REM IV Remedial Planning Activities at Selected Uncontrolled Hazardous Waste Sites–Zone II

Rec'd November 19, 1987 Kgf

FINAL

Environmental Protection Agency
Hazardous Site Control Division
Contract No. 68-01-7251

QUALITY ASSURANCE PROJECT PLAN

PHASE I
REMEDIAL INVESTIGATION/ FEASIBILITY STUDY
VOLUME II OF II

Moss-American
Milwaukee, Wisconsin

EPA WA 5-5LM7.0

CH2M HILL

Black & Veatch
ICF
PRC
Ecology and Environment

QUALITY ASSURANCE PROJECT PLAN

PHASE I
REMEDIAL INVESTIGATION/ FEASIBILITY STUDY
VOLUME II OF II

Moss-American
Milwaukee, Wisconsin

EPA WA 5-5LM7.0

October 15, 1987

Appendix G
SPECIAL ANALYTICAL SERVICES (SAS) PARAMETERS FOR SURFACE WATER/GROUNDWATER

.S. Environmental Protection Agency
LP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
HONE: (703)/557-2490 or FTS/557-2490

SAS Number

Approved for Scheduling

SPECIAL ANALYTICAL SERVICES
Client Request

☐ Regional Transmittal ☐ Telephone Request

. EPA Region/Client: Region V

. RSCC Representative: Dennis Wesolowski

C. Telephone Number: (312) 886-1971

. Date of Request:

E. Site Name: Moss-American, WI

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for our request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

. General description of analytical service requested: Analysis of biological oxygen demand (BOD) in water and wastewater. Samples will be unfiltered. Results are reported as mg/l oxygen.

. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentrations are assumed.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4 Estimated date(s) of collection: ______________________

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6 Number of days analysis and data required after laboratory receipt of samples:

Laboratory should report results within 30 days of receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

BOD "Standard Methods for the Examination of Water and Wastewater" 15th or 16th Edition, Method 507. All samples will be seeded unless otherwise stated.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Set-up 3 or more sample dilutions so that two or more sample dilutions overlap to result in a residual D.O. > or = to 1 mg/l and a D.O. depletion ≥ 2 mg/l. Measure the seed BOD using 2 or more dilutions (Section 5d). BOD results for 2 dilutions should agree within + or - 15%. Analyze unseeded dilution water blanks , and glucose-glutamic acid checks (Section 5b of Method 507), both in duplicate, in addition to sample dilutions. Determine the initial and final D.O. for each bottle. Store samples at 4°C until analysis. The holding time is not to exceed 48 hours from the time of the beginning of sample collection. Dilution water will be seeded so that calculated DO uptake from BOD of seed will be between 0.6 and 1.0 mg/l (Section 5d of Method 507). Do not use seeded blanks to estimate seed corrections. All procedures defined in the Method must be followed precisely. Check for interferences (Section 5e).

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

All measurements and calculations must be documented and submitted. Submit all raw data. Report initial and final D.O. from each bottle. Report BOD in mg/l for each bottle and the average of each fitting the depletion range listed above using calculations specified by "Standard Methods"(Section 6 of Method 507). Report results of duplicates, unseeded dilution water blank, BOD of seed, calculated DO uptake of seed in seeded dilution water, and glucose-glutamic acid check.
EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis will be provided for all reference samples used.

10. Other (use additional sheets or attach supplementary information, as needed):

____

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414/272-2426

I. DATA REQUIREMENTS

Parameter:	Detection Limit	Precision Desired (±% or Conc.)
BOD	2 mg/l	Differences in duplicate series of sample results shall not exceed 2 mg/l for concentrations less than 20mg/l.

II. QC REQUIREMENTS

Do not use any field blanks for QA audits.

Audits Required	Frequency of Audits	Limits* (% or Conc.)
Glucose-Glutamic acid checks	1 pair per set of samples	160-240 mg/l
Duplicate (full dilution series)	at least 1 per group of 10 or fewer samples	+ or -(10% or 2 mg/l)
Unseeded Dilution Water Blanks	1 pair per set of samples, including 1 pair for each lot of dilution water	< or = to 0.2 mg/l
DO Uptake of seed in seeded dilution water (calculated)	calculated for each lot of seeded dilution water	0.6 to 1.0 mg/l
1 set of EPA QC Demand Reference Samples (if specified) Yes ___ No ___	1 set of 2 per sample set	75 - 125% Recovery

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples - Contact Jay Thakkar (312) 886-1972 or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

5/020G-0-6/87 Total Organic Carbon in Water 6/30/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V

B. RSCC Representative: Dennis Wesolowski

C. Telephone Number: (312) 886-1971

D. Date of Request:

E. Site Name: Moss-American, WI

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for total organic carbon in water (surface waters, groundwaters, drinking waters, leachate, etc.). Most samples will be unfiltered, although certain aliquots can be filtered and preserved at the time of collection. Results are reported as mg/l C.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentration are assumed.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Number of days analysis and data required after laboratory receipt of samples:

Laboratory should report results within 30 days of receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

EPA Method 415.1 (combustion or oxidation).

Samples will be preserved with 1 ml/l H_2SO_4 to pH <2. Samples will be stored at 4°C until analysis and validation of results.

8. Special technical instruction (if outside protocol requirements) dilute and rerun samples with absorbances higher than the highest standard:

Check sample pH with (wide range pH paper). If pH >2 contact CPMS, CRL for instructions. The holding time is not to exceed 28 days from sample collection. Homogenize samples if necessary. Qualify results where suspended solids content may affect accuracy. Instruments with syringe injection will utilize 2 injections per measurement. If the 2 injections differ by more than 10% or 2 mg/l, repeat and report the average of 4 injections. Inorganic carbon will be purged from solution or, if determined separately, subtracted from total carbon values. Obtain approval of CPMS, CRL, prior to use of any other method. The calibration curve must include at least 5 standards. (One of the standards must be zero concentration).

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion:

Test procedures and specific instrument used will be clearly identified. Bench records tabulating order of calibration standards, lab blanks, samples lab control standards, spikes, duplicates etc., with resulting output on concentration readout will be provided along with worksheets used to calculate results. Specify the organic compound used to prepare standards and spikes. A photocopy of the instrument readout, i.e. stripcharts, printer, tapes, etc. must be included. Results are to be reported in mg/l C. Records of analysis and calculations must be legible and sufficient to recalculate all concentrations.

EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414/272-2426

I. DATA REQUIREMENTS

Parameter:	Detection Limit	Precision Desired (±% or Conc.)
TOC	2 mg/l	Difference in duplicate results should not exceed ± 10% for concentrations >20 mg/l or 2 mg/l for concentrations less than 20 mg/l.
NOTE: These are minimum requirements. Report actual detection limits used based on specified methodologies.		

II. QC REQUIREMENTS - Do not use designated field blanks for QA audits.

Audits Required	Frequency of Audits	Limits* (% or Conc.)
Matrix Spike*	at least 1 per group of 10 or fewer samples	85% - 115%
Lab Duplicate	at least 1 per group of 10 or fewer samples	± (10% or 2.0 mg/l)
Lab Blank	at least 1 per group of 10 or fewer samples	≤ 2.0 mg/l
Calibration verification standard	1 per group of 10 samples and end of set	90% - 110%
1 set of EPA demand QC reference samples (conc. 1 and 2)	1 per sample set	85% - 115%

*The matrix spike concentrations will be approximately 30% of sample concentrations, but spiked samples shall not exceed the working range of the standard curve.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples - Contact Jay Thakkar (312) 886-1972 or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

.S. Environmental Protection Agency
P Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved for Scheduling

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V

RSCC Representative: Dennis Wesolowski

C. Telephone Number: 312/886-1971

Date of Request:

Site Name: Moss-American, WI

Please provide below a description of your request for Special Analytical Services under e Contract Laboratory Program. In order to most efficiently obtain laboratory capability for our request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue esponse on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of chemical oxygen demand (COD) (Hi-level) (50 - 800 mg/l) and COD (Lo-level) (5 - 50 mg/l) in water (surface water, groundwater, leachate, wastewater, drinking water, etc.). Samples will be unfiltered. Any sample with COD values less than 50 mg/l will be determined and reported as COD (Lo-level). Samples with COD values greater than or equal to 50 mg/l will be determined and reported as COD (Hi-level). The COD (Lo-level) method is used for optimum precision and accuracy of measurement of low concentration COD values.

   If field specific conductance values are greater than or equal to 5000 umhos/cm, field personnel will indicate this on the SAS Packing Lists or any future RAS/SAS Traffic Report Forms, the field conductance values and the instruction "Check for Possible Chloride Interference in COD Test" for any such samples. If this is the case or if there is other definite knowledge of chlorides exceeding 2000 mg/l, the laboratory will determine the chloride content and inhibit chloride interference pursuant to Section 7.1 of EPA Method 410.3.

   NOTE: It is expected that few waters from Region V (<3%), will have chloride concentrations in excess of 2000 mg/l, however, it is the responsibility of field personnel to first identify any samples having a chloride interference for COD so that the COD test can be modified to compensate for any chloride interference.

   Results are reported as mg/l COD.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration): Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentration are assumed.

Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund, Enforcement

4. Estimated date(s) of collection: ____________________

Estimated date(s) and method of shipment: Daily by overnight carrier

6. Number of days analysis and data required after laboratory receipt of samples:

Laboratory should report results within 30 days of receipt of samples.

Analytical protocol required (attach copy if other than a protocol currently used in this program):

EPA Method 410.1 (Titrimetric, Mid-level) for COD $\geq$ 50 mg/l.
EPA Method 410.2 (Titrimetric, Low-level) for COD $\leq$ 50 mg/l.

Use Section 7.1 of Method 410.3 if chloride concentration exceeds 2000 mg/l in a sample. If titration blank is necessary for each different amount of mercuric sulfate used for inhibition of chloride interference, SAS Packing Lists will note the samples requiring assessment of chloride interferences. Measurement of chloride will be done using any method of "Standard Methods",16th ed., or "EPA Methods for Chemical Analysis of Water and Wastes", 1983 ed., whenever possible chloride interference is noted. Samples will be preserved with 1 ml of H_2SO_4 to pH less than 2 and kept at 4°C until sample analysis and validation of results are completed. Holding time is not to exceed 28 days from date of sample collection.

Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1. Check sample pH (wide range pH paper). If pH>2, contact CPMS, CRL for further instructions.
2. Use a) 50 ml sample aliquots for both methods, b) 0.250 N $K_2Cr_2O_7$ reagent and 0.25 N ferrous ammonium sulfate titrant for Method 410.1, and c) 0.0250 N $K_2Cr_2O_7$ reagent and 0.025 N ferrous ammonium sulfate titrant for Method 410.2.
3. Dilute and reanalyze (by Method 410.1) any samples with COD values > 800 mg/l or titrant volumes < 5.0 ml. Reanalyze samples (by Method 410.1) if initial sample values are > 50 mg/l COD by Method 410.2. Reanalyze samples (by Method 410.2) if initial sample values are < 50 mg/l COD by Method 410.1.
4. Any sample aliquots < 50 mls will be diluted to 50 mls so that the COD reaction mixture will be 50% H_2SO_4/ 50% water by volume.
5. Titration blanks will be determined, at least in duplicate each day of analysis and will not differ more than ± 0.1 ml titrant for Method 410.1 and ± 1.0 ml titrant for Method 410.2.
6. Separate sets of QA Audits will be performed for each method, if both methods are used.
7. Use potassium hydrogen phthalate as a matrix spike compound. Use 20 mg/l matrix spike concentration for Method 410.2.
8. Samples will be refluxed for at least 2 hours.
9. Homogenize sample aliquots, as necessary, to obtain sample aliquots of representative suspended solids.
10. Use only the method specified.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Bench records, tabulating titrant standardization, titration volumes for titration or sample blanks (2 or more in number), samples, and QA Audits will be provided for each method used. All records of analysis and calculations must be legible and sufficient to recalculate all sample concentrations and QA Audit results. Records of chloride analysis will be provided for any samples so specified on the RAS/SAS Traffic Report or SAS Packing List. Separate bench records will be provided for any COD determinations of high chloride samples (>2000 mg/l Cl) including weight of mercuric sulfate used, sample titration volume and titration blank volume for each sample type. EPA QC Reference samples, or any other reference samples, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414/272-2426

I. DATA REQUIREMENTS

Parameter:	Detection Limit	Precision Desired (±% or Conc.)
COD (Method 410.1)	50 mg/l	Method 410.1: Differences in sample duplicates are to be < or = to 0.2 ml titrant or ≤ 8 mg/l for concentrations ≤ 80 mg/l and < 10% for COD concentrations exceeding 80 mg/l.
COD (Method 410.2)	5 mg/l	Method 410.2: Differences in sample duplicate results are to be ≤ 1.0 ml titrant or ≤ 4 mg/l for concentrations less than 40 mg/l and are to be ≤ 5 mg/l for concentrations between 40 50 mg/l.
NOTE: These are minimum requirements. Report actual detection limits used based on specified methodologies.		

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (% or Conc.)
Matrix spike (KHP) Method 410.1* Method 410.2(Use 20 mg/l spike)	at least 1 per group of 10 or fewer samples	85 - 115% Recovery (410.1) 75 - 125% Recovery (410.2)
Lab duplicate	" " " "	Diff ≤ (8 mg/l or 10%) (410.1) Diff ≤ (4 mg/l - 5 mg/l) (410.2)
Titration blank (used for calculation of results)	at least 2 per sample set for each method used	Diff in titrant volumes shall not exceed 0.1 ml for 410.1 and 1.0 ml for 410.2
1 set of EPA QC Demand Reference samples - 2 concentration levels	1 per sample set for each method used	90 - 110% Recovery or ≤ 8 mg/l error for 410.1 and ≤ 5 mg/l error for 410.2 in aliquot tested

* - Matrix spike will be greater than 30% of the sample concentration, but spiked sample shall not exceed 800 mg/l for Method 410.1.

II. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples. Contact Jay Thakkar (312) 886-1972 or Chuck Elly (312) 353-9087.

Contact Region V RSCC Dennis Wesolowski (312) 886-1971 concerning questions on chloride interferences and modifications of COD test.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

/011G-0-7/87 Sulfate in Water July 30, 1987

U.S. Environmental Protection Agency
CLP Sample Management Office
. O. Box 818, Alexandria, Virginia 22313
HONE: (703)/557-2490 or FTS/557-2490

SAS Number:

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V

RSCC Representative: Dennis Wesolowski

C. Telephone Number: (312) 886-1971

D. Date of Request:

Site Name: Moss-American, WI

ease provide below a description of your request for Special Analytical Services under e Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue sponse on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for sulfate in water (surface water, groundwater, drinking water, leachate, etc.). Samples will be unfiltered. Results are reported as mg/l SO_4.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentrations are assumed.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5 Estimated date(s) and method of shipment: Daily by overnight carrier

6 Number of days analysis and data required after laboratory receipt of samples:

Laboratory should report results within 30 days of receipt of samples.

7 Analytical protocol required (attach copy if other than a protocol currently used in this program):

1. EPA Method 375.2 (Colorimetric Methylthmol Blue) - 1983 ed.
   - Note: This method requires 0.75 mg/l SO_4 in Dilution Water(See Reagent Section 6.8)
2. Method 426C of Standard Methods, 16th ed. (Turbidimetric)
   - Note; this last method provides for measurement of sulfate using 2 standard curves-1 for sulfate concentrations between 0 and 10mg/l, and 1 between 10 and 40 mg/l sulfate.

Samples will be kept at 4°C until validation of results.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Sample holding time is not to exceed 28 days from date of sample collection. Sulfate standards will be prepared daily from stock solution. Samples with absorbances or turbidities greater than that in the highest standard will be diluted and rerun. For Method 426C, 1) the reanalysis solution should contain between 20 and 40 mg/l sulfate, and 2) concentrations must be corrected for background turbidity and color per Section 5d of Method 426C using pH adjusted sample aliquots. Use only the methods specified. Calibration curves must include at least 6 points (including a zero concentration standard) for Method 375.2 and Buffer A of Method 426C.

9 Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

The test procedure used must be clearly identified. Results shall be reported as mg/l SO_4. Bench records tabulating the order of calibration standards, lab control standards, lab blanks, samples, spikes, etc., with resulting absorbances or concentration readouts, will be provided along with copies of worksheets used to calculate results. Background absorbances used for turbidity corrections must be tabulated for each sample aliquot tested. A photocopy of the instrument readout (ie. strip charts, printer tapes, etc.) must be included. All records of analysis must be legible and sufficient to calculate all concentrations and results.

EPA QC reference samples, or any other reference sample or initial calibration verification, will be identified as to source,lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414/272-2426

I. DATA REQUIREMENTS

Parameter:	Detection Limit	Precision Desired (±% or Conc.)
Sulfate	5 mg/l	Method 375.2: Differences in duplicate sample results are to be < 5 mg/l for concentrations < 50 mg/l, and < 10% for concentrations ≥ 50 mg/l. Method 426 C: Differences in duplicate sample results are to be ≤ 2 mg/l for concentrations ≤ 20 mg/l and ≤ 10% for concentrations > 20 mg/l in aliquot tested.
Note: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.		

II. QC REQUIREMENTS - Do not use designated field blanks for QA audits.

Audits Required	Frequency of Audits	Limits* (% or Conc.)
Matrix Spike*	1 per group of 10 or fewer samples	85-115%
Lab Duplicate	" "	± (10% or 5 mg/l) for Method 375.2 ± (10% or 2 mg/l) for Method 426C
Lab Blank (0 mg/l SO_4)	" "	< 5 mg/l - Method 375.2 -2 to +2mg/l-Buffer B of Method 426C or
Lab Blank (10 mg/l SO_4)	" "	8 to 10mg/l - Buffer A of Method 426C
Calibration Verification Standard	1 per group of 10 samples and at end of sample set	90 - 110%
1 Set of EPA QC Mineral Reference Samples	once per sample set	85-115% for each concentration.

*Matrix spike concentrations will be greater than 30% of sample concentrations, but spiked samples shall not exceed working range of standard curve.

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyze samples.

Contact Jay Thakkar (312) 886-1972 or Chuck Elly (312) 353-9087.

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

Approved for Scheduling

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V , Moss-American, WI

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) 312/886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for total suspended solids (103-105°C) in water (surface waters, groundwater, drinking water, leachate, etc.) Results are reported as mg/l total suspended solids.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentrations are assumed.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6. Approximate number of days results required after lab receipt of samples: 30

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

1. EPA Method 160.2, 1983 ed., (Gravimetric, Dried at 103° - 105° C) using glass fiber filter discs without organic binder such as: Millipore AP-40, Reeve Angel 934-AH, Gelman A/E, or equivalent. Use only membrane filter apparatus with 47 mm diameter glass fiber filter and a coarse (40-60 micron) fritted disc filter support. The filter and support specifications are mandatory. Samples will be held at 4°C until sample analysis and validation of results are completed. Holding time is 7 days from date of sample collection.

8. Specail technical instructionns (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1. Sample aliquot volumes are selected on the basis of the following factors. a) During initial sample filtratrion, filtration rate should not drop rapidly, or require more than 5 minutes of filtratrion time. (Increase the filter area or decrease the sample volume as needed for sample reanalysis), b) The sample aliquot filtered should provide a residue with greater than 1.0 mg for aliquots less than 200ml in volume, and c) Sample aliquots should not exceed 200ml in volume. 2. Duplicate sample aliquots will be filtered with 2 or more intervening samples. 3. Final residues are to be weighed either to constant weight pursuant to Section 7.6 of Method 160.1 (The final weight is to be used for calculations), or dried overnight (12 hours of drying time) with the single weight used for calculations. Constant weight is defined as less than 0.5 mg or less than 4% weight loss from the previous weight, whichever is smaller. 4. Use only the method specified above in items 7 and 8.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Identify EPA QC reference sample lot numbers used and their true values and 95% confidence intervals. Bench records of tare weights, final weights, volumes filtered, blanks, duplicate samples, and reference samples (all in the order filtered) will be provided along with copies of worksheets used to calculate results. Dates and time of a) filtration of initial 100ml volume, b) determination of tare weights, c) sample filtration, and d) determination of constant residue weights will be part of bench records. All records of analysis must be legible and sufficient to recalculate all sample concentrations and QA results.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414/272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
Suspended Solids	2-3 mg/l for 200 ml sample aliquot	Difference in duplicate results shall not exceed 0.5 mg for duplicate aliquots filtered.
Note: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.		

II. QUALITY CONTROL REQUIREMENTS

Do not use designated field blanks for QA Audits.

Audits Required	Frequency of Audits	Limits* (±% or Conc.)
1) Lab Duplicates (See item 8.3 on Page 2)	1 per group of 10 or fewer samples	less than 0.5 mg
2) Lab Blanks (200 ml aliquots)	1 per group or 10 or fewer samples	-0.5 to +0.5 mg
3) 1 set of 2 EPA QC Residue Reference Samples-2 concentration levels	1 per sample set	< 5 mg/l error for concentrations ≤ to 50 mg/l or < or = to 10% for nominal concentrations > than 50 mg/l

* Alternate reference samples must be approbed by Region V RSCC prior to analysis.

III. *Action Required if Limits are Exceeded:

Take corrective action and reanalyze samples.

Contact Jay Thakkar (312) 886-1972 or Chuck Elly (312) 353-9087.

5/0246-0-6/87 Total Dissolved Solids 6/29/87

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
Phone: (703) 557-2490 or FTS-557-2490

SAS Number

Special Analytical Services
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V Moss-AMerican, WI
B. Regional Representative: Dennis Wesolowski
C. Telephone Number: (312) 886-1971
D. Data request:
E. Site Name:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis of total dissolved solids (180°C) in water (surface waters, wastes, groundwaters, drinking water, leachate, etc.) Results are reported as mg/l dissolved solids.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentrations are assumed.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6. Approximate number of days results required after lab receipt of samples: 30 days

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

1. EPA Method 160.1, 1983 ed., or

2. Method 209B, "Standard Methods", 16th ed. Samples will be kept at 4°C until sample analysis and validation of results. Holding time is 7 days from date of sample collection.

8. Specail technical instructionns (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1) Use standard aliquots of 100ml; however do not use sample aliquots yielding more than 200 mg residue. If residue is greater than 200 mg, repeat the analysis using a smaller sample aliquot. 2) If the pH value is less than 4.0, raise the pH of the aliquot (using NaOH titrant) to between pH 4 and 8 and subtract the weight of sodium added from the weigth of the residue. 3) Residue will be weighed either to constant weight pursuant to Section 7.6 of Method 160.1 the final weight is to be used for calculations. Constant weight is defined as a) less than 0.5 mg or less than 4% weight loss from the previous weight, whichever is smaller, or b) dried overnight (12 hours drying time) with a single weight used for calculations.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Identify the QC reference sample lot numbers used and their true values with 95% confidence intervals. Bench records of tare weights, final weights, additional weights to determine constant weights, volumes filtered, blanks, duplicate samples, and reference samples will be provided with copies of work sheets used to calculate results . Dates and time of 1) determination of tare weights, 2) sample filtration, and 3) determination of residue weights and constant residue weights will be part of bench records. All records of analysis must be legible and sufficient to recalculate all sample concentrations and QA results.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414/272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
TDS	20 mg/l	Difference in duplicate sample aliquots shall not exceed 2 mg for residues. Duplicate differences shall not exceed 10% for sample values greater than 200 mg/l.
Note: These are minimum requirements. Report the actual detection limits used based on allowable methodology options.		

II. QUALITY CONTROL REQUIREMENTS

Do not use any designated field blanks for QA Audits.

Audits Required	Frequency of Audits	Limits* (±% or Conc.)
1. 1 set of EPA QC Mineral Reference Samples*- 2 concentration levels.	1 per sample set	85-115% Recovery
2. Lab Duplicate	At least 1 per group of 10 or fewer samples	± (10% or 2 mg of residue)
3. Lab Blanks (100 ml of filtered reagent water)	At least 1 per group of 10 or fewer samples	- 20 mg/l to + 20 mg/l

* Alternate reference samples must be approved by Region V RSCC prior to analysis.

III. *Action Required if Limits are Exceeded:

Take corrective action and retest samples. Contant Charles T. Elly (312/353-9087) or Jay Thakkar at (312/886-1972).

5/003G-0-6/87 Alk/Acid/pH 6/29/87

U.S. Environmental Protection Agency
CLP Sample Management Office
P. O. Box 818, Alexandria, Virginia 22313
PHONE: (703)/557-2490 or FTS/557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Client Request

Approved For Scheduling

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region/Client: Region V

B. RSCC Representative: Dennis Wesolowski

C. Telephone Number: 312/886-1971

D. Date of Request:

E. Site Name: Moss-American, WI

Please provide below a description of your request for Special Analytical Services under the Contract Laboratory Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Analysis for alkalinity, acidity (if necessary), and pH in waters (surface waters, groundwaters, drinking waters, leachates, etc.). Samples will be unfiltered. Determine alkalinity and pH first. Only those samples with pH values less than or equal to 5.0 or alkalinity values less than or equal to 20 mg/l $CaCO_3$ will be tested for acidity. Use attached SAS for acidity (titration after hydrogen peroxide addition and boiling), if any such determinations are required. Report alkalinity and acidity as mg/l $CaCO_3$.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration): Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentrations are assumed.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Number of days analysis and data required after laboratory receipt of samples:

Laboratory should report results within 30 days of receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

1) Alkalinity EPA Method 310.1 (Titrimetric, ph 4.5) or Standard Methods, 16th Edition, Method 403 4c and 4d.
2) pH - EPA Method 150.1 (Electrometric) - Initial pH of alkalinity titration is an acceptable procedure so long as sample has not been diluted.
3) Acidity - EPA Method 305.1 (Titrimetric) - Use attached SAS, and its specifications, for acidity. Determine acidity if sample pH $\leq$ 5.0 or alkalinity $\leq$ 20 mg/l $CaCO_3$.

Samples will be stored at 4°C until analysis and validation of results.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Sample holding time should not exceed 14 days from date of collection. Use potentiometric titration to pH 4.5 for alkalinity > 20 mg/l $CaCO_3$. For concentrations < 20 mg/l, use EPA Method 310.1 (Section 6.3) or Standard Methods, Method 403 4d. Do not use titrant volumes greater than 50 ml. Use only the Methods specified above.

Use Na_2CO_3 to standardize titrant. Standardize the pH meter and the titrant each day. Standardize the pH meter using at least two buffers which bracket the alkalinity end point. Record pH of each sample prior to titration.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

The test procedure used will be clearly identified. Bench records tabulating the order of analysis including pH meter calibration, titrant standardization, sample pH values, lab blanks, samples, lab control standards, duplicates, etc., with resulting titrant volumes or read-outs, will be provided along with calculation worksheets. All records will be legible and sufficient to recalculate all sample concentrations and QA audit results. Report method of titrant standardization.

EPA QC reference samples, or any other reference sample, will be identified as to source, lot number, and sample number. Corresponding "true" or target values and associated 95% confidence limits for analysis results will be provided for all reference samples used.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414-272-2426

I. DATA REQUIREMENTS

Parameter:	Detection Limit	Precision Desired (±% or Conc.)
Alkalinity (as mg/l $CaCO_3$)	2 mg/l for low level	± 2 mg/l for concentrations ≤ 20 mg/l $CaCO_3$
	20 mg/l for high level	± 10% for concentrations ≥ 20 mg/l $CaCO_3$
pH	not applicable	Report to nearest 0.1 pH values.

II. QC REQUIREMENTS Do not use any field blanks for QA audits.

Audits Required (Alkalinity)	Frequency of Audits	Limits* (% or Conc.)
lab blank	at least 1 per group of 10 or fewer samples	< 10 mg/l for high-level samples tested. ≤ 2 mg/l for low-level samples tested.
lab duplicate	at least 1 per group of 10 or fewer samples	± 10% or ± 2 mg/l
lab control sample	1 per sample set	90 - 110% recovery
1 set of EPA QC mineral reference samples		

III. ACTION REQUIRED IF LIMITS ARE EXCEEDED:

Take corrective action and reanalyzesamples. Contact Jay Thakkar (312) 886-1972

or Chuck Elly (312) 353-9087

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

Phenols

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) 312/886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze groundwater and surface water samples for total phenols.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 27 groundwater and 10 surface water samples including field duplicates and blanks. Whole aqueous samples of low concentrations are assumed.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6. Approximate number of days results required after lab receipt of samples:

Laboratory should report results within 30 days after receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

EPA Method 420.1 chloroform distillation for concentrations between 2 and 200ug/l or 420.1 direct photometric method for conc. greater than 200 ug/l or Standard Methods $_{510-A}$ followed by B for conc. from 2 to 200ug/l or c for conc.greater than 200 ug/l.

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Samples will be preserved with phosphoric acid and 1% $CuSO_4$ in the field to a pH 4. If the Chloroform extract is over 200ug/l the sample must be diluted and redistilled. Do not dilute the chloroform extract. Holding time is not to exceed 7 days. A 5 point calibration curve should be used (blank and 4 std.). Use only the methods specified above. Obtain approval from CPMs CRL prior to using any other method. Rerun samples with absorbances greater than the highest standard.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

The test procedure used must be clearly identified. Include a sample preparation log. Benc records tabulating the order of titrant standardization, lab blanks, samples, spikes duplic etc. whth resulting absorbance or conc. readouts will be provided along with copies of work sheets used to calculate results. all records of analysis and calculations must be legible

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: (414) 272-2426

Please return this request to the Sample Management Office as soon as possible to expedi processing of your request for special analytical services. Should you have any questior or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
Phenols	2 ug/1 for Chloroform	± 20% or 5 ug/1 for
	200 ug/1 for direct	conc. less than 20 ug/1
	photometric method	

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or Conc.)
Lab Blank (distilled)	At least 1 per analytical run and 1 per 10 samples	2 ug/1
Lab Duplicates	At least 1 per analytical run and 1 per 10 samples	20% or 5 ug/1
Matrix Spike (distilled)	At least 1 per analytical run and 1 per 10 samples	80% - 120%
Calibration verification check sample (Undistilled)	At the end of each run and 1 per 10	90% - 110%
EPA QC Phenol reference sample 1 set of 2 samples	1 per this project	80% -120%

Spike concentrations will be greater than 30% of the sample conc. but will not exceed the working range of the standard curve.

III. *Action Required If Limits are Exceeded:

Reanalyze the sample, contact Jay Thakkar or Chuck Elly at the Region V CRL

Appendix H
SPECIAL ANALYTICAL SERVICES (SAS) PARAMETERS FOR SOIL/SEDIMENT

Attachment H-1: HSL Organics
Attachment H-2: HSL Inorganics
Attachment H-3: Proximate Analysis
Attachment H-4: Ultimate Analysis
Attachment H-5: Heating Valve
Attachment H-6: Flash Point
Attachment H-7: Soil/Sediment pH
Attachment H-8: Soil/Sediment TOC
Attachment H-9: Water Soluble Chlorides
Attachment H-10: Dioxin
Attachment H-11: Particle Size Distribution
Attachment H-12: Atterberg Limits

Attachment H-1
HSL ORGANICS

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ **Regional Transmittal** ☐ **Telephone Request**

A. EPA Region and Site Name: Region V Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze soil and sediment samples for HSL volotiles, acid, base/neutral extractables and pesticides/PCB's. All samples should be analyzed using high level extraction techniques. Volatiles and pesticides/PCB's should be analyzed at medium level detection limits. The acid, base/neutrals should be analyzed at high level detection limits.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 16 high concentration soil samples and 10 high concentration sediment samples for the parameters listed above. The samples contain high levels of creosote.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Remedial

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6. Approximate number of days results required after lab receipt of samples:

Report results within 30 days of receipt of samples

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

As specified in proposed US EPA protocol for analysis of high/medium concentration organics. (Rev. 4/85)

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Analyze for volatiles and pesticide/PCB at medium level detection limits. Analyze for acid, base/neutral extractables at high level detection limits.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Provide deliverables as per proposed US EPA protocol for analysis of high/medium concentration organics (Rev. 4/85). Document sample preparation cleanup and analysis. Report all QA/QC data.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: (414) 272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
HSL volatiles	as per US EPA proposed protocol	
HSL BNA extractables	for high/medium organics	
HSL pesticides	analysis (Rev. 4/85)	

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or Conc.)

