy released by combustion of a unit quantity of refuse-derived fuel at constant volume or constant pressure in a suitable calorimeter under specified conditions such that all water in the products is in the liquid form. This is the measure of calorific value predominantly used in the United States. Synonym: higher heating value.

gross sample—a sample representing one lot, normally composed of a number of increments, on which neither reduction nor division has been performed.

higher heating value (HHV)—a synonym for gross calorific value.

increment—a portion of the lot collected by one individual manual or mechanical sampling operation and normally combined with other increments from the lot to make a gross sample.

laboratory sample—a representative portion of the gross sample received by the laboratory for analysis.

lot—a designated quantity of refuse-derived fuel that can be represented by a properly selected gross sample.

lower heating value (LHV)—a synonym for net calorific value.

milling—a reduction in particle size of refuse-derived fuel by shearing, cutting, or grinding to a suitable particle size for analysis and characterization (see **sample reduction**).

net calorific value—the energy released by combustion of a unit quantity of refuse-derived fuel at constant volume or constant pressure in a suitable calorimeter under specified conditions such that all water in the products remains in the gaseous form. The net calorific value is the lower heating value that can be calculated from the gross calorific value by making a correction for the heat of vaporization of the water. This is the measure of calorific value in Europe but is rarely used in the United States. Synonym: lower heating value.

noncombustible—that fraction of a macrosample remaining after moisture and combustibles are driven off by heat and combustion. It is composed of metallic and glass particles in addition to the residue from the combustion of organic substances.

precision—a term used to indicate the capability of a person, an instrument, or a method to obtain reproducible results; specifically, a measure of the random error as expressed by the variance, the standard error, or a multiple of the standard error.

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[1] These definitions are under the jurisdiction of ASTM Committee E-38 on Resource Recovery and are the direct responsibility of Subcommittee E38.01 on Energy.

Current edition approved Oct. 26, 1983. Published December 1983.

proximate analysis—the determination, by prescribed methods, of moisture, volatile matter, fixed carbon (by difference), and ash. Unless otherwise specified, the term proximate analysis does not include determinations of chemical elements or any determinations other than those named.

refuse-derived fuel (RDF-3)—refuse-derived fuel-3 (RDF-3) is defined as a shredded fuel derived from municipal solid waste (MSW) which has been processed to remove metal, glass, and other inorganic materials. This material has a particle size such that 95 weight % passes through a 2-in. square mesh screen.

NOTE 1—Other refuse-derived fuel may be classified as follows:
RDF-1—Wastes used in as-discarded form.
RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.
RDF-4—Combustible waste processed into powder form, 95 weight % passing 10-mesh screening.
RDF-5—Combustible waste densified (compressed) into the form of pellets, slugs, cubettes, or briquetes.
RDF-6—Combustible waste processed into liquid fuels.
RDF-7—Combustible waste processed into gaseous fuel.

residual moisture—the moisture content remaining in an RDF sample after it has been air-dried and milled down to an analysis sample.

representative sample—a sample collected in such a manner that it has characteristics equivalent to the lot.

sample—a portion of material taken from a larger quantity for the purpose of estimating properties or composition of the larger quantity. See **analysis sample, gross sample, laboratory sample, and representative sample.**

sample division—the process of obtaining a smaller sample from a larger sample so that the representative properties of the larger sample are retained. During this process it is assumed that no change in particle size or other characteristics occurs.

sample preparation—the process that includes drying, size reduction, division, and mixing of a laboratory sample for the purpose of obtaining an unbiased analysis sample.

sample reduction—the process whereby sample particle size is reduced without change in sample weight (see milling).

standard deviation—the square root of the variance.

systematic error—an error caused by undetected fundamental flaws in the test equipment by inadequate understanding of the theory underlying the measurement or by repetitious errors on the part of the analyst.

total moisture—the water contained in a sample. The determination of the total moisture is made by drying a sample under controlled conditions of temperature, time, and air flow. The determination may consist of a single-stage or a two-stage drying process.

ultimate analysis—the determination of the percentages of carbon, hydrogen, sulfur, nitrogen, chlorine, ash, and oxygen in a dry refuse-derived fuel sample. The percentage of oxygen may be obtained by difference between 100 % and the sum of the other determined elemental analyses.

variance—the mean square of deviations (or errors) of a set of observations; the sum of square deviations (or errors) of individual observations with respect to their arithmetic mean divided by the number of observations less one (degrees of freedom); the square of the standard deviation (or standard error).

volatile matter—those products, exclusive of moisture, given off by a material as gas or vapor, determined by definite prescribed methods.

Designation: E 954 – 88

Standard Test Method for Packaging and Shipping of Laboratory Samples of Refuse-Derived Fuel[1]

This standard is issued under the fixed designation E 954; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers a procedure for packaging a refuse-derived fuel sample at its point of origin for shipping this sample to the laboratory for subsequent analyses.[2]

1.2 This test method may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Additional hazard information is found in Section 7.

2. Referenced Document

2.1 *ASTM Standard:*

E 856 Definitions of Terms and Abbreviations Relating to the Physical and Chemical Characteristics of Refuse-Derived Fuel[3]

3. Definitions

3.1 *gross sample*—a sample representing one lot and composed of a number of increments on which neither reduction nor division has been performed.

3.2 *laboratory sample*—a representative portion of the gross sample (or lot) received by the laboratory for analysis.

3.3 *lot*—a large designated quantity (greater than the quantity of the final sample) of RDF which can be represented by a properly selected gross sample.

3.4 *forms of refuse-derived fuel* (RDF):

RDF-1 Waste used as a fuel in as-discarded form.

RDF-2—Waste processed to coarse particle size with or without ferrous metal separation.

RDF-3—shredded fuel derived from municipal solid waste (MSW) which has been processed to remove metal, glass, and other inorganics. This material has a particle size such that 95 weight % passes through a 2-in. square mesh screen.

RDF-4—Combustible waste processed into powder form, 95 weight % passing a 10-mesh screen.

RDF-5—Combustible waste densified (compressed) into the form of pellets, slugs, subettes, and briquettes.

RDF-6—Combustible waste processed into liquid fuel.

RDF-7—Combustible waste processed into gaseous fuel.

4. Summary of Test Method

4.1 A representative portion of a gross sample of RDF is packaged in such a manner that all physical and chemical properties of the material are retained during shipment to the laboratory for analyses. Labeling and chain-of-custody procedures are also included in this test method.

5. Significance and Use

5.1 The packaging of a laboratory sample as specified herein is intended to ensure that the physical and chemical characteristics of the sample as received in the laboratory are not changed during shipment.

6. Apparatus

6.1 *Polyethylene Bags,* 3 mL, having a capacity to hold 2 kg (1 to 2 ft^3) of RDF-3.

6.2 *Polyethylene Bag Seal,* twist tie or equivalent.

6.3 *Box,* corrugated.

6.4 *Box Seal,* strapping tape or equivalent.

7. Hazards

7.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when handling samples. Recommended hygienic practices include use of gloves when handling RDF; wearing; wearing a dust mask (NIOSH—approved type), especially when shredding samples; conducting tests under a negative pressure hood when possible; and washing hands before eating and smoking.

7.2 Sample handling shall be performed by trained personnel. All operations shall be done as rapidly as possible to avoid sample moisture changes due to atmospheric exposure.

7.3 At all times, RDF samples should be protected from moisture, sun or contact with absorbent materials.

7.4 Packaging must be done at the sampling site without delay between sampling and bagging.

8. Sampling

8.1 Refuse-Derived Fuel products are frequently nonhomogeneous. For this reason, significant care should be exercised to obtain a representative laboratory sample from the RDF lot to be characterized.

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

Current edition approved March 25, 1988. Published May 1988. Originally published as E 954 – 83. Last previous edition E 954 – 83.

[2] Supporting data for this test method are available on loan from ASTM Headquarters, 1916 Race St., Philadelphia, PA 19103. Request RR: E38-1001.

[3] *Annual Book of ASTM Standards,* Vol 11.04.

Client ______ Sampler ______
Sample Identification ______
Date sampled ______ Date packaged ______ weight of gross sample ______
Weight of sample, bags, and seals as shipped ______
Weight of bags and seals ______
Weight of sample as shipped ______
Weight of samples as received ______
Analyses requested ______
______
Method of shipment ______

Relinquished by ______ Received by ______ Date ______ Time ______
Relinquished by ______ Received by ______ Date ______ Time ______
Relinquished by ______ Received by ______ Date ______ Time ______

Other Information ______
______
______

NOTE—Remove tag before weighing.

FIG. 1 Typical Chain-of-Custody Tag

8.2 The sampling method should be based on an agreement between involved parties.

9. Packaging Package Marking

9.1 Place the sample as it is obtained into a preweighed 3-mil polyethylene bag. Secure the bag with a seal to prevent moisture loss.

9.2 Place the polyethylene bag containing the sample in 9.1 into a second preweighed 3-mil polyethylene bag. Secure the bag with a seal to prevent moisture loss.

9.3 Weigh the double-bagged sample, and record the weight of the bags and sample on a chain-of-custody tag. Attach the tag to the outside of the sample bag (see Fig. 1).

$$D = C - (A + B)$$

where:

A = weight in grams of polyethylene bag including seal in 9.1,
B = weight in grams of polyethylene bag including seal in 9.2,
C = weight in grams of sample, polyethylene bags, and seals in 9.3, and
D = weight in grams of sample as shipped.

9.4 Place the double-bagged sample into a corrugated container, seal the container, and ship to the testing laboratory. Any appropriate means of shipment may be used.

9.5 A chain-of-custody tag shall accompany the sample (see Fig. 1).

Designation: E 1126 - 87

Standard Terminology Relating to Biomass Fuels[1]

biomass—any material, excluding fossil fuels, which is or was a living organism that can be used as a fuel directly or after a conversion process.

NOTE—Wood, peanut hulls, agricultural waste, corn and other grains, sugar, and bagasse are all examples of biomass.

biomass fuel—fuel derived from biomass.

denatured fuel ethanol—fuel ethanol to which chemicals (denaturants) have been added to make the ethanol unfit for human consumption in accordance with the regulations of the Bureau of Alcohol, Tobacco, and Firearms of the U. S. Treasury Department.

densified particulate biomass fuels—a fuel made by mechanical compression of biomass to increase the bulk density and to press the fuel into a specific shape, such as pellets and briquettes. The fuel can have a maximum volume of 16.39 cm^3 (1 $in.^3$) such that the largest dimension is 7.62 cm (3 in.).

dry basis moisture content—of biomass fuels, the ratio of the weight of the water in a sample to the weight of the dry material. It is expressed as a percent.

fermentation fuel—a fuel produced by fermentation of biomass.

NOTE—Ethyl alcohol is the most common form of fermentation fuel.

fuel alcohol—ethyl, methyl, or higher alcohols with impurities (including water but excluding denatureants) produced for use as a fuel alone or as an addition to other fuels, such as gasoline.

fuel ethanol—ethanol with impurities (including water but excluding denaturants).

NOTE—Fuel ethanol produced by fermentation normally contains trace amounts of methanol and small quantities of higher alcohols. These higher alcohols are collectively called "fusel oils."

fuel ethanol manufacturing facility—a manufacturing facility of any size designed to produce fuel ethanol by a fermentation process.

hogged fuel—ground wood fuel that is usually a by-product of a wood products manufacturing process.

particulate wood fuel—any wood fuel with a maximum particle volume of 16.39 cm^3 (1 $in.^3$) such that the largest dimension is 7.62 cm (3 in.).

NOTE—These fuels include sanderdust, sawdust, pellets, green tree chips, and hogged fuel.

pelletized biomass fuel—see **densified particulate biomass fuels.**

refuse derived fuel 3 (RDF-3)—as defined by Committee E-38 on Resource Recovery, RDF-3 is a shredded fuel derived from municipal solid waste (MSW) that has been processed to remove metal, glass, and other inorganics. The material has a particle size such that 95 % weight passes through a 2 in. square mesh screen.

total weight basis moisture content—of biomass fuels, the ratio of the weight of the water in a sample to the weight of the wet material. It is expressed as a percent (also called wet basis moisture content).

wet basis moisture content—see **total weight basis moisture content.**

wood fuel—fuel derived from biomass composed of woody trees or shrubs.

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[1] This terminology is under the jurisdiction of ASTM Committee E-48 on Biotechnology and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion Systems.

Current edition approved Feb. 27, 1987. Published April 1987. Originally published as E 1126 - 86. Last previous edition E 1126 - 86.

APPENDIX B

CHARACTERIZATION AND TESTING:

ASTM STANDARDS

Designation: D 1102 - 84

Modification of
Technical Association of Pulp and Paper Industry
Standard Method T 211 OM-80

Standard Test Method for Ash in Wood[1]

1. Scope

1.1 This test method covers the determination of ash, expressed as the percentage of residue remaining after dry oxidation (oxidation at 580 to 600°C), of wood or wood products.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Significance and Use

2.1 The ash content is an approximate measure of the mineral content and other inorganic matter in wood.

3. Apparatus

3.1 *Crucibles*, with tightly fitting lids, having a capacity of 30 mL or more, shall be used. Platinum crucibles are preferred, but silica or porcelain crucibles may be used.

3.2 *Muffle Furnace*—An electric furnace is recommended for igniting the wood sample. A furnace fitted with an indicating pyrometer, so that the desired temperature can be maintained, is preferable.

3.3 *Analytical Balance*, sensitive to 0.1 mg.

3.4 *Drying Oven*, with temperature controlled between 100 and 105°C.

4. Test Specimen

4.1 The test specimen shall consist of approximately 2 g of wood that has been ground to pass a No. 40 (425-μm) sieve. Care shall be taken to ensure that it is representative of the entire lot of material being tested.

5. Procedure

5.1 Ignite the empty crucible and cover over a burner or in the muffle at 600°C, cool in a desiccator, and weigh to the nearest 0.1 mg. Place the 2-g test specimen in the crucible, determine the weight of crucible plus specimen, and place in the drying oven at 100 to 105°C with the crucible cover removed. After 1 h, replace the cover on the crucible, cool in a desiccator, and weigh. Repeat the drying and weighing until the weight is constant to within 0.1 mg. During the cooling and weighing periods, keep the crucible covered to prevent absorption of moisture from the air. Record the weight (crucible plus specimen minus weight of crucible) as the weight of the oven-dry test specimen.

5.2 Place the crucible and contents, with the cover removed, in the muffle furnace and ignite until all the carbon is eliminated. Heat slowly at the start to avoid flaming and protect the crucible from strong drafts at all times to avoid mechanical loss of test specimen. The recommended temperature of final ignition is 580 to 600°C. Avoid heating above this maximum.

5.3 Remove the crucible with its contents to a desiccator, replace the cover loosely, cool, and weigh accurately. Repeat the heating for 30-min periods until the weight after cooling is constant to within 0.2 mg.

6. Calculations and Report

6.1 Calculate the percentage of ash, based on the weight of the moisture-free wood, as follows:

$$\text{Ash, \%} = (W_1/W_2) \times 100$$

where:

W_1 = weight of ash, and

W_2 = weight of oven-dry sample.

6.2 Report the results to two decimal places.

7. Precision and Bias[2]

7.1 Data obtained by testing 60 wood samples in one laboratory gives a repeatability as ash content of 0.03 % and as a percentage of ash content of 6.6 %. The range of ash content was from 0.16 % to 0.84 %.

7.2 Reproducibility and comparability data are not available.

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[1] This test method is currently under the jurisdiction of ASTM Committee D-7 on Wood and is the direct responsibility of Subcommittee D07.01 on Fundamental Test Methods and Properties.

Current edition approved April 27, 1984. Published June 1984. Originally published as D 1102 - 50. Last previous edition D 1102 - 56 (1978).

[2] Data in this section was obtained from the Technical Association of the Pulp and Paper Industry, P.O. Box 105113, Atlanta, GA 30348.

Designation: D 3682 - 87

Standard Test Method for Major and Minor Elements in Coal and Coke Ash by Atomic Absorption[1]

This standard is issued under the fixed designation D 3682; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the analysis of the commonly determined major and minor elements in coal ash and coke ash.

NOTE 1—Test Methods D 1757 is used for determination of sulfur.

1.2 The values stated in SI units are to be regarded as the standard.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Method of Collection and Preparation of Coke Samples for Laboratory Analysis[2]
D 1193 Specification for Reagent Water[3]
D 1757 Test Methods for Sulfur in Ash from Coal and Coke[2]
D 2013 Method of Preparing Coal Samples for Analysis[2]
D 3174 Test Method for Ash in the Analysis Sample of Coal and Coke from Coal[2]
D 3180 Method for Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

3. Summary of Method

3.1 The coal or coke to be analyzed is ashed under standard conditions and ignited to constant weight. The ash is fused with lithium tetraborate ($Li_2B_4O_7$) followed by a final dissolution of the melt in dilute hydrochloric acid (HCl). The solution is analyzed by atomic absorption/emission for all elements.

4. Significance and Use

4.1 A compositional analysis of the ash in coal is often useful in the total description of the quality of the coal. Knowledge of ash composition is also useful in predicting the behavior of ashes and slags in combustion chambers. Utilization of the ash by-products of coal combustion sometimes depends on the chemical composition of the ash.

4.2 It should be noted that the chemical composition of laboratory-prepared coal ash may not exactly represent the composition of mineral matter in the coal or the composition of fly ash and slag resulting from commercial-scale burning of the coal.

5. Apparatus

5.1 *Ashing Furnace,* with an adequate air circulation and capable of having its temperature regulated between 700 and 750°C.

5.2 *Fusion Furnace,* with an operating temperature of 1000°C.

5.3 *Platinum Dish,* 35 to 85-mL capacity.

5.4 *Stirring Hotplate and Bars,* operating temperature of 200°C.

5.5 *Atomic Absorption Spectrometer*—Any dual-channel instrument using a deuterium (D_2) arc background corrector or other comparable simultaneous background correction system.

5.6 *Visible-Range Spectrophotometer and Absorption Cells.*

6. Reagents

6.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. It is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination. The lithium tetraborate and lanthanum chloride reagents in particular should be examined for alkali and alkaline earth contamination.

6.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as defined in Specification D 1193.

6.3 *Aluminum Stock Solution (1000 ppm Al).*

6.4 *Calcium Stock Solution (1000 ppm Ca).*

6.5 *Hydrochloric Acid (5+95)*—Dilute 50 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to 1000 mL.

6.6 *Iron Stock Solution (1000 ppm Fe).*

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[1] This test method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke, and is the direct responsibility of Subcommittee D 05.29 on Major Elements in Ash and Trace Elements in Coal.

Current edition approved Jan. 30, 1987. Published March 1987. Originally published as D 3682 – 78. Last previous edition D 3682 – 78 (1983).

[2] *Annual Book of ASTM Standards,* Vol 05.05.

[3] *Annual Book of ASTM Standards,* Vol 11.01.

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

6.7 *Lanthanum Chloride Solution (175 g/L $LaCl_3$ or equivalent 10 % La).*

6.8 *Lithium Tetraborate* ($Li_2B_4O_7$), powder.

6.9 *Magnesium Stock Solution (1000 ppm Mg).*

6.10 *Manganese Stock Solution (1000 ppm Mn).*

6.11 *Potassium Stock Solution (1000 ppm K).*

6.12 *Silicon Stock Solution (200 ppm Si)* (Note 2).

6.13 *Sodium Stock Solution (1000 ppm Na).*

6.14 *Titanium Stock Solution (1000 ppm Ti).*

NOTE 3—Commercial silicon standards prepared from sodium silicate have not proved satisfactory. A standard stock solution can be prepared by fusing 0.1070 g of reignited spectrographic grade silica (SiO_2) with 1 g of lithium tetraborate, dissolving in HCl (5+95), and diluting to 250 mL as described for sample preparation (8.3.1 and 8.3.2). This solution is 200 ppm Si. Preferable standard preparations for silica are made by fusion and dilution of ash sample(s) of known composition according to 8.3.1 and 8.3.2. The standard sample(s) should have a composition(s) similar to the unknown.

7. Preparation of Coal Ash and Coke Ash

7.1 Prepare the ash from a thoroughly mixed representative sample of air-dried coal or coke which has been ground to pass a No. 60 (250-µm) sieve. Spread the coal or coke in a layer not over ¼ in. (6 mm) in depth in a fireclay or porcelain roasting dish. Place in a cold muffle furnace and heat gradually so that the temperature reaches 500°C in 1 h and 750°C in 2 h. Ignite at 750°C until all carbonaceous matter is removed. Allow the ash to cool, transfer to an agate mortar, and grind to pass a No. 200 (74-µm) sieve. Reignite the ash at 750°C for 1 h, cool rapidly, and immediately weigh portions for analysis. If samples are stored, reignite the ash before weighing or determine loss on ignition at 750°C on a separate sample weighed out at the same time as the analysis sample and make the necessary corrections. Thoroughly mix each sample before weighing.

8. Procedure

8.1 The solutions and proportions described below are for typical ash samples as represented by American coals of bituminous rank. Therefore, stronger or weaker dilutions may be required to establish suitable concentrations for those elements of varying percentages outside the range of the typical sample. Each analyst must determine the sensitivity and linear range of calibration of his own equipment and choose concentration ranges for standards compatible with the samples and instrument specific to his own work.

8.1.1 Calculations used in subsequent sections are developed from the following general formula for percent concentration in moisture-free coal ash.

$$\text{Percent element oxide in ash} = [(C - B)/(A - B)] \times (N/M) \times F \times 100$$

where:

A = absorbance of standard,
B = absorbance of blank,
C = absorbance of sample solution,
N = element in standard, ppm,
M = sample of solution, ppm, and
F = conversion from element to oxide.

NOTE 3—Concentrations in the ash may be converted to the air-dried whole coal basis using the following expression:

$$C = (AB/100)$$

where:

C = percent in air-dried coal,
A = percent in ash, and
B = percent ash as prepared in 7.1.

See Method D 3180 for procedures to convert values to other bases.

8.2 To minimize the potential of contamination, the platinumware must be prepared by boiling in dilute HCl (5 + 95) and rinsing thoroughly with reagent-grade water. After this initial cleaning, the platinumware must be handled with *clean* tongs and protected from further contamination from table tops, etc. All glassware used in analyses must be equally clean and equally protected.

8.3 *Sample Fusion and Solution:*

8.3.1 Weigh 0.1 ± 0.0002 g of the sample as prepared in 7.1 into a platinum dish (5.3) (Note 4) and add 0.5 g of $Li_2B_4O_7$. Mix the ash and lithium tetraborate well, then add an additional 0.5 g of $Li_2B_4O_7$ to cover the mixture. Place the dish in a clean silica or refractory tray and place in a muffle preheated to 1000°C; 15 min at 1000°C is sufficient to fuse the mixture completely. Remove the tray and dish and cool to room temperature. Carefully rinse the bottom and outside of the platinum dish to remove possible contamination; then place it in a clean 250 (or 400)-mL beaker. Place a clean TFE-fluorocarbon-coated stirring magnet inside the dish, add 150 mL of HCl (5+95) (6.5) to the beaker and dish, and place immediately on the stirring hotplate. Heat the solution to just below boiling temperature and maintain for not more than 30 min with constant stirring. This time and temperature are sufficient to completely dissolve the melt. If stirring is not maintained constantly, some of the ash constituents are apt to precipitate and the analysis must be repeated.

NOTE 4—The use of graphite crucibles and subsequent dissolution of fused beads from them was not investigated; however, their successful use in similar methods has been reported.[5]

8.3.2 Remove the beaker from the hotplate and permit to cool to room temperature. Quantitatively transfer the solution to a 200-mL volumetric flask, wash the platinum dish and beaker with small amounts of HCl (5+95) and dilute to the 200-mL mark with the HCl. This solution is 500 ppm with respect to the total sample and contains 5 g/L of $Li_2B_4O_7$ solution.

8.3.3 *Solution 1*—Pipet 20 mL of the sample solution (8.3.2) into a 50-mL volumetric flask and dilute to volume with HCl (5+95). This solution is 200 ppm with respect to the total sample and contains 2 g/L of $Li_2B_4O_7$ solution.

8.3.4 *Solution 2*—Pipet 10 mL of the sample solution (8.3.2) into a 100-mL volumetric flask, add 10 mL of lanthanum solution (6.7), and dilute to volume with HCl (5 + 95) (Note 5). This solution is 50 ppm with respect to the total sample and contains 0.5 g/L of $Li_2B_4O_7$ solution.

NOTE 5—Lanthanum was included in the solution as a release agent in those determinations that may require it (for example, calcium).

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[5] Muter, R. B. and Nice, L. L., "Major and Minor Constituents in Siliceous Materials by Atomic Absorption Spectroscopy," Advances in Chemistry Series 141, *Trace Elements in Fuels*, American Chemical Society, Washington, DC, 1975, pp. 57–65.

Alternative measures, such as use of nitrous oxide flame, are permissible.

9. Silicon Dioxide (SiO_2)

9.1 *Preparation of Standards*—Prepare a series of standards by combining the following volumes of the silicon stock solution (6.12) with 1 mL of the aluminum stock solution (6.3) and diluting to 100 mL with the blank solution (9.2). Only those standards need be prepared which bracket the expected SiO_2 concentrations in the samples.

Silicon, mL Stock Solution (6.12)	Silicon, ppm	Equivalent %, SiO_2
25	50	53.5
20	40	42.8
15	30	32.1
10	20	21.4

9.2 *Blank Solution*—Prepare a solution of 2 g/L of $Li_2B_4O_7$ solution in HCl (5+95).

9.3 *Sample Solution*—Use the 200-ppm sample solution as prepared in 8.3.3.

9.4 *Atomic Absorption Operating Conditions*—Use a silicon hollow-cathode lamp and set the monochromator at 251.6 nm. Use a nitrous oxide/acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

9.5 *Determination*—Read out absorbance values for the blank solution, standard solutions, and sample solution. In this and all subsequent determinations, those instruments so equipped may be calibrated to read out "percent concentration" directly.

$$SiO_2, \% \ [(C - B)/(A - B)] \times N \times 1.07$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample, and
N = Si in standard, ppm.

10. Aluminum Oxide (Al_2O_3)

10.1 *Preparation of Standards*—Prepare standard solutions containing from 10 to 30 ppm Al and dilute with blank solution 9.2.

10.2 *Blank Solution*—Use the blank as prepared in 9.2.

10.3 *Sample Solution*—Use Solution 1 as prepared in 8.3.3.

10.4 *Atomic Absorption Operating Conditions*—Use an aluminum hollow-cathode lamp and set the monochromator at 309.2 nm. Use a nitrous oxide-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

10.5 *Determination*—Read out absorbance values for the blank solution, standard solutions, and sample solution.

$$Al_2O_3, \% = [(C - B)/(A - B)] \times N \times 0.94$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample, and
N = Al in standard, ppm.

11. Iron Oxide (Fe_2O_3)

11.1 *Preparation of Standards*—Prepare standard solutions containing from 2 to 10 ppm Fe and 10 mL of lanthanum solution per 100 mL. Dilute with blank solution (11.2).

11.2 *Blank Solution*—Prepare a solution of HCl (50 mL/L concentrated HCl) containing 0.5 g/L $Li_2B_4O_7$ solution and 100 mL/L of lanthanum solution.

11.3 *Sample Solution*—Use Solution 2 as prepared in 8.3.4.

11.4 *Atomic Absorption Operating Conditions*—Use an iron hollow-cathode lamp and set the monochromator at 248.3 nm. Use an air-acetylene flame of stoichiometric composition. Adjust other instrument parameters to optimum for the particular equipment used.

11.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution.

$$Fe_2O_3, \% = [(C - B)/(A - B)] \times N \times 2.86$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample, and
N = Fe in standard, ppm.

12. Calcium Oxide (CaO)

12.1 *Preparation of Standards*—Prepare standard solutions containing 1 to 10 ppm Ca and 10 mL of lanthanum solution per 100 mL. Dilute with the blank solution as described in 11.2.

12.2 *Blank Solution*—Use blank solution as described in 11.2.

12.3 *Sample Solution*—Use Solution 2 as described in 8.3.4.

12.4 *Atomic Absorption Operating Conditions*—Use a calcium hallow-cathode lamp and set the monochromator at 422.7 nm. Use an air-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

12.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution.

$$CaO, \% = [(C - B)/(A - B)] \times N \times 2.80$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample, and
N = Ca in standard, ppm.

13. Magnesium Oxide (MgO)

13.1 *Preparation of Standards*—Prepare standard solutions containing 0.5 to 2 ppm Mg and 10 mL of lanthanum solution per 100 mL. Dilute with blank solution as described in 11.2.

13.2 *Blank Solution*—Use blank solution as described in 11.2.

13.3 *Sample Solution*—Use Solution 2 as described in 8.3.4.

13.4 *Atomic Absorption Operating Conditions*—Use a magnesium hollow-cathode lamp and set the monochromator at 285.1 nm. Use an air-acetylene flame of stoichiometric composition. Adjust other instrument parameters to optimum for the particular equipment used.

13.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution.

$$MgO, \% = [(C - B)/(A - B)] \times N \times 3.32$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample, and
N = Mg in standard, ppm.

14. Sodium Oxide (Na_2O)

14.1 *Preparation of Standards*—Prepare standard solutions containing 0.5 to 2 ppm Na and 10 mL of lanthanum[6] solution per 100 mL. Dilute with blank solution as described in 11.2.

14.2 *Blank Solution*—Use blank solution as described in 11.2.

14.3 *Sample Solution*—Use Solution 2 as described in 8.3.4.

14.4 *Atomic Absorption Operating Conditions*—Use a sodium hollow-cathode lamp and set the monochromator at 589.0 nm. Use an air-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

14.5 *Determination*—Read the absorbance values for the blank solution, the standard solutions, and the sample solution.

$$Na_2O, \% = [(C - B)/(A - B)] \times N \times 2.70$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample, and
N = Na in standard, ppm.

NOTE 6—Alternatively, sodium may be determined by flame emission.

15. Potassium Oxide (K_2O)

15.1 *Standard Preparation*—Prepare standard solutions containing 0.5 to 2 ppm K and 10 mL of lanthanum[6] solution per 100 mL. Dilute with blank solution as described in 11.2.

15.2 *Blank Solution*—Use blank solution as described in 11.2.

15.3 *Sample Solution*—Use Solution 2 as described in 8.3.4.

15.4 *Atomic Absorption Operating Conditions*—Use a potassium hollow-cathode lamp and set the monochromator at 766.5 nm. Use an air-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

15.5 *Determination*—Read the absorbance values for the blank solution, the standard solution, and the sample solution.

$$K_2O, \% = [(C - B)/(A - B)] \times N \times 2.41$$

where:

A = absorbance of standard nearest C,
B = absorbance of blank,
C = absorbance of sample, and
N = K in standard, ppm.

NOTE 7—Alternatively, potassium may be determined by flame emission.

NOTE 8—It may be found convenient to combine the standards for iron, calcium, magnesium, sodium, and potassium in one solution.

16. Titanium Dioxide (TiO_2)

16.1 *Standard Preparation*—Prepare a standard solution containing 3 ppm Ti and 5 g/L of $Li_2 B_4O_7$ solution dissolved in HCl (5+95) (6.6). If required, successive dilutions may be made with the blank solution (16.2).

16.2 *Blank Solution*—Prepare a solution containing 5 g/L of $Li_2B_4O_7$ solution dissolved in HCl (5+95) (6.5).

16.3 *Sample Solution*—Use the original sample solution as prepared in 8.3.2.

16.4 *Atomic Absorption Operating Conditions*—Use a titanium hollow-cathode lamp and set the monochromator at 364.3 nm. Use a nitrous oxide-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

16.5 *Determination*—Read the absorbance for the blank solution, the standard solution and the sample solution.

$$TiO_2, \% = [(C - B)/(A - B)] \times 1.00$$

where:

A = absorbance of standard,
B = absorbance of blank, and
C = absorbance of sample.

17. Manganese Dioxide (MnO_2)

17.1 *Standard Preparation*—Prepare a standard solution containing 0.5 ppm Mn and 5 g/L of $Li_2B_4O_7$ solution in HCl (5+95) (6.5). If required, successive dilutions may be made with the blank solution (16.2).

17.2 *Blank Solution*—Use the blank solution (16.2).

17.3 *Sample Solution*—Use the original sample solution (8.3.2).

17.4 *Atomic Absorption Operating Conditions*—Use a manganese hollow-cathode lamp and set the monochromator at 279.5 nm. Use an air-acetylene flame. Adjust other instrument parameters to optimum for the particular equipment used.

17.5 *Determination*—Read the absorbance values for the blank solution, the standard solution, and the sample solution.

$$MnO_2, \% = [(C - B)/(A - B)] \times 0.16$$

where:

A = absorbance of standard,
B = absorbance of blank, and
C = absorbance of sample.

18. Precision and Bias

18.1 Repeatability and reproducibility for the elements determined by this test method are as described in Table 1.

18.2 *Bias:*

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[6] Supporting data are available on loan at ASTM Headquarters. Request RR:D05-1000.

TABLE 1 Repeatability and Reproducibility Ranges

Element	Percent of Moisture-free Ash			
	Repeatability	Range	Reproducibility	Range
SiO_2	2	10 to 60	4	10 to 60
Al_2O_3	1	5 to 30	3	5 to 30
Fe_2O_3	1.0	5 to 50	2	5 to 50
CaO	1.0	≥2	1.0	≥2
CaO	0.25	<2	0.5	<2
MgO	0.20	0.3 to 10	0.6	≥2
MgO			0.2	<2
Na_2O	0.5	≥5	0.7	≥5
Na_2O	0.1	<5	0.2	<5
K_2O	0.1	0.3 to 3	0.2	0.3 to 3
MnO_2	0.02	<0.2	0.07	<0.2
TiO_2	0.2	0.5 to 2	0.4	0.5 to 2

TABLE 2 Comparative Results for an Eastern and Western U.S. Coal Ash

Oxides	Percent of Moisture-free Ash						
	Eastern U.S. Coal Ash			Western U.S. Coal Ash			Reproducibility[C] (from Table 1)
	ASTM-1[A]	ASTM-2[A]	X-RF[B]	ASTM-1[A]	ASTM-2[A]	X-RF[B]	
SiO_2	51.56	51.45	52.16	37.61	36.72	37.12	4
Al_2O_3	32.60	31.65	32.89	17.01	15.94	17.42	3
Fe_2O_3	7.49	8.52	8.50	10.87	12.09	11.39	2
MgO	0.99	1.08	1.24	3.21	3.65	4.00	0.2 and 0.6
CaO	1.37	1.38	1.59	11.96	11.00	12.74	0.5 and 1
K_2O	2.44	2.18	2.31	0.55	0.47	0.47	0.2
Na_2O	0.99	0.82	—	0.16	0.18	—	0.2
TiO_2	1.42	1.28	1.47	0.67	0.68	0.66	0.4

[A] Mean of duplicate determinations from laboratory 1 or 2 using Test Method D 3682.

[B] Mean of duplicate X-ray fluorescence determinations.

[C] Applies to differences between Test Method D 3682 values only.

TABLE 3 Results of Analyses of USGS Standard Rock Samples

	Lab-1[A] AVG-1	Lab-2[A] AVG-1	Ref. Value AVG-1[B]	Lab-3[C] BHVO-1	Ref. Value BHVO-1[D]	Lab-3[C] MAG-1	Ref. Value MAG-1[D]	Lab-3[C] QLO-1	Ref. Value QLO-1
SiO_2	58.79	60.10	59.00	48.20	49.8	49.81	49.74	62.44	65.15
Al_2O_3	16.70	17.66	17.25	13.39	14.0	16.41	16.44	15.88	16.12
Fe_2O_3	6.97	6.54	6.76	12.23	11.95	7.05	6.70	4.34	4.42
MgO	1.50	1.33	1.53	6.72	7.2	2.77	2.98	0.94	0.94
CaO	4.97	5.11	4.90	11.64	11.3	1.36	1.50	3.24	3.17
K_2O	2.86	2.97	2.89	0.49	0.62	3.46	3.6	3.25	3.49
Na_2O	4.21	4.32	4.26	2.33	2.2	3.87	3.9	7.82	4.07
TiO_2	0.85	0.89	1.04	3.18	2.6	0.80	0.70	0.65	0.63
MnO	...	...	0.097	0.15	0.18	0.80	0.10	0.083	0.097

[A] Mean of duplicate determinations from laboratory 1 or 2 using Test Method D 3682

[B] Values for U.S. Geological Survey AVG-1 andesite standard rock reference material. Personal communication, July 1976, from F. J. Flanagan, U.S. Geological Survey, Reston, Va

[C] Mean of triplicate determinations from laboratory 3 using Test Method D 3682

[D] Values for U.S. Geological Survey standard rock samples BHVO-1 (basalt) MAG-1 (marine mud), and QLO-1 (quartz) latite were taken from U.S. Geological Survey Professional Paper 840 "Descriptions and Analyses of Eight New USGS Rock Standards" (1976) pages 34–35, 36, and 91 respectively, compiled and edited by F. J. Flanagan

18.2.1 Comparison of the analytical results obtained using Test Method D 3682 with those obtained for the same samples analyzed by an independent method is one measure of bias. Another is the comparison of published values for standard reference materials with values obtained by Test Method D 3682.

18.2.2 Table 2 gives examples where differences between means of duplicate determinations carried out by different laboratories using Test Method D 3682 fall within the established tolerances and agree well with the independently obtained X-ray fluorescence values.

18.2.3 In Table 3, values from Test Method D 3682 are compared with published values for various U.S. Geological Survey rock standard samples. These were used as comparative reference materials for Test Method D 3682 because no coal ash standard reference material was available.

18.2.4 Both tables indicate a suitable degree of bias for the method.

Designation: E 711 – 87

Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter[1]

This standard is issued under the fixed designation E 711; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the gross calorific value of a prepared analysis sample of solid-forms of refuse-derived fuel (RDF) by the bomb calorimeter method.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific cautionary and precautionary statements see 6.10 and Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

D 3177 Test Method for Total Sulfur in the Analysis Sample of Coal and Coke[3]

E 1 Specification for ASTM Thermometers[4]

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[5]

E 775 Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel[6]

E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[6]

E 829 Method of Preparing RDF-3 Laboratory Samples for Analysis[6]

3. Terminology

3.1 *Definitions:*

3.1.1 *calorific value*—the heat of combustion of a unit quantity of a substance. It may be expressed in joules per gram (J/g), British thermal units per pound (Btu/lb), or calories per gram (cal/g) when required.

NOTE 1—The unit equivalents are as follows:
1 Btu (International Table) = 1055.06 absolute joules
1 Calorie (International Table) = 4.1868 absolute joules
1 Btu/lb = 2.326 J/g
1.8 Btu/lb = 1.0 cal/g

3.1.2 *gross calorific value*—the heat produced by combustion of a unit quantity of solid fuel, at constant volume, in an oxygen bomb calorimeter under specified conditions such that all water in the products remains in liquid form.

3.1.3 *net calorific value*—a lower value calculated from the gross calorific value. It is equivalent to the heat produced by combustion of a unit quantity of solid fuel at a constant pressure of one atmosphere, under the assumption that all water in the products remains in the form of vapor.

3.2 *Descriptions of Terms Specific to This Method*:

3.2.1 *calorimeter*—describes the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

3.2.2 *energy equivalent*—the energy required to raise the temperature (Note 2) of the calorimeter system 1°C (or 1°F) per gram of sample. This is the number that is multiplied by the corrected temperature rise in degrees and divided by the sample weight in grams to give the gross calorific value after thermochemical corrections have been applied.

NOTE 2—Temperature change is measured in thermal units. Temperature changes may also be recorded in electromotive force, ohms, or other units when other types of temperature sensors are used. Consistent units must be used in both the standardization and actual calorific determination. Time is expressed in minutes. Weights are measured in grams.

3.2.3 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*:[7]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

4. Summary of Test Method

4.1 Calorific value is determined in this method by burning a weighed analysis sample in an oxygen bomb calorimeter under controlled conditions. The calorific value is computed from temperature observations made before and after combustion, taking proper allowance for thermometer and thermochemical corrections. Either isothermal or adiabatic calorimeter jackets may be used.

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E 38.01 on Energy.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 05.05.

[4] *Annual Book of ASTM Standards*, Vol 14.03.

[5] *Annual Book of ASTM Standards*, Vol 15.05.

[6] *Annual Book of ASTM Standards*, Vol 11.04.

[7] *Thesaurus on Resource Recovery Terminology*, *ASTM STP 832*, ASTM, 1983, p. 72.

5. Significance and Use

5.1 The calorific value, or heat of combustion, is a measure of the energy available from a fuel. Knowledge of this value is essential in assessing the commercial worth of the fuel and to provide the basis of contract between producer and user.

6. Apparatus

6.1 *Test Room*—The apparatus should be operated in a room or area free of drafts that can be kept at a reasonably uniform temperature and humidity for the time required for the determination. The apparatus should be shielded from direct sunlight and radiation from other sources. Controlled room temperature and humidity are desirable.

6.2 *Oxygen Bomb*, constructed of materials that are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base mmtal. The bomb shall be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There shall be no gas leakage during a test. The bomb shall be capable of withstanding a hydrostatic pressure test to 21 MPa (3000 psig) at room temperature without stressing any part beyond its elastic limit.

6.3 *Calorimeter*, made of metal (preferably copper or brass) with a tarnish-resistant coating and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C (0.02°F) starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low heat conductivity.

6.4 *Jacket*—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 10 mm from the jacket walls. The jacket may be arranged so as to remain at constant temperature or with provisions for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It shall be constructed so that any water evaporating from the jacket will not condense on the calorimeter.

6.5 *Thermometers*—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

6.5.1 *Mercury-in-Glass Thermometers*, conforming to the requirements for Thermometers 116°C or 117°C (56°F or 57°F) as prescribed in Specification E 1. Other thermometers of equal or better accuracy are satisfactory. These thermometers shall be tested for accuracy against a known standard (preferably by the National Bureau of Standards) at intervals no greater than 2.0°C (3.6°F) over the entire graduated scale. The maximum difference in correction between any two test points shall not be more than 0.02°C (0.04°F).

6.5.2 *Beckmann Differential Thermometer*, having a range of approximately 6°C in 0.01°C subdivisions reading upward and conforming to the requirements for Thermometer 115°C, as prescribed in Specification E 1. Each of these thermometers shall be tested for accuracy against a known standard at intervals no larger than 1°C over the entire graduated scale. The maximum difference between any two test points shall not be more than 0.02°C.

6.5.3 *Calorimetric-Type Platinum Resistance Thermometer, 25-*, tested for accuracy against a known standard.

6.5.4 *Other Thermometers*—A high precision electronic thermometer employing balanced thermistors or a quartz thermometer may be used, provided the temperature rise indication is accurate within ±0.003°C per 1°C rise.

6.6 *Thermometer Accessories*—A magnifier is required for reading mercury-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as to introduce no significant errors due to parallax. A Wheatstone bridge and galvanometer capable of measuring resistance to 0.0001 Ω are necessary for use with resistance thermometers.

6.7 *Sample Holder*—Samples shall be burned in an open crucible of platinum, quartz, or acceptable base-metal alloy. Base-metal alloy crucibles are acceptable if after a few preliminary firings the weight does not change significantly between tasks.

6.8 *Firing Wire* shall be 100 mm of No. 34 B & S nickel-chromium alloy wire or 100 mm of No. 34 B & S iron wire. Equivalent platinum or palladium wire may be used provided constant ignition energy is supplied, or measured, and appropriate corrections made.

6.9 *Firing Circuit*—A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A stepdown transformer connected to an alternating current lighting circuit or batteries may be used.

6.10 **CAUTION:** The ignition circuit switch shall be of momentary double-contact type, normally open, except when held closed by the operator. The switch should be depressed only long enough to fire the bomb.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[8] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type III, conforming to Specification D 1193.

7.3 *Benzoic Acid, Standard (C_6H_5COOH)*—Use National Bureau of Standards SRM (Standard Reference Material) benzoic acid. The crystals shall be pelletized before use. Commercially prepared pellets may be used provided they are made from National Bureau of Standards benzoic acid

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[8] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

The value of heat of combustion of benzoic acid, for use in the calibration calculations, shall be in accordance with the value listed in the National Bureau of Standards certificate issued with the standard.

7.4 *Methyl Orange, Methyl Red, or Methyl Purple Indicator* may be used to titrate the acid formed in the combustion. The indicator selected shall be used consistently in both calibrations and calorific determinations.

7.5 *Oxygen*, free of combustible matter. Oxygen manufactured from liquid air, guaranteed to be greater than 99.5 % pure, will meet this requirement. Oxygen made by the electrolytic process may contain a small amount of hydrogen rendering it unfit without purification.

7.6 *Sodium Carbonate, Standard Solution* (0.34 *N*)—One millilitre of this solution should be equivalent to 20.0 J in the nitric acid (HNO_3) titration. Dissolve 18.02 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 L. The Na_2CO_3 should be previously dried for 24 h at 105°C. The buret used for the HNO_3 titration shall be of such accuracy that estimations to 0.1 mL can be made. A more dilute standard solution may be used for higher sensitivity.

8. Precautions

8.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF and washing hands before eating or smoking.

8.2 The following precautions are recommended for safe calorimeter operation:

8.2.1 The weight of solid fuel sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

8.2.2 Bomb parts should be inspected carefully after each use. Threads on the main closure should be checked frequently for wear. The bomb should be returned to the manufacturer occasionally for inspection and possibly proof of firing.

8.2.3 The oxygen supply cylinder should be equipped with an approved type of safety device, such as a reducing valve, in addition to the needle valve and pressure gage used in regulating the oxygen feed to the bomb. Valves, gages, and gaskets must meet industry safety codes. Suitable reducing valves and adaptors for 2 to 3.5-MPa (300 to 500-psig) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

8.2.4 During ignition of a sample, the operator shall not permit any portion of his body to extend over the calorimeter.

9. Sampling[9]

9.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative laboratory sample for the RDF lot to be characterized.

9.2 The sampling method for this procedure should be based on agreement between the involved parties.

9.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Method E 829.

10. Standardization

10.1 Determine the energy equivalent of the calorimeter as the average of a series of ten individual runs, made over a period of not less than 3 days or more than 5 days. To be acceptable, the standard deviation of the series shall be 6.9 kJ/°C (6.5 Btu/°C) or less (see Appendix X1, Table X1). For this purpose, any individual run may be discarded only if there is evidence indicating incomplete combustion. If this limit is not met, repeat the entire series until a series is obtained with a standard deviation below the acceptable limit.

10.2 The weights of the pellets of benzoic acid in each series should be regulated to yield the same temperature rise as that obtained with the various samples tested in the individual laboratories. The usual range of weight is 0.9 to 1.3 g. Make each determination in accordance with the procedure described in Section 11, and compute the corrected temperature rise, *T*, as described in 12.1. Determine the corrections for HNO_3 and firing wire as described in 12.2 and substitute into the following equation:

$$E = [(H)(g) + e_1 + e_3 + e_4] \times t$$

where:

E = energy equivalent, J/°C,
H = heat of combustion of benzoic acid, as stated in the National Bureau of Standards certificate, J/g,
g = weight of benzoic acid, g,
t = corrected temperature rise, °C,
e_1 = titration correction, J,
e_3 = fuse wire correction, J, and
e_4 = correction for ignition energy if measured and corrected for, J.

10.3 Standardization tests should be repeated after changing any part of the calorimeter and occasionally as a check on both calorimeter and operating technique.

11. Procedure

11.1 *Weight of Sample*—Thoroughly mix the analysis sample of solid fuel in the sample bottle, taking care that the heavies and lights (fluff) are distributed in the sample (Note 3). Carefully weigh approximately 1 g of the sample directly into the crucible in which it is to be burned or into a tared weighing scoop from which the sample is transferred to the crucible. Weigh the sample to the nearest 0.1 mg. Some form of compaction may be necessary to ensure satisfactory ignition and complete combustion.

NOTE 3—In the event segregation of the heavies and lights cannot be avoided, attempt to remove sample from the bottle in such a way that a representative sample is transferred.

NOTE 4—Perform the residual moisture determination of the sample simultaneously using Test Method E 790.

11.2 *Water in Bomb*—Add 1.0 mL of water to the bomb by a pipet. Before adding this water, rinse the bomb, and drain the excess water, and leave undried.

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[9] ASTM Subcommittee E38.01 is currently in the process of developing procedures for sampling RDF-3 and the preparation of an analysis sample. The chairman of E 38.01 should be contacted for details.

11.3 *Firing Wire*—Connect a measured length of firing wire to the ignition terminals with enough slack to allow the firing wire to maintain contact with the sample.

11.4 *Oxygen*—Charge the bomb with oxygen to a consistent pressure between 20 and 30 atm (2.03 and 3.04 MPa). This pressure must remain the same for each calibration and for each calorific determination. If, by accident, the oxygen introduced into the bomb should exceed the specified pressure, do not proceed with the combustion. Detach the filling connection and exhaust the bomb in the usual manner. Discard this sample.

11.5 *Calorimeter Water*—It is recommended that calorimeter water temperature be adjusted before weighing as follows:

11.5.1 *Isothermal Jacket Method*, 1.6 to 2.0°C (3.0 to 3.5°F) below jacket temperature (Note 4).

11.5.2 *Adiabatic Jacket Method*, 1.0 to 1.4°C (2.0 to 2.5°F) below room temperature.

NOTE 5—This initial adjustment will ensure a final temperature slightly above that of the jacket for calorimeters having an energy equivalent of approximately 10 200 J/K (2450 cal/°C). Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is acceptable, provided it is used in all tests, including standardization. Use the same amount (±0.5 g) of water in the calorimeter vessel for each test and for calibration. The amount of water (2000 g is usual) can be most satisfactorily determined by weighing the calorimeter vessel and water together on a balance. The water may be measured volumetrically if it is always measured at the same temperature. Tap water may be satisfactory for use in calorimeter bucket.

11.6 *Observations, Isothermal Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Allow 5 min for attainment of equilibrium; then record the calorimeter temperatures (Note 6) at 1-min intervals for 5 min. Fire the charge at the start of the sixth minute and record the time and temperature, T^a. Add to this temperature 60 % of the expected temperature rise, and record the time at which the 60 % point is reached (Note 5). After the rapid-rise period (about 4 to 5 min), record temperatures at 1-min intervals on the minute until the difference between successive readings has been constant for 5 min.

NOTE 6—Use a magnifier and estimate all readings (except those during the rapid rise period) to the nearest 0.002°C (0.005°F) when using ASTM Bomb Calorimeter Thermometer 56C (56F). Estimate Beckmann thermometer readings to the nearest 0.001°C. Tap mercurial thermometers with a pencil just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

NOTE 7—When the approximate expected rise is unknown, the time at which the temperature reaches 60 % of the total can be determined by recording temperatures at 45, 60, 75, 90, and 105 s after firing and interpolating.

11.7 *Observations, Adiabatic Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Adjust the jacket temperature to be equal to or slightly lower than the calorimeter, and run for 5 min to obtain equilibrium. Adjust the jacket temperature to match the calorimeter with ±0.01°C (0.02°F) and hold for 3 min. Record the initial temperature (Note 6) and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise, and adjusting to within ±0.01°C (0.02°F) when approaching the final equilibrium temperature. Take calorimeter readings at 1-min intervals until the same temperature is observed in three successive readings. Record this as the final temperature. Do not record time intervals since they are not critical in the adiabatic method.

11.8 *Analysis of Bomb Contents*—Remove the bomb and release the pressure at a uniform rate, in such a way that the operation will require not less than 1 min. Examine the bomb interior and discard the test if unburned sample or sooty deposits are found. Carefully wash the interior of the bomb including the capsule with distilled or deionized water containing the titration indicator until the washings are free of acid. Collect the washings in a beaker and titrate the washings with standard carbonate solution. Remove and measure or weigh the combined pieces of unburned firing wire, and subtract from the original length or weight to determine the wire consumed in firing. Determine the sulfur content of the sample by any of the procedures described in Test Methods E 775.

12. Calculations

12.1 *Temperature Rise in Isothermal Jacket Calorimeter*—Using data obtained as prescribed in 11.6, compute the temperature rise, T, in an isothermal jacket calorimeter as follows:

$$T = T_c - T_a - r_1(b - a) - r_2(c - b)$$

where:

T = corrected temperature rise,
a = time of firing,
b = time (to nearest 0.1 min) when the temperature rise reaches 60 % of total,
c = time at beginning of period in which the rate of temperature change with time has become constant (after combustion),
T_a = temperature at time of firing, corrected for thermometer error (Note 7),
T_c = temperature at time c, corrected for thermometer error (Note 7),
r_1 = rate (temperature units per minute) at which temperature was rising during 5-min period before firing, and
r_2 = rate (temperature units per minute) at which temperature was rising during the 5-min period after time c. If the temperature is falling, r_2 is negative and the quantity r_2 $(c - b)$ is positive.

12.2 *Temperature Rise in Adiabiatic Jacket Calorimeter*—Using data obtained as prescribed in 11.7 compute the corrected temperature rise, T, as follows:

$$T = T_f - T_a$$

where:

T = corrected temperature rise, °C or °F,
T_a = initial temperature when charge was fired, corrected for thermometer error (Note 8), and
T_f = final temperature corrected for thermometer error.

NOTE 8—With all mercury-in-glass thermometers, it is necessary to make the following corrections if the total heat value is altered by 12 J/g or more. This represents a change of 0.001°C (0.002°F) in a calorimeter using approximately 2000 g of water. The corrections include the calibration correction as stated on the calibration certificate, the setting correction for Beckman thermometers according to the directions furnished by the calibration authority, and the correction for emergent stem. Directions for these corrections are given in Appendix X2.

12.3 *Thermochemical Corrections* (Appendix X3)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, J. Each millilitre of standard alkali is equivalent to 20.0 J.
e_2 = correction for heat of formation of H_2SO_4, J
= 55.2 × percent of sulfur in sample × weight of sample, g.
e_3 = correction for heat of combustion of firing wire, J (Note 10)
= 9.6 J/cm or 5980 J/g for No. 34 B & S gage Chromel C
= 11.3 J/cm or 7330 J/g for No. 34 B & S iron wire.
e_4 = correction for ignition energy of platinum or palladium if measured and corrected for.

NOTE 9—There is no correction for platinum or palladium wire, provided the ignition energy is constant.

12.4 *Calorific Value*:

12.4.1 Calculate the gross calorific value (gross heat of combustion) as follows:

$$H_s = [(T)(E) - e_1 - e_2 - e_3 - e_4]/g$$

where:

H_s = gross calorific value, J/g,
T = corrected temperature rise as calculated in 12.1 or 12.2, °C or °F, consistent with the water equivalent value,
E = energy equivalent (see Section 10),
e_1, e_2, e_3, e_4 = corrections as prescribed in 12.3, and
g = weight of sample, g.

12.4.2 Calculate the net calorific value (net heat of combustion) as follows:

$$H_i = H_s - 23.96\ (H \times 9)$$

where:

H_i = net calorific value (net heat of combustion), J/g,
H_s = gross calorific value (gross heat of combustion), J/g, and
H = total hydrogen, %.

13. Precision and Bias[10]

13.1 *Precision*—The standard deviations of individual determinations, in Btu/lb, are:

Average	Within-laboratory	Between-laboratories
HHV-1:		
6400	27.1	135.5
5200	48.8	239.6
HHV-2:		
7900	32.3	118.0
7400	38.1	227.8
HHV-3:		
9700	111.3	290.4
9500	99.2	249.2
9300	40.3	67.6

13.2 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

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[10] Supporting data are available on loan from ASTM Headquarters. Request RR:E38-1000.

APPENDIXES

(Nonmandatory Information)

X1. CALCULATION OF STANDARD DEVIATIONS FOR CALORIMETER STANDARDIZATION

X1.1 The example given in Table X1.1 illustrates the method of calculating standard deviations for calorimeter standardizations.

TABLE X1.1 Standard Deviations for Calorimeter Standardization[A]

Standardization Number	Column A Water Equivalent, (Btu/lb) × (g/°C)	Column B Code to 4400 (Column A-4400)	Column C (Column B)²
1	4412	12	144
2	4407	7	49
3	4415	15	225
4	4408	8	64
5	4404	4	16
6	4406	6	36
7	4409	9	81
8	4410	10	100
9	4412	12	144
10	4409	9	81
Sum		92	940

Average = $\bar{x}^2$ = x/10 = (92/10) + 4400 = 4409
Variance = s^2 = Column C − (Column B)²/n/n − 1 = 940 − (92)²/10/9 = 10.4
Standard deviation, s = Variance = 10.4 = 3.22

[A] In this example the values of water equivalent are typical for a calorimeter calibrated such that the water equivalent multiplied by the temperature rise in °C/g of sample will give the calorific value of the sample in Btu/lb.

X2. THERMOMETER CORRECTIONS

X2.1 It is necessary to make the following corrections in the event they result in an equivalent change of 0.001°C or more.

X2.1.1 *Calibration Correction* shall be made in accordance with the calibration certificate furnished by the calibration authority.

X2.1.2 *Setting Correction* is necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

X2.1.3 *Differential Emergent Stem Correction*—The calculation depends upon the way the thermometer was calibrated and how it is used. The following two conditions are possible:

(*a*) *Thermometers Calibrated in Total Immersion and Used in Partial Immersion*—This emergent stem correction is made as follows:

$$\text{Correction} = K(t_c - t_a)\,(t_c + t_a - L - T)$$

where:

K = 0.00016 for thermometers calibrated in °C, 0.00009 for thermometers calibrated in °F,
L = scale reading to which the thermometer was immersed,
T = mean temperature of emergent stem,
t_a = initial temperature reading, and
t_c = final temperature reading.

NOTE X2.1: *Example*—Suppose the point L, to which the thermometer was immersed was 16°C; its initial reading, t_a, was 24.127°C, its final reading, t_c, was 27.876°C, the mean temperature of the emergent stem, T, was 26°C,

then:

Differential stem correction

$$= +0.00016\,(28 - 24)\,(28 + 24 - 16 - 26)$$
$$= +\,0.006°\text{C}$$

(*b*) *Thermometers Calibrated and Used in Partial Immersion but at a Different Temperature than the Calibration Temperature*—This emergent stem correction is made as follows:

$$\text{Correction} = K\,(t_c - t_a)\,(t_1 - t^*)$$

where:

K = 0.00016 for thermometers calibrated in °C, 0.00009 for thermometers calibrated in °F,
t_a = initial temperature reading,
t_c = final temperature reading,
t_1 = observed stem temperature, and
t^* = stem temperature at which the thermometer was calibrated.

NOTE X2.2: *Example*—Suppose the initial reading, t_a, was 80°F, the final reading, t_c, was 86°F, and that the observed stem temperature, t_1, was 82°F, and the calibration temperature, t^*, was 72°F; then:

Differential stem correction

$$= 0.00009\,(86 - 90)(82 - 72)$$
$$= 0.005°\text{F}$$

X3. THERMOCHEMICAL CORRECTIONS

X3.1 *Heat of Formation of Nitric Acid*—A correction (e^1, in 12.3) of 20 J is applied for each 1 mL of standard Na_2CO_3 solution used in the acid titration. The standard solution (0.34 *N*) contains 18.02 g of Na_2CO_3/L. This correction is based on assumption that all the acid titrated is HNO_3 formed by the following reaction: ½ N_2 (g + 5/4 O_2 (g) + ½ H_2O (l) = HNO_3 (in 500 mol H_2O), and (*2*) the energy of formation of 1 mol of HNO_3 is approximately 500 mol of water under bomb conditions is 14.1 kcal/mol.[6] When H_2SO_4 is also present part of the correction for H_2SO_4 is contained in the e_1 correction and the remainder in the e_2 correction.

X3.2 *Heat of Formation of Sulfuric Acid*—By definition the gross calorific value is obtained when the product of the combustion of sulfur in the sample is SO_2 (g). However, in actual bomb combustion processes, the sulfur is found as H_2SO_4 in the bomb washings. A correction (e_2 in 12.4.1) of 55.2 J is applied for each percent of sulfur in the 1-g sample, that is converted to H_2SO_4. This correction is based upon the energy of formation of H_2SO_4 in solutions such as will be present in the bomb at the end of a combustion. This energy is taken as −70.5 kcal/mol.[11] A correction, of 2 × 14.1 kcal/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is 70.5 − (2 × 14.1) = 42.3 kcal/mol or 5520 J of sulfur in the sample (55.2 J × weight of sample in grams × % sulfur in sample).