As per US EPA proposed protocol for high/medium organics analysis (Rev. 4/85)

III. *Action Required if Limits are Exceeded:

Contact Chuck Elly (312) 353-9087

Attachment H-2
HSL INORGANICS

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☐ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze soil and sediment high hazard samples for HSL metals and cyanide. The samples are high in creosote and fuel oil. The metals should be analyzed using medium level detection limits.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 16 soil high concentration soil samples and 10 high concentration sediment samples for the parameters listed above. The samples contain high concentrations of creosote and fuel oil.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement.

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6. **Approximate number of days results required after lab receipt of samples:**

Report results within 30 days of receipt of samples

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

As specified in US EPA protocol for high concentration inorganics analysis (Feb, 1985)

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):** Medium concentrations are anticipated. The above methodologies are requested to provide analysis for oil matrix samples.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Provide deliverables as per US EPA protocol for high concentration inorganics analysis (Feb, 1985). Report all QA/QC data.

10. **Other (use additional sheets or attach supplementary information, as needed):**

11. **Name of sampling/shipping contact:** Jeff Keiser

Phone: 414-272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
HSL metals	as specified in US EPA protocol for high concentration inorganics analysis (Feb, 1985)	

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or Conc.)
As per US EPA protocol for high concentration inorganics analysis (Feb, 1985)		

III. *Action Required If Limits are Exceeded:

Contact Chuck Elly (312) 353-9087.

Attachment H-3
PROXIMATE ANALYSIS OF COAL AND COKE

Method: American Society for Testing Materials

Proximate Analysis of Coal and Coke:	D3172-73 (1979)
Moisture:	D3173-73 (1979)
Ash:	D3174-82
Volatile Matter:	D3175-82
Fixed Carbon:	D3172-73 (1979)

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. **General description of analytical service requested:**
Analyze soil and sediment samples for 1) Proximate analysis for: a) moisture content, b) ash, c) volatile matter, and d) fixed carbon. 2) Ultimate analysis for a) C, H, S, O, N 3) Heating Value, 4) Flash Point and 5) pH

2. **Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):**
Analyze 54 soil samples and 20 sediment samples for the parameters listed above. The samples will have low to high concentrations of creosote and fuel oil.

3. **Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):**
Superfund, Enforcement

4. **Estimated date(s) of collection:**

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Approximate number of days results required after lab receipt of samples:

Lab will report results within 30 days after receipt of samples

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

ASTM D 3172-73 (1979) proximate analysis for Coal and Cokes

(a) % Moistures	ASTM D 3173
(b) % Ash	ASTM D 3174
(c) % Volatile Matter	ASTM D 3175
(d) % Fixed Carbon	ASTM D 3172

See Attachment F-1

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Note that these samples may be toxic and/or flmmable.

See Safety Notice

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Report all sample, spikes, duplicates reports data legibly. Supply copies of all laboratory log books, reports forms related to these sample. QC samples and standards.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414-272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions

I. DATA REQUIREMENTS

Parameter	**Detection Limit**	**Precision Desired (±% or Conc.)**
Parameter	Detection Limit	≤.2% for Moisture Values < 5%
% Moisture	≤ 1%	< 0.3% for moisture Values > 5%
% Ash	≤ 1%	No Carbonates < 0.2%
		Carbonates < 0.3%
% Volatile Matter	≤ 1%	< 1%
% Fixed Carbon	≤ 1%	Not Established
(by difference)		

II. QUALITY CONTROL REQUIREMENTS

Audits Required	**Frequency of Audits**	**Limits* (±% or Conc.)**
Reference Material	1 per 10 Samples	% R 80 to 120%
		R % D < 10%
Duplicates	1 per 10 Samples	
		Report of all
		QC Values

% R = Percent recovery R % D = Relative % difference

III. *Action Required If Limits are Exceeded:

a) Reference Material - if % R is exceeded, rerun, if R % D is exceeded, rerun. Take best pair.

b) Duplicates - rerun sample in duplicate

If out, call Dennis Wesolowski 312-886-1971.

Designation: D 3172 – 73 (Reapproved 1979)

An American National Standard

Standard Method for
PROXIMATE ANALYSIS OF COAL AND COKE[1]

This standard is issued under the fixed designation D 3172; 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 moisture, volatile matter, and ash and the calculation of fixed carbon on coals and cokes sampled and prepared by prescribed methods and analyzed according to ASTM established procedures. Methods as herein described may be used to establish the rank of coals, 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.

2. Applicable Documents

2.1 *ASTM Standards:*

D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 388 Classification of Coals by Rank[2]

D 2013 Preparing Coal Samples for Analysis[2]

D 2234 Collection of a Gross Sample of Coal[2]

D 3173 Test for Moisture in the Analysis Sample of Coal and Coke[2]

D 3174 Test for Ash in the Analysis Sample of Coal and Coke[2]

D 3175 Test for Volatile Matter in the Analysis Sample of Coal and Coke[2]

3. Definition

3.1 *proximate analysis of coal and coke*—an assay of the moisture, ash, volatile matter, and fixed carbon as determined by prescribed methods. Other constituents such as sulfur and phosphorus are not included.

4. Sampling

4.1 Coal sample collection shall be in accordance with Sections 5 and 6 of Classification D 388 if the proximate analysis is to be used for classification of coal by rank. In all other cases, sample collection shall be in accordance with Methods D 2234. Preparation shall be in accordance with Method D 2013. Coke sampling shall be in accordance with Method D 346.

5. Test Methods

5.1 *Moisture*—Method D 3173.

5.2 *Ash*—Method D 3174.

5.3 *Volatile Matter*—Method D 3175. If the modified procedure is required, the report should show that the modified procedure was used.

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.

$$\%\ \text{Fixed carbon} = 100 - (\%\ \text{moisture} + \%\ \text{ash} + \%\ \text{volatile matter})$$

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[1] This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke.

Current edition approved April 27, 1973. Published July 1973.

[2] *1983 Annual Book of ASTM Standards*, Vol 05.05.

An American National Standard

AL AND COKE[1]

ıtely following the designation indicates the
.nber in parentheses indicates the year of last
revision or reapproval.

constituents such as sulfur and
are not included.

sample collection shall be in ac-
th Sections 5 and 6 of Classification
ie proximate analysis is to be used
:ation of coal by rank. In all other
le collection shall be in accordance
ds D 2234. Preparation shall be in
: with Method D 2013. Coke sam-
.l be in accordance with Method

ethods

isture—Method D 3173.
'—Method D 3174.
tile Matter—Method D 3175. If the
procedure is required, the report
ıow that the modified procedure was

ed Carbon—The fixed carbon is a
d value. It is the resultant of the
on of percentage moisture, ash, and
ıatter subtracted from 100. All per-
shall be on the same moisture refer-
:.

ırbon = 100 − (% moisture
+ % ash + % volatile matter)

ıethod is under the jurisdiction of ASTM Commit-
Coal and Coke.
edition approved April 27, 1973. Published

nnual Book of ASTM Standards, Vol 05.05.

*the validity of any patent rights asserted in connection
advised that determination of the validity of any such
esponsibility*

*committee and must be reviewed every five years and
either for revision of this standard or for additional
will receive careful consideration at a meeting of the
mments have not received a fair hearing you should
Philadelphia, Pa. 19103.*

Designation: D 3173 - 73 (Reapproved 1979)

Standard Test Method for

MOISTURE IN THE ANALYSIS SAMPLE OF COAL AND COKE[1]

This standard is issued under the fixed designation D 3173; 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 moisture in the analysis sample of coal or coke. It is used for calculating other analytical results to a dry basis. When used in conjunction with the air drying loss as determined in accordance with Method D 2013, Method D 2961, or Method D 346, each analytical result can be calculated to an as-received basis.

2. Applicable Documents

2.1 *ASTM Standards:*

D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Preparing Coal Samples for Analysis[2]

D 2961 Total Moisture in Coal Reduced to No. 8 (2.38 mm) Top Sieve Size (Limited Purpose Method)[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. Analysis Sample

4.1 The analysis sample is that sample which has been pulverized to pass 250-μm (No. 60) sieve as prepared in accordance with Method D 346 or Method D 2013.

5. Apparatus

5.1 *Drying Oven*, for coal samples:

5.1.1 For determining the moisture of coal, the oven shall be so constructed as to have a uniform temperature in all parts, have a minimum of air space, and be capable of temperature regulation between the limits of 104 and 110°C. It may be of the form shown in Fig. 1. Provision shall be made for renewing the reheated air in the oven at the rate of two to four times a minute, with the air dried bypassing it through a dessicant as defined in 6.1.

5.1.2 In the oven shown in Fig. 1, the door should contain a hole of approximately ⅛ in. (3.2 mm) in diameter near the bottom to permit a free flow of air through the oven space.

5.2 *Drying Oven*, for coke samples. For determining the moisture of coke, an ordinary drying oven with openings for natural air circulation and capable of temperature regulation between limits of 104 and 110°C may be used.

5.3 *Capsules*, with covers. A convenient form, which allows the ash determination to be made on the same sample, is a porcelain capsule, ⅞ in. (22 mm) in depth and 1¾-in. (44 mm) in diameter, or a fused silica capsule of similar shape. This shall be used with a well-fitting flat aluminum cover, illustrated in Fig. 2; Platinum crucibles or glass capsules with

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[1] This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke.

Current edition approved April 27, 1973. Published July 1973.

[2] *1983 Annual Book of ASTM Standards*, Vol 05.05.

ground-glass caps may also be used. They should be as shallow as possible, consistent with convenient handling

6. Reagents

6.1 *Desiccant:*

6.1.1 *Sulfuric Acid* (H_2SO_4, sp gr 1.84) (Note 1) or *Anhydrous Magnesium Perchlorate* ($Mg(ClO_4)_2$) approximately 2.36-mm (No. 8) sieve. As a safety precaution magnesium perchlorate should not be regenerated for reuse. It should be destroyed by dissolving in water and flushing down a drain

NOTE 1—H_2SO_4 (sp gr 1.84) is 95 % concentrated. Its affinity for water diminishes as the concentration decreases. The acid should be replaced with new acid (sp gr 1.84) when the original volume has increased by ⅔ (66 %).

7. Procedure for Sample Passing a 250-μm (No. 60) Sieve

7.1 Heat the empty capsules under the conditions at which the sample is to be dried, place the stopper or cover on the capsule, cool over a desiccant for 15 to 30 min and weigh. Dip out with a spoon or spatula from the sample bottle approximately 1 g of the sample. Put this quickly into the capsule, close, and weigh at once.

7.2 An alternative procedure for weighing the sample (more subject to error) is as follows: After transferring an amount of the sample slightly in excess of 1 g, bring to exactly 1 g in weight (±0.5 mg) by quickly removing the excess weight of the sample with a spatula. The utmost dispatch must be used in order to minimize the exposure of the sample until the weight is determined.

7.3 After removing the covers, quickly place the capsules in a preheated oven (at 105 to 110°C) through which passes a current of air dried by H_2SO_4 (sp gr 1.84) (Note 1) (The current of dry air is not necessary for coke.) Close the oven at once and heat for 1 h. Open the oven, cover the capsules quickly, cool in a desiccator over desiccant and weigh as soon as cold

7.4 Use the percentage of moisture in the sample passing a 250-μm (No. 60) sieve to calculate the results of the other analyses to a dry basis.

8. Calculations

8.1 Calculate the percent moisture in the analysis sample as follows:

$$\text{Moisture in analysis sample, \%} = [(A - B)/A] \times 100$$

where:

A = grams of sample used, and

B = grams of sample after heating.

9. Precision

9.1 The following criteria should be used for judging the acceptability of results:

9.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than 0.2 % for coals having less than 5 % moisture and 0.3 % for coals having more than 5 % moisture.

9.1.2 *Reproducibility*—The results submitted by two or more laboratories should not be considered suspect unless they differ by more than 0.3 % for coals having less than 5 % moisture and 0.5 % for coals having more than 5 % moisture.

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ch passes a current of air
gr 1.84) (Note 1). (The
s not necessary for coke.)
nce and heat for 1 h. Open
capsules quickly, cool in a
ccant and weigh as soon as

centage of moisture in the
250-μm (No. 60) sieve to
of the other analyses to a

percent moisture in the
follows:

mple, %
$= [(A - B)/A] \times 100$

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g criteria should be used for
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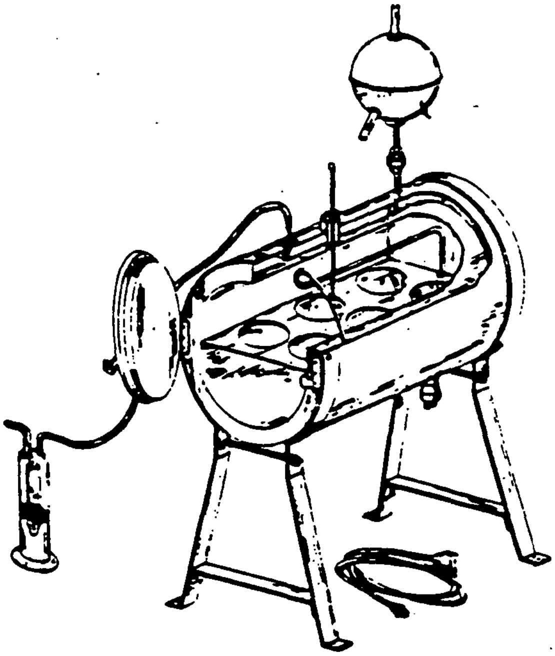
differ by more than 0.2 %
s than 5 % moisture and 0.3
more than 5 % moisture.
ibility—The results submit-
laboratories should not be
unless they differ by more
oals having less than 5 %
% for coals having more than



NOTE—Details in U.S. Bureau of Mines Bulletin No. 492, 1951, p 6

FIG. 1 Moisture Oven

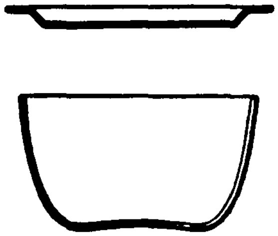


FIG. 2 Capsule for Use in Determining Moisture.

Designation: D 3174 - 82

Standard Test Method for
ASH IN THE ANALYSIS SAMPLE OF COAL AND COKE FROM COAL[1]

This standard is issued under the fixed designation D 3174; 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 the inorganic residue as ash in the analysis sample of coal or coke as prepared in accordance with Method D 2013 or Method D 346. The results obtained can be applied as the ash in the proximate analysis, Method D 3172, and in the ultimate analysis, Method D 3176. For the determination of the constituents in ash, reference is made to Method D 2795 and D 3682. See Definitions D 121 for definition of ash.

2. Applicable Documents

2.1 *ASTM Standards:*

D 121 Definitions of Terms Relating to Coal and Coke[2]
D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]
D 388 Classification of Coals by Rank[2]
D 1756 Test for Carbon Dioxide in Coal[2]
D 1757 Tests for Sulfur in Ash from Coal and Coke[2]
D 2013 Preparing Coal Samples for Analysis[2]
D 2795 Analysis of Coal and Coke Ash[2]
D 3172 Proximate Analysis of Coal and Coke[2]
D 3173 Test for Moisture in the Analysis Sample of Coal and Coke[2]
D 3176 Ultimate Analysis of Coal and Coke[2]
D 3180 Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]
D 3682 Test for Major and Minor Elements in Coal and Coke Ash by the Atomic Absorption Method[2]

3. Summary of Method

3.1 Ash is determined by weighing the residue remaining after burning the coal or coke under rigidly controlled conditions of sample weight, temperature, time, atmosphere, and equipment specifications.

4. Significance and Use

4.1 Ash, as determined by this method, is the residue remaining after burning the coal and coke. Ash obtained differs in composition from the inorganic constituents present in the original coal. Incineration causes an expulsion of all water, the loss of carbon dioxide from carbonates, the conversion of iron pyrites into ferric oxide, and other chemical reactions. Ash, as determined by this method, will differ in amount from ash produced in furnace operations and other firing systems because incineration conditions influence the chemistry and amount of the ash. References for correcting ash results determined by this method to a mineral-matter-free basis are listed in Method D 388, Section 8, Classification of Coal by Rank.

5. Apparatus

5.1 *Electric Muffle Furnace for Coal or Coke* (Note 1)—For determination of ash of coal, the furnace shall have an adequate air circulation and be capable of having its temperature regulated at 700 to 750°C. The furnace shall be equipped with a temperature indicator and means of controlling the temperature within

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[1] This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved March 3, 1982. Published May 1982.

Originally published as D 3174 – 73. Last previous edition D 3174-73 (1979).

[2] *1983 Annual Book of ASTM Standards*, Vol 05.05.

mits. Means shall be provided for
g air flow at a rate of 2 to 4 changes
see Figs. 1 and 2). Inlet and outlet
located and arranged to distribute
formly throughout the furnace area
e possibility of sweeping solid parti-
ie capsules. The temperature over
vorking area of the furnace floor
aintained within the specified tem-
mits.

Combustion gases shall be vented from

celain Capsules, about ⅞ in. (22 mm)
nd 1¾ in. (44 mm) in diameter, or
low dishes or platinum crucibles.
nce, sensitive to 0.1 mg.
cible Cover, aluminum, porcelain, or
rs.

rature Calibration

a preignited capsule with 1 g of
center of the working area of the
d by the use of a potentiometer and
uple or other suitable temperature
device measure the temperature of
the crucible. The crucible and sand
at temperature equilibrium with the
There should be 2 to 4 air changes per
ving throughout the furnace (the air
e measured by using a wet-test meter
nent calibrated at standard conditions
nnected to the ceramic-pipe exhaust).
furnace temperature until the poten-
ads 750°C ± 10 and then adjust or
temperature on the indicating pyrom-
this reading as the proper setting for
the furnace.

dure

nsfer approximately 1 g (weighed to
0.1 mg) of the thoroughly mixed
ote 2) to a weighed capsule and cover
An alternative way is to use the dried
the moisture determination in
3173. Place the capsule containing
e in a cold furnace and heat gradually
a rate that the temperature reaches 450
in 1 h.

—The sample shall be the material pul-
pass No. 60 (250-mm) sieve in accordance
thod D 2013 or Method D 346.

7.2 Continue heating so that a temperature of 700 to 750°C is reached by the end of the second hour. Continue the ashing at 700 to 750°C for two additional hours (Note 3). Remove the capsule from the muffle, place the cover on the capsule, cool under conditions to minimize moisture pickup, and weigh.

NOTE 3—While the 4-h incineration interval described is sufficient with most coals to reach a condition of complete burn-off, certain cokes and nonreactive coals may require additional time. If unburned carbon particles are observed, or if duplicate results are suspect, the samples should be returned to the furnace for sufficient time to reach a constant weight (± 0.001 g). By this means, pyritic sulfur will be oxidized and expelled before the calcite is decomposed. An ample supply of air in the muffle, "2 to 4 changes per minute," must be assured at all times to ensure complete oxidation of the pyritic sulfur and to remove the SO_2 formed. The 4-h time limit may be reduced if the sample reaches a constant weight at 700 to 750°C in less than 4 h.

NOTE 4—Some samples may be encountered that contain a high amount of carbonates (calcite) or pyrites, or both. In such cases sulfur retained as sulfates may be both unduly high and nonuniform between duplicate samples. In such cases sulfate sulfur in the ash can be determined in accordance with Method D 1757 and the value properly corrected. If such is done, the ash value should be reported and designated both as determined and corrected.

8. Calculations

8.1 Calculate the ash percent in the analysis sample as follows:

$$\text{Ash in analysis sample, \%} = [(A - B)/C] \times 100$$

where:

A = weight of capsule, cover, and ash residue, g,
B = weight of empty capsule and cover, g, and
C = weight of analysis sample used, g.

9. Report

9.1 For reporting analyses to other than as-determined basis, refer to Method D 3180.

10. Precision

10.1 The following criteria should be used for judging the acceptability of the results:

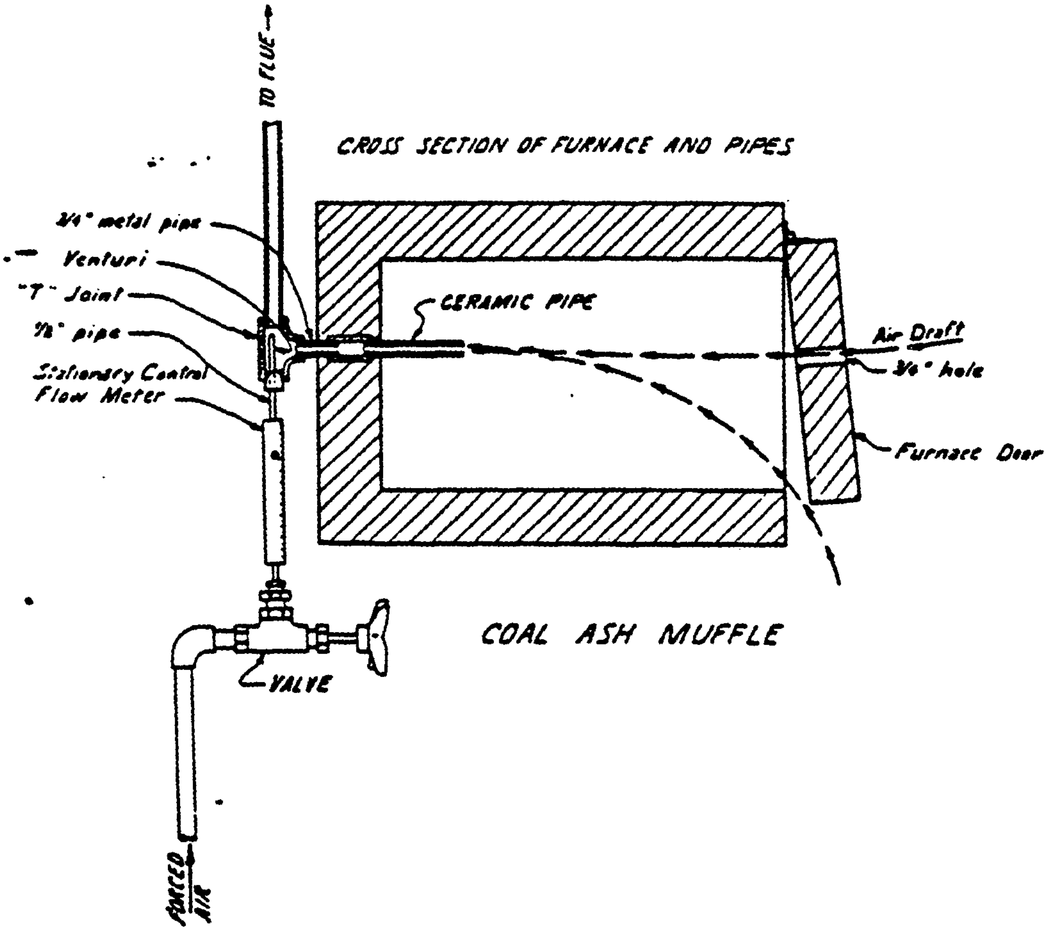
10.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than the following percentages:

No carbonates present	0.2 %
Carbonates present	0.3 %

Coals with more than 12 % ash containing carbonates and pyrites	0.5 %

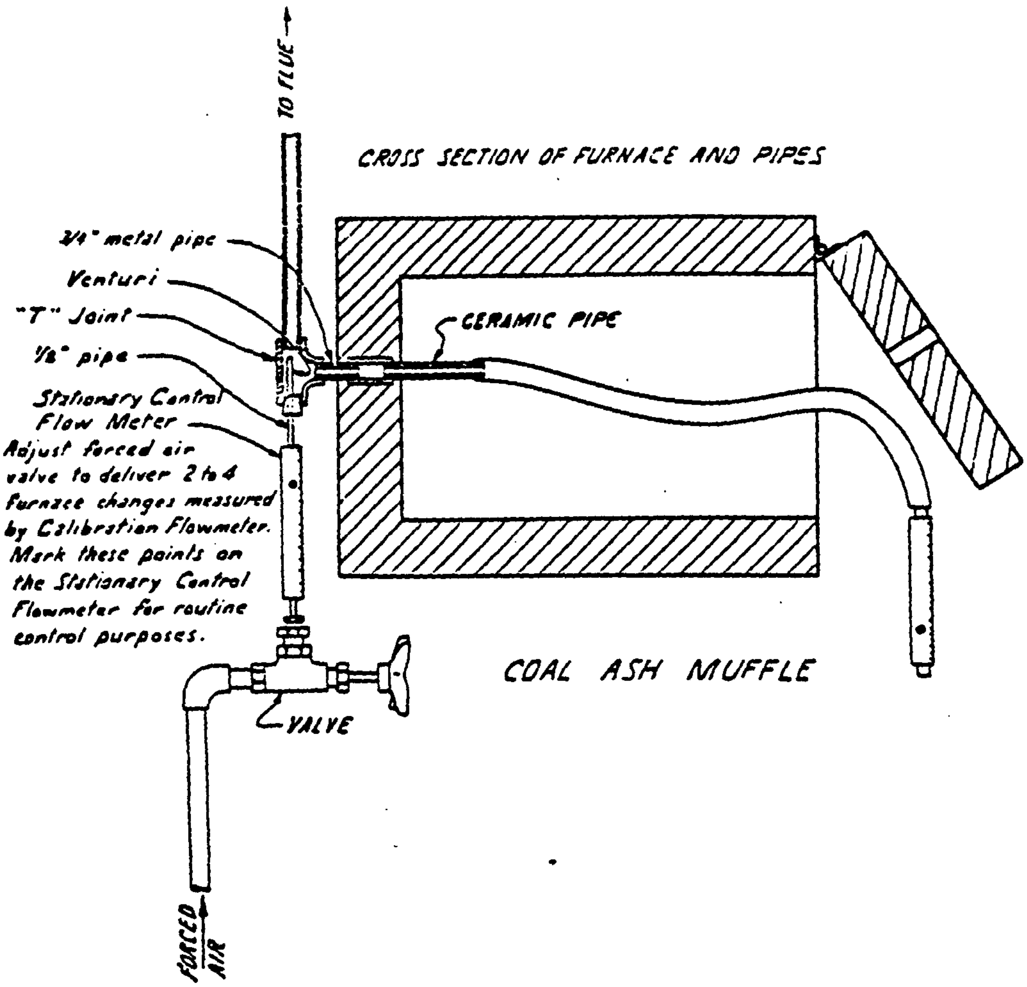
1.2 *Reproducibility*—Results submitted by two or more laboratories should not be considered suspect unless they differ by more than the following percentages:

No carbonates present	0.3 %
Carbonates present	0.5 %
Coals with more than 12 % ash containing carbonates and pyrites	1.0 %



(Suggested method for inducing regulated air flow through ashing furnace.)

FIG. 1 Air Aspirator



Calibration Flowmeter with Tubing—Ambient Air - For calibration use only. adjust forced air valve to deliver 2 to 4 furnace volume changes per minute (at standard temperature-pressure conditions.)

NOTE—Flowmeters are usually calibrated for one atmosphere at 70°F (760 mm Hg at 21.1°C).

(Suggested layout for calibration.)

FIG. 2 Air Aspirator

Designation: D 3175 - 82

Standard Test Method for
VOLATILE MATTER IN THE ANALYSIS SAMPLE OF COAL AND COKE[1]

This standard is issued under the fixed designation D 3175; 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 determines the percentage of gaseous products, exclusive of moisture vapor, in the analysis sample which are released under the specific conditions of the test.

2. Applicable Document

2.1 *ASTM Standard:*

D3173 Test for Moisture in the Analysis Sample of Coal and Coke[2]

3. Summary of Method

3.1 Volatile matter is determined by establishing the loss in weight resulting from heating a coal or coke under rigidly controlled conditions. The measured weight loss, corrected for moisture as determined in Method D 3173 establishes the volatile matter content. Two procedures are described to permit conformity with differences in sample behavior.

4. Significance and Use

4.1 Volatile matter, when determined as herein described, may be used to establish the rank of coals, to indicate coke yield on carbonization process, to provide the basis for purchasing and selling, or to establish burning characteristics.

5. Definition

5.1 *sparking fuels*—within the context of this standard, fuels that do not yield a coherent cake as residue in the volatile matter determination but do evolve gaseous products at a rate sufficient to mechanically carry solid particles out of the crucible when heated at the standard rate. Such coals normally include all low-rank noncaking coals and lignites but may also include those anthracites, semianthracites, bituminous, chars and cokes that lose solid particles as described above. These are defined as "sparking fuels" because particles escaping at the higher temperatures may become incandescent and spark as they are emitted.

6. Apparatus

6.1 *Platinum Crucible*, with closely fitting cover, for coal. 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.

6.2 *Platinum Crucible*, with closely fitting cover, for coke. The crucible shall be of 10-mL capacity, with capsule cover having thin flexible sides fitting down into crucible. Or the double-crucible method may be used, in which the sample is placed in 10-mL platinum crucible, which is then covered with another crucible of such a size that it will fit closely to the sides of the outer crucible and its bottom will rest [illegible] to ½ in. (8.5 to 12.7 mm) above the bottom of the outer crucible.

6.3 *Vertical Electric Tube Furnace*, for coal or coke. 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 thermocouple positioned in the furnace.

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[1] This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Aug. 27, 1982. Published December 1982. Originally published as D 3175 - 73. Last previous edition D 3175 - 77.

[2] *1983 Annual Book of ASTM Standards*, Vol 05.05.

rucedure

Procedure for nonsparking coals and

1 Weigh 1 g of the sample in a weighed
m crucible, close with a cover (Note 1),
on platinum or Nichrome-wire supports
sert directly into the furnace chamber,
shall be maintained at a temperature of
20°C, and lower immediately to the 950
Regulation of the temperature to within
scribed limits is critical. After the more
discharge of volatile matter has subsided
wn by the disappearance of the luminous
or, in the case of coke after 2 or 3 min,
the crucible (Note 2) to verify the lid is
operly seated. If necessary, reseat the lid
d against the admission of air into the
. Do this as rapidly as possible by rais-
crucible to the top of the furnace cham-
position the lid (Note 3) to more perfectly
crucible, then lower immediately back
950 zone. After heating for a total of
7 min, remove the crucible from the
and, without disturbing the cover, al-
to cool. Coke should be cooled in a
ator. Weigh as soon as cold. The per-
loss of weight minus the percentage
re equals the volatile matter.

1—The cover should fit closely enough so
carbon deposit from bituminous, subbitu-
and lignite coals does not burn away from
side.

2—Inspection of the crucible may be aided
use of a mirror held above the furnace well.

3—With some strongly caking low-volatile
ium-volatile bituminous coals, the coke but-
be broken with explosive violence, due to
ration of volatile matter within the button.
usually designated as "popping." Such pop-
blow the lid off the crucible and cause
cal losses of the coked material. When such
is observed, the determination shall be re-
d the test repeated until popping does not

Modified Procedure for All Sparking

Fuels that do not cake or cake weakly
volatile matter is determined shall be
d closely for sparking during the heating
(Note 2); also, at the end of the test the
cover shall be inspected for ash depos-
the presence of such deposits shall be
red as evidence of sparking.

All fuels that spark when the volatile is determined by the methods described in 7.1 shall be treated as follows: The sample shall be given a preliminary gradual heating such that a temperature of 600 ± 50°C is reached in 6 min (Note 4). After this preliminary heating the sample shall be heated for exactly 6 min at 950 ± 20°C. If sparking is then observed, the determination shall be rejected and the test repeated until no sparking occurs either during the preliminary heating or during the 6-min period at 950°C. Remove the crucible from the furnace, cool on a metal cooling block (Note 5) and weigh. The percentage loss in weight minus the percent moisture in accordance with Method D 3173, is the volatile matter. All analyses by this method shall be so marked when reported to indicate that the modified procedure was used.

NOTE 4—If a tubular furnace of the Fieldner type (Fig. 1) is used for the determination of volatile matter, the preliminary gradual heating may be accomplished by moving the crucible to predetermined positions in the cooler top zone of the furnace. Due to variations in the heating characteristics of the furnace, the operator must predetermine by thermocouple the proper positions to meet a preliminary heating rate as specified in 7.2.2. A mechanical device to lower the crucible into the furnace may be used to facilitate control of the lowering operation.

NOTE 5—To ensure uniformity of results, the cooling period should be kept constant and should not be prolonged beyond 15 min.

8. Calculations

8.1 Calculate the weight loss percent as follows:

$$\text{Weight loss, \%} = (A - B)/A \times 100$$

where:

A = weight of sample used, g, and
B = weight of sample after heating, g.

8.2 Calculate the volatile matter percent in the analysis samples as follows:

$$\text{Volatile matter in analysis sample, \%} = C - D$$

where:

C = weight loss, %, and
D = moisture, %.

9. Precision

9.1 The following criteria should be used for judging the acceptability of results:

9.1.1 *Repeatability*—Duplicate results by the same laboratory should not be considered suspect unless they differ by more than the following percentages:

High-temperature coke	0.2
Anthracite	0.3
Semianthracite, bituminous coal, low-temperature coke, and chars	0.5
Subbituminous	0.7
Lignite and peat	1.0

9.2.1 *Reproducibility*—The results submitted by two or more laboratories sho[illegible] not be considered suspect unless they diff[illegible] by more than the following percentages:

High-temperature coke	0.4
Anthracite	0.6
Semianthracite, bituminous coal, low-temperature coke, and chars	1.0
Subbituminous	1.4
Lignite and peat	2.0

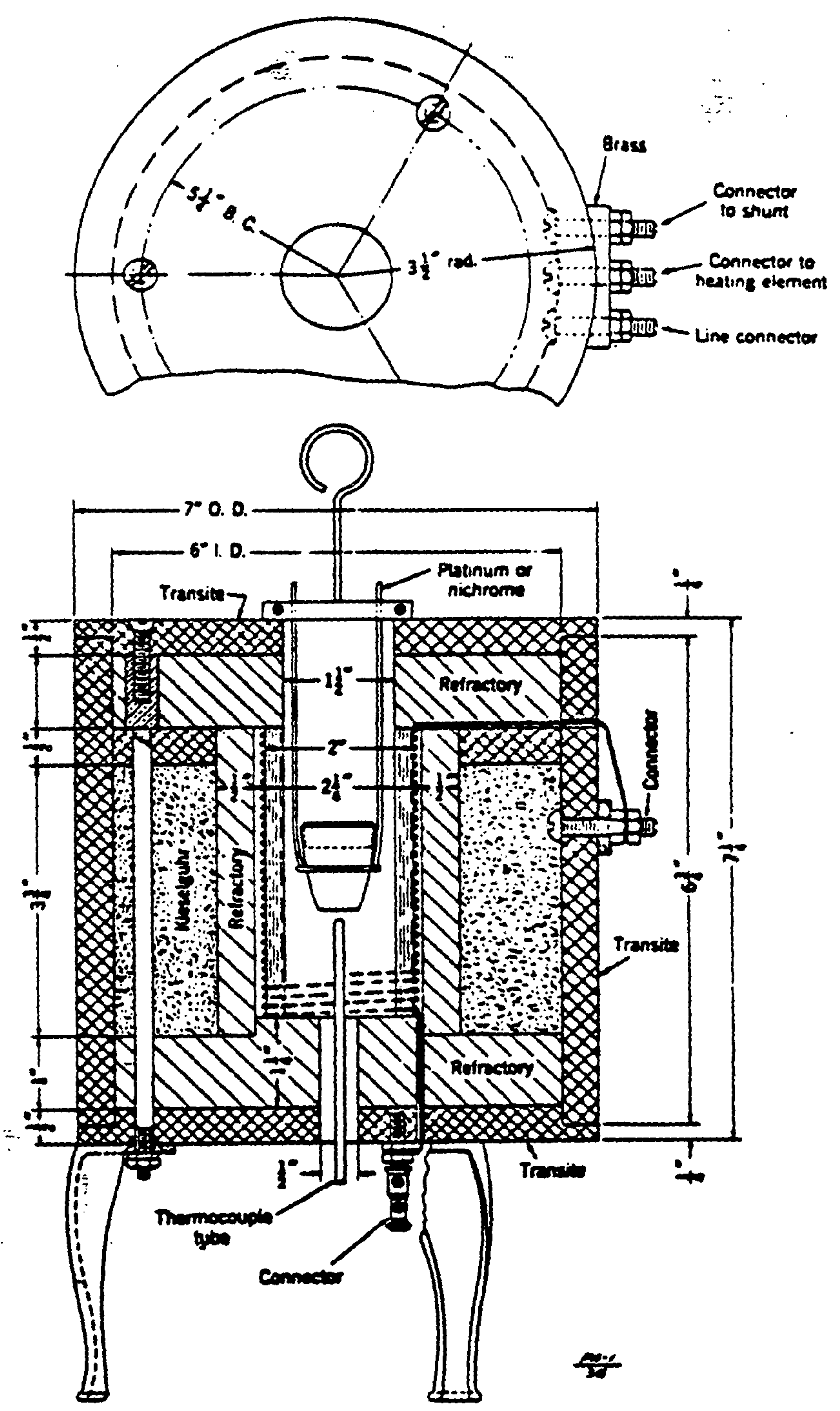

FIG. 1 Electric Furnace for Determining Volatile Matter

Attachment H-4
ULTIMATE ANALYSIS OF COAL AND COKE

Method: American Society for Testing Materials

Ultimate Analysis of Coal and Coke:	D3176-74 (1979)
Carbon and Hydrogen:	D3178
Sulfur:	D3177-82
Nitrogen:	D3179
Oxygen:	D3176

Note:

1. See Proximate Analysis for moisture, fixed carbon, volatile matter, and ash.
2. See Halogen Analysis.

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze soil and sediment samples for 1) Proximate analysis for: a) moisture content, b) ash, c) volatile matter, and d) fixed carbon. 2) Ultimate analysis for a) C, H, S, O, N 3) Heating Value, 4) Flash Point and 5) pH

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 54 soil samples and 20 sediment samples for the parameters listed above. The samples will have low to high concentrations of creosote and fuel oil.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Approximate number of days results required after lab receipt of samples:

Lab will report results within 30 days after receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

1) Elemental Analysis for carbon ASTM D3178 Ultimate Analysis of Coal and Coal D

3176-74 (1979) Hydrogen D 3178

Sulfur D 3177-82

Nitrogen D 3179

Oxygen by difference

See Attachment F-2

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

1) Note these samples may be toxic and/or flammable.

2) Note the special safety notice in each method

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

1) Supply copies of all lot notebook pages and related data. 2) Copies of all instrument data printouts. 3) All QC data, standards data and sample data

10. Other (use additional sheets or attach supplementary information, as needed):

Use a summary report form for sample reference and QC results

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414-272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, [illegible]

12. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (± % or Conc.)
% Sulfur	< 1%	See Table III
		Page 409
% Carbon/Hydrogen	< 1%	ASTM 05.05 1983
		D3176 (See attachment)
% Nitrogen	< 1%	D3176 for Table III
% Sulfur		
% Oxygen	By difference	

13. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits (± % or Conc.)
Blank	1 per 10 sample	< D.L.
Duplicate	1 per 10 sample	R % D < 10%
Reference Material*	1 per 10 sample	R % D < 10%
run in duplicates		% R 80-120%
		See Table 2 and 3
		D 3176

R% D = Relative Percent Difference
% R = Percent Recovery
*NBS or EPA approved test sample

14. ACTION REQUIRED IF LIMITS ARE EXCEEDED

1. Blank outliers rerun
2. Duplicate outliers rerun same sample
run different sample to varify matrix problem
3. Reference material. Rerun.

If outside limits call Dennis Wiscolowski 312-886-1971

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

Designation: D 3176 - 74 (Reapproved 1979)

An American National

Standard Method for
ULTIMATE ANALYSIS OF COAL AND COKE[1]

This standard is issued under the fixed designation D 3176. 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 term ultimate analysis as it is applied to the analysis of coal and coke. The information derived is intended for the general utilization by applicable industries. to provide the basis for evaluation. beneficiation. or for other purposes.

2. Applicable Documents

2.1 *ASTM Standards:*

D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 2013 Preparing Coal Samples for Analysis[2]

D 2234 Collection of a Gross Sample of Coal[2]

D 3173 Test for Moisture in the Analysis Sample of Coal and Coke[2]

D 3174 Test for Ash in the Analysis Sample of Coal and Coke[2]

D 3177 Test for Total Sulfur in the Analysis Sample of Coal and Coke[2]

D 3178 Test for Carbon and Hydrogen in the Analysis Sample of Coal and Coke[2]

D 3179 Test for Nitrogen in the Analysis Sample of Coal and Coke[2]

3. Definition

3.1 *ultimate analysis*—in the case of coal and coke. 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.

NOTE 1—The determination of phosphorus or chlorine is not by definition a part of the ultimate analysis of coal or coke. See Method D 2361 Test for Chlorine in Coal.[2] for the determination of chlorine and Method D 2795 Test for Analysis of Coal and Coke Ash.[2] for the determination of phosphorus

NOTE 2—Moisture is not by definition a part of the ultimate analysis of coal or coke but must be determined in order that analytical data may be converted to bases other than that of the analysis sample.

NOTE 3—Inasmuch as some coals contain mineral carbonates. and practically all contain clay or shale containing combined water. a part of the carbon. hydrogen. and oxygen found in the products of combustion may arise from these mineral components.

4. General Requirements

4.1 Coal sample collection shall be in accordance with Method D 2234. and sample preparation shall be in accordance with Method D 2013. Coke sampling and preparation shall be in accordance with Method D 346.

5. Specific Requirements

5.1 *Carbon and Hydrogen*—The carbon and hydrogen determination shall be made in accord with Method D 3178.

5.2 *Sulfur*—The sulfur determination shall be made in accordance with Method D 3177.

5.3 *Nitrogen*—The nitrogen determination shall be made in accordance with Method D 3179.

5.4 *Ash*—The ash determination shall be made in accordance with Method D 3174.

5.5 *Oxygen*—There being no satisfactory direct ASTM method of determining oxygen. it shall be calculated by subtracting from 100 the sum of the other components of the ultimate analysis. The result so obtained is affected by errors incurred in the other determinations of the ultimate analysis and also by the changes in

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[1] This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke.

Current edition approved May 27. 1974. Published June 1974.

[2] *1983 Annual Book of ASTM Standards*. Vol 05.05.

AND COKE[1]

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weight of the ash-forming constituents on ignition. By definition, oxygen calculated as a weight percentage of the analysis sample according to this procedure does not include oxygen in the mineral matter or in the ash, but does include oxygen in the free water (moisture) associated with the analysis sample. See Section 6 of this method for calculating and reporting results on other bases.

5.6 *Moisture*—The moisture determination shall be made in accordance with Method D 3173.

6. Calculating and Reporting Results

6.1 The results of an ultimate analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

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

6.3 It is recommended that for data reported on the as-received basis (or any other moist basis) a footnote or some other means be employed in the report to indicate whether the hydrogen and oxygen values reported do include or do not include the hydrogen and oxygen in the free water (moisture) associated with the sample.

6.4 Procedures for converting ultimate analysis sample data to other bases are presented in Table 1.

6.4.1 Symbols used in Table 1 are:

M = moisture, weight %
P = a symbol used interchangeably in the table to refer to ash, or carbon, or nitrogen, or sulfur, weight %
H = hydrogen, weight %
Ox = oxygen, weight %.

6.4.2 Subscripts used in Table 1 are

ad = as-determined from analysis sample
ar = as received or any other moisture-containing basis (that is, equilibrium capacity moisture basis, as-shipped moisture basis, bed moisture basis) if the appropriate moisture value is substituted for M_{ar} in the formulae
d = dry basis

6.4.3 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 as not containing the hydrogen and oxygen in water (moisture) reported on that basis. Alternative conversion procedures are shown in Table 1.

6.5 An example of ultimate analysis data tabulated for a hypothetical coal on various bases is given in Table 2.

7. Reproducibility of Results

7.1 The permissible differences between two or more determinations shall not exceed the values given in Table 3.

TABLE 1 Procedures for Converting As-Determined Values to Other Bases

Reporting Basis Parameter[A]	As-Determined[B]	Dry	As-Received[C, D]	
			H_{ar} and Ox_{ar} include H and Ox in Moisture (M_{ar})	H_{ar} and Ox_{ar} do not include H and Ox as M_{ar}
Ash Carbon Nitrogen (P) Sulfur	No corrections (See standard method)	$P_d = P_{ad} \times \left(\frac{100}{100 - M_{ad}}\right)$	$P_{ar} = P_{ad} \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)$	same as column at left
Hydrogen (H)	No corrections (See standard method)	$H_d = (H_{ad} - 0.1119M_{ad}) \times \left(\frac{100}{100 - M_{ad}}\right)$	$H_{ar} = \left[(H_{ad} - 0.1119M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)\right] + 0.1119M_{ar}$	$H_{ar} = (H_{ad} - 0.1119M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)$
Oxygen (Ox)	$Ox_{ad} = 100 - A_{ad} - C_{ad} - H_{ad} - N_{ad} - S_{ad}$	$Ox_d = (Ox_{ad} - 0.8881M_{ad}) \times \left(\frac{100}{100 - M_{ad}}\right)$ or $Ox_d = 100 - A_d - C_d - H_d - N_d - S_d$	$Ox_{ar} = \left[(Ox_{ad} - 0.8881M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)\right] + 0.8881M_{ar}$	$Ox_{ar} = (Ox_{ad} - 0.8881M_{ad}) \times \left(\frac{100 - M_{ar}}{100 - M_{ad}}\right)$

[A] All parameters expressed on a weight percent basis.

[B] Hydrogen and oxygen reported on as-determined basis include hydrogen and oxygen in free moisture associated with analysis sample.

[C] Alternative procedures are shown, differing on the basis of whether hydrogen and oxygen in the moisture are included or are not included in the reported values. A footnote or other means should be employed to indicate the basis used.

[D] To convert results to a moisture-containing basis other than as-received, as for example equilibrium capacity moisture, substitute the appropriate moisture value for M_{ar} in the equations.

TABLE 2 Ultimate Analysis Data

Test Parameter	As-Determined	Dry Basis	As-Received Basis	
	Hydrogen and oxygen include H and Ox in sample moisture (M_{ad})		Hydrogen and oxygen include H and Ox in sample moisture (M_{ar})	Hydrogen and oxygen do not include H and Ox in sample moisture (M_{ar})
Carbon, weight %	60.08	66.02	46.86	46.86
Hydrogen, weight %	5.44	4.87	6.70	3.46
Nitrogen, weight %	0.88	0.97	0.69	0.69
Sulfur, weight %	0.73	0.80	0.57	0.57
Ash, weight %	7.86	8.64	6.13	6.13
Oxygen, weight % (by difference)	25.01	18.70	39.05	13.27
Total %	100.00	100.00	100.00	70.98
Total moisture, weight % (as-received)	...		(29.02)	29.02
Moisture weight % (sample as-determined)	9.00			Total % 100.00

(Air-Dry Loss in accordance with Method D 2013 = 22.00%)

TABLE 3 Precision

	Permissible Differences, %	
	Same Laboratory	Different Laboratory
Sulfur:		
Coal, under 2 %	0.05	0.10
Coal, over 2 %	0.10	0.20
Coke	0.03	0.05
Carbon	0.3	...
Hydrogen	0.07	...
Nitrogen	0.05	...
Ash:		
No carbonates present	0.2	0.3
Carbonates present	0.3	0.5
Coals with more than 12% ash, containing carbonates and pyrites	0.5	1.0

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$\times \left(\frac{100}{100 - M_{ad}}\right)$

or

$Ox_d = 100 - A_d - C_d - H_d - N_d - S_d$

$\times \left(\frac{\ldots}{100 - M_{ad}}\right)\Big]$

$+ 0.8881 M_{ar}$

$\left(100 - M_{ad}\right)$

[A] All parameters expressed on a weight percent basis.

[B] Hydrogen and oxygen reported on as-determined basis include hydrogen and oxygen in free moisture associated with analysis sample.

[C] Alternative procedures are shown, differing on the basis of whether hydrogen and oxygen in the moisture are included or are not included in the reported values. A footnote or other means should be employed to indicate the basis used.

[D] To convert results to a moisture-containing basis other than as-received, as for example equilibrium capacity moisture, substitute the appropriate moisture value for M_{ar} in the equations.

Designation: D 3177 – 82

Standard Test Methods for
TOTAL SULFUR IN THE ANALYSIS SAMPLE OF COAL AND COKE[1]

1. Scope

1.1 These methods cover three alternative procedures for the determination of total sulfur in samples of coal and coke. Sulfur is included in the ultimate analysis of coal and coke.

1.2 The procedures appear in the following order.

	Sections
Method A—Eschka Method	5 to 8
Method B—Bomb Washing Method	9 to 11
Method C—High-Temperature Combustion Method	12 to 16

2. Applicable Documents

2.1 *ASTM Standards:*

D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Preparing Coal Samples for Analysis[2]

D 2015 Test for Gross Calorific Value of Solid Fuel by the Adiabatic Bomb Calorimeter[2]

D 3173 Test for Moisture in the Analysis Sample of Coal[2]

D 3176 Ultimate Analysis of Coal and Coke[2]

D 3180 Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

3. Summary of Methods

3.1 *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.

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

3.3 *High-Temperature Combustion Method*—A weighed sample is burned in a tube furnace at a temperature of 1350°C in a stream of oxygen. The sulfur oxides and chlorine formed are absorbed in a hydrogen peroxide (H_2O_2) solution yielding hydrochloric (HCl) and sulfuric (H_2SO_4) acids. The total acid content is determined by titration with sodium hydroxide (NaOH), and the amount of sodium chloride (NaCl) resulting from the titration of the HCl is converted to NaOH with a solution of mercuric oxycyanide (Hg(OH)CN). This sodium hydroxide is determined titrimetrically and used to correct the sulfur value which is equivalent to the amount of H_2SO_4 formed during combustion of the coal.

4. Sample

4.1 The sample shall be the material pulverized to pass No. 60 (250-μm) sieve in accordance with Method D 2013 or Method D 346.

4.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Method D 3173, so that calculation to other than the as determined basis can be made.

4.3 Procedures for converting as determined sulfur values obtained from the analysis sample to other bases are described in Method D 3176 and Method D 3180.

4.4 Standard Reference Material (SRM) 1631-Sulfur in Coal[4] consists of three different

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[1] These methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke and are the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Aug. 27, 1982. Published December 1982. Originally published as D 3177–73. Last previous edition D 3177 – 75 (1982).

[2] *1983 Annual Book of ASTM Standards*, Vol 05.05.

[3] *1983 Annual Book of ASTM Standards*, Vol 11.01.

[4] Available from the Office of Standard Reference Materials, Room B314, Chemistry Bldg., National Bureau of Standards, Washington, D.C. 20234.

MPLE OF COAL

following the designation indicates the
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ple is burned in a tube furnace
re of 1350°C in a stream of
fur oxides and chlorine formed
ı a hydrogen peroxide (H_2O_2)
·g hydrochloric (HCl) and sul-
cids. The total acid content is
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he amount of sodium chloride
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Reference Material (SRM)
Coal[4] consists of three different

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and Coke and are the direct responsibility
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low-volatile coal samples, each of which has a certified sulfur content. Sulfur values obtained by analyzing these coals, using any of the three methods described in this standard, may be used for checking the accuracy of analytical results.

ALTERNATIVE PROCEDURES

Method A—Eschka Method

5. Apparatus

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

NOTE 1—Gas may contain sulfur compounds.

5.2 *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 igniting the $BaSO_4$.

6. Reagents

6.1 *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 Available Reagents of the American Chemical Society, where such specifications are available.[5] 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.

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

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

6.4 *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.

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

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

6.7 *Methyl Orange Indicator Solution* (0.2 g/L)—Dissolve 0.02 g of methyl orange in 100 mL of hot water and filter.

6.8 *Sodium Carbonate, Saturated Solution*—Dissolve approximately 60 g of crystallized sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) or 22 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.

6.9 *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 the Na_2CO_3 solution.

7. Procedure

7.1 *Preparation of Sample and Mixture*—Thoroughly mix on glazed paper approximately 1 g of the sample, weighed to nearest 0.1 mg, and 3 g of Eschka mixture. The amount of sample to be taken will depend on the amount of $BaCl_2$ solution required in accordance with 7.3. Transfer to a porcelain capsule or porcelain crucible, or a platinum crucible, and cover with about 1 g of Eschka mixture.

7.2 *Ignition*—Heat the crucible over an alcohol, gasoline, or gas flame as described in 7.2.1, or in a gas or electrically heated muffle as described in 7.2.2 for coal and in 7.2.3 for coke. The use of artificial gas for heating the sample and the Eschka mixture is permissible only when the crucibles are heated in a muffle.

7.2.1 Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter which tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 min, gradually increase the temperature, and occasionally stir until all black particles have disappeared, which is an indication of the completeness of the procedure.

7.2.2 *For Coal*—Place the crucible in a cold-vented muffle and gradually raise the temperature to 800 ± 25°C in about 1 h. Maintain this maximum temperature until on stirring all

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[5] "Reagent Chemicals, American Chemical Society Specification," Am. Chemical Soc., Washington, D.C. 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, N.Y., and the "United States Pharmacopeia."

black particles have disappeared (about 1½ h).

7.2.3 *For Coke*—Place the crucible in a warm-vented muffle (about 200°C) and gradually raise the temperature to 800 ± 25°C in about 30 min. Maintain this maximum temperature until on stirring all black particles have disappeared.

7.3 *Subsequent Treatment*—Remove the crucible and empty the contents into a 200-mL beaker and digest with 100 mL of hot water for ½ to ¾ h. while stirring occasionally. By decantation, filter, and thoroughly wash the insoluble matter with hot water. After several washings in this manner, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated. Make the filtrate, amounting to about 250 mL, just neutral to methyl orange with NaOH or Na_2CO_3 solution; then add 1 mL of HCL (1 + 9). Boil again and add slowly from a pipet, while stirring constantly, 10 mL or more of $BaCl_2$ solution. The $BaCl_2$ solution must be 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. Continue boiling for 15 min and allow to stand for at least 2 h, or preferably overnight, at a temperature just below boiling. Filter through an ashless paper and wash 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.

7.3.1 Place the wet filter containing the precipitate of barium sulfate ($BaSO_4$) in a weighed platinum, porcelain, silica, or Alundum crucible, allowing a free access of air by folding the paper over the precipitate loosely to prevent spattering. Smoke the paper off gradually and at no time allow to burn with flame. After the paper is practically consumed, raise the temperature to approximately 925°C and heat to constant weight.

7.4 *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. 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 to 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 the conditions of precipitation prescribed, the solubility error for $BaSO_4$ is probably the largest one to be considered. Barium sulfate is soluble[6] in acids and 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 redissolve.

8. Calculation

8.1 Calculate the sulfur content as follows:

$$\text{Sulfur, \%, in the analysis sample} = \frac{(A - B) \times 13.73}{C}$$

where:

A = grams of $BaSO_4$ precipitated,
B = grams of $BaSO_4$ correction, and
C = grams of sample used.

Method B—Bomb Washing Method[7]

9. Reagents

9.1 *Purity of Reagents*—(See 6.1.)

9.2 *Purity of Water*—(See 6.2.)

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

9.4 *Hydrochloric Acid* (1 + 1)—(See 6.5)

9.5 *Sodium Carbonate Solution*—Dissolve 20.90 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.

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

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[6] *Journal of the American Chemical Society*, JACSA, Vol 32, 1910, p. 588; Vol 33, 1911, p. 829.

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

10. Procedure

10.1 *Ignition*—Sulfur is determined in the washings from the oxygen-bomb calorimeter following the calorimetric determination (Method D 2015). 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 (Sections 4 to 8 of Method D 2015). The bomb shall stand in the calorimeter water for not less than 5 min after firing.

10.2 *Subsequent Treatment*—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. 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 (9.6) 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.

10.3 Collect the washings in a 250-mL beaker and titrate with standard sodium carbonate solution (9.5) to obtain the "acid correction" for the heating value, as specified under the calorimetric determination D 2015. Adjust the pH to 5.5 to 7.0 with dilute NH_4OH, heat the solution to boiling, and filter through a qualitative paper. Wash the residue and paper thoroughly five or six times with hot water. Adjust the acidity of the filtrate and washings, amounting to about 250 mL, precipitate, and determine the sulfur as specified under the Eschka method, Sections 5 to 8.

Method C—High-Temperature Combustion Method[8]

11. Apparatus

11.1 *Tube Furnace*—Capable of heating a tube approximately 34-mm external diameter over a length of 150 mm to a temperature of 1350°C. It is heated electrically using either silicon carbide resistance rods or a resistance wire.

NOTE 2—Induction furnace techniques may be used provided it can be shown that they meet the precision requirements of Section 17.

11.2 *Combustion Tube*—Approximately 28-mm internal diameter with a 3-mm wall thickness and 750 mm in length, which is gas tight at working temperature. A high-temperature porcelain or zircon straight refractory tube has been found most efficient. It requires a silica (12.12) adaptor with a flared end that just fits inside the combustion tube and serves as an exit for the gases. Alternatively, the combustion may be carried out in a tapered end tube that is directly connected to the elbow of the fritted gas bubbler (12.8) or to a 10/30 standard-taper ground-joint which is attached to a borosilicate glass right-angle bend. The temperature at the tapered end of the tube should be high enough to prevent condensation in the tube itself.

11.3 *Oxgen Cylinder*, fitted with pressure regulator and needle valve to control flow rate of oxygen.

11.4 *Flowmeter*, for measuring an oxygen flow rate of 300 mL/min.

11.5 *Sample Combustion Boats*—Iron-free, unglazed porcelain or zircon boats. A convenient size is 100-mm long, 19-mm wide, and 11-mm deep.

11.6 *Heat-Resistant Wire*, 1.5-mm thick with bent end to remove boats from combustion tube.

11.7 *Silica Pusher or Heat-Resistant Rod*, with a disk end for pushing the combustion boat into the hot zone. The pusher passes through a T-piece which is fitted into a rubber stopper at the inlet end of the combustion tube. The open end of the T-piece is sealed with a rubber tube or one-holed stopper to permit movement of the pusher and prevent escape of oxygen which enters at the side limb of the T. The rubber stopper or tube should be changed periodically to avoid leakage.

11.8 *Gas Absorption Bottles with Fritted Disk*, 125-mL capacity, for gas absorption. Fritted

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[8] Based on the method of Mott, R. A., and Wilkinson, H. C., "Determination of Sulfur in Coal and Coke By the Sheffield High Temperature Method," *Fuel*, FUEL B, Vol 35, 1956, p. 6. This method is designed for the rapid determination of sulfur in coal and coke. It is not applicable to coals or coal density fractions that have been subjected to treatment with chlorinated hydrocarbons because of the potentially high acidity of the combustion gases.

glass end porosity should be 15 to 40 μm. The bottle should be of such a diameter that the fritted end is covered by peroxide solution to a depth of at least 50 mm. The bottles are fitted, in a series of two per combustion tube, to the outlet end of a combustion tube. Alternatively a single narrow gas absorber may be used so that the fritted bubbler is covered to a depth of at least 90 mm.

11.9 *Vacuum Regulating Bottle*, containing mercury with an open-ended tube dipping into it.

11.10 *U-tube*, packed with soda-asbestos.

11.11 *Vacuum Source*.

11.12 *Silica Adaptor*, 300-mm long by 8 mm in outside diameter and flared at one end to 26 mm.

12. Reagents

12.1 *Purity of Reagents*—(See 6.1.)

12.2 *Purity of Water*—(See 6.2.)

12.3 *Aluminum Oxide* (Al_2O_3), finely divided and dried at 1350°C.

12.4 *Hydrogen Peroxide* (H_2O_2) *Solution*—One volume percent (50 mL of 30 % H_2O_2 with 1450 mL of water). The pH is adjusted (using NaOH or H_2SO_4 as appropriate) to that which is used for the end point in the titration. Solutions should be discarded after 2 or 3 days.

12.5 *Indicator*—Indicators that change color (titration end point) between pH 4 and 5 are recommended, but in no case should the pH exceed 7. Adequate lighting and stirring to ensure proper detection of the end point is essential. A choice of indicators or use of a pH meter is permitted. Directions for preparing two acceptable mixed indicators are as follows:

12.5.1 Mix 1 part methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) with 3 parts bromcresol green solution (dissolve 0.083 g in 20 mL of ethanol and dilute to 100 mL with water). Discard the mixed solution after 1 week.

12.5.2 Mix equal volumes of methyl red solution (dissolve 0.125 g in 60 mL of ethanol and dilute to 100 mL with water) and methylene blue solution (dissolve 0.083 g in 100 mL) of ethanol and store in a dark glass bottle). Discard the mixed solution after 1 week.

12.6 *Mercuric Oxycyanide Hg(OH)CN* (Note 3)—One g/80 mL of water. Prepare fresh solution every 2 or 3 days.

NOTE 3—This is a highly poisonous substance and will explode when touched with a flame or by percussion.

12.7 *Soda-Asbestos*, 8 to 20 mesh.

12.8 *Sodium Hydroxide* (*NaOH*) *Solution*, 0.050 *N*.

12.9 *Sulfuric Acid* (H_2SO_4), 0.050 *N*.

13. Procedure

13.1 Raise the temperature of the furnace to 1350°C at such a rate that the combustion tubes will withstand the thermal shock. Measure 100 mL of 1 % H_2O_2 (12.4) into two gas absorption bottles so that at least 50 mm of the fritted disk is covered in the first bottle, or pour the whole amount into a single absorption bottle. Assemble the apparatus as shown in Fig. 1 except do not connect the rubber tube from the oxygen supply to the soda-asbestos U-tube. Draw air through at about 350 mL/min. The rate of flow can be adjusted by changing the depth of penetration into the mercury of the open-ended glass tube in the vacuum regulating bottle. Connect the oxygen supply to the U-tube and adjust the rate of flow of oxygen to 300 mL/min. This flow rate, at a temperature of 1350°C, will prevent the formation of oxides of nitrogen. The preliminary adjustment to 350 mL/min of air ensures that the connections at the outlet end of the combustion tube are under slightly reduced internal pressure and no leak of combustion products will occur.