X3.2.1 The value of 5520 J/g of sulfur is based on a coal containing about 5 % sulfur and about 5 % hydrogen. The assumption is also made that the H_2SO_4 is dissolved entirely in water condensed during combustion of the sample.[12] If a 1-g sample of such a fuel is burned, the resulting H_2SO_4 condensed with water formed on the walls of the bomb will have a ratio of about 15 mol of water to 1 mol of H_2SO_4. For this concentration the energy of the reaction.

$$SO_2\ (g) + \tfrac{1}{2}O_2\ (g) + H_2O\ (l) = H_2SO_4\ (\text{in 15 mol } H_2O)$$

under the conditions of the bomb process is −70.5 kcal/mol.

X3.2.2 Basing the calculation upon a sample of comparatively large sulfur content reduces the overall possible errors, because for smaller percentages of sulfur the correction is smaller.

X3.3 *Fuse Wire*—Calculate the heat in SI units contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the heat of combustion of No. 34 B & S gage Chromel C wire

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[11] Calculated from data in National Bureau of Standards Circular 500.

[12] Mott, R. A., and Parker, C., "Studies in Bomb Calorimetry IX-Formation of Sulfuric Acid," *Fuel*, Vol 37, 1958, p. 371.

is equivalent to 9.6 J/cm or 5980 J/g and that of No. 34 B & S gage iron wire is equivalent to 11.3 J/cm or 7330 J/g. There is no correction for platinum or palladium wire provided the ignition energy is constant.

X4. REPORTING RESULTS IN OTHER UNITS

X4.1 *Reporting Results in British Thermal Units (Btu) per Pound*—The gross calorific value can be expressed in British thermal units by using the thermochemical correction factors in Table X4.1 and the water equivalent expressed in (Btu/lb) × (g/°C).

TABLE X4.1 Thermochemical Correction Factors (Units in BTU)

Correction	Multiplication Factor	Multiply by
e_1 (HNO_3)	10.0	mL of 0.394 *N* Na_2CO_3 solution
e_2 (H_2SO_4)	23.7	% of sulfur in sample times weight of sample in grams
e_3 (fuse wire)	4.1 or	cm of No. 34 B & S gage Chromel C wire
	2570	weight (g) of Chromel C wire
e_3 (fuse wire)	4.9 or	cm of No. 34 B & S gage iron wire
	3150	weight (g) of iron wire

Designation: E 775 – 87

Standard Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel[1]

1. Scope

1.1 These test methods cover two alternative procedures for the determination of total sulfur in prepared analysis samples of solid forms of refuse-derived fuel (RDF). Sulfur is included in the ultimate analysis of RDF.

1.2 The test methods appear in the following order:

Test	Sections
Eschka Method	8 to 11
Bomb Washing Method	12 to 13

1.3 These test methods may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.4 The values stated in inch-pound units are to be regarded as standard. The values given in parentheses are for information only.

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

E 711 Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter[4]

E 829 Method of Preparing RDF-3 Laboratory Samples for Analysis[4]

3. Description of Term Specific to This Standard

3.1 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*:[5]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

4. Summary of Methods

4.1 *Eschka Method*—A weighed sample and Eschka mixture are ignited together and the sulfur is precipitated from the resulting solution as barium sulfate ($BaSO_4$). The precipitate is filtered, ashed, and weighed.

4.2 *Bomb Washing Method*—Sulfur is precipitated as $BaSO_4$ from the oxygen-bomb calorimeter washings and the precipitate is filtered, ashed, and weighed.

5. Significance and Use

5.1 The standards are available to producers and users of RDF for determining the total sulfur content of the fuel.

6. Precautions

6.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under negative pressure hood when possible; and washing hands before eating or smoking.

7. Sampling

7.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative laboratory sample from the RDF lot to be characterized.

7.2 The sampling method for this procedure should be based on agreement between the involved parties.

7.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in methods E 829. This procedure must be performed carefully to preserve the sample's representative characteristics (other than particle size) while preparing the analysis sample to be used in the procedures.

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[1] These test methods are under the jurisdiction of ASTM Committee E-38 on Resource Recovery and are the direct responsibility of Subcommittee E38.01 on Energy.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] *Annual Book of ASTM Standards*, Vol 11.04.

[5] *Thesaurus on Resource Recovery Terminology*, *ASTM STP 832*, ASTM, 1983, p. 72.

TEST METHOD A—ESCHKA METHOD

8. Apparatus

8.1 *Gas (Note 1) or Electric Muffle Furnace or Burners*, for igniting the sample with Eschka mixture and for igniting the barium sulfate ($BaSO_4$).

NOTE 1—Gas may contain sulfur compounds in sufficient quantities to affect the results.

8.2 *Crucibles or Capsules*—Porcelain capsules, ⅞ in. (22 mm) in depth and 1¾ in. (44 mm) in diameter, or porcelain crucibles of 30-mL capacity, high or low-form, or platinum crucibles of similar size shall be used for igniting the sample with the Eschka mixture. Porcelain, platinum, Alundum, or silica crucibles of 10 to 15-mL capacity shall be used for the final ignition step (see 10.3.8).

9. Reagents

9.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available. Other grades[6] may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

9.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type III conforming to Specification D 1193.

9.3 *Barium Chloride Solution* (100 g/L)—Dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) and dilute to 1 L with water.

9.4 *Bromine Water* (saturated)—Add an excess of bromine to 1 L of water.

9.5 *Eschka Mixture*—Thoroughly mix 2 parts by weight of light calcined magnesium oxide (MgO) with 1 part of anhydrous sodium carbonate (Na_2CO_3). Both materials should be as free as possible from sulfur.

9.6 *Hydrochloric Acid* (1 + 1)—Mix equal volumes of concentrated HCl (sp gr 1.19) and water.

9.7 *Hydrochloric Acid* (1 + 9)—Mix 1 volume of concentrated HCl (sp gr 1.19) with 9 volumes of water.

9.8 *Methyl Orange Indicator Solution* (0.2 g/L)—Dissolve 0.2 g of methyl orange in 1000 mL of hot water and filter.

9.9 *Sodium Carbonate* (saturated solution)—Dissolve approximately 60 g of crystallized sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) or 20 g of anhydrous sodium carbonate (Na_2CO_3) in 100 mL of water, using a sufficient excess of Na_2CO_3 to ensure a saturated solution.

9.10 *Sodium Hydroxide Solution* (100 g/L)—Dissolve 100 g of sodium hydroxide ($NaOH$) in 1 L of water. This solution may be used in place of Na_2CO_3 solution.

10. Procedure

10.1 *Preparation of Sample and Eschka Mixture*—Weigh to the nearest 0.1 mg about 1 g of mixed air-dried analysis sample and 3 g of Eschka mixture on glazed paper. Mix thoroughly. The amount of sample to be taken will depend on the amount of $BaCl_2$ solution required (see 10.3.5 and Note 2).

10.1.1 Quantitatively transfer the mixture to a porcelain capsule or porcelain crucible or platinum crucible, and cover with about 1 g of Eschka mixture.

10.2 *Ignition*—Heat the crucible over a gas flame as described in 10.2.1, or in a gas- or electrically heated muffle furnace as described in 10.2.2. The use of artificial gas for heating the sample and Eschka mixture is permissible only when the crucibles are heated in a muffle (see Note 2).

10.2.1 Heat the crucible, placed in a slanting position partially covered on a triangle, over a very low flame. This prevents rapid expulsion of the volatile matter and affords more complete oxidation of the sulfur. After 30 min of low flame heating, gradually increase the temperature and occasionally stir the mixture until all black particles have disappeared, which is an indication of complete combustion.

10.2.2 Place the crucible in a cold muffle furnace and gradually raise the temperature to 800 ± 25°C in about 1 h. Maintain this maximum temperature until upon stirring all black particles have disappeared (about 1½ h).

10.3 *Subsequent Treatment:*

10.3.1 Remove the crucible, cool, and empty the contents quantitatively into a 200-mL beaker. Digest with 100 mL of hot water for ½ to ¾ h with occasional stirring.

10.3.2 Decant the supernatant liquid through a filter into a 600-mL beaker. Wash the insoluble matter with hot water several times using 25 mL of water at each washing and filter the washings through the filter paper into the 600-mL beaker. After washing, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated, collecting the wash waters in the 600-mL beaker.

10.3.3 Treat the filtrate with 10 to 20 mL of saturated bromine water. Make slightly acid with HCl and boil to expel the liberated bromine.

10.3.4 Neutralize using methyl orange indicator with $NaOH$ or Na_2CO_3 solution; then add 1 mL of HCl solution (1 + 9).

10.3.5 Boil again and then, while stirring constantly, add slowly from a pipet 10 mL or more of $BaCl_2$ solution.

NOTE 2—Barium chloride solution must be added in excess. If more than 10 mL of $BaCl_2$ solution is required, reduce the weight of sample to about 0.5 g and repeat the ignition and digestion.

10.3.6 Continue boiling for 15 min and allow to stand for at least 2 h, or preferrably overnight, at a temperature just below boiling.

NOTE 3—When standing overnight at a temperature slightly less than boiling, cover the flask with a watchglass to prevent the solution from evaporating to dryness and to protect it from external contamination.

10.3.7 Filter the solution and the precipitate of barium sulfate ($BaSO_4$) through an ashless paper and wash the $BaSO_4$ residue with hot water until 1 drop of silver nitrate ($AgNO_3$) solution produces no more than a slight opalescence when added to 8 to 10 mL of filtrate.

10.3.8 Place the wet filter containing the precipitate of barium sulfate ($BaSO_4$) in a preweighed platinum, porcelain, silica, or Alundum crucible, allowing a free access of air by

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[6] "Reagent Chemicals, American Chemical Society Specification," *American Chemical Society*, Washington, DC. For suggestions on testing of reagents not listed by the American Chemical Society, see *Reagent Chemicals and Standards* (1967 revised edition) by Joseph Rosin, D. Van Nostrand Co., Inc., New York and the *United States Pharmacopeia*

folding the paper over the precipitate loosely to prevent spattering.

10.3.9 Smoke the paper off gradually over a gas burner or in a gas or electrically heated muffle furnace. At no time allow it to burn with a flame (see Note 4). After charring of the paper, raise the temperature to approximately 925°C and heat to constant weight.

NOTE 4—Partially covering the crucible while smoking and smoldering will aid in the prevention of the flaming of the paper.

10.3.10 Transfer the crucibles to a desiccator and weigh when cooled to room temperature.

10.4 *Blanks and Corrections*—In all cases a correction must be applied. Either a reagent blank may be run exactly as described above, using the same amount of all reagents that were employed in the routine determination, or a more accurate correction may be made by analyzing a weighed portion of a standard sulfate using the prescribed reagents and operations.

NOTE 5—If the latter procedure is carried out once a week, or whenever a new supply of a reagent is used for a series of solutions covering the approximate range of sulfur concentrations in the samples, it is only necessary to add or subtract from the weight of $BaSO_4$ determined for the sample the deficiency or excess found by the appropriate "check" determination. This procedure is more accurate than the simple reagent blank because, for the amounts of sulfur in question and condition of precipitation prescribed, the solubility error for $BaSO_4$ is probably the largest one considered. Barium sulfate is soluble in acids[7] and in pure water, and the solubility limit is reached almost immediately on contact with the solvent. Hence, if very high-purity reagents are used or extra precaution is exercised, there may be no sulfate apparent in the "blank." In other words, the solubility limit for $BaSO_4$ has not been reached or at any rate not exceeded; consequently, some sulfate in the sample may remain in solution or has redissolved.

11. Calculations

11.1 Calculate the sulfur content as follows:

$$\text{Sulfur, \%} = (A - B) \times 13.738/W$$

where:

A = grams of $BaSO_4$ precipitated,
B = grams of $BaSO_4$ correction,
W = grams of sample used, and
13.738 = percentage of sulfur in $BaSO_4$.

TEST METHOD B—BOMB WASHING METHOD[8]

12. Reagents

12.1 *Purity of Reagents*—see 9.1.

12.2 *Purity of Water*—see 9.2.

12.3 *Ammonium Hydroxide* (sp gr 0.90)—Concentrated ammonium hydroxide (NH_4OH).

12.4 *Bromine Water* (saturated)—see 9.4.

12.5 *Hydrochloric Acid* (1 + 1)—see 9.6.

12.6 *Sodium Carbonate Solution*—Dissolve 18.02 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 L. The Na_2CO_3 should be previously dried for 24 h at 105°C.

NOTE 6—Other concentrations of sodium carbonate solution may be used.

12.7 *Wash Solution*—Dilute 1 mL of a saturated solution of methyl orange to 1 L of water.

13. Procedure

13.1 *Ignition*—Sulfur is determined in the washings from the oxygen-bomb calorimeter following calorimetric determination in accordance with Test Method E 711. The type of bomb, amount of water in the bomb, oxygen pressure, and amount of sample taken shall be the same as specified under the calorimetric determination. The bomb shall stand in the calorimeter water for not less than 5 min after firing.

13.2 *Subsequent Treatment:*

13.2.1 Remove the bomb from the calorimeter water and open the valve carefully so as to allow the gases to escape at an approximately even rate so the pressure is reduced to atmospheric in not less than 1 min. Bombs equipped with valves other than needle valves, such as compression valves, shall be provided with a device so the valve can be controlled to permit a slow and uniform release of the gases.

13.2.2 Open the bomb and examine the inside for traces of unburned material or sooty deposit. If these are found, discard the determination. Wash carefully all parts of the interior of the bomb, including the capsule with a fine jet of water containing methyl orange (12.7) until no acid reaction is observed. It is essential to wash through the valve opening in the case of bombs equipped with compression valves, or other types of valves with large openings, as considerable spray may collect in such valve openings.

13.2.3 Collect the washings in a 250-mL beaker and titrate with standard sodium carbonate solution (12.6) to obtain the acid correction for the heating value, as specified in the calorimetric determination of Test Method E 711.

13.2.4 Adjust the pH to between 5.5 and 7.0 with dilute NH_4OH and heat the solution to boiling.

13.2.5 Filter through a qualitative filter paper and wash the residue and paper thoroughly five or six times with hot water collecting the filtrate and washings.

13.2.6 To the filtrate and washings add 1 mL of saturated bromine water (12.4) and sufficient HCl (12.5) to make it slightly acid. Boil the solution to expel the excess bromine.

13.2.7 Adjust the acidity, precipitate and determine the sulfur as described in 10.3.4 through 11.1 inclusive.

14. Precision and Bias[9]

14.1 *Precision:*

14.1.1 The standard deviation of individual determinations in percent absolute, are as follows:

Typical average value	0.35 %
Within-laboratory	0.03 %
Between-laboratory	0.06 %

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[7] Allen, E. T., and Johnston, John, "The Exact Determination of Sulfur in Soluble Sulfates," *Journal of the American Chemical Society*, Vol 32, No. 5, 1910, pp. 588-617; and Johnston, John, and Adams, L. H., "The Phenomenon of Acclusion in Precipitates of Barium Sulfate, and its Relation to the Exact Determination of Sulfate," *Journal of the American Chemical Society*, Vol 33, No. 6, 1911, pp. 829-845.

[8] Selvic, W. A. and Fieldner, A. C., "Check Determinations of Sulfir in Coal and Coke by the Eschka, Bomb Washing and Sodium Peroxide Fusion Methods," *Industrial and Engineering Chemistry*, Vol 29, 1927, pp. 729-733.

[9] Data from preliminary testing and round-robin tests are on file in ASTM Research Report RR-E38-1000. A copy of the report is available on loan from ASTM Headquarters, 1916 Race St., Philadelphia, PA 19103.

14.1.2 The above precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.[9]

14.2 *Bias*—The bias of this test method has not been determined because of the lack of a recognized standard reference material.

Designation: E 777 – 87

Standard Test Method for Carbon and Hydrogen in the Analysis Sample of Refuse-Derived Fuel[1]

This standard is issued under the fixed designation E 777; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of total carbon and hydrogen in a sample of refuse-derived fuel (RDF). Both carbon and hydrogen are determined in one operation. This test method yields the total percentages of carbon and hydrogen in RDF as analyzed and the results include not only the carbon and hydrogen in the organic matter, but also the carbon present in mineral carbonates and the hydrogen present in the free moisture accompanying the analysis sample as well as hydrogen present as water of hydration.

NOTE 1—It is recognized that certain technical applications of the data derived from this test procedure may justify additional corrections. These corrections could involve compensation for the carbon present as carbonates, the hydrogen of free moisture accompanying the analysis sample, and the calculated hydrogen present as water of hydration.

1.2 This test method may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements see Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

E 790 Test Method for Residual Moisture in Refuse-Derived Fuel Analysis Sample[4]

E 791 Method for Calculating Refuse-Derived Fuel Analysis Data From As-Determined to Different Bases[4]

E 829 Method of Preparing RDF-3 Laboratory Samples for Analysis[4]

3. Description of Term Specific to This Standard

3.1 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*:[5]

RDF-1— Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-inch square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

4. Summary of Test Method

4.1 The determination is made by burning the sample to convert all of the carbon to carbon dioxide and all of the hydrogen to water. The combustion is carried out by high purity oxygen that has been passed through a purifying train. The carbon dioxide and water are recovered in an absorption train. The combustion tube packing is used to remove any interfering substances. This test method gives the total percentages of carbon and hydrogen in the RDF as analyzed, including the carbon in carbonates and the hydrogen in any form of water.

5. Significance and Use

5.1 The standard sample is available to producers and users of RDF as a method of determining the weight percent of carbon and hydrogen in the analysis sample.

5.2 Carbon and hydrogen are part of the ultimate analysis of a fuel and can be used for calculations of combustion parameters.

6. Apparatus

6.1 *Oxygen-Purifying Train*—The high-purity oxygen is passed through water and carbon dioxide absorbers prior to use for combustion. The oxygen-purifying train consists of the following three units in order of passage of oxygen (see Fig. 1):

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

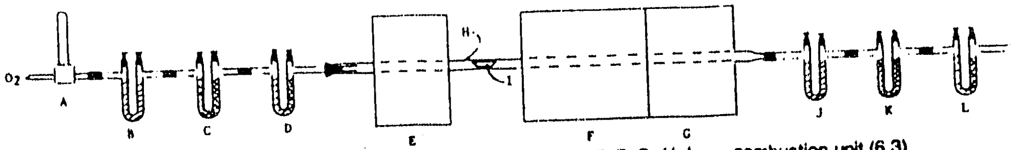
Current edition approved Aug. 28, 1987. Published October 1987. Originally published as E 777 – 81. Last previous edition E 777 – 81.

[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] *Annual Book of ASTM Standards*, Vol 11.04.

[5] *Thesaurus on Resource Recovery Terminology*, *ASTM STP 832*, ASTM, 1983, p. 72.



A = flowmeter (6.2)
B, C, D = oxygen purifying train (6.1)
B = first water absorber (6.1.1)
C = carbon dioxide absorber (6.1.2)
D = second water absorber (6.1.3)

E, F, G, H, I = combustion unit (6.3)
E = furnace section 1 (6.3.1)
F = furnace section 2 (6.3.2)
G = furnace section 3 (6.3.3)
H = combustion tube (6.3.4)
I = combustion boat (6.3.5)

J, K, L = absorption train (6.4)
J = first water absorber (6.4.1)
K = carbon dioxide absorber (6.4.2)
L = guard tube (6.4.3)

NOTE—*C* and *K* can substitute a Vanier bulb if liquid absorbent is used.

FIG. 1 Set-Up of Apparatus

6.1.1 *First Water Absorber*—A container constructed so that the oxygen must pass through a column of reagent. The container shall have a capacity for at least 45 cm^3 of solid reagent, and the minimum gas travel through the reagent shall be at least 80 mm. A container of large volume and long path of oxygen travel through the reagent will be found to be advantageous where many carbon and hydrogen determinations are made.

6.1.2 *Carbon Dioxide Absorber*—If solid reagents are used for carbon dioxide absorption, the container shall be as described in 6.1.1. If a solution is used, the container shall be a Vanier bulb. It shall provide a column of reagent adequate to remove the carbon dioxide completely.

6.1.3 *Second Water Absorber*—Same as specified in 6.1.1.

6.2 *Flowmeter*, used to permit volumetric measurement of the rate of flow of oxygen during the determination. It shall be suitable for measuring flow rates within the range from 50 to 100 mL/min (standard temperature and pressure). The use of a double-stage pressure-reducing regulator with gage and needle valve is recommended to permit easy and accurate adjustment to the rate of flow.

6.3 *Combustion Unit*, consisting of three electrically heated furnace sections, individually controlled, which may be mounted on rails for easy movement. The upper part of each furnace may be hinged so that it can be opened for inspection of the combustion tube. The three furnace sections shall be as follows (see Fig. 1):

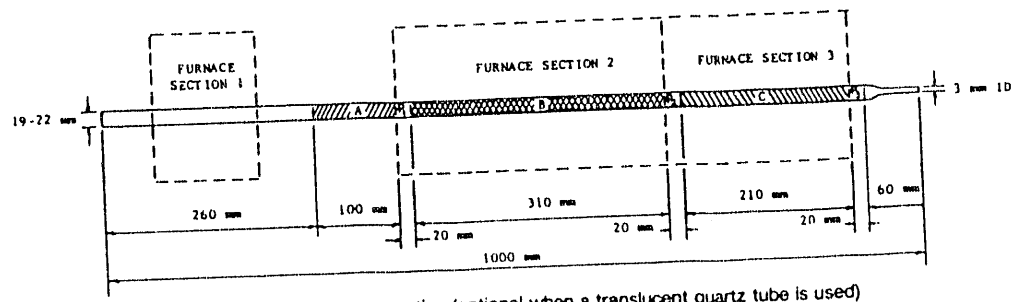
6.3.1 *Furnace Section 1*—Furnace section 1 is nearest the oxygen inlet end of the combustion tube, approximately 130 mm long and used to heat the inlet end of the combustion tube and the sample. It shall be capable of rapidly attaining an operating temperature of 875 ± 25°C.

NOTE 2—Combustion tube temperature shall be measured by means of a thermocouple placed immediately adjacent to the tube near the center of the appropriate tube section.

6.3.2 *Furnace Section 2*—Furnace section 2 shall be approximately 330 mm in length and used to heat that portion of the tube filled with cupric oxide. The operating temperature shall be 850 ± 20°C (see Note 2).

6.3.3 *Furnace Section 3*—Furnace section 3 shall be approximately 230 mm long, and used to heat that portion of the tube filled with lead chromate or silver. The operating temperature shall be 500 ± 50°C.

6.3.4 *Combustion Tube*, made of fused quartz, or high-silica glass and having a nominal inside diameter which may vary within the limits of 19 to 22 mm and a minimum total length of 970 mm. The exit end shall be tapered down to provide a tubulated section for connection to the absorption train. The tubulated section shall have a length of 20 to 25 mm, an internal diameter of not less than 3 mm, and an



A = clear fused quartz section (optional when a translucent quartz tube is used)
B = cupric oxide filling
C = lead chromate or silver gauze filling
P_1, P_2, P_3 = oxidized copper gauze plugs

NOTE—When furnace sections longer than those specified in 6.3 are to be used, changes in the above dimensions shall be in accordance with provisions of Note 5.

FIG. 2 Arrangement of Tube Filling for Combustion Tube external diameter of approximately 7 mm. The total length of the reduced end shall not exceed 60 mm. If a translucent fused quartz tube is used, a transparent section 190 mm long, located 250 mm from the oxygen inlet end of the tube, will be found convenient (see Fig. 2).

6.3.5 *Combustion Boat,* made of glazed porcelain, fused silica, or platinum. Boats with internal dimensions of approximately 70 by 8 by 8 mm have been found convenient.

6.4 *Absorption Train,* identical to the oxygen absorption train indicated in 5.1 to obtain system equilibrium. Therefore, the absorption train shall consist of the following units arranged as listed in the order of passage of oxygen (see Fig. 1):

6.4.1 *First Water Absorber,* as described in 5.1.1.

6.4.2 *Carbon Dioxide Absorber,* as described in 5.1.2.

6.4.3 *Second Water Absorber,* as described in 6.1.3. The second water absorber is also known as a guard tube.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean reagent water, Type III, conforming to Specification D 1193.

7.3 *Oxygen,* with minimum acceptable purity 99.5 %.

NOTE 3—If the blank tests for flow (see 9.3.2) indicate interfering impurities in the oxygen supply by consistent weight-gain in the absorbers, eliminate these impurities by using a preheater furnace and tube, filled with cupric oxide. Operate this preheater at 850 ± 20°C and insert in series between the supply tank of oxygen and the purification train.

7.4 *Combustion Tube Reagents:*

7.4.1 *Cupric Oxide* (CuO), wire form, dust-free.

7.4.2 *Fused Lead Chromate* ($PbCrO_4$), approximately 2.38 to 0.84 mm in size.

7.4.3 *Silver Gauze,* 99.9 % silver minimum purity, 0.84 mm, made from approximately No. 27 B&S gage wire.

7.4.4 *Copper Gauze,* 99.0 % copper minimum purity, 0.84 mm, made from approximately No. 26 B&S gage wire.

7.5 *Purification and Absorption Train Reagents:*

7.5.1 *Water Absorbent*—Anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) approximately 2.38 to 0.35 mm in size.[7]

7.5.2 *Carbon Dioxide Absorbent*—If a solid reagent is used, it shall be sodium or potassium hydroxide (NaOH or KOH) impregnated in an inert carrier approximately 2.38 to 0.84 mm in size. Use of soda lime in place of the above or in admixture with them is permissible (Note 4). If a solution is used, it shall be 30 weight % potassium hydroxide (KOH).

NOTE 4—Acceptable carbon dioxide absorbing reagents using sodium or potassium hydroxide are sold under the tradenames: Ascarite, Caroxite, and Mikohbite. If soda lime is used in admixture with any of the foregoing, it should not exceed 30 weight % of the total reagent. In using Ascarite it may be necessary to add a few drops of water to the reagent to assure complete absorption of carbon dioxide.

8. Precautions

8.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under a negative pressure hood when possible; and washing hands before eating or smoking.

9. Preparation of Apparatus

9.1 *Combustion Tube Packing*—To ensure complete oxidation of combustion products and complete removal of interfering substances such as oxides of sulfur, the combustion tube shall be packed with cupric oxide and lead chromate or silver gauze. The arrangement and lengths of the tube fillings and separating plugs shall be as shown in Fig. 2 (see Note 5). It is recommended that the tube be placed in a vertical position (constricted end downward) for packing. When filling the tube with lead chromate, any residual reagent adhering to the walls of the empty portion of the tube must be removed. When silver gauze is used as a tube filling, the required length of filling may be prepared conveniently from three or four strips 150 to 200 mm in length, by rolling each strip into a cylindrical plug and inserting the strips end-to-end in the tube.

NOTE 5—Longer furnaces with appropriate lengths of tube packing will be satisfactory.

9.2 *Purification and Absorption Trains:*

9.2.1 *Water Absorbers*—Fill a container, described in 6.1.1, with a permissible solid desiccant, as described in 7.5.1, by adding the required amount in small portions and settling each portion by gently tapping between additions. Place a glass wool plug between the reagent and absorber outlet to prevent loss of reagent dust.

9.2.2 *Carbon Dioxide Absorbers*—If a solid reagent is used for the retention of carbon dioxide, 7.5.2, fill the absorber, 6.1.2, as described in 9.2.1. Place a layer or cap of desiccant in the outlet section of the container; it shall be the same as that used in the water absorber. This layer shall have a bulk volume not less than one fourth nor more than one third of the combined volume of both reagents.

9.2.2.1 If a liquid absorbent is used, fill the inner tube of the Vanier bulb with the same desiccant used in the water absorber. If a solid absorbent is used, place a glass wool plug in the outlet section of the container to prevent loss of reagent dust.

9.2.3 *Guard Tube*—Pack a container, as described in 5.1.1, with equal volumes of the water absorbent and a solid carbon dioxide absorbent.

9.2.4 *Connections*—To ensure a closed system from the supply tank of oxygen to the guard tube at the end of the absorption train, it is recommended that all connections be glass-to-glass or glass-to-quartz butt joints with short lengths

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[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Reagent Chemicals and Standards* (1967 revised edition), by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the *United States Pharmacopeia*.

[7] Tradenames of this reagent are Anhydrone or Dehydrite.

of flexible tubing as seals. The connection between the purification train and the combustion tube may be made by means of a rubber stopper or other suitable device. All connections shall be gas tight. No lubricant shall be used for making tubing connections in the absorption train.

9.3 *Conditioning of Apparatus.*

9.3.1 *Newly Packed Combustion Tube*—Burn a sample of RDF as described in 11.4 except that the products of combustion need not be fixed in a weighed absorption train.

9.3.2 *Used Combustion Tube*—After any extended shut down (one day or more) test the combustion train under procedure conditions, but without burning a sample, for 40 min with weighed absorbers connected. A variation of not more than 0.5 mg of both water and carbon dioxide absorbers shall be considered satisfactory (see Note 3).

9.3.3 *Absorption Train*—Condition freshly packed absorbers and guard tubes by burning a sample of RDF, as described in 11.4, except that the absorber weights need not be determined.

9.3.4 Make standard checks frequently, particularly when intermittent use of the combustion train is common or when any changes have been made in the system. Burn a standard substance of certified analysis, such as benzoic acid or sucrose as furnished by the National Bureau of Standards, as described in Section 11. A variation from the theoretical of not more than 0.07 % for hydrogen nor more than 0.30 % for carbon shall be considered satisfactory.

10. Sampling

10.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative laboratory sample from the RDF lot to be characterized.

10.2 The sampling method for this procedure should be based on agreement between the involved parties.

10.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Method E 829. This procedure must be performed carefully to preserve the sample's representative characteristics (other than particle size) while preparing the analysis sample to be used in the procedures.

11. Procedure

11.1 After the combustion tube and absorbers have been conditioned as prescribed in Section 9, conduct the test as follows:

11.2 *Absorption Train*—Bring the water and carbon dioxide absorbers to room temperature near the balance for 15 to 20 min, vent momentarily to the atmosphere, wipe with a chamois or lint-free cloth in the areas where handled, and weigh the water and carbon dioxide absorbers to the nearest 0.1 mg.

11.3 *Sample*—After thoroughly mixing the RDF analysis sample to provide the best possible mix of heavy fines with milled fluff, weigh approximately 0.2 g to the nearest 0.1 mg of sample into a combustion boat.

NOTE 6—The final milling stage may produce a suitably mixed analysis sample without further mixing. It is important that no unwanted segregation of particle sizes take place. True representation of the analysis sample must be contained in the 200 mg used for the analysis.

11.4 *Sample Analysis*—With furnace sections 2 and 3 at specified temperatures and positioned as shown in Fig. 2, perform the following operations in rapid succession in the order listed:

11.4.1 If a conventional type of sample heating furnace is used for heating furnace section 1, place it so that its left-hand edge is about 100 mm from the oxygen inlet end of the combustion tube.

11.4.2 Attach the weighed absorption train to the combustion tube.

11.4.3 Push the sample boat containing the weighed sample into the combustion tube to a point within approximately 20 mm from plug P_1 (see Fig. 2).

11.4.4 Close the tube and adjust the oxygen flow to a rate of 50 to 100 mL/min (standard temperature and pressure), being the same as used in blanking (see 9.3.2).

11.4.5 Apply full heat to heating section 1 to bring it to an operating temperature of 850 to 900°C as rapidly as possible. Move the heater slowly toward the boat so that it completely covers the boat and is brought into contact with furnac section 2 over a period of 10 to 20 min (Note 7). Allow it to remain in this position for an additional 5 to 10 min, and then shut off the heat and return the sample heater to its original position. Continue the flow of oxygen through the system for 10 min (Note 9), close the absorbers under a positive pressure of oxygen and detach them from the train. Remove the absorbers to the vicinity of the balance, allow them to cool to room temperature for 15 to 20 min, vent momentarily to the atmosphere, wipe them with a chamoi or lint-free cloth in the areas handled, and finally weigh them to the nearest 0.1 mg. While the absorbers are cooling, it i recommended that the ash remaining in the combustion boat be examined for tracers of unburned carbon which, i present, will nullify the determination.

NOTE 7—Some variation in operating technique and heater manipulation may be permitted at the discretion of the analyst, provided tha it is conducive to a gradual and controlled release of volatile matter Conditions that lead to visible burning (flame combustion) of th sample shall be avoided.

NOTE 8—Since water may condense in the cooler outlet end of th combustion tube or in the inlet arm of the water absorber, the use of a external or internal heat-conducting device (a metal heat bridge) i recommended to prevent such condensation or promote reevaporatio during this flushing period.

12. Calculations

12.1 Calculate the percentage of carbon in the analysi sample as follows:

$$\text{Carbon, } \% = \frac{A}{B} \times 27.289$$

where:

A = increase in weight of CO_2 absorber, g,
B = grams of sample used, and
27.289 = percentage of carbon in CO_2.

12.2 Calculate the percentage of hydrogen in the analys sample as follows (see Note 7).

$$\text{Hydrogen, } \% = \frac{C}{B} \times 11.19$$

where:

C = increase in weight of water absorber, g,
B = grams of sample used, and
11.19 = percentage of hydrogen in water.

NOTE 9—The water absorbed in the water absorber includes not only water formed as a product of combustion, but also free water (moisture) in the sample and water of hydration of materials that may be contained in RDF.

13. Report

13.1 The results of the carbon and hydrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

13.2 The numerical moisture value established by Test Method E 790 shall be used for converting carbon and hydrogen data on the as-determined basis to the dry basis as in Test Method E 791.

14. Precision and Bias[8]

14.1 *Precision:*

14.1.1 The standard deviations of individual determinations, in percent absolute, are as follows:

Typical Average Value, %	Within-Laboratory, %	Between-Laboratories, %
Carbon:		
40	0.5	1.6
Hydrogen:		
5.4	0.2	0.5

14.1.2 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

14.2 *Bias*—The bias of this test method has not been determined because of the lack of a recognized standard reference material.

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[8] Supporting data are available on loan from ASTM Headquarters. Request RR:E38-1000.

Designation: E 778 — 87

Standard Test Methods for Nitrogen in the Analysis Sample of Refuse-Derived Fuel[1]

1. Scope

1.1 These test methods cover the determination of total Kjeldahl nitrogen in (prepared analysis) samples of (solid forms) of refuse-derived fuel (RDF). The procedures measure free ammonia or ammonia formed from the conversion of organic nitrogenous compounds such as amino acids and proteins. However, the procedures may not convert the nitrogenous compounds of some wastes to ammonia. Examples of such compounds that may not be measured are nitro compounds, hydrozones, oxines, nitrates, semicarbazones, pyridines, and some refractory tertiary amines.

1.2 Two alternatives are described for the final determination of the ammonia, the Kjeldahl-Gunning Test Method and the Acid-Titration Test Method.

1.3 The analytical data from these test methods are to be reported as part of the ultimate analysis where ultimate analysis is requested.

1.4 These test methods may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements see 7.4.1 and Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analysis[3]

E 790 Test Method for Residual Moisture in Refuse-Derived Fuel Analysis Sample[4]

E 791 Test Method for Calculating Refuse-Derived Fuel Analysis Data From As-Determined to Different Bases[4]

E 829 Method of Preparing RDF-3 Laboratory Samples for Analysis[4]

3. Description of Term Specific to This Standard

3.1 *refuse-derived fuel*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*.[5]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

4. Summary of Test Methods

4.1 The determination of nitrogen is made by either the Kjeldahl-Gunning Test Method (Section 11) or the Acid-Titration Test Method (Section 12). In both these methods the nitrogen in the sample is converted into ammonium salts by destructive digestion of the sample with a hot, catalyzed mixture of concentrated sulfuric acid and potassium sulfate. The salts are subsequently decomposed in a hot alkaline solution from which the ammonia is recovered by distillation, and finally determined by alkalimetric or acidimetric titration.

5. Significance and Use

5.1 The standard sample is available to producers and users of RDF as a method for determining the weight percent of nitrogen in the analysis sample.

5.2 Nitrogen is part of the ultimate analysis and can be used for calculation of combustion parameters.

6. Apparatus

6.1 *Digestion Unit*—An electrical heater of approximately 500-W minimum rating or a gas burner of comparable capacity. Either type of heater shall be provided with adequate means of control to maintain digestion rates as described in 11.1 (Note 1). Commercially made, multiple-unit digestion racks provided with fume exhaust ducts may be used.

NOTE 1—If commercially made electrical heaters are used, auxiliary voltage control equipment, such as an autotransformer, may be needed to maintain the specified rates of digestion and distillation.

6.2 *Distillation Unit* (Fig. 1)—An electrical heater or gas burner as described in 6.1. Either type shall be provided with adequate means of control to maintain rates as described in

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[1] These test methods are under the jurisdiction of ASTM Committee E-38 on Resource Recovery and are the direct responsibility of Subcommittee E38.01 on Energy.

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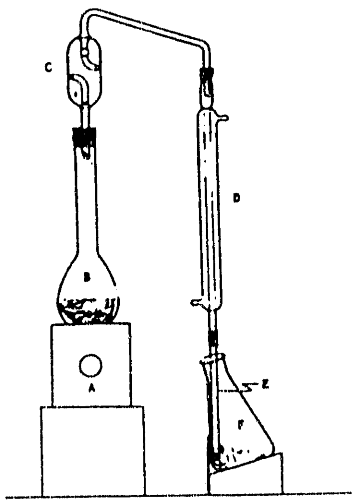
[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] *Annual Book of ASTM Standards*, Vol 11.04.

[5] *Thesaurus on Resource Recovery Terminology, ASTM STP 832*, ASTM, 1983, p. 72.



A = electric heater
B = Kjeldahl digestion flask
C = Kjeldahl connecting bulb
D = condenser
E = connecting tube
F = receiving flask

FIG. 1 Kjeldahl Distillation Apparatus

11.2. Commercially made, multiple-unit distillation racks provided with water-cooled glass or block tin condensers may be used.

6.3 *Condenser*, glass, water-cooled, having a minimum jacket length of 500 mm.

6.4 *Kjeldahl Digestion Flask*, of heat-resistant glass, having a capacity of 500 or 800 mL. Borosilicate glass has been found satisfactory for this purpose.

6.5 *Kjeldahl Connecting Bulb*, cylindrical type, 45 mm in diameter by 100 mm long, or larger, with curved inlet and outlet tubes.

6.6 *Receiving Flasks*—Erlenmeyer flask having a capacity of 250 or 300 mL.

6.7 *Connecting Tube*—Glass tubing approximately 10 mm in outside diameter by 200 mm in length.

6.8 *Pure Gum Rubber Tubing*.

7. Reagents

7.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[6] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

7.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean reagent water, Type II, conforming to Specification D 1193, prepared by the passage through an ion-exchange column containing a strongly acid cation resin in the hydrogen form.

7.3 *Potassium Sulfate* (K_2SO_4), crystals.

NOTE 2—Other satisfactory and permissible catalysts for the digestion, together with the quantities of K_2SO_4 required in their use, are as follows:

(a) Five grams of a mixture containing 32 parts by weight of K_2SO_4, 5 parts by weight of mercuric sulfate ($HgSO_4$), and 1 part by weight of selenium.

(b) Three-tenths gram of mercuric selenite ($HgSeO_3$) with 7 to 10 g of K_2SO_4.

(c) Three-tenths gram of cupric selenite dihydrate ($CuSeO_2 \cdot 2H_2O$) with 7 to 10 g of K_2SO_4. When this mixture is used, the addition of a sulfide to the alkali solution is not necessary.

7.4 *Mercury*, metal (see Note 2).

7.4.1 **Precaution**—Appropriate safety precautions should be used when handling and disposing of mercury and selenium compounds.

7.5 *Sulfuric Acid* (sp gr 1.84)—Concentrated sulfuric acid (H_2SO_4).

7.6 *Potassium Permanganate* ($KMnO_4$), crystals.

7.7 *Zinc*, mossy or granular.

7.8 *Alkali Solution*—Dissolve 8.0 g of potassium sulfide (K_2S) and 500 g of sodium hydroxide (NaOH) in water and dilute to 1 L. The use of appropriate amounts of sodium sulfide (Na_2S) or potassium hydroxide (KOH) may be substituted for the above, if desired (Note 2 (*c*)).

7.9 *Ethyl Alcohol* (95 %)—Ethyl alcohol conforming to Formula No. 30 or 2A of the U.S. Bureau of Internal Revenue. Methyl alcohol may be substituted.

7.10 *Sucrose*—National Bureau of Standards primary standard grade.

7.11 *Reagents Required for Kjeldahl-Gunning Test Method*:

7.11.1 *Methyl Red Indicator Solution* (0.4 to 1 g/L)—Dissolve 0.04 to 0.1 g of methyl red in 50 mL of 95 % ethyl alcohol or methyl alcohol and add 50 mL of water. Bromcresol green indicator solution of equal concentration may be used.

7.11.2 *Sodium Hydroxide, Standard Solution* (0.1 to 0.2 *N*)—Prepare and standardize a 0.1 to 0.2 *N* sodium hydroxide (NaOH) solution against a primary standard, as described in Practice E 200.

7.11.3 *Sulfuric Acid, Standard Solution* (0.2 *N*)—Prepare and standardize a 0.2 *N* sulfuric acid (H_2SO_4) solution as described in Practice E 200.

7.12 *Reagents Required Only for Acid-Titration Test Method*:

7.12.1 *Boric Acid Solution* (50 g/L)—Dissolve 5 g of boric acid (H_3BO_3) in 100 mL of boiling water. Allow to cool to room temperature before use.

7.12.2 *Mixed Indicator Solution*—Prepare a solution containing 0.125 % methyl red and 0.083 % methylene blue in 95 % ethyl alcohol or in methyl alcohol. Prepare fresh solution at bimonthly intervals.

7.12.3 *Sulfuric Acid, Standard Solution* (0.1 to 0.2 *N*)—Prepare and standardize a 0.1 to 0.2 *N* sulfuric acid (H_2SO_4) solution. Hydrochloric acid (HCl) of similar concentration, as described in Practice E 200, may be substituted.

8. Precautions

8.1 Due to the origins of RDF in municipal waste,

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[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Reagent Chemicals and Standards*, by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the *United States Pharmacopoeia*.

common sense dictates that precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under a negative pressure hood when possible; and washing hands before eating or smoking.

8.2 The hot acidic and basic solutions in this procedure pose a significant potential hazard. Proper laboratory safety practices and equipment should be employed throughout this procedure.

9. Sampling

9.1 RDF products are frequently nonhomogeneous. For this reason significant care should be exercised to obtain a representative laboratory sample from the RDF lot to be characterized.

9.2 The sampling method for this procedure should be based on agreement between the involved parties.

9.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Method E 829. This procedure must be performed carefully to preserve the sample's representative characteristics, other than particle size, while preparing the analysis sample to be used in the procedures.

10. Interferences and Limitations

10.1 Because of the nature of RDF, nitrogenous compounds may be present which will not readily be converted to ammonia by this test method (1.1). Modifications to the digestion of the waste may enhance the conversion of these nitrogenous compounds to the ammonium salts.[7]

11. Procedure for Kjeldahl-Gunning Test Method

11.1 *Digestion of Sample.*

11.1.1 After thoroughly mixing the RDF analysis sample to provide the best possible mix of heavy fines with milled fluff, weigh approximately 1 g to the nearest 1 mg of sample into a weighing scoop.

11.1.2 Carefully transfer the sample into a 500 or 800-mL Kjeldahl flask containing 7 to 10 g of K_2SO_4 and 0.6 to 0.8 g of mercury (see Note 3).

11.1.3 Add 30 mL of H_2SO_4 (sp gr 1.84) to the mixture by pouring it down the neck of the flask while rotating the flask to wash any sample adhering to the walls into the mixture. Swirl the contents of the flask several times to ensure thorough mixing and wetting of the sample.

11.1.4 Incline the flask at an angle of 45 to 60° on the digestion heater in a fume hood (Note 3). Heat the contents gradually. If frothing or foaming occurs, or both, lower the heat and digest at a lower temperature until the frothing or foaming ceases.

NOTE 3—When fume exhaust ducts or hoods are not available another method must be used to exhaust fumes from the flask, such as aspiration.

11.1.5 Heat the contents to boiling, controlling the heat input in such a manner that the H_2SO_4 vapors condense no more than halfway up the neck of the flask (see Note 1). Continue the digestion until all sample particles are oxidized, as evidenced by a nearly colorless solution, or for at least 2 h after the solution has reached a straw color. The total time of digestion will require 3 to 6 h.

11.1.6 When the digestion is completed and the solution has cooled, a few crystals of $KMnO_4$ may be added to ensure complete oxidation; further heating may be necesary to destroy the excess permanganate and decolorize the solution.

11.2 *Distillation of Digestate* (see Fig. 1).

11.2.1 Dilute the cooled digestion mixture to about 300 mL with water and remove any heat of dilution by cooling the flask under running water or by allowing it to stand until cool.

11.2.2 Accurately pipet 20.0 mL of 0.2 N H_2SO_4 into a 250 or 300-mL Erlenmeyer flask. Add 6 drops of methyl red or bromcresol green indicator solution.

11.2.3 Attach the glass connecting tube to the discharge end of the condenser, using a short piece of rubber tubing as a seal.

11.2.4 Incline the Erlenmeyer flask at a suitable angle and insert this tube so that the end is immersed well below the surface of the acid solution (see Fig. 1).

11.2.5 Add 1 to 2 g of granular zinc to the digestion mixture in the Kjeldahl flask (two or three small pieces, if mossy zinc is used), and slowly add 100 mL of alkali solution so that it forms a distinct layer under the acid solution. This may be accomplished by inclining the flask at an angle of 45 to 60° and pouring the alkali solution slowly down the neck of the flask. Failure to maintain discrete layers during the operation may lead to a fairly fast exothermic reaction and loss of ammonia.

11.2.6 Quickly connect the flask to the distilling condenser through the Kjeldahl connecting bulb and swirl the contents to promote thorough mixing.

NOTE 4—All connections must be air-tight so no loss of ammonia will be experienced.

11.2.7 Bring the contents of the Kjeldahl flask to a boil carefully in order to avoid bumping or foaming, or both, and distill the ammonia over into the acid solution in the Erlenmeyer flask.

11.2.8 Continue the distillation at a maximum rate of approximately 350 mL/h until 100 to 150 mL of distillate have been collected.

11.2.9 Discontinue the boiling, and remove the glass connecting tube from the condenser and Erlenmeyer flask. Rinse the tube with water, collecting the washings in the Erlenmeyer flask.

11.2.10 Titrate the excess acid in the Erlenmeyer flask to a methyl red or bromcresol green end point, using 0.1 to 0.2 N NaOH solution as the titrant.

11.3 *Blank Determination*—Run a blank determination in the same manner as described in 11.1 and 11.2, using approximately 1 g of sucrose (weighed to the nearest 1 mg) as the sample material.

NOTE 5—A blank determination must be made with every series of analyses performed. The blank determination serves two principal functions:

(1) Since the principle of the method is ascertaining the amount of standardized acid being consumed in a reaction and a back-titration is

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[7] Kolthoff, I. M., and Stenger, V. A., *Volumetric Analysis II*, Interscience Publishers, Inc., New York, NY, pp. 173–176.

necessary, the blank is a check on the concentration of the standard solutions.

(2) The blank serves as a correction for nitrogen from sources other than the sample.

12. Calculation

12.1 Calculate the percentage of nitrogen in the analysis sample as follows:

$$\text{Nitrogen, \%} = \frac{(B - A)\,N \times 0.014}{C} \times 100$$

where:

A = millilitres of NaOH solution required for titration of the sample,
B = millilitres of NaOH solution required for titration of the blank,
N = normality of the NaOH solution,
C = grams of sample used, and
0.014 = milliequivalent weight of nitrogen.

13. Procedure for Acid-Titration Test Method

13.1 *Digestion of Sample.*

13.1.1 Digest the sample as described in 11.1.

13.2 *Distillation of Digestate* (see Fig. 1).

13.2.1 Dilute the cooled digestion mixture to about 300 mL with water and remove any heat of dilution by cooling the flask under running water or by allowing it to stand until cool.

13.2.2 Add 20 mL of H_3BO_3 solution into a 250 or 300-mL Erlenmeyer flask and add 6 drops of mixed indicator solution.

13.2.3 Set up the distillation apparatus and distill as described in 11.2.3 thorugh 11.2.9.

13.2.4 Titrate the ammonia collected in the Erlenmeyer flask containing the H_3BO_3 to the mixed indicator end point using 0.2 N H_2SO_4 as the titrant.

13.3 *Blank*—Run a blank determination in the same manner as described in 11.1 and 11.2, using approximately 1 g (weighed to the nearest 1 mg) of sucrose as the samp material (Note 5 (*2*)).

14. Calculation

14.1 Calculate the percent of nitrogen in the analys sample as follows:

$$\text{Nitrogen, \%} = \frac{(A - B)\,N \times 0.014}{C} \times 100$$

where:

A = millilitres of H_2SO_4 required for titration of sample,
B = millilitres of H_2SO_4 required for titration of the bl
N = normality of H_2SO_4,
C = grams of sample used, and
0.014 = milliequivalent weight of nitrogen.

15. Report

15.1 The results of the nitrogen analysis may be reported on any number of bases, differing from each other in the manner by which moisture is treated.

15.2 The numerical moisture value established by Test Method E 790, shall be used for converting nitrogen data from the as-determined basis to the dry basis as in Test Method E 791.

16. Precision and Bias[8]

16.1 *Precision:*

16.1.1 The standard deviations of individual determinations, in percent absolute, are as follows:

Typical Average Value, %	Within-Laboratory, %	Between-Laboratories, %
0.6	0.04	0.05

16.1.2 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

16.2 *Bias*—The bias of this test method can not be determined due to the lack of a recognized standard reference material.

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[8] Supporting data are available on loan from ASTM Headquarters. Request RR:E38-1000.

Designation: E 790 – 87

Standard Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[1]

This standard is issued under the fixed designation E 790; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the measurement of the residual moisture in an analysis sample of RDF. It is used to calculate to the dry basis other determinations performed on the analysis sample. It is used with the air-dry moisture results to calculate total moisture (Note 1). The total moisture is used to calculate as-received values or other analyses performed on the sample.

NOTE 1—In some instances RDF moisture may change during the size-reduction steps of the analysis sample preparation procedure. This moisture change, unless suitable corrections are made, will affect the accuracy of the total moisture value as calculated from the air-dry and residual moisture results.

1.2 The values stated in acceptable metric units are to be regarded as standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For more specific precautionary information see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D3173 Test Method for Moisture in the Analysis Sample of Coal and Coke[2]

E 180 Practice for Developing Precision Data on ASTM Methods for Analysis and Testing of Industrial Chemicals[3]

3. Description of Terms Specific to This Standard

3.1 *air drying*—a process of partial drying of RDF to bring its moisture content near to equilibrium with the atmosphere in which further reduction, division, and characterization of the sample are to take place. In order to bring about the equilibrium, the RDF is usually subjected to drying under controlled temperature conditions ranging from 30 to 40°C.

3.2 *analysis sample*—the final subsample prepared from the air-dried laboratory sample but reduced by passing through a mill with a 0.5-mm (0.02-in.) size or smaller final screen.

3.3 *bias*—a systematic error that is consistently negative or consistently positive. The mean of errors resulting from a series of observations that does not tend towards zero.

3.4 *gross sample*—a sample representing one lot and composed of a number of increments on which neither reduction nor division has been performed.

3.5 *laboratory sample*—a representative portion of the gross sample received by the laboratory for analysis.

3.6 *lot*—a large designated quantity (greater than the quantity of the final sample) of RDF which can be represented by a properly selected gross sample.

3.7 *precision*—a term used to indicate the capability of a person, an instrument, or a method to obtain reproducible results; specifically, a measure of the random error as expressed by the variance, the standard error, or a multiple of the standard error.

3.8 *refuse-derived fuels*—solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832*:[4]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

3.9 *representative sample*—a sample collected in such a manner that it has characteristics equivalent to the lot sample.

3.10 *sample division*—the process of extracting a smaller sample from a sample so that the representative properties of the larger sample are retained. During this process it is assumed that no change in particle size or other characteristics occurs.

3.11 *sample preparation*—the process that includes drying, size reduction, division, and mixing of a laboratory sample for the purpose of obtaining an unbiased analysis sample.

3.12 *sample reduction*—the process whereby sample particle size is reduced without change in sample weight.

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

Current edition approved Aug. 28, 1987. Published October 1987. Originally published as E 790 – 81. Last previous edition E 790 – 81.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 15.05.

[4] *Thesaurus on Resource Recovery Terminology*, *ASTM STP 832*, ASTM, 1983, p. 72.

3.13 *significant loss*—any loss that introduces a bias in final results that is of appreciable importance to concerned parties.

4. Summary of Test Method

4.1 This test method is based on the loss in weight of an air-dried analysis sample of RDF under rigidly controlled conditions of temperature, time, and air flow.

4.2 The total moisture is calculated from the loss or gain in air drying and the residual moisture as determined by this test method.

5. Significance and Use

5.1 The treatment of the sample as specified herein is intended for the purpose of determining the residual moisture present in an analysis sample of RDF.

5.2 The residual moisture value is used to convert as-determined analyses such as gross heating value, sulfur, and ash to a dry sample basis.

6. Apparatus

6.1 *Drying Oven*:

6.1.1 *Referee Type*—The oven shall be so constructed as to have a uniform temperature within the specimen chamber, have a minimum excess air volume, and be capable of constant temperature regulation at 107 ± 3°C. Provision shall be made for renewing the preheated air in the oven at the rate of two to four times a minute, with the intake air dried by passing it through a desiccant. An oven similar to the one illustrated in Fig. 1 of Test Method D 3173 is suitable.

6.1.2 *Routine Type*—A drying oven of either the mechanical or natural circulation type which is capable of constant uniform temperature within the specimen chamber regulated at 107 ± 3°C.

NOTE 2—Either type of oven may be used for routine determinations. However, the referee-type oven shall be used to resolve differences between determinations.

6.2 *Containers*—A convenient form that allows the ash determination to be made on the same sample is a porcelain capsule 22 mm in depth and 44 mm in diameter or a fused silica capsule of similar shape. This shall be used with a well-fitting flat aluminum cover. Platinum crucibles or glass capsules with ground-glass caps may also be used. They should be as shallow as possible consistent with convenient handleability.

6.3 *Analytical Balance*, with 0.1 mg sensitivity.

6.4 *Analysis Sample Containers*—Heavy (minimum 4 mil), vapor-impervious bags, properly sealed; or noncorroding cans, glass jars, or plastic bottles with air-tight sealing covers to store RDF samples for analysis. Containers shall be checked for suitability by measuring weight loss or gain of the sample and container stored for 1 week under ambient laboratory conditions. The weight loss or gain should be less than 0.5 % of the sample weight stored in the container.

7. Precautions

7.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially when shredding RDF samples; conducting tests under negative pressure hood when possible; and washing hands before eating or smoking.

7.2 Laboratory sample handling shall be performed by trained personnel. All operations shall be done rapidly as possible to avoid sample moisture changes due to atmospheric exposure.

7.3 Since heavy fine particles tend to segregate rapidly in the RDF analysis sample, the analyst should exercise care to assure that the analysis sample is well-mixed prior to performing this determination.

7.4 When the residual moisture is to be used for the determination of total moisture, special care shall be taken to avoid any change in sample moisture between the completion of air drying and analysis for residual moisture. It is recommended that the delay between sample preparation and the determination of residual moisture be a maximum of 72 h.

8. Sampling[5]

8.1 RDF products are frequently nonhomogeneous. For this reason, significant care should be exercised to obtain a representative laboratory sample from the RDF lot to be characterized.

8.2 The sample method for this procedure should be based on agreement between the involved parties.

8.3 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen for this analysis. This procedure must be performed carefully to preserve the sample's representative characteristics (other than particle size) while preparing the analysis sample to be used in this procedure.

9. Procedure

9.1 Heat the empty containers and covers under the conditions at which the sample is to be dried, place the stopper or cover on the container, cool over a desiccant for about 15 to 20 min, and weigh. Mix the sample, if necessary, and dip out with a spoon or spatula from the sample bottle approximately 1 g of the sample. Put the sample quickly into the container, cover, and weigh at once.

NOTE 3—If weighing bottles with air-tight covers are used, it may not be necessary to preheat the moisture analysis container nor to desiccate it after drying.

9.2 Remove the cover and place in a desiccator. Quickly place the uncovered container into an oven preheated to 107 ± 3°C through which is passed a current of dry air. Close the oven at once and heat for 1 hr. Open the oven, remove, cover the container quickly, and cool in a desiccator over desiccant. Weigh the sample and container as soon as cooled to room temperature.

10. Calculations (see Note 1)

10.1 Calculate the percent residual moisture, R, in the analysis sample as follows:

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[5] ASTM Subcommittee E38.01 is currently in the process of developing procedures for sampling RDF and the preparation of an analysis sample. The chairman of E38.01 should be contacted for details.

$$R = \frac{S - B}{S} \times 100$$

where:

S = grams of analysis sample used, and

B = grams of sample after heating.

10.2 Calculate the percent total moisture in the laboratory sample, as follows:

$$M = \frac{R\,(100 - A)}{100} + A$$

where:

R = residual moisture, %, and

A = air dry loss determined during preparation of the analysis sample, %.

10.3 To convert other parameters determined on the analysis sample, such as ash, sulfur, and gross calorific value, to a dry sample basis, the following equation can be used:

$$P_{dry} = \frac{P_{ad}\,(100)}{100 - R}$$

where:

P_{ad} = parameter, % "as-determined" on the analysis sample,

R = residual moisture, % (see 10.1), and

P_{dry} = parameter, % expressed on a dry sample basis.

11. Precision and Bias

11.1 *Precision:*

11.1.1 The standard deviations of individual determinations, in percent absolute are as follows:

Typical Average Value	Within Laboratories	Between Laboratories
2.5–4.5 %	0.15 %	0.50 %

11.1.2 The above precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

11.2 *Bias*—The bias of this test method has not been determined due to a lack of a recognized standard reference material.

Designation: E 828 – 81 (Reapproved 1987)$^{\epsilon 2}$

Standard Test Method for Designating the Size of RDF-3 From its Sieve Analysis[1]

This standard is issued under the fixed designation E 828; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

$^{\epsilon 1}$ NOTE—Sections 3, 4, and 5 were renumbered editorially in July 1987.
$^{\epsilon 2}$ NOTE—Figures in Annex were editorially renumbered in March 1989.

1. Scope

1.1 This test method of designating the size of refuse-derived fuel from its sieve analysis is applicable to the classified light fraction (RDF-3) of shredded municipal or industrial waste materials less than 0.15 m (6 in.) in size.

1.2 The values stated in acceptable metric units are to be regarded as standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For more specific precautionary information see Section 7.

2. Referenced Documents

2.1 *ASTM Standards:*

D 2234 Method for Collection of a Gross Sample of Coal[2]
E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]
E 177 Practice for Use of the Terms Precision and Bias in ASTM Test Methods[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *air drying*—a process of partial drying of RDF-3 to bring its moisture content near to equilibrium with the atmosphere in the room in which the sieving is to take place.

3.1.2 *gross sample*—a sample representing a lot of RDF and composed of a number of increments on which neither reduction nor division has been performed.

3.1.3 *laboratory sample*—a representative portion of the gross sample delivered to the laboratory for further analysis.

3.1.4 *lot*—a large designated quantity of RDF-3.

3.1.5 *representative sample*—a sample collected in such a manner that it has characteristics equivalent to the material being sampled.

3.1.6 *sample division*—the process of extracting a smaller sample from a gross sample wherein the representative properties of the large sample are retained.

3.2 *Description of Term Specific to This Standard:*

3.2.1 *refuse-derived fuel* (RDF-3)—a shredded fuel derived from municipal solid waste (MSW) that has been processed to remove metal, glass, and other inorganics. This material has a particle size such that 95 weight % passes through a 2-in. square-mesh screen.