13.2 Weigh about 0.5 g of the analysis sample (Note 4) to the nearest 0.1 mg and spread evenly in a combustion boat previously lined with a thin layer of Al_2O_3 (0.02 to 0.05 g); then cover with approximately 0.5 g of Al_2O_3.

NOTE 4—It may be necessary to grind coals of high mineral matter content to pass through a No. 100 (150-μm) sieve.

13.3 Put the charged boat into the inlet end of the combustion tube so that the center of the boat is 270 mm from the center of the combustion tube hot zone, and if necessary readjust the rate of flow of oxygen to 300 mL/min. Move the boat forward a distance of 30 mm at the beginning of each minute with the exception of the sixth minute, for the next 10 min. The boat should be left at the fifth minute position until the seventh minute to ensure a slow heating rate. At the end of the 10-min period the combustion boat will be in the center of the hot zone. Withdraw the pusher after each movement to prevent distortion of the rod.

Keep the boat in the hot zone for an additional 4 min. Disconnect the gas absorption bottles and withdraw the boat onto a sheet of asbestos. This heating program has been established for all types of coal, and where it is shortened for a particular coal, results should be checked against those obtained by using the longer heating schedule.

13.4 Pour the content of the absorption bottles into a suitable titration flask. Wash the bottles and the interior of the silica adaptor with water (12.2) and add the washings to the flask. Add 5 or 6 drops of indicator solution and titrate with 0.050 *N* NaOH solution (12.8). The total acidity, due to oxides of sulfur and chlorine, is given according to the following reactions:

$$SO_2 + H_2O_2 \rightarrow H_2SO_4$$
$$Cl_2 + H_2O_2 \rightarrow 2\ HCl + O_2$$

13.5 After titration, the chloride ion is present in solution as NaCl. Convert the NaCl to NaOH by adding 20 mL of Hg(OH)CN (13.6) solution (sufficient for coals containing up to 1.2 % chlorine):

$$NaCl + Hg(OH)CH \rightarrow HgClCN + NaOH$$

13.6 Titrate the liberated NaOH with the 0.050 *N* H_2SO_4 (12.9). Make a blank determination in the same manner but without sample.

14. Calculation

14.1 Calculate the percentage sulfur in coal as follows:

$$S = \frac{1.603\ [F_1(a-a_1) - F_2(b-b_1)]}{W}$$

where:

S = percent sulfur in coal,
a = millilitre of NaOH solution used in full determination,
a_1 = millilitre of NaOH solution used in blank determination,
b = millilitre of H_2SO_4 used in full determination,
b_1 = millilitre of H_2SO_4 used in blank determination,
F_1 = normality of the NaOH solution,
F_2 = normality of the H_2SO_4 solution, and
W = grams of coal taken.

15. Report

15.1 The results of the sulfur analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

15.2 Use the percentage of moisture in the sample passing a No. 60 (260-μm) sieve to calculate the results of the analysis sample to a dry basis.

15.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Specifications D 3176 and D 3180.

PRECISION

16. Eschka and Bomb-Washing Methods

16.1 *Repeatability*—Results of two consecutive determinations carried out on the same sample in the same laboratory by the same operator using the same apparatus should not differ more than the following:

	%
Coal containing less than 2 % sulfur	0.05
Coal containing 2 % sulfur or more	0.10
Coke	0.03

16.2 *Reproducibility*—The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ by more than the following:

	%
Coal containing less than 2 % sulfur	0.10
Coal containing 2 % sulfur or more	0.20
Coke	0.05

17. High-Temperature Combustion Method

17.1 *Repeatability*—Results of two consecutive determinations carried out on the same sample in the same laboratory by the same operator using the same apparatus should not differ more than 0.05 % sulfur for all coal and coke.

17.2 *Reproducibility*—The means of results of duplicate determinations carried out by different laboratories on representative samples taken from the same bulk sample after the last stage of reduction should not differ more than the following:

	%
Coals containing less than 2 % sulfur	0.15
Coals containing 2 % sulfur or more	0.25
Coke	0.15

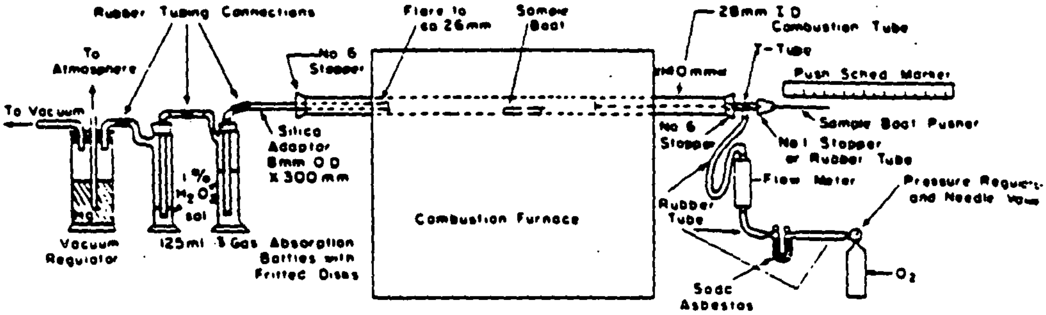

FIG. 1 High-Temperature Combustion Tube Furnace for the Determination of Total Sulfur in Coal

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ATTACHMENT C

Designation: D 3178 - 73

Standard Test Methods for
CARBON AND HYDROGEN IN THE ANALYSIS SAMPLE OF COAL AND COKE[1]

This Standard is issued under the fixed designation D 3178; 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.

1. Scope

1.1 These methods cover the determination of total carbon and hydrogen in samples of coal or coke. Both the carbon and hydrogen are determined in one operation. This method yields the total percentages of carbon and hydrogen in the coal 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 sample as well as hydrogen present as water of hydration of silicates.

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 sample and the calculated hydrogen present as water of hydration of silicates.

1.2 When data are converted and reported on the "dry" basis the hydrogen value is corrected for the hydrogen present in the free moisture accompanying the sample.

2. Applicable Documents

2.1 *ASTM Standards:*

D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]
D 1193 Specification for Reagent Water[3]
D 2013 Preparing Coal Sample for Analysis[2]
D 3173 Test for Moisture in the Analysis Sample of Coal[2]
D 3176 Ultimate Analysis of Coal and Coke[2]
D 3180 Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

3. Sample

3.1 The sample shall be the material pulverized to pass No. 60 (250-μm) sieve and well mixed according to Method D 346 or Method D 2013. It may be beneficial to grind the ash, pit ash, calcined coke and high mineral content materials to pass a No. 100 (150-μm) sieve.

3.2 The test sample should be weighed just prior to commencing the analysis to minimize chance for moisture change. A change in moisture content would introduce error in the hydrogen analysis. In order to provide the data necessary to correct for the hydrogen present in the moisture and ensuing final calculations of both the hydrogen and carbon, a separate sample should be weighed out at the same time for a moisture analysis, and analyzed in accordance with Method D 3173.

TOTAL CARBON AND TOTAL HYDROGEN

4. Summary of Method

4.1 The determination of carbon and hydrogen is made by burning a weighed quantity of sample in a closed system and fixing the products of combustion in an absorption train after complete oxidation and purification from interfering substances. This method gives the total percentages of carbon and hydrogen in the coal as analyzed, and includes the carbon in carbonates and the hydrogen in the moisture and in the water of hydration of silicates.

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[1] These methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke.

Current edition approved Nov. 27, 1973. Published March 1974.

[2] *Annual Book of ASTM Standards*, Part 26.

[3] *Annual Book of ASTM Standards*, Part 31.

5. Apparatus

5.1 *Oxygen Purifying Train*, consisting of the following units arranged as listed in the order of passage of oxygen:

5.1.1 *First Water Absorber*—A container for the solid dehydrating reagent. It shall be so constructed that the oxygen must pass through a column of reagent adequate to secure water equilibrium equal to that secured in the prescribed absorption train. 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.

5.1.2 *Carbon Dioxide Absorber*—A container for solid carbon dioxide absorbing agent. It shall be constructed as described in 5.1.1 and shall provide for a column of reagent adequate to remove carbon dioxide completely.

5.1.3 *Second Water Absorber*, same as specified in 5.1.1.

5.2 *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 preceding the first water absorber is recommended to permit easy and accurate adjustment of the rate of flow.

5.3 *Combustion Unit*—The combustion unit shall consist 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:

5.3.1 *Furnace Section 1*, 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 850 to 900°C (Note 2).

5.3.2 *Furnace Section 2*, 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 (Note 2).

5.3.3 *Furnace Section 3*, 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.

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.

5.3.4 *Combustion Tube*—The combustion tube shall be made of fused quartz or high-silica glass[4] and shall have 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 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. 1).

5.3.5 *Combustion Boat*—This shall be either glazed porcelain, fused silica, or platinum. Boats with internal dimensions of approximately 70 by 8 by 8 mm have been found convenient.

5.4 *Absorption Train*—The absorption train shall consist of the following units arranged as listed in the order of passage of oxygen:

5.4.1 *Water Absorber*, having a capacity for 45 cm³ of solid reagent and a minimum length of gas travel through the reagent of 80 mm.[5]

5.4.2 *Carbon Dioxide Absorber*—If solid reagents are used for carbon dioxide absorption the container shall be as described in 5.4.1. If a solution is used, the container shall be a Vanier bulb.

5.4.3 *Guard Tube*—A container as described in 5.4.1.

6. Reagents

6.1 *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 availabl
used, provided it is
reagent is of sufficie
its use without lesse
determination.

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[4] Vycor has been found satisfactory for this purpose.

[5] Glass-stoppered containers such as the Nesbitt, Schwartz U-tube and the Stetser-Norton bulbs have been found satisfactory.

6.2 *Purity of Wat*
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to mean reagent wat
cation D 1193.
6.3 *Oxygen*, 99.5
6.4 *Combustion T*
6.4.1 *Cupric Oxid*
free.
6.4.2 *Fused Lead*
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6.4.3 *Silver Gauz*
purity, 0.84 mm, m
No. 27 B&S gage wi
6.4.4 *Copper Gau*
mum purity, 0.84
mately No. 26 B&S
6.5 *Purification*
Reagents:
6.5.1 *Water Absor*
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mately 2.38 to 0.35

NOTE 3—Trade nam
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6.5.2 *Carbon Dio*
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complete absorption

7. Preparation of

7.1 *Combustion*
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limits of 19 to
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d mm. If a
is used, a trans-
located 250 mm
the tube, will be

This shall be either
lica, or platinum.
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have been found

he absorption train
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aving a capacity for
a minimum length
eagent of 80 mm.[9]
Absorber—If solid
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ts—Reagent grade
in all tests. Unless
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ty, where such speci-

fications are available.[9] 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.

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

6.3 *Oxygen*, 99.5 % purity or better (Note 6).

6.4 *Combustion Tube Reagents:*

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

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

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

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

6.5 *Purification and Absorption Train Reagents:*

6.5.1 *Water Absorbent*—Anhydrous magnesium perchlorate ($Mg(ClO_4)_2$) of approximately 2.38 to 0.35 mm size.

NOTE 3—Trade names of the reagents are Anhydrone and Dehydrite.

6.5.2 *Carbon Dioxide Absorbent*—If a solid reagent is used, it shall be sodium or potassium hydroxide (NaOH or KOH) impregnated in an inert carrier of approximately 2.38 to 0.84 mm 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—Trade names of the sodium and potassium hydroxide permissible solid carbon dioxide absorbing reagents are: 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 this reagent to assure complete absorption of carbon dioxide.

7. Preparation of Apparatus

7.1 *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. The arrangement and [illegible] shall be as shown in Fig. 1. 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 is used as a tube filling, the required length of filling may be prepared conveniently from three or four strips of silver gauze 150 to 200 mm long, 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.

7.2 *Absorption Train:*

7.2.1 *Water Absorber*—A container is filled with a permissible solid desiccant by adding the required amount in small portions and settling each portion by gentle tapping between additions. A glass wool plug shall be placed between the reagent and the absorber outlet to prevent loss of reagent "dust".

7.2.2 *Carbon Dioxide Absorber*—If a solid reagent is used for the retention of carbon dioxide, the absorber shall be filled as described in 7.2.1. A layer or "cap" of desiccant shall be placed in the outlet section of the container and 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. If a liquid absorbent is used, the inner tube of the Vanier bulb shall be filled with the same desiccant used in the water absorber. A glass wool plug shall be placed in the outlet section of the container to prevent loss of reagent "dust".

7.2.3 *Guard Tube*, packed with equal volumes of the water absorbent and a solid carbon dioxide absorbent.

7.2.4 *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 of flexible tubing as seals. The connection between the purification train and the

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[9] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. 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, N. Y., and the "United States Pharmacopeia."

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.

7.3 *Conditioning of Apparatus:*

7.3.1 *Newly Packed Combustion Tube*—Burn a sample of coal or coke as described in 8.4 except that the products of combustion need not be fixed in a weighed absorption train.

7.3.2 *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 absorption bulbs connected. A variation of not more than 0.5 mg of either bulb shall be considered satisfactory.

NOTE 6—If the blank tests for flow indicate interfering impurities in the oxygen supply by consistent weight-gain in the absorption bulbs, eliminate these impurities by using a preheater furnace and tube, filled with cupric oxide. Operate this preheater furnace at 850 ± 20°C and insert in series between the supply tank of oxygen and the purification train.

7.3.3 *Absorption Train*—Condition freshly packed absorber and guard tubes by burning a sample of coal or coke as described in 8.4 except that tube weights need not be determined.

7.3.4 *Standard Checks* shall be made frequently, particularly when intermittent use of the combustion train is common or when any changes have been made in the system. A standard substance of certified analysis, such as benzoic acid or sucrose as furnished by the National Bureau of Standards shall be burned as described in Section 8. A variation from the theoretical of not more than 0.07 % for hydrogen nor more than 0.30 % for carbon shall be considered satisfactory.

8. Procedure

8.1 After the combustion tube and absorbers have been conditioned as prescribed in Section 7, conduct the test as follows:

8.2 *Absorption Train*—Bring the absorption tubes 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 to the nearest 0.1 mg.

8.3 *Sample*—Weigh approximately 0.2 g (weighed to the nearest 0.1 mg) of air-dry sample ground to pass a No. 60 (250-μm) sieve into a combustion boat.

8.4 *Sample Analysis*—With furnace Section 5.3.2 and 5.3.3 at specified temperatures and positioned as shown in Fig. 1, perform the following operations in rapid succession in the order listed:

8.4.1 If a conventional type of sample heating furnase is used for heating 5.3.1, place it so that its left-hand edge is about 100 mm from the oxygen inlet end of the combustion tube.

8.4.2 Attach the weighed absorption train to the tube:

8.4.3 Push the sample boat into the tube to a point within approximately 20 mm from plug P_3;

8.4.4 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 7.3.2).

8.4.5 Apply full heat to heating section No. 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 heating 5.3.2 in 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 tube for 10 min (Note 8), 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 atmosphere, wipe them with a chamois or lint-free cloth in the areas handled, and finally weigh them to the nearest 0.1 mg. While the absorbers are cooling, it is recommended that the ash remaining in the combustion boat be examined for traces of unburned carbon which, if present, will nullify the determination.

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

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

9. Calculations

9.1 Calculate the pe
9) in the analysis samp

Carbon, % = (

where:

A = increase in weig
bulb, g, and

B = grams of samplec

NOTE 9—It is recognize
of nitrogen during the co
lead to slightly high resu
extensive study of this effe
to the conclusion that erro
significant in commercia
research applications, wh
order is required, means
nitrogen prior to water and
should be included

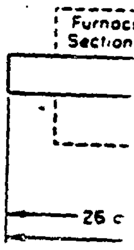
9.2 *Hydroge*- Calc
hydrogen in the analys
follows:

Hydrogen, % =

where:

B = grams of sample u

C = increase of weigh
bulb, g.



A—Clear fused quartz sectio
B—Cupric oxide filling.
C—Lead chromate or silver
P_1, P_2, or P_3—oxidized copp
NOTE—All dimensions ar
changes in the above dimensio

9. Calculations

9.1 Calculate the percentage of carbon (Note 9) in the analysis sample as follows:

$$\text{Carbon, \%} = (A \times 27.289)/B$$

where:

A = increase in weight of CO_2 absorption bulb, g, and

B = grams of sampled used.

NOTE 9—It is recognized that formation of oxides of nitrogen during the combustion procedure may lead to slightly high results for carbon. However, extensive study of this effect by five laboratories led to the conclusion that error so incurred would not be significant in commercial application. In certain research applications, where accuracy of a higher order is required, means of removing oxides of nitrogen prior to water and carbon dioxide absorption should be included.

9.2 *Hydrogen*—Calculate the percentage of hydrogen in the analysis sample (Note 10) as follows:

$$\text{Hydrogen, \%} = (C \times 11.19)/B$$

where:

B = grams of sample used, and

C = increase of weight of water absorption bulb, g.

NOTE 10—The water absorbed in the water absorption tube includes not only water formed as a product of combustion, but also free water (moisture) in the sample and water of hydration of any clay minerals present

10. Report

10.1 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.

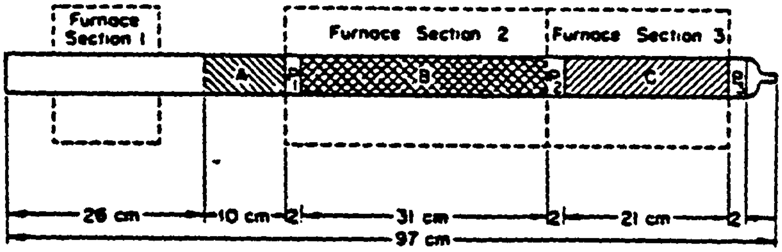
10.2 Use the percentage of moisture in the sample passing a No. 60 (250-μm) sieve to calculate the results of the analysis sample to a dry basis.

10.3 Procedures for converting the values obtained on the analysis sample to other bases are described in D 3176 and D 3180.

11. Precision

11.1 The permissible differences between two or more determinations shall not exceed the following values:

	Repeatability, %	Reproducibility, %
Carbon	0.3	...
Hydrogen	0.07	...



A—Clear fused quartz section (optional) when a translucent quartz tube is used

B—Cupric oxide filling.

C—Lead chromate or silver filling

P_1, P_2, or P_3—oxidized copper gauze plugs.

NOTE—All dimensions are given in centimeters. When furnace sections longer than those specified in 5.3 are to be used, changes in the above dimensions shall be in accordance with the provisions of Note 5.

FIG. 1 Arrangement of Tube Fillings for Combustion Tube.

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ASTM Designation: D 3179 – 73 (Reapproved 1979)

An American National Standard

Standard Test Methods for
NITROGEN IN THE ANALYSIS SAMPLE OF COAL AND COKE[1]

This standard is issued under the fixed designation D 3179; 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 These methods cover the determination of total nitrogen in samples of coal or coke. The analytical data from these methods are to be reported as part of ultimate analysis where ultimate analysis is requested. If ultimate analysis is not requested the value is to be reported according to the request.

2. Applicable Documents

2.1 *ASTM Standards:*

- D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]
- D 1193 Specification for Reagent Water[3]
- D 2013 Preparing Coal Samples for Analysis[2]
- D 3173 Test for Moisture in the Analysis Sample of Coal and Coke[2]
- D 3176 Ultimate Analysis of Coal and Coke[2]
- D 3180 Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

3. Summary of Methods

3.1 The determination of nitrogen is made by either the Kjeldahl-Gunning method (Section 7) or the alternative method (Section 8). In these procedures nitrogen is converted into ammonium salts by destructive digestion of the sample with a hot, catalyzed mixture of concentrated sulfuric acid and potassium sulfate. These 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.

4. Apparatus

4.1 *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 7.1 (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 autotransformer, may be needed to maintain the specified rates of digestion and distillation.

4.2 *Distillation Unit*—An electrical heater or gas burner as described in 4.1; either type shall be provided with adequate means of control to maintain distillation rates as described in 7.1. Commercially made, multiple-unit distillation racks provided with water-cooled glass or block tin condensers may be used.

4.3 *Condenser*, glass, water-cooled, having a minimum jacket length of 500 mm. This apparatus is not ordinarily required when a commercially made distillation rack is used.

4.4 *Kjeldahl Digestion Flask*, of heat-resistant[4] glass, having a capacity of 500 or 800 ml.

4.5 *Kjeldahl Connecting Bulb*, cylindrical type, 45 mm in diameter by 100 mm long, or larger, with curved inlet and outlet tubes.

4.6 *Erlenmeyer Flask*, having a capacity of 250 or 300 ml.

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[1] These methods are under the jurisdiction of ASTM Committee D-5 on Coal and Coke.

Current edition approved Nov. 27, 1973. Published March 1974.

[2] *1983 Annual Book of ASTM Standards*, Vol 05.05.

[3] *1983 Annual Book of ASTM Standards*, Vol 11.01.

[4] Borosilicate glass has been found satisfactory for this purpose.

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ASTM Standards, Vol 05.05.
of *ASTM Standards*, Vol 11.01.
has been found satisfactory for this pur-

4.7 *Glass Connecting Tube*, approximately 10 mm in outside diameter by 200 mm long.

4.8 *Rubber Tubing*, short piece.

5. Reagents

5.1 *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.[3] 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, references to water shall be understood to mean reagent water conforming to Specification D 1193.

5.3 *Alkali Solution*—Dissolve 8.0 g of potassium sulfide (K_2S) and 500 g of sodium hydroxide (NaOH) in water and dilute to 1 litre. The use of appropriate amounts of sodium sulfide (Na_2S) or potassium hydroxide (KOH) may be substituted for the above, if desired (Note 2 (*3*)).

5.4 *Ethyl Alcohol* (95%)—Ethyl alcohol conforming to Formula No. 30 or 2A of the U. S. Bureau of Internal Revenue. Methyl alcohol may be used.

5.5 *Mercury*, metal.

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:

(*1*) 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.

(*2*) Three-tenths gram of mercuric selenite ($HgSeO_3$) with 7 to 10 g of K_2SO_4.

(*3*) Three-tenths gram of cupric selenite dihydrate ($CuSeO_3 \cdot 2H_2O$) 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.

5.6 *Potassium Permanganate* ($KMnO_4$), crystals.

5.7 *Potassium Sulfate* (K_2SO_4), crystals.

5.8 *Sucrose*, National Bureau of Standards primary-standard grade.

5.9 *Sulfuric Acid* (*sp gr 1.84*)—Concentrated sulfuric acid (H_2SO_4).

5.10 *Zinc*, mossy or granular.

Reagents Required Only for Kjeldahl-Gunning Method

5.11 *Methyl Red Indicator Solution* (*0.4 to 1 g/litre*)—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 solutions of equal concentrations may be used.

5.12 *Sodium Hydroxide, Standard Solution* (*0.1 to 0.2 N*)—Prepare and accurately standardize a 0.1 to 0.2 *N* sodium hydroxide (NaOH) solution against a primary standard.

5.13 *Sulfuric Acid* (*0.2 N*)—Prepare and standardize a 0.2 *N* sulfuric acid (H_2SO_4) solution. The solution need not be standardized against a primary standard.

Reagents Required Only for Alternate Method

5.14 *Boric Acid Solution* (*50 g/litre*)—Dissolve 5 g of boric acid (H_3BO_3) in 100 ml of boiling water. Allow to cool before use.

5.15 *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 a fresh solution at bimonthly intervals.

5.16 *Sulfuric Acid* (*0.1 to 0.2 N*)—Prepare and accurately standardize a 0.1 to 0.2 *N* sulfuric acid (H_2SO_4) solution against a primary standard; hydrochloric acid (HCl) of similar concentration may be substituted.

6. Sample

6.1 The sample shall be the material pulverized to pass No. 60 (250-μm) sieve and well mixed in accordance with Method D 346 or Method D 2013.

6.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Method D 3173, etc. in order to allow calculation of the as-analyzed data to other bases.

6.3 Weigh approximately 1 g (weighed to the nearest 1 mg) of the analysis sample ground to pass a No. 60 (250-μm) or finer sieve, into a weighing scoop. In the case of coke and anthra-

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[3] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D. C. 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, N. Y., and the "United States Pharmacopeia."

cite, grinding the sample to pass a No. 200 (75-µm) or finer sieve is recommended.

7. Procedure for Kjeldahl-Gunning Method

7.1 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 of mercury (Note 2). Add 30 ml of H_2SO_4 (sp gr 1.84) to the mixture by pouring it down the neck of the flask with rotation, in order to wash any adherent sample material into the mixture. Swirl the contents of the flask several times to ensure thorough mixing and wetting of the sample. Incline the flask at an angle of 45 to 60 deg on the digestion heater in a fume hood (Note 3), and 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 (Note 1). Continue the boiling 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-colored stage. The total time of digestion will require 3 to 6 h, except in the case of coke and anthracite, which may require 12 to 16 h (Note 4). 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 necessary to destroy the excess permanganate and decolorize the solution.

NOTE 3—When fume exhaust ducts or hoods are not available a Hengar tube may be inserted in the neck of the flask.

NOTE 4—Addition of 0.1 g of chromic anhydride (CrO_3) to the digestion mixture has been found very helpful in reducing the time of digestion for coke.

7.2 Dilute the cooled digestion mixture to about 300 ml with cold water, and remove any heat of dilution by cooling with water. Meanwhile, pipet into the 250 or 300-ml Erlenmeyer flask, 20.0 ml of 0.2 *N* H_2SO_4 and add 6 drops of methyl red or bromcresol green indicator solution. Attach the glass connecting tube to the discharge end of the condenser, using the short piece of rubber tubing as a seal. Incline the Erlenmeyer flask at a suitable angle, and insert this tube so that the end is immersed to the maximum depth in the acid. Add 1 to 2 g of granular zinc to the mixture in the Kjeldahl flask (two or three small pieces if mossy zinc is used), and slowly add 100 ml of the 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 deg and pouring the alkali solution down the neck. Failure to maintain discrete layers during this operation may lead to loss of ammonia. Quickly connect the flask to the distilling condenser through the Kjeldahl connecting bulb, and then swirl the contents to promote thorough mixing.

7.3 Bring the contents of the Kjeldahl flask to a boil carefully, in order to avoid violent bumping, and then distill the ammonia over into the acid solution in the Erlenmeyer flask. Continue the distillation at a maximum rate of approximately 350 ml/h until 150 to 175 ml of distillate have been collected. Discontinue the boiling, and remove the glass connecting tube from the condenser and Erlenmeyer flask. Rinse the tube with distilled water, collecting the washings in the Erlenmeyer flask, and then back-titrate the excess acid with 0.1 to 0.2 *N* NaOH solution.

7.4 Run a blank determination in the same manner as described above, using approximately 1 g of sucrose (weighed to the nearest 1 mg) as the sample material.

NOTE 5—Blank determinations must be made to correct for nitrogen from sources other than the sample. A blank determination shall be made whenever a new batch of any one reagent is used in the analysis.

7.5 *Calculation*—Calculate the percentage of nitrogen in the analysis sample as follows:

$$\text{Nitrogen, \%} = [((B - A)\,N \times 0.014)/C] \times 100$$

where:

A = millilitres of 0.1 to 0.2 *N* NaOH solution required for titration of the sample,
B = millilitres of 0.1 to 0.2 *N* NaOH solution required for titration of the blank,
N = normality of the NaOH solution, and
C = grams of sample used

8. Procedure for Alternative Method

8.1 Digest the sample as described in 7.1.

8.2 Dilute and cool the digestion mixture as described in 7.2. Add to the 250 or 300-ml Erlenmeyer flask approximately 20 ml of H_3BO_3 solution and 6 drops of mixed indicator solution. Then proceed as described in the remainder of 7.2.

8.3 Distill the ammonia into the H_3BO_3

This may be accomplished by
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$[((B - A) N \times 0.014)/C] \times 100$

of 0.1 to 0.2 N NaOH solution
or titration of the sample,
of 0.1 to 0.2 N NaOH solution
for titration of the blank,
of the NaOH solution, and
sample used

or Alternative Method

sample as described in 7.1.
d cool the digestion mixture as
2. Add to the 250 or 300-ml
ask approximately 20 ml of
and 6 drops of mixed indicator
proceed as described in the
.2.
he ammonia into the H_3BO_3

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solution exactly as described in 7.3 and finally titrate the ammonia with 0.2 N H_2SO_4.

8.4 Run a blank determination in the same manner as described above, using approximately 1 g (weighed to the nearest 1 mg) of sucrose as the sample material (Note 5).

8.5 *Calculation*—Calculate the percentage of nitrogen in the sample as follows:

$$\text{Nitrogen, \%, in the analysis sample} = [(A - B) N \times 1.4]/C$$

where:

A = millitres of 0.2 N H_2SO_4 required for titration of the sample,
B = millilitres of 0.2 N H_2SO_4 required for titration of the blank,
N = normality of the H_2SO_4, and
C = grams of the sample used.

9. Report

9.1 The results of the nitrogen analysis may be reported on any of a number of bases, differing from each other in the manner by which moisture is treated.

9.2 Use the percentage of moisture in the sample passing a No. 60 (250-μm) sieve to calculate the results of the analysis sample to a dry basis.

9.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Specifications D 3176 and D 3180.

10. Precision

10.1 The permissible differences between two or more determinations shall not exceed the following values:

	Repeatability, %	Reproducibility, %
Nitrogen	0.05	...

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103.

Attachment H-5
HEATING VALUE

Method: American Society for Testing Materials

Gross Calorific Value of Solid Fuel by Adiabatic Bomb Calorimeter: D2015-77 (1978)

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze soil and sediment samples for 1) Proximate analysis for: a) moisture content, b) ash, c) volatile matter, and d) fixed carbon. 2) Ultimate analysis for a) C, H, S, O, N 3) Heating Value, 4) Flash Point and 5) pH

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 54 soil samples and 20 sediment samples for the parameters listed above. The samples will have low to high concentrations of creosote and fuel oil.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

Heating Value

6. Approximate number of days results required after lab receipt of sample:

Lab will report results within 30 days after receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

A.) Heating value ASTM Method D 2015-77

See Attachment F-3

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.): 1.) Exact compliance to the specific requirements of the method must be met. particularly the restandardization requirements.

2.) A reference standard of Benzoic Acid from the NBS for heating value must be run with each sample set. The acceptable range is ± 6 BTU/°C.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). if not completed, format of results will be left to program discretion.

1.) Copies of Thermometer's Certificate to NBS Certification

2.) Logs of restandardization data.

3.) Copies of all log pages particularly the calculations.

10. Other (use additional sheets or attach supplementary information, as needed):

The correlation coefficient for standards must be calculated and supplied.

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414-272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
Heat Valve	Repeatability	<50 BTU/lbs Dry Weight
(Adiabatic Bomb Calorimeter)		

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or Conc.)
Restandardization	After changing any part of the calorimeter and at least once a month.	
Duplicates	1 per 10 samples	<50 BTU/lbs Dry Weight

III. *Action Required If Limits are Exceeded:

Call Dennis Wesolowski (312) 886-1971

ASTM Designation: D 2015 - 77 (Reapproved 1978)

An American National Standard

Standard Test Method for
GROSS CALORIFIC VALUE OF SOLID FUEL BY THE ADIABATIC BOMB CALORIMETER[1]

This standard is issued under the fixed designation D 2015; 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 determination of the gross calorific value of solid fuel by the adiabatic bomb calorimeter.

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

2. Applicable Documents

2.1 *ASTM Standards:*

D 121 Definitions of Terms Relating to Coal and Coke[2]

D 346 Collection and Preparation of Coke Samples for Laboratory Analysis[2]

D 1193 Specification for Reagent Water[3]

D 2013 Preparing Coal Samples for Analysis[2]

D 3173 Moisture in the Analysis Sample of Coal and Coke[2]

D 3177 Total Sulfur in the Analysis Sample of Coal and Coke[2]

D 3180 Calculating Coal and Coke Analyses from As-Determined to Different Bases[2]

E 1 Specification for ASTM Thermometers[4]

E 144 Recommended Practice for Safe Use of Oxygen Combustion Bombs[5]

3. Sample

3.1 The sample shall be the material pulverized to pass No. 60 (250-μm) sieve and well-mixed in accordance with either Methods D 346 or D 2013.

3.2 A separate portion of the analysis sample should be analyzed simultaneously for moisture content in accordance with Methods D 2013 and D 3173 so that calculation to other than the as-determined basis can be made.

4. Summary of Method

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

NOTE 1—Oxidation after sampling of susceptible low-rank coal or lignite may result in a reduction of calorific value. Unnecessary exposure of the sample to air from the time of sampling or delay in analysis shall be avoided.

NOTE 2—The moisture determination of the sample shall be performed simultaneously in accordance with Method D 3173.

5. Definitions

5.1 *calorific value*—the heat of combustion of a substance. It is usually expressed in British thermal units (Btu) per pound. (Calorific value may also be computed in calories per gram or joules per gram when required.)

NOTE 4—The unit equivalents are as follows:

1 Btu = 1055.06 J
1 cal[A] = 4.1868 J
1 Btu/lb = 2.326 J/g
1.8 Btu/lb = 1.0 cal/g

[A] International Tables calorie.

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[1] This method is under the jurisdiction of ASTM Committee D-5 on Coal and Coke and is the direct responsibility of Subcommittee D05.21 on Methods of Analysis.

Current edition approved Oct. 28, 1977. Published December 1977. Originally published as D 2015 - 62 T. Last previous edition D 2015 - 66 (1972).

[2] *1983 Annual Book of ASTM Standards*, Vol 05.05.

[3] *1983 Annual Book of ASTM Standards*, Vol 11.01.

[4] *1983 Annual Book of ASTM Standards*, Vol 14.01.

[5] *1983 Annual Book of ASTM Standards*, Vol 14.02.

5.2 *gross calorific value* (*gross heat of combustion at constant volume*). Q_v (*gross*)—see definition contained in Definitions D 121.

5.3 *net calorific value* (*net heat of combustion at constant pressure*). Q_p (*net*)—see definition contained in Definitions D 121.

5.4 *water equivalent or energy equivalent*—in this method, the calorific value (Btu's per pound) required to raise the temperature (Note 4 of the calorimeter 1°C or 1°F per gram of sample. This is the number that is multiplied by the temperature rise in degrees and divided by the sample weight in grams to give the heating value in Btu per pound (Note 5).

NOTE 4—*Temperature* is measured in either degrees Celsius or Fahrenheit. Temperatures may also be recorded in ohms or other units when using electric thermometers. Consistent units must be used in both the standardization and actual calorific determination.

Time is expressed in minutes.

Weights are measured in grams.

NOTE 5—Energy units for quantities listed throughout this method are such that the number of energy units per gram of sample corresponds exactly to the number of Btu's per pound of sample. For brevity these are referred to as Btu's. The actual energies are smaller than those stated by the ratio of the number of pounds per gram (1/453.59 ---). The energy equivalent of the calorimeter has the units (Btu/lb) × (g/deg).

6. Apparatus

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

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 metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to a gage pressure of 3000 psi (approximately 20 MPa) at room temperature without stressing any part beyond its elastic limit.

6.3 *Calorimeter* (Note 6), 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.

NOTE 6—As used in this method, the term "calorimeter" describes the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

6.4 *Jacket*—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides; to, and bottom are approximately 1 cm from the jacket walls. The jacket shall be arranged with provisions for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It must 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 116C, 117C, 56C, or 56F as prescribed in Specification E 1, may be used. 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 larger than 2.5°F or 2.0°C over the entire graduated scale. The maximum difference in correction between any two test points shall not be more than 0.02°C or 0.05°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 115C, as prescribed in Specification E 1, may be used. Each of these thermometers shall be tested for accuracy against a known standard (preferably by the National Bureau of Stan-

(Note 6). made of metal
or brass) with a tarnish-
and with all outer surfaces
its size shall be such that the
npletely immersed in water
neter is assembled. It shall
stirring the water thoroughly
m rate, but with minimum
inuous stirring for 10 min
he calorimeter temperature
C (0.02°F) starting with iden-
es in the calorimeter, room,
e immersed portion of the
oupled to the outside through
w heat conductivity.

ed in this method, the term "calo-
the bomb, the vessel with stirrer,
which the bomb is immersed.

The calorimeter shall be com-
d within a stirred water jacket
so that its sides, to, and bottom
ately 1 cm from the jacket walls.
all be arranged with provisions
justing the jacket temperature
of the calorimeter for adiabatic
must be constructed so that any
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he calorimeter.
ometers—Temperatures in the
and jacket shall be measured with
thermometers or combinations

cury-in-Glass Thermometers con-
the requirements for Thermome-
17C, 56C, or 56F as prescribed
tion E 1, may be used. Other
ers of equal or better accuracy are
These thermometers shall be
curacy against a known standard
by the National Bureau of Stan-
intervals no larger than 2.5°F or
r the entire graduated scale. The
difference in correction between
st points shall not be more than
0.05°F.
Beckmann Differential Thermome-
a range of approximately 6°C in
bdivisions reading upward and con-
to the requirements for Thermometer
prescribed in Specification E 1, may
Each of these thermometers shall be
or accuracy against a known standard
ably by the National Bureau of Stan-

dards) at intervals no larger than 1°C over the entire graduated scale. The maximum difference in the correction between any two test points shall not be more than 0.02°C.

6.5.3 *Calorimetric Type Platinum Resistance Thermometer*, 25-Ω, tested for accuracy against a known standard (preferably by the National Bureau of Standards).

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 tests.

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. Platinum wire No. 38 B & S gage may be used provided constant ignition energy is supplied. Alternatively, a cotton thread may be used for ignition in conjunction with the firing wire. In this case, the firing wire shall be just long enough to stretch tautly between the ignition terminals. The lengths of the firing wire and cotton thread shall remain constant for all calibrations.

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 step-down transformer connected to an alternating current lighting circuit or batteries may be used. **Caution**—The ignition circuit switch shall be of the 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.[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 distilled water or water of equal purity.

7.3 *Benzoic Acid, Standard* (C_6H_5COOH)—Use National Bureau of Standards 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. 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 for the acid titration. 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* (20.9 g/litre)—One millilitre of this solution should be equivalent to 10.0 Btu in the nitric acid (HNO_3) titration (Note 4). Dissolve 20.9 g of anhydrous sodium carbonate (Na_2CO_3) in water and dilute to 1 litre. 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.

8. Standardization (Note 5)

8.1 Determine the water equivalent of the calorimeter as the average of a series of ten

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[6] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D.C. 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, N.Y., and the "United States Pharmacopeia."

individual runs, made over a period of not less than 3 days, nor more than 5 days. To be acceptable, the standard deviation of the series shall be 6.5 Btu/°C (3.6 Btu/°F) or less. (See Appendix X1, Table X1.1.) 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.

8.2 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 coal 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 10 and compute the corrected temperature rise, t, as described in 11.1. Determine the corrections for HNO_3 and firing wire as described in 11.2 and substitute into the following equation:

$$W = [(H)(g) + e_1 + e_3 + e_4]/t$$

where:

W = water equivalent,

H = heat of combustion of benzoic acid, as stated in the National Bureau of Standards certificate, Btu/lb,

g = weight of benzoic acid, g,

t = corrected temperature rise, (see 11.1),

e_1 = titration correction, Btu, (see 11.2),

e_3 = fuse wire correction, Btu, (see 11.2), and

e_4 = cotton thread correction, if used, Btu, (see 11.2).

9. Restandardization (Note 5)

9.1 Make checks on the standard water equivalent after changing any part of the calorimeter and at least once a month. The test procedure for checking the standard water equivalent factor shall be in accordance with Section 8, except that the required number of individual runs shall be determined as follows:

9.1.1 If a single new standard value exceeds the old standard by ±6 Btu/°C (±4 Btu/°F), the old standard is suspect, thereby requiring a second test.

9.1.2 The difference between the two new standards must not exceed 8 Btu/°C (5 Btu/°F), and the average of the two new standards must not differ from the old standard by more than ±4 Btu/°C (±3 Btu/°F). If these requirements are met, do not change the standard on the calorimeter.

9.1.3 If the requirements given in 9.1.2 are not met, two more standards must be run. The range of the four new standards must not exceed 14 Btu/°C (8 Btu/°F), and the average of the four new standards must not differ from the old standard by more than ±3 Btu/°C (±2 Btu/°F). If these requirements are met, do not change the standard on the calorimeter.

9.1.4 If the requirements given in 9.1.3 are not met, a fifth and sixth standard must be run. The range of the six new standards must not exceed 17 Btu/°C (10 Btu/°F), and the average of the six new standards must not differ from the old standard by more than ±2 Btu/°C (±2 Btu/°F). If these requirements are met, do not change the standard on the calorimeter.

9.1.5 If the requirements given in 9.1.4 are not met, four more standards must be run to complete a series of ten runs. The range of these ten results must not exceed 20 Btu/°C (12 Btu/°F), and the average of the ten new standards must not differ from the old standard by more than ±1 Btu/°C (±1 Btu/°F). If these requirements are met, do not change the standard on the calorimeter.

9.1.6 If the requirements given in 9.1.5 are not met, the average value from the ten new standards must be used for the new standard water equivalent, provided that the standard deviation of the series does not exceed 6.5 Btu/°C (3.6 Btu/°F).

9.2 The summary of the numerical requirements at each stage of restandardization is given in Table 1.

10. Procedure (Notes 1 and 2)

10.1 *Weight of Sample*—Thoroughly mix the analysis sample of coal or coke in the sample bottle and carefully weigh approximately 1 g of it into the crucible in which it is to be burned. The sample shall be weighed to the nearest 0.1 mg.

NOTE 7—The balance should be checked periodically to determine its sensitivity.

NOTE 8—For anthracite, coke, and coal of high ash content, which do not readily burn completely,

of the two new standards
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°C (±3 Btu/°F). If these
net, do not change the
rimeter.
uirements given in 9.1.2
more standards must be
the four new standards
Btu/°C (8 Btu/°F), and
four new standards must
old standard by more than
°F). If these requirements
ange the standard on the

quirements given in 9.1.3
h and sixth standard must
of the six new standards
17 Btu/°C (10 Btu/°F), and
six new standards must not
standard by more than ±2
'F). If these requirements
change the standard on the

quirements given in 9.1.4
more standards must be run
ies of ten runs. The range of
must not exceed 20 Btu/°C
the average of the ten new
not differ from the old stan-
an ±1 Btu/°C (±1 Btu/°F). If
its are met, do not change
he calorimeter.
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e average value from the ten
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ion of the series does not
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stage of restandardization is
1.

Notes 1 and 2)

of Sample—Thoroughly mix
imple of coal or coke in the
and carefully weigh approxi-
into the crucible in which it is
The sample shall be weighed to
mg.

balance should be checked period-
se its sensitivity.
r anthracite, coke, and coal of high
uch do not readily burn completely.

the following procedures are recommended: (*1*) The inside of the crucible is lined completely with ignited asbestos in a thin layer pressed well down into the angles, and the sample is then sprinkled evenly over the surface of the asbestos; or (*2*) The weight of the sample may be varied to obtain good ignition. If the weight is varied, it will be necessary to recalibrate the calorimeter so that the water equivalent will be based on the same temperature rise as that obtained with the new sample weight; or (*3*) A known amount of benzoic acid may be mixed with the sample. Proper allowance must be made for the heat of combustion of benzoic acid when determining the calorific value of the sample.

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

10.3 *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. If cotton thread is used, connect the firing wire tautly across the ignition terminal, and tie the cotton thread around it at about the center. Arrange the ends of the cotton thread so that they are in contact with the sample. Assemble the bomb in the normal manner.

10.4 *Oxygen*—Charge the bomb with oxygen to a consistent pressure between 20 and 30 atm (3 MPa). This pressure must remain the same for each calibration and for each calorific determination. For the calorific value of coke, it is necessary to use 30-atm oxygen pressure. If, by accident, the oxygen introduced into the bomb should exceed the specific pressure, *do not* proceed with the combustion. Detach the filling connection and exhaust the bomb in the usual manner. Discard this sample.

10.4.1 **Caution**—The following precautions are recommended for safe calorimeter operation. Additional precautions are given in Recommended Practice E 144.

10.4.1.1 The weight of coal or coke sample and the pressure of the oxygen admitted to the bomb must not exceed the bomb manufacturer's recommendations.

10.4.1.2 Bomb parts should be inspected carefully after each use. Threads on the main closure should be checked frequently for wear. Cracked or significantly worn parts should be replaced. The bomb should be returned to the manufacturer occasionally for inspection and possibly proof firing.

10.4.1.3 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 code. Suitable reducing valves and adaptors for 300 to 500-psi (2070 to 3440-kPa) discharge pressure are obtainable from commercial sources of compressed gas equipment. The pressure gage shall be checked periodically for accuracy.

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

10.4.1.5 Extreme caution must be exercised when combustion aids are employed so as not to exceed the bomb manufacturer's recommendations and to avoid damage to the bomb. Do not fire loose fluffy material such as unpelleted benzoic acid, unless thoroughly mixed with the sample.

10.4.1.6 Admit oxygen slowly into the bomb so as not to blow powdered material from the crucible.

10.4.1.7 Do not fire the bomb if it has been filled to greater than 30 atm (3 MPa) pressure with oxygen, the bomb has been dropped or turned over after loading, or there is evidence of a gas leak when the bomb is submerged in the calorimeter water.

10.5 *Calorimeter Water*—Adjust the calorimeter water temperature to 1.0 to 1.4°C (2.0 to 2.5°F) below room temperature, but not lower than 20°C (68°F). Use the same weight measured to ±0.5 g of water in each experiment. For 2000-ml calorimeters, the proper quantity can be obtained by use of a volumetric flask calibrated to deliver 2000 ± 0.5 g. As the density of water varies with temperature, suitable corrections shall be made if the water temperature varies from the temperature at which the flask was calibrated.

10.6 *Observations*—Transfer the bomb to the calorimeter, check that it is gastight, and connect it to the firing circuit. Place the stirrers, thermometers, and cover in position. Start the stirrers and keep them in continuous operation throughout the determination. Stir for at least 5 min before reading any temperatures (Note 9). Adjust the jacket temperature to match the calorimeter within ±0.01°C (0.02°F) and maintain for 3 min. Record the "initial temperature", 20°C (68°F) or higher, to within one-tenth of the smallest thermometer subdivision 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 temperature readings at 1-min intervals until the *same* temperature (within one tenth of the smallest thermometer subdivision) is observed in three successive readings. Record this as the "final temperature."

NOTE 10—Before taking any readings, tap the thermometer lightly and examine for mercury separation. Mercury separation will cause erroneous readings and should be corrected before proceeding. In addition, the entire thermometer should be examined daily.

10.7 *Analysis of Bomb Contents*—Remove the bomb and release the pressure at a uniform rate, such 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. Wash the interior of the bomb with distilled water containing the titration indicator, until the washings are free of acid, and titrate the washings with standard carbonate solution using an indicator specified in 7.4. 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 Method D 3177.

11. Calculations (Note 5)

11.1 *Temperature Rise*—Using data obtained as prescribed in 10.5, 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 10), and

t_f = "final temperature" corrected for thermometer error.

NOTE 10—With all mercury-in-glass thermometers, it is necessary to make the following corrections if the total heat value is altered by 5.0 Btu or more. This represents a change of 0.001°C or 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 Beckmann 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, Section X2.1.1.

11.2 *Thermochemical Corrections* (Appendix X2, Section X2.2.1)—Compute the following for each test:

e_1 = correction for the heat of formation of HNO_3, Btu. Each millilitre of standard alkali is equivalent to 10.0 Btu.

e_2 = correction for heat of formation of H_2SO_4, Btu,
= 23.7 times percent of sulfur in sample times weight of sample, g,

e_3 = correction for heat of combustion of firing wire, Btu (Note 11),
= 0.41 Btu/mm or 2.6 Btu/mg for No. 34 B & S gage Chromel C,
= 0.49 Btu/mm or 3.2 Btu/mg for No. 34 B & S gage iron wire (Note 11), and

e_4 = correction for heat of combustion of cotton thread (if used), in Btu. The heat supplied by the ignition of cotton thread is preferably determined by combustion in the bomb. As an alternative, it can be determined from the calorific value of cellulose, which is equivalent to 7.52 Btu/mg.

NOTE 11—There is no correction for platinum wire provided the ignition energy is constant.

11.3 *Calorific Value:*

11.3.1 Calculate the gross calorific value (gross heat of combustion at constant volume) Q_v (gross) as follows:

$$Q_v\ (\text{gross}) = [(t)(W) - e_1 - e_2 - e_3 - e_4]/g$$

where:

Q_v (gross) = gross calorific value, Btu/lb,

t = corrected temperature rise as calculated in 11.1, °C or °F, consistent with the water equivalent value,

W = water equivalent (see Section 8)

e_1, e_2, e_3, e_4 = corrections as prescribed in 11.2, and

g = weight of sample, g.

11.3.2 Calculate the net calorific value

mercury-in-glass thermome-
make the following correc-
alue is altered by 5.0 Btu or
change of 0.001°C or 0.002
ng approximately 2000 g of
include the calibration cor-
e calibration certificate. the
r Beckmann thermometers.
ons furnished by the calibra-
he correction for emergent
hese corrections are given in
X2.1.1.

nical Corrections (Appen-
2.2.1)—Compute the fol-

r the heat of formation of
Each millilitre of standard
valent to 10.0 Btu.
or heat of formation of

ercent of sulfur in sample
of sample, g.
or heat of combustion of fir-
(Note 11).
m or 2.6 Btu/mg for No. 34
Chromel C,
m or 3.2 Btu/mg for No. 34
iron wire (Note 11), and
for heat of combustion of
ead (if used), in Btu. The
ied by the ignition of cotton
preferably determined by
in the bomb. As an alter-
can be determined from the
alue of cellulose, which is
to 7.52 Btu/mg.

is no correction for platinum
gnition energy is constant.

Value:
ate the gross calorific value
mbustion at constant volume)
llows:

$(t)(W) - e_1 - e_2 - e_3 - e_4]/g$

oss calorific value, Btu/lb.
temperature rise as calculated
°C or °F, consistent with the
uivalent value.
uivalent (see Section 8)
corrections as prescribed in
d
of sample, g.
ulate the net calorific value

(net heat of combustion at a constant pressure) Q_p (net) as follows:

$$Q_p\,(\text{net}) = Q_v\,(\text{gross}) - 10.30\,(\text{H} \times 9)$$

where:

Q_p (net) = net calorific value, Btu/lb,
Q_v (gross) = gross calorific value, Btu/lb, and
H = total hydrogen, %.

12. Report

12.1 The results of the calorific value may be reported on any of a number of bases, differing from each other in the manner which moisture is treated.

12.2 Use the percentage of moisture in the sample passing a No. 60 (250-μm) sieve to calculate the results of the analysis sample to a dry basis.

12.3 Procedures for converting the value obtained on the analysis sample to other bases are described in Method D 3180.

13. Precision

13.1 The following criteria should be used for judging the acceptability of results (95 % probability) on split 60-mesh (250-μm) samples.

13.1.1 *Repeatability*—Duplicate results by the same laboratory on different days, using the same operator and equipment, should not be considered suspect unless they differ by more than 50 Btu/lb, dry basis.

13.1.2 *Reproducibility*—The results submitted by two or more laboratories (different equipment, operators, date of test, and different portions of the same pulp) should not be considered suspect unless the two results differ by more than 100 Btu/lb, dry basis.

TABLE 1 Summary of Numerical Requirements

(Note 5)

NOTE—Test values exceeding table limits require additional runs.[A]

Number of Runs	Maximum Range of Results		Maximum Difference between $\bar{X}_1$ and $\bar{X}_2$[B]	
	Btu/°C	Btu/°F	Btu/°C	Btu/°F
1	...	...	±6	±4
2	8	5	±4	±3
4	14	8	±3	±2
6	17	10	±2	±2
10	20	12	±1	±1

[A] Values in this table have been rounded off after statistical calculation, and are therefore not precisely in a ratio of 1.8 to 1.0.

[B] $\bar{X}_1$ = average of original standard.
$\bar{X}_2$ = average of check runs.

APPENDIXES

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.

X2. CORRECTIONS (Note 7)

X2.1 Thermometer Corrections

X2.1.1 It is necessary to make the following corrections in the event they result in an equivalent change of 5.0 Btu or more.

X2.1.1.1 *Calibration Correction* shall be made in accordance with the calibration certificate furnished by the calibration authority.

X2.1.1.2 *Setting Correction* is necessary for the Beckmann thermometer. It shall be made in accordance with the directions furnished by the calibration authority.

X2.1.1.3 *Differential Emergent Stem Correction*—The calculation of differential stem correction depends upon the way the thermometer was calibrated and how it is used. Two conditions are possible:

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

$$\text{Correction} = K\,(t_f - t_o)\,(t_f + t_o - L - T)$$

where:

K = 0.00016 for thermometers calibrated in degrees Celsius.
0.00009 for thermometers calibrated in degrees Fahrenheit.
L = scale reading to which the thermometer was immersed.
T = mean temperature of emergent stem.
t_o = initial temperature reading, and
t_f = final temperature reading.

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

$$\begin{aligned}\text{Differential stem correction}\\ &= 0.00016\,(28 - 24)\,(28 + 24 - 16 - 26)\\ &= +0.006°\text{C}\end{aligned}$$

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

$$\text{Correction} = K\,(t_f - t_o)\,(t^1 - t^0)$$

where:

K = 0.00016 for thermometers calibrated in degrees Celsius.
0.00009 for thermometers calibrated in degrees Fahrenheit.
t_o = initial temperature reading.
t_f = final temperature reading.
t^1 = observed stem temperature, and
t^0 = stem temperature at which the thermometer was calibrated.

Note X2.2: *Example*—Suppose the initial reading t_o was 80°F, the final reading t_f was 86°F, and that the observed stem temperature t^1 was 82°F, and the calibration temperature t^0 was 72°F; then:

$$\begin{aligned}\text{Differential stem correction}\\ &= 0.0009\,(86 - 90)\,(82 - 72)\\ &= 0.005°\text{F}\end{aligned}$$

X2.2 Thermochemical Corrections

X2.2.1 *Energy of Formation of Nitric Acid*—A correction (e_1, in 11.2) of 10.0 Btu for calculations in Btu/lb (23.2 J for calculations in J/g is applied for each millilitre of standard Na_2CO_3 solution used in the acid titration. The standard solution contains 20.9 g of Na_2CO_3/litre. This correction is based on the assumption that (*1*) all the acid titrated is HNO_3 formed by the following reaction: $\frac{1}{2}\,N_2\,(g) \times \frac{5}{4}\,O_2\,(g) + \frac{1}{2}\,H_2O\,(l) = HNO_3$ (in 500 mol H_2O), and (*2*) that the energy of formation of one mol of HNO_3 in approximately 500 mol of water under bomb conditions is −59.0 kJ/mol.[7] 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.

X2.2.2 *Energy of Formation of Sulfuric Acid*—By definition (see Definitions D 121), 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 11.2) of 23.7 Btu for calculations in Btu/lb (55.2 J for calculations in J/g is applied for each percent of sulfur in the 1-g sample, which 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 −295 kJ/mol.[7] A correction of 2 × 59.0 kJ/mol of sulfur was applied in the e_1 correction, so the additional correction necessary is 295 − (2 × 59.0) = 177 kJ/mol or 2300 Btu/g of sulfur in the sample (23.7 Btu × weight of sample in grams × percent sulfur in sample). The factor 23.7 is 177/(32.06 × 2.326) = 55.2/2.326.

X2.2.2.1 The value of 2370 Btu/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 the water condensed during combustion of the sample.[8] 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 −295 kJ/mol.

X2.2.2.2 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.

X2.2.3 *Fuse Wire*—Calculate the heat in British thermal units contributed by burning the fuse wire in accordance with the directions furnished by the supplier of the wire. For example, the energy of combustion of No. 34 B & S gage Chromel C wire is 6.0 J/mg or approximately 0.95 J/mm equivalent to 2.6 Btu/mg or 0.41 Btu/mm for calculations of calorific value in Btu/lb, and that of No. 34 B & S gage iron wire is 7.33 J/mg or approximately 1.15 J/mm. There is no correction of platinum wire provided the ignition energy is constant. The heat supplied by ignition of cotton thread, if used, is preferably determined by combustion in the bomb. As an alternative, it can be determined from the calorific value of cellulose, 17.5 J/mg, which is equivalent to 7.52 Btu/mg for calculations in Btu/lb (7.52 = 17.5/2.326).

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

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

ing the maximum height above the principal surface of the liquid to which oil rises on the hydrometer scale when the hydrometer in question is immersed in a transparent oil having a surface tension similar to that of the sample under test (see Fig. 2).

NOTE 7—Alternatively, corrections as given in Table 1 may be applied.

9.8 Immediately after observing the hydrometer scale value, again cautiously stir the sample with the thermometer keeping the mercury thread fully immersed. Record the temperature of the sample to the nearest 0.2°C (0.5°F) (Note 8). Should this temperature differ from the previous reading by more than 0.5°C (1°F), repeat the hydrometer test and then thermometer observations until the temperature becomes stable within 0.5°C (1°F).

NOTE 8—After use at a temperature higher than 38°C (100°F), allow all hydrometers of the lead shot in wax type to drain and cool in a vertical position.

10. Calculations and Report

10.1 Apply any relevant corrections to the observed thermometer reading (for scale or bulb) and to the hydrometer reading (scale). For opaque samples, make the appropriate correction to the observed hydrometer reading as given in 9.7. Record to the nearest 0.0001 density or relative density (specific gravity) or 0.1° API the final corrected hydrometer scale reading (Note 9). After application of any relevant corrections record to the nearest 0.5°C or 1°F, the mean of the temperature values observed immediately before and after the final hydrometer reading.

NOTE 9—Hydrometer scale readings at temperatures other than calibration temperatures (15°C or 60°F) should not be considered as more than scale readings since the hydrometer bulb changes with temperature.

10.2 To convert corrected values from 10.1 to standard temperature, use the following from the Petroleum Measurement Tables (D 1250):

10.2.1 When a density scaled hydrometer has been employed, use Tables 53 A or 53 B to obtain density at 15°C.

10.2.2 When a relative density (specific gravity) hydrometer has been employed, use Tables 23 A or 23 B to obtain Relative Density (Specific Gravity) 60/60 F, and

10.2.3 When an API gravity scaled hydrometer has been employed, use Tables 5 A or 5 B to obtain the gravity in API degrees.

10.3 When a value is obtained with a hydrometer scaled in one of the units described herein and a result is required in one of the other units, make the conversion by one of the appropriate tables given in Standard D 1250, Physical Data Tables. For conversion from density at 15°C, use Table 51; from relative density (specific gravity) 60/60 F, use Table 21; from API gravity, use Table 3.

10.4 Report the final value as density in kilograms per litre at 15°C, or as relative density (specific gravity) at 60/60°F, or as gravity in degrees API, as applicable.

11. Precision

11.1 The following criteria should be used for judging the acceptability of results:

11.1.1 *Repeatability*—Duplicate results by the same operator should be considered suspect if the results differ by more than the following amounts:

Product	Temperature Range	Units	Repeatability
Transparent	−2 to 24.5°C	density	0.0005
Nonviscous	29 to 76°F	relative density (specific gravity)	0.0005
	42 to 78°F	API gravity	0.1
Opaque	−2 to 24.5°C	density	0.0006
	29 to 76°F	relative density (specific gravity)	0.0006
	42 to 78°F	API gravity	0.2

11.1.2 *Reproducibility*—The results submitted by each of two laboratories should not be considered suspect unless the results differ by more than the following amounts:

Product	Temperature Range	Units	Reproducibility
Transparent	−2 to 24.5°C	density	0.0012
Nonviscous	29 to 76°F	relative density (specific gravity)	0.0012
	42 to 78°F	API gravity	0.3
Opaque	−2 to 24.5°C	density	0.0015
	29 to 76°F	relative density (specific gravity)	0.0015
	42 to 78°F	API gravity	0.5

11.1.3 For very viscous products, or when the conditions given in 11.1.1 and 11.1.2 are not compiled with, no specific variations can be given.

. is -59.0 kJ/mol.[7] When
part of the correction for
the e_1 correction and the
ection.
rmation of Sulfuric Acid—
finitions D 121), the gross
ed when the product of the
in the sample is SO_2 (g).
omb combustion processes.
$_2SO_4$ in the bomb washings.
.2) of 23.7 Btu for calcula-
J for calculations in-J/g is
it of sulfur in the 1-g sample.
H_2SO_4. This correction is
of formation of H_2SO_4 in
e present in the bomb at the
This energy is taken as -295
of 2 × 59.0 kJ/mol of sulfur
correction, so the additional
s $295 - (2 \times 59.0) = 177$
of sulfur in the sample (23.7
le in grams × percent sulfur =
23.7 is $177/(32.06 \times 2.326)$.

e of 2370 Btu/g of sulfur is
aining about 5 % sulfur and
The assumption is also made
solved entirely in the water
nbustion of the sample.[8] If a
fuel is burned, the resulting
h water formed on the walls
e a ratio of about 15 mol of
$_2SO_4$. For this concentration
tion

$H_2O(l)$
$= H_2SO_4$ (in 15 mol H_2O)

of the bomb process is -295

he calculation upon a sample
ge sulfur content reduces the
s, because for smaller percent-
rection is smaller.
—Calculate the heat in British
outed by burning the fuse wire
he directions furnished by the
. For example, the energy of
4 B & S gage Chromel C wire
imately 0.95 J/mm equivalent
1 Btu/mm for calculations of
/lb, and that of No. 34 B & S
3 J/mg or approximately 1.15
correction of platinum wire
energy is constant. The heat
of cotton thread, if used, is
d by combustion in the bomb.
t can be determined from the
cellulose, 17.5 J/mg, which is
Btu/mg for calculations in Btu/
126).

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lata in National Bureau of Standards

nd Parker, C., "Studies in Bomb
rmation of Sulfuric Acid," *Fuel*,
8, p. 371.

TABLE X1 Standard Deviations for Calorimeter Standardization (Note 3)

Standardization Number	Column A	Column B	Column C
	Water Equivalent, Btu/°C	Code to 4400 (Column A − 4400)	(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 $= \bar{X} = \Sigma x/10 = (92/10) + 4400 = 4409$

Variance $= s^2$

$$= \frac{\Sigma \text{ Column C} - [(\Sigma \text{ Column B})^2/n]}{n - 1}$$

$$= 940 - [(92)^2/10]/9 = 10.4$$

Standard deviation $= s = \sqrt{\text{variance}} = \sqrt{10.4} = 3.22$

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103.