NOTE 1—Other refuse-derived fuel may be classified as follows:

RDF-1—Wastes used as a fuel in as-discarded form.
RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.
RDF-4—Combustible waste processed into powder form, 95 weight % passing 10-mesh screening.
RDF-5—Combustible waste densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.
RDF-6—Combustible waste processed into liquid fuel.
RDF-7—Combustible waste processed into gaseous fuel.

4. Summary of Test Method

4.1 This test method covers the separation of an RDF sample into defined size fractions and expressing those fractions as a weight percent of an air-dried sample.

5. Significance and Use

5.1 The purpose of this test method is to provide a means of designating the size classification of RDF-3 for use by consumers and producers of RDF-3.

6. Apparatus

6.1 *Sieves:*

6.1.1 Use sieves conforming to Specification E 11. For recommended sizes see Table 1.

6.1.1.1 For RDF-3 and larger than 50 mm (2 in.) screens having rectangular frames 0.6 to 0.7 m^2 (6 to 8 ft^2) sieve area are satisfactory.

6.1.1.2 For RDF-3 50 mm (2 in.) or smaller, rectangular frames having 2 to 4 ft^2 (0.2 to 0.4 m^2) sieve area are satisfactory.

6.1.1.3 For RDF-3 smaller than 0.01 m (0.5 in.), circular sieves 0.3 m (12 in.) or 0.2 m (8 in.) in diameter are satisfactory.

6.2 *Sieving Devices:*

6.2.1 Hand sieving is permissible.

6.2.2 Sieving machines that provide the necessary agitation and tumbling action may be used. See Annex A1 for recommended screen sizes and machines.

6.3 *Balance* (laboratory sample), having sufficient capacity to weigh the sample and container with a sensitivity of 0.5 g in 1000 g.

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

Current edition approved July 31, 1981. Published February 1982.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

TABLE 1 Recommended Sieve Sizes (ASTM E 11 - 70)

For screening RDF-3 the following screen series is recommended:	
Standard (mm)	Alternative (in. or mesh)
100 mm	4 in.
50 mm	2 in.
25 mm	1 in.
12.5 mm	1/2 in.
6.3 mm	1/4 in.
3.35 mm	No. 6
1.70 mm	No. 12
850 µm	No. 20
425 µm	No. 40
The following intermediate screen sizes may be used as needed:	
Standard (mm)	Alternative (in. or mesh)
75 mm	3 in.
37.5 mm	1.5 in.
19.0 mm	3/4 in.
9.5 mm	3/8 in.
4.75 mm	No. 4
2.36 mm	No. 8
1.18 mm	No. 16
600 µm	No. 30

7. Precautions

7.1 Due to the origins of RDF-3 in municipal waste, common sense dictates that some precautions be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF-3; wearing masks (NIOSH-approved type), especially while shredding RDF-3 samples; conducting tests under a negative pressure hood when possible; and washing hands before eating or smoking.

8. Sampling

8.1 Collect increments regularly and systematically so that the entire quantity of RDF sampled will be representative proportionately in the gross sample, and with such frequency that a gross sample of the required amount shall be collected. No sampling procedure shall be used that alters the particle size distribution.

8.2 Establish the sampling procedures to be used, the number and size of samples required to obtain a representative sample, and the method of division of the gross sample into the laboratory sample in accordance with an agreement between purchaser and supplier.

NOTE 2—The statistical methods described in Method D 2234 may be applicable in determining the number and size of samples.

8.3 Division of the gross sample into the laboratory sample may be done by coning and quartering, riffling, or by other appropriate method.

8.4 The sample shall be approximately 2 kg (4.4 lb) in weight.

8.5 Air-dry the sample in a ventilated drying oven to constant weight at 10 to 15°C above the ambient temperature. (Calculate the loss in weight to percentage of moisture that shall constitute the air-dry loss in the sieve analysis sample.)

9. Procedure

9.1 Weigh the air-dried sample.

9.2 *Hand Sieving:*

9.2.1 Starting with the sieve having the largest opening, sieve a portion of the RDF-3 in such an increment as will allow the individual pieces to be in direct contact with the meshes of the screen after the completion of shaking of each increment. In shaking, apply a vertical as well as horizontal motion in order to allow all small particles to pass through the openings, until no more material will pass. Hand fitting is not permitted.

9.2.2 Pass the material through successively smaller sieves in increments small enough to avoid matting of the material to the extent that the undersized material cannot reach and pass the screen.

9.2.3 Continue to shake the sieve after each increment is added until no significant amount of material passes through the screen.

9.3 *Machine Sieving:*

9.3.1 When sieving machines are used, test their thoroughness of sieving by comparison with hand methods as described in 9.2.

9.3.2 Stack the sieves progressively starting with the smallest aperture size, above the pan, to the largest aperture size at the top.

9.3.3 Introduce the air-dried sample above the largest screen in small enough increments such that matting of the material does not occur to an extent that prevents the undersize material from reaching and passing the screen. The amount of RDF-3 added to the top screen in any increment must not exceed one third of the volume of the screen, in order to prevent matting or blinding.

9.3.4 After adding each increment, assemble the pans or trays in the machine and turn on agitation for 10 min, or up to 15 min if necessary, to complete screening.

9.3.5 Inspect each screen for evidence of matting. If a screen is mostly or entirely covered with a mat, decrease the size of the initial increments such that no mat forms on any sieve, and repeat the tests.

9.3.6 When sieving of each increment is complete, promptly determine the weight of material remaining on each screen to the nearest 0.5 g. If more than one increment is sieved to pass the entire sample, add the incremental weights remaining on each sieve. If the sum of the weights show a loss of 2 % or more, reject the analysis and make another test using a second sample.

NOTE 3—In order to obtain a complete characterization of the size range of an RDF-3 sample, it is necessary that the number of sieves be such that no more than 25 % of the gross sample weight will be retained on any given sieve. The recommended screen series are listed in Table 1.

NOTE 4—The sand and glass contained in a sample of RDF-3 has a strong tendency to segregate from the light fraction. For this reason great care must be taken to include the entire sample in the sieve analysis. When a sample is divided, the sand will probably not divide equally into the sample portions. Samples may be divided for convenience in feeding the sieving apparatus, but the weights of all portions of the sample must be properly summed so that the entire sample has been included in the sieve analysis.

NOTE 5—Some abrasion and physical degradation of the sample by the screen can occur during the sieving operation. The analyst shall monitor and report his observations of any sample degradation.

10. Report

10.1 Report the weights of the size fractions as a percentage of the weight of the air-dried laboratory sample of RDF-3. Calculate to the nearest 0.5 % the percentages of the size fractions remaining on each sieve, and the percentage

REPORT OF SIEVE ANALYSIS OF RDF-3

All weights in grams

Sample identification no. ____________________

Date sampled: ____________________

Sample rec'd. ____________________

Source: ____________________

____

AIR DRY LOSS

Weight Before ____________________

Weight After ____________________

Weight Loss ____________________

% A-D Loss ____________________

Sieve No. (mm)	Alternative (in. mesh)	Weight retained	% retained	% cumulative greater than size
100 mm	4 in.			
50 mm	2 in.			
25 mm	1 in.			
12.5 mm	½ in.			
6.3 mm	¼ in.			
3.35 mm	No. 6			
1.70 mm	No. 12			
850 μm	No. 20			
425 μm	No. 40			
In pan through 425 μm	No. 40			
(Total)				

NOTE 1—Calculate percentages to the nearest 0.5 %.
NOTE 2—If the sum of the weights shows a loss of over 2 %, reject the analysis and make another test.
NOTE 3—Nominal top size sieve shall retain 1 % to 5 % of A-D sample weight. The nominal bottom size sieve shall allow no more than 15 % of A-D sample to pass.

Analyst: ____________________

Date: ____________________

FIG. 1 Sample Report Form

passing through the smallest aperture sieve. See sample report form in Fig. 1.

10.2 Record the results starting with the largest aperture size. If desirable, the percentage can also be reported on a cumulative basis, as cumulative percentage greater than size or cumulative percentage less than size where size refers to sieve aperture size or mesh number.

10.3 The sieve aperture defining the upper particle size limit shall be that sieve of the series with the smallest aperture size that will retain less than 5 % of the sample weight. This sieve size is the nominal top particle size (see Annex A2 for definition).

10.4 The sieve aperture size defining the lower particle size limit shall be the smallest aperture sieve of the series which passes less than 15 % of the sample weight. This sieve size is the nominal bottom particle size (see Annex A2 for definition).

10.5 The term defining particle sizes shall be written with the nominal top size first, followed by the nominal bottom size.

10.6 International Standard sieve sizes shall be expressed as millimetre (mm), or micrometre, (μm), representing the actual size of the sieve opening. U.S. Standard sieve sizes shall be expressed as inches (in.) or by mesh numbers representing the number of mesh wires per inch. For sieves No. 4 and smaller sieve sizes, the abbreviation No., shall be used each time a sieve is indicated by a mesh number.

11. Precision and Bias

11.1 The precision and bias of this test method are yet to be determined.

ANNEXES

(Mandatory Information)

A1. SIEVING DEVICES

A1.1 Horizontal Rotating Cylindrical Screens

A1.1.1 Horizontal rotating cylindrical screens are preferable for screening flat materials such as RDF-3, because they readily provide the lifting and tumbling action required to bring all materials to the screen surface. However, no screens of this sort are commercially available at this time.

A1.2 Rectangular Testing Screen[4] (Fig. A1.1)

A1.2.1 Trays have 0.46 by 0.66-m (18 by 26-in.) clear screen area, designed primarily for the 0.1 m (4 in.) to No. 4 mesh size, but will handle small amounts of finer material

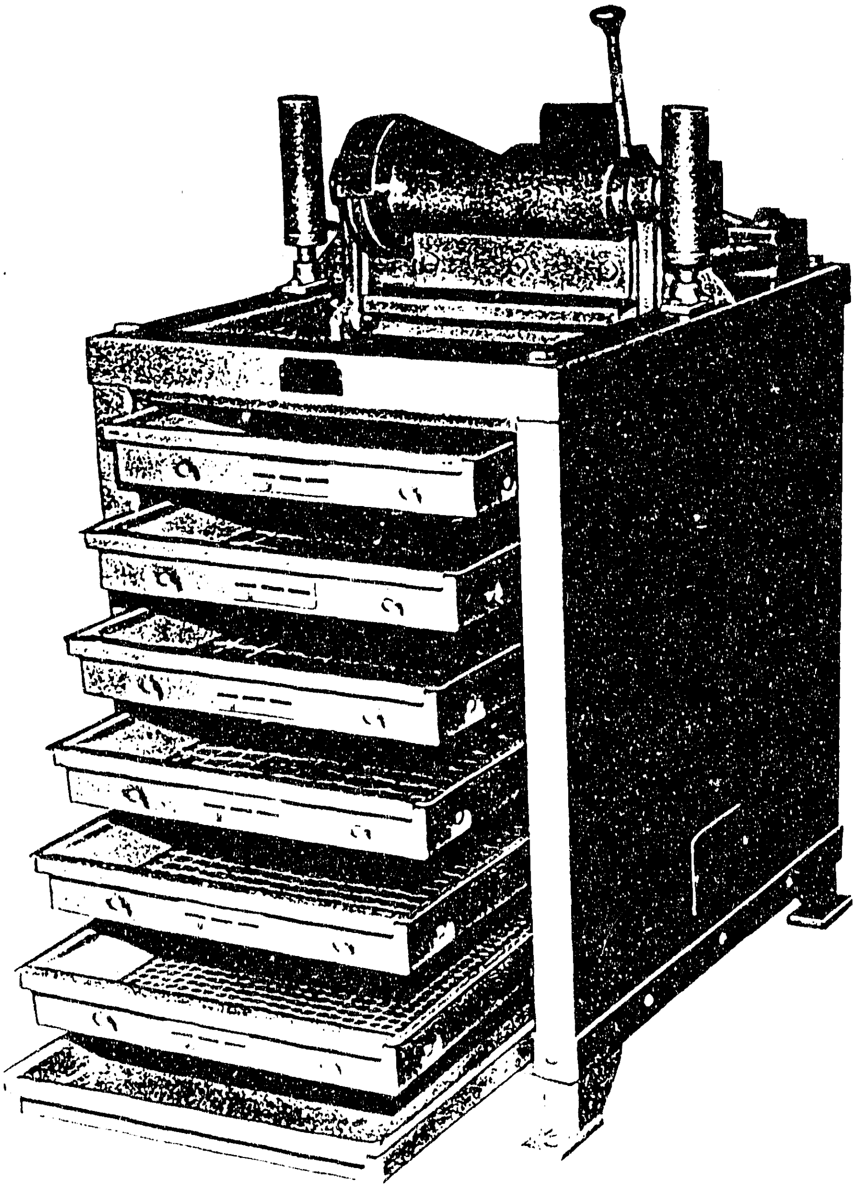

FIG. A1.1 Rectangular Testing Screen

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[4] Gilson testing screen model TS-1, having six screens and a pan 0.46 by 0.66 m (18 by 26 in.), has been found to be satisfactory for RDF-3 under 0.05 mm (2 in.), when equipped with a special low-amplitude drive shaft. Available from Gilson Screen Co., P.O. Box 99-T, Malinta, OH 43535.

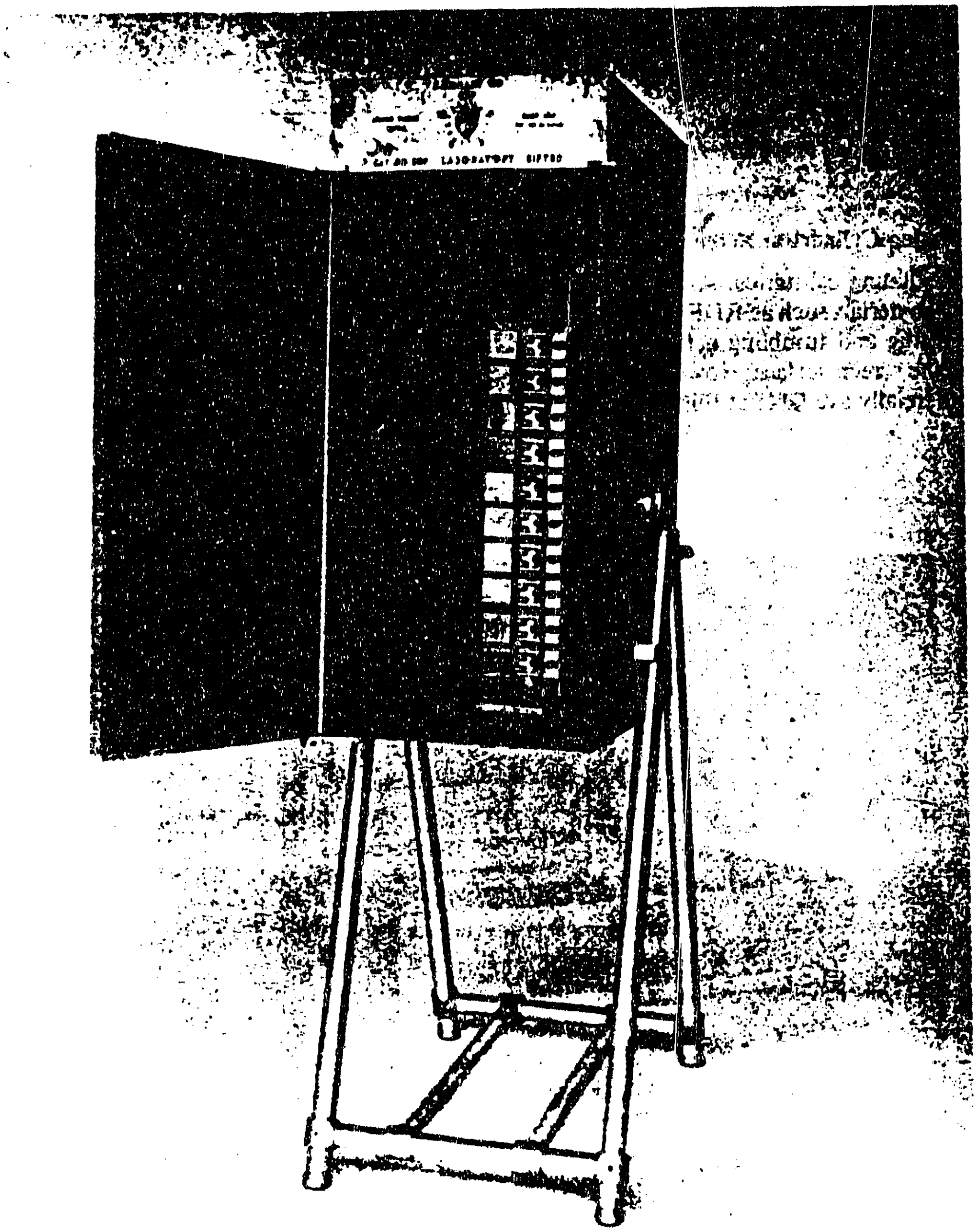

FIG. A1.2 Rotary Pan Sieve

down to No. 200 mesh. The screens handle samples up to a maximum of 1 ft^3 (0.03 m^3). Screening motion is essentially a vertical variation, which is factory set for the type of material to be tested. Up to six screen trays can be held in the vibrating unit.

A1.3 Rotary Pan Sieve[5] (Fig. A1.2)

A1.3.1 This device can be operated with up to nine full height 200 mm (8-in.) or 300 mm (12-in.) sieving screens and a pan, assembled together in a set, and held at an angle of 45° while rapping and rotating the assembly. A timer is provided to stop the mechanical action after time intervals up to 15 min.

A1.4 Testing Sieve Shaker[6]

A1.4.1 This device reproduces the circular and tapping motion given testing sieves in hand-sieving, and can hold a series of size full-height, 200-mm (8-in.) sieves in one operation of the machine.

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[5] Rainhart Rotary Pan Sieve using 300-mm (12-in.) or 200-mm (8-in.) circular sieves has been found to be satisfactory for RDF-3 under 12.5 mm (0.5 in.) Available from Rainhart Co. (Testing Equipment), 604-T Williams, Austin, TX 78752.

[6] A Rotap screening machine with 200-mm (8-in.) circular sieve has been found to be satisfactory for RDF-3 under 12.5 mm (0.5 in.). Available from W. S. Tyler Co., Inc., 8200 Tyler Blvd., Mentor, OH 44060.

A2. METHOD FOR DETERMINATION OF NOMINAL AND MEAN PARTICLE SIZES

2.1 Graphical Form

A2.1.1 The graphical form (see Fig. A2.1) is suitable for cording the sieve analysis data, determining the percentage tained, the cumulative percentage, and for plotting the umulative percentage on the Rosin-Rammler graph.

A2.1.2 The characteristics of the size distribution can be etermined from the plotted cumulative percentage, reulting in a distribution coefficient *n* and an absolute onstant, or mean particle size *x* in accordance with the echniques of Rosin-Rammler analysis.

2.2 Procedure for Determining Coefficients

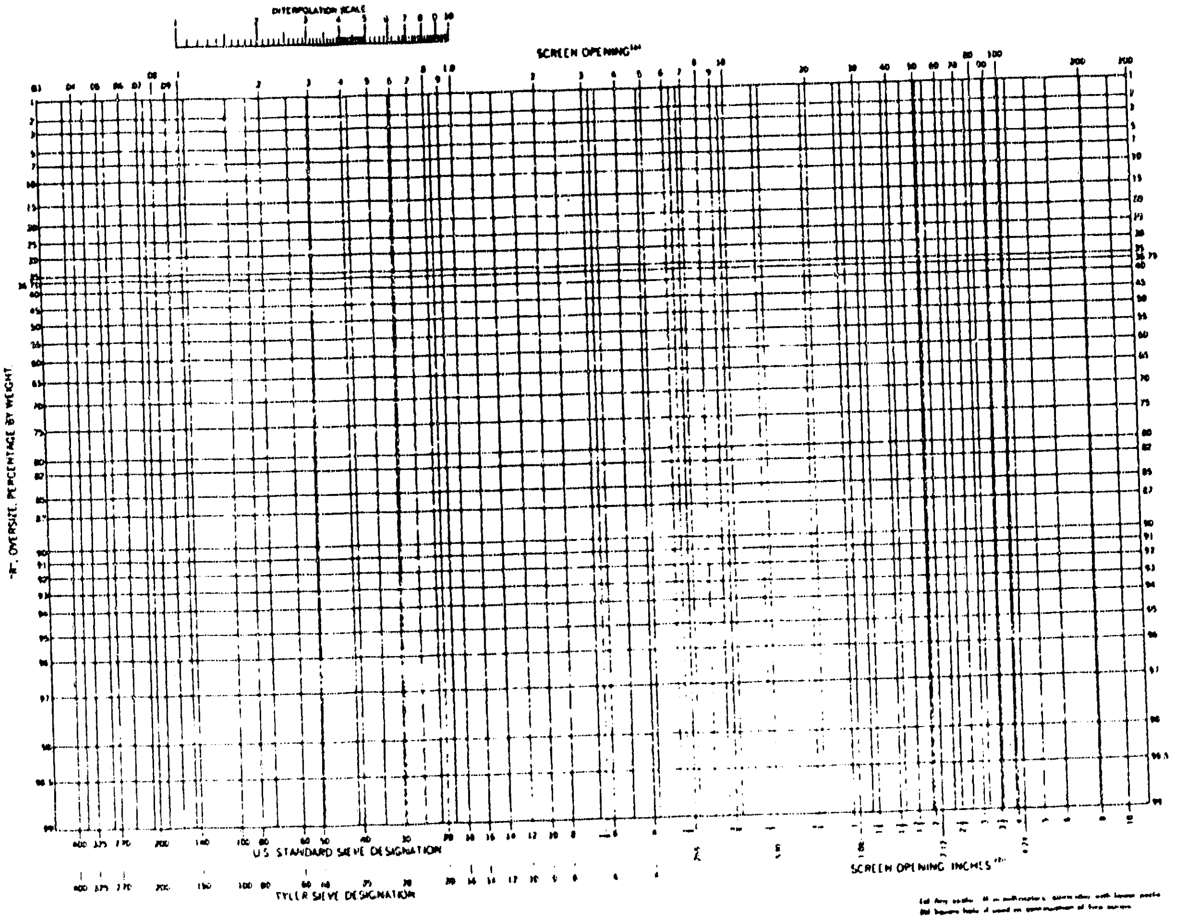
A2.2.1 Plot "Percent Cumulative Greater than Size" against size on the Graphical Form.

A2.2.2 Note the size retaining 36.79 %. This is the mean particle size. Use the nearest-standard screen opening or mesh designation to describe the mean particle size.

A2.2.3 Draw a straight line through the plotted points, passing through the mean particle size, and extend this line to the upper axis (1 % oversize).

A2.2.4 Read the size at 5 % oversize. Determine the next larger standard screen opening. This is the "Nominal Top Particle Size" of the sample, defined as the size retaining less than 5 % of the sample.

A2.2.5 Read the size at 85 % oversize. Determine the next



GRAPHICAL FORM FOR REPRESENTING DISTRIBUTION OF SIZES OF BROKEN COAL

Average particle size (intersection of size distribution line with 63.21 % passing line) $\bar{X}$

Slope of size distribution line (tangent of angle) N

[A] Any scale, if in millimetres, coincides with lower scale.

[B] Square hole if used as continuation of fine series

[C] From: Landers, W. S., and Reid, W. T., A Graphical Form for Applying the Rosin and Rammler Equation to the Size Distribution of Broken Coal, Bureau of Mines Inf Circular 7346, 1946. Pristine forms are available from ASTM Headquarters. Order PCN 12-508280-4.

FIG. A2.1 Graphical Form for Representing Distribution of Sizes[C] smaller standard screen opening. This is the "Nominal Bottom Particle Size."

A2.2.6 Select two points, "A" one screen size less than and "B" one size greater than the mean particle size, lying on the straight line drawn through the plotted points.

A2.2.6.1 Measure the horizontal distance of points A and B from the left axis in mm (or inches), and enter them in the table "characteristics" along with the percentage retained. Take the difference between x and y.

A2.2.6.2 The distribution coefficient, n, is the slope of the line, $\frac{\Delta y}{\Delta x}$.

A2.2.6.3 Measure the horizontal distance, x, of points A and B from the left vertical axis, and record in the table "characteristics."

A2.2.6.4 Measure the vertical distance, y, of points A and B from the bottom axis. Record in the table and subtract the x and y measurements to obtain the differences, Δx and Δy.

Designation: E 830 – 87

Standard Test Method for Ash in the Analysis Sample of Refuse-Derived Fuel[1]

This standard is issued under the fixed designation E 830; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers determination of the ash content in the analysis sample of refuse-derived fuel (RDF). The results obtained can be applied as the weight percent ash in the proximate analysis and in the ultimate analysis.

1.2 The values stated in acceptable metric units are to be regarded as standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[3]

E 829 Method of Preparing RDF-3 Laboratory Samples for Analysis[3]

3. Description of Term Specific to This Standard

3.1 *refuse-derived fuel*—Solid forms of refuse-derived fuels from which appropriate analytical samples may be prepared are defined as follows in *ASTM STP 832:*[4]

RDF-1—Wastes used as a fuel in as-discarded form with only bulky wastes removed.

RDF-2—Wastes processed to coarse particle size with or without ferrous metal separation.

RDF-3—Combustible waste fraction processed to particle sizes, 95 % passing 2-in. square screening.

RDF-4—Combustible waste fraction processed into powder form, 95 % passing 10-mesh screening.

RDF-5—Combustible waste fraction densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

4. Summary of Test Method

4.1 Ash is determined by weighing the residue remaining after burning the prepared analysis sample under rigidly controlled conditions of sample weight, temperature, and furnace atmosphere.

5. Significance and Use

5.1 This test method is available to producers and users of RDF as a method of determining the weight percent of ash in the analysis sample.

6. Apparatus

6.1 *Electric Furnace*—For determination of the ash content of RDF, the furnace shall have adequate air ventilation and shall be capable of temperature regulation up to at least 750 ± 25°C. An air change rate of 1 to 4 furnace volumes of air per minute has been found adequate.

NOTE 1—It may be possible to reduce the rate of air flow below the suggested minimum without adversely affecting results of the ash determination.

6.2 *Porcelain Capsules*, about 22 mm (7/8 in.) in depth, and 44 mm (1¾ in.) in diameter, or similar containers.

NOTE 2—Weighing bottles of borosilicate glass may be safely used without deformation or softening at temperatures of 600°C or less.

7. Precautions

7.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under a negative pressure hood when possible; and washing hands before eating or smoking.

8. Sampling

8.1 The laboratory sample shall be obtained in accordance with sampling methods developed for materials of similar physical form.

8.2 The laboratory sample must be air-dried and particle size reduced to pass a 0.5-mm screen as described in Method E 829.

9. Procedure

9.1 After thoroughly mixing the analysis sample analysis sample to provide the best possible mix of heavy fines with the milled fluff, transfer approximately 1 g of the sample to a tared, previously fired container (weighed to the nearest 0.1 mg) with a scoop or spatula. Quickly weigh sample and container to the nearest 0.1 mg. As an alternate method use

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

Current edition approved Aug. 28, 1987. Published October 1987. Orginally published as E 830 – 81. Last revised E 830 – 81.

[2] *Annual Book of ASTM Standards*, 15.05.

[3] *Annual Book of ASTM Standards*, 11.04

[4] *Thesaurus on Resource Recovery Terminology, ASTM STP 832*, ASTM, 1983, p. 72.

the dried analysis sample from the residual moisture determination. See Test Method E 790.

9.2 Place the uncovered container containing the sample in the furnace at low temperature and gradually heat to ignition at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter.

9.3 Finish the ignition to constant weight 9±0.001 g/h) at 575 ± 25°C. It may be determined that a constant weight can be routinely established by allowing a sample to ash within the prescribed temperature range for a set period of time.

NOTE 3—Experience has shown that particles of glass and sand tend to sinter to each other and also to porcelain crucibles at temperatures close to 675°C. If laboratory conditions necessitate maintaining consistency in the maximum furnace temperature used for ash tests of other fuels, the ignition may be finished to constant weight (±0.001 g/h) at a temperature of 725 ± 25°C. If this option is invoked, it should be also noted that prolonged exposure to high temperatures may actually result in changes in weight due to possible chemical reactions.

9.4 Cool in a desiccator over desiccant and weigh as soon as possible after the container and ash reach the temperature of the area in which weighing is performed.

10. Calculations

10.1 Calculate the ash percent in the analysis sample as follows:

$$\text{Ash as-determined, } \% = [(A - B)/C] \times 100$$

where:

A = weight of container and ash residue, g,
B = weight of empty container, g, and
C = weight of ash analysis sample, g (includes residual moisture).

10.2 Use the numerical moisture value established by Test Method E 790 for converting ash data on the as-determined basis to the dry basis.

11. Report

11.1 Difficulty may be experienced in securing satisfactory check determinations of ash in the same or different laboratories for RDF rich in heavy fines. This is caused by siliceous matter such as glass and sand as well as a wide variety of other particles of different densities entrained in the milled RDF in nonuniform strata. When such a condition is anticipated or encountered, a paired set of determinations should be made, and the results reported as an average. If one determination of a paired set is accidentally ruined, another pair must be run. An off or unusual value does not constitute a ruined determination. In such cases, an additional set of duplicate determinations should be run and all values reported as an average of the two sets.

12. Precision and Bias

12.1 *Precision:*

12.1.1 The standard deviations of individual determinations in percent absolute are as follows:

Typical Average Value, %	Within-Laboratory, %	Between-Laboratories, %
20.0	0.6	1.3

12.1.2 These precision estimates are based on an interlaboratory study conducted in accordance with Practice E 180.

12.2 *Bias*—The bias of this test method can not be determined due to the lack of a recognized standard reference material.

Designation: E 870 – 82 (Reapproved 1987)$^{\epsilon 1}$

Standard Test Methods for Analysis of Wood Fuels[1]

This standard is issued under the fixed designation E 870; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

$^{\epsilon 1}$ NOTE—Sections were rearranged editorially in March 1987.

1. Scope

1.1 These test methods cover the proximate and ultimate analysis of wood fuels and the determination of the gross caloric value of wood fuels sampled and prepared by prescribed test methods and analyzed according to ASTM established procedures. Test methods as herein described may be used to establish the rank of fuels, to show the ratio of combustible to incombustible constituents, to provide the basis for buying and selling, and to evaluate for beneficiation or for other purposes.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1102 Test Method for Ash in Wood[2]

E 711 Test Method for Gross Calorific Value of Refuse-Derived Fuel (RDF-3) By the Bomb Calorimeter[3]

E 775 Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel[3]

E 777 Test Method for Carbon and Hydrogen in the Analysis Sample of Refuse-Derived Fuel[4]

E 778 Test Method for Nitrogen in the Analysis Sample of Refuse-Derived Fuel[3]

E 871 Method of Moisture Analysis of Particulate Wood Fuels[3]

E 872 Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels[3]

3. Definitions

3.1 *proximate analysis*—an assay of the moisture, ash, volatile matter, and fixed carbon as determined by prescribed test methods. Other constituents such as sulfur and phosphorus are not included.

3.2 *ultimate analysis*—the determination of carbon and hydrogen in the material, as found in the gaseous products of its complete combustion, the determination of sulfur, nitrogen, and ash in the material as a whole, and the calculation of oxygen by difference.

4. Significance and Use

4.1 These test methods of analysis described herein can be used for the proximate analysis, ultimate analysis, and the determination of the gross caloric value of wood fuels.

5. Procedures

5.1 *Moisture*—Method E 871.

5.2 *Ash*—Test Method D 1102.

5.3 *Volatile Matter*—Test Method E 872.

5.4 *Fixed Carbon*—The fixed carbon is a calculated value. It is the resultant of the summation of percentage moisture, ash, and volatile matter subtracted from 100. All percentages shall be on the same moisture reference base.

5.5 *Carbon and Hydrogen*—Test Method E 777.

5.6 *Sulfur*—Test Method E 775.

5.7 *Nitrogen*—Test Method E 778.

5.8 *Oxygen*—The oxygen is a calculated value. It is the resultant of the summation of percentages carbon, hydrogen, sulfur, nitrogen, and ash subtracted from 100. All percentages shall be on the same moisture reference base.

5.9 *Gross Calorific Value*—Test Method E 711.

6. Precision and Bias

6.1 The precision and bias of the test methods described herein are contained in these individual test methods.

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[1] These test methods are under the jurisdiction of ASTM Committee E-48 on Biotechnology and are the direct responsibility of Subcommittee E48.05 on Biomass Conversion Systems.

Current edition approved Nov. 26, 1982. Published January 1983.

[2] *Annual Book of ASTM Standards*, Vol 04.09.

[3] *Annual Book of ASTM Standards*, Vol 11.04.

[4] *Annual Book of ASTM Standards*, Vol 14.02.

Designation: E 871 – 82 (Reapproved 1987)

Standard Method for Moisture Analysis of Particulate Wood Fuels[1]

This standard is issued under the fixed designation E 871; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This method covers the determination of total weight basis moisture in the analysis sample of particulate wood fuel. The particulate wood fuel may be sanderdust, sawdust, pellets, green tree chips, hogged fuel, or other type particulate wood fuel having a maximum particle volume of 16.39 cm^3 (1 in.^{3}). It is used for calculating other analytical results to a dry basis. Moisture, when determined as herein described, may be used to indicate yields on processes, to provide the basis for purchasing and selling, or to establish burning characteristics.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Methods of Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Method of Preparing Coal Samples for Analysis[2]

3. Summary of Method

3.1 Moisture is determined by establishing the loss in weight of the sample when heated under rigidly controlled conditions of temperature, time and atmosphere, sample weight, and equipment specifications.

4. Significance and Use

4.1 The test procedures described in this method can be used to determine the total weight basis moisture of any particulate wood fuel meeting the requirements specified in this method.

5. Apparatus

5.1 *Drying Oven*—For determining the moisture of wood, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation of 103 ± 1°C shall be used.

5.2 *Open Containers*, nonporous glass, metal, or ceramic and of a configuration so as to accommodate the test sample. The minimum volume shall be 32.18 cm^3 (2 in.^{3}).

5.3 *Desiccator*, of sufficient size to contain the open container.

6. Procedure

6.1 *Sampling:*

6.1.1 *Place of Sampling*—Take the sample where the wood is being loaded into or unloaded from means of transportation or when discharged from storage bins or conveyors.

NOTE—Samples collected from the surface of piles are, in general, unreliable because of the exposure to the environment. If necessary, collect nine increments from a foot or more below the surface at nine points covering the pile.

6.1.2 *Collection of Gross Sample:*

6.1.2.1 Collect increments regularly, systematically, and with such frequency that the entire quantity of wood sampled will be represented proportionally in the gross sample.

6.1.2.2 The quantity of the sample shall be large enough to be representative but not less than 10 kg (22 lb).

6.1.2.3 Place the samples in an airtight container immediately after collection. Maintain the samples in the airtight container whenever possible to prevent gains or losses in moisture from the atmosphere.

6.1.3 Sample reduction may be done by two methods, a coning and dividing process, or by using a riffle. The operations of mixing, coning, and quartering are described in Methods D 346.

6.1.3.1 Accomplish coning and dividing reduction by placing the gross sample on a sheet of rubber or oil cloth. Thoroughly mix it by raising first one corner of the cloth and then the other. After mixing cone and quarter sample, continue the operations until the sample is reduced sufficiently so that one quarter weighs about 50 g (0.11 lb). This shall constitute a laboratory sample.

6.1.3.2 Accomplish riffle reduction using a standard coal riffle. Riffle the gross sample repeatedly until one half of the riffle sample equals about 50 g (0.11 lb), which will constitute a laboratory sample. Riffles and procedures are described in Method D 2013.

6.2 Dry sample container for 30 min at 103 ± 1°C in the oven, then cool in desiccator to room temperature. Weigh to the nearest 0.02 g and record as container weight, W_c. Place a minimum of 50 g of sample in the container, weigh the sample and container to the nearest 0.01 g, and record as initial weight, W_i.

6.3 Place the sample and container in the oven for 16 h at 103 ± 1°C.

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[1] This method is under the jurisdiction of ASTM Committee E-48 on Biotechnology and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion Systems.

Current edition approved May 28, 1982. Published December 1982.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

6.4 Remove the sample and the container from the oven and cool in the desiccator to room temperature. Remove the sample and container from the desiccator, weigh immediately to the nearest 0.01 g, and record the weight.

6.5 Return the sample and container to the oven at 103 ± 1°C for 2 h. Repeat 6.4.

6.6 Continue 6.4 until the total weight change between weighings varies less than 0.2 % and record as the final weight, W_f.

7. Calculation

7.1 Calculate the percent moisture in the analysis sample as follows:

$$\text{Moisture in analysis sample, \%} = [(W_i - W_f)/(W_i - W_c)] \times 100$$

where:

W_c = container weight, g,
W_i = initial weight, g, and
W_f = final weight, g.

8. Precision and Bias

8.1 The following criteria should be used for judging the acceptability of results:

8.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than 0.5 %.

8.2.1 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than 1 %.

Designation: E 872 – 82 (Reapproved 1987)

Standard Test Method for Volatile Matter in the Analysis of Particulate Wood Fuels[1]

This standard is issued under the fixed designation E 872; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method determines the percentage of gaseous products, exclusive of moisture vapor, in the analysis sample of particulate wood fuel that is released under the specific conditions of the test. The particulate wood fuel may be sanderdust, sawdust, pellets, green tree chips, hogged fuel, or other type particulate wood fuel having a maximum particle volume of 16.39 cm^3 (1 $in.^3$). Volatile matter, when determined as herein described, may be used to indicate yields on processes to provide the basis for purchasing and selling or to establish burning characteristics.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Methods of Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Method of Preparing Coal Samples for Analysis[2]

E 871 Method of Moisture Analysis of Particulate Wood Fuels[3]

3. Summary of Test Method

3.1 Volatile matter is determined by establishing the loss in weight resulting from heating wood under rigidly controlled conditions. The measured weight loss, corrected for moisture as determined in Method E 871, establishes the volatile matter content.

4. Significance and Use

4.1 The test procedures described in this test method can be used to determine the percentage of gaseous products, exclusive of moisture vapor, of any particulate wood fuel meeting the requirements specified in this test method.

5. Apparatus

5.1 *Platinum Crucible,* with closely fitting cover, or a nickel-chromium crucible, with closely fitting cover, prefired to oxidize and stabilize the weight. The crucible shall be of not less than 10 or more than 20-mL capacity, not less than 25 or more than 35 mm in diameter, and not less than 30 or more than 35 mm in height.

5.2 *Vertical Electric Tube Furnace*—The furnace may be of the form shown in Fig. 1. It shall be regulated to maintain a temperature of 950 ± 20°C in the crucible, as measured by a thermocouple positioned in the furnace.

6. Procedure

6.1 *Sampling:*

6.1.1 *Place of Sampling*—Take sample where wood is being loaded into or unloaded from means of transportation or when discharged from storage bins or conveyors.

NOTE 1—Samples collected from the surface of piles are, in general, unreliable because of the exposure to the environment. If necessary, collect nine increments from a foot or more below the surface at nine points covering the pile.

6.1.2 *Collection of Gross Sample:*

6.1.2.1 Collect increments regularly, systematically, and with such frequency that the entire quantity of wood sampled will be represented proportionally in the gross sample.

6.1.2.2 The quantity of the sample shall be large enough to be representative but not less than 10 kg (22 lb).

6.1.2.3 Place samples in an airtight container immediately after collection. Maintain samples in the airtight container whenever possible to prevent gains or losses in moisture from the atmosphere.

6.1.3 Sample reduction may be done by two methods, a coning and dividing process, or by using a riffle. Mixing, coning, and quartering are described and illustrated in Methods D 346.

6.1.3.1 Coning and dividing reduction is accomplished by placing the gross sample on a sheet of rubber or oil cloth. Thoroughly mix it by raising first one corner of the cloth and then the other. After mixing, cone and quarter sample. Continue the operations until the sample is reduced sufficiently so that one quarter weighs about 50 g (0.11 lb). This shall constitute a laboratory sample.

6.1.3.2 Riffle reduction is accomplished by using a standard coal riffle. The gross sample is riffled repeatedly until one half of the riffle sample equals about 50 g (0.11 lb) which will constitute a laboratory sample. Riffles and procedures are described in Method D 2013.

6.2 Reduce the sample to a smaller particle size by use of cutting or shearing type laboratory mill. The final product should pass through a 1-mm or smaller screen. Depending

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[1] This test method is under the jurisdiction of ASTM Committee E-48 on Biotechnology and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion Systems.

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[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 11.04.

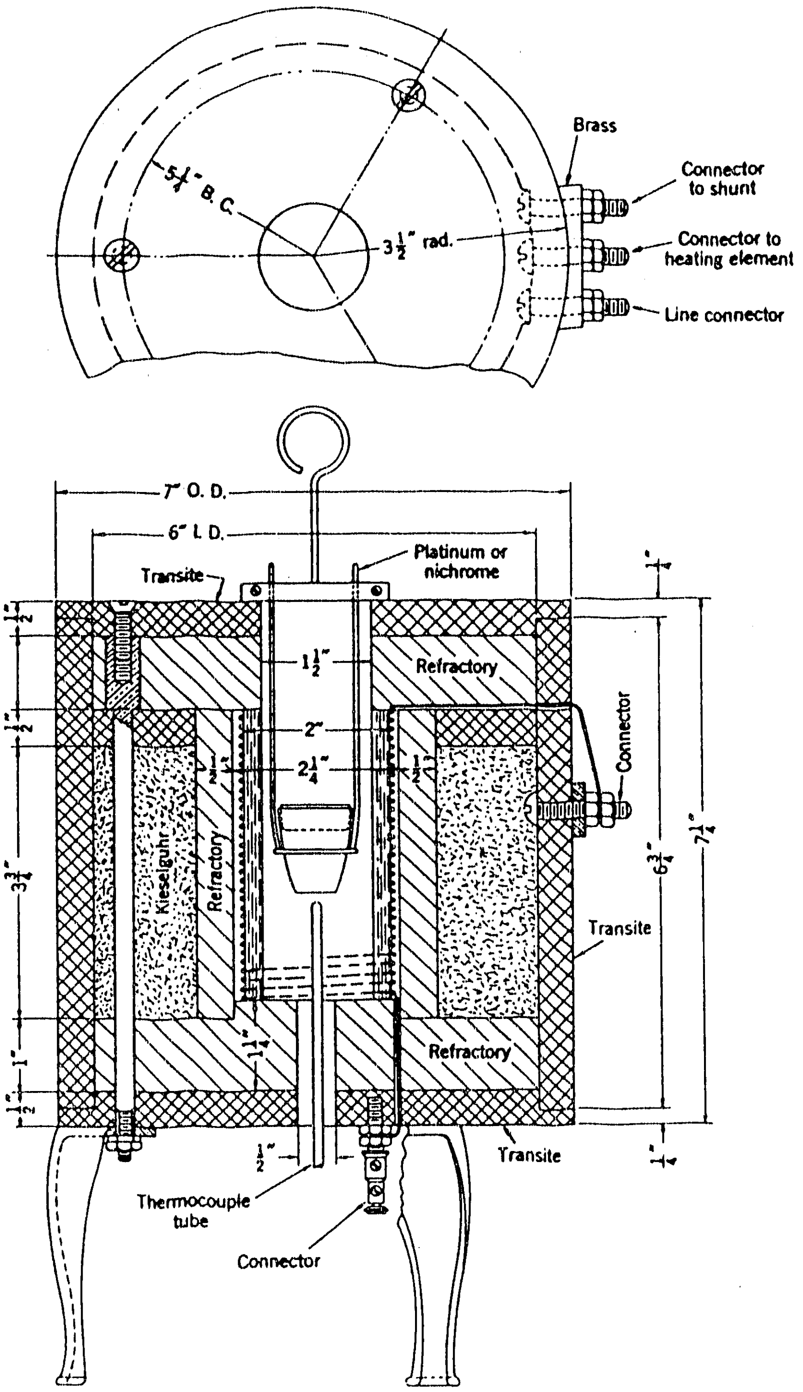

FIG. 1 Electric Furnace for Determining Volatile Matter

on the specific product this step may involve more than one stage of reduction, that is, passing the sample through a mill with a larger size screen first and then milled to pass the final screen. Minimum atmospheric exposure is recommended and the milling process should be conducted to avoid significant moisture means to ensure thorough intermix of heavy fines and milled fluff.

6.3 Weigh the crucible and cover to the nearest 0.01 g and record as crucible weight, W_c. Place approximately 1 g of sample in the crucible, cover, weigh the crucible, cover, and sample to the nearest 0.01 g, and record as initial weight, W_i.

6.4 Place the covered crucible with sample on platinum or nickel-chromium wire supports and insert directly into the furnace chamber, which shall be maintained at a temperature of 950 ± 20°C, and lower immediately to the 950°C zone. Regulation of the temperature to within the prescribed limits is critical. After the more rapid discharge of volatile matter has subsided as shown by the disappearance of the luminous flame, inspect the crucible (Note 2) to verify the lid is still properly seated. If necessary, reseat the lid to guard against the admission of air into the crucible. Do this as rapidly as possible by raising the crucible to the top of the furnace chamber, reposition the lid as described in Method D 2013 to more perfectly seal the crucible, then lower immediately back to the 950°C zone. After heating for a total of exactly 7 min, remove the crucible from the furnace and, without disturbing the cover, allow it to cool in a desiccator. Weigh the covered crucible with sample as soon as cold to the nearest 0.1 mg and record as final weight, W_f.

NOTE 2—Inspection of the crucible may be aided by the use of a mirror held above the furnace well.

7. Calculations

7.1 Calculate the weight loss percent as follows:

$$\text{Weight loss, \%} = 100 \times (W_i - W_f)/(W_i - W_c) = A$$

where:

W_c = weight of crucible and cover, g,
W_i = initial weight, g, and
W_f = final weight, g.

7.2 Calculate the volatile matter percent in the analysis samples as follows:

$$\text{Volatile matter in analysis sample, \%} = A - B$$

where:

A = weight loss %, and
B = moisture, %, as determined using Method E 871.

8. Precision and Bias

8.1 The following criteria should be used for judging the acceptability of results:

8.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than 0.3 %.

8.1.2 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than 1.0 %.

Designation: E 873 – 82 (Reapproved 1987)

Standard Test Method for Bulk Density of Densified Particulate Biomass Fuels[1]

This standard is issued under the fixed designation E 873; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the procedure for the determination of bulk density (or bulk specific weight) of densified particulate biomass fuels with a maximum particle volume of 16.39 cm^3 (1 $in.^3$).

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Significance and Use

2.1 The test procedures described in this test method can be used to determine the bulk density (or bulk specific weight) of any densified particulate biomass fuel meeting the requirements specified in this test method.

3. Apparatus

3.1 *Box* of nominal 305 by 305 by 305-mm (12 by 12 by 12-in.) dimensions with handles. The box material shall be dimensionally stable. The volume shall be determined to within 16.39 cm^3 (1 $in.^3$).

3.2 *Scales* of such capacity as to weigh the box and sample to within 100 g.

4. Sampling

4.1 *Place of Sampling*—Sample fuel while it is being loaded into or unloaded from means of transportation or when discharged from storage bins or conveyors.

NOTE—Samples collected from the surface of piles are, in general, unreliable because of the exposure to the environment. If necessary, collect nine increments from a foot or more below the surface at nine points covering the pile.

4.2 *Collection of Gross Sample:*

4.2.1 Collect increments regularly, systematically, and with such frequency that the entire quantity of pellets sampled will be represented proportionally in the gross sample.

4.2.2 The quantity of the sample shall be large enough to be representative but not less than 45.45 kg (100 lb).

5. Procedure

5.1 Weigh and record the empty box weight within 100 g (0.22 lb). Fill the box by pouring from a height of 610 mm (2 ft) above the top edge of the container. Drop the box five times from a height of 150 mm (6 in.) on to a nonresilient surface to allow settling. Add additional sample and strike off the excess sample level with the top edge.

5.2 Then weigh the box and sample to within 100 g (0.22 lb) and record the total weight.

6. Calculation

6.1 Calculate bulk density as follows:

$$\text{Bulk density, g/cm}^3 = \frac{\text{(weight of box and sample)} - \text{(weight of box)}}{\text{(volume of box)}}$$

7. Precision and Bias

7.1 Precision and bias statements are in the process of being balloted. Subsequently, they will be added to this test method.

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[1] This test method is under the jurisdiction of ASTM Committee E-48 on Biotechnology and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion Systems.

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Designation: E 887 – 88

Standard Test Method for Silica in Refuse-Derived Fuel (RDF) and RDF Ash[1]

This standard is issued under the fixed designation E 887; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of silica in RDF, RDF ash, fly ash, bottom ash, or slag.

1.2 The test method is an acid dehydration gravimetric procedure and is independent of interferences.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For hazard statement, see Section 6.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1193 Specification for Reagent Water[2]

E 791 Method for Calculating Refuse-Derived Fuel Analysis Data from As-Determined to Different Bases[3]

E 829 Method for Preparing RDF Laboratory Samples for Analysis[3]

E 830 Test Method for Ash in the Analysis Sample of Refuse-Derived Fuel[3]

E 856 Definitions of Terms and Abbreviations Relating to Physical and Chemical Characteristics of Refuse-Derived Fuel[3]

3. Summary of Test Method

3.1 Silicon compounds in RDF ash, fly ash, bottom ash, or slag are dissolved by alkali fusion and dehydrated with hydrochloric acid (HCl). Dehydration is completed by ignition, and the silica is volatilized as silicon tetrafluoride.

4. Apparatus

4.1 *Analytical Balance*, capable of weighing to 0.0001 g.

4.2 *Muffle Furnace*—The furnace shall have an operating temperature of up to 1200°C.

4.3 *Hot Plate or Steam Bath.*

4.4 *Platinum Crucibles*, 35 to 85-mL capacity.

4.5 *Graphite Crucibles*, 35 to 85-mL capacity.

4.6 *Fused Quartz Dishes*, 35 to 85-mL capacity.

5. Reagents and Materials

5.1 *Purity of Reagents*—Reagent grade chemicals shall be used in this test. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society where such specifications are available.[4] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*—Unless otherwise indicated, reference to water shall be understood to mean at least Type III reagent water conforming to Specification D 1193.

5.3 *Sodium Carbonate* (Na_2CO_3), anhydrous powder.

5.4 *Hydrochloric Acid* (HCl), concentrated, sp gr 1.19.

5.5 *Hydrochloric Acid* (1+3)—Mix 1 volume of concentrated HCl with 3 volumes of water.

5.6 *Hydrochloric Acid* (1+1)—Mix 1 volume of concentrated HCl with 1 volume of water.

5.7 *Hydrochloric Acid* (1+99)—Mix 1 volume of concentrated HCl with 99 volumes of water.

5.8 *Sulfuric Acid* (1+1)—Mix 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) with 1 volume of water.

5.9 *Hydrofluric Acid* (HF), concentrated 48 to 51 %.

6. Hazards

6.1 Due to the origins of RDF in municipal waste, common sense dictates that precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type), especially while milling RDF samples; conducting tests under negative pressure hoods when possible; and washing hands before eating or smoking.

7. Sampling

7.1 *Refuse-Derived Fuel (RDF):*

NOTE 1—ASTM Subcommittee E38.01 is currently in the process of developing procedures for sampling RDF.

7.1.1 RDF products are frequently nonhomogeneous. For this reason, significant care should be exercised to obtain a representative laboratory sample from the RDF lot to be characterized.

7.1.2 The sampling method for these procedures should be based on agreement between involved parties.

7.1.3 The laboratory sample must be air-dried and particle

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

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[2] *Annual Book of ASTM Standards*, Vol 11.01.

[3] *Annual Book of ASTM Standards*, Vol 11.04.

[4] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards", by Joseph Rosin, D. Van Nostrand Co., Inc., New York, NY, and the "United States Pharmacopeia."

size reduced to pass a 0.5-mm screen for analysis. This procedure must be performed carefully to preserve the sample's representative characteristics (other than particle size) while preparing the analysis sample to be used in this procedure (see Method E 829).

7.2 *Refuse-Derived Fuel Ash, Fly Ash, Bottom Ash, or Slag*—The method of sampling for this procedure should be based on agreement between involved parties.

8. Sample Preparation

8.1 *Refuse-Derived Fuel:*

8.1.1 Weigh accurately 30 to 50 g of RDF analysis sample as prepared in 7.1 into a conditioned and preweighed fused quartz dish.

8.1.2 Spread out the analysis sample of RDF in a layer not over 38.1 mm (1½ in.) in depth.

8.1.3 Place the dish in the muffle at a low temperature (not greater than 100°C) and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter.

8.1.4 Complete the conversion to ash at a temperature of 800 to 900°C (1470 to 1650°F).

8.1.5 Cool in a desiccator and stir the ash to ensure homogeneity of particle sizes. Be careful not to lose any ash from the dish during this stirring.

8.1.6 Spread the ash in a thin layer in the disn, and ignite in a stream of oxygen for 1½ h at 800 to 850°C (1470 to 1560°F) to ensure complete and uniform oxidation of the ash.

8.1.7 Cool the ash to room temperature in a desiccator.

8.1.8 Weigh the dish and the ash.

8.1.9 Calculate the percent ash as follows:

$$\% \text{ Ash} = (C - A)/(B - A) \times 100$$

where:

A = weight of fused quartz, g,
B = weight of fused quartz dish and sample, g, and
C = weight of fused quartz dish and ash, g.

8.2 *Refuse-Derived Fuel Ash, Fly Ash, Bottom Ash, or Slag:*

8.2.1 Prepare the RDF ash, fly ash, bottom ash, or slag by grinding the sample in an agate mortar to a particle size to pass a No. 200 (75-μm) sieve.

8.2.2 Weigh accurately 6 to 10 g of RDF ash, fly ash, bottom ash, or slag as prepared in 8.2.1 into a conditioned preweighed fused quartz dish.

8.2.3 Spread out the analysis sample of the ash to be analyzed in a layer not over 6.4 mm (¼ in.) in depth.

8.2.4 Place the dish in the muffle at a low temperature (not greater than 100°C), and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter.

8.2.5 Complete the conversion to ash at a temperature of 800 to 900°C (1470 to 1659°F).

8.2.6 Cool in a desiccator and stir the ash to ensure homogeneity of particle sizes. Be careful not to lose any ash from the dish during this stirring.

8.2.7 Spread the ash in a thin layer in the dish and ignite in a stream of oxygen for 1½ h at 800 to 850°C (1470 to 1560°F) to ensure complete and uniform oxidation of the ash.

8.2.8 Cool the ash to room temperature in a desiccator.

8.2.9 Weigh the dish and the ash.

8.2.10 Calculate the percent residue after ignition as follows:

$$\% \text{ Residue after ignition} = (F - D)/(E - D) \times 100$$

where:

D = weight of fused quartz dish, g,
E = weight of fused quartz dish and sample, of RDF ash, fly ash, bottom ash or slag, g, and
F = weight of fused quartz dish and residue after ignition of RDF ash, fly ash, bottom ash, or slag, g.

9. Procedure

9.1 *Sample Fusion:*

9.1.1 Weigh accurately 0.010 to 0.100 g of the prepared RDF ash as prepared in 8.1 or the residue of RDF ash, fly ash, bottom ash, or slag as prepared in 8.2 into a platinum or graphite crucible.

9.1.2 Add 1.0 g of Na_2CO_3. Mix the ash and Na_2CO_3 well, then add an additional 0.5 g of Na_2CO_3 to cover the mixture.

9.1.3 Place the crucible into a clean silica or refractory tray, and place in a muffle furnace preheated to 1000°C and maintain until the mass is quiescent (about 45 min).

9.1.4 Set the crucible aside to cool.

9.1.5 Rinse off the outside of the crucible, and place it on its side in a 300-mL casserole or beaker about one-third full of water. Warm and stir until the cake disintegrates and can be easily removed.

9.1.6 By means of platinum tipped tongs, lift the crucible out of the liquid, rinsing it thoroughly with water followed by rinsing with dilute hydrochloric acid (HCl, 1+3); adding the rinse to the casserole or beaker.

9.2 *Acid Dehydration:*

9.2.1 Very slowly and cautiously add 20 mL of concentrated hydrochloric acid (HCl, sp gr 1.19) to the covered casserole or beaker (see Note 2). Remove the cover and rinse. If any gritty particles are present, the fusion is incomplete and must be repeated, using a new sample and a larger amount of Na_2CO_3.

NOTE 2—This solution will tend to "creep" over the rim of the casserole unless the rim is kept hot and dry. This can be accomplished by applying heat from above by means of infrared lamps.

9.2.2 Evaporate the solution to dryness on a steam bath.

9.2.3 Without heating the residue any further, treat it with 5 to 10 mL of HCl (concentrated), wait at least 2 min, then add an equal amount of water.

9.2.4 Cover the casserole or beaker, and digest for 10 min on the steam bath or hot plate.

9.2.5 Dilute the solution with an equal volume of hot water, immediately filter through medium-textured ashless paper, and wash the residue thoroughly with hot HCl (1+99), then with hot water.

9.2.6 Reserve the residue.

9.2.7 Again, evaporate the filtrate to dryness and bake the residue in an oven for 1 h at 105 to 110°C.

9.2.8 Cool, add 10 to 15 mL HCl (1+1) and digest on the steam bath or hot plate for 10 min.

9.2.9 Dilute with an equal volume of water, filter immediately on a fresh filter paper, and wash the small amount of residue thoroughly with hot HCl (1+99), then with hot water.

9.2.10 Transfer the papers containing the residues (from

9.2.6 and 9.2.9) to a weighed conditioned platinum crucible.

9.2.11 Dry and ignite the papers, first at a low heat until the carbon of the filter paper is completely consumed without flaming, and finally ignite at 1100 to 1200°C until the weight becomes constant. Record weight of residue after ignition.

9.3 *Volatilization of Silicon Tetrafluoride*:

9.3.1 Treat the silica (SiO_2) thus obtained, which will contain impurities, in the crucible with 0.5 to 1 mL of water, 2 drops of H_2SO_4 (1+1) and 10 mL of HF.

9.3.2 Cautiously evaporate to dryness on a hot plate or hot sand bath.

9.3.3 Finally, ignite the small residue at 1050 to 1100°C (1922 to 2012°F) for 5 min.

9.3.4 Cool in a desiccator and weigh.

9.3.5 The difference between this weight and the weight previously obtained in 9.2.11 represents the amount of SiO_2.

9.4 *Blank*—Make a blank determination, following the same procedures as used in 9.1.2 through 9.3.5 using the same amounts of reagents and correct the obtained in the analysis accordingly.

10. Calculation

10.1 Calculate the concentration of SiO_2 as follows:

10.1.1 Percent SiO_2 on prepared sample as used in 9.1.1.

$$\% \ SiO_2 = (W_1 - W_2) - (W_3 - W_4)/W_5 \times 100$$

where:

W_1 = weight of residue after first ignition as in 9.2.11, g,

W_2 = weight of blank after first ignition, g,

W_3 = weight of residue after treatment with HF and second ignition as in 9.3.4, g,

W_4 = weight of blank after treatment with HF and second ignition, g, and

W_5 = weight of sample of prepared RDF, RDF ash, fly ash, bottom ash, or slag as used in 9.1.1, g.

10.1.2 Percent SiO_2 in RDF (8.1).

$$\% \ SiO_2 \text{ in RDF} = (G \times H)/(100)$$

where:

G = ash as found in 8.1.9, %, and

H = SiO_2 as found in 10.1.1, %.

10.1.3 Percent SiO_2 in RDF ash, fly ash, bottom ash, or slag (8.2).

$$\% \ SiO_2 \text{ in RDF Ash, fly ash, bottom ash, or slag} = (I \times H)/(100)$$

where:

I = residue after ignition as found in 8.2.10, %, and

H = SiO_2 as found in 10.1.1, %.

See Method E 791 for procedures to convert values to other bases.