Attachment H-6
FLASH POINT

Method: Federal EPA "Test Methods for Evaluating Solid Waste," July 1982, SW846, 2nd Edition, No. 1010 and 1020

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze soil and sediment samples for 1) Proximate analysis for: a) moisture content, b) ash, c) volatile matter, and d) fixed carbon. 2) Ultimate analysis for a) C, H, S, O, N 3) Heating Value, 4) Flash Point and 5) pH

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 54 soil samples and 20 sediment samples for the parameters listed above. The samples will have low to high concentrations of creosote and fuel oil.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Approximate number of days results required after lab receipt of samples:

Laboratory will provide results within 30 days after reciept of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Flash Point

Reference: "Test Methods for Evaluating Solid Waste"

July 1982 SW 846 2nd Edition

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Note the special precautionary statement in the method

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

1) Supply copies of all notebook pages 2) Copies of all instrument data printouts/ charts 3) All QC data 4) All standards data. 5) Specify the method used.

10. Other (use additional sheets or attach supplementary information, as needed):

Use a summary report form for sample reference and QC results.

11. Name of sampling/shipping contact: Jeff Keiser

Phone: 414-272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

12. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (± % or Conc.)
Flash point		< 1°C or 1.5°F

13. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits (Percent or Conc.)
Duplicate	1 per 10 Samples	R % D < 20%
Reference Material	1 per 10 Samples	27° ± 0.8°C
run in duplicate		81 ± 1.5°F
p-xylene is the		
recommended		
reference material		

R % D = Relative Percent Difference

14. ACTION REQUIRED IF LIMITS ARE EXCEEDED

Call Dennis Wesolowski 312-663-9415

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

METHOD 1010[1]

MODIFIED PENSKY-MARTENS CLOSED-CUP METHOD

1.0 Scope and Application

1.1 A modified Method 1010 uses the Pensky-Martens closed-cup tester to determine the flash point of soils.

2.0 Summary of Method

2.1 The sample is heated at a slow, constant rate. A small flame is directed into the cup at regular intervals. The flash point is the lowest temperature at which application of the test flame ignites the vapor above the sample.

3.0 Interferences

3.1 Ambient pressure, sample homogeneity, uneven heating, drafts, and operator bias can affect flash point values.

4.0 Apparatus

4.1 Pensky-Martens Closed Flash Tester, as described in Annex A1 of ASTM Method D93-77. (Automatic flash point testers are available and may be advantageous since they save testing time, permit the use of smaller samples, and exhibit other advantages. If automatic testers are used, the user must be sure to follow all the manufacturer's instructions for calibrating, adjusting, and operating the instrument. In any cases of dispute, the flash point as determined manually shall be considered the referee test.)

4.2 Thermometers: Two standard thermometers shall be used with the ASTM Pensky-Marten tester.

4.2.1 For tests in which the indicated reading falls with -7° to +110°C (20° to 230°F), inclusive: either (1) an ASTM Pensky-Martens Low Range or Tag Closed Tester Thermometer having a range from -7° to +110°C (20° to 230°F) and conforming to the requirements for Thermometers 9C (9F) and as prescribed in ASTM Specification E1, or (2) an IP Thermometer 15C (15F) conforming to specifications given to Annex A3 of ASTM D93-77.

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[1] This method is based on ASTM Method D93-77. Refer to D93-77 or D93-80 for more information.

4.2.2 For tests in which the indicated reading falls within 110° to 370°C (230° to 700°F): either (1) an ASTM Pensky-Martens High Range Thermometer having a range from 90° to 370°C (200° to 700°F) and conforming to the requirements for Thermometers 10C (16F) conforming to specifications given in Annex A3 of ASTM D93-77.

5.0 Reagents

5.1 Calcium chloride

5.2 p-Xylene reference standard

6.0 Sample Collection, Preservation, and Handling

6.1 All samples must be collected using a sampling plan that addresses the considerations discussed in Section One of this manual.

6.2 Samples shall not be stored in plastic bottles since volatile materials may diffuse through the walls of the bottle.

7.0 Procedure

7.1 Routine Procedure

7.1.1 Thoroughly clean and dry all parts of the cup and its accessories before starting the test. Be sure to remove any solvent that was used to clean the apparatus. Fill the cup with the sample to be tested to the level indicated by the filling mark. Place the lid on the cup and set the latter in the stove. Be sure to properly engage the locating or locking device. Insert the thermometer. Light the test flame and adjust it to a diameter of 5/32 in (4 mm). Supply the heat at such a rate that the temperature as indicated by the thermometer increases 5° to 6°C (9° to 11°F)/min.

7.1.2 If the sample is expected to have a flash point of 110°C (230°F) or below, apply the test flame when the temperature of the sample is from 17°C (30°F) to 28°C (50°F) below the expected flash point and thereafter at a temperature reading that is a multiple of 1°C (2°F). Apply the test flame by operating the mechanism on the cover which controls the shutter and test flame burner so that the flame is lowered into the vapor space of the cup in 0.5 sec, left in its lowered position for 1 sec, and quickly raised to its high position. Do not stir the sample while applying the test flame.

7.1.3 If the sample is expected to have a flash point above 110°C (230°F), apply the test flame in the manner just described at each temperature that is a multiple of 2°C (5°F), beginning at a temperature of 17°C (30°F) to 28°C (50°F) below the expected flash point. NOTE: When testing materials to determine if volatile contaminants are present, it is not necessary to adhere to the temperature limits for initial flame application as stated in 7.2.2 and 7.2.3.

7.1.4 Record as the flash point the temperature read on the thermometer at the time the test flame application causes a distinct flash in the interior of the cup. Do not confuse the true flash point with the bluish halo that sometimes surrounds the test flame at applications preceding the one that causes the actual flash. The actual flash will have occurred when a large flame propagates itself over the surface of the sample.

7.2 Calculation and Report

7.2.1 Observe and record the ambient barometric pressure at the time of the test. When the pressure differs from 760 mm Hg (101.3 kPa), correct the flash point as follows:

(A) Corrected flash point = $C + 0.25\ (101.3 - p)$
(B) Corrected flash point = $F + 0.06\ (760 - P)$
(C) Corrected flash point = $C = 0.033\ (760 - P)$

where:

F = observed flash point, °F
C = observed flash point, °C
P = ambient barometric pressure, mm Hg
p = abmient barometric pressure, kPa

NOTE: The barometric pressure used in this calculation must be the ambient pressure for the laboratory at the time of test. Many aneroid barometers, such as those used at weather stations and airports, are precorrected to give sea level readings. These must not be used.

7.2.2 Record the corrected flash point to the nearest 0.5°C (or 1°F).

7.2.3 Report the recorded flash point as the Pensky-Martens Closed Cup Flash Point ASTM D93-IP 34, of the sample tested.

7.3 Refer to Method ASTM D93-77 for more details and background on the Pensky-Marten method.

8.0 Quality Control

8.1 All quality control data should be available for review.

8.2 Duplicates and standard reference materials should be routinely analyzed.

8.3 The flash point of the p-xylene reference standard must be determined in duplicate at least once per sample batch. The average of the two analyses should be 27° ± 0.8°C (81° ± 1.5°F).

Attachment H-7
SOIL pH PAPER TEST

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American
B. Regional Representative: Dennis Wesolowski
C. Telephone Number: ( ) (312) 886-1971
D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:
Analyze soil and sediment samples for 1) Proximate analysis for: a) moisture content,
b) ash, c) volatile matter, and d) fixed carbon. 2) Ultimate analysis for
a) C, H, S, O, N 3) Heating Value, 4) Flash Point and 5) pH

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):
Analyze 54 soil samples and 20 sediment samples for the parameters listed above. The samples will have low to high concentrations of creosote and fuel oil.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):
Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

Laboratory will provide results within 30 days after reciept of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

See Attachment

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Report: 1) Water reaction 2) Wide range PH 3) Narrow range PH and narrow range PH duplicate within 0.5 Incerment.

10. **Other (use additional sheets or attach supplementary information, as needed):**

11. **Name of sampling/shipping contact:** Jeff Keiser

Phone: 414-272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions

12. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (± % or Conc.)
pH	0.1 pH unit	± 0.1 pH unit
		See pH paper
		manufacture's
		specifications

13. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits (Percent or Conc.)
Duplicate	See method	See pH paper
		manufacture's
		specification.

14. ACTION REQUIRED IF LIMITS ARE EXCEEDED

Call Dennis Wesolowski 312-886-1971

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please contact your Regional representative at the Sample Management Office.

pH Test

I Equipment

A. pH Paper

1. Wide range 0 to 12 pH units
2. Narrow range Q1pH units

B. Deionized/distilled water

1. ASTM D 1143 Reagent water

C. Glass Ware

1. Beakers Griffen; 150, 250 ml
2. Glass stirring rod 6 to 8 inches by 1/4 inch.
3. Test tubes; glass or plastic 150 to 250 ml volume and rubber stopper to close the top of the test tube for shaking.

II Water Reaction Test

Warning: This test in used to evaluate the reaction of the sample with water. Caustic, sulfuric acid or other reaction compounds may be present.

1. In a beaker, place 50 ml water.
2. Add about 10 grams of sample.
3. Carefully stir with a glass rod.
4. Note any reaction which would create a hazard in this test Report any reaction.

III pH Touch Test

1. Using a wide range paper, wet the paper with water and touch to the sample.
2. Record wide range pH.
3. If necessary use a narrow range paper and touch the narrow range, wet paper to the sample
4. Repeat #3

Report: Reaction to Water
Wide range pH
Narrow range pH for both samples tested

IV pH Shake Test

1. Place about 50 grams (or 50 ml) of sample into a test tube.
2. Add 15-20 ml water.
3. Carefully stir the sample and the water with glass rod.

WARNING! Be careful of any reaction!!!

4. **ANY REACTION?**
   a) Yes. Stop and evaluate
   b) No. Proceed to 5
5. Shake gently then
6. Shake vigorously if no reaction occurs.
7. Let stand for phase separation
8. Measure pH of aquious phase first with wide range paper then with narrow range paper. Repeat narrow range test

   Report: Water reaction
   Wide range pH
   Narrow range test for both samples tested.

Notice:

These samples may be toxic, flammable and/or react with water. Use good safety lab, sample and operational procedures.

Attachment H-8
SOIL/SEDIMENT TOTAL ORGANIC CARBON

Method: By Versar, Inc. using the Dohrmann DC-80 Carbon Analyzer

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze soil and sediment samples for total organic carbon (TOC).

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 54 soil samples and 20 sediment samples for the parameters listed above. The samples will have low to high concentrations of creosote and fuel oil.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

Laboratory should report results within 30 days after receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

See attached method.

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Homogenize the samples. Inorganic carbon values will be subtracted from the total carbon values or purged from the samples prior to measurement. Use a minimum of 5 point standard curve (blank and 4 std.). Report results on a dry weight basis. Rerun samples with results greater than the highest standard. Obtain approval of CPM's, CRL prior to use of any other method.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The test procedure and specific instrument used will be clearly identified. Bench records tabulating the order of calibration standards, lab blanks, samples, duplicates and spikes, etc., with resulting output of concentration readouts will be provided along with worksheet used to calculate results. Specify the organic compound used to prepare standards and spikes. All records of analysis must be legible.

10. **Other (use additional sheets or attach supplementary information, as needed):**

11. **Name of sampling/shipping contact:** Jeff Keiser

Phone: (414) 272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

Soil TOC

I. DATA REQUIREMENTS

Parameter	**Detection Limit**	**Precision Desired (±% or Conc.)**
TOC	0.1 mg/gm	± 20% for conc. greater than 1.0 mg/gm or .2 mg/g for conc. less than 1.0 mg/gm

II. QUALITY CONTROL REQUIREMENTS

Audits Required	**Frequency of Audits**	**Limits* (±% or Conc.)**
Lab Blanks	At least 1 per analytical run and 1 per 20 samples	0.1 mg/gm
Lab Duplicate	At least 1 per analytical run and 1 per 20 samples	± 20% or 0.2 mg/g
Matrix Spike	At least 1 per analytical run and 1 per 20 samples	80%-120% recovery
NBS Reference Standard	1 per this project	80%-120%

III. *Action Required If Limits are Exceeded:

Rerun the samples in the affected batch. If limits are still exceeded contact CPM's of the CRL.

Versar INC.

VERSAR, INC.
LABORATORY OPERATIONS

DRAFT

Analyte: TOC

Matrix: Soil/Sediment

Method: Dohrmann DC-80 Carbon Analyzer

Reference: (1) Methods of Soil Analysis, Part 2, 2nd Ed., ASA, 1982.

(2) DC-80 Total Organic Carbon Systems Manual, 5th Ed., Dohrmann/Xertex, 1982.

(3) Methods for Chemical Analysis of Water and Wastes, EPA 600/4-79-020, USEPA, 1983.

(4) Standard Versar Quality Control Plan

1. GENERAL. The DC-80 carbon analyzer is designed mainly for analysis of water samples by MCAWW method 415.2 (3). The PRG-1 furnace and sludge/sediment sampler modules allow introduction of soil/sediment samples, either as a solid or as a slurry. The instrument is capable of determining TOC at sub-ppm levels. This sensitivity may lead to problems when analyzing soils, which typically range from 1 to 4 percent TOC. The instrumental sensitivity requires introduction of a very small sample (on the order of 1 to 100 mg) depending on TOC content. Since soils are inherently non-homogeneous, the analyst must take care that a representative subsample is analyzed. The procedure which follows has been shown to meet this requirement.

The DC-80 sludge/sediment sampler determines TOC by oxidizing carbon in an 800°C furnace. The evolved CO_2 is then measured with a non-dispersive infrared detector (NDIR). Thus, CO_2 and other inorganic forms of carbon are a positive interference. The relatively low levels of CO_2 in humid region soils are not a major concern. Some sediments and many arid soils, however, may contain percent levels of carbonates which must be destroyed prior to analysis. The $H_2SO_4/FeSO_4$ pretreatment described in reference (1) has been found to be suitable to the DC-80, with some modifications.

2. SAMPLE PREPARATION

2.1 Mix the sample thoroughly. Reserve about 5 grams for moisture determination, and spread the remainder of the sample on a large watch glass. Allow to air dry at room temperature. Depending on the nature of the sample, this will take from 8 to 48 hours. Thoroughly mix the dry sample and reduce to a convenient size by halving and quartering, as necessary. Grind the subsample in a mortar and pestle.

[NOTE: Fine textured sludges and muds may not require drying and grinding. Peats, mucks, and some industrial sludges should not be dried, since these materials resist rewetting.]

2.2 Test for inorganic carbon. Place a few mg of ground sample on a spot plate or small watch glass, and perform the inorganic carbon spot test as described in ref. (1), sec. 29-3.3.1. If carbonates are not present, prepare the sample for injection according to 2.3.1. If carbonates are present, proceed according to 2.3.2.

2.3 Preparation of Slurry.

2.3.1 Carbonates not present. Weigh accurately 100 to 500 mg of sample into a dilution tube. Add 10.00 ml of reagent water; cover, and allow to stand 5 minutes. Acidify and sparge to remove CO_2, as directed by ref. (2), pg. 3-12. Place the sample on a vortex mixer and mix at high speed for 5 to 10 seconds. Proceed IMMEDIATELY to section 3.2.2, below.

2.3.2 Carbonates present. Weigh accurately 100 to 500 mg of sample into a dilution tube. Add 10.00 ml of H_2SO_4-$FeSO_4$ digestion reagent (see ref. 1, sec. 29-3.3.2.2) a few drops at a time. Swirl to mix and allow to digest at room temperature for 30 minutes. Sparge to remove CO_2, as directed by reference (2), pg. 3-2. [NOTE: Omit the addition of 10% HNO_3.] Place the sample on a vortex mixer and mix at high speed for 5 to 10 seconds. Proceed IMMEDIATELY to section 3.2.2, below.

ANALYSIS

3.1 Instrument Preparation.

3.1.1 Prepare the instrument as directed by ref. (2), p. 11-4. Make certain the pump and UV lamp are both off.

3.1.2 Combust the empty boat for 2 minutes; then, determine the system blank as directed by reference (2), section 11c.

3.1.3 Prepare a calibration curve by injecting a suitable series of standards. Use a minimum of 5 standards covering the range 0-1000 mg/l. Do not use the one-point calibration method in reference (2).

3.2 TOC Determination.

3.2.1 Using a sharp razor blade, remove abour 3/16" from the tip of a 1000 ul (blue) Eppendorf pipet tip.

3.2.2 IMMEDIATELY after mixing ceases (2.3.1 or 2.3.2, above) pipet a suitable aliquot (normally 200 to 400 ul) into the sample boat. Analyze as directed in reference (2), section 11.

3.2.3 Determine TOC in the sample from the calibration curve.

4. REPORT

4.1 Report TOC in mg/Kg, dry basis.

4.2 Analyze and report calibration standards, blanks, duplicates, and spiked samples as required by contract provisions. In the absence of contractual QC requirements, the provisions of reference (4) are to be followed.

4.3 Duplicate analyses must come from two separately prepared slurries. Duplicate injections from a single slurry are not acceptable.

Attachment H-9
WATER SOLUBLE CHLORIDES

Method: Methods of Soil Analysis, Part 2, Chemical and Microbiological Properties, 1973, 62-3.5, American Society of Agronomy

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze soil and sediment samples for water soluble chlorides.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 54 soil samples and 20 sediment samples for the parameters listed above.

The samples will contain high and low concentrations of creosote.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement.

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. **Approximate number of days results required after lab receipt of samples:**

Laboratory should report results within 30 days after receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

Methods of Soil Analysis 62-3.5 See Attachment

8. **Special technical instructions (If outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Standardize the silvernitrate solution (0.025N) before each run. If more than 10 ml of titrant is necessary to achieve the end point, rerun the analysis with a smaller sample amount. At least 2 lab blanks should be prepared per analytical run and an average value used for calculating the chloride concentration. Report results in mg/Kg Cl.

9. **Analytical results required (If known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

The test procedure used will be clearly identified. Bench records tabulating the order of titrant standardization, lab blanks, samples, duplicates. spikes etc., with resulting titrant volumes will be provided along with copies of worksheets used to calculate results. All records of analysis and calculations must be legible.

10. **Other (use additional sheets or attach supplementary information, as needed):**

11. **Name of sampling/shipping contact:** Jeff Keiser

Phone: (414) 272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
Chloride	50mg/kg	± 10 mg/kg for conc. less than 50 mg/kg or ± 20% for concentrations greater than 50 mg/kg.

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or Conc.)
Lab blank	2 per run	50 mg/kg
Lab Duplicate	At least 1 per analytical run and 1 per 20 samples	± 20% or 10mg/kg
Lab Matrix Spike *	At least 1 per analytical run and 1 per 20 samples	80% - 120% recovery
EPA QC Mineral reference std. (use only the high std.)	one per this project.	85% - 115% recovery

Matrix spike will provide chloride value greater than 30% of the sample concentration but will not exceed the maximum 10 ml titrant.

III. *Action Required if Limits are Exceeded:

Reanalyze the samples, contact the CPMS, CRL if problems persist.

; a measure of CO_3^{2-}, and
nt provides a measure of

f phenolphthalein in 100 ml.

ethyl orange in 100 ml. of

sually 5 ml.) of the soil-
.. of HCO_3^-, into a beaker.
tart the stirrer. Add 2 drops
lor is produced, titrate the
ling a drop every 2 or 3
the buret reading. To the
iginal solution if no color
ops of methyl orange (re-
yl orange end point without
buret. Reserve the solution
eterminations after adding
make corrections if neces-

ality of standard H_2SO_4)

reach the phenolphthalein

ality of standard H_2SO_4)

d to reach the methyl orange
uired to reach the phenol-

Table 62-2. The titration of hydroxide, carbonate, and bicarbonate ions in the presence of phenolphthalein and methyl orange indicators.

Result of titration*	Titration value related to each ion		
	Hydroxide	Carbonate	Bicarbonate
P = 0	0	0	T
P < 1/2 T	0	2P	T - 2P
P = 1/2 T	0	2P	0
P > 1/2 T	2P - T	2(T - P)	0
P = T	T	0	0

* P = ml. of standard strong acid used in titration to the phenolphthalein end point.
T = total ml. of standard strong acid used in titration to the methyl orange end point.

To facilitate calculations, a table similar to that shown in Am. Public Health Assoc. standard methods (1960) is included (Table 62-2). Report the results to 3 significant figures, but do not report more than 1 place to the right of the decimal.

62-3.4.2.4 Comments. The results of the titrations are satisfactorily reproducible and are generally accurate to about 0.1 me. per liter.

Water extracts from sodic soils are often so dark in color that it is difficult or impossible to titrate CO_3^{2-} and HCO_3^- with color indicators. Under such circumstances, the titrations can be made by using a glass electrode pH meter instead of the indicators. Carbonate is titrated to pH 8.2, and HCO_3^- to pH 4.5.

62-3.5 Chloride

62-3.5.1 INTRODUCTION

The chlorides of Ca, Mg, K, and Na are all very soluble. Chloride is usually the principal anion in extracts of saline soils, and the concentration may reach several hundred me. per liter.

Chloride is specifically toxic to some tree and vine crops. Chloride is more toxic to many plants where present as $CaCl_2$ than as NaCl (U. S. Salinity Laboratory Staff, 1954).

The well-known Mohr volumetric method is satisfactory for the determination of chloride in aqueous soil extracts. The chloride is titrated with a standard silver nitrate solution, using potassium chromate as the indicator. As the equivalence point is passed, the excess of silver combines with the chromate to form a red or reddish-brown precipitate of silver chromate. This color change is easily recognized and serves as the end point of the titration. Other methods for chloride are found in sections 81-3 and 81-4.

62-3.5.2 *METHOD*

62-3.5.2.1 Special Apparatus.

1. Magnetic stirrer.
2. Titration assembly including a 10-ml. buret.

62-3.5.2.2 Reagents.

1. Potassium chromate (K_2CrO_4) indicator: Dissolve 5 g. of K_2CrO_4 in approximately 75 ml. of water. Add a saturated solution of $AgNO_3$ until a small quantity of red Ag_2CrO_4 precipitates. Set the solution in the dark for 24 hours. Then filter it to remove the Ag_2CrO_4, and make the volume to 100 ml.
2. Standard silver nitrate ($AgNO_3$) solution, 0.025*N*: Dissolve 4.2472 g. of $AgNO_3$ in water, and dilute the solution to a volume of 1 liter. Check the normality by titrating an aliquot of the 0.01*N* KCl conductivity reference solution reagent (section 62–2.2.2).
3. Sodium bicarbonate ($NaHCO_3$), saturated solution: Renew the solution every few weeks because it has a tendency to lose CO_2 and become too alkaline. Dispense the solution from a dropping bottle.

62–3.5.2.3 Procedure. Place the solution from the carbonate-bicarbonate titration in the titration assembly, and start the stirrer. If this solution is not available, take a new aliquot of the sample. Adjust the pH with $NaHCO_3$ solution (reagent 3) so that the solution is alkaline to methyl orange but acid to phenolphthalein. Usually a single drop of the $NaHCO_3$ solution is sufficient. Add K_2CrO_4 indicator (reagent 1), 1 drop per 5-ml. aliquot, and titrate the solution with the standard silver nitrate (reagent 2) until the appearance of a red or reddish-brown precipitate.

Determine a blank correction by titrating a like volume of Cl-free distilled water. The normal blank correction is 0.02 to 0.05 ml., depending on the final volume.

Calculation:

me. of Cl per liter

$$= \frac{1{,}000}{\text{ml. of sample}} \times (\text{ml. of AgNO}_3 - \text{blank}) \times \text{Normality of AgNO}_3.$$

62–3.5.2.4 Comments. The end point is sharper if the titration is done under a yellow light.

In general, the reproducibility and accuracy are of the order of 0.05 me. per liter in the aliquot titrated.

Difficulty is encountered if the solutions are highly colored, as may happen with extracts from sodic soils. These can be titrated potentiometrically, using an Ag-AgCl half-cell, as described in section 81–3.

62-3.6.1 *INTRODUCTI*

Boron tends to
trations of B in th
values of several h
have been found i
leached from the
necessary to reclai

Methods for th
studies are not we
without dilution,
veloped for toxici
purpose. The cor
toxicity investigati
oped in the samp
hours and obeys t
as overnight dryin
tion, are seldom re
in from 1 to 2 ho

Carmine or car
red to a bluish red

Nitrate and nit
extracts that interf
of concentrated H

62-3.6.2 *METHOD*[9]

62–3.6.2.1 Sp

1. A spectrophoto
14 Universal s
satisfactory.)
2. Flasks, alkali-r
ml., of Corning

62–3.6.2.2 R
free containers.

1. Sodium hydrox
in water, and di
2. Hydrochloric a
3. Hydrochloric a
trated HCl to 1
4. Sulfuric acid (

---

[9] Hatcher and Wil

Attachment H-10
DIOXIN (all isomers)

Method: Based on "Analytical Chemistry," 1980, 52, 2045-2054

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☒ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: ( ) (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested:

Analyze for 2,3,7,8 specific tetrachlorinated dibenzodioxin and dibenzofuran, total tetra through octa polychlorinated debenzodioxins and dibenzo furans and percent moisture. Do not subcontract without prior Regional approval.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

Analyze 54 soil samples and 20 sediment samples for the parameters listed above. The samples will have low to high concentrations of creosote and fuel oil.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier.

6. Approximate number of days results required after lab receipt of samples: Extract within days VTSR, analyze within days.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program): (See Attachment F-8)

Extraction: Benzene soxhlet as described in Anal. Chem. 1980, 52, 2045-2054. (Appendix I)

Clean Up: HPLC/RPHPLC as described in above reference or Dioxin IFB WA 86-K357 options including carbon column cleanup as needed to meet surrogate percent recovery limits. (Appendix II)

Instrument: Use HRMS or LRMS to meet target detection limits.

8. Special technical instruction (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

(1) Determine and report % moisture (use CLP IFB protocol - Appendix III)

(2) Report all data on dry weight basis.

(3) Stir soil samples for 30 seconds before removing aliquot.

(4) Quantitation and standards requirements. (Appendix IV)

(5) MUST monitor for the masses of the polychlorinated diphenyl ether interferences in all furan isomer groups.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Appendix V for deliverables.

Appendix VI for suggested data report format.

Remember to report % moisture.

10. Other (use additional sheets or attach supplementary information as needed):

DO NOT SUBCONTRACT WITHOUT PRIOR REGIONAL APPROVAL.

11. Name of sampling/shipping contact: **Jeff Keiser**

Phone: 414-272-2426

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should you have any questions or need any assistance, please call the Sample Management Office.

DATA REQUIREMENTS

Parameter:	TARGET Detection Limit	Precision Desired (±% or Conc.)
2378-TCDD/TCDF	5 ppt	See Dioxin page 4,c.
Total TCDD/TCDF	5 ppt	
Total Penta CDD/CDF	20 ppt	
Total Hexa CDD/CDF	20 ppt	
Total Hepta CDD/CDF	20 ppt	
OCDD/OCDF	50 ppt	

II. QC REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (% or Conc.)
Method Blank	1 per 20 SPLS or run	< Target D.L.
In lab matrix spike		see attachment
Matrix spike duplicate		see attachment
Surrogate spikes	In every sample	

III. *ACTION REQUIRED IF LIMITS ARE EXCEEDED:

1) FOLLOW PROCEDURES SPECIFIED IN DIOXIN IFB WA86-K357 (Appendix II).

2) Call Region V if problem persists. [Frank Thomas 312-886-5482]

Surrogate, Duplicate and Matrix Spike Limits

In Laboratory Matrix Spike

Compound	Level		Recovery Limits
2378-TCDD	$\leq$ 50 ppt		70 - 130%
2378-TCDF	$\leq$ 50 ppt		70 - 130%
enta CDD/CDF	$\leq$ 200 ppt	*	40 - 160%
exa CDD/CDF	$\leq$ 200 ppt	*	40 - 160%
pta CDD/CDF	$\leq$ 200 ppt	*	40 - 160%
OCDD/OCDF	$\leq$ 500 ppt	*	40 - 160%

t least one isomer from each of these classes should be used in the spike solution.

Surrogate Spikes (required in every sample)

Surrogate	Level ^{a}	Recovery Limits
l_4 2378-TCDD	5 ng	50 - 115%
C_{12} or $^{37}Cl_4$ 2378-TCDF	5 ng	50 - 115%
l_4-OCDD or ^{13}C-HpCDD	10 - 20 ng	40 - 110%

ded to 10g sample

In Matrix Spike Duplicate

Class	RPD Limit
78- TCDD/TCDF	$\leq$ 30% RPD
enta CDD/CDF	$\leq$ 60% RPD
Hexa CDD/CDF	$\leq$ 60% RPD
Hepta CDD/CDF	$\leq$ 60% RPD
OCDD/OCDF	$\leq$ 30% RPD

Anal. Chem. 1980, 5[illegible]045–2054

tion of Tetra-, Hexa-, Hepta-, and odibenzo-*p*-dioxin Isomers in Particulate Samples at Trillion Levels

and T. J. Nestrick

s, 574 Building, Dow Chemical U.S.A., Midland, Michigan 48640

edure is presented which permits the iso- mination of tetra-, hexa-, hepta-, and octa- dioxins simultaneously at parts per trillion Typical data are presented to establish its ariety of environmental particulate samples. y specific sample clean-up procedure based omatographies is shown to permit the iso- termination of 2,3,7,8-tetrachlorodibenzo-*p*- DD) by packed-column gas chromatogra- on mass spectrometry in the presence of any DD isomers.

nation of parts per trillion (10^{-12} g/g, pptr) s of chemical residues generally requires the use ly selective sample purification procedures ecific detectors (*1, 2*). As detection limits are umber of possible interferences present at oncentrations increases dramatically (*3*). Don- surmized that every known organic chemical cted in water at a level of 10^{-15} g/g or higher. sidering an analysis at the 10 pptr concentration nple matrix that is 99.9% pure, interferences from ^{5} compounds at concentrations 10^3 times higher ponent of interest are possible. Naturally the interferences from sources other than the sample make this task formidable. Such contamination reagents by a multitude of compounds has been *19*). Indeed, in some cases, the controlling factor ing the limit of detection (LoD) for a given analysis instrumental sensitivity of the detector but the sponse observed in reagent blanks (*20–22*).

er reports the development of an analytical pro- ich permits the isomer-specific determination of D at low parts per trillion concentrations, even in at have been intentionally fortified with equivalent f each of the other 21 TCDD isomers. Higher ted dioxins, including hexachlorodibenzo-*p*-dioxins 10 possible isomers), heptachlorodibenzo-*p*-dioxins 2 possible isomers), and octachlorodibenzo-*p*-dioxin can also be determined at low parts per trillion levels this technique. In regards to the isomer-specific nation of 2378-TCDC, the other 21 TCDD isomers be considered as possible interferences. Several ons have recently appeared which demonstrate CDD nation capabilities but do not provide complete TCDD pecificity (*23–32*).

EXPERIMENTAL SECTION

ents. The preparation of 44% concentrated sulfuric acid 10% silver nitrate on silica, basic alumina, and purified (Femtogas) have been described (*1*).

This adsorbent is prepared from chromatographic grade id as described for the preparation of 44% sulfuric acid (*1*).

1 M Sodium Hydroxide on Silica. The silica support red as described (*1*). Activated silica is weighed into an iately sized glass bottle. On the basis of the support weight, the amount of 1 M aqueous sodium hydroxide necessary to yield a reagent containing 33% by weight is added in a stepwise fashion with shaking to produce a uniformly coated, free-flowing powder.

Chemicals and Solvents. All solvents used are Burdick and Jackson, distilled-in-glass quality. Laboratory chemicals (H_2SO_4, $AgNO_3$, NaOH) are ACS reagent grade. These materials are tested by subjecting them to the analytical procedure to verify the absence of contamination. Spectrophotometric grade Gold-label *n*-hexadecane was obtained from Aldrich Chemical Co. (Milwaukee, WI) and was purified by passage through basic alumina.