11. Precision and Bias

11.1 Precision and bias statements cannot be made at this time for the measurement of SiO_2 by this test method.

Designation: E 897 - 88

Standard Test Method for Volatile Matter in the Analysis Sample of Refuse-Derived Fuel[1]

1. Scope

1.1 This test method covers the determination of the percentage of gaseous products, exclusive of moisture vapor, in the analysis sample which is released under specific conditions of the test. The knowledge of the volatile matter content assists in predicting burning characteristics of RDF.

1.2 This test method may be applicable to any waste material from which a laboratory analysis sample can be prepared.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 790 Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample[3]

E 829 Method of Preparing RDF Laboratory Samples for Analysis[3]

3. Definition

3.1 *refuse-derived fuel* (RDF):

RDF-1—Waste used as a fuel in as-discarded form.

RDF-2—Waste processed to coarse particle size with or without ferrous metal separation.

RDF-3—shredded fuel derived from municipal solid waste (MSW) that has been processed to remove metal, glass, and other inorganics. This material has a particle size such that 95 weight % passes through a 2-in. square mesh screen.

RDF-4—Combustible waste processed into powder form—95 weight % passing a 10-mesh screen.

RDF-5—Combustible waste densified (compressed) into the form of pellets, slugs, cubettes or briquettes.

RDF-6—Combustible waste processed into liquid fuel.

RDF-7—Combustible waste processed into gaseous fuel.

4. Summary of Test Method

4.1 Volatile matter is determined by establishing the loss in weight resulting from heating refuse-derived fuel under rigidly-controlled conditions. The measured weight loss, corrected for moisture as determined in Test Method E 790, establishes the volatile matter content

5. Apparatus

5.1 *Platinum or Fused Quartz Crucible*, with closely fitting cover. The crucible shall be of not less than 10 nor more than 20 mL capacity, not less than 25 nor more than 35 mm in diameter, and not less than 30 nor more than 35 mm in height.

5.2 *Vertical Electric Tube Furnace*—The furnace may be of the form shown in Fig. 1. It shall be regulated to maintain a temperature of 950 ± 20°C in the crucible, as measured by a thermocouple positioned in the furnace.

6. Hazards

6.1 Due to the origins of RDF in municipal waste, common sense dictates that precautions should be observed when conducting tests on the samples. Recommended hygienic practices include use of gloves when handling RDF, wearing dust masks (NIOSH-approved type), especially while milling RDF samples, conducting tests under a negative-pressure hood when possible, and washing hands before eating or smoking.

NOTE 1—Caution—Exercise care when placing the sample into the volatile furnace. The possibility of an explosion always exists when heating samples of unknown origin.

7. Procedure

7.1 Weigh to the nearest 0.1 mg about 1 g of thoroughly mixed air-dried analysis RDF sample in a weighed crucible. Close with a cover (Note 2), place on a platinum or Nichrome-wire support and insert directly into the furnace chamber, which shall be maintained at a temperature of 950 ± 20°C. Lower the crucible immediately to the 950°C zone. Regulation of the temperature to within the prescribed limits is critical. After the more rapid discharge of volatile matter has subsided as shown by disappearance of the luminous flame, inspect the crucible to verify that the lid is still seated. If necessary, reseat the lid to guard against the admission of air into the crucible. Do this as rapidly as possible by raising the crucible to the top of the furnace chamber, reposition the lid to more perfectly seal the crucible, then lower immediately back to the 950°C zone.

NOTE 2—The cover should fit closely enough so that the carbon deposit from the refuse-derived fuel does not burn away from the underside.

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E38.01 on Energy.

Current edition approved March 25, 1988. Published May 1988. Originally published as E 897 - 82. Last previous edition E 897 - 82.

[2] *Annual Book of ASTM Standards*, Vol 15.05.

[3] *Annual Book of ASTM Standards*, Vol 11.04.

7.2 After heating for a total of exactly 7 min, remove the crucible from the furnace and, without disturbing the cover, allow it to cool on a metal cooling block. Weigh as soon as cold (Note 3). The percentage loss of weight minus the percentage moisture in accordance with Test Method E 790 is the volatile matter.

NOTE 3—To ensure uniformity of results, the cooling period should be kept constant and should not be prolonged beyond 15 min.

8. Calculation

8.1 Calculate the percentage of volatile matter on an "as-determined" basis, V_{ad} as follows:

$$V_{ad} = \left[\frac{A - B}{A} \times 100\right] - M_{ad}$$

where:

A = weight of sample used, g,
B = weight of sample after heating, g, and
$M_{(ad)}$ = moisture (as-determined), %.

9. Precision and Bias

9.1 *Precision:*

9.1.1 The standard deviation of individual determinations, in percent absolute, is as follows:

Typical Average Value, 69 %
Within-Laboratory, 0.7 %
Between-Laboratories, 2.1 %

9.1.2 The precision estimates in 8.1.1 are based on an interlaboratory study conducted in accordance with Practice E 180.

9.2 *Bias:*

9.2.1 The bias of this test method has not been determined.

9.2.2 Precision estimates are based on ASTM Report No. RR:E 38-1000 which describes the preliminary testing and round-robin tests.[4]

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[4] Supporting data are available on loan from ASTM Headquarters. Request RR:E 38-1000.

Designation: E 953 - 88

Standard Test Method for Fusibility of Refuse-Derived Fuel (RDF) ASH[1]

1. Scope

1.1 This test method covers the observation of the temperatures at which triangular pyramids (cones) prepared from RDF ash attain and pass through certain stages of fusing and flow when heated at a specific rate in controlled, mildly-reducing, and oxidizing atmospheres.

1.2 The test method is empirical, and strict observance of the requirements and conditions is necessary to obtain reproducible temperatures and enable different laboratories to obtain concordant results.

1.3 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* See Section 6 for additional hazard information.

2. Referenced Documents

2.1 *ASTM Standards:*

E 180 Practice for Determining the Precision Data of ASTM Methods for Analysis and Testing of Industrial Chemicals[2]

E 829 Method of Preparing RDF Laboratory Samples for Analysis[3]

3. Definitions and Symbols

3.1 The critical temperature points to be observed are as follows, denoting the atmosphere used:

3.1.1 *initial deformation temperature, IT*—the temperature at which the first rounding of the apex of the cone occurs. Shrinking or warping of the cone is ignored if the tip remains sharp. In Fig. 1, the first cone shown is an unheated one; the second cone, IT, is a typical cone at the initial deformation stage.

3.1.2 *softening temperature, ST*—the temperature at which the cone has fused down to a spherical lump in which the height is equal to the width at the base as shown by the third cone, ST, in Fig. 1.

3.1.3 *hemispherical temperature, HT*—the temperature at which the cone has fused down to a hemispherical lump at which point the height is one half the width of the base as shown by the fourth cone, HT, in Fig. 1.

3.1.4 *fluid temperature, FT*—the temperature at which the fused mass has spread out in a nearly flat layer with a maximum height of 1.6 mm (1/16 in.) as shown in the fifth cone, FT, in Fig. 1.

3.2 *forms of refuse-derived fuel* (RDF):

RDF-1—Waste used as a fuel in as-discarded form.

RDF-2—Waste processed to coarse particle size with or without ferrous metal separation.

RDF-3—Shredded fuel derived from municipal solid waste (MSN) that has been processed to remove metal, glass, and other inorganics. This material has a particle size such that 95 weight % passes through a 2-in. square mesh screen.

RDF-4—Combustible waste processed into powder form, 95 weight % passing a 10-mesh screening.

RDF-5—Combustible waste densified (compressed) into the form of pellets, slugs, cubettes, or briquettes.

RDF-6—Combustible waste processed into liquid fuel.

RDF-7—Combustible waste processed into gaseous fuel.

4. Significance and Use

4.1 The standard is available to producers and users of RDF to use in determining the fusibility of ash produced from RDF.

4.2 *Limitations of Ash Fusibility Data*—Ash fusibility data are too often over-interpreted. In practice, types of burning equipment, rate of burning, temperature and thickness of fire bed or ball, distribution of ash forming mineral matter in the RDF, and viscosity of the molten ash may influence ash behavior more than the ash fusibility characteristics determined by the laboratory test. Furthermore, conditions existing during applied combustion of RDF are so complex that they are impossible to duplicate completely in a small-scale laboratory test. Therefore, the test should be considered an empirical one and the data, at best, only qualitative.

5. Apparatus

5.1 *Furnace*—Any gas-fired or electric furnace conforming to the following requirements may be used.

5.1.1 The furnace shall be capable of maintaining a uniform temperature zone in which to heat the ash cones. This zone shall be such that the difference in the melting point of 12.7 mm (½ in.) pieces of pure gold wire when mounted in place of the ash cones on the cone support shall be not greater than 11°C (20°F) in a reducing atmosphere test run.

5.1.2 The furnace shall be capable of maintaining the desired atmosphere surrounding the cones during heating.

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[1] This test method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E 38.01 on Energy.

Current edition approved March 25, 1988. Published May 1988. Originally published as E 953 -83. Last previous edition E 953 - 83.

[2] *Annual Book of ASTM Standards*, Vol 15.05.

[3] *Annual Book of ASTM Standards*, Vol 11.04.

The composition of the atmosphere, reducing or oxidizing, shall be maintained within the limits specified in Section 7. The desired atmosphere in the gas-fired furnace surrounding the cones shall be obtained by regulation of the ratio of gas to air in the combustion mixture. The desired atmosphere in the electric furnace shall be obtained by means of gases introduced into the heating chamber. The muffle shall be gas-impervious, free from cracks, and the closure-plug tight fitting. Since state-of-the-art furnaces vary somewhat in design, the gas supply inlet tube shall be installed per instructions of furnace manufacturer.

5.1.3 The furnace shall be capable of regulation so that the rate of temperature rise shall be 8 ± 3°C (15 ± 5°F) per minute.

5.1.4 The furnace shall provide a means of observing the ash cones during the heating. Observation shall be on the same horizontal plane as the cone-support surface.

5.2 *Cone Mold*—A commercially available cone mold as shown in Fig. 2 shall be used. The cone shall be 19 mm (¾ in.) in height and 6.4 mm (¼ in.) in width at each side of the base which is an equilateral triangle.

5.2.1 A steel spatula with a pointed tip, ground off to fit the cone depression in the mold, is suitable for removal of the ash cone.

5.3 *Optical Pyrometer or Thermocouple*, for temperature measurements, conforming to the following requirements:

5.3.1 *Optical Pyrometer*—An optical pyrometer of the disappearing filament type shall be used. The instrument shall have been calibrated to be accurate within 11°C (20°F) up to 1400°C (2550°F) and within 16°C (30°F) from 1400 to 1600°C (2550°F to 2900°F) (Note 2). The pyrometer filament shall be sighted on the cones until the softening point temperature (Fig. 1) has been passed, and then sighted on the cone support. The pyrometer shall have readable graduations not larger than 5.5°C (10°F).

NOTE 2—The pyrometer equipment shall be standardized periodically by a suitably equipped standardizing laboratory such as that of the National Bureau of Standards, or checked periodically against equipment certified by the National Bureau of Standards.

5.3.2 *Thermocouple*—A thermocouple of platinum and platinum-rhodium, protected from the furnace gases by a glazed porcelain sheath, shall be used with a high-resistance millivoltmeter or potentiometer accurate and readable to within 5.5°C (10°F). The sheath shall be sealed to the furnace wall by alundum cement. The hot junction of the thermocouple shall touch the end of the sheath and shall be located in the center of the muffle and immediately to the rear of the cones. The thermocouple protective sheath shall be checked periodically for cracks. The thermocouple and its meter shall meet the requirements of Section 10. The potentiometer or millivoltmeter shall be located or shielded adequately as to prevent radiant or convection heating of the cold junction. The room temperature compensator shall be adjusted to the existing temperature.

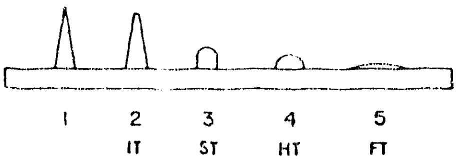
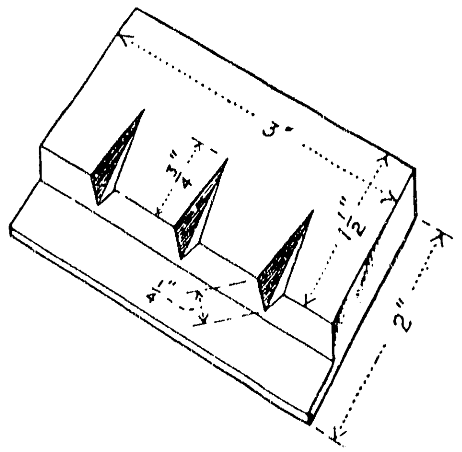


FIG. 1 Critical Temperature Points



U.S. Customary Units, in.	SI Units, mm
¼	6.4
¾	19.1
1½	38.1
2	50.2
3	76.2

FIG. 2 Brass Cone Mold

5.4 *Ash-Cone Refractory Support*—The ash cone shall be mounted on a refractory base composed of a mixture of equal parts by weight of kaolin and alumina conforming to the following requirements:

5.4.1 *Kaolin*—NF-Grade powder passing a No. 200 (0.074 mm) sieve.

5.4.2 *Aluminum Oxide*—Reagent grade powder passing a No. 100 (0.149 mm) sieve.

5.5 *Refractory Support Mold*—A mold with flat top and bottom surfaces to provide a refractory support of suitable thickness to minimize warping shall be used. A side mold not over ¼ in. (6.4 mm) high of any convenient shape, placed on an iron plate so that the top surface of the refractory mix can be struck off flat and parallel to the base by means of a straightedge, is satisfactory. For electric furnace use, legs not over 3 mm (⅛ in.) long may be provided on the corners of the cone support by suitable holes bored in the iron base plate of the mold.

5.6 *Gold Wire*,[4] Twenty-four gage or larger round wire of 99.98 % purity, but drawn from metal of 99.99 % purity, and having a melting point of 1063°C (1945°F).

5.7 *Nickel Wire*,[5] Twenty-four gage or larger round wire of CP nickel 99.98 % pure, fully annealed, and having a melting point of 1452°C (2645°F).

6. Hazards

6.1 Due to the origins of RDF in municipal waste, common sense dictates that some precautions should be observed

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[4] Gold wire of this purity can be purchased from the Baker Dental Division of Engelhard Industries, Inc., 850 Passaic Ave., East Newark NJ 07029.

[5] Nickel wire of this purity can be purchased with the additional specifications of having a minimum coefficient of resist for 0 to 100°C of 0.00673 Ohm/Ohm °C, from the Baker Dental Division of Engelhard Industries, Inc., 850 Passaic Ave., East Newark, NJ 07029.

when conducting tests on the samples. Recommended hygenic practices include use of gloves when handling RDF; wearing dust masks (NIOSH-approved type); especially while milling RDF samples; conducting tests under a negative pressure hood when possible; and washing hands before eating or smoking.

6.2 Good laboratory practices dictate the precautions that should be observed when using compressed gases such as hydrogen or carbon monoxide as reducing gases.

7. Test Atmosphere[6]

7.1 *Gas Fired Furnace:*

7.1.1 *Reducing Atmosphere Test*—A mildly reducing atmosphere surrounding the cones shall be maintained during the test in the gas-fired furnace. Hydrogen, hydrocarbons, and carbon monoxide shall be considered as reducing gases; oxygen, carbon dioxide, and water vapor shall be considered as oxidizing gases. Nitrogen is inert. The ratio by volume of reducing gases to oxidizing gases in the atmosphere shall be between the limits of 20 to 80 %, that is, on a nitrogen-free basis, the total amount of reducing gases present shall be between the limits of 20 and 80 volume %. A flame 150 to 200 mm (6 to 8 in.) in height and tinged with yellow above the furnace outlet has been found to provide an atmosphere within the specified limits.

7.1.2 *Oxidizing Atmosphere Test*—An atmosphere containing a minimum amount of reducing gases shall be maintained surrounding the cones during the test in the gas-fired furnace. On a nitrogen-free basis, the volume of the reducing gases present in the atmosphere will not exceed 10 volume %. Combustion with the maximum possible quantity of air with preservation of the specified rate of temperature increase has been found to provide an atmosphere within the specified limits. A completely blue flame, not over 50 mm (2 in.) in height above the outlet at the beginning of the test, provides the desired atmosphere; and, by regulation of the combustion gas-air ratio, the specified atmosphere and temperature rise can be maintained.

7.2 *Electric Furnace:*

7.2.1 *Reducing Atmosphere Test*—A regulated flow of gas of the nominal composition, 60 % carbon monoxide and 40 ± 5 volume % carbon dioxide,[7] shall be maintained in the heating chamber throughout the test (Note 2) in the electric furnace. The gas stream shall be regulated by any convenient means to provide a measured flow of 1.3 to 1.5 furnace volumes per minute.

NOTE 2—New cylinders of the mixed gas for which a certified analysis is not available should be mixed before use by laying the cylinder on its side with the protective screw cap in place. The cylinder should then be rolled back and forth, 6 to 10 ft in each direction, approximately 15 times. Certified analyses of each cylinder or batch can be obtained for a small extra charge.

7.2.2 *Oxidizing Atmosphere Test*—A regulated stream of air shall be maintained throughout the test in the electric furnace. The gas stream shall be regulated by any convenient means to provide a measured flow of 1.3 to 1.5 furnace volumes per minute.

8. Preparation of Ash

8.1 Use RDF milled to passing a 0.5-mm (0.02-in.) sieve prepared in accordance with Method E 829 to obtain the ash by incineration in a well-ventilated muffle furnace. The quantity of RDF required will vary with the ash content; usually 3 to 5 g of ash will suffice for cones for several check determinations. Spread out the analysis sample of RDF in a layer approximately 6.4 mm (¼ in.) in depth in a fireclay or porcelain roasting dish. Place the dish in the muffle at a low temperature, and gradually heat to redness at such a rate as to avoid mechanical loss from too rapid expulsion of volatile matter. The rate of temperature rise of 500°C (932°F) in 1 h was found to be satisfactory. Complete the conversion to ash at a temperature of 800 to 900°C (1470 to 1650°F). Transfer the ash to an agate mortar (Note 3), and grind so it will pass a No. 200 (0.074 mm) sieve.

NOTE 3—A mechanical agate mortar grinder will save time where many determinations are made. An iron mortar or pestle is not recommended because of metallic contamination.

8.2 Spread the ash in a thin layer in a fireclay, silica, or porcelain dish and ignite it in a stream of oxygen for 1½ h at 800 to 850°C (1470 to 1560°F) to ensure complete and uniform oxidation of the ash. Any tube or muffle-type furnace which, when supplied with an oxygen flow of not less than one furnace volume in 5 min will maintain a highly oxidizing atmosphere, is suitable.

NOTE 4—It has been found that in most samples, the initial ignition outlined in 8.1 is sufficient to convert the RDF to ash and the reignition step in 8.2 is not necessary. Reignition of the ash should be made only if an observable amount of noncombustible matter or carbon is present.

9. Preparation of Cones

9.1 Thoroughly mix the ignited ash in a mechanical mixer or on a sheet of glazed paper or oil cloth by raising first one corner to roll the ash over, and then raising each of the other corners in rotation in the same manner until each corner has been raised five times or more.

9.2 Take sufficient ash for the number of cones desired from various parts of the bulk ash. Moisten the ash with a few drops of a clear, filtered (if necessary) 10 % solution of dextrin containing 0.1 % salicylic acid as a preservative, and work it into a stiff plastic mass with a spatula. Press the plastic material firmly with a spatula into the cone mold to form the triangular pyramids. Strike off the exposed surfaces of the material smooth and remove the cones from the mold by applying pressure at the base with a suitably pointed spatula. Previous coating of the mold with a thin layer of petroleum jelly, thinned with kerosine (if necessary), aids in preventing adherence of the cones to the mold and in providing the sharp point and edges desired in the cone.

9.3 Place the cones in a suitable location to dry sufficiently to permit handling without deformation. Mount the dried cone vertically on a freshly prepared refractory base. Moisten a portion of the well-mixed kaolin-alumina mixture with a minimum amount of water to make a workable, but stiff, plastic mass and firmly press it into the support mold. Strike off the surface of the mass flat and smooth with a steel spatula, moistening with one or two drops of water is neces-

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[6] For information concerning the effect of various atmospheres, see U.S. Bureau of Mines Bulletin 129, 1918.

[7] This gas is available from the Matheson Division of Searle Medical Products USA, Inc.

sary to obtain a smooth surface. A number of cones may be mounted on one base. Make shallow triangular depressions, not over 0.8 mm (1/32 in.) in depth, with a triangular file ground to the correct size to produce a depression to fit the base of the cone, and locate the cones sufficiently distant from adjacent cones so that no merging of the fusing material of the cones shall occur during the test. Mount the cones vertically in the depressions while the base is still wet without the use of ash or refractory as mounting aid.

NOTE 5—The intent of the triangular depression is to enable the cones to be mounted in a sufficiently stable manner to permit handling of the prepared support with cones.

NOTE 6—Gold wires can be mounted on each cone support beside the ash cones, and the gold melting point observed concurrently with the ash cones in both oxidizing and reducing atmospheres.

9.4 For the calibration check run of Section 10, mount 12.7 mm (½ in.) lengths of gold and nickel wire as described in 5.6 and 5.7 vertically on a support similar to those prepared as described in 9.3, but on which no ash cones are mounted. Insert the pieces of wire into the support before drying. Two or more pieces of each kind of wire should be mounted on this support in locations which correspond to ash cone positions. Dry the support as described in 9.5 but do not ignite. At least one such support with mounted pieces of gold and nickel wire shall be prepared for each week of observation of ash fusibility.

9.5 Dry the mounted cones at 110°C (230°F), and ignite at 750°C (1382°F) to remove all carbonaceous material.

10. Calibration

10.1 At least once during each week of operation, check the optical pyrometer or the thermocouple and its meter for calibration in place under routine test conditions with the reducing atmosphere by observing the melting point of gold. At the same time, check the adequacy of the furnace atmosphere by observing the melting point of nickel.

10.1.1 Insert a support with mounted pieces of gold and nickel wire into the test furnace. Locate at the position used for tests of ash cones.

10.1.2 Establish the reducing gas atmosphere, and heat the furnace chamber in accordance with 11.1.

10.1.3 Observe the temperatures shown on the meter when the pieces of wire melt.

10.1.4 The indicated melting points should be within ±10°F (5.5°C) of the following:

Gold	1945°F (1063°C)
Nickel	2645°F (1452°C)

10.1.5 If the indicated melting point of gold wire frequently falls outside of the desired range, readjust or calibrate the meter so that the average temperature from several observations of the gold melting point is within the specified range.

10.1.6 If the indicated melting point for nickel wire frequently falls outside the desired range after applying the corrections in 10.1.5, the consistency of indicated temperatures and the subsequent appearance of the specimen should be examined closely. Erratic readings of failures to obtain melting at 2645°F (1452°C) can be due to nickel oxidation caused by an insufficient reducing atmosphere. If a consistent error of more than 25°F (14°C) is found, the furnace atmosphere and the temperature measurement equipment should be suspected of having faults; necessary corrections should be made.

11. Procedure

11.1 *Reducing Atmosphere Test:*

11.1.1 Place the mounted test cones in the furnace at a temperature of not over 1470°F (800°C) for the gas-fired furnace and not over 750°F (400°C) for the electric furnace in order to provide sufficient time to purge the air from the uniform temperature zone and establish the desired atmosphere.

11.1.2 If the furnace temperature is below the respective temperature specified in 11.1.1, raise it rapidly to the specified temperature; then control the rate of heating to give a rate of temperature increase of 15 ± 5°F (8 ± 3°C) per minute. Maintain this rate throughout the test.

11.1.3 Establish the mildly reducing atmosphere surrounding the cones, as specified in 7.1.1 and 7.2.1, at the temperature specified in 11.1.1 for the respective furnace type. Maintain this atmosphere throughout the test.

NOTE 7—At temperatures of the order of 2500 to 2600°F (1370 to 1430°C) and above in the gas-fired furnace, it may not be possible to maintain the reducing gases above the 20-volume % limit specified while also preserving the specified rate of temperature increase. At such temperatures, the effect of the atmosphere is not so critical as the maintenance of the specified heating rate. Make every effort to maintain the reducing gases as near the 20- volume % level as possible at such temperature.

11.2 *Oxidizing Atmosphere Test:*

11.2.1 Place the mounted test cones in the furnace at a temperature of not over 800°C (1470°F) for the gas-fired furnace, and not over 400°C (750°F) for the electric furnace. If the furnace temperature is below the respective temperature specified, raise it rapidly to the specified temperature, then control the rate of heating to give a rate of temperature increase of 8 ± 3°C (15 ± 5°F) per minute. Maintain this rate throughout the test.

11.2.2 Establish the oxidizing atmosphere surrounding the cones, as specified in 7.1.2 and 7.2.2 at the temperature specified in 11.2.1 for the respective furnace type. Maintain this atmosphere throughout the test.

12. Report

12.1 Report the following information:

12.1.1 Type of atmosphere,

12.1.2 Initial deformation temperature, IT,

12.1.3 Softening temperature, ST,

12.1.4 Hemispherical temperature, HT, and

12.1.5 Fluid temperature, FT.

13. Precision and Bias

13.1 *Precision:*[8]

13.1.1 The standard deviations of individual determinations are given in Table 1:

13.1.2 The precision estimates in Table 1 apply to both reducing and oxidizing atmospheres. The standard deviation

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[8] Supporting data describing the preliminary testing and round-robin tests on which precision estimates are based is available on loan from ASTM Headquarters Request RR: E 38 - 1000.

TABLE 1 Standard Deviations of Individual Determinations

Temperature Range		Standard Deviation			
°C	(°F)	Within-Laboratory		Between-Laboratories	
		Sw		Sb	
1049-1177	(1920-2150)	8.9°C	(16°F)	36.7°C	(66°F)
1204-1260	(2200-2300)	11.0°C	(20°F)	92.2°C	(166°F)

for the 1049-1177°C (1950-2150°F) range include initial deformation (IT), softening temperature (ST), and hemispherical temperature (HT). The standard deviations for the 1204-1260°C (2200-2300°F) range cover fluid temperature (FT).

13.1.3 The precision estimates in Table 1 are based on an interlaboratory study conducted in accordance with Practice E 180.

13.2 *Bias*—The bias of this test method has not been determined.

Designation: E 1037 – 84

Standard Method for Measuring Particle Size Distribution of RDF-5[1]

1. Scope

1.1 This method is used to determine the size distribution of a RDF-5 sample. Size is defined as the maximum length of the particle, where length is determined by the RDF-5 manufacturing process. That is, a pellet, cubette, or briquette all have a recognizable length. Figure 1 displays the sizes and shapes of some RDF-5 particles.

1.2 An air dried RDF-5 sample is separated into categories of differing particle sizes. The size distribution is measured as the weight percentage of each size category. A graph of a function of the cumulative fraction of material by weight finer than particle size versus particle size is plotted. From this plot are taken values which describe the size distribution—the uniformity constant and the characteristic particle size.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Significance and Use

2.1 The particle size distribution of RDF-5 strongly influences the storage and handling characteristics of the fuel. Small particles tend to block flow through storage bins and feed hoppers, although correct bin and hopper designs will alleviate this problem of blockage.

2.2 This method of measuring size by hand allows accurate description of RDF-5 particle size distribution. Measurement by hand is superior to sieving techniques, wherein particles may be broken by the size separation technique itself. However, hand measurement is more time-consuming than sieving techniques.

3. Definition

3.1 *RDF-5*—solid fuel derived from municipal solid waste in which the processed combustible fraction is densified (compressed) into the form of pellets, cubettes or briquettes.

4. Apparatus

4.1 *Labelled Containers,* used to hold the particles which are separated by size. Appropriate containers are beakers or pans labelled "≥70 mm", "≥60 mm – <70 mm", etc. The tare weight of each container shall be recorded to 0.1 g.

4.2 *Scale,* capable of weighing the sample and container with an accuracy of 0.1 g.

4.3 *Vernier Calipers,* a length-measuring instrument having an accuracy of 0.1 mm.

5. Procedure

5.1 The sample shall weigh 1.0 ± 0.1 kg (2.2 ± 0.2 lb) unless otherwise specified. Record the weight of the sample to the nearest 0.1 g.

5.2 Beginning with the largest particles, measure the length of each particle in the sample. Separate the particles into containers labelled as the size categories of less than 10 mm, 10 to less than 20 mm, 20 to less than 30 mm, 30 to less than 40 mm, etc. as needed.

5.3 Record the weight of each size category to 0.1 g.

5.4 Add the weights of the size components. If this sum differs by more than 2 % from the sample weight recorded initially, then reject the analysis and begin another test.

5.5 Use the sum of the separate size categories as the total weight to determine weight percentages of each size fraction. If the weight percentage of any fraction is greater than or equal to 25 %, then separate that fraction into two portions of 5-mm size categories. Continue separating the size fraction into categories of 2.5 mm, 1.25 mm, etc., until the weight percentage of each fraction is less than 25 %.

6. Calculations

6.1 With each particle size for which there is data, calculate y, the cumulative fraction of the sample less than that particle size. This is found by summing the weight percentages of all fractions less than that size. Also calculate the value of the Rosin-Rammler function for each particle size, as follows:

$$ln\left(\frac{1}{1-y}\right)$$

6.2 Plot $\ln[1/(1-y)]$ versus particle size on log-log paper. Data points will yield a straight line.

6.3 Determine two values which characterize this line—the uniformity constant and the characteristic particle size. The uniformity constant, n, is defined as the slope of the line. The characteristic particle size, x_0, is defined as the size at which 63.2 % of the particles (by weight) are smaller. The characteristic particle size is the size corresponding to $ln[1/(1-y)] = 1.0$. Figure 2 is an example of this plot.

7. Report

7.1 Report the uniformity constant, n (a dimensionless

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[1] This method is under the jurisdiction of ASTM Committee E-38 on Resource Recovery and is the direct responsibility of Subcommittee E-38.08 on Processing Equipment and Unit Operations.

Current edition approved Dec. 28, 1984. Published June 1985.

TABLE 1 Results of Precision Testing

		Uniformity Constant	Characteristic Size
Intra-laboratory	Sample mean	2.42	3 g
	Standard deviation	0.16	2 mm
Inter-laboratory	Sample mean	2.65	36 mm
	Standard deviation	0.18	2 mm

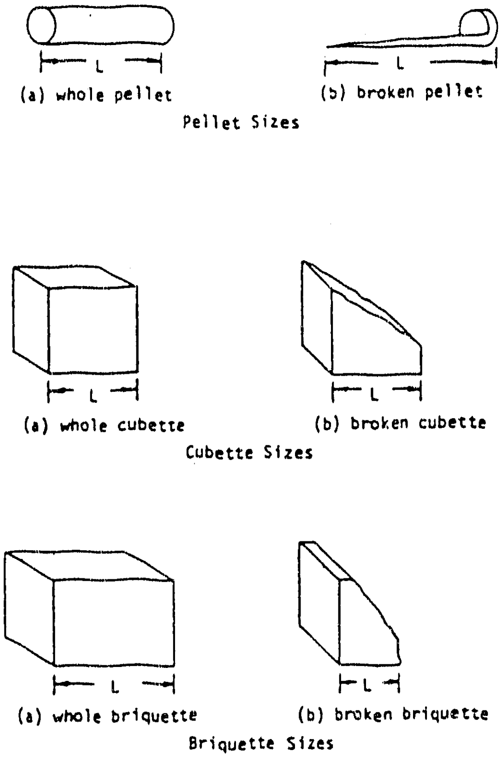

FIG. 1 RDF-5 Sizes

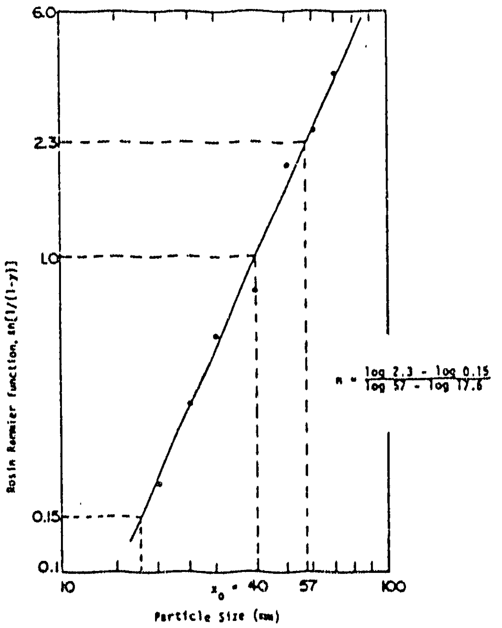

FIG. 2 Size Distribution Example—Test Number 1

number), and the characteristic particle, x_0 (millimeters).

8. Precision

8.1 Table 1 presents the results of intra- and inter-laboratory precision testing. Intra-laboratory and inter-laboratory tests were performed on different populations of RDF-5.

Designation: E 1288 − 89

Standard Test Method for The Durability of Biomass Pellets[1]

This standard is issued under the fixed designation E 1288; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the relative durability of biomass fuel pellets by tumbling and sieve analysis.

1.2 The values stated in SI units are to be regarded as the standard. The values given in parentheses are for information only.

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 346 Methods for Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Method for Preparing Coal Samples for Analysis[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purpose[3]

3. Apparatus

3.1 *Square Hole Woven-Wire Cloth Sieves*, of the following sizes conforming to ASTM Specification E 11:

(1) 2.36 mm (No. 8)
(2) 1.18 mm (No. 16)
(3) 600 μm (No. 30)
(4) 300 μm (No. 50)
(5) 150 μm (No. 100)
(6) 75 μm (No. 200)

Optionally a seventh sieve, the next size opening smaller than the pellet diameter, can be included.

3.2 *Air-Tight Gross Sample Containers*, of a size as to contain the sample (see Note 1).

NOTE 1—The containers need to be air tight so as to minimize changes in the moisture content of the sample that may affect the test results. Heavy plastic bags are ideal since they minimize trapped air.

3.3 *Metal or Glass Laboratory Containers*, of such configuration as to facilitate the collection and weighing of samples during testing.

3.4 *Metal Tumbler*, 304 by 304 and 127 mm, (12 in. by 12 in. and 5 in. deep), rotated about an axis perpendicular to and centered in the 304-mm (12-in.) sides. A 508 by 229-mm (2 by 9-in.) plate is affixed symmetrically along one of its 229-mm (9-in.) sides to a diagonal of one of the 304 by 304-mm (12 by 12-in.) sides. A dust-tight door (or doors) may be placed in any side. Projections shall be kept to a minimum and well rounded.

4. Sampling

4.1 *Place of Sampling:*

4.1.1 Sample pellets while they are being loaded into or unloaded from means of transportation or when they are discharged from storage bins or conveyors.

NOTE 2—Samples collected from surface of piles are, in general, unreliable because of the exposure to the environment. If necessary, collect nine increments from a foot or more below the surface at nine points covering the pile.

4.2 *Collection of the Gross Sample:*

4.2.1 Collect increments regularly, systematically, and with such frequency, so that the entire quantity of pellets sampled will be represented proportionally in the gross sample.

4.2.2 The quantity of the sample shall be large enough to be representative but not less than 45.45 kg (100 lb).

4.2.3 Sample reduction may be done by two methods, a coning and dividing process, or by using a riffle.

4.2.3.1 Coning and dividing reduction is accomplished by placing the gross sample on a sheet of rubber or oil cloth. Thoroughly mix it by raising first one corner of the cloth and then the other. After mixing, cone and quarter the sample. Continue the operation until the sample is reduced sufficiently so that one fourth of the coning sample weighs about 1 kg (2.2 lb). This shall constitute a laboratory sample.

NOTE 3—The operations of mixing, coning, and quartering, are described and illustrated in Methods D 346.

4.2.3.2 Riffle reduction is accomplished by using a standard coal riffle. The gross sample is riffled repeatedly until one half of the riffle sample equals about 1 kg (2.2 lb) that will constitute a laboratory sample.

NOTE 4—Riffles and procedures are described in Method D 2013.

5. Procedure

TUMBLER TEST

5.1 *Laboratory Sample:*

5.1.1 Sieve the pellets to be tested through the largest sieve, and consider 250 g of the retained pellets a laboratory sample.

NOTE 5—Pellets should be at approximately ambient temperature so as to reflect true handling behavior.

5.2 *Procedure:*

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[1] This test method is under the jurisdiction of ASTM Committee E-48 on Biotechnology and is the direct responsibility of Subcommittee E48.05 on Biomass Conversion.

Current edition approved Feb. 24, 1989. Published April 1989.

[2] *Annual Book of ASTM Standards*, Vol 05.05.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

5.2.1 Place the laboratory sample in the tumbler and seal ie tumbler. Then tumble for 5 min at 50 r/min. After that me, stop the tumbler and allow to stand for a sufficient me so as to allow the dust to settle. Then remove the ontents and place in a preweighed laboratory container. lean the interior of the tumbler from dust using a 25.4-mm l-in.) bristle brush. Add the resulting material to the iboratory container. Weigh the laboratory container and ample to the nearest 0.01 g. Determine the weight of the ample by subtracting the weight of the laboratory container rom the total weight. If more than 0.5 % (that is, 1.25 g) has een lost, then reject the sample and tumble another sample. f the sample is satisfactory, then sieve it using the procedure lescribed in the Sieve Test.

SIEVE TEST

5.3 *Procedure:*

5.3.1 Place the 250-g sample from four samples on the argest sieve of the stack of sieves in descending order, with a ollection pan under the 75-µm (No. 200) sieve. Place a tight-fitting cover over the top sieve and place in a mechanical shaker. Shake the sieves for 2 min at 150 rotations/min. Remove the sieves and brush the bottom of each sieve to loosen dust; then resume shaking for another 1 min. Remove the stack of sieves from the shaker and weigh the material retained on each sieve and in the pan to the nearest 0.01.

6. Calculation

6.1 Calculate the fineness from the weights of the residues on the sieves, and express as percentages of the weight of the original sample. Apply sieving value corrections for the 75-µm (No. 200) sieve, as determined by the NIST, to the material sieved on the 75-µm sieve.

7. Report

7.1 The fineness test shall be reported as follows:

Retained on Sieve	Passing Sieve	Percent
2.36 mm (No. 8)	. . .	. . .
1.18 mm (No. 16)	2.36 mm (No. 8)	. . .
600 µm (No. 30)	1.18 mm (No. 16)	. . .
300 µm (No. 50)	600 µm (No. 30)	. . .
150 µm (No. 100)	300 µm (No. 50)	. . .
75 µm (No. 200)	150 µm (No. 100)	. . .
. . .	75 µm (No. 200)	. . .

8. Reproducibility of Results

8.1 Duplicate determinations by the same operator, using the same sieves, shall check within 1 % on all sizes. Different operators, using different sieves, shall check within 3 % on the material sieved on the 75-µm (No. 200) sieve.

APPENDIX C

CHARACTERIZATION AND TESTING:

EPA METHOD: TCLP

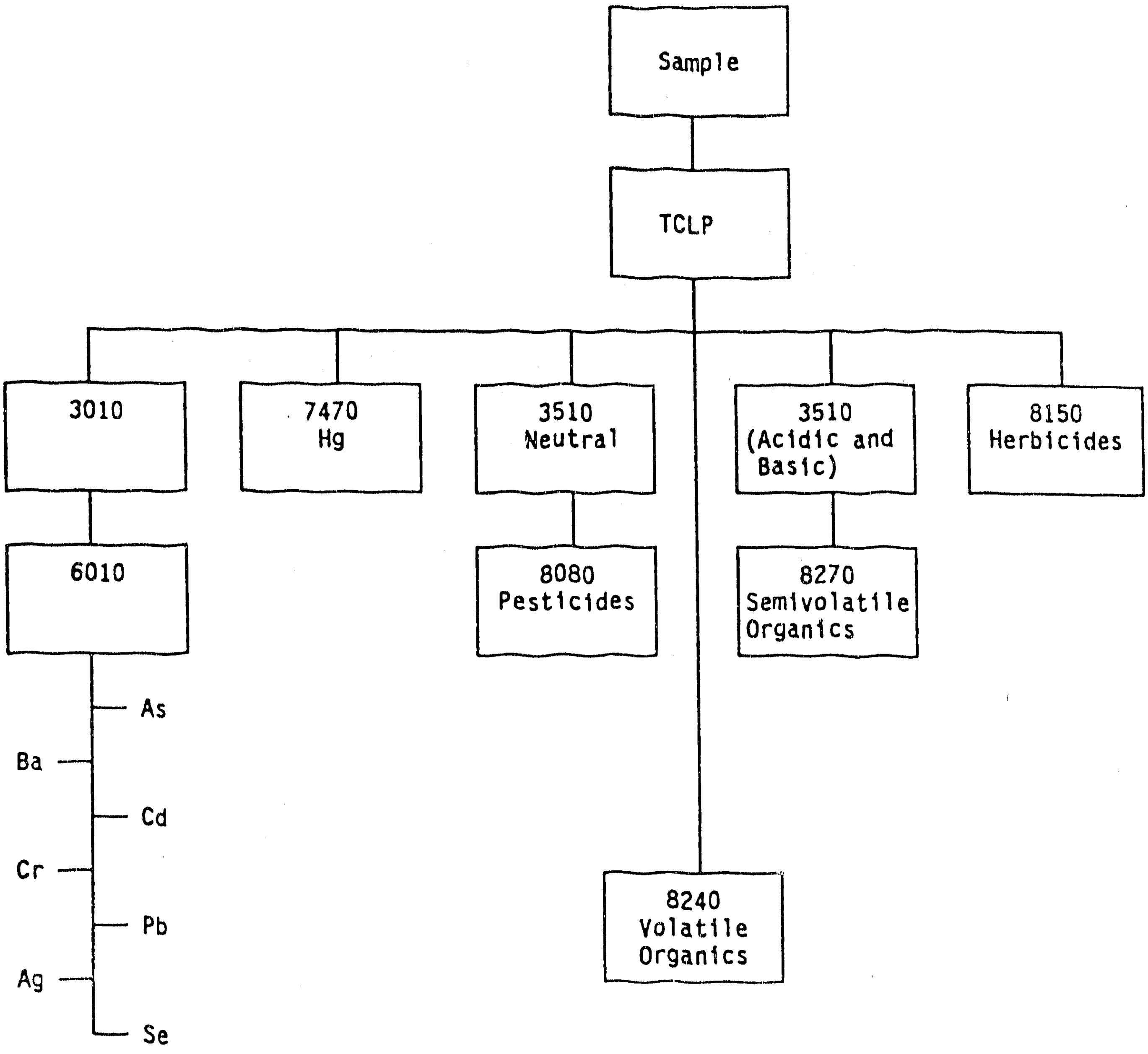


Figure 2-6B. TCLP.

TABLE II.2.—TOXICITY CHARACTERISTIC CONSTITUENTS AND REGULATORY LEVELS

EPA HW No.[1]	Constituent (mg/L)	CAS No.[2]	Chronic toxicity reference level (mg/L)	Regulatory level (mg/L)
D004	Arsenic	7440-38-2	0.05	5.0
D005	Barium	7440-39-3	1.0	100.0
D018	Benzene	71-43-2	0.005	0.5
D006	Cadmium	7440-43-9	0.01	1.0
D019	Carbon tetrachloride	56-23-5	0.005	0.5
D020	Chlordane	57-74-9	0.0003	0.03
D021	Chlorobenzene	108-90-7	1	100.0
D022	Chloroform	67-66-3	0.06	6.0
D007	Chromium	7440-47-3	0.05	5.0
D023	o-Cresol	95-48-7	2	[4] 200.0
D024	m-Cresol	108-39-4	2	[4] 200.0
D025	p-Cresol	106-44-5	2	[4] 200.0
D026	Cresol		2	[4] 200.0
D016	2,4-D	94-75-7	0.1	10.0
D027	1,4-Dichlorobenzene	106-46-7	0.075	7.5
D028	1,2-Dichloroethane	107-06-2	0.005	0.5
D029	1,1-Dichloroethylene	75-35-4	0.007	0.7
D030	2,4-Dinitrotoluene	121-14-2	0.0005	[3] 0.13
D012	Endrin	72-20-8	0.0002	0.02
D031	Heptachlor (and its hydroxide)	76-44-8	0.00008	0.008
D032	Hexachlorobenzene	118-74-1	0.0002	[3] 0.13
D033	Hexachloro-1,3-butadiene	87-68-3	0.005	0.5
D034	Hexachloroethane	67-72-1	0.03	3.0
D008	Lead	7439-92-1	0.05	5.0
D013	Lindane	58-89-9	0.004	0.4
D009	Mercury	7439-97-6	0.002	0.2
D014	Methoxychlor	72-43-5	0.1	10.0
D035	Methyl ethyl ketone	78-93-3	2	200.0
D036	Nitrobenzene	98-95-3	0.02	2.0
D037	Pentachlorophenol	87-86-5	1	100.0
D038	Pyridine	110-86-1	0.04	[3] 5.0
D010	Selenium	7782-49 2	0.01	1.0
D011	Silver	7440-22-4	0.05	5.0
D039	Tetrachloroethylene	127-18-4	0.007	0.7
D015	Toxaphene	8001-35-2	0.005	0.5
D040	Trichloroethylene	79-01-6	0.005	0.5
D041	2,4,5-Trichlorophenol	95-95-4	4	400.0
D042	2,4,6-Trichlorophenol	88-06-2	0.02	2.0
D017	2,4,5-TP (Silvex)	93-72-1	0.01	1.0
D043	Vinyl chloride	75-01-4	0.002	0.2

[1] Hazardous waste number.

[2] Chemical abstracts service number.

[3] Quantitation limit is greater than the calculated regulatory level. The quantitation limit therefore becomes the regulatory level.

[4] If *o-*, *m-*, and *p-cresol* concentrations cannot be differentiated, the total cresol (D026) concentration is used. The regulatory level for total cresol is 200 mg/l.

5. Section 261.30 is amended by revising paragraph (b) to read as follows:

§ 261.30 General.

* * * * *

(b) The Administrator will indicate his basis for listing the classes or types of wastes listed in this subpart by employing one or more of the following Hazard Codes:

Ignitable Waste	(I)
Corrosive Waste	(C)
Reactive Waste	(R)
Toxicity Characteristic Waste	(E)
Acute Hazardous Waste	(H)
Toxic Waste	(T)

Appendix VII identifies the constituent which caused the Administrator to list the waste as a Toxicity Characteristic Waste (E) or Toxic Waste (T) in §§ 261.31 and 261.32.

* * * * *

6. Appendix II of part 261 is revised to read as follows:

Appendix II—Method 1311 Toxicity Characteristic Leaching Procedure (TCLP)

1.0 Scope and Application

1.1 The TCLP is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes.

1.2 If a total analysis of the waste demonstrates that individual contaminants are not present in the waste, or that they are present but at such low concentrations that the appropriate regulatory thresholds could not possibly be exceeded, the TCLP need not be run.

1.3 If an analysis of any one of the liquid fractions of the TCLP extract indicates that a regulated compound is present at such high levels that even after accounting for dilution from the other fractions of the extract the concentration would be above the regulatory threshold for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile contaminant exceeds the regulatory threshold for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory threshold.

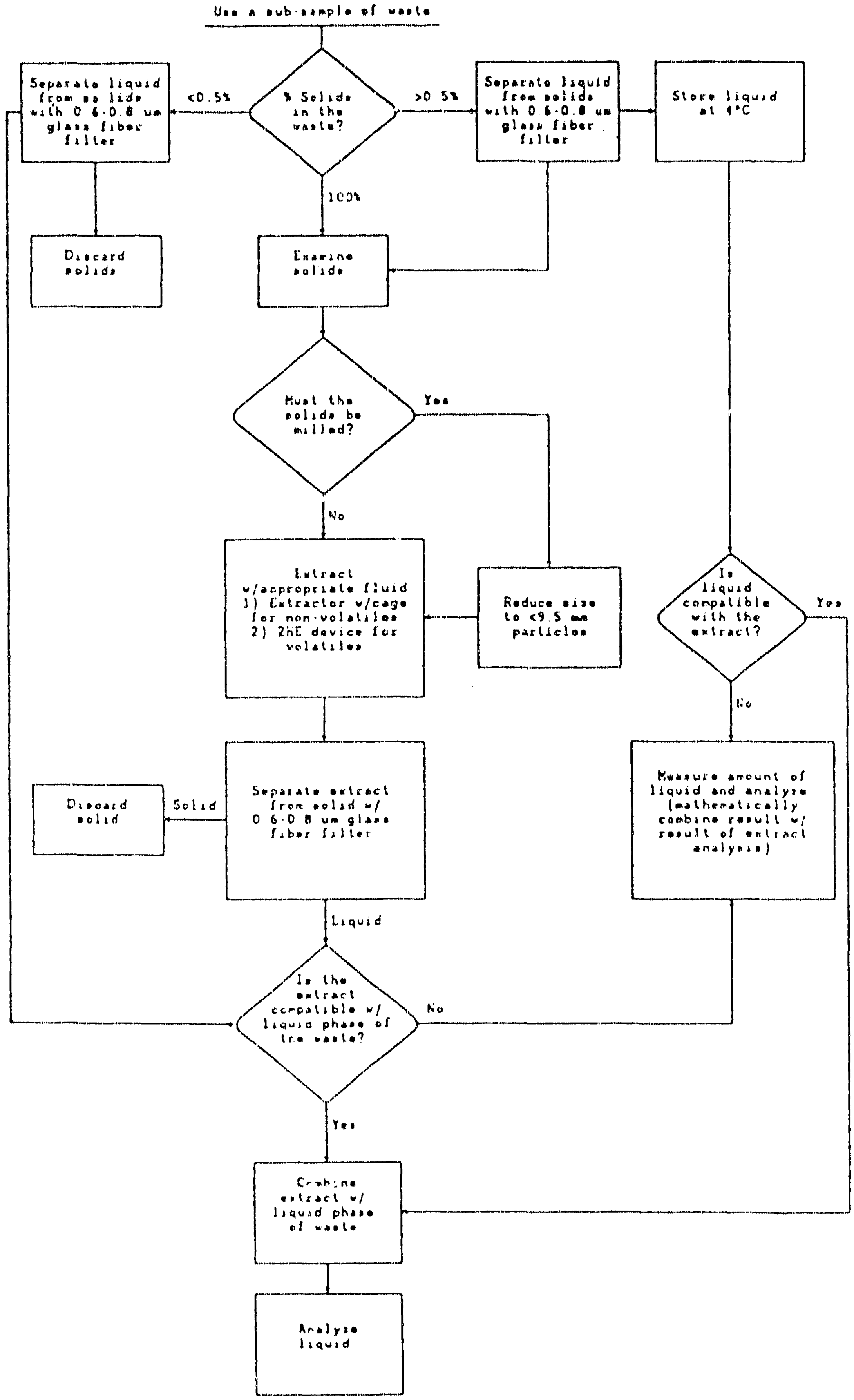
2.0 Summary of Method (see Figure 1)

2.1 For liquid wastes (i.e., those containing less than 0.5 percent dry solid material), the waste, after filtration through a 0.6 to 0.8-um glass fiber filter, is defined as the TCLP extract.

2.2 For wastes containing greater than or equal to 0.5 percent solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the solid phase, if necessary, is reduced in particle size. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the alkalinity of the solid phase of the waste. A special extractor vessel is used when testing for volatile contaminants (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the solid phase by filtration through a 0.6 to 0.6-um glass fiber filter.

BILLING CODE 6560-50-M

Figure 1 Method 1311 Flowchart



BILLING CODE 6560-50-C

TABLE 1.—VOLATILE CONTAMINANTS [1]

Compound	CAS no.
Acetone	67-64-1
Benzene	71-43-2
n-Butyl alcohol	71-36-3
Carbon disulfide	75-15-0
Carbon tetrachloride	56-23-5
Chlorobenzene	108-90-7
Chloroform	67-66-3
1,2-Dichloroethane	107-06-2
1,1-Dichloroethylene	75-35-4
Ethyl acetate	141-78-6
Ethyl benzene	100-41-4
Ethyl ether	60-29-7
Isobutanol	78-83-1
Methanol	67-56-1
Methylene chloride	75-09-2
Methyl ethyl ketone	78-93-3
Methyl isobutyl ketone	108-10-1
Tetrachloroethylene	127-18-4
Toluene	108-88-3
1,1,1-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
Trichlorofluoromethane	75-69-4
1,1,2-Trichloro-1,2,2-trifluoroethane	76-13-1
Vinyl chloride	75-01-4
Xylene	1330-20-7

[1] When testing for any or all of these contaminants, the zero-headspace extractor vessel shall be used instead of the bottle extractor.

2.3 If compatible (i.e., multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

3.0 Interferences

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 Apparatus and Materials

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 2) at 30 + 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessel:

4.2.1 Zero-Headspace Extraction Vessel (ZHE). This device is for use only when the waste is being tested for the mobility of volatile constituents (i.e., those listed in Table 1). The ZHE (depicted in Figure 3) allows for liquid/solid separation within the device, and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see step 4.3.1). The vessels shall have an internal volume of 500–600 mL and be equipped to accommodate a 90–110 mm filter. The devices contain VITON ® [1] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

BILLING CODE 6560-50-M

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[1] VITON ® is a trademark of Du Pont.

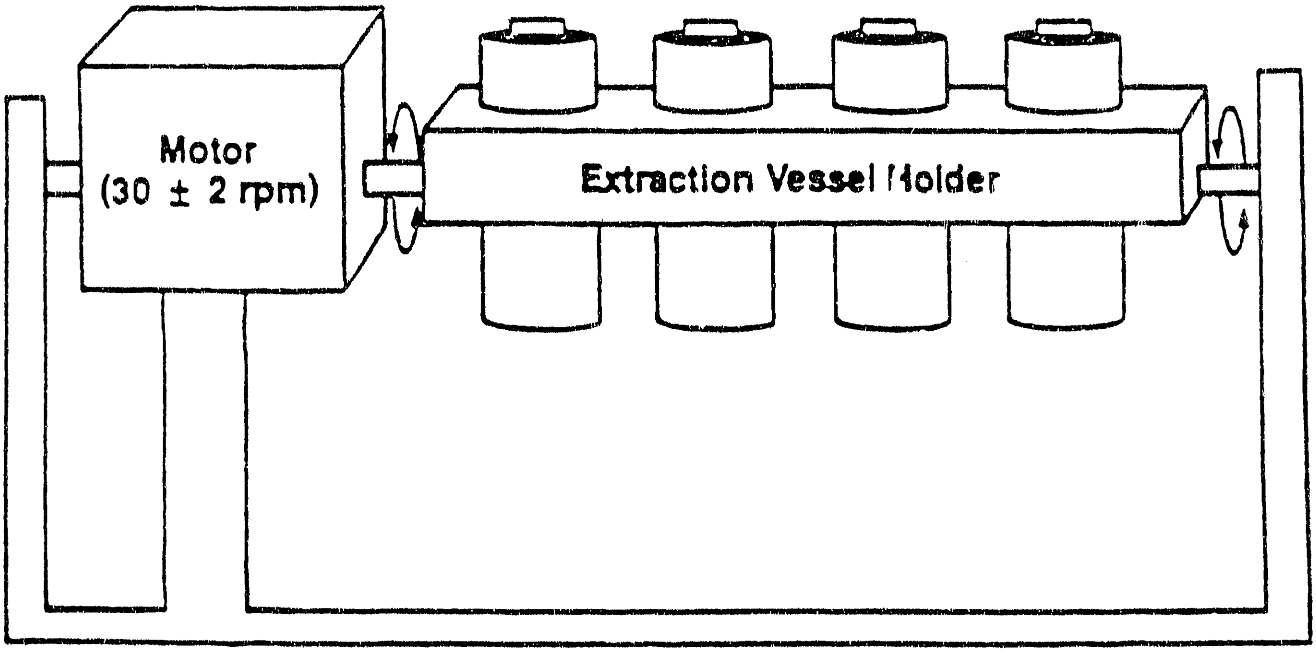

Figure 2. Rotary Agitation Apparatus

TABLE 2.—SUITABLE ROTARY AGITATION APPARATUS [1]

Company	Location	Model no.
Analytical Testing and Consulting Services, Inc	Warrington, PA (215) 343-4490	2-ZHE or 4-bottle extractor (DC20S); 4-ZHE or 8-bottle extractor (DC20); 6-ZHE or 12-bottle extractor (DC20B).
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	2-vessel (3740-2). 4-vessel (3740-4). 6-vessel (3740-6). 8-vessel (3740-8). 12-vessel (3740-12). 24-vessel (3740-24).
Environmental Machine and Design, Inc	Lynchburg, VA (804) 845-6424	8-vessel (08-00-00). 4-vessel (04-00-00).
IRA Machine Shop and Laboratory	Santurce, PR (809) 752-4004	8-vessel (011001).
Lars Lande Manufacturing	Whitmore Lake, MI (313) 449-4116.	10-vessel (10VRE). 5-vessel (5 VRE).
Millipore Corp.	Bedford, MA (800) 225-3384	4-ZHE or 4 1-liter bottle extractor (YT30ORAHW).

[1] Any device that rotates the extraction vessel in an end-over-end fashion at 30 +2 rpm is acceptable.

BILLING CODE 6560-50-M

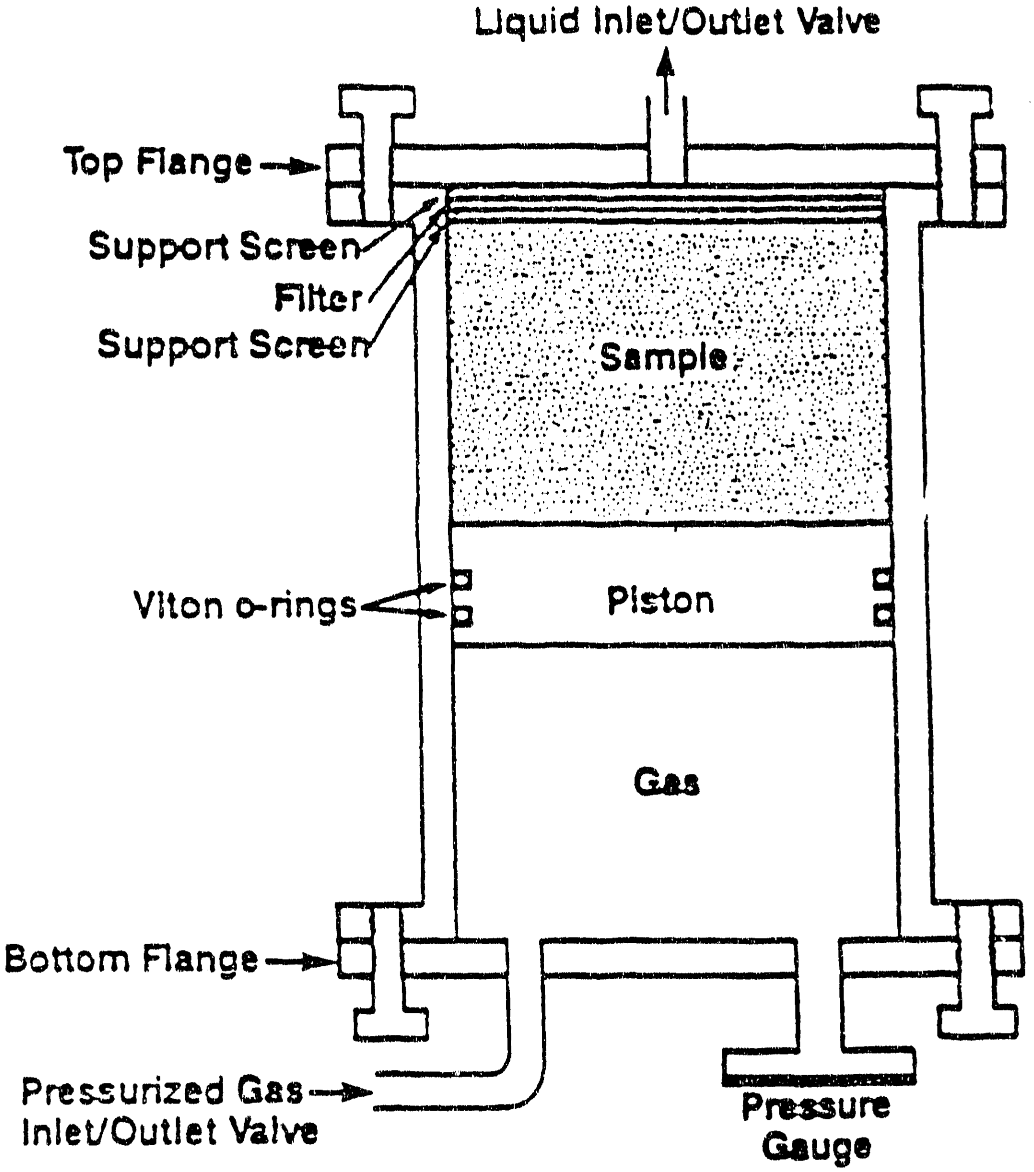

Figure 3. Zero-Headspace Extractor (ZHE)

BILLING CODE 6560-50-C

TABLE 3.—SUITABLE ZERO-HEADSPACE EXTRACTOR VESSELS [1]

Company	Location	Model no.
Analytical Testing & Consulting Services, Inc	Warrington, PA (215) 343-4490	C102, Mechanical Pressure Device.
Associated Design and Manufacturing Company	Alexandria, VA (703) 549-5999	3745-ZHE, Gas Pressure Device.
Lars Lande Manufacturing [2]	Whitmore Lake, MI (313) 449-4116.	ZHE-11, Gas Pressure Device.
Millipore Corporation	Bedford, MA (800) 225-3384	YT3009OHW, Gas Pressure Device.
Environmental Machine and Design, Inc	Lynchburg, VA (804) 845-6424	VOLA-TOX1, Gas Gas Pressure Device.