Expendables. Pyrex glass wool, silica boiling stones, and disposable pipettes are cleaned before use. Glass wool and boiling stones are Soxhlet extracted ~1 h consecutively with the following solvents: methanol, chloroform + benzene (1:1 by volume), benzene, and methylene chloride. They are then dried in a hot air oven at ~160 °C for ~1 h. Disposable pipettes are cleaned ultrasonically in deionized water and then methanol and finally methylene chloride prior to drying at ~160 °C. Final sample residues are stored in Reacti-Vials obtained from Pierce Chemical Co. (Rockford, IL). The vials are cleaned by washing with detergent and water and then boiled sequentially in benzene + chloroform + methanol (1:1:1 by volume), benzene + chloroform (1:1 by volume), benzene, and finally methylene chloride. They are air-dried and again rinsed with methylene chloride immediately before use.

Dioxin Standards. The primary standard of 2378-TCDD was prepared by W. W. Muelder (Dow Chemical Co.) and its structure was confirmed by single-crystal X-ray diffraction techniques (*33*). Purity was assessed at 98% by mass spectrometry. Standards of other TCDD isomers were synthesized and isolated as previously described (*34*). Primary standards of 1,2,3,4,6,7,8-heptachlorodibenzo-*p*-dioxin (1234678-H_7CDD) and OCDD were synthesized by H. G. Fravel and W. W. Muelder (Dow Chemical Co.). A standard containing two HCDD isomers was prepared by Aniline (*35*). Standards of 1234679-H_7CDD and the 10 HCDD isomers were synthesized and isolated in a manner similar to that reported for TCDDs (*34*). Isotope-enriched ^{13}C-2378-TCDD and ^{13}C-123478-HCDD were synthesized by A. S. Kende (University of Rochester, Rochester, NY). Mass spectrometric analysis indicated these standards to be 86 atom % and 43 atom % ^{13}C, respectively. Perchlorination of the ^{13}C-2378-TCDD provided ^{13}C-OCDD.

Apparatus. *Reverse-Phase High-Performance Liquid Chromatography (RP-HPLC).* Residues containing chlorinated dioxins are injected into the RP-HPLC system: column, two 6.2 × 250 mm Zorbax-ODS (DuPont Instruments Division, Wilmington, DE) columns in series; isocratic eluent, methanol at 2.0 mL/min; pump, Altex Model 110A; column temperature, 50 °C; UV detector, Perkin-Elmer Model LC-65T liquid chromatographic column oven and detector operated at 0.02 aufs at 235 nm; injector, Rheodyne Model 7120 with 50-μL sample loop.

Normal-Phase Adsorption High-Performance Liquid *Chromatography (Silica-HPLC).* Residues containing TCDDs are injected into the silica-HPLC system: column, two 6.2 × 250 mm Zorbax-SIL (DuPont Instruments Division) columns in series; isocratic eluent, hexane at 2.0 mL/min; pump, Altex Model 110A; column temperature, ambient; UV detector, Laboratory Data Control Model 1204 variable-wavelength detector at 0.05 aufs at 235 nm; injector, Rheodyne Model 7120 with 100-μL sample injection loop. The columns were activated by the procedure of Bredeweg et al. (*36*).

Packed-Column Gas Chromatography–Low-Resolution Mass Spectrometry (GC-LRMS). Chlorinated dioxin quantification

Reprinted from Analytical Chemistry, 1980, 52, 2045.

was accomplished by GC-LRMS using a Hewlett-Packard Model 5992-A operating in the selected ion mode (SIM) at unit resolution: column, 2 mm i.d. × 210 cm silylated glass; packing, 0.60% OV-17 silicone + 0.40% Poly S-179 on 80/100 mesh Permabond Methyl Silicone-10 cycle (HNU Systems Inc., Newton, MA); injection port temperature, 280 °C on-column; carrier gas, helium at 14 cm^3/min; separator, single stage glass jet operating at column temperature; electron energy, 70 eV. TCDD analyses conditions: column temperature, 246 °C isothermal; ions monitored, native TCDDs at m/e 320, 322, and 324, and ^{13}C-2378-TCDD internal standard at m/e 332. Higher chlorinated dioxin analyses conditions: column temperature, programmed from 230 to 300 °C at 10 °C/min and hold at maximum; ions monitored, native HCDDs at m/e 388, 390, and 392, native H$_7$CDDs at m/e 422, 424, and 426, and native OCDD at m/e 458, 460, and 462. ^{13}C-123478-HCDD and ^{13}C-OCDD are monitored at m/e 398 and 470, respectively.

Environmental Particulate Samples. *Industrial Dust.* Particulates were removed from the air intake filtration system from a research building located in Midland, MI.

Electrostatically Precipitated Fly Ash. Particulates were collected from the ash-removal system associated with the electrostatic precipitator on the Nashville Thermal Transfer Corp. refuse incinerator located in Nashville, TN.

Activated Municipal Sludge. Representative samples were removed from the center of a commercially purchased 20-kg bag of Milwaukee Milorganite.

Urban Particulate Matter. Standard Reference Material No. 1648 was obtained from the National Bureau of Standards (NBS).

European Fly Ash. Particulate emissions from a municipal trash incinerator were collected on filter paper by a nonisokinetic sampling procedure. The location of the sampling port was downstream from the electrostatic precipitator. This incinerator was not operated to recover energy for power generation.

Sample Preparation. Prior to GC-LRMS SIM quantification, the sample is prepared by using five basic steps: (1) chlorinated dioxins removal from the matrix via hydrocarbon extraction, (2) chemically modified adsorbent treatment of the extract to remove easily oxidizable species, (3) adsorbent treatment to remove common chemical interferences, (4) RP-HPLC residue fractionation to remove residual chemically similar interferences and to separate dioxins present into groups according to their degree of chlorination, and (5) silica-HPLC refractionation of the RP-HPLC TCDD fractions to provide a second high-efficiency chromatographic separation having different selectivity to remove residual interferents and to permit TCDD isomer specificity.

An appropriately sized all-glass Soxhlet extraction apparatus equipped with a water-cooled condenser, a 43 × 125 mm glass thimble with coarse frit, a 250-mL boiling flask, and a temperature-controlled heating mantle is assembled. Each of the parts is thoroughly scrubbed with an aqueous detergent solution, rinsed with deionized water followed by acetone, methanol, and methylene chloride, and finally air-dried. Depending on the particulate sample size (larger samples require most), 5–15 g of silica is charged into the thimble followed by a plug of glass wool large enough to cover the silica bed completely. The assembled system (thimble installed) is charged with benzene (~250 mL) and allowed to reflux at a recycle rate of ~20 mL/min for a minimum period of 2 h. Following this preextraction period, the system is permitted to cool and the total benzene extract is discarded. The extraction thimble is removed and allowed to drain completely on a clean wire stand in a fume hood. The glass wool plug is removed with clean forceps while a representative particulate sample, ranging from 50 mg for filtered airborne particulates to 100 g for heavy soils, is quickly charged on top of the silica bed. The glass wool plug is replaced and the thimble returned to the Soxhlet extractor body. At this time aliquots of isooctane internal standard solutions containing isotopically labeled 2378-TCDD, 123478-HCDD, and OCDD are introduced directly into the particulates bed. The system is recharged with fresh benzene and exhaustively extracted at the rate previously described for a minimum period of 16 h. Each sample or set should have at least one system treated as described for the sample to serve as a reagent blank.

Upon completion of the prescribed extraction period, the flask containing the benzene extract is removed and fitted with a three- to six-stage Snyder distillation column. The volume of the extra solution is then reduced by atmospheric pressure distillation the benzene solvent to a final volume of approximately 25 mi The concentrated benzene extract is then diluted with a rough equal volume of hexane when cool.

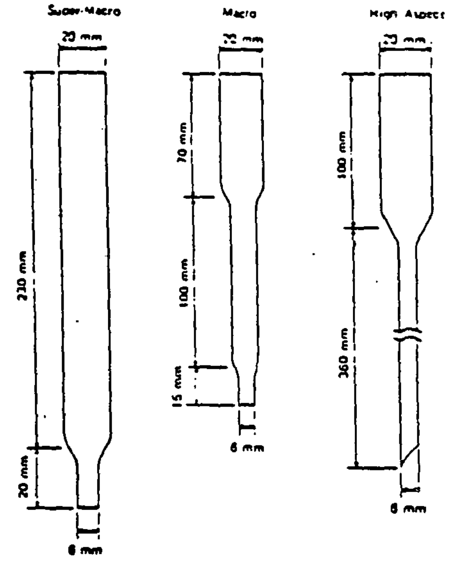

Figure 1. Liquid chromatographic clean-up columns.

Bulk matrix (benzene extractables other than CDDs) remov is accomplished by passing the residue extract solution throug a Super-Macro chromatographic column (see Figure 1) prepare as follows. The column is thoroughly washed and dried just pric to use via the same procedure described for the Soxhlet extracto A glass wool plug is inserted into the end of the column to serv as a bed support, and the following reagents are then carefull weighed directly into the column: 1.0 g of silica (bottom layer 2.0 g of 33% 1 M sodium hydroxide on silica, 1.0 g of silica, 4. g of 44% concentrated sulfuric acid on silica, and 2.0 g of silic (top layer). The freshly packed column is then immediate prewashed with 30 mL of hexane and the effluent discarded. Th residue extract is then passed through the column followed b 3 × 5-mL hexane rinses of the boiling flask vessel. Following the rinses an additional 30 mL of hexane is passed through th column. The total effluent is collected in a 150-mL beaker an then evaporated to dryness under a stream of Femtogas nitroge A single drop of n-hexadecane (~25 mg) is added to the reage blank prior to its evaporation to dryness as a means of improvi internal standard recovery.

Common chemical interferences are removed by passage of t residue through a dual column system consisting of a top Mac chromatographic column draining into a bottom High Aspe column. (See Figure 1.) Each of these columns is cleaned previously described and a glass wool bed support inserted ju prior to use. The Macro column is packed with 1.5 g of 10% silv nitrate on silica and prewashed with 15 mL of hexane prior use. The High Aspect column is packed with 5.0 g of bas alumina. When the top Macro column prewash has drained. is positioned over the High Aspect column reservoir. The samp residue is dissolved in ~15 mL of hexane and introduced in the top column followed by 3 × 5-mL hexane beaker rinse Following the rinses, an additional 30 mL of hexane is pass through the system. When drained, the top column is discarde After the hexane has drained to bed level in the High Aspe column, 50 mL of 50% (v/v) carbon tetrachloride in hexane passed through. The total effluent to this point can be discarde A 25-mL glass vial (cleaned same as chromatographic colum is used to collect the total effluent after 22.5 mL of 50% (v/ methylene chloride in hexane is introduced into the colum When elution is complete this fraction which contains chlorinat dioxins is evaporated to dryness under a stream of Femtog nitrogen (*1*).

RP-HPLC fractionation of the residue is initiated by calibrati of the appropriate collection zones for TCDDs, HCDDs, H$_7$CDI and OCDD. This is accomplished by injecting a calibrati

ble I. TCDD Isomer RP-HPLC Fractionation Scheme
d Specific Retention Indices

DD isomer	RP-HPLC abs RT,[a] min	silica-HPLC rel RT[b]	GC packed column rel RT[c]
	RP-Iso No. 1 Fraction		
1269	11.6-13.0	1.702	0.998
1469	11.6-13.0	1.497	0.912
1267/1289	12.2-12.9	1.623	1.081
	12.2-12.9	1.795	1.200
1268/1279	13.3-13.9	1.238	0.956
	13.3-13.9	1.291	1.065
1369/1478	13.3-13.9	1.220	0.802
	13.3-13.9	1.340	0.907
	RP-2378 Fraction		
1246/1249	13.7-14.5	1.328	0.896
	13.7-14.5	1.411	0.898
2378	13.8-14.5	1.000	1.006[d]
1236/1239	13.8-14.4	1.356	1.037
	14.4-15.2	1.350	0.969
1278	14.0-14.7	1.288	0.893
1237/1238	14.0-15.0	1.100	0.979
	14.0-15.0	1.128	0.990
1247/1248	14.2-15.1	1.154	0.854
	14.2-15.1	1.199	0.857
	RP-Iso No. 2 Fraction		
1378	14.9-15.7	1.000	0.858
1379	14.9-15.9	0.940	0.771
1368	~~15.9~~-16.8	0.977	0.729
1234	15.8-16.8	1.248	0.960

[a] RP-HPLC abs RT = absolute retention time (±0.1 min) to collect peak. [b] Silica-HPLC rel RT = retention time relative to 2378-TCDD (±0.010). [c] GC-packed column rel RT = retention time relative to ^{13}C-2378-TCDD (±0.005). [d] Native 2378-TCDD elutes slightly later than ^{13}C-2378-TCDD.

subjected to reverse-phase high-performance liquid chromatography fractionation. The resultant liquid chromatograms monitored by a UV detector at 235 nm (~λ_{max} for TCDDs) and 0.02 aufs are shown in Figure 3b–f. Shown in Figure 3a is the chromatogram obtained for a CDD calibration standard by RP-HPLC. Although the appropriate CDD collection zones, denoted by dotted lines, were initially established by individual injections of 22 TCDD isomers, 10 HCDD isomers, 2 H_7CDD isomers, and OCDD, we routinely compute their location from the observed retention times of only a few selected species. The specific RP-HPLC retention indices for TCDDs are given in Table I and those for HCDDs, H_7CDDs, and OCDD are listed in Table II.

As indicated, all 22 TCDD isomers can be fractionated from a sample residue by collecting the column effluent beginning at ~11.5 and ending at ~17.0 min. The initial stage of TCDD isomer specificity is achieved by collecting the 22 isomers in three separate fractions as shown. TCDD Iso No. 1 (RP-HPLC TCDD isomer fraction no. 1) can contain the following isomers: 1269-, 1469-, 1267-, 1289-, 1268-, 1279-, 1369-, and 1478-TCDD. The TCDD 2378 fraction contains 1246-, 1249-, 2378-, 1236-, 1239-, 1278-, 1237-, 1238-, 1247-, and 1248-TCDD. TCDD Iso No. 2 contains the remaining four isomers: 1378-, 1379-, 1368-, and 1234-TCDD. Preliminary evidence, gained by fortifying samples with roughly equal amounts of all 22 TCDD isomers at approximately the 150 pptr concentration level, has indicated that three of the possible isomers in TCDD Iso No. 1 must be sacrificed in order to ensure quantitative collection of 2378-TCDD in the following fraction. This consequence will be discussed later. Its occurrence is related to the RP-HPLC retention times for the isomers: 1369-TCDD, 1478-TCDD, and one of the pair 1268- or 1279-TCDD having Sil rel RT 1.238 (normal-phase silica HPLC retention time relative to 2378-TCDD). Their retention times are very close to the fraction boundary separating Iso No. 1 and 2378 and are split rather irreproducibly between these fractions. Although these isomers do not necessarily interfere with the quantitation of the isomers expected to the present in the TCDD 2378 fraction, their quantitation essentially becomes impossible. For cases where quantitation of these three TCDDs is required, a second aliquot of sample residue can be fractionated by RP-HPLC in such a manner so as to expand the Iso No. 1 fraction to ensure their collection.

Table II. HCDDs, H_7CDDs, and OCDD Retention Indices

CDD isomer	silica-HPLC rel RT[a]	RP-HPLC abs RT[b]	GC-packed column rel RT[c]
HCDDs			
123469-HCDD	1.081	19.23	0.954
123467-HCDD	1.192	19.47	1.077
124679/124689-HCDD	0.958	19.62	0.805
124679/124689-HCDD	0.972	19.70	0.806
123678/123789-HCDD	1.060	20.07	1.103
123679/123689-HCDD	0.970	20.20	0.903
123679/123689-HCDD	1.039	20.28	0.908
123678/123789-HCDD	0.974	20.85	1.016
123478-HCDD	0.941	21.02	1.006[d]
123468-HCDD	0.890	21.37	0.861
H_7CDDs			
1234679-H_7CDD		24.00	
1234678-H_7CDD		24.65	
OCDD		29.40	

[a] Silica-HPLC rel RT = retention time relative to 2378-TCDD (±0.010). [b] RP-HPLC abs RT = absolute retention (±0.1 min) at peak maximum. [c] GC packed column rel RT = retention time relative to ^{13}C-123478-HCDD. [d] Native 123478-HCDD elutes slightly later than ^{13}C-123478-HCDD.

The 10 HCDD isomers are collected in accordance with Figure 3 and Table II. Although isomer-specific HCDD determinations are possible by using essentially the same chromatography procedures described for TCDDs (i.e., RP-HPLC → silica-HPLC → GC), we have not yet applied this system to samples. Similarly, the two H_7CDD isomers are collected in a single fraction, as is OCDD.

The RP-HPLC residue fractionation chromatograms in Figure 3 are typical of those associated with particulate samples. The presence of higher chlorinated species, such as H_7CDDs and OCDD, can often be observed at this point in the analysis. Although the UV detector has been adjusted for maximum sensitivity for TCDDs, under these conditions a detectable response for HCDDs, H_7CDDs, and OCDD is obtained for approximately 5 ng. Similarly, heptachlorodibenzofurans (H_7CDFs) and octachlorodibenzofuran (OCDF) may also be observed in the RP-HPLC fractionation. Because of the lack of availability of authenticated chlorinated dibenzofuran (CDFs) standards, we have made no attempt to quantitate these species. Via collection of appropriate RP-HPLC fractions, and capillary GC-EC and GC-LRMS, we have established the possible presence of four H_7CDF isomers and OCDF in a variety of particulate samples.

Refractionation of the RP-HPLC TCDD fractions via normal-phase HPLC (silica-HPLC) is the final stage of the sample cleanup prior to GC-LRMS analysis. Normally monitoring of these chromatograms with a UV detector at 0.05 aufs and 235 nm does not produce observable peaks with the exception of the ^{13}C-2378-TCDD internal standard. For this reason example chromatograms are omitted. Table I lists the individual TCDD isomers contained in each RP-HPLC TCDD fraction. Included are the RP-HPLC, silica-HPLC, and GC packed column retention indices for each species. By use of standard containing approximately 10–20 ng each: 2378-TCDD, HCDD(s), H_7CDD(s), and OCDD in no more than 30 μL of chloroform. In accordance with the chromatogram obtained, appropriate collection zones are established for each of these species (see Discussion section). Following calibration, the injector is rinsed with copious quantities of chloroform, to include multiple consecutive injections of 50 μL of chloroform into the column to ensure that no residual chlorinated dioxins remain.

The residue is prepared for RP-HPLC fractionation by quantitative transfer to a 0.3-mL Reacti-Vial. Quantitative injection requires complete residue solubility in 30 μL or less of chloroform. Larger injections of chloroform into this RP-HPLC system severely reduce column efficiency. An aliquot of no more than 30 μL can be fractionated if the sample residue requires greater amounts of chloroform to be dissolved. Appropriate chlorinated dioxin fractions are collected in 25-mL volumetric flasks, equipped with ground glass stoppers, containing ~1 mL of hexane. The chlorinated dioxins are recovered by addition of 2% (w/v) aqueous sodium bicarbonate. The hexane layer is transferred to a 5-mL glass vial and the aqueous phase is extracted three additional times with ~1 mL of hexane. The combined extracts are then evaporated to dryness under a stream of Femtogas nitrogen. HCDD, H_7CDD, and OCDD fractions are quantitatively transferred to 0.3-mL Reacti-Vials and diluted to appropriate volumes for determination by GC-LRMS.

Regarding the case for an isomer-specific 2378-TCDD determination, additional silica-HPLC fractionation of the RP-HPLC 2378-TCDD fraction is required (see Discussion section). Calibration of the appropriate collection zone is accomplished by injecting approximately 10 ng of 2378-TCDD into the silica-HPLC in 60–80 μL of hexane and monitoring the chromatogram obtained. Adequate isomer specificity is obtained when the silica-HPLC columns are sufficiently dry so as to provide a 2378-TCDD retention time ranging from a minimum of 12.5 min to maximum of 17 min (*24*). Following injection of the residue fraction, the chromatogram is monitored and the appropriate 2378-TCDD fraction is collected in a 5-mL glass vial. This fraction is then evaporated to dryness under a stream of Femtogas nitrogen and diluted to appropriate volume for determination by GC-LRMS. This procedure can also be used to collect other TCDD isomers as described in the Discussion section; see Figure 2.

DISCUSSION

The purpose of this paper is to demonstrate the feasibility of using a single multiple-step procedure to accomplish the isomer-specific determination of TCDDs, HCDDs, H_7CDDs, and OCDD at low part per trillion concentrations in a variety of environmental particulate samples. There were two prerequisites for our development of the methodology. First, the sample cleanup must be capable of recovering each of the listed chlorinated dioxin (CDD) groups from a single sample and from a single workup. And second, all procedures must use the least sophisticated and most reliable instrumentation possible so that such analyses could be conducted in the greatest number of analytical facilities. These prerequisites have determined the means by which the described analyses can be accomplished. That is, a neutral or acid extraction procedure must be used. Any treatment of either the sample or its extracts with strong bases is known to cause degradation of the higher chlorinated dioxins (*21, 37*). In accordance with ease of handling and the general solubility characteristics of higher chlorinated dioxins (least soluble species), continuous benzene extraction was found to be adequate for all particulate samples examined. The selection of packed-column gas chromatography–low-resolution mass spectrometry as opposed to capillary column gas chromatography–high-resolution mass spectrometry represents our attempt to use the least sophisticated instrumentation for CDD determination. Because packed-column GC-LRMS is inherently more subject to possible interference than capillary column GC-HRMS, a more rigorous sample preparation is required. The approach of combining classical extraction and adsorbent clean-up techniques with consecutive RP-HPLC and silica-HPLC residue fractionations can be one solution to this problem. Under these circumstances a significant portion of the method capabilities to prevent MS interferences during the identification and quantification of CDDs is relegated to the cleanup rather than to the final gas chromatographic separation. This can be advantageous when dealing with highly contaminated samples because the chromatographic capacity of the clean-up steps is usually much greater than that of the GC column, especially when capillaries are used. In addition, this approach incorporates the consecutive RP-HPLC and silica-HPLC steps that we have published for the separation and isolation of the 22 TCDD isomers (*34*). Their described application in this procedure permits the analyst to predetermine which possible TCDD isomers can be present in a given residue fraction. Hence, the necessity of using a capillary GC column to obtain improved TCDD isomer separations is eliminated. This capability may be of utmost importance as the authors are not aware of any published data suggesting that all 22 TCDD isomers can be separated simultaneously using a single capillary GC column. The described methodology will address this problem.

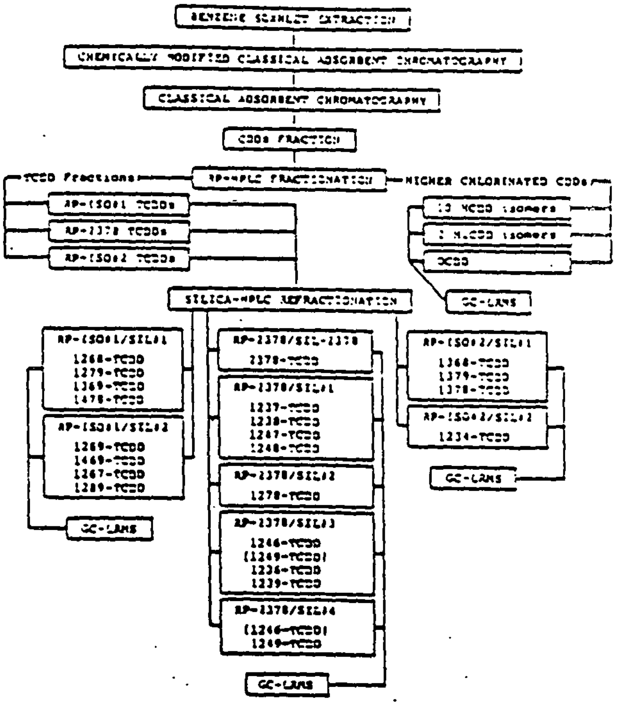

Figure 2. Block diagram for CDD sample preparation.

It is to be understood that this procedure has been developed and used for survey purposes on a variety of different environmental particulates. A complete method validation including controls, fortifications, and replicates would be required for each specific matrix before its absolute degree of reliability can be established. The inclusion of isotopically enriched TCDD, HCDD, and OCDD internal standards provide a reasonable degree of reliability under the circumstances of its described uses.

The samples 1.0 g of NBS urban particulate matter, 1.0 g of industrial dust, 1.0 g of electrostatically precipitated fly ash from a municipal burner (fly ash), 16.7 g of Milorganite, and 0.3968 g of European flyash were Soxhlet extracted with benzene for ~16 h and the resulting residues processed through the preliminary liquid chromatographic clean-up steps. Each sample, to include a reagent blank, was fortified with 5–20 ng of isotopically enriched internal standard CDDs (^{13}C enrichment) prior to analysis. After transfer to a 0.3-mL Reacti-Vial and evaporation of the solvent, all samples yielded

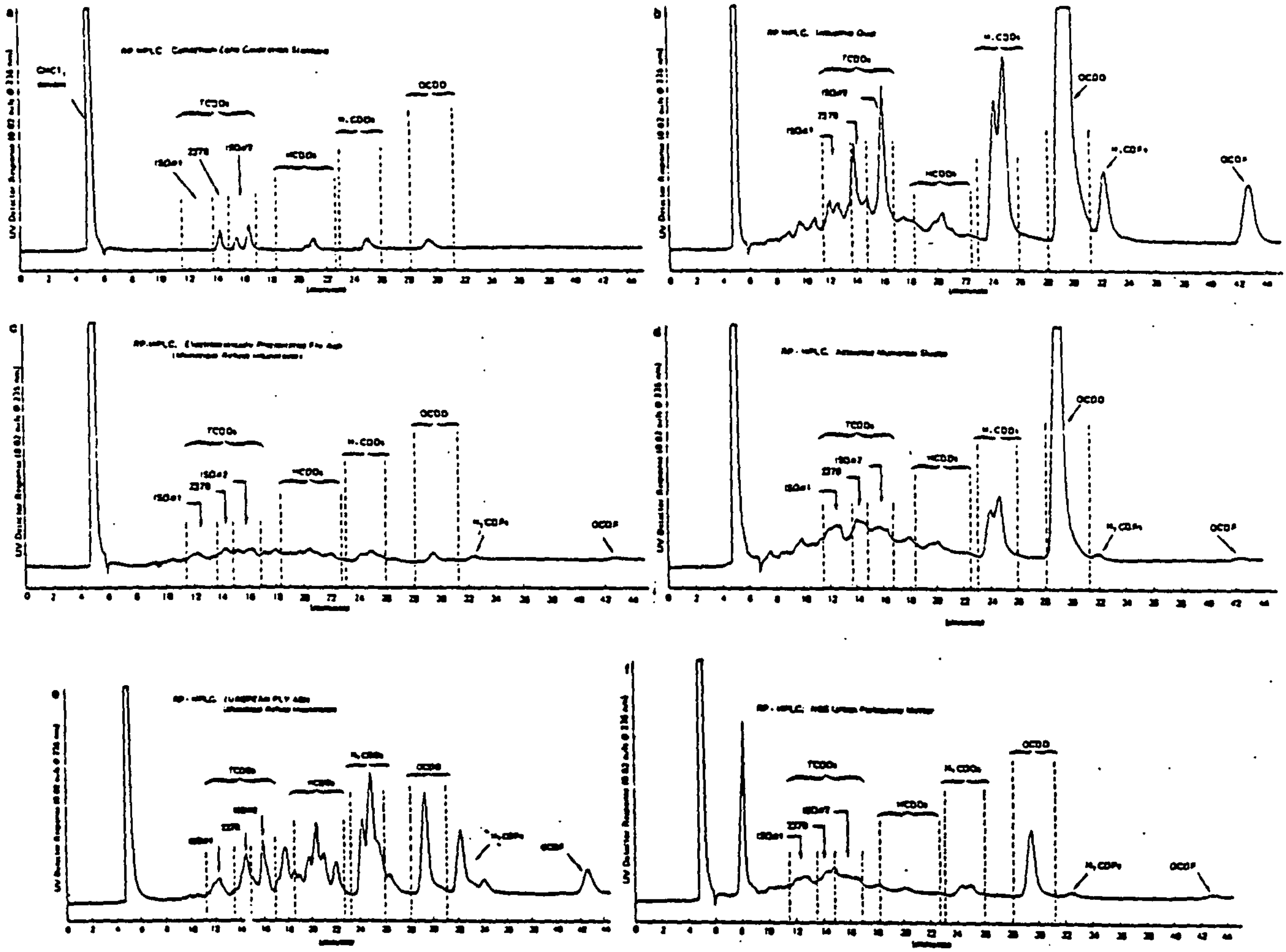

Figure 3. RP-HPLC fractionation chromatograms: (a) calibration standard, (b) industrial dust, (c) electrostatic fly ash, (d) municipal sludge, (e) European fly ash, (f) NBS urban particulates.

this information, appropriate fractions can be collected from the silica-HPLC which permit isomer-specific GC-LRMS identification and quantitation.

The silica-HPLC TCDDs fractionation scheme in Table III is designed to provide maximum isomer-specific information when using our packed-column GC-LRMS analysis, while minimizing the total number of fractions collected. Remembering that the primary goal was to provide the highest quality analytical data for 2378-TCDD, this scheme is adequate. Examination of the GC packed column relative retention times (GC rel RT, TCDD retention time relative to ^{13}C-2378-TCDD) for all TCDDs present in the RP-2378-TCDD fraction indicates that four other TCDDs have GC rel RTs within ±0.050 (~12 s for 4 min absolute retention time for ^{13}C-2378-TCDD) of 2378-TCDD. Arbitrarily defining GC rel RT ±0.050 as the minimum GC pakced column separation for qualitative identification of a TCDD isomer from 2378-TCDD and then direct GC-LRMS analysis of the RP-2378-TCDD fraction would yield a 2378-TCDD value which could include a maximum of four other TCDD isomers (2378-TCDD + 4). However, examination of the silica HPLC relative retention times (Sil rel RT, TCDD retention time relative to 2378-TCDD) for these TCDDs indicates that 2378-TCDD is the first isomer to elute. The next isomer to elute is 1237/1238-TCDD (Sil rel RT 1.10); however, even at the minimum acceptable silica-HPLC retention time for 2378-TCDD which is ~12.5 min, this isomer is separated by ~1.75 min. The remaining nine TCDD isomers, other than 2378-TCDD, present in the RP-2378-TCDD fraction can be determined as single isomers with the exception of those in Sil Fraction No. 1. Although 1237-, 1238-, 1247-, and 1248-TCDD are essentially baseline separated by silica-HPLC, attempts to collect them in individual fractions under conditions where the species cannot be observed by a UV detector would be difficult. Hence a single fraction is collected for GC-LRMS analysis. As indicated by the respective GC rel RTs, these isomers can be determined as a total for 1237- and 1238-TCDD and a total for 1247- and 1248-TCDD.