[1] Any device that meets the specifications listed in Section 4.2.1 of the method is suitable.

[2] This device uses a 110 mm filter.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for TCLP analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see section 9.0) refers to pounds-per-square-inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the waste is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

The extraction bottles may be constructed from various materials, depending on the contaminants to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extractor Vessel (ZHE): When the waste is evaluated for volatiles, the zero-headspace extraction vessel described in section 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

Note: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the waste is evaluated for other than volatile compounds, any filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater and equipped to accommodate a 142 mm diameter filter are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 percent) and for highly granular liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb waste components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene, or polyvinyl chloride may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are constituents of concern.

TABLE 4.—SUITABLE FILTER HOLDERS [1]

Company	Location	Model/Catalogue no.	Size (um)
Nucleopore Corporation	Pleasanton, CA (800) 882-7711	425910 410400	142 mm 47 mm
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	302400 311400	142 mm 47 mm
Millipore Corporation	Bedford, MA (800) 225-3384	YT30142HW XX1004700	142 mm 47 mm

Any device capable of separating the liquid from the solid phase of the waste is suitable, providing that it is chemically compatible with the waste and the constituents to be analyzed. Plastic devices (not listed above) may be used when only inorganic contaminants are of concern. The 142 mm size filter holder is recommended.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8-um or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH meters: The meter should be accurate to +0.05 units at 25 °C.

TABLE 5 —SUITABLE FILTER MEDIA [1]

Company	Location	Model	Pore size
Millipore Corporation	Bedford, MA (800) 225-3384	AP40	0.7
Nucleopore Corporation	Pleasanton, CA (415) 463-2530	211625	0.7
Whatman Laboratory Products, Inc	Clifton, NJ (201) 773-5800	GFF	0.7
Micro Filtration Systems	Dublin, CA (800) 334-7132 (415) 828-6010	GF75	0.7

[1] Any filter that meets the specifications in Section 4.4 of the Method is suitable.

4.6 ZHE extract collection devices: TEDLAR®[2] bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract of the waste when using the ZHE device. The devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (i.e., < 1 percent of total waste), the TEDLAR® bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (i.e., > 1 percent of total waste), the syringe or the TEDLAR® bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 percent solid) or has no significant solid phase (is 100 percent liquid), either the TEDLAR® bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE extraction fluid transfer devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (e.g., a positive displacement or peristaltic pump, a gas tight syringe, pressure filtration unit (See Step 4.3.2), or other ZHE device).

4.8 Laboratory balance: Any laboratory balance accurate to within +0.01 grams may be used (all weight measurements are to be within +0.1 grams).

5.0 Reagents

5.1 Reagent water. Reagent water is defined as water in which an interferant is not observed at or above the methods detection limit of the analyte(s) of interest. For nonvolatile extractions, ASTM Type II water or equivalent meets the definition of reagent water. For volatile extractions, it is recommended that reagent water be generated by any of the following methods. Reagent water should be monitored periodically for impurities.

5.1.1 Reagent water for volatile extractions may be generated by passing tap water through a carbon filter bed containing about 500 grams of activated carbon (Calgon Corp., Filtrasorb-300 or equivalent).

5.1.2 A water purification system (Millipore Super-Q or equivalent) may also be used to generate reagent water for volatile extractions.

5.1.3 Reagent water for volatile extractions may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the water temperature at 90 + 5 °C, bubble a contaminant-free inert gas (e.g., nitrogen) through the water for 1 hour. While still hot, transfer the water to a narrow mouth screw-cap bottle under zero-headspace and seal with a Teflon-lined septum and cap.

5.2 Hydrochloric acid (1N), HCl, made from ACS reagent grade.

5.3 Nitric acid (1N), HNO_3, made from ACS reagent grade.

5.4 Sodium hydroxide (1N), NaOH, made from ACS reagent grade.

5.5 Glacial acetic acid, HOAc, ACS reagent grade.

5.6 Extraction fluid.

5.6.1 Extraction fluid #1: Add 5.7 mL glacial HOAc to 500 mL of the appropriate water (See Step 5.1), add 64.3 mL of 1N NaOH, and dilute to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 4.93 + 0.05.

5.6.2 Extraction fluid #2: Dilute 5.7 mL glacial HOAc with ASTM Type II water (See Step 5.1) to a volume of 1 liter. When correctly prepared, the pH of this fluid will be 2.88 + 0.05.

Note: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.7 Analytical standards prepared according to the appropriate analytical method.

6.0 Sample Collection, Preservation, and Handling

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 The TCLP may place requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the contaminants of concern. An aliquot is needed for preliminary evaluation of which extraction fluid is to be used for the nonvolatile contaminant extraction procedure. Another aliquot may be needed to actually conduct the nonvolatile extraction (see section 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the waste is to be evaluated for volatile contaminants, care shall be taken to minimize the loss of volatiles. Samples shall be taken and stored in a manner to prevent the loss of volatile contaminants (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4 °C, until ready to be opened prior to extraction).

6.6 TCLP extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic contaminant determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see section 8.14 if precipitation occurs). Extracts or portions of extracts for organic contaminant determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See section 10.0 (QA requirements) for acceptable sample and extract holding times.

7.0 Preliminary Evaluations

Perform preliminary TCLP evaluations on a minimum 100 gram aliquot of waste. This aliquot may not actually undergo TCLP extraction. These preliminary evaluations include: (1) determination of the percent solids; (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration; (3) determination of whether the solid portion of the waste requires particle size reduction; and (4) determination of which of the two extraction fluids are to be used for the nonvolatile TCLP extraction of the waste.

7.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1 If the waste will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solids) proceed to Step 7.3

7.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.1.3 through 7.1.9.

7.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

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[2] TEDLAR® is a registered trademark of Du Pont.

7.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.7 Quantitatively transfer the waste sample to the filter holder (liquid and solid phases). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature then allow the sample to warm up to room temperature in the device before filtering.

Note: If waste material (>1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.5 to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1–10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10-psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase.

Note: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 7.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the waste sample by subtracting the weight of the liquid phase from the weight of the total waste sample, as determined in Step 7.1.5 or 7.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.9)}}{\text{Total weight of waste (Step 7.1.5 or 7.1.7)}} \times 100$$

7.2 If the percent solids determined in Step 7.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.3 to determine whether the solid material requires particle size reduction or to Step 7.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.9 is less than 0.5%, then proceed to Step 8.9 if the nonvolatile TCLP is to be performed and to section 9.0 with a fresh portion of the waste if the volatile TCLP is to be performed.

7.2.1 Remove the solid phase and filter from the filtration apparatus.

7.2.2 Dry the filter and solid phase at 100 +20 °C until two successive weighing yield the same value within +1 percent. Record the final weight.

Note: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{\text{(Weight of dry waste + filter)} - \text{tared weight of filter}}{\text{Initial weight of waste (Step 7.1.5 or 7.1.7)}} \times 100$$

7.2.4 If the percent dry solids is less than 0.5 percent, then proceed to Step 8.9 if the nonvolatile TCLP is to be performed, and to Section 9.0 if the volatile TCLP is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile TCLP is to be performed, return to the beginning of this Section (7.0) and, with a fresh portion of waste, determine whether particle size reduction is necessary (Step 7.3) and determine the appropriate extraction fluid (Step 7.4). If only the volatile TCLP is to be performed, see the note in Step 7.4.

7.3 Determination of whether the waste requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the waste, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm², or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken, see Step 9.6.

Note: Surface area criteria are meant for filamentous (e.g., paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.4 Determination of appropriate extraction fluid: If the solid content of the waste is greater than or equal to 0.5 percent and if TCLP extraction for nonvolatile constituents will take place (Section 8.0), perform the determination of the appropriate fluid (Step 5.6) to use for the nonvolatiles extraction as follows:

Note: TCLP extraction for volatile constituents uses only extraction fluid #1 (Step 5.6.1). Therefore, if TCLP extraction for nonvolatiles is not required, proceed to Section 9.0.

7.4.1 Weigh out a small subsample of the solid phase of the waste, reduce the solid (if necessary) to a particle-size of approximately 1 mm in diameter or less, and transfer 5.0 grams of the solid phase of the waste to a 500-mL beaker or Erlenmeyer flask.

7.4.2 Add 96.5 mL of reagent water (ASTM Type II) to the beaker, cover with a watchglass, and stir vigorously for 5 minutes using a magnetic stirrer. Measure and record the pH. If the pH is <5.0, use extraction fluid #1. Proceed to Section 8.0.

7.4.3 If the pH from Step 7.4.2 is >5.0, add 3.5 mL 1N HCl, slurry briefly, cover with a watchglass, heat to 50 °C, and hold at 50 °C for 10 minutes.

7.4.4 Let the solution cool to room temperature and record the pH. If the pH is <5.0, use extraction fluid #1. If the pH is >5.0, use extraction fluid #2. Proceed to Section 8.0.

7.5 If the aliquot of the waste used for the preliminary evaluation (Steps 7.1–7.4) was determined to be 100% solid at Step 7.1.1, then it can be used for the Section 8.0 extraction (assuming at least 100 grams remain), and the section 9.0 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 9.0. The aliquot of the waste subjected to the procedure in Step 7.1.7 might be appropriate for use for the section 8.0 extraction if an adequate amount of solid (as determined by Step 7.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 8.10 of the nonvolatile TCLP extraction.

8.0 Procedure When Volatiles Are Not Involved

A minimum sample size of 100 grams (solid and liquid phases) is required. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of TCLP extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single TCLP extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

8.1 If the waste will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 percent solid, see Step 7.1), weigh out a subsample of the waste (100 gram minimum) and proceed to Step 8.9.

8.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 8.3 to 8.8.

8.3 Pre-weigh the container that will receive the filtrate.

8.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

Note: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.

8.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight. If the waste contains <0.5 percent dry solids (Step 7.2), the liquid portion of the waste, after filtration, is defined as the TCLP extract. Therefore, enough of the sample should be filtered so that the amount of filtered liquid will support all of the analyses required of the TCLP extract. For wastes containing >0.5 percent dry solids (Step 7.1 or 7.2), use the percent solids information obtained in Step 7.1 to determine the optimum sample size (100 gram minimum) for filtration. Enough solids should be generated by filtration to support the analyses to be performed on the TCLP extract.

8.6 Allow slurries to stand to permit the solid phase to settle. Wastes that settle slowly may be centrifuged prior to filtration. Use centrifugation only as an aid to filtration. If the waste is centrifuged, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

8.7 Quantitatively transfer the waste sample (liquid and solid phases) to the filter holder (see Step 4.3.2). Spread the waste sample evenly over the surface of the filter. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

Note: If waste material (>1 percent of the original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 8.5, to determine the weight of the waste sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1–10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when the liquid flow has ceased at 50 psi (i.e., filtration does not result in any additional filtrate within a 2-minute period), stop the filtration.

Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

8.8 The material in the filter holder is defined as the solid phase of the waste, and the filtrate is defined as the liquid phase. Weigh the filtrate. The liquid phase may now be either analyzed (See Step 8.12) or stored at 4 °C until time of analysis.

Note: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying vacuum or pressure filtration, as outlined in Step 8.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the extraction as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

8.9 If the waste contains <0.5 percent dry solids (see Step 7.2), proceed to Step 8.13. If the waste contains >0.5 percent dry solids (see Step 7.1 or 7.2), and if particle-size reduction of the solid was needed in Step 7.3, proceed to Step 8.10. If the waste as received passes a 9.5 mm sieve, quantitatively transfer the solid material into the extractor bottle along with the filter used to separate the initial liquid from the solid phase, and proceed to Step 8.11.

8.10 Prepare the solid portion of the waste for extraction by crushing, cutting, or grinding the waste to a surface area or particle-size as described in Step 7.3. When the surface area or particle-size has been appropriately altered, quantitatively transfer the solid material into an extractor bottle. Include the filter used to separate the initial liquid from the solid phase.

Note: Sieving of the waste is not normally required. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended. If sieving is necessary, a Teflon-coated sieve should be used to avoid contamination of the sample.

8.11 Determine the amount of extraction fluid to add to the extractor vessel as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Step 7.1)} \times \text{weight of waste filtered (Step 8.5 or 8.7)}}{100}$$

Slowly add this amount of appropriate extraction fluid (see Step 7.4) to the extractor vessel. Close the extractor bottle tightly (it is recommended that Teflon tape be used to ensure a tight seal), secure in rotary agitation device, and rotate at 30 + 2 rpm for 18 + 2 hours. Ambient temperature (i.e., temperature of room in which extraction takes place) shall be maintained at 22 + 3 °C during the extraction period.

Note: As agitation continues, pressure may build up within the extractor bottle for some types of wastes (e.g., limed or calcium carbonate containing waste may evolve gases such as carbon dioxide). To relieve excess pressure, the extractor bottle may be periodically opened (e.g., after 15 minutes, 30 minutes, and 1 hour) and vented into a hood.

8.12 Following the 18 + 2 hour extraction, separate the material in the extractor vessel into its component liquid and solid phases by filtering through a new glass fiber filter, as outlined in Step 8.7. For final filtration of the TCLP extract, the glass fiber filter may be changed, if necessary, to facilitate filtration. Filter(s) shall be acid-washed (see Step 4.4) if evaluating the mobility of metals.

8.13 Prepare the TCLP extract as follows:

8.13.1 If the waste contained no initial liquid phase, the filtered liquid material obtained from Step 8.12 is defined as the TCLP extract. Proceed to Step 8.14.

8.13.2 If compatible (e.g., multiple phases will not result on combination), combine the filtered liquid resulting from Step 8.12 with the initial liquid phase of the waste obtained in Step 8.7. This combined liquid is defined as the TCLP extract. Proceed to Step 8.14.

8.13.3 If the initial liquid phase of the waste, as obtained from Step 8.7, is not or may not be compatible with the filtered liquid resulting from Step 8.12, do not combine these liquids. Analyze these liquids, collectively defined as the TCLP extract, and combine the results mathematically, as described in Step 8.14.

8.14 Following collection of the TCLP extract, the pH of the extract should be recorded. Immediately aliquot and preserve the extract for analysis. Metals aliquots must be acidified with nitric acid to pH <2. If precipitation is observed upon addition of nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses shall not be acidified and the extract shall be analyzed as soon as possible. All other aliquots must be stored under refrigeration (4 °C) until analyzed. The TCLP extract shall be prepared and analyzed according to appropriate analytical methods. TCLP extracts to be analyzed for metals shall be acid digested except in those instances where digestion causes loss of metallic contaminants. If an analysis of the undigested extract shows that the concentration of any regulated metallic contaminant exceeds the regulatory level, then the waste is hazardous and digestion of the extract is not necessary. However, data on undigested extracts alone cannot be used to demonstrate that the waste is not hazardous. If the individual phases are to be analyzed separately, determine the volume of the individual phases (to +0.5 percent), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final analyte concentration} = \frac{(V_1)(C_1)+(V_2)(C_2)}{V_1+V_2}$$

where:
V_1 = The volume of the first phase (L).
C_1 = The concentration of the contaminant of concern in the first phase (mg/L).
V_2 = The volume of the second phase (L).
C_2 = The concentration of the contaminant of concern in the second phase (mg/L).

8.15 Compare the contaminant concentrations in the TCLP extract with the thresholds identified in the appropriate regulations. Refer to § 10.0 for quality assurance requirements.

9.0 Procedure When Volatiles Are Involved

Use the ZHE device to obtain TCLP extract for analysis of volatile compounds only. Extract resulting from the use of the ZHE shall not be used to evaluate the mobility of nonvolatile analytes (e.g., metals, pesticides, etc.).

The ZHE device has approximately a 500-mL internal capacity. The ZHE can thus accommodate a maximum of 25 grams of solid (defined as that fraction of a sample from which no additional liquid may be forced out by an applied pressure of 50 psi), due to the need to add an amount of extraction fluid equal to 20 times the weight of the solid phase.

Charge the ZHE with sample only once and do not open the device until the final extract (of the solid) has been collected. Repeated filling of the ZHE to obtain 25 grams of solid is not permitted.

Do not allow the waste, the initial liquid phase, or the extract to be exposed to the atmosphere for any more time than is absolutely necessary. Any manipulation of these materials should be done when cold (4 °C) to minimize loss of volatiles.

9.1 Pre-weigh the (evacuated) filtrate collection container (See Step 4.6) and set aside. If using a TEDLAR® bag, express all liquid from the ZHE device into the bag, whether for the initial or final liquid/solid separation, and take an aliquot from the liquid in the bag for analysis. The containers listed in Step 4.6 are recommended for use under the conditions stated in 4.6.1–4.6.3.

9.2 Place the ZHE piston within the body of the ZHE (it may be helpful first to moisten the piston O-rings slightly with extraction fluid). Adjust the piston within the ZHE body to a height that will minimize the distance the piston will have to move once the ZHE is charged with sample (based upon sample size requirements determined from Section 9.0, Step 7.1 and/or 7.2). Secure the gas inlet/outlet flange (bottom flange) onto the ZHE body in accordance with the manufacturer's instructions. Secure the glass fiber filter between the support screens and set aside. Set liquid inlet/outlet flange (top flange) aside.

9.3 If the waste is 100 percent solid (see Step 7.1), weigh out a subsample (25 gram maximum) of the waste, record weight, and proceed to Step 9.5.

9.4 If the waste contains <0.5 percent dry solids (Step 7.2), the liquid portion of waste, after filtration, is defined as the TCLP extract. Filter enough of the sample so that the amount of filtered liquid will support all of the volatile analyses required. For wastes containing >0.5 percent dry solids (Steps 7.1 and/or 7.2), use the percent solids information obtained in Step 7.1 to determine the optimum sample size to charge into the ZHE. The recommended sample size is as follows:

9.4.1 For wastes containing <0.5 percent solids (see Step 7.1), weigh out a 500-gram subsample of waste and record the weight.

9.4.2 For wastes containing >0.5 percent solids (see Step 7.1), determine the amount of waste to charge into the ZHE as follows:

$$\text{Weight of waste to charge ZHE} = \frac{25}{\text{Percent solids (Step 7.1)}} \times 100$$

Weigh out a subsample of the waste of the appropriate size and record the weight.

9.5 If particle-size reduction of the solid portion of the waste was required in Step 7.3, proceed to Step 9.6. If particle-size reduction was not required in Step 7.3, proceed to Step 9.7.

9.6 Prepare the waste for extraction by crushing, cutting, or grinding the solid portion of the waste to a surface area or particle-size as described in Step 7.3.1. Wastes and appropriate reduction equipment should be refrigerated, if possible, to 4 °C prior to particle-size reduction. The means used to effect particle-size reduction must not generate heat in and of itself. If reduction of the solid phase of the waste is necessary, exposure of the waste to the atmosphere should be avoided to the extent possible.

Note: Sieving of the waste is not recommended due to the possibility that volatiles may be lost. The use of an appropriately graduated ruler is recommended as an acceptable alternative. Surface area requirements are meant for filamentous (e.g., paper, cloth) and similar waste materials. Actual measurement of surface area is not recommended.

When the surface area or particle-size has been appropriately altered, proceed to Step 9.7.

9.7 Waste slurries need not be allowed to stand to permit the solid phase to settle. Do not centrifuge wastes prior to filtration.

9.8 Quantitatively transfer the entire sample (liquid and solid phases) quickly to the ZHE. Secure the filter and support screens onto the top flange of the device and secure the top flange to the ZHE body in accordance with the manufacturer's instructions. Tighten all ZHE fittings and place the device in the vertical position (gas inlet/outlet flange on the bottom). Do not attach the extract collection device to the top plate.

Note: If waste material (>1% of original sample weight) has obviously adhered to the container used to transfer the sample to the ZHE, determine the weight of this residue and subtract it from the sample weight determined in Step 9.4 to determine the weight of the waste sample that will be filtered.

Attach a gas line to the gas inlet/outlet valve (bottom flange) and, with the liquid inlet/outlet valve (top flange) open, begin applying gentle pressure of 1–10 psi (or more if necessary) to force all headspace slowly out of the ZHE device into a hood. At the first appearance of liquid from the liquid inlet/outlet valve, quickly close the valve and discontinue pressure. If filtration of the waste at 4 °C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering. If the waste is 100 percent solid (see Step 7.1), slowly increase the pressure to a maximum of 50 psi to force most of the headspace out of the device and proceed to Step 9.12.

9.9 Attach the evacuated pre-weighed filtrate collection container to the liquid inlet/outlet valve and open the valve. Begin applying gentle pressure of 1–10 psi to force the liquid phase of the sample into the filtrate collection container. If no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10-psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When liquid flow has ceased such that continued pressure filtration at 50 psi does not result in any additional filtrate within a 2-minute period, stop the filtration. Close the liquid inlet/outlet valve, discontinue pressure to the piston, and disconnect and weigh the filtrate collection container.

Note: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

9.10 The material in the ZHE is defined as the solid phase of the waste and the filtrate is defined as the liquid phase.

Note: Some wastes, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid. Even after applying pressure filtration, this material will not filter. If this is the case, the material within the filtration device is defined as a solid and is carried through the TCLP extraction as a solid.

If the original waste contained <0.5 percent dry solids (see Step 7.2), this filtrate is defined as the TCLP extract and is analyzed directly. Proceed to Step 9.15.

9.11 The liquid phase may now be either analyzed immediately (See Steps 9.13 through 9.15) or stored at 4 °C under minimal headspace conditions until time of analysis. Determine the weight of extraction fluid #1 to add to the ZHE as follows:

$$\text{Weight of extraction fluid} = \frac{20 \times \text{percent solids (Step 7.1)} \times \text{weight of waste filtered (Step 9.4 or 9.8)}}{100}$$

9.12 The following steps detail how to add the appropriate amount of extraction fluid to the solid material within the ZHE and agitation of the ZHE vessel. Extraction fluid #1 is used in all cases (See Step 5.6).

9.12.1 With the ZHE in the vertical position, attach a line from the extraction fluid reservoir to the liquid inlet/outlet valve. The line used shall contain fresh extraction fluid and should be preflushed with fluid to eliminate any air pockets in the line. Release gas pressure on the ZHE piston (from the gas inlet/outlet valve), open the liquid inlet/outlet valve, and begin transferring extraction fluid (by pumping or similar means) into the ZHE. Continue pumping extraction fluid into the ZHE until the appropriate amount of fluid has been introduced into the device.

9.12.2 After the extraction fluid has been added, immediately close the liquid inlet/outlet valve and disconnect the extraction fluid line. Check the ZHE to ensure that all valves are in their closed positions. Manually rotate the device in an end-over-end fashion 2 or 3 times. Reposition the ZHE in the vertical position with the liquid inlet/outlet valve on top. Pressurize the ZHE to 5–10 psi (if necessary) and slowly open the liquid inlet/outlet valve to bleed out any headspace (into a hood) that may have been introduced due to the addition of extraction fluid. This bleeding shall be done quickly and shall be stopped at the first appearance of liquid from the valve. Re-pressurize the ZHE with 5–10 psi and check all ZHE fittings to ensure that they are closed.

9.12.3 Place the ZHE in the rotary agitation apparatus (if it is not already there) and rotate at 30+2 rpm for 18+2 hours. Ambient temperature (i.e., temperature of room in which extraction occurs) shall be maintained at 22+3 °C during agitation.

9.13 Following the 18 +2 hour agitation period, check the pressure behind the ZHE piston by quickly opening and closing the gas inlet/outlet valve and noting the escape of gas. If the pressure has not been maintained (i.e., no gas release observed), the device is leaking. Check the ZHE for leaking as specified in Step 4.2.1, and perform the extraction again with a new sample of waste. If the pressure within the device has been maintained, the material in the extractor vessel is once again separated into its component liquid and solid phases. If the waste contained an initial liquid phase, the liquid may be filtered directly into the same filtrate collection container (i.e., TEDLAR® bag) holding the initial liquid phase of the waste. A separate filtrate collection container must be used if combining would create multiple phases, or there is not enough volume left within the filtrate collection container. Filter through the glass fiber filter, using the ZHE device as discussed in Step 9.9. All extract shall be filtered and collected if the TEDLAR® bag is used, if the extract is multiphasic, or if the waste contained an initial liquid phase (see Steps 4.6 and 9.1).

Note: An in-line glass fiber filter may be used to filter the material within the ZHE if it is suspected that the glass fiber filter has been ruptured.

9.14 If the original waste contained no initial liquid phase, the filtered liquid material obtained from step 9.13 is defined as the TCLP extract. If the waste contained an initial liquid phase, the filtered liquid material obtained from Step 9.13 and the initial liquid phase (Step 9.9) are collectively defined as the TCLP extract.

9.15 Following collection of the TCLP extract, immediately prepare the extract for analysis and store with minimal headspace at 4 °C until analyzed. Analyze the TCLP extract according to the appropriate analytical methods. If the individual phases are to be analyzed separately (i.e., are not miscible), determine the volume of the individual phases (to 0.5%), conduct the appropriate analyses, and combine the results mathematically by using a simple volume-weighted average:

$$\text{Final analyte concentration} \; \frac{(V_1)\,(C_1) + (V_2)\,(C_2)}{V_1 + V_2}$$

where:

V_1 = The volume of the first phases (l).

C_1 = The concentration of the contaminant of concern in the first phase (mg/l).

V_2 = The volume of the second phase (l).

C_2 = The concentration of the contaminant of concern in the second phase (mg/l).

9.16 Compare the contaminant concentrations in the TCLP extract with the thresholds identified in the appropriate regulations. Refer to section 10.0 for quality assurance requirements.

10.0 Quality Assurance Requirements

10.1 Maintain all data, including quality assurance data, and keep it available for reference or inspection.

10.2 A minimum of one blank (extraction fluid #1) for every 10 extractions that have been conducted in an extraction vessel shall be employed as a check to determine if any memory effects from the extraction equipment are occurring.

10.3 A matrix spike shall be performed for each waste unless the result exceeds the regulatory level and the data is being used solely to demonstrate that the waste property exceeds the regulatory level. If more than one sample of the same waste is being tested, a matrix spike needs to be performed for every twenty samples and the average percent recovery applied to the waste characterization.

10.3.1 Matrix spikes are to be added after filtration of the TCLP extract and before preservation. Matrix spikes should not be added prior to TCLP extraction of the sample.

10.3.2 Matrix spike levels should be made at the appropriate regulatory threshold limits. However, if the extract contaminant concentration is less than one half the threshold limit, the spike level may be one half the contaminant concentration but not less than the quantitation limit or a fifth of the threshold limit.

10.3.3 The purpose of the matrix spike is to monitor the adequacy of the analytical methods used on the TCLP extract and to determine whether matrix interferences exist in analyte detection. If the matrix spike recoveries are less than 50%, then the analytical methods are not performing adequately or use of the methods is inadequate. Use of internal calibration quantitation methods, modification of the analytical methods, or use of alternate analytical methods may be needed to accurately measure the contaminant concentration in the TCLP extract.

10.3.4 Use of internal quantitation methods is also required when the contaminant concentration is within 20% of the regulatory level. (See section 10.5 concerning the use of internal calibration methods.)

10.3.5 Matrix spike recoveries are calculated by the following formula:

$$\text{Percent recovery} = \frac{A-B}{C} \times 100\%$$

where A = the concentration of the spiked sample,

B = the concentration of the unspiked sample, and

C = the spike level

10.4 All quality control measures described in the appropriate analytical methods shall be followed.

10.5 The use of internal calibration quantitation methods shall be employed for a contaminant if: (1) Recovery of the contaminant from the TCLP extract is not at least 50% and the concentration does not exceed the regulatory level, and (2) The concentration of the contaminant measured in the extract is within 20% of the appropriate regulatory level.

10.5.1 The method of standard additions shall be employed as the internal calibration quantitation method for each metallic contaminant.

10.5.1.1 The method of standard additions requires preparing calibration standards in the sample matrix rather than reagent water or blank solution. It requires taking four identical aliquots of the solution and adding known amounts of standard to three of these aliquots. The fourth aliquot is the unknown. Preferably, the first addition should be prepared so that the resulting concentration is approximately 50% of the expected concentration of the sample. The second and third additions should be prepared so that the concentrations are approximately 100% and 150% of the expected concentration of the sample. All four aliquots are maintained at the same final volume by adding reagent water or a blank solution, and may need dilution adjustment to maintain the signals in the linear range of the instrumental technique. All four aliquots are analyzed.

10.5.1.2 Prepare a plot, or subject data to linear regression, of instrumental signals or external-calibration-derived concentrations as the dependent variable (y-axis) versus concentrations of the additions of standard as the independent variable (x-axis). Solve for the intercept of the abscissa (the independent variable, x-axis) which is the concentration in the unknown.

10.5.1.3 Alternately, subtract the instrumental signal or external-calibration-derived concentration of the unknown (unspiked) sample from the instrumental signals or external-calibration-derived concentrations of the standard additions. Plot or subject data to linear regression of the corrected instrumental signals or external-calibration-derived concentrations as the dependent variable versus the independent variable. Derive concentrations for unknowns using the internal calibration curve as if it were an external calibration curve.

10.6 Samples must undergo TCLP extraction within the following time periods:

SAMPLE MAXIMUM HOLDING TIMES

[Days]

	From: Field collection To: TCLP extraction	From: TCLP extraction To: Preparative extraction	From: Preparative extraction To: Determinative analysis	Total elapsed time
Volatiles	14	NA	14	26
Semi-volatiles	7	7	40	54
Mercury	28	NA	28	56
Metals, except mercury	180	NA	180	360

NA = Not applicable.

If sample holding times are exceeded, the values obtained will be considered minimal concentrations. Exceeding the holding time is not acceptable in establishing that a waste does not exceed the regulatory level. Exceeding the holding time will not invalidate characterization if the waste exceeds the regulatory level.

PART 264—STANDARDS FOR OWNERS AND OPERATORS OF HAZARDOUS WASTE TREATMENT, STORAGE, AND DISPOSAL FACILITIES

7. The authority citation for part 264 continues to read as follows:

Authority: 42 U.S.C. 6905, 6912, 6924, and 6925.

8. Section 264.301 is amended by revising paragraph (e)(1) to read as follows:

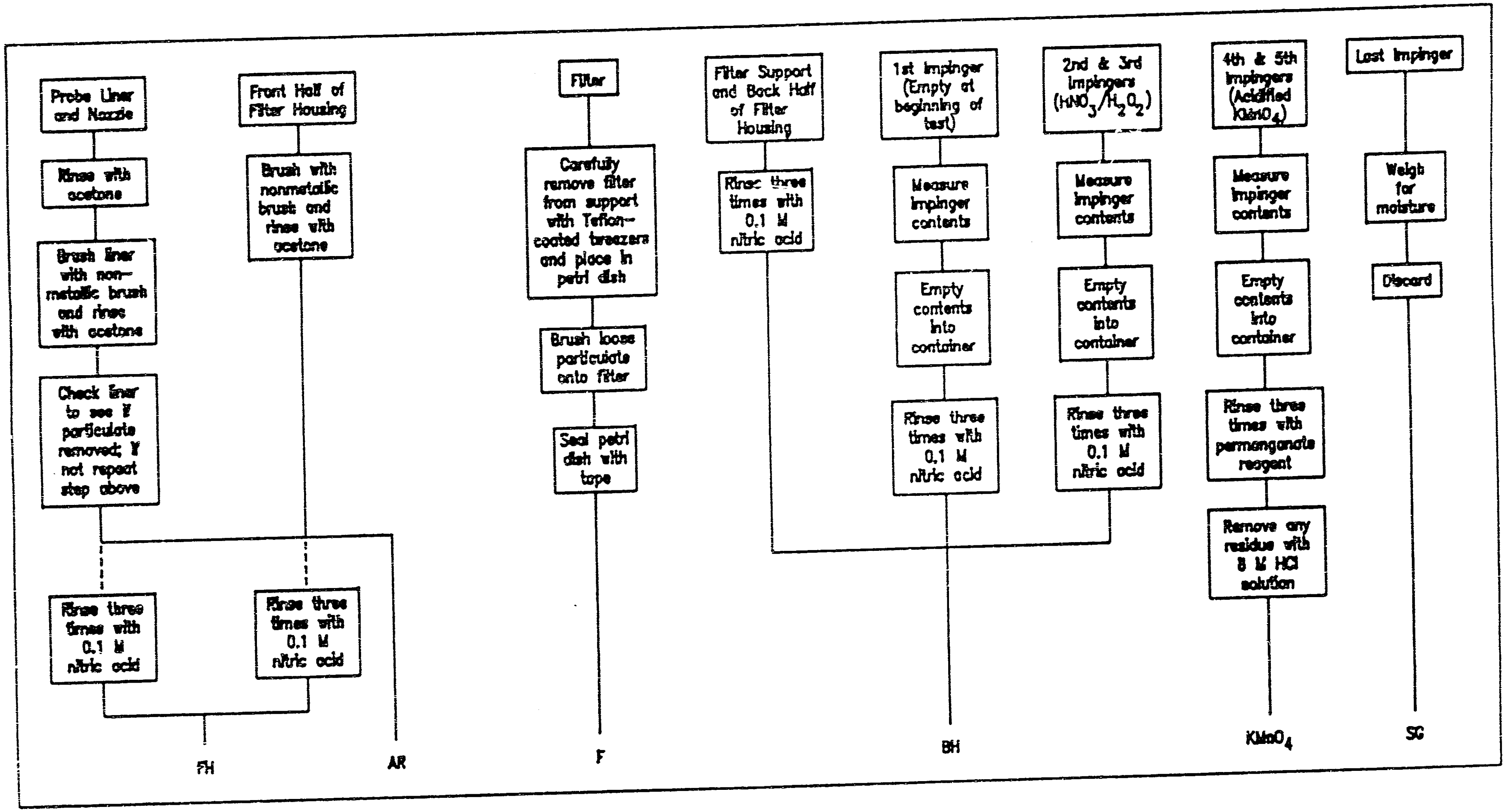
§ 264.301 Design and operating requirements.

* * * * *

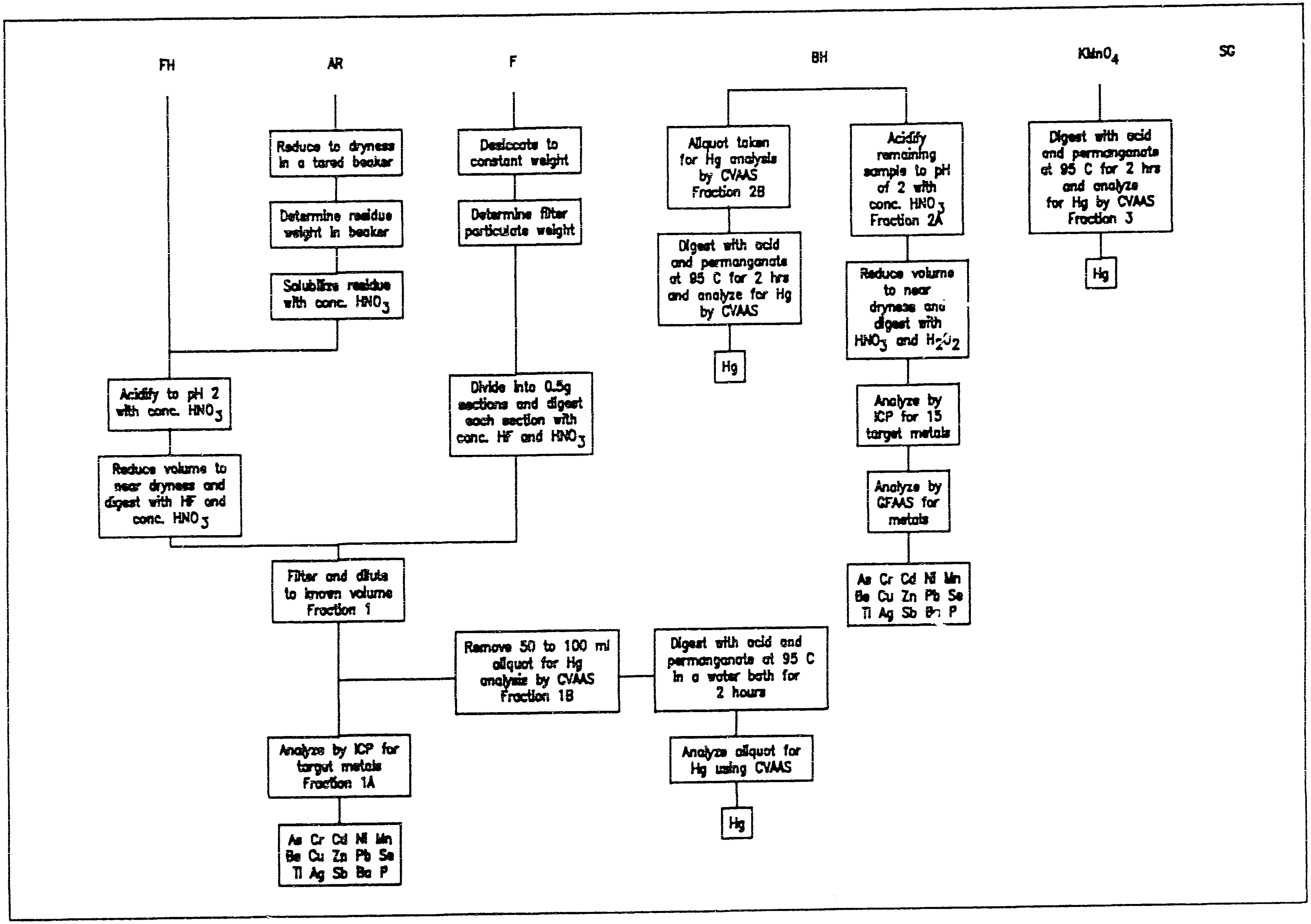
APPENDIX D

CHARACTERIZATION AND TESTING:
TOTAL METALS

TOTAL METALS TEST SAMPLE PREPARATION



TOTAL METALS TEST SAMPLE ANALYSIS



METHODOLOGY FOR THE DETERMINATION OF METALS EMISSIONS IN EXHAUST GASES FROM HAZARDOUS WASTE INCINERATION AND SIMILAR COMBUSTION PROCESSES

1. Applicability and Principle

1.1 Applicability. This method is applicable for the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) emissions from hazardous waste incinerators and similar combustion processes. This method may also be used for the determination of particulate emissions following the additional procedures described. Modifications to the sample recovery and analysis procedures described in this protocol for the purpose of determining particulate emissions may potentially impact the front half mercury determination.*

1.2 Principle. The stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in a series of chilled impingers containing a solution of dilute nitric acid in hydrogen peroxide in two impingers, and acidic potassium permanganate solution in two (or one) impingers. Sampling train components are recovered and digested in separate front and back half fractions. Materials collected in the sampling train are digested with acid solutions to dissolve inorganics and to remove organic constituents that may create analytical interferences. Acid digestion is performed using conventional Parr^R Bomb or microwave digestion techniques. The nitric acid and hydrogen peroxide impinger solution, the acidic potassium permanganate impinger solution, and the probe rinse and digested filter solutions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS). Except for the permanganate solution, the remainder of the sampling

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*Field tests to date have shown that of the total amount of mercury measured by the method, only 0 to <2% was measured in the front half. Therefore, it is tentatively concluded, based on the above data, that particulate emissions may be measured by this train, without significantly altering the mercury results.

train catches are analyzed for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of antimony, arsenic, cadmium, lead, selenium, and thallium, if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analyses of all metals if the resulting in-stack method detection limits meet the goal of the testing program. For convenience, aliquots of each digested sample fraction can be combined proportionally for a single analytical determination. The efficiency of the analytical procedure is quantified by the analysis of spiked quality control samples containing each of the target metals including actual sample matrix effects checks.

2. Range, Sensitivity, Precision, and Interferences

2.1 Range. For the analyses described in this methodology and for similar analyses, the ICAP response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter (ug/ml) range in the analytical finish solution can be analyzed using this technique. Samples containing greater than approximately 50 ug/ml of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 ug/ml of cadmium should be diluted to that level before analysis.

2.2 Analytical Sensitivity. 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), 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), Ti (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (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). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml. The use of GFAAS can give added sensitivity compared to the use of direct aspiration AAS for the following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (3) a volume of 300 ml for the front half and 150 ml for the back half samples, and (4) a stack gas sample volume of 1.25 m^3, the corresponding in-stack method detection limits are presented in Table A-1 and calculated as shown:

$$\frac{A \times B}{C} = D$$

where: A = analytical detection limit, ug/ml.
B = volume of sample prior to aliquot for analysis, ml.
C = stack sample volume, dscm (dsm^3).
D = in-stack detection limit, ug/m^3.

Values in Table A-1 are calculated for the front and back half and/or the total train.

To ensure optimum sensitivity in obtaining the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition should be used to establish the quality of the data.

Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table A-1 for a specific test by using one or more of the following options:

- A normal 1-hour sampling run collects a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased and 5 m^3 are collected, the in-stack method detection limits would be one fourth of the values shown in Table A-1 (this means that with this change, the method is four times more sensitive than normal).
- The in-stack detection limits assume that all of the sample is digested (with exception of the aliquot for mercury) and the final liquid volumes for analysis are 300 ml for the front half and 150 ml for the

TABLE A-1. IN-STACK METHOD DETECTION LIMITS (ug/m^3) FOR TRAIN FRACTIONS USING ICAP AND AAS

Metal	Front Half Fraction 1 Probe and Filter	Back Half$_1$ Fraction 2 Impingers 1-3	Back Half$_2$ Fraction 3 Impingers 4-5	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)*
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	0.05**	0.03**	0.03**	0.11**
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

( )* Detection limit when analyzed by GFAAS.
** Detection limit when analyzed by CVAAS.
Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

back half sample. If the front half volume is reduced from 300 ml to 30 ml, the front half in-stack detection limits would be one tenth of the values shown above (ten times more sensitive). If the back half volume is reduced from 150 ml to 25 ml, the in-stack detection limits would be one sixth of the above values. Matrix effects checks are necessary on analyses of samples and typically are of greater significance for samples that have been concentrated to less than the normal sample volume. A volume less than 25 ml may not allow resolubilization of the residue and may increase interference by other compounds.

- When both of the above two improvements are used on one sample at the same time, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front and back halves is reduced by factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive).

- Conversely, reducing stack gas sample volume and increasing sample liquid volume will increase limits. The front half and back half$_1$ samples (Fractions 1 and 2) can be combined prior to analysis. The resultant liquid volume (excluding Fraction 3, which must be analyzed separately) is recorded. Combining the sample as described does not allow determination (whether front or back half) of where in the train the sample was captured. The in-stack method detection limit then becomes a single value for all metals except mercury, for which the contribution of Fraction 3 must be considered.
- The above discussion assumes no blank correction. Blank corrections are discussed later in this method.

2.3 Precision. The precisions (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

2.4 Interferences. Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICAP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Refer to EPA Method 6010 (SW-846) for details on potential interferences for this method. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

3. Apparatus

3.1 Sampling Train. A schematic of the sampling train is shown in Figure A-1. It is similar to the Method 5 train. The sampling train consists of the following components.

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. Glass nozzles are required unless an alternate probe tip prevents the possibility of contamination or

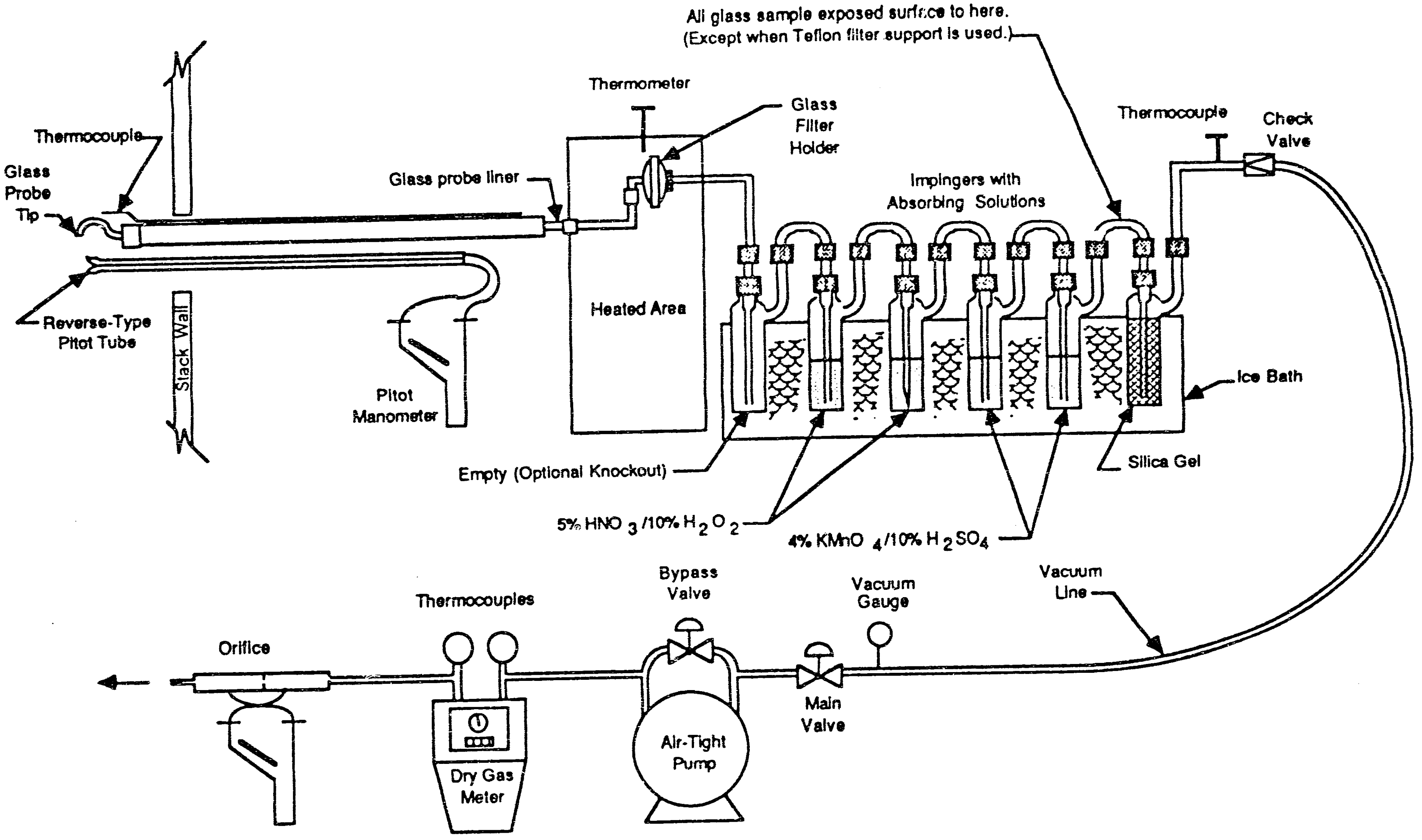


Figure A-1. Schematic of multiple metals sampling train.

4174 7/89

interference of the sample with its materials of construction. If a probe tip other than glass is used, no correction of the stack sample test results can be made because of the effect on the results by the probe tip.

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 that a Teflon filter support must be used to replace the glass frit.

3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.5 Condenser. The following system shall be used for the condensation and collection of gaseous metals and for determining the moisture content of the stack gas. The condensing system should consist of four to six impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a water knockout trap for use during test conditions which require such a trap. The impingers to be used in the metals train are now described. When the first impinger is used as a water knockout, it shall be appropriately-sized for an expected large moisture catch and constructed generally as described for the first impinger in Method 5, Paragraph 2.1.7. The second impinger (or the first HNO_3/H_2O_2 impinger) shall also be as described for the first impinger in Method 5. The third impinger (or the impinger used as the second HNO_3/H_2O_2 impinger) shall be the same as the Greenburg Smith impinger with the standard tip described as the second impinger in Method 5, Paragraph 2.1.7. All other impingers used in the metals train are the same as the second impinger (the first HNO_3/H_2O_2 impinger) previously described in this paragraph. In summary, the first impinger should be empty, the second and third shall contain known quantities of a nitric acid/hydrogen peroxide solution (Section 4.2.1), the fourth (and fifth, if required) shall contain a known quantity of acidic potassium permanganate solution (Section 4.2.2), and the last impinger shall contain a known quantity of silica gel or equivalent desiccant. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knockout impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers are removed.

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 on the sampling train.

3.2 Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Nonmetallic Probe-Liner and Probe-Nozzle Brushes, 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 Nonmetallic Probe-Liner and Probe-Nozzle Brushes. For quantitative recovery of materials collected in the front half of the sampling train. Description of acceptable all-Teflon component brushes to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps, 1000- and 500-ml, shall be used for $KMnO_4$-containing samples and blanks. 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 identification of 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. For the analysis, the following equipment is needed:

3.3.1 Volumetric Flasks, 100 ml, 250 ml, and 1000 ml. For preparation of standards and sample dilution.

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).

3.3.4 Beakers and Watchglasses. 250 ml beakers for sample digestion with watchglasses to cover the tops.

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 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

3.3.8 Disposable Pasteur Pipets and Bulbs.

3.3.9 Volumetric Pipets.

3.3.10 Analytical Balance. Accurate to within 0.1 mg.

3.3.11 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures.

3.3.12 Hot Plates.

3.3.13 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.3.13.1 Graphite Furnace Attachment. With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium).

3.3.13.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. Same as EPA Method 7470.

3.3.14 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010.

4. Reagents

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.

4.1 Sampling. The reagents used in sampling are as follows:

4.1.1 Filters. The filters shall contain less than 1.3 ug/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders shall be used. The filters should exhibit 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 D2986-71 (incorporated by reference). For particulate determination in sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3, as described in EPA Method 5. Quartz fiber filters meeting these requirements are recommended.

4.1.2 Water. To conform to ASTM Specification D1193.77, Type II (incorporated by reference). Analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

4.1.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.1.5 Hydrogen Peroxide, 30 Percent (V/V).

4.1.6 Potassium Permanganate.

4.1.7 Sulfuric Acid. Concentrated.

4.1.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

4.2 Pretest Preparation for Sampling Reagents.

4.2.1 Nitric Acid (HNO_3)/Hydrogen Peroxide (H_2O_2) Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add 50 ml of concentrated HNO_3 and 333 ml of 30 percent H_2O_2 to a 1000-ml volumetric flask or graduated cylinder containing approximately 500 ml of water. Dilute to volume with water. The reagent shall contain less than 2 ng/ml of each target metal.

4.2.2 Acidic Potassium Permanganate ($KMnO_4$) Absorbing Solution, 4 Percent $KMnO_4$ (W/V). Prepare fresh daily. Dissolve 40 g of $KMnO_4$ in sufficient 10 percent H_2SO_4 to make 1 liter. Prepare and store in glass bottles to prevent degradation. The 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 reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottle; these bottles should not be fully filled and should be vented both to relieve excess pressure and prevent explosion due to pressure buildup. Venting is highly recommended, but should not allow contamination of the sample; a No. 70-72 hole drilled in the container cap and Teflon liner has been used.

4.2.3 Nitric Acid, 0.1 N. Add 6.3 ml of concentrated HNO_3 (70 percent) to a graduated cylinder containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.2.4 Hydrochloric Acid (HCl), 8 N. Add 690 ml of concentrated HCl to a graduated cylinder containing 250 ml of water. Dilute to 1000 ml with water. Mix well. The reagent shall contain less than 2 ng/ml of Hg.

4.3 Glassware Cleaning Reagents.

4.3.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

4.3.2 Water. To conform to ASTM Specifications D1193-77, Type II.

4.3.3 Nitric Acid, 10 Percent (V/V). Add 500 ml of concentrated HNO_3 to a graduated cylinder containing approximately 4000 ml of water. Dilute to 5000 ml with water.

4.4 Sample Digestion and Analysis Reagents.

4.4.1 Hydrochloric Acid, Concentrated.

4.4.2 Hydrofluoric Acid, Concentrated.

4.4.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

4.4.4 Nitric Acid, 10 Percent (V/V). Add 100 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.5 Nitric Acid, 5 Percent (V/V). Add 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Reagent shall contain less than 2 ng/ml of each target metal.

4.4.6 Water. To conform to ASTM Specifications D1193-77, Type II.

4.4.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See EPA Method 7470 for preparation.

4.4.8 Stannous Chloride.

4.4.9 Potassium Permanganate, 5 Percent (W/V)

4.4.10 Sulfuric Acid, Concentrated.

4.4.11 Nitric Acid, 50 Percent (V/V).

4.4.12 Potassium Persulfate, 5 Percent (W/V).

4.4.13 Nickel Nitrate, $Ni(NO_3)_2 \cdot 6H_2O$.

4.4.14 Lanthanum Oxide, La_2O_3.

4.4.15 AAS Grade Hg Standard, 1000 ug/ml.

4.4.16 AAS Grade Pb Standard, 1000 ug/ml.

4.4.17 AAS Grade As Standard, 1000 ug/ml.

4.4.18 AAS Grade Cd Standard, 1000 ug/ml.

4.4.19 AAS Grade Cr Standard, 1000 ug/ml.

4.4.20 AAS Grade Sb Standard, 1000 ug/ml.

4.4.21 AAS Grade Ba Standard, 1000 ug/ml.

4.4.22 AAS Grade Be Standard, 1000 ug/ml.

4.4.23 AAS Grade Cu Standard, 1000 ug/ml.

4.4.24 AAS Grade Mn Standard, 1000 ug/ml.

4.4.25 AAS Grade Ni Standard, 1000 ug/ml.

4.4.26 AAS Grade P Standard, 1000 ug/ml.

4.4.27 AAS Grade Se Standard, 1000 ug/ml.

4.4.28 AAS Grade Ag Standard, 1000 ug/ml.

4.4.29 AAS Grade Tl Standard, 1000 ug/ml.

4.4.30 AAS Grade Zn Standard, 1000 ug/ml.

4.4.31 AAS Grade Al Standard, 1000 ug/ml.

4.4.32 AAS Grade Fe Standard, 1000 ug/ml.

4.4.33 The metals standards may also be made from solid chemicals as described in EPA Method 200.7. EPA Method 7470 or Standard Methods for the Analysis of Water and Wastewater. 15th Edition, Method 303F should be referred to for additional information on mercury standards.

4.4.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 ug/ml intermediate mercury standard by adding 5 ml of 1000 ug/ml mercury stock solution to a 500 ml volumetric flask; dilute to 500 ml by first adding 20 ml of 15 percent HNO_3 and then adding water. Prepare a working mercury standard solution fresh daily: add 5 ml of the 10 ug/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. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until in the range of the calibration.

4.4.35 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 ug/ml solutions with 5 percent nitric acid. A minimum of one standard and a blank can be used to form each calibration curve. However, a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve should be prepared. Suggested standard levels are 50 ug/ml for Al, 25 ug/ml for Cr and Pb, 15 ug/ml for Fe, and 10 ug/ml for the remaining elements. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.4.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Lead, Selenium, and Thallium. Prepare a 10 ug/ml standard by adding 1 ml of 1000 ug/ml standard to a 100 ml volumetric flask. Dilute to 100 ml with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/ml standard by adding 1 ml of the 10 ug/ml standard to a 100 ml volumetric flask and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by dilution of the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 ug/ml standard and diluting until it is in the range of the samples. Standards containing less than 1 ug/ml of metal should be prepared daily. Standards containing greater than 1 ug/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.4.37 Matrix Modifiers.

4.4.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $Ni(NO_3)_2 \cdot 6H_2O$ in approximately 50 ml of water in a 100 ml volumetric flask. Dilute to 100 ml with water.

4.4.37.2 Nickel Nitrate, One-tenth 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 AAS analysis for As.

4.4.37.3 Lanthanum. Dissolve 0.5864 g of La_2O_3 in 10 ml of concentrated HNO_3 and dilute to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for Pb.

5. Procedure

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

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. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled, prior to sampling.

5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train. Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the nitric acid/hydrogen peroxide solution (Section 4.2.1) in the two HNO_3/H_2O_2 impingers (normally the second and third impingers), place 100 ml of the acidic potassium permanganate solution (Section 4.2.2) in the fourth and fifth impinger, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

Several options are available to the tester based on the sampling conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers is calculated or determined to be less than 150 ml. The tester shall include two impingers containing the acidic potassium permanganate solution for the first test run, unless past testing experience at the same or similar sources has shown that only one is necessary. The last permanganate impinger may be discarded if both permanganate impingers have retained their original deep purple permanganate color. A maximum of 200 ml in each permanganate impinger (and a maximum of three permanganate impingers) may be used, if necessary, to maintain the desired color in the last permanganate impinger.

Retain for reagent blanks, 100 ml of the nitric acid/hydrogen peroxide solution and 100 ml of the acidic potassium permanganate solution. These solutions should be labeled and treated as described in Section 7. Set up the sampling train as shown in Figure A-1. If necessary to ensure leak-free sampling train connections, Teflon tape should be used instead of silicone grease to prevent contamination.

Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic potassium permanganate) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent hydrogen peroxide from mixing with the acidic potassium permanganate.

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. 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. 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. This normally causes a vacuum to form in the filter holder, thus causing the undesired result of drawing liquid from the impingers into the filter.

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 off 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.

Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled, if this procedure is followed: 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.

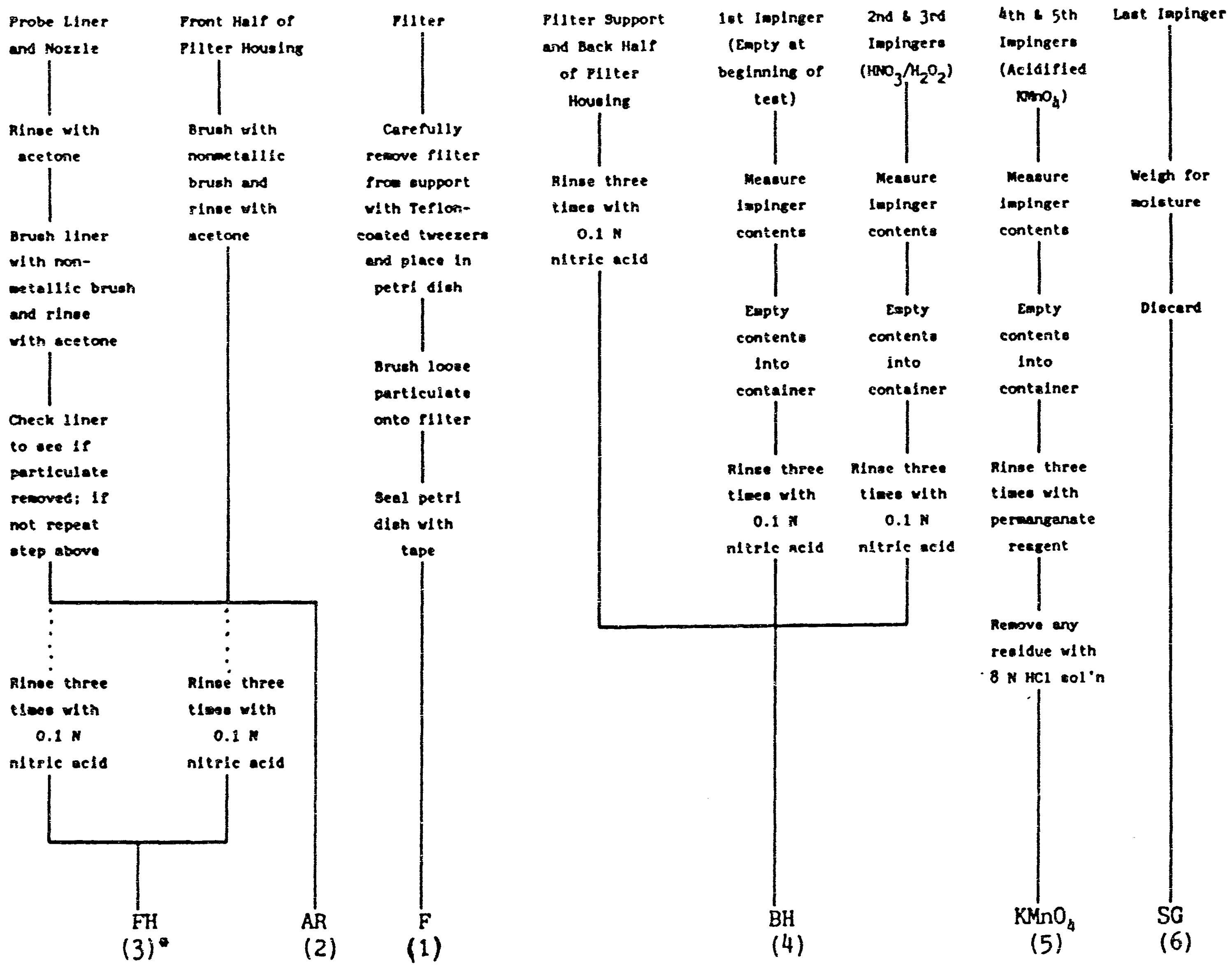
Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. The sample is recovered and treated as follows (see schematic in Figure A-2). Assure that all items necessary for recovery of the sample do not contaminate it.

5.2.1 Container No. 1 (Filter). Carefully remove the filter from the filter holder and place it in its identified petri dish container. Acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water should be used to handle the filters. 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.

5.2.2 Container No. 2 (Acetone Rinse). Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, 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 100 ml of acetone and placing the wash in a glass container. Note: 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. Perform the acetone rinses as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a nonmetallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok 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 nonmetallic 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 through the probe; hold a sample



* Number in parantheses indicates container number.

Figure A-2. Sample recovery scheme.

container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe three times or more 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.

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 nonmetallic nylon bristle 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 on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Label the container clearly to identify its contents.

5.2.3 Container No. 3 (Probe Rinse). Rinse the probe liner, probe nozzle, and front half of the filter holder thoroughly with 100 ml of 0.1 N nitric acid and place the wash into a sample storage container. Note: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as described in Method 12, Section 5.2.2. Record the volume of the combined rinse. 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.

5.2.4 Container No. 4 (Impingers 1 through 3, Contents and Rinses). Due to the large quantity of liquid involved, the tester may place the impinger solutions in more than one container. Measure the liquid in the first three impingers volumetrically to within 0.5 ml using a graduated cylinder. Record the volume of liquid present. 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 nitric acid as described in Method 12, Section 5.2.4. Note: The use of exactly 100 ml of 0.1 N nitric acid rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the volume. Calculate the 0.1 N nitric acid rinse volume by difference. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Seal the container and clearly label the contents.

5.2.5 Container No. 5 (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 4 & 5). Pour all the liquid from the permanganate impingers (fourth and fifth, if two permanganate impingers are used) 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. Using 100 ml total of the acidified potassium permanganate solution, rinse the permanganate impinger(s) and connecting glass pieces a minimum of three times. Combine the rinses with the permanganate impinger solution. Finally, rinse the permanganate impinger(s) and connecting glassware with 50 ml of 8 N HCl to remove any residue. Note: The use of exactly 100 ml and 50 ml for the two rinses is necessary for the subsequent blank correction procedures. Place the combined rinses and impinger contents in a labeled glass storage bottle. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.2.2 and properly seal the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

5.2.6 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. 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 may 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.

5.2.7 Container No. 7 (Acetone Blank). Once during each field test, place 100 ml of the acetone used in the sample recovery process into a labeled container for use in the front half field reagent blank. Seal the container.

5.2.8 Container No. 8 (0.1 N Nitric Acid Blank). Once during each field test, place 200 ml of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use in the front half and back half field reagent blanks. Seal the container.

5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Blank). Once during each field test, place 200 ml of the 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use in the back half field reagent blank. Seal the container.

5.2.10 Container No. 10 (Acidified Potassium Permanganate Blank). Once during each field test, place 300 ml of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container.

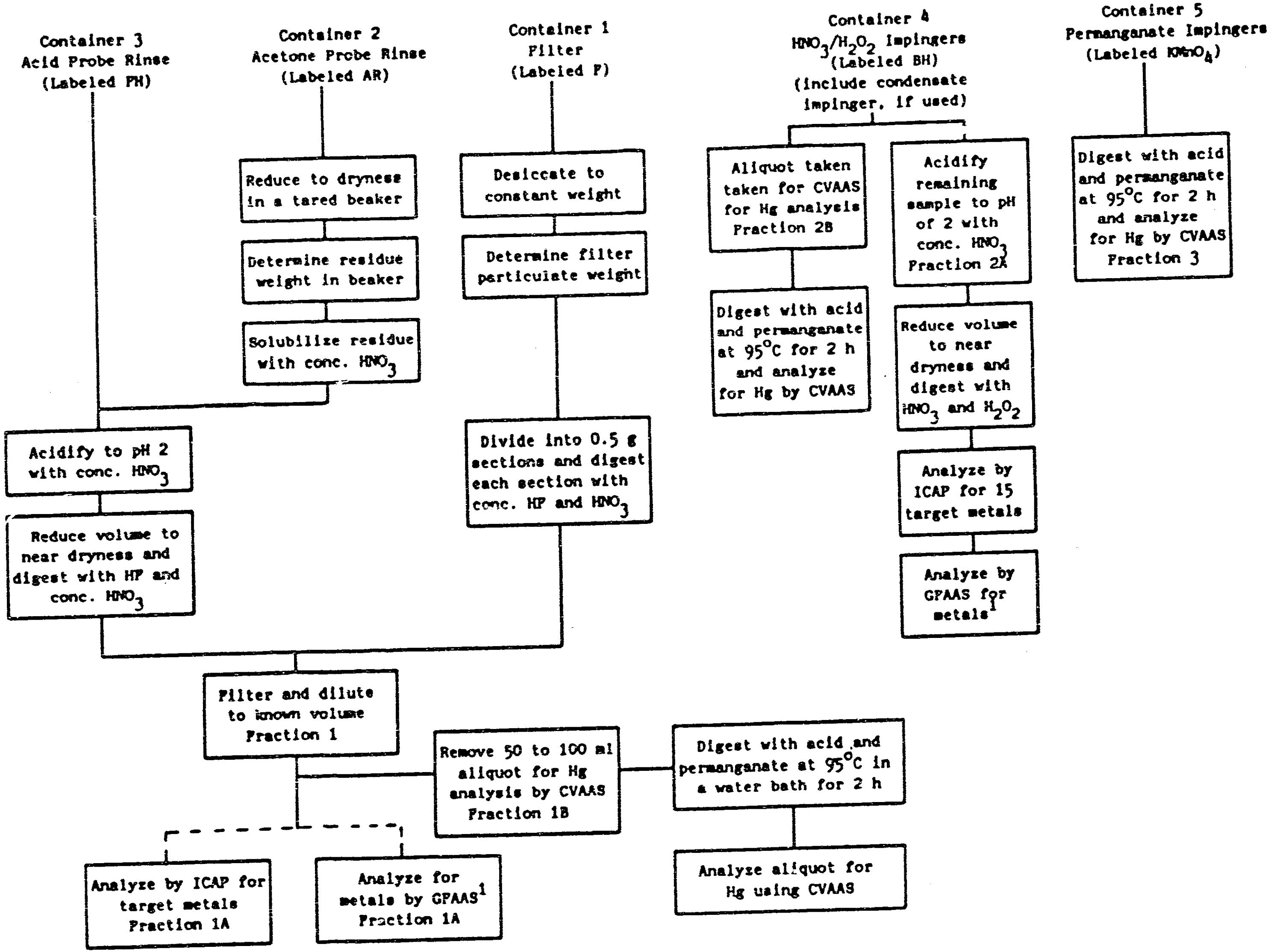
Note: This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

5.2.11 Container No. 11 (8 N HCl Blank). Once during each field test, place 50 ml of the 8 N hydrochloric acid used to rinse the acidified potassium permanganate impingers into a labeled container for use in the back half reagent blank for mercury.

5.2.12 Container No. 12 (Filter Blank). Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. This will be used in the front half field reagent blank.

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 A-3.

5.3.1 Container No. 1 (Filter). If particulatre emissions are being determined, then desiccate the filter and filter catch without heat and weigh to



[1] Analysis by AAS for metals found at less than 2 μg/ml in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

Figure A-3. Sample preparation and analysis scheme.

a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr[R] Bombs. Add 6 ml of concentrated nitric acid and 4 ml of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr 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, below.

Notes: 1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.

2. If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

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 to ±1 ml or gravimetrically to ±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 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. Resolubilize the residue with concentrated nitric acid and combine the resultant sample including all liquid and any particulate matter with Container No. 3 prior to beginning the following Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified with concentrated nitric acid to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced to approximately 50 ml by heating on a hot plate at a temperature just below boiling. Inspect the sample for visible particulate matter, and depending on the results of the inspection, perform one of the following. If no particulate matter is observed, combine the sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. If particulate matter is observed, digest the sample in microwave vessels or Parr^R Bombs following the procedures described in Section 5.3.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. Measure and record the combined volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50 ml aliquot and label as Fraction 1B. Label the remaining 250 ml portion as Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front half mercury.

5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 50 ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as Fraction 2A. The Fraction 2B aliquot should be prepared and analyzed as described in Section 5.4.3. Fraction 2A shall be pH 2 or lower. If necessary, use concentrated nitric acid to lower Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker should be covered with a ribbed watchglass. The sample volume should be reduced 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 and 5.3.4.2, below.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent hydrogen peroxide 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.

5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent nitric acid and heat for 6 minutes in intervals of 1 to 2 minutes at 600 Watts. Allow the sample to cool. Add 10 ml of 3 percent hydrogen peroxide 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.

Note: 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. 5 (Impingers 4 & 5). Measure and record the total volume of this sample to within 0.5 ml. This sample is referred to as Fraction 3. Follow the analysis procedures described in Section 5.4.3.

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. (This step may be conducted in the field.)

5.4 Sample Analysis. For each sampling train, five individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure A-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 5.4.1 and/or 5.4.2. Fraction 1B is for determination of front half mercury as described in Section 5.4.3.

The back half of the train was used to prepare the third through fifth samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the H_2O and HNO_3/H_2O_2 Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury.

The fifth sample, labeled Fraction 3, consists of the impinger contents and rinses from the permanganate Impingers 4 and 5. This sample is analyzed for mercury as described in Section 5.4.3. The total back half mercury catch is determined from the sum of Fraction 2B and Fraction 3.

5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using EPA Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 200.7. The quality control procedures described in Section 7.3.1 of this method shall be followed. Recommended wavelengths for use in the analysis are listed below.

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference.

Initially, analyze all samples for the target metals plus iron and aluminum. If iron and aluminum are present in the sample, the sample may have to be diluted so that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic and lead.

Note: When analyzing samples in a hydrofluoric acid matrix, an alumina torch should be used; since all front half samples will contain hydrofluoric acid, use an alumina torch.

5.4.2 AAS by Direct Aspiration and/or Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table A-2 should be used to determine which techniques and methods should be applied for each target metal. Table A-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

5.4.3 Cold Vapor AAS Mercury Analysis. Fraction 1B, Fraction 2B, and Fraction 3 should be analyzed for mercury using cold vapor atomic absorption spectroscopy following the method outlined in EPA Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up

TABLE A-2. APPLICABLE TECHNIQUES, METHODS, AND MINIMIZATION OF INTEFERENCE FOR AAS ANALYSIS

Metal	Technique	Method No.	Wavelength (nm)	Interference	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/ml Pb Ni, Cu, or acid	Use secondary wavelenght 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 volatization Aluminium	Spiked samples & add nickel nitrate solution to digestates prior to analyses Use Zeeman background correction
Ba	Aspiration	7080	553.6	Calcium Barium ionization	High hollow cathode current & narrow band set 2 mL of KCl per 100 mL of sample
Be	Aspiration	7090	234.9	500 ppm Al High Mg & Si	Add 0.1% flouride Use method of standard additions
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to miminize effects
Cd	Aspiration	7130	228.8	Absorption & light scattering	Background correction is required
Cd	Furnace	7131	228.8	As above Excess chloride Pipet tips	As above Ammonium phosphate used as a matrix modifier Use cadmium-free tips
Cr	Aspiration	7190	357.9	Alkali metal Absorption & scatt	KCl ionization suppressant in sample & stand Consult manufacturer's literature
Cr	Furnace	7191	357.9	200 mg/L calcium & phosphate	All calcium nitrate for a know constant effect and to eliminate effect of phosphate

(continued)

TABLE A-2 (CONTINUED)

Metal	Technique	Method No.	Wavelength (nm)	Interference Cause	Interference Minimization
Cu	Aspiration	7210	324.7	Absorpt & scatter	Consult manufacturer's manual
Fe	Aspiration	7380	248.3	Contamination	Great care taken to aviod contamination
Pb	Aspiration	7420	283.3	217.0 nm alternat	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 alternat	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternat	Background correction required
				Fe, Co, & Cr	Matrix matching or a nitrous-oxide/acety flame
				Nonlinear respons	Sample dilution or use 352.4 nm line
Se	Furnace	7740	196.0	Volitality	Spike samples & reference materials & add nickel nitrate to minimize volatilization
				Adsorpt & scatter	Background correction is required & Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Absorpt & scatter	Background correction is required
				AgCl insoluble	Avoid hydrochloric acid unless silver is in solution as a chloride complex
				Viscosity	Sample & standards monitored for apiration rate
Tl	Aspiration	7840	276.8		Background correction is required Hydrochloric acid should not be used
Tl	Furnace	7841	276.8		Background correction is required
				Hydrochloric acid or chloride	Verify that losses are not occuring for volitization by spiked samples or standad addt Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu & P	Strontium removes Cu and phosphate
				Contamination	Care should be taken to avid contamination

the calibration curve as described in Section 7.3 of Method 303F. Add approximately 5 ml of each sample to BOD bottles. Record the amount of sample added. The amount used is dependent upon the expected levels of mercury. Dilute to approximately 120 ml with mercury-free water. Add approximately 15 ml of 5 percent potassium permanganate solution to the Fraction 2B and Fraction 3 samples. Add 5 percent potassium permanganate solution to the Fraction 1B sample as needed to produce a purple solution lasting at least 15 minutes. A minimum of 25 ml is suggested. Add 5 ml of 50 percent nitric acid, 5 ml of concentrated sulfuric acid, and 9 ml of 5 percent potassium persulfate to each sample and each standard. Digest the solution in the capped BOD bottle at 95°C (205°F) in a convection oven or water bath for 2 hours. Cool. Add 5 ml of hydroxylamine hydrochloride solution and mix the sample. Then add 7 ml of stannous chloride to each sample and analyze immediately.

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 4.4. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. The instrument calibration should be checked once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed.

6.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in Section 4.4. Calibrate the spectrometer using these prepared standards. Calibration procedures are also outlined in the EPA methods referred to in Table A-2 and in Standard Methods for Water and Wastewater, 15th Edition, Method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

7. Quality Control

7.1 Sampling. Field Reagent Blanks. The blank samples in Container Numbers 7 through 12 produced previously in Sections 5.2.7 through 5.2.11, respectively, shall be processed, digested, and analyzed as follows. Digest and process Container No. 12 contents per Section 5.3.1, Container No. 7 per Section 5.3.2, and half of Container No. 8 per Section 5.3.3. This produces Fraction Blank 1A and Fraction Blank 1B from Fraction Blank 1. Combine the remaining half of Container No. 8 with the contents of Container No. 9 and digest and process the resultant volume per Section 5.3.4. This produces Fraction Blank 2A and Fraction Blank 2B from Fraction Blank 2. Container No. 10 and Container No. 11 contents are Fraction Blank 3. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 5.4.1 and/or 5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blank 3 per Section 5.4.3. The analysis of Fraction Blank 1A produces the front half reagent blank correction values for the metals except mercury; the analysis of Fraction Blank 1B produces the front half reagent blank correct value for mercury. The analysis of Fraction Blank 2A produces the back half reagent blank correction values for the metals except mercury, while separate analysis of Fraction Blanks 2B and 3 produce the back half reagent blank correction value for mercury.

7.2 An attempt may be made to determine if the laboratory reagents used in Section 5.3 caused contamination. They should be analyzed by the procedures in Section 5.4. The Administrator will determine whether or not the laboratory blank reagent values can be used in the calculation of the stationary source test results.

7.3 Quality Control Samples. The following quality control samples should be analyzed.

7.3.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010. For the purposes of a three run test series, these requirements have been modified to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by standard addition), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 5% of average or repeat all analysis).

7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Chromium, Lead, Nickel, Manganese, Mercury, Phosphorus, Selenium, Silver, Thallium, and Zinc. All samples should be analyzed in duplicate. Perform a matrix spike on 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 additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10% or the calibration repeated.

7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 10% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA Method 7470 or in Standard Methods for Water and Wastewater, 15th Edition, 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 data obtained from this test, 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 Mercury) in Source Sample.

8.4.1 Fraction 1A, Front Half, Metals (except Hg). Calculate the amount of each metal collected in Fraction 1 of the sampling train using the following equation:

$$M_{fh} = C_a \; F_d \; V_{soln,1} \qquad \text{Eq. 1*}$$

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*If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

where:

M_{fh} = total mass of each metal (except Hg) collected in the front half of the sampling train (Fraction 1), ug.
C_a = concentration of metal in sample Fraction 1A as read from the standard curve (ug/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_a. For example, when the dilution of Fraction 1A is from 2 to 10 ml, $F_d = 5$).
$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), ml.

8.4.2 Fraction 2A, Back Half, Metals (except Hg). Calculate the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh} = C_a F_a V_a \qquad \text{Eq. 2*}$$

where:

M_{bh} = total mass of each metal (except Hg) collected in the back half of the sampling train (Fraction 2), ug.
C_a = concentration of metal in sample Fraction 2A, as read from the standard curve (ug/ml).
F_a = aliquot factor, volume of Fraction 2 divided by volume of aliquot Fraction 2A.
V_a = volume of digested sample analyzed (concentrated Fraction 2A), ml.

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:

$$M_t = (M_{fh} - M_{fhb}) + (M_{bh} - M_{bhb}) \qquad \text{Eq. 3*}$$

where:

M_t = total mass of each metal (separately stated for each metal) collected in the sampling train, ug.
M_{fhb} = blank correction value for mass of metal detected in front half field reagent blank, ug.
M_{bhb} = blank correction value for mass of metal detected in back half field reagent blank, ug.

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*If Fractions 1A and 2A are combined, proportional aliquots must be used. Appropriate changes must be made in Equations 1-3 to reflect this approach.

Note: If the measured blank value for the front half (m_{fhb}) is in the range 0.0 to A ug [where A ug equals the value determined by multiplying 1.4 ug per square inch (1.4 ug/in.^{2}) times the actual area in square inches (in.^{2}) of the filter used in the emission sample], m_{fhb} may be used to correct the emission sample value (m_{fh}); if m_{fhb} exceeds A ug, the greater of the two following values (either I. or II.) may be used:

I. A ug, or

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 ug, m_{bhb} may be used to correct the emission sample value (m_{bh}); if m_{bhb} exceeds 1 ug, the greater of the two following values may be used: 1 ug or 5 percent of m_{bh}.

8.5 Mercury in Source Sample.

8.5.1 Fraction 1B, Front Half, Hg. Calculate the amount of mercury collected in the front half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}} \times V_{soln,1} \qquad \text{Eq. 4}$$

where:

Hg_{fh} = total mass of mercury collected in the front half of the sampling train (Fraction 1), ug.

Q_{fh} = quantity of mercury in analyzed sample, ug.

$V_{soln,1}$ = total volume of digested sample solution (Fraction 1), ml.

V_{f1B} = volume of Fraction 1B analyzed, ml. See the following Note.

Note: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction 1B were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100 ml dilution was analyzed, V_{f1B} would be 0.01.

8.5.2 Fraction 2B and Fraction 3, Back Half, Hg. Calculate the amount of mercury collected in Fractions 2 and 3 using Equations 5 and 6, respectively. Calculate the total amount of mercury collected in the back half of the sampling train using Equation 7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f1B}} \times V_{soln,2} \qquad \text{Eq. 5}$$

where:

Hg_{bh2} = total mass of mercury collected in Fraction 2, ug.
Q_{bh2} = quantity of mercury in analyzed sample, ug.
V_{f2B} = volume of Fraction 2B analyzed, ml (see Note in Section 8.5.1).
$V_{soln,2}$ = total volume of Fraction 2, ml.

$$Hg_{bh3} = \frac{Q_{bh3}}{V_{f2B}} \times V_{soln,3} \qquad \text{Eq. 6}$$

where:

Hg_{bh3} = total mass of mercury collected in Fraction 3, ug.
Q_{bh3} = quantity of mercury in analyzed sample, ug.
V_{f3} = volume of Fraction 3 analyzed, ml (see Note in Section 8.5.1).
$V_{soln,3}$ = total volume of Fraction 3, ml.

$$Hg_{bh} = Hg_{bh2} + Hg_{bh3} \qquad \text{Eq. 7}$$

where:

Hg_{bh} = total mass of mercury collected in the back half of the sampling train, ug.

8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Equation 8.

$$M_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \qquad \text{Eq. 8}$$

where:

M_t = total mass of mercury collected in the sampling train, ug.
Hg_{fhb} = blank correction value for mass of mercury detected in front half field reagent blank, ug.
Hg_{bhb} = blank correction value for mass of mercury detected in back half field reagent blank, ug.

Note: If the total of the measured blank values (Hg_{fhb} + Hg_{bhb}) is in the range of 0 to 3 ug, then the total may be used to correct the emission sample value (Hg_{fh} + Hg_{bh}); if it exceeds 3 ug, the greater of the following two values may be used: 3 ug or 5 percent of the emission sample value (Hg_{fh} + Hg_{bh}).

8.6 Metal Concentration of Stack Gas. Calculate the cadmium, total chromium, arsenic, nickel, manganese, beryllium, copper, lead, phosphorus, thallium, silver, barium, zinc, selenium, antimony, and mercury concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

$$C_s = K_4 \left(M_t / V_{m(std)}\right) \qquad \text{Eq.9}$$

where:

C_s = concentration of each metal in the stack gas, mg/dscm.
K_4 = 10^{-3} mg/ug.
M_t = total mass of each metal collected in the sampling train, ug.
$V_{m(std)}$ = 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

9.1 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.

9.2 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.

9.3 EPA Method 200.7, Code of Federal Regulations, Title 40, Part 136, Appendix C. July 1, 1987.

9.4 EPA Methods 1 through 5, Code of Federal Regulations, Title 40, Part 60, Appendix A, July 1, 1987.

APPENDIX E

CHARACTERIZATION AND TESTING:

EPA METHODS: STACK SAMPLING

METHOD 1A—SAMPLE AND VELOCITY TRAVERSES FOR STATIONARY SOURCES WITH SMALL STACKS OR DUCTS

1. Applicability and Principle

1.1 The applicability and principle of this method are identical to Method 1, except this method's applicability is limited to stacks or ducts less than about 0.30 meter (12 in.) in diameter or 0.071 m^2 (113 $in.^2$) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter or 0.0081 m^2 (12.57 $in.^2$) in cross-sectional area.

1.2 In these small diameter stacks or ducts, the conventional Method 5 stack assembly (consisting of a Type S pitot tube attached to a sampling probe, equipped with a nozzle and thermocouple) blocks a significant portion of the cross section of the duct and causes inaccurate measurements. Therefore, for particulate matter (PM) sampling in small stacks or ducts, the gas velocity is measured using a standard pitot tube downstream of the actual emission sampling site. The straight run of duct between the PM sampling and velocity measurement sites allows the flow profile, temporarily disturbed by the presence of the sampling probe, to redevelop and stabilize.

1.3 The cross-sectional layout and location of traverse points and the verification of the absence of cyclonic flow are the same as in Method 1, Sections 2.3 and 2.4, respectively. Differences from Method 1, except as noted, are given below.

2. Procedure

2.1 Selection of Sampling and Measurement Sites.

2.1.1 PM Measurements. Select a PM sampling site located preferably at least 8 equivalent stack or duct diameters downstream and 10 equivalent diameters upstream from any flow disturbances such as bends, expansions, or contractions in the stack, or from a visible flame. Next, locate the velocity measurement site 8 equivalent diameters downstream of the PM sampling site. See Figure 1A-1. If such locations are not available, select an alternative PM sampling site that is at least 2 equivalent stack or duct diameters downstream and 2½ diameters upstream from any flow disturbance. Then, locate the velocity measurement site 2 equivalent diameters downstream from the PM sampling site. Follow Section 2.1 of Method 1 for calculating equivalent diameters for a rectangular cross section.

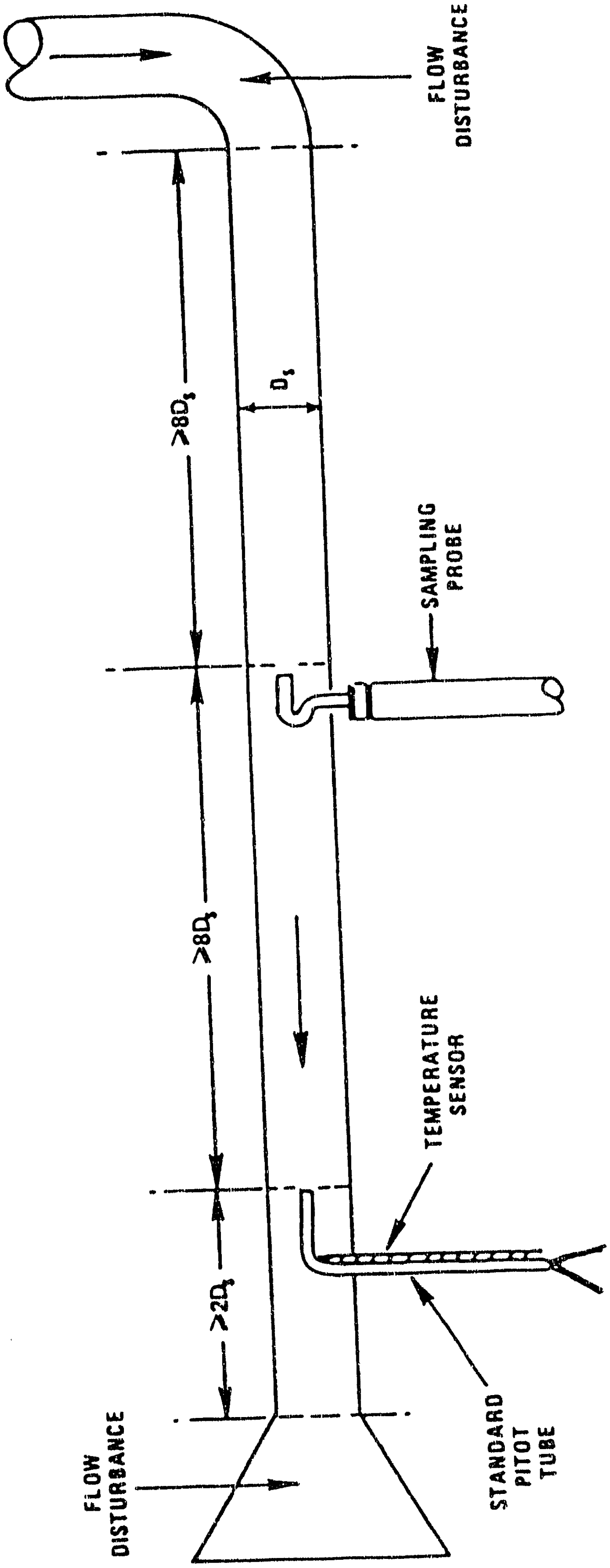

Figure 1A-1. Recommended sampling arrangement for small ducts.

2.1.2 PM Sampling (Steady Flow) or only Velocity Measurements. For PM sampling when the volumetric flow rate in a duct is constant with respect to time, Section 2.1 of Method 1 may be followed, with the PM sampling and velocity measurement performed at one location. To demonstrate that the flow rate is constant (within 10 percent) when PM measurements are made, perform complete velocity traverses before and after the PM sampling run, and calculate the deviation of the flow rate derived after the PM sampling run from the one derived before the PM sampling run. The PM sampling run is acceptable if the deviation does not exceed 10 percent.

2.2 Determining the Number of Traverse Points.

2.2.1 PM Sampling. Use Figure 1-1 of Method 1 to determine the number of traverse points to use at both the velocity measurement and PM sampling locations. Before referring to the figure, however, determine the distances between both the velocity measurement and PM sampling sites to the nearest upstream and downstream disturbances. Then divide each distance by the stack diameter or equivalent diameter to express the distances in terms of the number of duct diameters. Next, determine the number of traverse points from Figure 1-1 of Method 1 corresponding to each of these four distances. Choose the highest of the four numbers of traverse points (or a greater number) so that, for circular ducts, the number is a multiple of four, and for rectangular ducts, the number is one of those shown in Table 1-1 of Method 1. When the optimum duct diameter location criteria can be satisfied, the minimum number of traverse points required is eight for circular ducts and nine for rectangular ducts.

2.2.2 PM Sampling (Steady Flow) or Velocity Measurements. Use Figure 1-2 of Method 1 to determine the number of traverse points, following the same procedure used for PM sampling traverses as described in Section 2.2.1 of Method 1. When the optimum duct diameter location criteria can be satisfied, the minimum number of traverse points required is eight for circular ducts and nine for rectangular ducts.

3. Bibliography

1. Same as in Method 1, Section 3, Citations 1 through 6.

2. Vollaro, Robert F. Recommended Procedure for Sample Traverses in Ducts Smaller Than 12 Inches in Diameter. U.S. Environmental Protection Agency, Emission Measurement Branch, Research Triangle Park, North Carolina. January 1977.

METHOD 2C—DETERMINATION OF STACK GAS VELOCITY AND VOLUMETRIC FLOW RATE IN SMALL STACKS OR DUCTS (STANDARD PITOT TUBE)

1. Applicability and Principle

1.1 Applicability.

1.1.1 The applicability of this method is identical to Method 2, except this method is limited to stationery source stacks or ducts less than about 0.30 meter (12 in.) in diameter or 0.071 m^2 (113 $in.^2$) in cross-sectional area, but equal to or greater than about 0.10 meter (4 in.) in diameter or 0.0081 m^2 (12.57 $in.^2$) in cross-sectional area.

1.1.2 The apparatus, procedure, calibration, calculations, and biliography are the same as in Method 2, Sections 2, 3, 4, 5, and 6, except as noted in the following sections.

1.2 Principle. The average gas velocity in a stack or duct is determined from the gas density and from measurement of velocity heads with a standard pitot tube.

2. Apparatus

2.1 Standard Pitot Tube (instead of Type S). Use a standard pitot tube that meets the specifications of Section 2.7 of Method 2. Use a coefficient value of 0.99 unless it is calibrated against another standard pitot tube with an NBS-traceable coefficient.

2.2 Alternative Pitot Tube. A modified hemispherical-nosed pitot tube (see Figure 2C-1), which features a shortened stem and enlarged impact and static pressure holes, may be used. This pitot tube is useful in liquid drop-laden gas streams when a pitot "back purge" is ineffective. Use a coefficient value of 0.99 unless the pitot is calibrated as mentioned in Section 2.1 above.

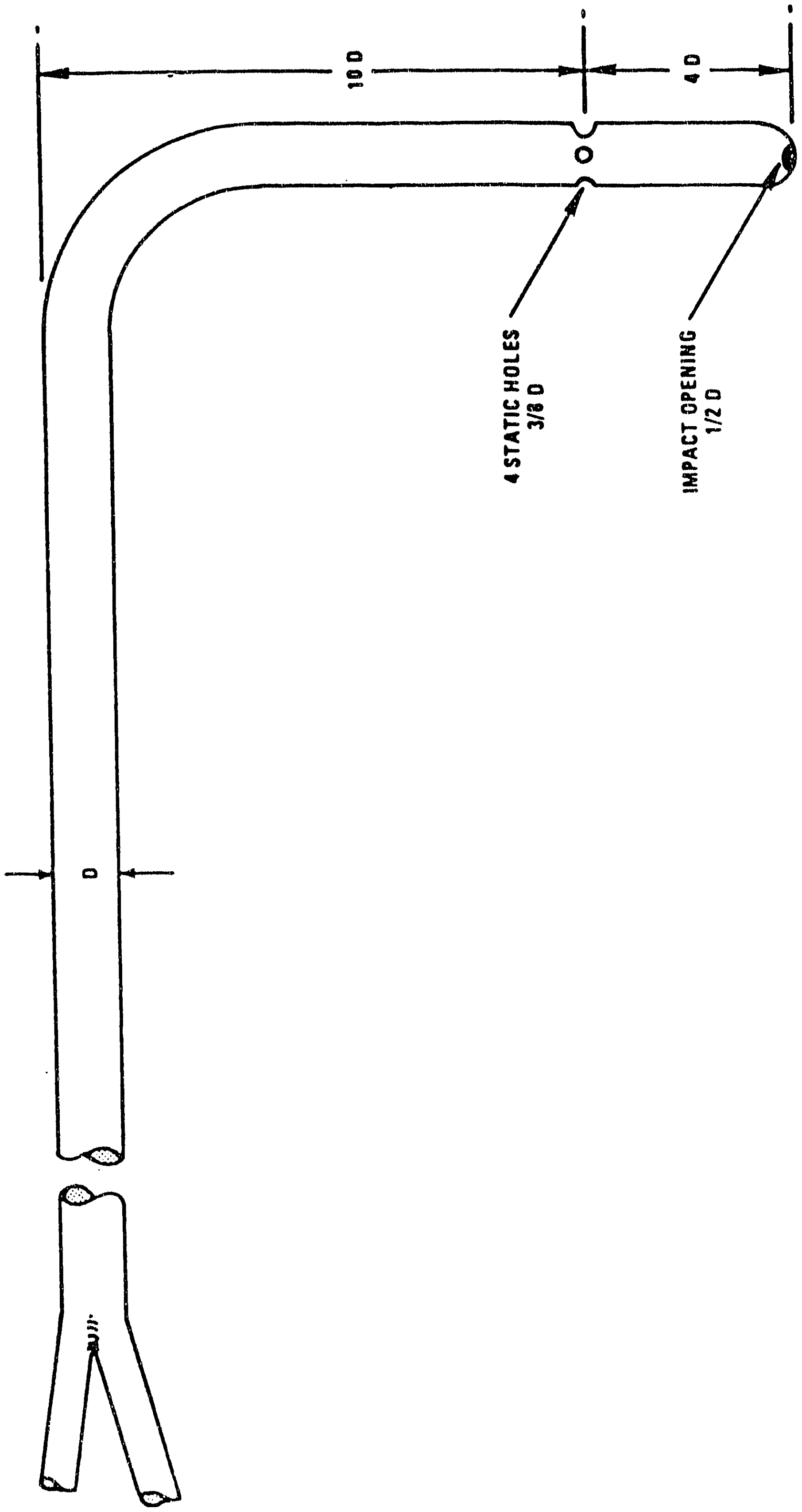

Figure 2C-1. Modified hemispherical-nosed pitot tube.

3. Procedure

Follow the general procedures in Section 3 of Method 2, except conduct the measurements at the traverse points specified in Method 1A. The static and impact pressure holes of standard pitot tubes are susceptible to plugging in PM-laden gas streams. Therefore, the tester must furnish adequate proof that the openings of the pitot tube have not plugged during the traverse period; this proof can be obained by first recording the velocity head (Δp) reading at the final traverse point, then cleaning out the impact and static holes of the standard pitot tube by "back-purging" with pressurized air, and finally by recording another Δp reading at the final traverse point. If the Δp reading made after the air purge is within 5 percent of the reading during the traverse, then the traverse is acceptable. Otherwise, reject the run. Note that if the Δp at the final traverse point is so low as to make this determination too difficult, then another traverse point may be selected. If "back purging" at regular intervals is part of the procedure, then take comparative Δp readings, as above, for the last two back purges at which suitable high Δp readings are observed.

METHOD 2D—MEASUREMENT OF GAS VOLUMETRIC FLOW RATES IN SMALL PIPES AND DUCTS

1. Applicability and Principle

1.1 Applicability. This method applies to the measurement of gas flow rates in small pipes and ducts, either before or after emission control devices.

1.2 Principle. To measure flow rate or pressure drop, all the stack gas is directed through a rotameter, orifice plate or similar flow rate measuring device. The measuring device has been previously calibrated in a manner that insures its proper calibration for the gas or gas mixture being measured. Absolute temperature and pressure measurements are also made to calculate volumetric flow rates at standard conditions.

2. Apparatus

Specifications for the apparatus are given below. Any other apparatus that has been demonstrated (subject to approval of the Administrator) to be capable of meeting the specifications will be considered acceptable.

2.1 Flow Rate Measuring Device. A rotameter, orifice plate, or other flow rate measuring device capable of measuring all the stack flow rate to within 5 percent of its true value. The measuring device shall be equipped with a temperature gauge accurate to within 2 percent of the minimum absolute stack temperature and a pressure gauge accurate to within 5 mm Hg. The capacity of the measuring device shall be sufficient for the expected maximum and minimum flow rates at the stack gas conditions. The magnitude and variability of stack gas flow rate, molecular weight, temperature, pressure, compressibility, dew point, corrosiveness, and pipe or duct size are all factors to consider in choosing a suitable measuring device.

2.2 Barometer. Same as in Method 2, Section 2.5.

2.3 Stopwatch. Capable of incremental time measurement to within 1 second.

3. Procedure

3.1 Installation. Use the procedure in Method 2A, Section 3.1.

3.2 Leak Check. Use the procedure in Method 2A, Section 3.2.

3.3 Flow Rate Measurement.

3.3.1 Continuous, Steady Flow. At least once an hour, record the measuring device flow rate reading, and the measuring device temperature and pressure. Make a minimum of twelve equally spaced readings of each parameter during the test period. Record the barometric pressure at the beginning and end of the test period. Record the data on a table similar to Figure 2D-1.

Plant____________________
Date__________ Run number______
Sample location________________
Barometric pressure, mm (in.) Hg
Start_____ Finish_____
Operators ________________
Measuring device number_____ Calibration coefficient_____
Calibration gas______
Last date calibrated______

Time	Flow rate reading	Static pressure mm (in.) Hg	Temperature	
			°C (°F)	°K (°R)
	Average.......			

Figure 2D-1. Flow rate measurement data.

3.3.2 Noncontinuous and Nonsteady Flows. Use flow rate measuring devices with particular caution. Calibration will be affected by variation in stack gas temperature, pressure, compressibility, and molecular weight. Use the procedure in Section 3.3.1. Record all the measuring device parameters on a time interval frequency sufficient to adequately profile each process cyclical or noncontinuous event. A multichannel continuous recorder may be used.

4. Calibration

4.1 Flow Rate Measuring Device. Use the procedure in Method 2A, Section 4, and apply the same performance standards. Calibrate the measuring device with the principal stack gas to be measured (e.g., air, nitrogen) against a standard reference meter. A calibrated dry gas meter is an acceptable reference meter. Ideally, calibrate the measuring device in the field with the actual gas to be measured. For measuring devices that have a volume rate readout, calculate the measuring device calibration coefficient, Y_m, for each run as follows:

$$Y_m = \frac{(Q_r)\,(T_r)\,P_{bar}}{(Q_m)\,(T_m)\,(P_{bar} + P_g)} \qquad \text{Eq. 2D-1}$$

where:

Q_r=reference meter flow rate reading, m^3/min (ft^3/min).

Q_m=measuring device flow rate reading, m^3/min (ft^3/min).

T_r=reference meter average absolute temperature, °K (°R).

T_m=measuring device average absolute temperature, °K (°R).

P_{bar}=barometric pressure, mm Hg (in. Hg).

P_g=measuring device average static pressure, mm Hg (in. Hg).

For measuring devices that do not have a readout as flow rate, refer to the manufacturer's instructions to calculate the Q_m corresponding to each Q_r.

4.2 Temperature Gauge. Use the procedure and specifications in Method 2A, Section 4.2. Perform the calibration at a temperature that approximates field test conditions.

4.3 Barometer. Calibrate the barometer to be used in the field test with a mercury barometer prior to the field test.

5. Gas Flow Rate Calculation

Calculate the stack gas flow rate, Q_s, as follows:

$$Q_s = K_1 Y_m Q_m \frac{(P_{bar} + P_g)}{T_m} \qquad \text{Eq. 2D-2}$$

where:

K_1 = 0.3858 for international system of units (SI); 17.64 for English units.

6. Bibliography

1. Spink, L.K. Principles and Practice of Flowmeter Engineering. The Foxboro Company. Foxboro, MA. 1967.

2. Benedict, Robert P. Fundamentals of Temperature, Pressure, and Flow Measurements. John Wiley and Sons, Inc. New York, NY. 1969.

3. Orifice Metering of Natural Gas. American Gas Association. Arlington, VA. Report No. 3. March 1978. 88 p.

METHOD 4—DETERMINATION OF MOISTURE CONTENT IN STACK GASES

1. *Principle and Applicability*

1.1 Principle. A gas sample is extracted at a constant rate from the source; moisture is removed from the sample stream and determined either volumetrically or gravimetrically.

1.2 Applicability. This method is applicable for determining the moisture content of stack gas.

Two procedures are given. The first is a reference method, for accurate determinations of moisture content (such as are needed to calculate emission data). The second is an approximation method, which provides estimates of percent moisture to aid in setting isokinetic sampling rates prior to a pollutant emission measurement run. The approximation method described herein is only a suggested approach; alternative means for approximating the moisture content, e.g., drying tubes, wet bulb-dry bulb techniques, condensation techniques, stoichiometric calculations, previous experience, etc., are also acceptable.

The reference method is often conducted simultaneously with a pollutant emission measurement run; when it is, calculation of percent isokinetic, pollutant emission rate, etc., for the run shall be based upon the results of the reference method or its equivalent; these calculations shall not be based upon the results of the approximation method, unless the approximation method is shown, to the satisfaction of the Administrator, U.S. Environmental Protection Agency, to be capable of yielding results within 1 percent H_2O of the reference method.

NOTE: The reference method may yield questionable results when applied to saturated gas streams or to streams that contain water droplets. Therefore, when these conditions exist or are suspected, a second determination of the moisture content shall be made simultaneously with the reference method, as follows: Assume that the gas stream is saturated. Attach a temperature sensor [capable of measuring to ±1° C (2° F)] to the reference method probe. Measure the stack gas temperature at each traverse point (see Section 2.2.1) during the reference method traverse; calculate the average stack gas temperature. Next, determine the moisture percentage, either by: (1) using a psychrometric chart and making appropriate corrections if stack pressure is different from that of the chart, or (2) using saturation vapor pressure tables. In cases where the pyschrometric chart or the saturation vapor pressure tables are not applicable (based on evaluation of the process), alternate methods, subject to the approval of the Administrator, shall be used.

2. *Reference Method*

The procedure described in Method 5 for determining moisture content is acceptable as a reference method.

2.1 Apparatus. A schematic of the sampling train used in this reference method is shown in Figure 4-1. All components shall be maintained and calibrated according to the procedure outlined in Method 5.

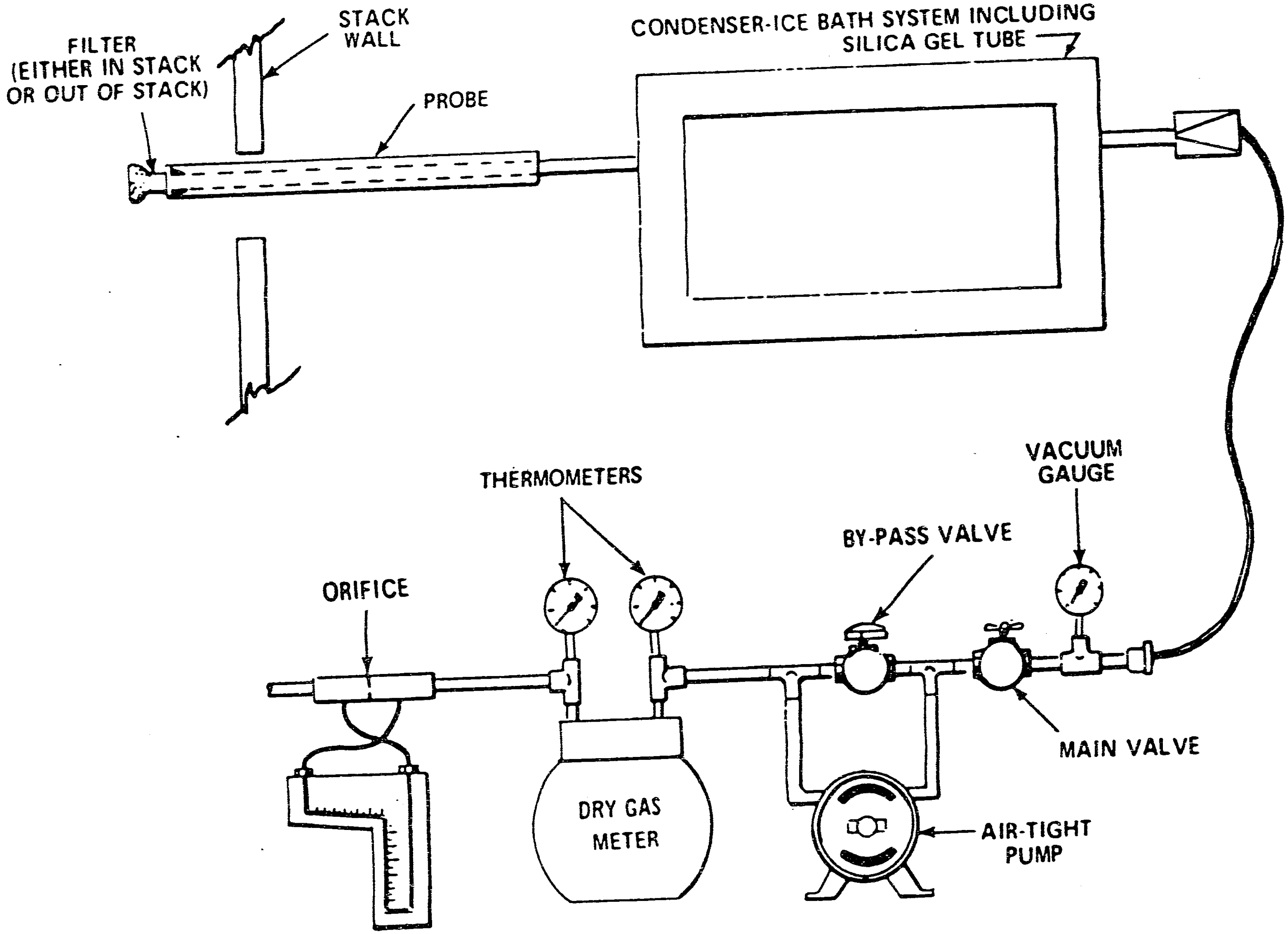

Figure 4-1. Moisture sampling train-reference method.

2.1.1 Probe. The probe is constructed of stainless steel or glass tubing, sufficiently heated to prevent water condensation, and is equipped with a filter, either in-stack (e.g., a plug of glass wool inserted into the end of the probe) or heated out-stack (e.g., as described in Method 5), to remove particular matter.

When stack conditions permit, other metals or plastic tubing may be used for the probe, subject to the approval of the Administrator.

2.1.2 Condenser. The condenser consists of four impingers connected in series with ground glass, leak-free fittings or any similarly leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with a 1.3 centimeter (½ inch) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator.

The first two impingers shall contain known volumes of water, the third shall be empty, and the fourth shall contain a known weight of 6- to 16-mesh indicating type silica gel, or equivalent desiccant. If the silica gel has been previously used, dry at 175° C (350° F) for 2 hours. New silica gel may be used as received. A thermometer, capable of measuring temperature to within 1° C (2° F), shall be placed at the outlet of the fourth impinger, for monitoring purposes.

Alternatively, any system may be used (subject to the approval of the Administrator) that cools the sample gas stream and allows measurement of both the water that has been condensed and the moisture leaving the condenser, each to within 1 ml or 1 g. Acceptable means are to measure the condensed water, either gravimetrically or volumetrically, and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures, or (2) passing the sample gas stream through a tared silica gel (or equivalent desiccant) trap, with exit gases kept below 20° C (68° F), and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump, to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

2.1.3 Cooling System. An ice bath container and crushed ice (or equivalent) are used to aid in condensing moisture.

2.1.4 Metering System. This system includes a vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment as shown in Figure 4-1. Other metering systems, capable of maintaining a constant sampling rate and determining sample gas volume, may be used, subject to the approval of the Administrator.

2.1.5 Barometer. Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg) may be used. In many cases, the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and the sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.6 Graduated Cylinder and/or Balance. These items are used to measure condensed water and moisture caught in the silica gel to within 1 ml or 0.5 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. These balances are suitable for use here.

2.2 Procedure. The following procedure is written for a condenser system (such as the impinger system described in Section 2.1.2) incorporating volumetric analysis to measure the condensed moisture, and silica gel and gravimetric analysis to measure the moisture leaving the condenser.

2.2.1 Unless otherwise specified by the Administrator, a minimum of eight traverse points shall be used for circular stacks having diameters less than 0.61 m (24 in.), a minimum of nine points shall be used for rectangular stacks having equivalent diameters less than 0.61 m (24 in.), and a minimum of twelve traverse points shall be used in all other cases. The traverse points shall be located according to Method 1. The use of fewer points is subject to the approval of the Administrator. Select a suitable probe and probe length such that all traverse points can be sampled. Consider sampling from opposite sides of the stack (four total sampling ports) for large stacks, to permit use of shorter probe lengths. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point. Place known volumes of water in the first two impingers. Weigh and record the weight of the silica gel to the nearest 0.5 g, and transfer the silica gel to the fourth impinger; alternatively, the silica gel may first be transferred to the impinger, and the weight of the silica gel plus impinger recorded.

2.2.2 Select a total sampling time such that a minimum total gas volume of 0.60 scm (21 scf) will be collected, at a rate no greater than 0.021 m^3/min (0.75 cfm). When both moisture content and pollutant emission rate are to be determined, the moisture determination shall be simultaneous with, and for the same total length of time as, the pollutant emission rate run, unless otherwise specified in an applicable subpart of the standards.

2.2.3 Set up the sampling train as shown in Figure 4-1. Turn on the probe heater and (if applicable) the filter heating system to temperatures of about 120° C (248° F), to prevent water condensation ahead of the condenser; allow time for the temperatures to stabilize. Place crushed ice in the ice bath container. It is recommended, but not required, that a leak check be done, as follows: Disconnect the probe from the first impinger or (if applicable) from the filter holder. Plug the inlet to the first impinger (or filter holder) and pull a 380 mm (15 in.) Hg vacuum; a lower vacuum may be used, provided that it is not exceeded during the test. A leakage rate in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, is unacceptable. Following the leak check, reconnect the probe to the sampling train.

2.2.4 During the sampling run, maintain a sampling rate within 10 percent of constant rate, or as specified by the Administrator. For each run, record the data required on the example data sheet shown in Figure 4-2. Be sure to record the dry gas meter reading at the beginning and end of each sampling time increment and whenever sampling is halted. Take other appropriate readings at each sample point, at least once during each time increment.

2.2.5 To begin sampling, position the probe tip at the first traverse point. Immediately start the pump and adjust the flow to the desired rate. Traverse the cross section, sampling at each traverse point for an equal length of time. Add more ice and, if necessary, salt to maintain a temperature of less 20° C (68° F) at the silica gel outlet.

2.2.6 After collecting the sample, disconnect the probe from the filter holder (or from the first impinger) and conduct a leak check (mandatory) as described in Section 2.2.3. Record the leak rate. If the leakage rate exceeds the allowable rate, the tester shall either reject the test results or shall correct the sample volume as in Section 6.3 of Method 5. Next, measure the volume of the moisture condensed to the nearest ml. Determine the increase in weight of the silica gel (or silica gel plus impinger) to the nearest 0.5 g. Record this information (see example data sheet, Figure 4-3) and calculate the moisture percentage, as described in 2.3 below.

2.2.7 A quality control check of the volume metering system at the field site is suggested before collecting the sample following the procedure in Method 5, Section 4.4

2.3 Calculations. Carry out the following calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

FIGURE 4-2—FIELD MOISTURE DETERMINATION REFERENCE METHOD

Plant ....
Location ....
Operator ....
Date ....
Run No. ....
Ambient temperature ....
Barometric pressure ....
Probe length m (ft) ....

SCHEMATIC OF STACK CROSS SECTION

Traverse point number	Sampling time (θ), min.	Stack temperature °C (°F)	Presure differential across orifice meter ΔH mm (in.) H_2O	Meter reading gas sample volume m^3 (ft^3)	ΔV_m m^3 (ft^3)	Gas Sample temperature at dry gas meter		Temperaturem of gas leaving condenser or last impinger °C (°F)
						Inlet (Tm_{in}), °C (°F)	Outlet (Tm_{out}), °C (°F)	
Total					Avg.	Avg.	Avg.	
Average								

FIGURE 4-3—ANALYTICAL DATA—REFERENCE METHOD

	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Difference		

2.3.1 Nomenclature.

B_{ws}=Proportion of water vapor, by volume, in the gas stream.

M_w=Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).

P_m=Absolute pressure (for this method, same as barometric pressure) at the dry gas meter, mm Hg (in. Hg).

P_{std}=Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R=Ideal gas constant, 0.06236 (mm Hg) (m³)/(g-mole) (°K) for metric units and 21.85 (in. Hg) (ft³)/(lb-mole) (°R) for English units.

T_m=Absolute temperature at meter, °K (°R).

T_{std}=Standard absolute temperature, 293° K (528°R).

V_m=Dry gas volume measured by dry gas meter, dcm (dcf).

ΔV_m=Incremental dry gas volume measured by dry gas meter at each traverse point, dcm (dcf).

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

$V_{wc(std)}$=Volume of water vapor condensed corrected to standard conditions, scm (scf).

$V_{wsg(std)}$=Volume of water vapor collected in silica gel corrected to standard conditions, scm (scf).

V_f=Final volume of condenser water, ml.

V_i=Initial volume, if any, of condenser water, ml.

W_f=Final weight of silica gel or silica gel plus impinger, g.

W_i=Initial weight of silica gel or silica gel plus impinger, g.

Y=Dry gas meter calibration factor.

ρ_w=Density of water, 0.9982 g/ml (0.002201 lb/ml).

2.3.2 Volume of Water Vapor Condensed.

$$V_{wc(std)} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w}$$

$$= K_1(V_f - V_i)$$

Eq. 4-1

Where:

K_1=0.001333 m³/ml for metric units
=0.04707 ft³/ml for English units

2.3.3 Volume of Water Vapor Collected in Silica Gel.

$$V_{wsg(std)} = \frac{(W_f - W_i) R T_{std}}{P_{std} M_w}$$

$$= K_2(W_f - W_i)$$

Eq. 4-2

Where:

K_2=0.001335 m³/g for metric units
=0.04715 ft³/g for English units

2.3.4 Sample Gas Volume.

$$V_{m(std)} = V_m Y \frac{(P_m)(T_{std})}{(P_{std})(T_m)}$$

$$= K_3 Y \frac{V_m P_m}{T_m}$$

Eq. 4-3

Where:

K_3=0.3858 °K/mm Hg for metric units
=17.64 °R/in. Hg for English units

NOTE: If the post-test leak rate (Section 2.2.6) exceeds the allowable rate, correct the value of V_m in Equation 4-3, as described in Section 6.3 of Method 5.

2.3.5 Moisture Content.

$$B_{ws} = \frac{V_{wc(std)} + V_{wsg(std)}}{V_{wc(std)} + V_{wsg(std)} + V_{m(std)}}$$

Eq. 4-4

NOTE: In saturated or moisture droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one using a value based upon the saturated conditions (see Section 1.2), and another based upon the results of the impinger analysis. The lower of these two values of B_{ws} shall be considered correct.

2.3.6 Verification of Constant Sampling Rate. For each time increment, determine the ΔV_m. Calculate the average. If the value for any time increment differs from the average by more than 10 percent, reject the results and repeat the run.

3. *Approximation Method*

The approximation method described below is presented only as a suggested method (see Section 1.2).

3.1 Apparatus.

3.1.1 Probe. Stainless steel glass tubing, sufficiently heated to prevent water condensation and equipped with a filter (either in-stack or heated out-stack) to remove particulate matter. A plug of glass wool, inserted into the end of the probe, is a satisfactory filter.

3.1.2 Impingers. Two midget impingers, each with 30 ml capacity, or equivalent.

3.1.3 Ice Bath. Container and ice, to aid in condensing moisture in impingers.

3.1.4 Drying Tube. Tube packed with new or regenerated 6- to 16-mesh indicating-type silica gel (or equivalent desiccant), to dry the sample gas and to protect the meter and pump.

3.1.5 Valve. Needle valve, to regulate the sample gas flow rate.

3.1.6 Pump. Leak-free, diaphragm type, or equivalent, to pull the gas sample through the train.

3.1.7 Volume Meter. Dry gas meter, sufficiently accurate to measure the sample volume within 2%, and calibrated over the range of flow rates and conditions actually encountered during sampling.

3.1.8 Rate Meter. Rotameter, to measure the flow range from 0 to 3 lpm (0 to 0.11 cfm).

3.1.9 Graduated Cylinder. 25 ml.

3.1.10 Barometer. Mercury, aneroid, or other barometer, as described in Section 2.1.5 above.

3.1.11 Vacuum Gauge. At least 760 mm Hg (30 in. Hg) gauge, to be used for the sampling leak check.

3.2 Procedure.

3.2.1 Place exactly 5 ml distilled water in each impinger.

Leak check the sampling train as follows: Temporarily insert a vacuum gauge at or near the probe inlet; then, plug the probe inlet and pull a vacuum of at least 250 mm Hg (10 in. Hg). Note, the time rate of change of the dry gas meter dial; alternatively, a rotameter (0–40 cc/min) may be temporarily attached to the dry gas meter outlet to determine the leakage rate. A leak 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.

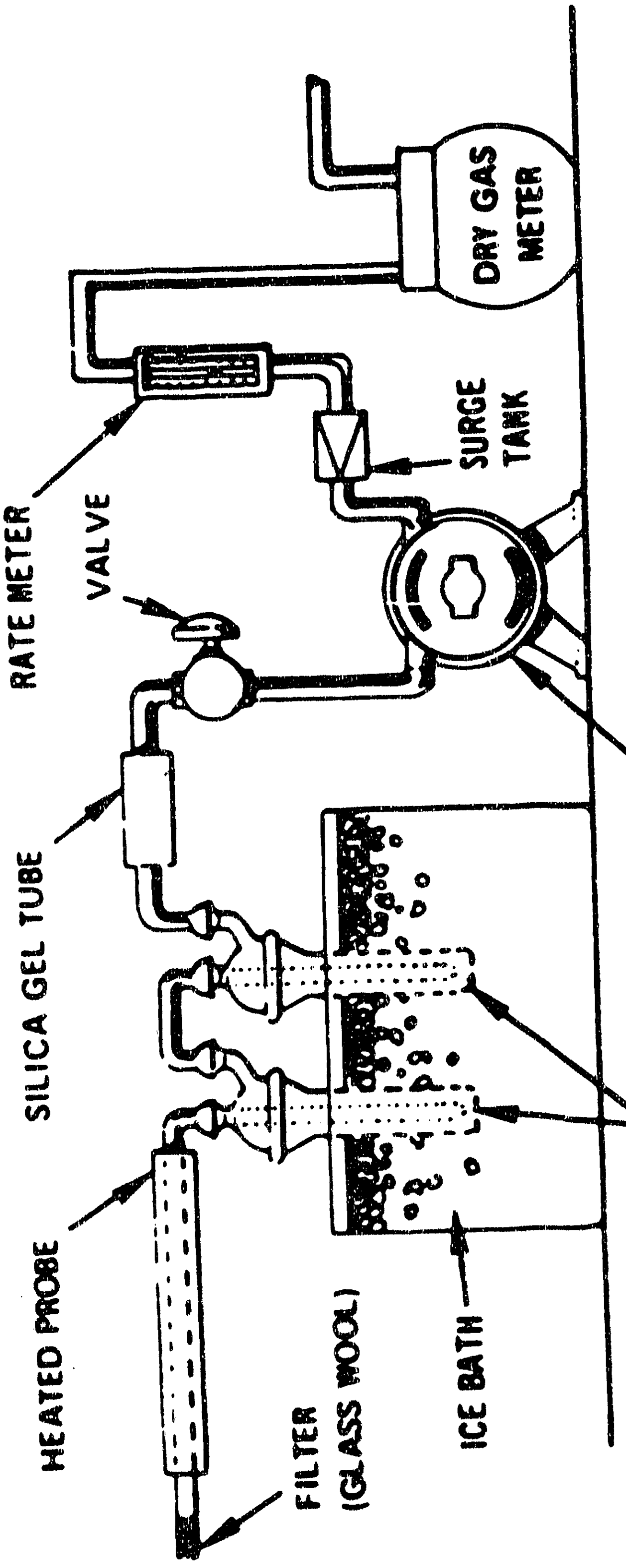

Figure 4-4. Moisture-sampling train - approximation method.

FIGURE 4-5—FIELD MOISTURE DETERMINATION—APPROXIMATION METHOD

Location.. Comments:
Test....:...
Date ....
Operator ....
Barometric pressure ....

Clock time	Gas volume through meter, (V_m), m^3 (ft^3)	Rate meter setting m^3/min (ft^3/min)	Meter temperature, °C (°F)

3.2.2 Connect the probe, insert it into the stack, and sample at a constant rate of 2 lpm (0.071 cfm). Continue sampling until the dry gas meter registers about 30 liters (1.1 ft^3) or until visible liquid droplets are carried over from the first impinger to the second. Record temperature, pressure, and dry gas meter readings as required by Figure 4-5.

3.2.3 After collecting the sample, combine the contents of the two impingers and measure the volume to the nearest 0.5 ml.

3.3 Calculations. The calculation method presented is designed to estimate the moisture in the stack gas; therefore, other data, which are only necessary for accurate moisture determinations, are not collected. The following equations adequately estimate the moisture content, for the purpose of determining isokinetic sampling rate settings.

3.3.1 Nomenclature.

B_{wm}=Approximate proportion, by volume, of water vapor in the gas stream leaving the second impinger, 0.025.
B_{ws}=Water vapor in the gas stream, proportion by volume.
M_w=Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole).
P_m=Absolute pressure (for this method, same as barometric pressure) at the dry gas meter.
P_{std}=Standard absolute pressure, 760 mm Hg (29.92 in. Hg).
R=Ideal gas constant, 0.06236 (mm Hg) (m^3)/(g-mole) (°K) for metric units and 21.85 (in. Hg) (ft^3)/lb-mole) (°R) for English units.
T_m=Absolute temperature at meter, °K (°R).
T_{std}=Standard absolute temperature, 293° K (528° R).
V_f=Final volume of impinger contents, ml.
V_i=Initial volume of impinger contents, ml.
V_m=Dry gas volume measured by dry gas meter, dcm (dcf).
$V_{m(std)}$=Dry gas volume measured by dry gas meter, corrected to standard conditions, dscm (dscf).
$V_{wc(std)}$=Volume of water vapor condensed, corrected to standard conditions, scm (scf).
ρ_w=Density of water, 0.9982 g/ml (0.002201 lb/ml).
Y=Dry gas meter calibration factor.

3.3.2 Volume of Water Vapor Collected.

$$V_{wc} = \frac{(V_f - V_i)\rho_w R T_{std}}{P_{std} M_w}$$

$$= K_1(V_f - V_i)$$

Eq. 4-5

Where:
K_1=0.001333 m^3/ml for metric units
=0.04707 ft^3/ml for English units.

3.3.3 Gas Volume.

$$V_{m(std)} = V_m\left(\frac{P_m}{P_{std}}\right)\left(\frac{T_{std}}{T_m}\right)$$

$$= K_2 \frac{V_m P_m}{T_m}$$

Equation 4-6

where:
K_2=0.3858 °K/mm Hg for metric units
=17.64 °R/in. Hg for English units

3.3.4 Approximate Moisture Content.

$$B_{ws} = \frac{V_{wc}}{V_{wc} + V_{m(std)}} + B_{wm}$$

$$= \frac{V_{wc}}{V_{wc} + V_{m(std)}} + (0.025)$$

Equation 4-7

4. *Calibration*

4.1 For the reference method, calibrate equipment as specified in the following sections of Method 5: Section 5.3 (metering system); Section 5.5 (temperature gauges); and Section 5.7 (barometer). The recommended leak check of the metering system (Section 5.6 of Method 5) also applies to the reference method. For the approximation method, use the procedures outlined in Section 5.1.1 of Method 6 to calibrate the metering system, and the procedure of Method 5, Section 5.7 to calibrate the barometer.

5. *Bibliography*

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Air Quality Planning and Standards. Research Triangle Park, NC. Publication No. AP-40. 1973.

2. Devorkin, Howard. et al. Air Pollution Source Testing Manual. Air Pollution Control District, Los Angeles, CA. November, 1963.

3. Methods for Determination of Velocity, Volume, Dust and Mist Content of Gases. Western Precipitation Division of Joy Manufacturing Co., Los Angeles, CA. Bulletin WP-50. 1968.

METHOD 5—DETERMINATION OF PARTICULATE EMISSIONS FROM STATIONARY SOURCES

1. *Principle and Applicability*

1.1 Principle. Particulate matter is withdrawn isokinetically from the source and collected on a glass fiber filter maintained at a temperature in the range of 120±14° C (248±25° F) or such other temperature as specified by an applicable subpart of the standards or approved by Administrator, U.S. Environmental Protection Agency, for a particular application. The particulate mass, which includes any material that condenses at or above the filtration temperature, is determined gravimetrically after removal of uncombined water.

1.2 Applicability. This method is applicable for the determination of particulate emissions from stationary sources.

2. *Apparatus*

2.1 Sampling Train. A schematic of the sampling train used in this method is shown in Figure 5-1. Complete construction details are given in APTD-0581 (Citation 2 in Bibliography); commercial models of this train are also available. For changes from APTD-0581 and for allowable modifications of the train shown in Figure 5-1, see the following subsections.

The operating and maintenance procedures for the sampling train are described in APTD-0576 (Citation 3 in Bibliography). Since correct usage is important in obtaining valid results, all users should read APTD-0576 and adopt the operating and maintenance procedures outlined in it, unless otherwise specified herein. The sampling train consists of the following components:

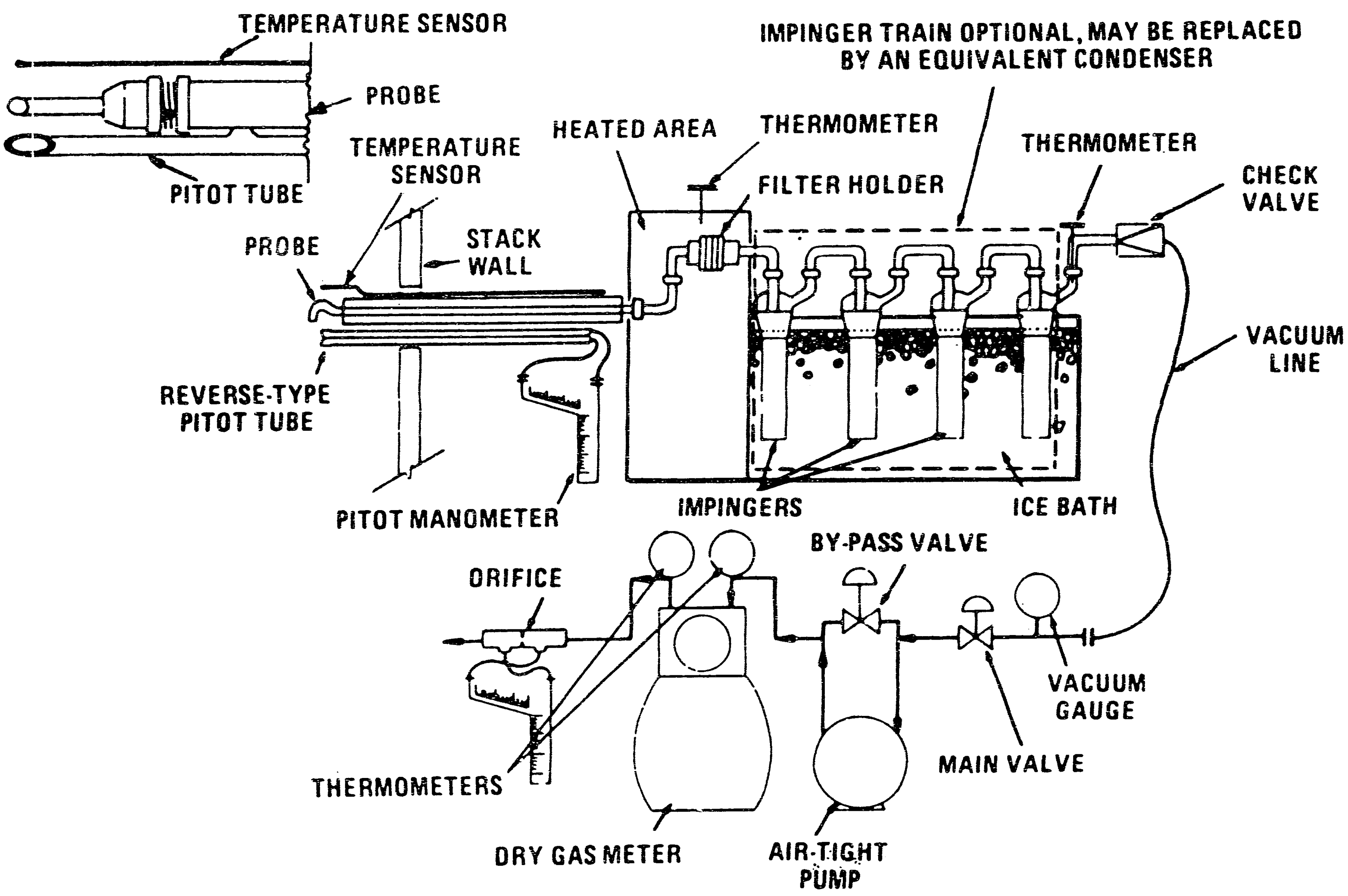

Figure 5-1. Particulate-sampling train.

2.1.1 Probe Nozzle. Stainless steel (316) or glass with sharp, tapered leading edge. The angle of taper shall be <30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise specified by the Administrator. If made of stainless steel, the nozzle shall be constructed from seamless tubing; other materials of construction may be used, subject to the approval of the Administrator.

A range of nozzle sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (⅛ to ½ in.)—or larger if higher volume sampling trains are used—inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.

2.1.2 Probe Liner. Borosilicate or quartz glass tubing with a heating system capable of maintaining a gas temperature at the exit end during sampling of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. (The tester may opt to operate the equipment at a temperature lower than that specified.) Since the actual temperature at the outlet of the probe is not usually monitored during sampling, probes constructed according to APTD-0581 and utilizing the calibration curves of APTD-0576 (or calibrated according to the procedure outlined in APTD-0576) will be considered acceptable.

Either borosilicate or quartz glass probe liners may be used for stack temperatures up to about 480° C (900° F) quartz liners shall be used for temperatures between 480 and 900° C (900 and 1,650° F). Both types of liners may be used at higher temperatures than specified for short periods of time, subject to the approval of the Administrator. The softening temperature for borosilicate is 820° C (1,508° F), and for quartz it is 1,500° C (2,732° F).

Whenever practical, every effort should be made to use borosilicate or quartz glass probe liners. Alternatively, metal liners (e.g., 316 stainless steel, Incoloy 825,[2] or other corrosion resistant metals) made of seamless tubing may be used, subject to the approval of the Administrator.

2.1.3 Pitot Tube. Type S, as described in Section 2.1 of Method 2, or other device approved by the Administrator. The pitot tube shall be attached to the probe (as shown in Figure 5-1) to allow constant monitoring of the stack gas velocity. The impact (high pressure) opening plane of the pitot tube shall be even with or above the nozzle entry plane (see Method 2, Figure 2-6b) during sampling. The Type S pitot tube assembly shall have a known coefficient, determined as outlined in Section 4 of Method 2.

2.1.4 Differential Pressure Gauge. Inclined manometer or equivalent device (two), as described in Section 2.2 of Method 2. One manometer shall be used or velocity head (Δp) readings, and the other, for orifice differential pressure readings.

2.1.5 Filter Holder. Borosilicate glass, with a glass frit filter support and a silicone rubber gasket. Other materials of construction (e.g., stainless steel, Teflon, Viton) may be used, subject to approval of the Administrator. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe (or cyclone, it used).

2.1.6 Filter Heating System. Any heating system capable of maintaining a temperature around the filter holder during sampling of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator for a particular application. Alternatively, the tester may opt to operate the equipment at a temperature lower than that specified. A temperature gauge capable of measuring temperature to within 3° C (5.4° F) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling. Heating systems other than the one shown in APTD-0581 may be used.

2.1.7 Condenser. The following system shall be used to determine the stack gas moisture content: Four impingers connected in series with leak-free ground glass fittings or any similar leak-free non-contaminating fittings. The first, third, and fourth impingers shall be of the Greenburg-Smith design, modified by replacing the tip with 1.3 cm (½ in.) ID glass tube extending to about 1.3 cm (½ in.) from the bottom of the flask. The second impinger shall be of the Greenburg-Smith design with the standard tip. Modifications (e.g., using flexible connections between the impingers, using materials other than glass, or using flexible vacuum lines to connect the filter holder to the condenser) may be used, subject to the approval of the Administrator. The first and second impingers shall contain known quantities of water (Section 4.1.3), the third shall be empty, and the fourth shall contain a known weight of silica gel, or equivalent desiccant. A thermometer, capable of measuring temperature to within 1° C (2° F) shall be placed at the outlet of the fourth impinger for monitoring purposes.

Alternatively, any system that cools the sample gas stream and allows measurement of the water condensed and moisture leav-

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[2] Mention of trade names or specific product does not constitute endorsement by the Environmental Protection Agency.

ing the condenser, each to within 1 ml or 1 g may be used, subject to the approval of the Administrator. Acceptable means are to measure the condensed water either gravimetrically or volumetrically and to measure the moisture leaving the condenser by: (1) monitoring the temperature and pressure at the exit of the condenser and using Dalton's law of partial pressures; or (2) passing the sample has stream through a tared silica gel (or equivalent desiccant) trap with exit gases kept below 20° C (68° F) and determining the weight gain.

If means other than silica gel are used to determine the amount of moisture leaving the condenser, it is recommended that silica gel (or equivalent) still be used between the condenser system and pump to prevent moisture condensation in the pump and metering devices and to avoid the need to make corrections for moisture in the metered volume.

NOTE: If a determination of the particulate matter collected in the impingers is desired in addition to moisture content, the impinger system described above shall be used, without modification. Individual States or control agencies requiring this information shall be contacted as to the sample recovery and analysis of the impinger contents.

2.1.8 Metering System. Vacuum gauge, leak-free pump, thermometers capable of measuring temperature to within 3° C (5.4° F), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 5-1. Other metering systems capable of maintaining sampling rates within 10 percent of isokinetic and of determining sample volumes to within 2 percent may be used, subject to the approval of the Administrator. When the metering system is used in conjunction with a pitot tube, the system shall enable checks of isokinetic rates.

Sampling trains utilizing metering systems designed for higher flow rates than that decribed in APTD-0581 or APDT-0576 may be used provided that the specifications of this method are met.

2.1.9 Barometer. Mercury aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases the barometric reading may be obtained from a nearby National Weather Service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

2.1.10 Gas Density Determination Equipment. Temperature sensor and pressure gauge, as described in Sections 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The temperature sensor shall, preferably, be permanently attached to the pitot tube or sampling probe in a fixed configuration, such that the tip of the sensor extends beyond the leading edge of the probe sheath and does not touch any metal. Alternatively, the sensor may be attached just prior to use in the field. Note, however, that if the temperature sensor is attached in the field, the sensor must be placed in an interference-free arrangement with respect to the Type S pitot tube openings (see Method 2, Figure 2-7). As a second alternative, if a difference of not more than 1 percent in the average velocity measurement is to be introduced, the temperature gauge need not be attached to the probe or pitot tube. (This alternative is subject to the approval of the Administrator.)

2.2 Sample Recovery. The following items are needed.

2.2.1 Probe-Liner and Probe-Nozzle Brushes. Nylon bristle brushes with stainless steel wire handles. The probe brush shall have extensions (at least as long as the probe) of stainless steel, Nylon, Teflon, or similarly inert material. The brushes shall be properly sized and shaped to brush out the probe liner and nozzle.

2.2.2 Wash Bottles—Two. Glass wash bottles are recommended; polyethylene wash bottles may be used at the option of the tester. It is recommended that acetone not be stored in polyethylene bottles for longer than a month.

2.2.3 Glass Sample Storage Containers. Chemically resistant, borosilicate glass bottles, for acetone washes, 500 ml or 1000 ml. Screw cap liners shall either be rubber-backed Teflon or shall be constructed so as to be leak-free and resistant to chemical attack by acetone. (Narrow mouth glass bottles have been found to be less prone to leakage.) Alternatively, polyethylene bottles may be used.

2.2.4 Petri Dishes. For filter samples, glass or polyethylene, unless otherwise specified by the Administrator.

2.2.5 Graduated Cylinder and/or Balance. To measure condensed water to within 1 ml or 1 g. Graduated cylinders shall have subdivisions no greater than 2 ml. Most laboratory balances are capable of weighing to the nearest 0.5 g or less. Any of these balances is suitable or use here and in Section 2.3.4.

2.2.6 Plastic Storage Containers. Airtight containers to store silica gel.

2.2.7 Funnel and Rubber Policeman. To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

2.2.8 Funnel. Glass or polyethylene, to aid in sample recovery.

2.3 Analysis. For analysis, the following equipment is needed.

2.3.1 Glass Weighing Dishes.

2.3.2 Desiccator.

2.3.3 Analytical Balance. To measure to within 0.1 mg.

2.3.4 Balance. To measure to within 0.5 g.

2.3.5 Beakers. 250 ml.

2.3.6 Hygrometer. To measure the relative humidity of the laboratory environment.

2.3.7 Temperature Gauge. To measure the temperature of the laboratory environment.

3. *Reagents*

3.1 Sampling. The reagents used in sampling are as follows:

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 D2986-71 (Reapproved 1978) (incorporated by reference—see § 60.17). Test data from the supplier's quality control program are sufficient for this purpose. In sources containing SO_2 or SO_3, the filter material must be of a type that is unreactive to SO_2 or SO_3. Citation 10 in Section 7 Bibliography, may be used to select the appropriate filter.

3.1.2 Silica Gel. Indicating type, 6 to 16 mesh. If previously used, 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, subject to the approval of the Administrator.

3.1.3 Water. When analysis of the material caught in the impingers is required, distilled water shall be used. Run blanks prior to field use to eliminate a high blank on test samples.

3.1.4 Crushed Ice.

3.1.5 Stopcock Grease. Acetone-insoluble, heat-stable silicone grease. This is not necessary if screw-on connectors with Teflon sleeves, or similar, are used. Alternatively, other types of stopcock grease may be used, subject to the approval of the Administrator.

3.2 Sample Recovery. Acetone-reagent grade, <0.001 percent residue, in glass bottles—is required. Acetone from metal containers generally has a high residue blank and should not be used. Sometimes, suppliers transfer acetone to glass bottles from metal containers; thus, acetone blanks shall be run prior to field use and only acetone with low blank values (<0.001 percent) shall be used. In no case shall a blank value of greater than 0.001 percent of the weight of acetone used be subtracted from the sample weight.

3.3 Analysis. Two reagents are required for the analysis:

3.3.1 Acetone. Same as 3.2.

3.3.2 Desiccant. Anhydrous calcium sulfate, indicating type. Alternatively, other types of desiccants may be used, subject to the approval of the Administrator.

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. It is suggested that sampling equipment be maintained according to the procedure described in APTD-0576.

Weigh several 200 to 300 g portions of silica gel in air-tight containers 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 need not be preweighed, but may be weighed directly in the impinger or sampling holder just prior to train assembly.

Check filters visually against light for irregularities and flaws or pinhole leaks. Label filters of the proper diameter on the back side near the edge using numbering machine ink. As an alternative, label the shipping containers (glass or plastic petri dishes) and keep the filters in these containers at all times except during sampling and weighing.

Desiccate the filters at 20±5.6° C (68±10° F) and ambient pressure for at least 24 hours and weigh at intervals of at least 6 hours to a constant weight, i.e., 0.5 mg change from previous weighing; record results to the nearest 0.1 mg. During each weighing the filter must not be exposed to the laboratory atmosphere for a period greater than 2 minutes and a relative humidity above 50 percent. Alternatively (unless otherwise specified by the Administrator), the filters may be oven dried at 105° C (220° F) for 2 to 3 hours, desiccated for 2 hours, and weighed. Procedures other than those described, which account for relative humidity effects, may be used, subject to the approval of the Administrator.

4.1.2 Preliminary Determinations. Select the sampling site and the minimum number of sampling points according to Method 1 or as specified by the Administrator. Determine the stack pressure, temperature, and the range of velocity heads using Method 2; it is recommended that a leak-check of the pitot lines (see Method 2, Section 3.1) be performed. Determine the moisture content using Approximation Method 4 or its alternatives for the purpose of making isokinetic sampling rate settings. Determine the stack gas dry molecular weight, as described in Method 2, Section 3.6; if integrated Method 3 sampling is used for molecular weight determination, the integrated bag sample shall be taken simultaneously with, and for the same total length of time as, the particulate sample run.

Select a nozzle size based on the range of velocity heads, such that it is not necessary to change the nozzle size in order to maintain isokinetic sampling rates. During the run, do not change the nozzle size. Ensure that the proper differential pressure gauge is chosen for the range of velocity heads encountered (see Section 2.2 of Method 2).

Select a suitable probe liner and probe length such that all traverse points can be sampled. For large stacks, consider sampling from opposite sides of the stack to reduce the length of probes.

Select a total sampling time greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry such that (1) the sampling time per point is not less than 2 min (or some greater time interval as specified by the Administrator), and (2) the sample volume taken (corrected to standard conditions) will exceed the required minimum total gas sample volume. The latter is based on an approximate average sampling rate.

It is recommended that the number of minutes sampled at each point be an integer or an integer plus one-half minute, in order to avoid timekeeping errors. The sampling time at each point shall be the same.

In some circumstances, e.g., batch cycles, it may be necessary to sample for shorter times at the traverse points and to obtain smaller gas sample volumes. In these cases, the Administrator's approval must first be obtained.

4.1.3 Preparation of Collection Train. During preparation and assembly of the sampling train, keep all openings where contamination can occur covered until just prior to assembly or until sampling is about to begin.

Place 100 ml of water in each of the first two impingers, leave the third impinger empty, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the fourth impinger. More silica gel may be used, but care should be taken to ensure that it is not entrained and carried out from the impinger during sampling. Place the 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.

Using a tweezer or clean disposable surgical gloves, place a labeled (identified) and weighed filter in the filter holder. Be sure that the filter is properly centered and the gasket properly placed so as to prevent the sample gas stream from circumventing the filter. Check the filter for tears after assembly is completed.

When glass liners are used, install the selected nozzle using a Viton A O-ring when stack temperatures are less than 260° C (500° F) and an asbestos string gasket when temperatures are higher. See APTD-0576 for details. Other connecting systems using either 316 stainless steel or Teflon ferrules may be used. When metal liners are used, install the nozzle as above or by a leak-free direct mechanical connection. Mark the probe with heat resistant tape or by some other method to denote the proper distance into the stack or duct for each sampling point.

Set up the train as in Figure 5-1, using (if necessary) a very light coat of silicone grease on all ground glass joints, greasing only the outer portion (see APTD-0576) to avoid possibility of contamination by the silicone grease. Subject to the approval of the Administrator, a glass cyclone may be used between the probe and filter holder when the total particulate catch is expected to exceed 100 mg or when water droplets are present in the stack gas.

Place crushed ice around the impingers.

4.1.4 Leak-Check Procedures.

4.1.4.1 Pretest Leak-Check. A pretest leak-check is recommended, but not required. If the tester opts to conduct the pretest leak-check, the following procedure shall be used.

After the sampling train has been assembled, turn on and set the filter and probe heating systems at the desired operating temperatures. Allow time for the temperatures to stabilize. If a Viton A O-ring or other leak-free connection is used in assembling the probe nozzle to the probe liner, leak-check the train at the sampling site by plugging the nozzle and pulling a 380 mm Hg (15 in. Hg) vacuum.

NOTE: A lower vacuum may be used, provided that it is not exceeded during the test.

If an asbestos string is used, do not connect the probe to the train during the leak-check. Instead, leak-check the train by first plugging the inlet to the filter holder (cyclone, if applicable) and pulling a 380 mm Hg (15 in. Hg) vacuum (see Note immediately above). Then connect the probe to the train and leak-check at about 25 mm Hg (1 in. Hg) vacuum; alternatively, the probe may be leak-checked with the rest of the sampling train, in one step, at 380 mm Hg (15 in. Hg) vacuum. Leakage rates in excess of 4 percent of the average sampling rate or 0.00057 m^3/min (0.02 cfm), whichever is less, are unacceptable.

The following leak-check instructions for the sampling train described in APTD-0576 and APTD-0581 may be helpful. Start the pump with bypass valve fully open and coarse adjust valve, completely closed. Partially open the coarse adjust valve and slowly close the bypass valve until the desired vacuum is reached. Do not reverse direction of bypass value; this will cause water to back up into the filter holder. If the desired vacuum is exceeded, either leak-check at this higher vacuum or end the leak-check as shown below and start over.

When the leak-check is completed, first slowly remove the plug from the inlet to the probe, filter holder, or cyclone (if applicable) and immediately turn off the vacuum pump. This prevents the water in the impingers from being forced backward into the filter holder and silica gel from being entrained backward into the third impinger.

4.1.4.2 Leak-Checks During Sample Run. If, during the sampling run, a component (e.g., filter assembly or impinger) change becomes unnecessary, a leak-check shall be conducted immediately before the change is made. The leak-check shall be done according to the procedure outlined in Section 4.1.4.1 above, except that it shall be done at a vacuum equal to or greater than the maximum value recorded up to that point in the test. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction will need to be applied to the total volume of dry gas metered; if, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and plan to correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

Immediately after component changes, leak-checks are optional; if such leak-checks are done, the procedure outlined in Section 4.1.4.1 above shall be used.

4.1.4.3 Post-test Leak-Check. A leak-check is mandatory at the conclusion of each sampling run. The leak-check shall be done in accordance with the procedures outlined in Section 4.1.4.1, except that it shall be conducted at a vacuum equal to or greater than the maximum value reached during the sampling run. If the leakage rate is found to be no greater than 0.00057 m^3/min (0.02 cfm) or 4 percent of the average sampling rate (whichever is less), the results are acceptable, and no correction need be applied to the total volume of dry gas metered. If, however, a higher leakage rate is obtained, the tester shall either record the leakage rate and correct the sample volume as shown in Section 6.3 of this method, or shall void the sampling run.

4.1.5 Particulate Train Operation. During the sampling run, maintain an isokinetic sampling rate (within 10 percent of true isokinetic unless otherwise specified by the Administrator) and a temperature around the filter of 120±14° C (248±25° F), or such other temperature as specified by an applicable subpart of the standards or approved by the Administrator.

For each run, record the data required on a data sheet such as the one shown in Figure 5-2. Be sure to record the initial dry gas meter reading. Record the dry gas meter readings at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted. Take other readings required by Figure 5-2 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate. Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling deposited material. To begin sampling, remove the nozzle cap, verify that the filter and probe heating systems are up to temperature, and that the pitot tube and probe are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream. Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient is 0.85±0.02, and the stack gas equivalent density (dry molecular weight) is equal to 29±4. APTD-0576 details the procedure for using the nomographs. If C_p and M_d are outside the above stated ranges do not use the nomographs unless appropriate steps (see Citation 7 in Bibliography) are taken to compensate for the deviations.

FIGURE 5-2—PARTICULATE FIELD DATA

Plant
Location
Operator
Date
Run No
Sample box No
Meter box No.
Meter ΔH@
C factor
Pitot tube coefficient, Cp

SCHEMATIC OF STACK CROSS SECTION

Ambient temperature
Barometric pressure
Assumed moisture, %
Probe length, m. (ft.)
Nozzle identification No.
Average calibrated nozzle diameter, cm (in.)
Probe heater setting
Leak rate, m³/min, (cfm)
Probe liner material
Static pressure, mm. Hg (in. Hg)
Filter No.

Traverse point number	Sampling time	Vacuum	Stack temperature	Velocity head	Pressure differential across orifice meter	Gas sample volume	Gas sample temperature at dry gas meter		Filter holder temperature	Temperature of gas leaving condenser or last impinger
							Inlet	Outlet		
	(θ). min.	mm Hg (in. Hg)	(T_s). °C (° F)	(ΔP_s). mm (in.) H_2O	mm H_2O (in. H_2O)	m³ (ft³)	°C (° F)	° C (° F)	° C (° F)	° C (° F)
Total							Avg.	Avg.		
Average							Avg.			

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe into the stack to prevent water from backing into the filter holder. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

Traverse the stack cross-section, as required by Method 1 or as specified by the Administrator, being careful not to bump the probe nozzle into the stack walls when sampling near the walls or when removing or inserting the probe through the portholes; this minimizes the chance of extracting deposited material.

During the test run, make periodic adjustments to keep the temperature around the filter holder at the proper level; add more ice and, if necessary, salt to maintain a temperature of less than 20° C (68° F) at the condenser/silica gel outlet. Also, periodically check the level and zero of the manometer.

If the pressure drop across the filter becomes too high, making isokinetic sampling difficult to maintain, the filter may be replaced in the midst of a sample run. It is recommended that another complete filter assembly be used rather than attempting to change the filter itself. Before a new filter assembly is installed, conduct a leak-check (see Section 4.1.4.2). The total particulate weight shall include the summation of all filter assembly catches.

A single train shall be used for the entire sample run, except in cases where simultaneous sampling is required in two or more separate ducts or at two or more different locations within the same duct, or, in cases where equipment failure necessitates a change of trains. In all other situations, the use of two or more trains will be subject to the approval of the Administrator.

Note that when two or more trains are used, separate analyses of the front-half and (if applicable) impinger catches from each train shall be performed, unless identical nozzle sizes were used on all trains, in which case, the front-half catches from the individual trains may be combined (as may the impinger catches) and one analysis of front-half catch and one analysis of impinger catch may be performed. Consult with the Administrator for details concerning the calculation of results when two or more trains are used.

At the end of the sample run, turn off the coarse adjust valve, remove the probe and nozzle from the stack, turn off the pump, record the final dry gas meter reading, and conduct a post-test leak-check, as outlined in Section 4.1.4.3. Also, leak-check the pitot lines as described in Method 2, Section 3.1; the lines must pass this leak-check, in order to validate the velocity head data.

4.1.6 Calculation of Percent Isokinetic. Calculate percent isokinetic (see Calculations, Section 6) to determine whether the run was valid or another test run should be made. If there was difficulty in maintaining isokinetic rates due to source conditions, consult with the Administrator for possible variance on the isokinetic rates.

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. Allow the probe to cool.

When the probe can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a cap over it to prevent losing or gaining particulate matter. Do not cap off the probe tip tightly while the sampling train is cooling down as this would create a vacuum in the filter holder, thus drawing water from the impingers into the filter holder.

Before moving the sample train to the cleanup site, remove the probe from the sample train, wipe off the silicone grease, and cap the open outlet of the probe. Be careful not to lose any condensate that might be present. Wipe off the silicone grease from the filter inlet where the probe was fastened and cap it. Remove the umbilical cord from the last impinger and cap the impinger. If a flexible line is used between the first impinger or condenser and the filter holder, disconnect the line at the filter holder and let any condensed water or liquid drain into the impingers or condenser. After wiping off the silicone grease, cap off the filter holder outlet and impinger inlet. Either ground-glass stoppers, plastic caps, or serum caps may be used to close these openings.

Transfer the probe and filter-impinger assembly to the cleanup area. This area should be clean and protected from the wind so that the chances of contaminating or losing the sample will be minimized.

Save a portion of the acetone used for cleanup as a blank. Take 200 ml of this acetone directly from the wash bottle being used and place it in a glass sample container labeled "acetone blank."

Inspect the train prior to and during disassembly and note any abnormal conditions. Treat the samples as follows:

Container No. 1. Carefully remove the filter from the filter holder and place it in its identified petri dish container. Use a pair of tweezers and/or clean disposable surgical gloves 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 petri dish any particulate matter and/or filter fibers which adhere to the filter holder gasket, by using a dry Nylon bristle brush and/or a sharp-edged blade. Seal the container.

Container No. 2. Taking care to see that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter or any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with acetone and placing the wash in a glass container. 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. Perform the acetone rinses as follows:

Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a Nylon bristle brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

Brush and rinse the inside parts of the Swagelok 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. Let the acetone drain from the lower end into the sample container. A funnel (glass or polyethylene) may be used to aid on transferring liquid washes to the container. Follow the acetone rinse with a 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 through the probe; hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed from the probe. Run the brush through the probe three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. With stainless steel or other metal probes, run the brush through in the above prescribed manner at least six times since metal probes have small crevices in which particulate matter can be entrapped. 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.

It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contaminations.

After ensuring that all joints have been wiped clean of silicone grease, clean the inside of the front half of the filter holder by rubbing the surfaces with a Nylon bristle 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. Carefully rinse out the glass cyclone, also (if applicable). After all acetone washings and particulate matter have been collected in the sample container, tighten the lid on the sample container so that acetone will not leak out when it is shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occured during transport. Label the container to clearly identify its contents.

Container No. 3. Note the color of the indicating silica gel to determine if it has been completely spent and make a notation of its condition. Transfer the silica gel from the fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall and are difficult to remove. Since the gain in weight is to be used for moisture calculations, do not use any water or other liquids to transfer the silica gel. If a balance is available in the field, follow the procedure for container No. 3 in Section 4.3.

Impinger Water. Treat the impingers as follows; Make a notation of any color or film in the liquid catch. Measure the liquid which is 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 (if one is available). 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, unless analysis of the impinger catch is required (see Note, Section 2.1.7).

If a different type of condenser is used, measure the amount of moisture condensed either volumetrically or gravimetrically.

Whenever possible, containers should be shipped in such a way that they remain upright at all times.

4.3 Analysis. Record the data required on a sheet such as the one shown in Figure 5-3. Handle each sample container as follows:

FIGURE 5-3—ANALYTICAL DATA

Plant————————————
Date————————————
Run No.————————————
Filter No.————————————
Amount liquid lost during transport————
Acetone blank volume, ml————————
Acetone wash volume, ml————————
Acetone blank concentration, mg/mg (Equation 5-4)————————
Acetone wash blank, mg (Equation 5-5)——

Container number	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1			
2			
Total			
Less acetone blank			
Weight of particulate matter			

	Volume of liquid water collected	
	Impinger volume, ml	Silica gel weight, g
Final		
Initial		
Liquid collected		
Total volume collected		g* ml

*Convert weight of water to volume by dividing total weight increase by density of water (1 g/ml).

$$\frac{\text{Increase, g}}{(1\ \text{g/ml})} = \text{Volume water, ml}$$

Container No. 1. Leave the contents in the shipping container or transfer the filter and any loose particulate from the sample container to a tared glass weighing dish. Desiccate for 24 hours in a desiccator containing anhydrous calcium sulfate. Weigh to a constant weight and report the results to the nearest 0.1 mg. For purposes of this Section, 4.3, the term "constant weight" means a difference of no more than 0.5 mg or 1 percent of total weight less tare weight, whichever is greater, between two consecutive weighings, with no less than 6 hours of desiccation time between weighings.

Alternatively, the sample may be oven dried at 105° C (220° F) for 2 to 3 hours, cooled in the desiccator, and weighed to a constant weight, unless otherwise specified by the Administrator. The tester may also opt to oven dry the sample at 105° C (220° F) for 2 to 3 hours, weigh the sample, and use this weight as a final weight.

Container No. 2. 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 to ±1 ml or gravimetrically to ±0.5 g. Transfer the contents to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Container No. 3. Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

NOTE: At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

4.4 Quality Control Procedures. The following quality control procedures are suggested to check the volume metering system calibration values at the field test site prior to sample collection. These procedures are optional for the tester.

4.4.1 Meter Orifice Check. Using the calibration data obtained during the calibration procedure described in Section 5.3, determine the $\Delta H_@$ for the metering system orifice. The $\Delta H_@$ is the orifice pressure differential in units of in. H_2O that correlates to 0.75 cfm of air at 528°R and 29.92 in. Hg. The $\Delta H_@$ is calculated as follows:

$$\Delta H_@ = 0.0319\ \Delta H \ \frac{T_m}{P_{bar}} \ \frac{\Theta^2}{Y^2 V_m^2} \qquad \text{Eq. 5-9}$$

Where:

ΔH=Average pressure differential across the orifice meter, in. H_2O.

T_m=Absolute average dry gas meter temperature, °R.

P_{bar}=Barometric pressure, in. Hg.

Θ=Total sampling time, min.

Y=Dry gas meter calibration factor, dimensionless.

V_m=Volume of gas sample as measured by dry gas meter, dcf.

$0.0319=(0.0567\ \text{in. Hg/°R}) \times (0.75\ \text{cfm})^2$.

Before beginning the field test (a set of three runs usually constitutes a field test), operate the metering system (i.e., pump, volume meter, and orifice) at the $\Delta H_@$ pressure differential for 10 minutes. Record the volume collected, the dry gas meter temperature, and the barometric pressure. Calculate a dry gas meter calibration check value, Y_c, as follows:

$$Y_c = \frac{10}{V_m} \left[\frac{0.0319\ T_m}{P_{bar}} \right]^{1/2}$$

Eq. 5-10

Where:

Y_c = Dry gas meter calibration check value, dimensionless.

10 = 10 minutes of run time.

Compare the Y_c value with the dry gas meter calibration factor Y to determine that:

$$0.97Y < Y_c < 1.03Y$$

If the Y_c value is not within this range, the volume metering system should be investigated before beginning the test.

4.4.2 Calibrated Critical Orifice. A calibrated critical orifice, calibrated against a wet test meter or spirometer and designed to be inserted at the inlet of the sampling meter box may be used as a quality control check by following the procedure of Section 7.2.

5. *Calibration*

Maintain a laboratory log of all calibrations.

5.1 Probe Nozzle. Probe nozzles shall be calibrated before their initial use in the field. Using a micrometer, measure the inside diameter of the nozzle to the nearest 0.025 mm (0.001 in.). Make three separate measurements using different diameters each time, and obtain the average of the measurements. The difference between the high and low numbers shall not exceed 0.1 mm (0.004 in.). When nozzles become nicked, dented, or corroded, they shall be reshaped, sharpened, and recalibrated before use. Each nozzle shall be permanently and uniquely identified.

5.2 Pitot Tube. The Type S pitot tube assembly shall be calibrated according to the procedure outlined in Section 4 of Method 2.

5.3 Metering System.

5.3.1 Calibration Prior to Use. Before its initial use in the field, the metering system shall be calibrated as follows: Connect the metering system inlet to the outlet of a wet test meter that is accurate to within 1 percent. Refer to Figure 5.5. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev). A spirometer of 400 liters (14 ft^3) or more capacity, or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should be periodically calibrated with a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained. Run the metering system pump for about 15 minutes with the orifice manometer indicating a median reading as expected in field use to allow the pump to warm up and to permit the interior surface of the wet test meter to be thoroughly wetted. Then, at each of a minimum of three orifice manometer settings, pass an exact quantity of gas through the wet test meter and note the gas volume indicated by the dry gas meter. Also note the barometric pressure, and the temperatures of the wet test meter, the inlet of the dry gas meter, and the outlet of the dry gas meter. Select the highest and lowest orifice settings to bracket the expected field operating range of the orifice. Use a minimum volume of 0.15 m^3 (5 cf) at all orifice settings. Record all the data on a form similar to Figure 5.6, and calculate Y, the dry gas meter calibration factor, and $\Delta H_@$, the orifice calibration factor, at each orifice setting as shown on Figure 5.6. Allowable tolerances for individual Y and $\Delta H_@$, values are given in Figure 5.6. Use the average of the Y values in the calculations in Section 6.

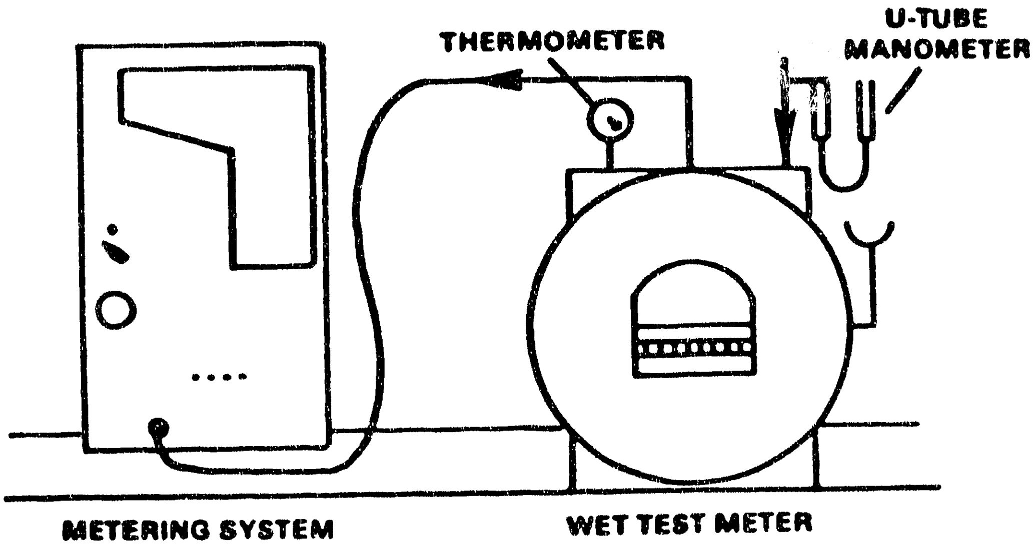

Figure 5.5 Equipment arrangement for metering system calibration.

Date________________________

Metering System Identification:____________________

Barometric pressure, P_b = _______ in. Hg

Orifice manometer setting ΔH in. H_2O	Spirometer (wet meter) gas volume V_w ft^3	Dry gas meter volume V_m ft^3	Temperatures				Time θ min
			Spirometer (wet meter) t_w °F	Dry Gas Meter			
				Inlet t_i °F	Outlet t_o °F	Average t_m °F	

Calculations

ΔH in. H_2O	Y	$\Delta H@$
	$\frac{V_w P_b (t_m + 460)}{V_m \left[P_b + \frac{\Delta H}{13.6}\right] (t_w + 460)}$	$\frac{0.0317\ \Delta H}{P_b (t_o + 460)} \left[\frac{(t_w + 460)\ \theta}{V_w}\right]^2$
Average		

Y = Ratio of reading of wet test meter to dry test meter; tolerance for individual values ±0.02 from average.

$\Delta H@$ = Orifice pressure differential that equates to 0.75 cfm of air @ 68°F and 29.92 inches of mercury, in. H_2O; tolerance for individual values ±0.20 from average.

Figure 5.6. Example data sheet for calibration of metering system (English units).

Before calibrating the metering system, it is suggested that a leak-check be conducted. For metering systems having diaphragm pumps, the normal leak-check procedure will not detect leakages within the pump. For these cases the following leak-check procedure is suggested: make a 10-minute calibration run at 0.00057m^3/min (0.02 cfm); at the end of the run, take the difference of the measured wet test meter and dry gas meter volumes; divided the difference by 10, to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 cfm).

5.3.2 Calibration After Use. After each field use, the calibration of the metering system shall be checked by performing three calibration runs at a single, intermediate orifice setting (based on the previous field test), with the vacuum set at the maximum value reached during the test series. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system. Calculate the average value of the dry gas meter calibration factor. If the value has changed by more than 5 percent, recalibrate the meter over the full range of orifice settings, as previously detailed.

Alternative procedures, e.g., rechecking the orifice meter coefficient may be used, subject to the approval of the Administrator.

5.3.3 Acceptable Variation in Calibration. If the dry gas meter coefficient values obtained before and after a test series differ by more than 5 percent, the test series shall either be voided, or calculations for the test series shall be performed using whichever meter coefficient value (i.e., before or after) gives the lower value of total sample volume.

5.4 Probe Heater Calibration. The probe heating system shall be calibrated before its initial use in the field.

Use a heat source to generate air heated to selected temperatures that approximate those expected to occur in the sources to be sampled. Pass this air through the probe at a typical simple flow rate while measuring the probe inlet and outlet temperatures at various probe heater settings. For each air temperature generated, construct a graph of probe heating system setting versus probe outlet temperature. The procedure outlined in APTD-0576 can also be used. Probes constructed according to APTD-0581 need not be calibrated if the calibration curves in APTD-0576 are used. Also, probes with outlet temperature monitoring capabilities do not require calibration.

5.5 Temperature Gauges. Use the procedure in Section 4.3 of Method 2 to calibrate in-stack temperature gauges. Dial thermometers, such as are used for the dry gas meter and condenser outlet, shall be calibrated against mercury-in-glass thermometers.

5.6 Leak Check of Metering System Shown in Figure 5-1. That portion of the sampling train from the pump to the orifice meter should be leak checked prior to initial use and after each shipment. Leakage after the pump will result in less volume being recorded than is actually sampled. The following procedure is suggested (see Figure 5-4): Close the main valve on the meter box. Insert a one-hole rubber stopper with rubber tubing atached into the orifice exhaust pipe. Disconnect and vent the low side of the orifice manometer. Close off the low side orifice tap. Pressurize the system to 13 to 18 cm (5 to 7 in.) water column by blowing into the rubber tubing. Pinch off the tubing and observe the manometer for one minute. A loss of pressure on the manometer indicates a leak in the meter box; leaks, if present, must be corrected.

5.7 Barometer. Calibrate against a mercury barometer.

6. *Calculations*

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after the final calculation. Other forms of the equations may be used as long as they give equivalent results.

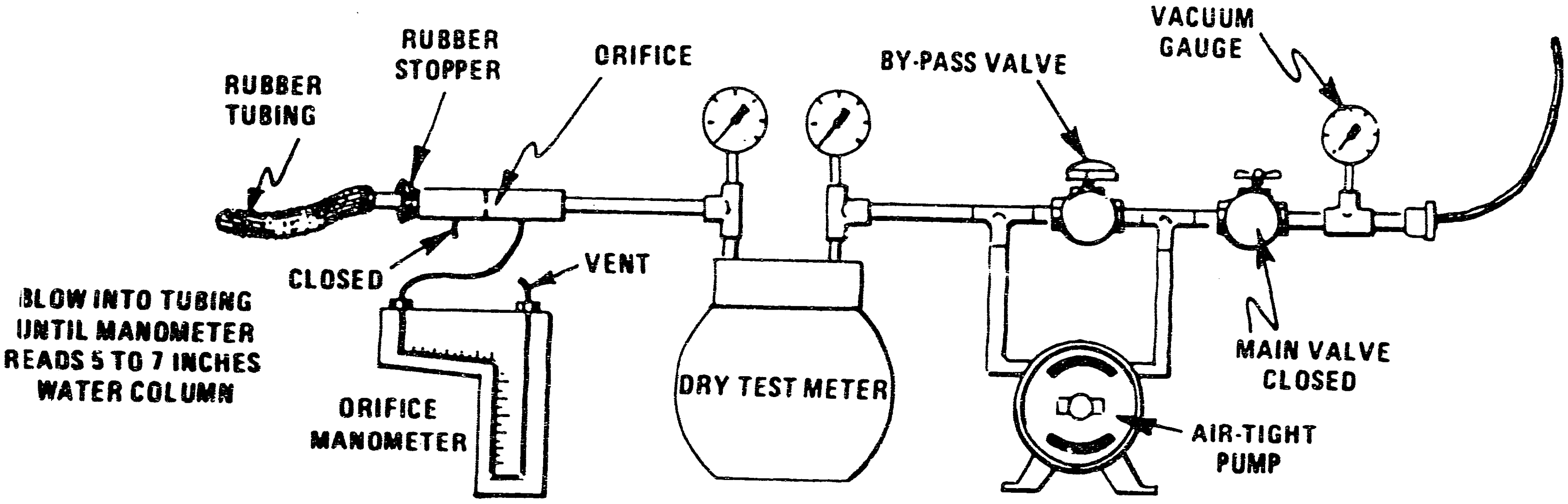

Figure 5–4. Leak check of meter box.

6.1 Nomenclature.

A_n = Cross-sectional area of nozzle, m² (ft²).

B_{ws} = Water vapor in the gas stream, proportion by volume.

C_a = Acetone blank residue concentration, mg/mg.

c_s = Concentration of particulate matter in stack gas, dry basis, corrected to standard conditions, g/dscm (g/dscf).

I = Percent of isokinetic sampling.

L_a = Maximum acceptable leakage rate for either a pretest leak check or for a leak check following a component change; equal to 0.0057 m³/min (0.02 cfm) or 4 percent of the average sampling rate, whichever is less.

L_i = Individual leakage rate observed during the leak check conducted prior to the "i^{th}" component change (i = 1, 2, 3....n), m³/min (cfm).

L_p = Leakage rate observed during the post-test leak check, m³/min (cfm).

m_a = Mass of residue of acetone after evaporation, mg.

m_n = Total amount of particulate matter collected, mg.

M_w = Molecular weight of water, 18.0 g/g-mole (18.0lb/lb-mole).

P_{bar} = Barometric pressure at the sampling site, mm Hg (in. Hg).

P_s = Absolute stack gas pressure, mm Hg (in. Hg).

P_{std} = Standard absolute pressure, 760 mm Hg (29.92 in. Hg).

R = Ideal gas constant, 0.06236 mm Hg-m³/°K-g-mole (21.85 in. Hg-ft³/°R-lb-mole).

T_m = Absolute average dry gas meter temperature (see Figure 5-2), °K (°R).

T_s = Absolute average stack gas temperature (see Figure 5-2), °K (°R).

T_{std} = Standard absolute temperature, 293° K (528° R).

V_a = Volume of acetone blank, ml.

V_{aw} = Volume of acetone used in wash, ml.

V_{lc} = Total volume of liquid collected in impingers and silica gel (see Figure 5-3), ml.

V_m = Volume of gas sample as measured by dry gas meter, dcm (dscf).

$V_{m(std)}$ = Volume of gas sample measured by the dry gas meter, corrected to standard conditions, dscm (dscf).

$V_{w(std)}$ = Volume of water vapor in the gas sample, corrected to standard conditions, scm (scf).

v_s = Stack gas velocity, calculated by Method 2, Equation 2-9, using data obtained from Method 5, m/sec (ft/sec).

W_a = Weight of residue in acetone wash, mg.

Y = Dry gas meter calibration factor.

ΔH = Average pressure differential across the orifice meter (see Figure 5-2), mm H_2O (in. H_2O).

ρ_a = Density of acetone, mg/ml (see label on bottle).

ρ_w = Density of water, 0.9982 g/ml (0.002201 lb/ml).

θ = Total sampling time, min.

θ_1 = Sampling time interval, from the beginning of a run until the first component change, min.

θ_i = Sampling time interval, between two successive component changes, beginning with the interval between the first and second changes, min.

θ_p = Sampling time interval, from the final (n^{th}) component change until the end of the sampling run, min.

13.6 = Specific gravity of mercury.

60 = Sec/min.

100 = Conversion to percent.

6.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop. See data sheet (Figure 5-2).

6.3 Dry Gas Volume. Correct the sample volume measured by the dry gas meter to standard conditions (20° C, 760 mm Hg or 68° F, 29.92 in. Hg) by using Equation 5-1.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right) \left[\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right]$$

$$= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m}$$

Equation 5-1

Where;

K_1 = 0.3858 °K/mm Hg for metric units

= 17.64 °R/in. Hg for English units

NOTE: Equation 5-1 can be used as written unless the leakage rate observed during any of the mandatory leak checks (i.e., the post-test leak check or leak checks conducted prior to component changes) exceeds L_a. If L_p or $_i$ exceeds L_a, Equation 5-1 must be modified as follows:

(a) Case I. No component changes made during sampling run. In this case, replace V_m in Equation 5-1 with the expression:

$$[V_m - (L_p - L_a)\theta]$$

(b) Case II. One or more component changes made during the sampling run. In this case, replace V_m in Equation 5-1 by the expression:

$$\left[V_m - (L_1 - L_a)\theta_1 - \sum_{i=2}^{n} (L_i - L_a)\theta_i - (L_p - L_a)\theta_p\right]$$

and substitute only for those leakage rates (L_i or L_p) which exceed L_a.

6.4 Volume of Water Vapor.

Equation 5-2

$$V_{w(std)}=V_{1c}\left(\frac{\rho_w}{M_w}\right)\left(\frac{RT_{std}}{P_{std}}\right)=K_2V_{1c}$$

Where:

K_2=0.001333 m³/ml for metric units

=0.04707 ft³/ml for English units.

6.5 Moisture Content.

$$B_{ws}=\frac{V_{w\,(std)}}{V_{m\,(std)}+V_{w\,(std)}}$$

Eq. 5-3

NOTE: In saturated or water droplet-laden gas streams, two calculations of the moisture content of the stack gas shall be made, one from the impinger analysis (Equation 5-3), and a second from the assumption of saturated conditions. The lower of the two values of B_w shall be considered correct. The procedure for determining the moisture content based upon assumption of saturated conditions is given in the Note of Section 1.2 of Method 4. For the purposes of this method, the average stack gas temperature from Figure 5-2 may be used to make this determination, provided that the accuracy of the in-stack temperature sensor is ±1° C (2° F).

6.6 Acetone Blank Concentration.

$$C_a=\frac{m_a}{V_a\rho_a}\qquad \text{Eq. 5-4}$$

6.7 Acetone Wash Blank.

$$W_a=C_a\,V_{aw}\rho_a\qquad \text{Eq. 5-5}$$

6.8 Total Particulate Weight. Determine the total particulate catch from the sum of the weights obtained from Containers 1 and 2 less the acetone blank (see Figure 5-3).

NOTE: Refer to Section 4.1.5 to assist in calculation of results involving two or more filter assemblies or two or more sampling trains.

6.9 Particulate Concentration.

$$c_s=(0.001\ g/mg)\ (m_n/V_{m\,(std)})$$

Eq. 5-6

6.10 Conversion Factors:

From	To	Multiply by
scf	m³	0.02832.
g	mg	0.001
g/ft³	gr/ft³	15.43.
g/ft³	lb/ft³	2.205×10⁻³.
g/ft³	g/m³	35.31.

6.11 Isokinetic Variation.

6.11.1 Calculation From Raw Data.

$$I=\frac{100\ T_s[K_3V_{lc}+(V_m\ Y/T_m)(P_{bar}+\Delta H/13.6)]}{60\theta v_s\ P_s\ A_n}$$

Eq. 5-7

Where:

K_3=0.003454 mm Hg−m³/ml−°K for metric units.

=0.002669 in. Hg−ft³/ml−°R for English units.

6.11.2 Calculation From Intermediate Values.

$$I=\frac{T_sV_{m\,(std)}P_{std}100}{T_{std}v_s\theta A_nP_s60(1-B_{ws})}$$

$$=K_4\frac{T_sV_{m\,(std)}}{P_sV_sA_n\theta(1-B_{ws})}$$

Equation 5-8

where:

K_4=4.320 for metric units

=0.09450 for English units.

6.12 Acceptable Results. If 90 percent < I < 110 percent, the results are acceptable. If the particulate results are low in comparison to the standard, and I is over 110 percent or less than 90 percent, the Administrator may accept the results. Citation 4 in the bibliography section can be used to make acceptability judgments. If I is judged to be unacceptable, reject the particulate results and repeat the test.

6.13 Stack Gas Velocity and Volumetric Flow Rate. Calculate the average stack gas velocity and volumetric flow rate, if needed, using data obtained in this method and the equations in Sections 5.2 and 5.3 of Method 2.

7. *Alternative Procedures*

7.1 Dry Gas Meter as a Calibration Standard. A dry gas meter may be used as a calibration standard for volume measurements in place of the wet test meter specified in Section 5.3, provided that it is calibrated initially and recalibrated periodically as follows:

7.1.1 Standard Dry Gas Meter Calibration.

7.1.1.1 The dry gas meter to be calibrated and used as a secondary reference meter should be of high quality and have an appropriately sized capacity, e.g., 3 liters/rev (0.1 ft^3/rev). A spirometer (400 liters or more capacity), or equivalent, may be used for this calibration, although a wet test meter is usually more practical. The wet test meter should have a capacity of 30 liters/rev (1 ft^3/rev) and capable of measuring volume to within ±1.0 percent; wet test meters should be checked against a spirometer or a liquid displacement meter to ensure the accuracy of the wet test meter. Spirometers or wet test meters of other sizes may be used, provided that the specified accuracies of the procedure are maintained.

7.1.1.2 Set up the components as shown in Figure 5.7. A spirometer, or equivalent, may be used in place of the wet test meter in the system. Run the pump for at least 5 minutes at a flow rate of about 10 liters/min (0.35 cfm) to condition the interior surface of the wet test meter. The pressure drop indicated by the manometer at the inlet side of the dry gas meter should be minimized [no greater than 100 mm H_2O (4 in. H_2O) at a flow rate of 30 liters/min (1 cfm)]. This can be accomplished by using large diameter tubing connections and straight pipe fittings.

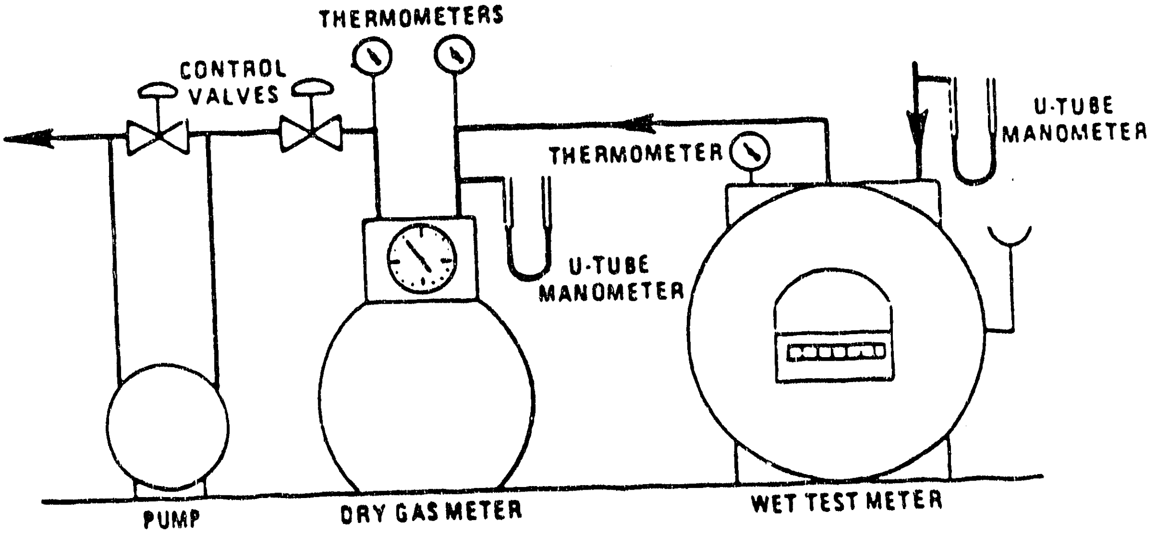

Figure 5.7 Equipment arrangement for dry-gas meter calibration.

7.1.1.3 Collect the data as shown in the example data sheet (see Figure 5-8). Make triplicate runs at each of the flow rates and at no less than five different flow rates. The range of flow rates should be between 10 and 34 liters/min (0.35 and 1.2 cfm) or over the expected operating range.

DATE:________________________

DRY GAS METER IDENTIFICATION:________________

BAROMETRIC PRESSURE (P_b):________________ in. Hg

APPROXIMATE FLOW RATE ($\tilde{Q}$) cfm	SPIROMETER (WET METER) GAS VOLUME (V_s) ft³	DRY GAS METER VOLUME (V_{dg}) ft³	TEMPERATURES				DRY GAS METER PRESSURE (Δp) in. H₂O	TIME (Θ) min.	FLOW RATE (Q) cfm	METER METER COEFFICIENT (Y_{ds})	AVERAGE METER COEFFICIENT ($\bar{Y}_{ds}$)
				DRY GAS METER							
			SPIROMETER (WET METER) (t_s) °F	INLET (t_i) °F	OUTLET (t_o) °F	AVERAGE ($\bar{t}_d$) °F					
0.40											
0.60											
0.80											
1.00											
1.20											

$$Q = 17.65 \cdot \frac{V_s}{\Theta} \cdot \frac{P_b}{(t_s + 460)} \qquad Y_{ds} = \frac{V_s}{V_{dg}} \cdot \frac{(\bar{t}_d + 460)}{(t_s + 460)} \cdot \frac{P_b}{\left(P_b + \frac{\Delta p}{13.6}\right)}$$

Figure 5.8. Example data sheet for calibration of a standard dry gas meter for method 5 sampling equipment (English units)

7.1.1.4 Calculate flow rate, Q, for each run using the wet test meter gas volume, V_w, and the run time, θ. Calculate the dry gas meter coefficient, Y_{ds}, for each run. These calculations are as follows:

$$Q = K_1 \frac{P_{bar}}{t_w + t_{std}} \frac{V_w}{\theta}$$

$$Y_{ds} = \frac{V_w}{V_{ds}} \frac{(t_{ds}+t_{std})}{(t_w+t_{std})} \frac{P_{bar}}{(P_{bar}+\frac{\Delta p}{13.6})}$$

Where:

K_1=0.3858 for international system of units (SI); 17.64 for English units.

V_w=Wet test meter volume, liters (ft³).

V_{ds}=Dry gas meter volume, liters (ft³).

t_{ds}=Average dry gas meter temperature, °C (°F).

t_{std}=273° C for SI units; 460° F for English units.

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

P_{bar}=Barometric pressure, mm Hg (in. Hg).

Δp=Dry gas meter inlet differential pressure, mm H_2O (in. H_2O).

θ=Run time, min.

7.1.1.5 Compare the three Y_{ds} values at each of the flow rates and determine the maximum and minimum values. The difference between the maximum and minimum values at each flow rate should be no greater than 0.030. Extra sets of triplicate runs may be made in order to complete this requirement. In addition, the meter coefficients should be between 0.95 and 1.05. If these specifications cannot be met in three sets of successive triplicate runs, the meter is not suitable as a calibration standard and should not be used as such. If these specifications are met, average the three Y_{ds} values at each flow rate resulting in five average meter coefficients, Y_{ds}.

7.1.1.6 Prepare a curve of meter coefficient, Y_{ds}, versus flow rate, Q, for the dry gas meter. This curve shall be used as a reference when the meter is used to calibrate other dry gas meters and to determine whether recalibration is required.

7.1.2 Standard Dry Gas Meter Recalibration.

7.1.2.1 Recalibrate the standard dry gas meter against a wet test meter or spirometer annually or after every 200 hours of operation, whichever comes first. This requirement is valid provided the standard dry gas meter is kept in a laboratory and, if transported, cared for as any other laboratory instrument. Abuse to the standard meter may cause a change in the calibration and will require more frequent recalibrations.

7.1.2.2 As an alternative to full recalibration, a two-point calibration check may be made. Follow the same procedure and equipment arrangement as for a full recalibration, but run the meter at only two flow rates [suggested rates are 14 and 28 liters/min (0.5 and 1.0 cfm)]. Calculate the meter coefficients for these two points, and compare the values with the meter calibration curve. If the two coefficients are within ±1.5 percent of the calibration curve values at the same flow rates, the meter need not be recalibrated until the next date for a recalibration check.

7.2 Critical Orifices As Calibration Standards. Critical orifices may be used as calibration standards in place of the wet test meter specified in Section 5.3, provided that they are selected, calibrated, and used as follows:

7.2.1 Section of Critical Orifices.

7.2.1.1 The procedure that follows describes the use of hypodermic needles or stainless steel needle tubings which have been found suitable for use as critical orifices. Other materials and critical orifice designs may be used provided the orifices act as true critical orifices; i.e., a critical vacuum can be obtained, as described in Section 7.2.2.2.3. Select five critical orifices that are appropriately sized to cover the range of flow rates between 10 and 34 liters/min or the expected operating range. Two of the critical orifices should bracket the expected operating range.

A minimum of three critical orifices will be needed to calibrate a Method 5 dry gas meter (DGM); the other two critical orifices can serve as spares and provide better selection for bracketing the range of operating flow rates. The needle sizes and tubing lengths shown below give the following approximate flow rates:

Gauge/cm	Flow rate (liters/min)	Gauge/cm	Flow rate (liters/min)
12/7.6	32.56	14/2.5	19.54
12/10.2	30.02	14/5.1	17.27
13/2.5	25.77	14/7.6	16.14
13/5.1	23.50	15/3.2	14.16
13/7.6	22.37	15/7.6	11.61
13/10.2	20.67	15/10.2	10.48

7.2.1.2 These needles can be adapted to a Method 5 type sampling train as follows: Insert a serum bottle stopper, 13- by 20-mm sleeve type, into a ½-inch Swagelok quick connect. Insert the needle into the stopper as shown in Figure 5-9.

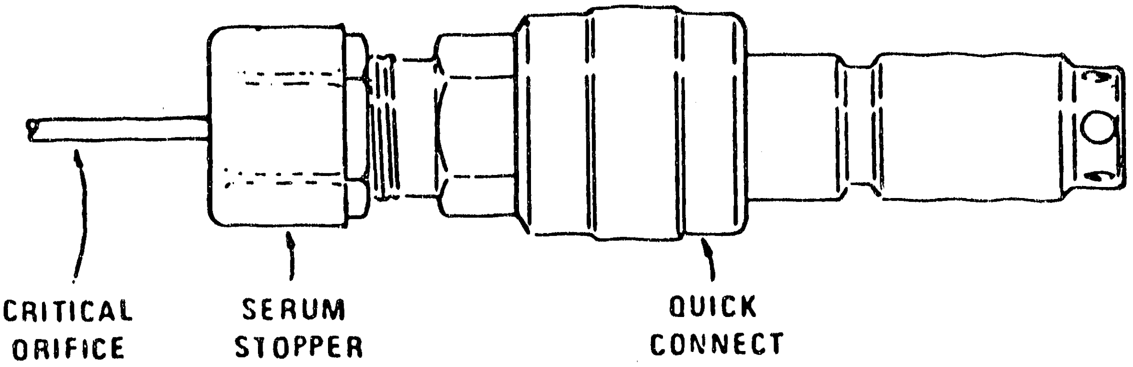

Figure 5-9. Critical orifice adaptation to Method 5 metering system.

7.2.2 Critical Orifice Calibration. The procedure described in this section uses the Method 5 meter box configuration with a DGM as described in Section 2.1.8 to calibrate the critical orifices. Other schemes may be used, subject to the approval of the Administrator.

7.2.2.1 Calibration of Meter Box. The critical orifices must be calibrated in the same configuration as they will be used; i.e., there should be no connections to the inlet of the orifice.

7.2.2.1.1 Before calibrating the meter box, leak check the system as follows: Fully open the coarse adjust valve, and completely close the by-pass valve. Plug the inlet. Then trun on the pump, and determine whether there is any leakage. The leakage rate shall be zero; i.e., no detectable movement of the DGM dial shall be seen for 1 minute.

7.2.2.1.2 Check also for leakages in that portion of the sampling train between the pump and the orifice meter. See Section 5.6 for the procedure; make any corrections, if necessary. If leakage is detected, check for cracked gaskets, loose fittings, worn O-rings, etc., and make the necessary repairs.

7.2.2.1.3 After determining that the meter box is leakless, calibrate the meter box according to the procedure given in Section 5.3. Make sure that the wet test meter meets the requirements stated in Section 7.1.1.1. Check the water level in the wet test meter. Record the DGM calibration factor, Y.

7.2.2.2 Calibration of Critical Orifices. Set up the apparatus as shown in Figure 5-10.

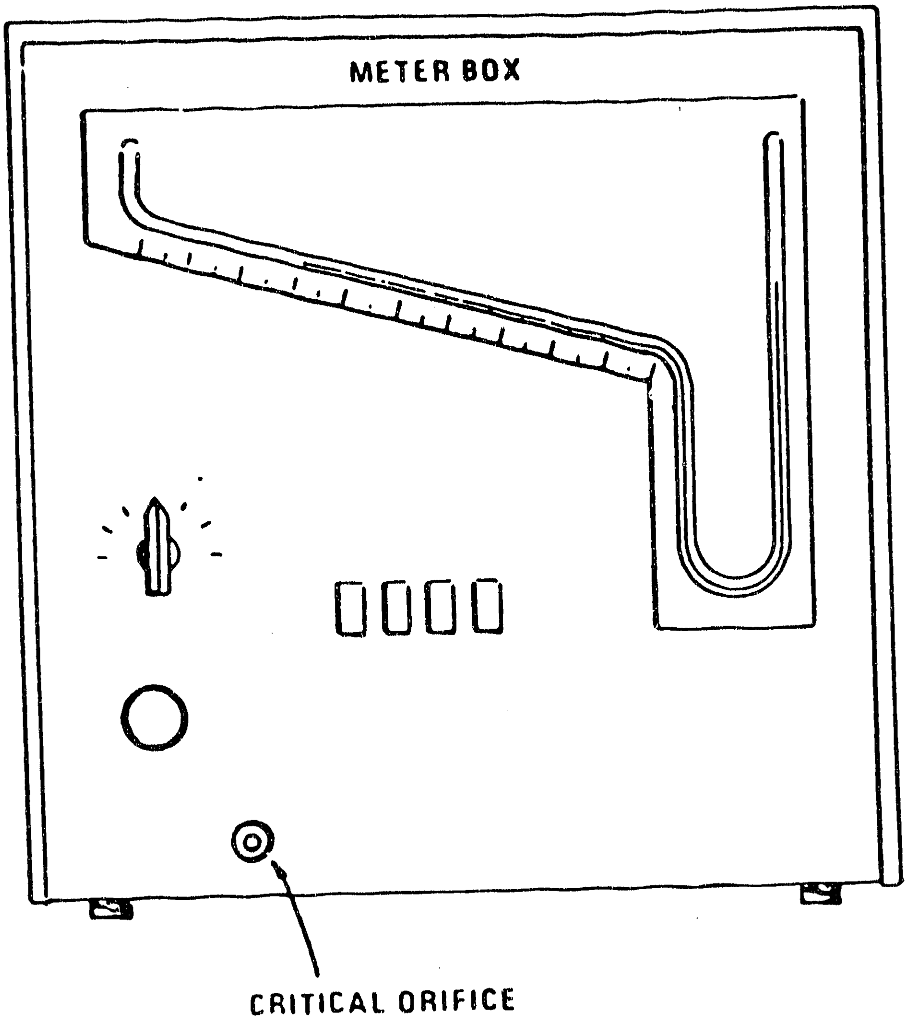

Figure 5-10. Apparatus setup.

7.2.2.2.1 Allow a warm-up time of 15 minutes. This step is important to equilibrate the temperature conditions through the DGM.

7.2.2.2.2 Leak check the system as in Section 7.2.2.1.1. The leakage rate shall be zero.

7.2.2.2.3 Before calibrating the critical orifice, determine its suitability and the appropriate operating vacuum as follows: Turn on the pump, fully open the coarse adjust valve, and adjust the by-pass valve to give a vacuum reading corresponding to about half of atmospheric pressure. Observe the meter box orifice manometer reading, H. Slowly increase the vacuum reading until a stable reading is obtained on the meter box orifice manometer. Record the critical vacuum for each orifice. Orifices that do not reach a critical value shall not be used.

7.2.2.2.4 Obtain the barometric pressure using a barometer as described in Section 2.1.9. Record the barometric pressure, P_{bar}, in mm Hg (in. Hg).

7.2.2.2.5 Conduct duplicate runs at a vacuum of 25 to 50 mm Hg (1 to 2 in. Hg) above the critical vacuum. The runs shall be at least 5 minutes each. The DGM volume readings shall be in increments of 0.00283 m^3 (0.1 ft^3) or in increments of complete revolutions of the DGM. As a guideline, the times should not differ by more than 3.0 seconds (this includes allowance for changes in the DGM temperatures) to achieve ± 0.5 percent in K'. Record the information listed in Figure 5-11.

7.2.2.2.6 Calculate K' using Equation 5-9.

Where:

$$K' = \frac{K_1 V_m Y \left(P_{bar} + \Delta H/13.6\right) \sqrt{T_{amb}}}{P_{bar}\, T_m \Theta} \qquad \text{Eq. 5-9}$$

K' = Critical orifice coefficient, $\frac{(m^3)(°K)^{1/2}}{(mm.\ Hg)\,(min)} \left[\frac{(ft^3)(°R)^{1/2}}{(in.\ Hg)\,(min)}\right]$

T_{amb}=Absolute ambient temperature, °K (°R).

Average the K' values. The individual K' values should not differ by more than ±0.5 percent from the average.

7.2.3 Using the Critical Orifices as Calibration Standards.

7.2.3.1 Record the barometric pressure.

Date ______ Train ID ______ DGM cal. factor ______ Critical orifice ID ______

Dry gas meter		Run number	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		
Difference, V_m	m^3 (ft^3)		
Inlet/Outlet temperatures:			
Initial	°C (°F)	/	/
Final	°C (°F)	/	/
Avg. Temperature, t_m.	°C (°F)		
Time, Θ	min/sec	/	/
	min		
Orifice man. rdg., ΔH	mm (in.) H_2O		
Bar. pressure, P_{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}.	°C (°F)		
Pump vacuum	mm (in.) Hg		
K' factor			
Average			

Figure 5-11. Data sheet for determining K' factor.

7.2.3.2 Calibrate the metering system according to the procedure outlined in Sections 7.2.2.2.1 to 7.2.2.2.5. Record the information listed in Figure 5.12.

7.2.3.3 Calculate the standard volumes of air passed through the DGM and the critical orifices, and calculate the DGM calibration factor, Y, using the equations below:

$$V_m(std) = K_1\, V_m \frac{P_{bar} + (\Delta H/13.6)}{T_m} \qquad \text{Eq. 5-10}$$

$$V_{cr}(std) = K' \frac{P_{bar}\Theta}{T_{amb}} \qquad \text{Eq. 5-11}$$

$$Y = \frac{V_{cr(std)}}{V_{m(std)}} \qquad \text{Eq. 5-12}$$

where:

$V_{cr(std)}$=Volume of gas sample passed through the critical orifice, corrected to standard conditions, dsm³ (dscf).

K_1=0.3858 °K/mm Hg for metric units =17.64 °R/in. Hg for English units.

7.2.3.4 Average the DGM calibration values for each of the flow rates. The calibration factor, Y, at each of the flow rates should not differ by more than ±2 percent from the average.

7.2.3.5 To determine the need for recalibrating the critical orifices, compare the DGM Y factors obtained from two adjacent orifices each time a DGM is calibrated; for example, when checking 13/2.5, use orifices 12/10.2 and 13/5.1. If any critical orifice yields a DGM Y factor differing by more than 2 percent from the others, recalibrate the critical orifice according to Section 7.2.2.2.

Date ______ Train ID ______ Critical orifice ID ______ Critical orifice K' factor ______

Dry gas meter		Run number	
		1	2
Final reading	m^3 (ft^3)		
Initial reading	m^3 (ft^3)		

Dry gas meter		Run number	
		1	2
Difference, V_m	m^3 (ft^3)		
Inlet/outlet temperatures:			
Initial	°C (°F)	/	/
Final	°C (°F)	/	/
Avg. Temperature, t_m	°C (°F)		
Time, Θ	min/sec	/	/
	min		
Orifice man. rdg., ΔH	mm (in.) H_2O.		
Bar. pressure, P_{bar}	mm (in.) Hg		
Ambient temperature, t_{amb}	°C (°F)		
Pump vacuum	mm (in.) Hg		
$V_{m(std)}$	m^3 (ft^3)		
$V_{cr(std)}$	m^3 (ft^3)		
DGM cal. factor, Y			

Figure 5-12. Data sheet for determining DGM Y factor.

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APPENDIX F

CHARACTERIZATION AND TESTING:

EPA METHOD 23: DIOXINS/FURANS

Method 23—Determination of Polychlorinated Dibenzo-p-Dioxins Polychlorinated Dibenzofurans From Stationary Sources

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) 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 PCDDs and PCDFs 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. The train is identical to that described in Section 2.1 of Method 5 of this appendix with the following additions:

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

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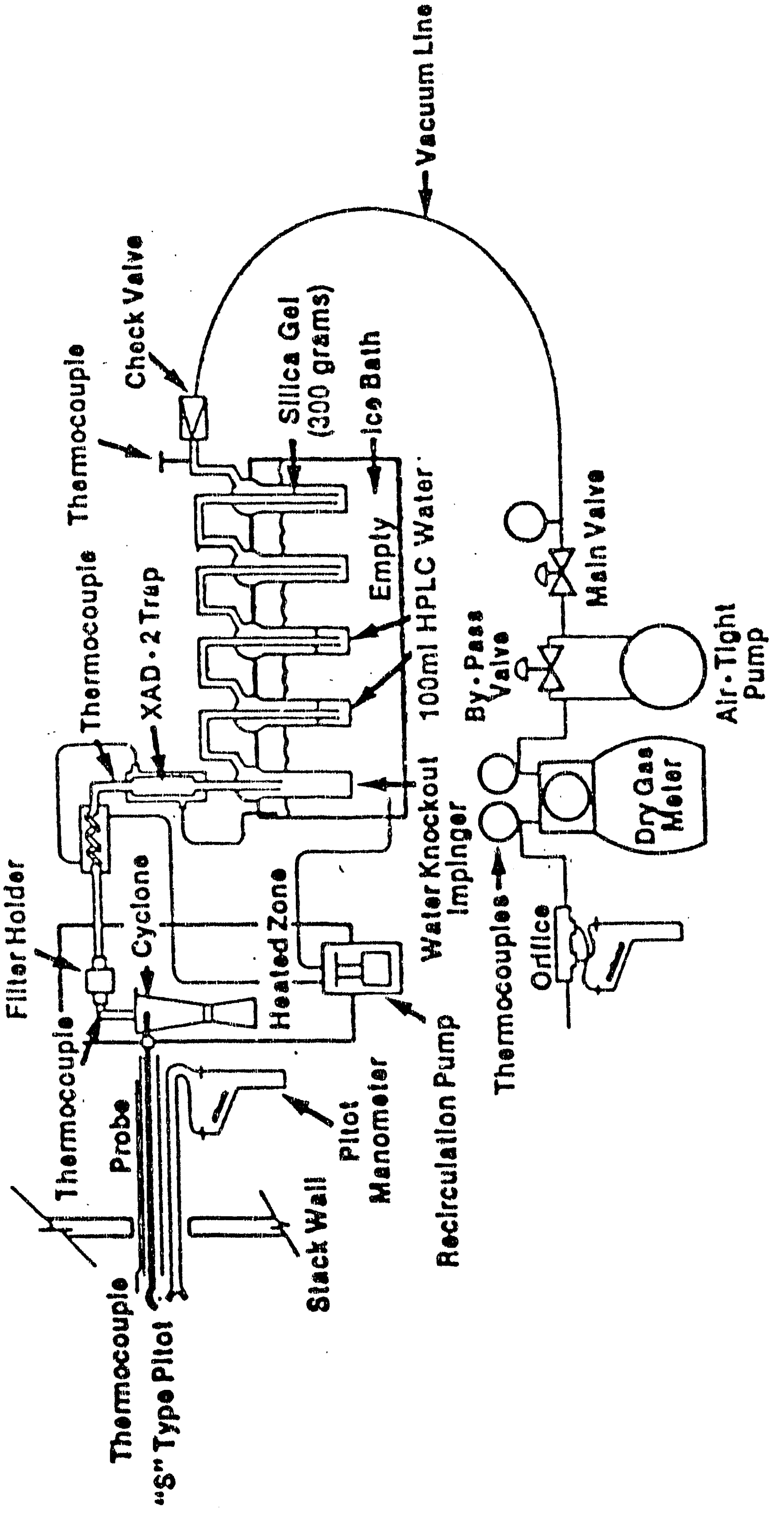

Figure 1. CDD/CDF Sampling Train Configuration

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2.1.2 Sample Transfer Lines. The sample transfer lines, if needed, shall be heat traced, heavy walled TFE (½ in. OD with ⅛ 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 Adsorbent Module. Glass container to hold the solid adsorbent. A schematic 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.

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

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

2.2 Sample Recovery.

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

2.2.2 Wash Bottle. Teflon, 500-ml.

2.2.3 Probe Liner and Probe-Nozzle 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 probe liner and nozzle.

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

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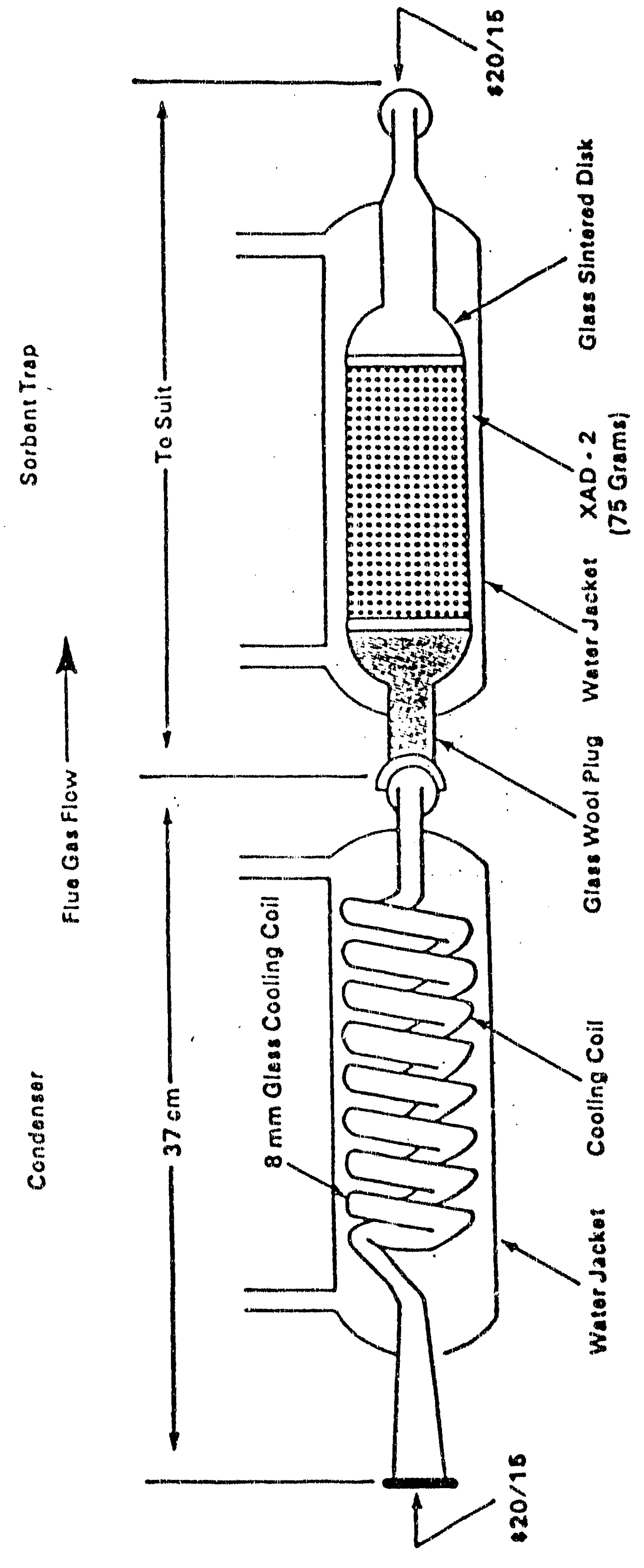

FIGURE 2. CONDENSER AND SORBENT TRAP FOR COLLECTION OF GASEOUS PCDDs AND PCDFs

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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 43×123 mm extraction thimbles.

2.3.4 Pasteur Pipettes. For preparing liquid chromatographic columns.

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

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

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

2.3.8 Separatory Funnels. Glass, 2-liter.

2.3.9 Gas Chromatograph. Consisting of the following components:

2.3.9.1 Oven. Capable of maintaining the separation column at the proper operating temperature ±1 °C and performing programmed increases in temperature at rates of at least 3 °C/min.

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

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

2.3.9.4 Capillary Columns. A fused silica column, 60 m×25 mm inside diameter (ID), coated with DB-5 and a fused silica column, 30 m×25 mm ID coated with SP-2331.

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

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

2.3.12 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 D2986-71 (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 three hours. Remove the toluene and discard it, but retain the silica gel. Place no more than 50 filters in the thimble onto the bed of silica gel 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 toluene extract, and retain it for analysis. Remove the filters and dry them under a clean N_2 stream. Store the filters tightly wrapped in cleaned aluminum foil.

3.1.1.2 Quality Control Check. Analyze the toluene extract from Section 3.1.1.1 as described in Sections 5.2 and 5.3. If any TCDD or TCDF is present at a concentration above the minimum detectable level, repeat the cleaning procedure and reanalyze the extract until no TCDD or TCDF is detectable.

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-coarse frit is used for extraction of XAD-2. The frit is recessed 10-15 mm above a crenellated 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.
Methylene chloride (fresh).	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 as shown in Figure 23-3.

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 rate of flow should be high enough to gently agitate the particles but not high enough to cause the particles to fracture.

3.1.2.3 Quality Control Check. The adsorbent must be checked for residual methylene chloride as well as TCDDs and TCDFs.

3.1.2.3.1 Methylene Chloride Residue.

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

3.1.2.3.1.2 Analysis. Inject a 5 μl sample of the extract into a gas chromatograph operated under the following conditions:

Column: 6 ft x ⅛ in stainless steel containing 10% 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 until it reaches 250 °C; return to 30 °C after 1000 seconds.

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

3.1.2.3.2 TCDDs and TCDFs. Extract the sample as described in Section 5.1.1. Analyze the extract as described in §§ 5.2 and 5.3. If any of the TCDDs or TCDFs are present at concentrations above the MDL, the adsorbent must be recleaned by repeating the last step of the cleaning procedure. The MDL can be calculated as ⅓ of the theoretical minimum quantifiable level (TMQL). The TMQL is calculated in § 9.8.

3.1.2.4 Storage. The adsorbent must be used within four 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 Teflon film and elastic bands.

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

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

3.1.5 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 quality.

3.2.3 Toluene. Pesticide quality.

3.3 Analysis.

3.3.1 Potassium Hydroxide. Reagent grade.

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 Isooctane. 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.

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 PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Internal Standards" in 10 ml of isooctane.

3.3.21 Surrogate Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Surrogate Standards" in 10 ml of isooctane.

3.3.22 Recovery Standard Solution. Prepare a stock standard solution containing the isotopically labelled PCDDs and PCDFs at the concentrations shown in Table 1 under the heading "Recovery Standards" in 10 ml of isooctane.

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 should not be loaded in the field. Fill a trap with 20 to 30 g of XAD–2. Follow the XAD–2 with glass wool and tightly cap both ends of the 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 or wrapped in aluminum foil.

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.

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

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

4.1.3.3 Place the 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 TCDDs and TCDFs.

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

4.1.5 Sample Train Operation. Same as Method 5, § 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/or filter fibers which adhere to the filter holder gasket, by using a dry inert bristle brush and/or a sharp-edged blade. Seal the container.

4.2.2 Absorbent 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 Cyclone Catch. If the optional cyclone is used, quantitatively recover the particulate into a glass container and cap.

4.2.4 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, the connecting line between the filter and the condenser, and the condenser, if using a separate condenser and absorbent trap, sequentially, three times each, with acetone and methylene chloride. Collect all the rinses in Container No. 2 and mark the level of the liquid on the container.

4.2.5 Container No. 3. Repeat the rinsing described in section 4.2.4 using toluene as the rinse solvent. Collect the rinses in Container No. 3 and mark the level of the liquid on the container.

4.2.6 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 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 fourth impinger to its original container and seal. A funnel may make it easier to pour the silica gel without spilling. A rubber policeman may be used as an aid in removing the silica gel from the impinger.

5. Analysis

5.1 Sample Extraction.

5.1.1 Container No. 1. Place a glass extraction thimble and 1 g of silica gel and a plug of glass wool into the Soxhlet appara charge the apparatus with toluene, and reflux for a minimum of 3 hours. Remove the toluene and discard it, but retain the silica gel. Suspend the adsorbent module directly over the extraction thimble described in section 5.1.1. The glass frit of the module should be in the up position. The thimble is contained in a clean beaker, which will serve to catch the solvent rinses. Using a Teflon squeeze bottle, flush the XAD–2 into the thimble onto the bed of cleaned silica gel. Thoroughly rinse the glass module with toluene into the beaker containing the thimble. Add the XAD–2 glass wool plug to the thimble, add the contents of container No. 1, and add the concentrate from Section 5.1.2. For low level samples, add 20 ul of the internal standard solution (section 3.3.20), for high level samples, add 100 ul of the solution. Low level samples are those samples that contain less than 200 pg of any TCDD of TCDF. Cover the XAD–2 in the thimble with the cleaned glass wool plug to prevent the resin from floating into the solvent reservoir of the extractor. If the resin is wet, effective extraction can be accomplished by loosely packing the resin in the thimble. The thimble is placed in the extractor, and the toluene contained in the beaker is added to the solvent reservoir. Additional toluene is added to make the reservoir approximately two—thirds full. Add Teflon boiling chips and assemble the apparatus. Adjust the heat source to cause the extractor to cycle 5–8 times per hour. Extract the resin 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 8 ml. Use nitrogen evaporation to further reduce the sample to about 1 ml. Split the sample in half. Store one half and analyze the other according to the procedures in sections 5.2 and 5.3.

5.1.2 Container No. 1. Transfer the contents directly to the glass thimble of the extractor and extract them simultaneously with the XAD–2 resin.

5.1.3 Container No. 2. 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 as described in section 5.1.1.

5.1.4 Container No. 3. 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 toluene and add these to the concentrated solution and concentrate further to near dryness. Analyze the extract according to the procedures in sections 5.2 and 5.3.

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 bottom 0.5 inch from the tip of a 9-ml disposable Pasteur pipette. Insert a filter paper 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. 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 eluates. 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 4 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 in a freezer, shielded from light prior to analysis.

5.3 Analysis. Analyze the sample using a gas chromatograph coupled to a mass spectrometer (GC/MS) using the instrumental parameters in sections 5.3.1 and 5.3.2. A 1 to 5 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 PCDDs and PCDFs (tetra-through octa-). If tetra-chlorinated dibenzofurans are detected in this analysis, then another aliquot of the sample is analyzed in a separate run, using the SP 2331 column to measure the 2,3,7,8 tetra-chlorodibenzofuran isomer.

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 ballistically 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. 8000–10000 m/e.

5.3.2.2 Ionization Mode. Electron impact, 70 eV.

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 4.

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 5.

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 4 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 RRTs found in the continuing calibration.

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

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 PCDFs, 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 PCDDs or PCDFs in its homologous series. For example the $^{13}C_{12}$-1,2,3,4-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 for low level samples or Table 3 for high level samples. 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 6. 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 5.

6.1.2 Daily Performance Check.

6.1.2.1 Calibration Check. Inject one μl of solution number 4 from Table 2 or solution number 3 from Table 3. Calculate the relative response factors (RRF's) for each compound and compare each of them 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 6. In addition the ion-abundance ratios shall be within the allowable control limits shown in Table 5.

6.1.2.2 Column Separation Check. Inject a solution of a mixture of PCDDs and PCDFs 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% of the lower of the two peaks.

7. Quality Control

7.1 Sampling Train Collection Efficiency Check. Add 100 μl of the surrogate standards in Table 1 to the adsorbent cartridge of each train before each test.

7.2 Internal Standard Percent Recoveries. Recoveries of the internal standards must be between 40 to 130% for the tetrathrough hexachlorinated compounds while the range is 25 to 130% for the higher hepta- and octachlorinated homologues. If the internal standards do not meet the recovery requirements, the data will still be acceptable provided that the signal is equal to or greater than ten times the noise level.

7.3 Surrogate Recoveries. The surrogate recoveries are measured relative to the internal standards and are a measure of collection efficiency. All recoveries shall be between 70 and 130%. 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%, 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 samples.

7.4 Toluene Quality Assurance Rinse. Report the results of the toluene quality assurance 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.

8.2 Audit Procedure. 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. If this condition is met, auditing of subsequent compliance analyses for any enforcement agency within seven days is not required.

8.3 Audit Sample Availability. The audit sample 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. The STAC will return the EPA response to the laboratory being audited. Include this EPA response with the results of the compliance samples in appropriate reports to the EPA regional office or the appropriate enforcement agency. Include this information with subsequent analyses for any enforcement agency during the seven-day period.

8. Calculations

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

9.1 Nomenclature.

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

A^*_{ci} = Integrated ion current of the two ions characteristic of the internal standard i in the 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_s = Concentration of the compound of interest in the most dilute calibration solution, pg/μl.

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

m^*_{ci} = Mass of labeled compound i in the calibration standard injected into the analyzer, pg.

m^*_i = Mass of internal standard i added to the sample, pg.

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

m_s = Mass of surrogate compound i in the calibration standard.

RRF_i = Relative response factor.

RRF_{rs} = Recovery standard response factor.

V = Final extract volume, μl.

9.2 Relative Response Factor.

$$RRF = 1/n \sum A_{ci} m^*_{ci}/(A^*_{ci} m_{ci}) \qquad \text{Eq. 23-1}$$

9.3 Concentration of the PCDDs and PCDFs.

$$C_i = m^*_i A_i/(A^*_i RRF_i V_{m(ml)}) \qquad \text{Eq. 23-2}$$

9.4 Recovery Standard Response Factor.

$$RRF_{rs} = A^*_{ci} m_{rs}/(A_{rs} m^*_{ci}) \qquad \text{Eq. 23-3}$$

9.5 Recovery of Internal Standards (R^*).

$$R^* = (A^*_i m_{rs}/A_{rs} RF_{rs} m^*_i) \times 100\% \qquad \text{Eq. 23-4}$$

9.6 Surrogate Compound Response Factor.

$$RRFs = A^*_{ci} m_s/(A_{csi} m^*_{ci}) \qquad \text{Eq. 23-5}$$

9.7 Recovery of Surrogate Compounds (R_s).

$$R_s = (A_s m^*_i/A^*_i RRF_s m_s) \times 100\% \qquad \text{Eq. 23-6}$$

9.8 Theoretical Minimum Quantifiable Level (TMQL).

$$TMQL = C_s V/R^* \qquad \text{Eq. 23-7}$$

9. Bibliography

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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
$^{13}C_{12}$-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
$^{13}C_{12}$-2,3,1,6,7,8 HpCDF	100
Surrogate Standards:	
$^{37}C_{l4}$-2,3,7,8-TCDD	100
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	100
$^{13}C_{12}$-2,3,1,7,8-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 (LOW)

Compound	Concentrations (pg/µL)—Solution No.— 1	2	3	4	5
Unlabeled analytes:					
2,3,7,8-TCDD	0.5	1	5	50	100
2,3,7,8-TCDF	0.5	1	5	50	100
1,2,3,7,8-PeCDD	2.5	5	25	250	500
1,2,3,7,8-PeCDF	2.5	5	25	250	500
2,3,4,7,8-PeCDF	2.5	5	25	250	500
1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
1,2,3,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,7,8,9-HxCDD	2.5	5	25	250	500
1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
1,2,3,6,7,8-HxCDF	2.5	5	25	250	500
1,2,3,7,8,9-HxCDF	2.5	5	25	250	500
2,3,4,6,7,8-HxCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDD	2.5	5	25	250	500
1,2,3,4,6,7,8-HpCDF	2.5	5	25	250	500
1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
OCDD	5	10	50	500	1000
OCDF	5	10	50	500	1000
Internal standards:					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate standards:					
$^{37}Cl_4$-2,3,7,8-TCDD	0.5	1	5	50	100
$^{13}C_{12}$-2,3,4,7,8-PeCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	2.5	5	25	250	500
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	2.5	5	25	250	500
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

TABLE 3.—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS (HIGH)

Compound	Concentrations (pg/µL)—Solution No.— 1	2	3	4	5
Unlabeled analytes:					
2,3,7,8-TCDD	5	50	100	500	1000
2,3,7,8-TCDF	5	50	100	500	1000
1,2,3,7,8-PeCDD	25	250	500	2500	5000
1,2,3,7,8-PeCDF	25	250	500	2500	5000
2,3,4,7,8-PeCDF	25	250	500	2500	5000
1,2,3,4,7,8-HxCDD	25	250	500	2500	5000
1,2,3,6,7,8-HxCDD	25	250	500	2500	5000
1,2,3,7,8,9-HxCDD	25	250	500	2500	5000
1,2,3,4,7,8-HxCDF	25	250	500	2500	5000
1,2,3,6,7,8-HxCDF	25	250	500	2500	5000
1,2,3,7,8,9-HxCDF	25	250	500	2500	5000
2,3,4,6,7,8-HxCDD	25	250	500	2500	5000
1,2,3,4,6,7,8-HpCDD	25	250	500	2500	5000
1,2,3,4,6,7,8-HpCDF	25	250	500	2500	5000
1,2,3,4,7,8,9-HpCDF	25	250	500	2500	5000
OCDD	50	500	1000	5000	10000

TABLE 3.—COMPOSITION OF THE INITIAL CALIBRATION SOLUTIONS (HIGH)—Continued

Compound	Concentrations (pg/µL)—Solution No.— 1	2	3	4	5
OCDF	50	500	1000	5000	10000
Internal standards:					
$^{13}C_{12}$-2,3,7,8-TCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDD	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDD	100	100	100	100	100
$^{13}C_{12}$-OCDD	200	200	200	200	200
$^{13}C_{12}$-2,3,7,8-TCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,7,8-PeCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,6,7,8-HxCDF	100	100	100	100	100
$^{13}C_{12}$-1,2,3,4,6,7,8-HpCDF	100	100	100	100	100
Surrogate standards:					
$^{37}Cl_4$-2,3,7,8-TCDD	5	50	100	500	1000
$^{13}C_{12}$-2,3,4,7,8-PeCDF	25	250	500	2500	5000
$^{13}C_{12}$-1,2,3,4,7,8-HxCDD	25	250	500	2500	5000
$^{13}C_{12}$-1,2,3,4,7,8-HxCDF	25	250	500	2500	5000
$^{13}C_{12}$-1,2,3,4,7,8,9-HpCDF	25	250	500	2500	5000
Alternate standard:					
$^{13}C_{12}$-1,2,3,7,8,9-HxCDF	5	50	100	500	1000
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

TABLE 4.—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDDS AND PCDFS

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
1	303.9016	M	$C_{12}H_4{}^{35}Cl_4O$	TCDF
	305.8987	M+2	$C_{12}H_4{}^{35}Cl_3{}^{37}ClO$	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	$C_{12}H_4{}^{35}Cl_4O_2$	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)
	331.9368	M	$^{13}C_{12}H_4{}^{35}Cl_4O_2$	TCDD (S)
	333.9339	M+2	$^{13}C_{12}H_4{}^{35}Cl_3{}^{37}ClO_2$	TCDD (S)
	375.8364	M+2	$C_{12}H_4{}^{35}Cl_5{}^{37}ClO$	HxCDPE
	354.9792	LOCK	C_9F_{13}	PFK
2	339.8597	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PECDF
	341.8567	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF
	351.9000	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO$	PeCDF (S)
	353.8970	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O$	PeCDF (S)
	355.8546	M+2	$C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD
	357.8516	M+4	$C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD
	367.8949	M+2	$^{13}C_{12}H_3{}^{35}Cl_4{}^{37}ClO_2$	PeCDD (S)
	369.8919	M+4	$^{13}C_{12}H_3{}^{35}Cl_3{}^{37}Cl_2O_2$	PeCDD (S)
	409.7974	M+2	$C_{12}H_3{}^{35}Cl_6{}^{37}ClO$	HpCPDE
	354.9792	LOCK	C_9F_{13}	PFK
3	373.8208	M+2	$C_{12}H_2{}^{35}Cl_5{}^{37}ClO$	HxCDF
	375.8178	M+4	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	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	$C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O_2$	HxCDD
	401.8559	M+2	$^{13}C_{12}H_2{}^{35}Cl_5{}^{37}ClO_2$	HxCDD (S)
	403.8529	M+4	$^{13}C_{12}H_2{}^{35}Cl_4{}^{37}Cl_2O$	HxCDD (S)
	445.7555	M+4	$C_{12}H_2{}^{35}Cl_6{}^{37}Cl_2O$	OCDPE
	430.9729	LOCK	C_9F_{17}	PFK
4	407.7818	M+2	$C_{12}H{}^{35}Cl_6{}^{37}ClO$	HpCDF
	409.7789	M+4	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O$	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	$C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD
	435.8169	M+2	$^{13}C_{12}H{}^{35}Cl_6{}^{37}ClO_2$	HpCDD (S)
	437.8140	M+4	$^{13}C_{12}H{}^{35}Cl_5{}^{37}Cl_2O_2$	HpCDD (S)
	479.7165	M+4	$C_{12}H{}^{35}Cl_7{}^{37}Cl_2O$	NCPDE
	430.9729	LOCK	C_9F_{17}	PFK
5	441.7428	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO$	OCDF
	443.7399	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O$	OCDF
	457.7377	M+2	$C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD
	459.7348	M+4	$C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD
	469.7779	M+2	$^{13}C_{12}{}^{35}Cl_7{}^{37}ClO_2$	OCDD (S)
	471.7750	M+4	$^{13}C_{12}{}^{35}Cl_6{}^{37}Cl_2O_2$	OCDD (S)

TABLE 4.—ELEMENTAL COMPOSITIONS AND EXACT MASSES OF THE IONS MONITORED BY HIGH RESOLUTION MASS SPECTROMETRY FOR PCDDS AND PCDFS—Continued

Descriptor No.	Accurate mass	Ion type	Elemental composition	Analyte
	513.6775 442.9728	M+4 LOCK	$C_{12}{}^{35}Cl_8{}^{37}Cl_2O$ $C_{10}F_{17}$	DCDPE 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

TABLE 5.—ACCEPTABLE RANGES FOR ION-ABUNDANCE RATIOS OF PCDDS AND PCDFS

Number 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[1]	M/M+2	0.51	0.43	0.59
7[2]	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

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

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

TABLE 6.—MINIMUM REQUIREMENTS FOR INITIAL AND DAILY CALIBRATION RESPONSE FACTORS

Compound	Relative Response Factors	
	Initial calibration RSD	Daily calibration percentage 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,-PeCDD	25	25
${}^{13}C_{12}$-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
Alternate Standard:		
${}^{13}C_{12}$-1,2,3,7,8,9-HxCDF	25	25

APPENDIX G

CHARACTERIZATION AND TESTING:

EPA METHOD 26: HYDROCHLORIC ACID

* * * * *

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 hydrogen chloride (HCl) emissions from stationary sources.

1.2 Principle. An integrated sample is extracted from the stack and passed through dilute sulfuric acid. In the dilute acid, the HCl gas is dissolved and forms chloride (Cl^-) ions. The Cl^- is analyzed by ion chromatography (IC).

1.3 Interferences. Volatile materials which produce chloride ions upon dissolution during sampling are obvious interferences. Another likely interferent is diatomic chlorine (Cl_2) gas which reacts to form HCl and hypochlorous acid (HOCl) upon dissolving in water. However, Cl_2 gas exhibits a low solubility in water and the use of acidic, rather than neutral or basic collection solutions, greatly reduces the chance of dissolving any chlorine present. This method does not experience a significant bias when sampling a 400 ppm HCl gas stream containing 50 ppm Cl_2. Sampling a 220 ppm HCl gas stream containing 180 ppm Cl_2 results in a positive bias of 3.4 percent in the HCl measurement.

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 Stability. The collected samples can be stored for up to 4 weeks before analysis.

1.6 Detection Limit. The analytical detection limit of the method is 0.1 μg/ml.

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 ⅜-in. (9-mm) I.D. with a heating system to prevent moisture condensation. A ⅜-in. I.D. Teflon elbow should be attached to the inlet of the probe and a 1-in. (25-mm) length of ⅜-in. I.D. Teflon tubing should be attached to the open end of the elbow to permit the opening of the probe to be turned away from the gas stream. This reduces the amount of particulate entering the train. This probe configuration should be used when the concentration of particulate matter in the emissions is high. When high concentrations are not present, the Teflon elbow is not necessary, and the probe inlet may be perpendicular to the gas stream. A glass wool plug should *not* be used to remove particulate matter since a negative bias in the data could result. Instead, a Teflon filter (see § 2.1.5) should be installed at the inlet (for stack temperatures ≤300 °F) or outlet (for stack temperatures >300 °F) of the probe.

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

2.1.3 Impingers. Four 30-ml midget impingers with leak-free glass connectors. Silicone grease may be used, if necessary, to prevent leakago.

BILLING CODE 6560-50-M

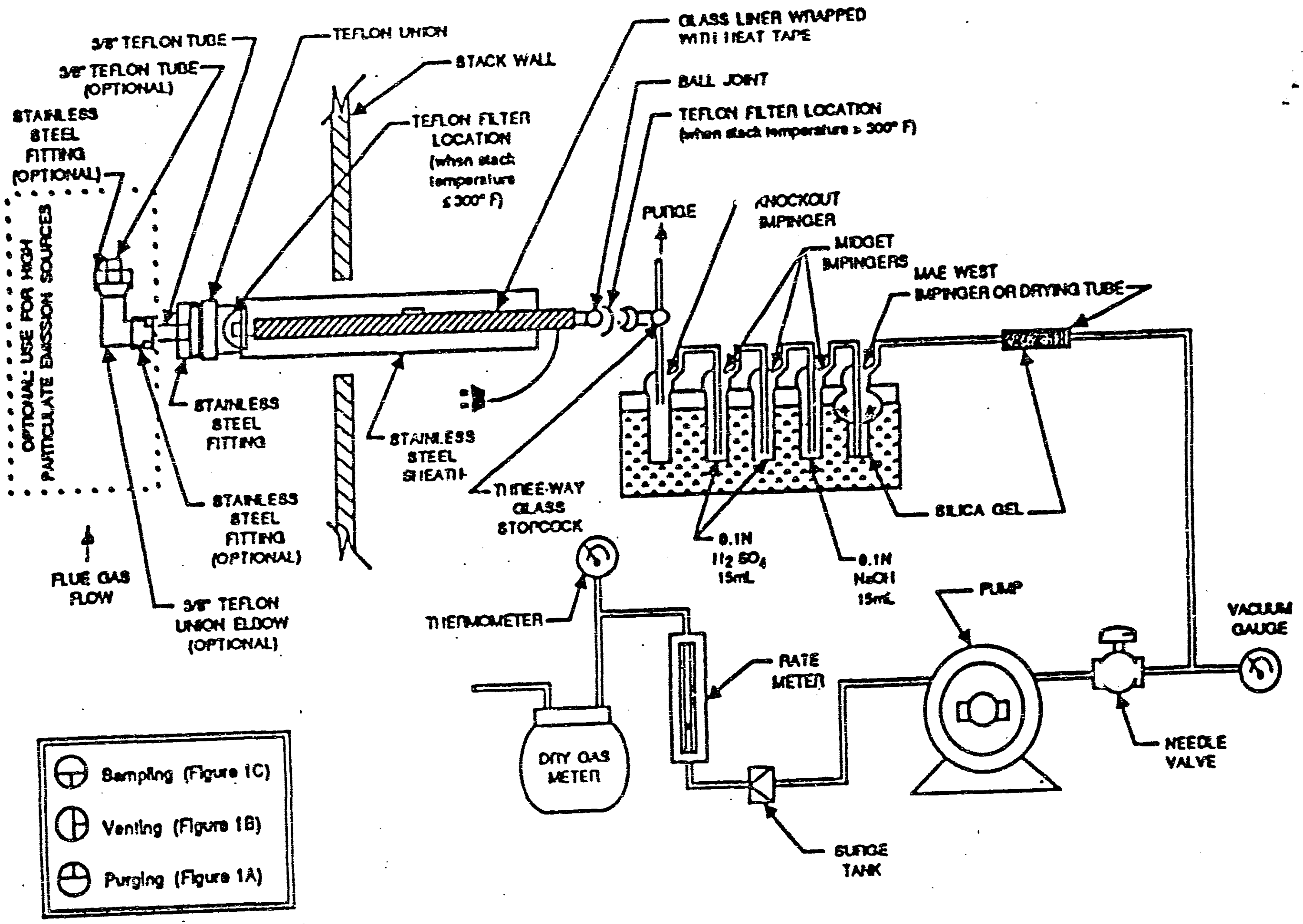

Figure 26-1. Sampling Train

BILLING CODE 6560-50-C

For sampling at high moisture sources or for sampling times greater than one 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.

2.1.5 Filter. A 25-mm Teflon mat, Pallflex TX40H175 or equivalent. Locate between the probe liner and Teflon elbow in a glass or quartz filter holder in a filter box heated to 250 °F.

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

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

2.1.8 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.

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

2.2 Sample Recovery.

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

2.2.2 Storage Bottles. 100-ml glass, with Teflon-lined lids, to store impinger samples (two per sampling run). During clean-up, the two front impinger contents (0.1 N H_2SO_4) should be combined. The contents of the two rear impingers (0.1 N NaOH) may be discarded, as these solutions are included only to absorb Cl_2, and thus protect the pump.

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 non-suppressed, 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 provided the 5 percent repeatability criteria for sample analysis and the linearity criteria for the calibration curve can be met.

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 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.

3.1.3 Chlorine Scrubber 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.

3.2 Sample Preparation and Analysis.

3.2.1 Water. Same as in Section 3.1.1.

3.2.2 Blank Solution. A separate blank solution of the absorbing reagent should be prepared for analysis with the field samples. Dilute 30 ml of absorbing solution to 100 ml with water in a separate volumetric flask.

3.2.3 Sodium Chloride (NaCl) Stock Standard Solution. Solutions containing a nominal certified concentration of 1000 mg/l are commercially available as convenient stock solutions from which working standards can be made by appropriate volumetric dilution. Alternately, concentrated stock solutions may be produced from reagent grade NaCl. The NaCl should be dried at 110 °C for 2 or more hours and 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. The exact Cl^- concentration can be calculated using Eq. 20–1.

$$\mu g\ Cl^-/ml = g\ of\ NaCl \times 10^3 \times 35.453/58.44$$

Eq. 26–1

Refrigerate the stock standard solution and store no longer than one month.

3.2.4 Chromatographic Eluent. Effective eluents for non-suppressed 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 absorbing solution into each of the first two impingers, and add 15 ml of scrubber solution to the third and fourth impingers. Connect the impingers in series with the knockout impinger first, followed by the two impingers containing absorbing solution and the two containing the scrubber solution. Place a fresh charge of silica gel, or equivalent, in the drying tube or Mae West impinger.

4.1.2 Leak-Check Procedures. Leak-check the probe and three-way stopcock before inserting the probe into the stack. Connect the stopcock to the outlet of the probe, and connect the sample line to the needle valve. Plug the probe inlet, turn on the sample pump, and pull a vacuum of at least 250 mm Hg (10 in. Hg). Turn off the needle valve, and note the vacuum gauge reading.The vacuum should remain stable for at least 30 seconds. Place the probe in the stack at the sampling location, and adjust the probe and stopcock heating system to a temperature sufficient to prevent water condensation. Connect the first impinger to the stopcock, and connect the sample line to the last impinger and the needle valve. Upon completion of a sampling run, remove the probe from the stack and leak-check as described above. If a leak has occurred, the sampling run must be voided. Alternately, the portion of the train behind the probe may be leak-checked between multiple runs at the same site as follows: Close the stopcock to the first impinger (see Figure 1A of Figure 28-1), and turn on the sampling pump. Pull a vacuum of at least 250 mm Hg, turn off the needle valve, and note the vacuum gauge reading. The vacuum should remain stable for at least 30 seconds. Release the vacuum on the impinger train by turning the stopcock to the vent position to permit ambient air to enter (see Figure 1B of Figure 20-2). If this procedure is used, the full train leak-check described above must be conducted following the final run, and all preceding sampling runs must be voided if a leak has occurred.

4.1.3 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 28-1). Turn on the purge pump, and adjust the purge rate to 2 liters/min. Purge for at least 5 minutes before sampling.

4.1.4 Sample Collection. Turn on the sampling pump, pull a slight vacuum of approximately 25 mm Hg (1 in. Hg) on the impinger train, and turn the stopcock to permit stack gas to be pulled through the impinger train (see Figure 1C of Figure 28-3). 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 five minutes during the run. A sampling time of one 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 first three impingers (the knockout impinger and the two absorbing solution impingers) to a leak-free storage bottle. Add the water rinses of each of these impingers and connecting glassware to the storage bottle. The contents of the scrubber impingers and connecting glassware rinses may be discarded. The sample bottle should be sealed, shaken to mix, and labeled. The fluid level should be marked so that if any sample is lost during transport, a correction proportional to the lost volume can be applied.

4.3 Sample Preparation for Analysis. Check the liquid level in each sample, and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, the volume lost can be determined from the difference between the initial and final solution levels, and this value can be used to correct the analytical results. Quantitatively transfer the sample solution to a 100-ml volumetric flask, and dilute the solution to 100 ml with water.

4.4 Sample Analysis.

4.4.1 The IC conditions will depend upon analytical column type and whether suppressed or non-suppressed IC is used. An example chromatogram from a non-suppressed 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.

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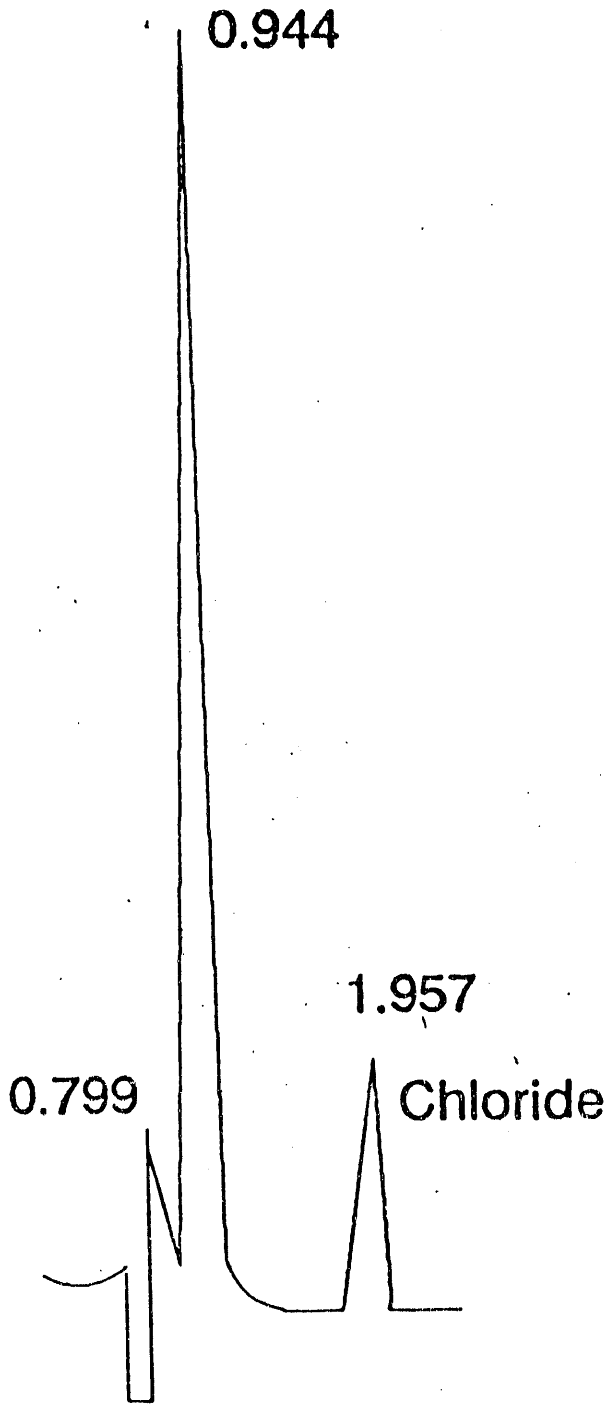

Figure 26-2. Example Chromatogram

4.4.2 Before sample analysis, establish a stable baseline. Next, inject a sample of water, and determine if any Cl^- appears in the chromatogram. If Cl^- is present, repeat the load/injection procedure until no Cl^- is present. At this point, the instrument is ready for use.

4.4.3 First, inject the calibration standards covering an appropriate concentration range, starting with the lowest concentration standard. Next, inject in duplicate, a QC sample followed by a water blank and the field samples. Finally, repeat the injection of calibration standards to allow compensation for any drift in the instrument during analysis of the field samples. Measure the Cl^- peak areas or heights of the samples. Use the average response from the duplicate injections to determine the field sample concentrations using a linear calibration curve generated from the standards.

4.5 Audit Analysis. There is currently no validated audit sample for this method. It is recommended to analyze a QC sample along with the field samples as described above.

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 Calibration Curve for Ion Chromatograph. To prepare calibration standards, dilute given volumes (1.0 ml or greater) of the stock standard solution, with 0.1 N H_2SO_4 (section 3.1.2) to convenient volumes. Prepare at least four standards that are within the linear range of the instrument and which cover the expected concentration range of the field samples. Analyze the standards as instructed in section 4.4.3, beginning with the lowest concentration standard. Determine the peak measurements, and plot individual values versus Cl^- concentration in μg/ml. Draw a smooth curve through the points. Use linear regression to calculate a formula describing the resulting linear curve.

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 samples 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 of 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. 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.

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.

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 Per Sample.

$$m = (S - B)(100)(36.46)/(35.453) = (102.84)(S - B) \qquad \text{Eq. 26–2}$$

Where:

m = Mass of HCl in sample, μg.
S = Concentration of sample, μg Cl^-/ml.
B = Concentration of blank, μg Cl^-/ml.
100 = Volume of filtered and diluted sample, ml.
36.46 = Molecular weight of HCl, μg/μg-mole.
35.453 = Atomic weight of Cl, μg/μg-mole.

7.3 Concentration of HCl in the Flue Gas.

$$C = K\, m/V_{m(std)} \qquad \text{Eq. 26–3}$$

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. *Bibliography*

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

3. Entropy Environmentalists Inc., "Laboratory Evaluation of a Sampling and Analysis Method for Hydrogen Chloride Emissions from Stationary Sources: Interim Report," EPA Contract No. 68–02–4442, Research Triangle Park, North Carolina, January 22, 1988.

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