Three of the TCDD isomers present in RP-Iso No. 1 are sacrificed in order to ensure maximum recovery of 2378-TCDD in the following RP-HPLC fraction. The consequence of this situation is the possible presence of 1268/1279-TCDD (Sil rel RT 1.238), 1369-TCDD, and 1478-TCDD in the RP-2378-TCDD fraction. Regarding their effect upon the isomer-specific determination of 2378-TCDD, it can be observed that no interference occurs by virtue of both their respective silica-HPLC rel RTs and their GC-packed column rel RTs. However, under circumstances where the 1268/1279-TCDD (Sil rel RT 1.238) isomer is relatively high in concentration, it could be misidentified as 1237- and 1238-TCDD present in Sil Fraction No. 1 of the RP-2378-TCDD fraction. This interference results from similar GC rel RTs for these isomers as indicated in Table III. The 1369/1478-TCDD (Sil rel RT 1.220) will not cause any similar interference problems with those TCDDs present in RP-2378-TCDD fraction—Sil Fraction No. 1 because of its GC rel RT of 0.802. The remaining isomer, 1369/1478-TCDD (Sil rel RT 1.340), if present in high concentration may interfere with 1246/1249-TCDD (Sil rel RT 1.411) in RP-2378-TCDD fraction-Sil Fraction No. 3.

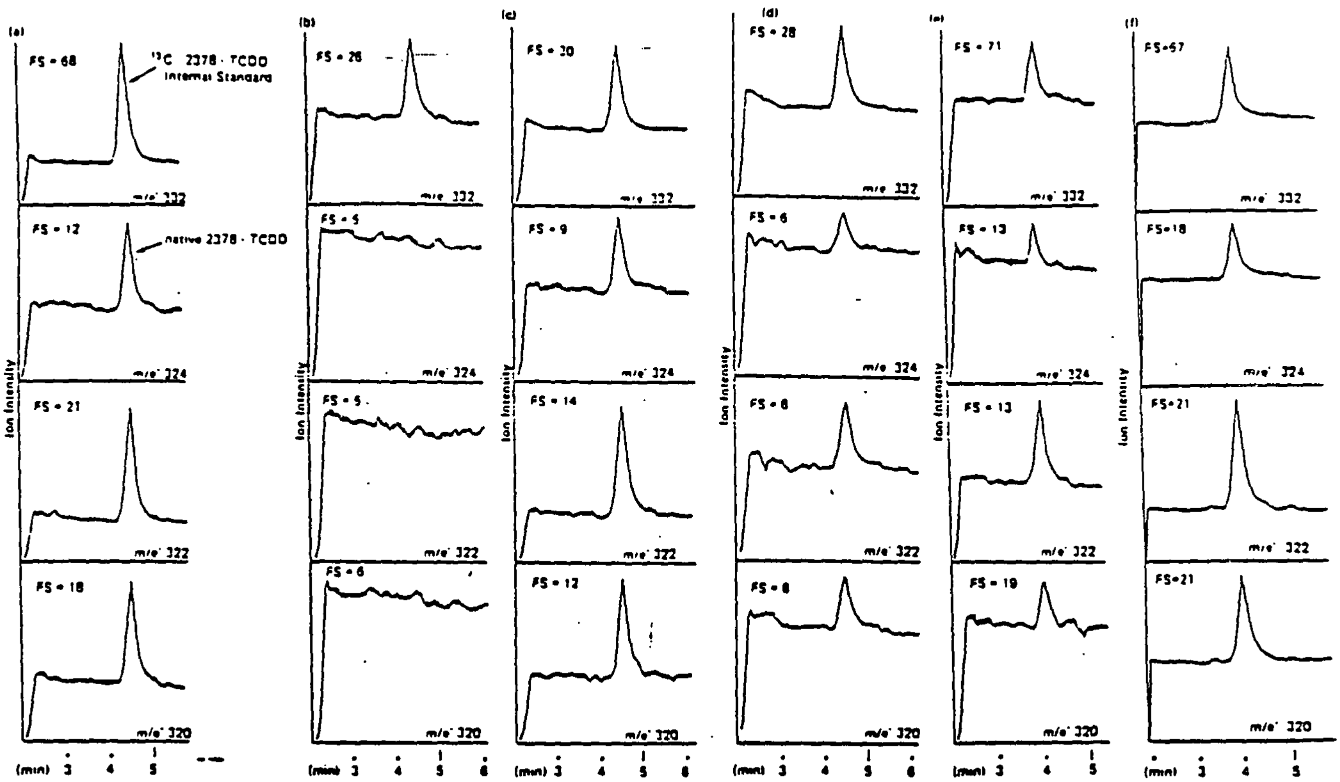

Figure 4. Isomer-specific 2378-TCDD GC-LRMS mass chromatograms: (a) calibration standard, (b) reagent blank, (c) industrial dust, (d) electrostati fly ash, (e) municipal sludge, (f) European fly ash.

GC-LRMS mass chromatograms for the isomer-specific 2378-TCDD fractions of each particulate sample analyzed are shown in Figure 4. Native 2378-TCDD is monitored at m/e 320, 322, and 324 and ^{13}C-2378-TCDD at 332. The calibration standard (Figure 4a shown is typical for a 2-μL injection of a reference standard containing 100 pg/μL of native 2378-TCDD and 500 pg/μL of ^{13}C-2378-TCDD.

The GC-LRMS mass chromatograms in Figure 5 compare the analysis of the RP-2378-TCDD fraction from electrostatically precipitated fly ash for 2378-TCDD, before and after silica-HPLC refractionation. As a means of ensuring homogeneity, a 2-g portion of sample was processed through the cleanup including RP-HPLC fractionation. At this point the RP-2378-TCDD fraction was divided into two equal portions, each equivalent to 1 g of original sample. One portion was analyzed directly by GC-LRMS as illustrated in Figure 5a. The other portion was further fractionated by silica-HPLC, the Sil Fraction 2378 collected, and this residue analyzed by GC-LRMS (Figure 5b). Comparison of 2378-TCDD quantitation for these residues yields 1500 pptr before silica-HPLC refractionation, and 430 pptr after. The value obtained before silica-HPLC refractionation must be qualified as being the concentration of 2378-HPLC plus four possible unseparated isomers (see Table IV).

Isomer-specific TCDD analysis data for each of the described particulate samples appear in Tables IV and V. Quantitation of TCDDs was accomplished by averaging the observed response at m/e 320, 322, and 324 for all cases except where denoted. Instrumental calibration for all TCDD isomers was based upon the observed responses for a primary standard of 2378-TCDD. The listed concentrations for 2378-TCDD have been corrected for recovery of the ^{13}C-2378-TCDD internal standard as given in Table V. Concentrations given for all other TCDD isomers represent absolute observed values. The limit of detection (LoD) for all species was defined as 2.5 × peak-to-valley noise in a region nearby the expected elution time. Observed concentrations less than the LoD are listed as not detected (ND).

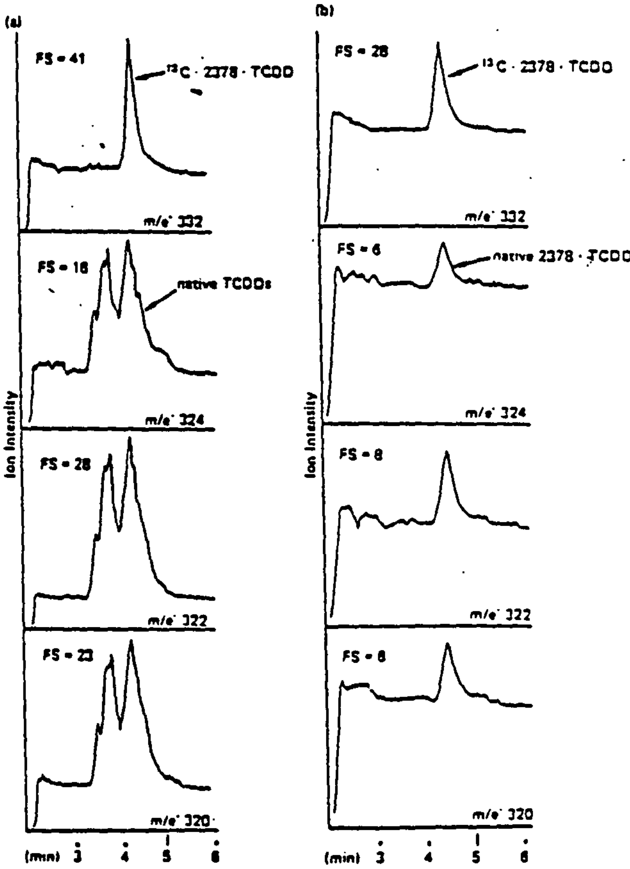

Figure 5. Comparative 2378-TCDD GC-LRMS mass chromatogram for electrostatic fly ash (a) after RP-HPLC (RP-2378 fraction) (b) afte silica-HPLC (silica-2378 fraction).

As a means of investigating the degree of reliability asso ciated with the isomer-specific determination of 2378-TCD in a sample containing equivalent concentrations of all 21 oth

III. TCDD Isomer Silica-HPLC Fractionation and Specific Retention Indices

CDD isomer	silica-HPLC rel RT[a]	Sil collection zone rel RT[a]	GC packed column rel RT[b]
RP-Isol No. 1 Fraction TCDDs			
raction no. 1		1.180-1.370	
68/1279-TCDD	1.238[c]		0.956
	1.291		1.065
9/1478-TCDD	1.220[c]		0.802
	1.340[c]		0.907
raction no. 2		1.455-1.850	
69-TCDD	1.702		0.998
9-TCDD	1.497		0.912
57/1289-TCDD	1.623		1.081
	1.795		1.200
RP-2378 Fraction TCDDs			
action 2378		0.950-1.050	
78-TCDD	1.000		1.006[d]
fraction no. 1		1.050-1.244	
237/1238-TCDD[e]	1.100		0.979
	1.128		0.990
47/1248-TCDD[e]	1.154		0.854
	1.199		0.857
fraction no. 2		1.244-1.300	
78-TCDD	1.288		0.893
action no. 3		1.300-1.385	
46/1249-TCDD	1.328		0.896
1236/1239-TCDD	1.356		1.037
	1.350		0.969
raction no. 4		1.385-1.450	
46/1249-TCDD	1.411		0.898
RP-Iso No. 2 Fraction TCDDs			
fraction no. 1[f]		0.900-1.050	
168-TCDD	0.940		0.729
379-TCDD	0.977		0.771
1378-TCDD	1.000		0.858
fraction no. 2[f]		1.210-1.288	
234-TCDD	1.248		0.960

lica-HPLC rel RT = retention time relative to 2378-DD (±0.010). [b] GC packed column rel RT = retention e relative to ^{13}C-2378-TCDD (±0.005). [c] See text for ery information. [d] Native 2378-TCDD elutes ly later than ^{13}C-2378-TCDD. [e] Related isomers ally reported as a total. [f] Fractions typically com- ed prior to GC-LRMS analysis.

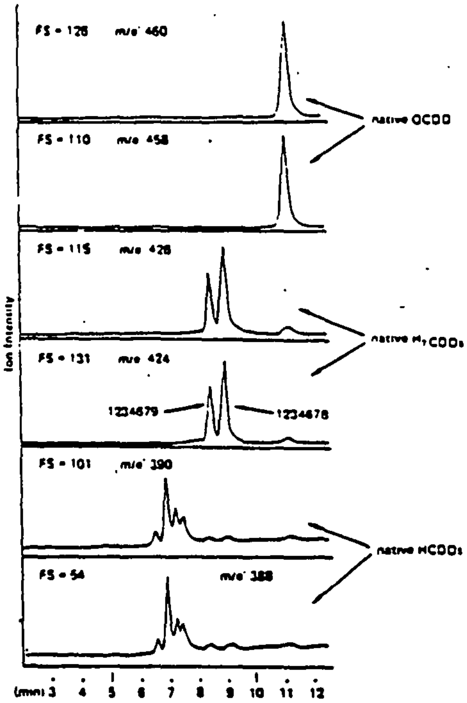

Figure 6. Higher chlorinated dioxin GC-LRMS mass chromatograms for electrostatic fly ash.

D isomers, we intentionally fortified a second portion of ipal sludge with each TCDD isomer at the levels shown Table VI. Neither 1237- or 1238-TCDD was added due heir natural presence at 230 pptr (see Table V). Analysis e fortified sample yielded the recovery data shown in VI. Regarding the 2378-TCDD data, the amount found s corrected for the recovery of the ^{13}C-2378-TCDD and also he 20 pptr natural 2378-TCDD previously observed in the sample. These data indicate that no other TCDD isomer interferes with the determination of 2378-TCDD when this analytical procedure is used. Recovery values given for all other TCDD isomers represent absolute observed values and were corrected for natural levels when necessary as listed in Table VI.

Typical temperature programmed GC-LRMS mass chromatograms for the determination of higher chlorinated dioxins appear in Figure 6. For the analysis of electrostatically precipitated fly ash the RP-HPLC HCDDs, H$_7$CDDs, and OCDD fractions were combined prior to GC-LRMS examination (see Figure 3c). As a means of overcoming problems associated with samples having relatively large amounts of native chlorinated dioxins compared to the 1–20 ng of fortified internal standards, a complete method validation study was conducted for HCDDs, H$_7$CDDs, and OCDD ranging from 50 pptr to 10 ppm (μg/g) and from 10 pptr to 5 ppb for 2378-TCDD. The control particulate sample used was a sandy loam soil, to which was added $\sim$150 μL of Mobile 1 synthetic engine lubricant per 20 g, as a means of increasing the total organics content to better simulate typical particulates. The following native CDD standards were used for sample fortification: 2378-TCDD, 123678-HCDD, 123679/123689-HCDD (Sil rel RT 1.039), 1234678-H$_7$CDD, and OCDD. The results of this

e IV. Chlorinated Dioxins Observed in Environmental Particulate Samples

CDDs	reagent blank, ng	parts per billion				
		industrial dust	electrostatic flyash	municipal sludge	European flyash	NBS urban particulates
2378-TCDD + 4 isomers[a]	ND (0.06)	...[b]	1.5[b]	...[b]	...[b]	0.12 (0.12)[e]
other TCDDs (17 isomers)	ND (0.04)	...[b]	...[b]	...[b]	...[b]	0.16 (0.08)
HCDDs[c] (10 isomers)	ND (0.18)	ND (14)	14	2.1	550[d]	2 (2)
1234679-H$_7$CDD[c]	ND (0.14)	200	11	14	470	16
1234678-H$_7$CDD[c]	ND (0.14)	220	17	15	570	18
OCDD[c]	ND (0.29)	4000	30	180	650	210

RP-HPLC RP-2378 fraction analyzed directly by GC-LRMS and not isomer specific as described in text. [b] Sample fully tionated for isomer-specific results given in Table V. [c] Observed values without correction run as part of validation ork reported in Table VII. [d] For "semi" isomer specific see Table VIII. [e] ^{13}C-2378-TCDD recovery 78% and value listed as been corrected, see Table V for others, and ND = compound not detected at limit of detection in parentheses and no entheses indicates detected signal ≥10× limit of detection.

Table V. Isomer-Specific TCDD Analyses of Environmental Particulate Samples

		parts per trillion			
TCDD isomer	reagent blank, pg	industrial dust	electrostatic flyash	municipal sludge	European flyash
2378-TCDD^{a}	ND (40)	1100	430 (110)	20 (2)	2300
1269-TCDD	ND (20)	ND (40)	190 (60)	ND (2)	1000 (140)
1469-TCDD	ND (20)	ND (50)	ND (50)	ND (2)	250 (140)
1267/1289-TCDD Sil rel RT 1.623	ND (20)	ND (50)	100 (60)	ND (2)	300 (140)
1267/1289-TCDD Sil rel RT 1.795	ND (20)	ND (50)	120 (60)	ND (2)	500 (140)
1268/1279-TCDD Sil rel RT 1.238	ND (30)	...^{b}	190 (90)^{c}	...	1000^{c}
1268/1279-TCDD Sil rel RT 1.291	ND (30)	ND (50)	310 (90)	3 (3)^{d}	1500
1369/1478-TCDD Sil rel RT 1.220	...	...	...	...	...
1369/1478-TCDD Sil rel RT 1.340	...	...	...	...	...
1278-TCDD	ND (60)	ND (40)	ND (80)	ND (3)	3100
1236/1239-TCDD Sil rel RT 1.356	ND (60)	ND (60)	280 (110)	ND (3)	1500
1236/1239-TCDD Sil rel RT 1.350	ND (60)	ND (60)	150 (110)	ND (3)	800 (400)
1237/1238-TCDD Sil rel RT 1.100	ND (60)	240 (50)^{e}	720^{e}	230^{e}	8500^{e}
1237/1238-TCDD Sil rel RT 1.128					
1246/1249-TCDD Sil rel RT 1.328	ND (60)	ND (60)^{e}	730 (110)^{e}	ND (3)^{e}	2000^{e}
1246/1249-TCDD Sil rel RT 1.411					1500
1247/1248-TCDD Sil rel RT 1.154	ND (60)	140 (50)	310 (70)	8 (2)	6900
1247/1248-TCDD Sil rel RT 1.199					
1378-TCDD	ND (20)	560 (110)	1370 (150)	23 (5)	13200
1379-TCDD	ND (20)	1340	1160 (150)	13 (5)	7000
1368-TCDD	ND (20)	2780	1320 (150)	13 (5)	16200
1234-TCDD	ND (20)	180	370 (150)	ND (30)	2100
total TCDDs	ND	6340	7750	310	69800
^{13}C-2378-TCDD % recovery	63%	59%	54%	61%	56%

^{a} Corrected for ^{13}C-2378-TCDD recovery and all other isomers are absolute observed. ^{b} ··· = not recovered as described in text. ^{c} Observed but recovery questionable. ^{d} Detected on *m/e* 322 only. ^{e} Possible isomer interference as described in text.

Table VI. Isomer-Specific TCDD Analysis of Municipal Sludge after Fortification

	concn in pptr		
TCDD isomer	added	found	% recovery
2378-TCDD	143	140	98^{a}
1269-TCDD	150	108	72
1469-TCDD	166	122	73
1267/1289-TCDD Sil rel RT 1.623	150	126	84
1267/1289-TCDD Sil rel RT 1.795	171	145	85
1268/1279-TCDD Sil rel RT 1.238	137	...^{b}	...
1268/1279-TCDD Sil rel RT 1.291	140	69	49
1369/1478-TCDD Sil rel RT 1.220	143	...	...
1369/1478-TCDD Sil rel RT 1.340	151	...	...
1278-TCDD	160	104	65
1236/1239-TCDD Sil rel RT 1.356	147	103	70
1236/1239-TCDD Sil rel RT 1.350	146	80	55
1237/1238-TCDD Sil rel RT 1.100	^{c}	(180)^{d}	
1237/1238-TCDD Sil rel RT 1.128			
1246/1249-TCDD Sil rel RT 1.328	141	220^{e}	75
1246/1249-TCDD Sil rel RT 1.411	151		
1247/1248-TCDD Sil rel RT 1.154	131	203^{e}	69
1247/1248-TCDD Sil rel RT 1.199	163		
1378-TCDD	171	151	88
1379-TCDD	171	138	81
1368-TCDD	101	45	45
1234-TCDD	143	122	85

^{a} Corrected for recovery of ^{13}C-2378-TCDD (72%) and native 2378-TCDD present given in Table V, all other isomers are absolute observed. ^{b} ··· = not recovered as described in text. ^{c} Total not added. High native concentration given in Table V. ^{d} Absolute amount observed in this sample. ^{e} Total.

study appear in Table VII. These data indicate that the average recoveries of HCDDs, H$_7$CDDS, and OCDD over the described concentrations range are reasonably constant and are between 70 and 80%. Because typical particulate samples contain higher chlorinated CDDs within this range, recovery factors derived from the validation can be used. Since ^{13}C-labeled internal standards are added to all samples, whenever very low native concentrations are observed appropriate correction factors can be applied. Note that recovery values reported for TCDD have been corrected for the observed ^{13}C-2378-TCDD internal standard recoveries after RP-HPLC fractionation.

Chlorinated Dioxin Recovery and Precision Data for Fortified Sandy Loam Soil[a]

2373-TCDD[b]			HCDD			H.CDD			OCDD		
dded, pptr	found, pptr	%	added, pptr	found, pptr	%	added, pptr	found, pptr	%	added, pptr	found, pptr	%
10	13	130	50	30	60	50	46	92	200	160	80
20	28	140	100	72	72	100	75	75	400	330	83
20	21	105	100	57	57	100	65	65	400	260	65
50	49	98	250	160	64	250	170	68	1000	730	73
50	45	90	250	180	72	250	200	80	1000	820	82
50	51	102	250	170	68	250	200	80	1000	780	78
50	53	106	250	170	68	250	170	68	1000	720	72
50	50	100	250	190	76	250	210	84	1000	880	88
50	50	100	250	160	64	250	160	64	1000	700	70
50	47	94	250	180	72	250	180	72	1000	690	69
50	52	104	250	170	68	250	160	64	1000	690	69
100	97	97	500	410	82	500	430	86	2000	1900	95
100	109	109	500	440	88	500	460	92	2000	2060	103
5000	5350	107	1×10^6	8.1×10^5	87	5×10^6	4.5×10^6	90	10×10^6	8.4×10^6	84
5000	5400	108	1×10^6	9.1×10^5	91	5×10^6	4.7×10^6	94	10×10^6	9.0×10^6	90
		106			73			78			80
		13			10			11			11
50	49.6	99.2	250	173	69	250	181	72	1000	751	75
	2.6	5.2		10.4	6.0		19.6	10.8		69.4	9.2

a for all species obtained by GC-LRMS analysis of appropriate RP-HPLC fractions. 2378-TCDD values corrected for 8-TCDD internal standard recovery, other CDDs are absolute observed. [b] Corrected for ^{13}C-2378-TCDD where ecovery was 59.8% for all samples. [c] $\bar{x}$ all and σ all represent the mean and standard deviation of all samples. [d] $\bar{x}$ σ prec represent the mean and standard deviation of samples 4–11 to determine precision of the analysis.

VIII. "Semi" Isomer-Specific HCDD Analysis Data for European Flyash, Absolute Values Reported

HCDD isomer[a]	parts per billion reagent blank	parts per billion European flyash
124679/124689-HCDD Sil rel RT 0.958 124679/124689-HCDD Sil rel RT 0.972	ND (0.13)[b,c]	82[c]
123468-HCDD	ND (0.13)	9 (9)
123679/123689-HCDD Sil rel RT 0.970 123679/123689-HCDD Sil rel RT 1.039 123469-HCDD	ND (0.13)[c]	260[c]
123478-HCDD 123678/123789-HCDD Sil rel RT 0.974	ND (0.13)[c]	110[c]
123678/123789-HCDD Sil rel RT 1.060 123467-HCDD	ND (0.13)[c]	85 (9)[c]

ICDD Sil rel RT = retention time relative to 2378-TCDD by silica-HPLC (Table II). [b] ND (0.13) is not detected with of detection in ppb based on flyash sample size. [c] Total.

-LRMS analysis data for higher chlorinated CDDs ap- : in Tables IV and VIII. Table VIII illustrates a format HCDD determination that is "semi"-isomer specific. In ase, the total RP-HCDDs fraction was analyzed directly cked-column GC-LRMS. However, because GC rel RTs e been experimentally determined (see Table II) for all ndividual HCDD isomers, we can separate the HCDDs rved into five distinct groups. Within each group only ited number of isomers are possible. These analyses are complished by using isothermal column condition (~270 so as to maximize the separation power of the column and nprove relative retention time measurements.

CONCLUSIONS

Although this paper demonstrates the applicability of a ltiple-step procedure to isomer-specifically determine a iety of CDDs in environmental particulate samples, we have so applied the technique to many other matrices successfully. nple modification of the preliminary matrix extraction has rmitted the analysis of tissues, human milk, vegetable atter, chemical products, and wastes without sacrificing high ensitivity or isomer specificity. This procedure, utilizing cked-column GC-LRMS, has provided reliable results for veral heavily contaminated matrices where the combination of a less sophisticated cleanup followed by both packed and capillary column GC-HR MS has failed. Interested individuals may request a more thorough discussion of the method development experiments from the authors.

ACKNOWLEDGMENT

The authors express their gratitude to O. Hutzinger for graciously suppling the European fly ash sample and to R. Bumb, W. Crummett, and V. Stenger for their help in repairing this manuscript.

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RECEIVED for review January 28, 1980. Resubmitted May 1980. Accepted July 31, 1980.

Secondary Ion Mass Spectra of Diquaternary Ammonium Salts

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Molecular dications emitted by momentum transfer processes are observed in secondary ion mass spectra (SIMS) of diquaternary ammonium salts. The relationship between molecular structure and the observation of dications is explored. Large intercharge separations, corresponding to lessened intramolecular coulombic repulsions, are observed to correlate with dication detection. Fragmentation with charge separation is facilitated by small intercharge distances and can preclude observation of the dication. Electron attachment to yield the monocation is an alternative to dication emission when the structure of the dication facilitates reduction. This occurs, for example, for the herbicide diquat (*N,N′*-ethylene-2,2′-bipyridyl dibromide) which is detected as its monocation. Complete spectra of diquaternaries can be taken with nanogram size samples.

Secondary ion mass spectrometry (SIMS) has recently been shown to be a sensitive method for the characterization of organic salts (*1–4*). Reported here is the observation of intact organic dications emitted from diquaternary ammonium salts upon sputtering. This constitutes the first observation of multiply charged organic molecular ions in SIMS. The result is of interest with regard to both analytical applications of SIMS and the fundamentals of ionization during sputtering. Specifically, some biologically important compounds, such as the herbicides paraquat and diquat and the curare alkaloids, have the diquaternary structure, so that SIMS may facilitate their characterization. In addition, studies on organic dications reflect the degree to which electron attachment occurs during sputtering. This process yields observable charged products for dications, but neutrals are sputtered when monocations are reduced during ion bombardment.

EXPERIMENTAL SECTION

All compounds were synthesized by using standard methods for the preparation of quaternary ammonium salts. The organic salts were burnished onto a 1 cm^2 roughened foil of either silver or platinum prior to SIMS analysis using argon primary ions at 5 keV and 0.3–0.5 nA primary ion current. Beam diameter was approximately 1 mm and pressures in the ultra-high-vacuum chamber remained below 1×10^{-4} torr during the course of the experiments.

All spectra were taken with Riber SIMS system using a quadrupole mass analyzer, Channeltron electron multiplier, and pulse-counting electronics.

Intercharge distances were measured by using Dreiding models; charge localization on nitrogen was assumed and the maximum distance in the unstrained molecule is reported. Intercharge distances (r) were used to calculate coulombic repulsive energies (T) from T (eV) = $14.6/r$ (Å).

RESULTS AND DISCUSSION

The SIMS spectrum of *N,N′*-bis(dimethyl)-4,4′-trimethylenedipiperidine diiodide (1) is shown in Figure 1. This spectrum provides both the molecular weight (inferred from the highest mass doubly charged ion, 268^{2+}) and structural information on the compound. Emission of the doubly charged species is confirmed by the observation of the ^{13}C isotope peak one-half mass unit above the dication peak (m/z 134.5 in Figure 2). Changing the counterion does not affect the SIMS spectrum; for example, the dibromide and diiodide of compound 1 gave identical SIMS spectra.

Analogous results were obtained for *N,N′*-bis(ethylmethyl)-4,4′-trimethylenedipiperidine diiodide (2) and for the aromatic compounds *N,N′*-bis(trimethyl)-4,4′-methylenedianiline diiodide (3) and *N,N′*-bis(dimethylethyl)-4,4′-methylenedianiline diiodide (4). The spectrum of compound 3 is shown in Figure 3; the dication, 284^{2+} at m/z 142 is of relatively low abundance, but its ^{13}C isotope is well resolved in high-resolution scans.

A considerable number of diquaternary salts (5–19, Table I) did not exhibit observable dications. Compounds 18 and 19, while they did not yield molecular dications, did show the corresponding singly charged ions in their SIMS spectra. Compounds 5–17 may fail to exhibit dications because they fragment by a favorable charge separation route, $M^{2+} \rightarrow M_1^{+} + M_2^{+}$. This is indicated by the absence of both singly and doubly charged molecular ions for these samples.

0003-2700/80/0352-2054$01.00/0

APPENDIX II

11.1.2.9 Transfer the concentrated extract to an 8-mL glass culture tube. Rinse the evaporator flask with three 5-mL portions of hexane; transfer each rinse to the culture tube. Between additions of hexane rinse, reduce the extract volume in the culture tube enough to allow addition of another 5-mL volume of rinse. To reduce the volume, place the culture tube in a water bath adjusted to operate at 50°C and position the tube so that the surfaces of the extract and the water are at about the same level. Evaporate the solvent with a stream of nitrogen (flow rate of approximately 150 mL/min) with the tip of the nitrogen delivery tube 2 cm above the solution.

11.1.2.10 After the final rinse has been added, reduce the extract volume to approximately 1 mL.

11.2 Column Chromatography

11.2.1 Column Preparation

11.2.1.1 Column 1: Place 1.0 g of silica gel into a 1 cm x 20 cm column and tap the column gently to settle the silica gel. Add 2 g sodium hydroxideimpregnated silica gel, 1 g silica gel, 4.0 g of sulfuric acid-impregnated silica gel, and 2 g silica gel. Tap column gently after each addition.

11.2.1.2 Column 2: Place 6.0 g of alumina into a 1 cm x 30 cm column and tap the column gently to settle the alumina. Add a 1-cm layer of purified sodium sulfate to the top of the alumina.

11.2.1.3 Add hexane to each column until the packing is free of channels and air bubbles. A small positive pressure (5 psi) of clean nitrogen can be used if needed.

11.2.2 Quantitatively transfer the hexane sample extract from the culture tube to the top of the sulfuric acid-impregnated silica gel in Column 1. Rinse the culture tube with two 0.5 mL portions of hexane; transfer rinses to Column 1.

11.2.3 With 90 mL of hexane, elute the extract from Column 1 directly into Column 2 containing alumina and sodium sulfate.

11.2.4 Add 20 mL of hexane to Column 2 and elute until the hexane level is just below the top of the sodium sulfate; discard the eluted hexane.

11.2.5 Add 20 mL of 20% methylene chloride/80% hexane (volume/volume) to Column 2 and collect the eluate.

11.2.6 Reduce the volume of eluate with a gentle stream of filtered dry nitrogen. When the volume is about 1 to 2 mL, transfer aliquots to a 1-mL amber mini-vial with conical reservoir. Concentrate and add additional aliquots with further concentration until entire eluate is transferred. Rinse eluate container with two 0.5-mL portions of hexane; transfer rinses to the mini-vial, with further concentration as necessary. CAUTION: Do not evaporate sample extract to dryness.

11.2.7 With the final sample extract volume at approximately 1 mL, store the extract until time for GC/MS analysis.

11.3 GC/MS Analysis

11.3.1 Remove the sample extract or blank from storage and allow it to warm to ambient laboratory temperature if necessary.

With a stream of dry, filtered nitrogen, reduce the extract/blank volume to near dryness. Immediately before GC/MS analysis, adjust the extract or blank volume to 50 μL with toluene.

11.3.2 Inject a 2-μL aliquot of the extract into the GC, operated under conditions previously used (Sect. 9) to produce acceptable results with the performance check solution.

11.3.3 Acquire mass spectral data for the following selected characteristic ions: m/z 257, 320, and 322 for unlabeled 2,3,7,8-TCDD; m/z 328 for $^{37}Cl_4$-2,3,7,8-TCDD; and m/z 332 and 334 for $^{13}C_{12}$-2,3,7,8-TCDD. Use the same data acquisition time and MS operating conditions previously used (Sect. 9.3.8) to determine response factors.

11.4 Identification Criteria. NOTE: Refer to Exhibit E, Section 7, for application of identification criteria.

11.4.1 Retention time (at maximum peak height) of the sample component must be within 3 seconds of the retention time of the $^{13}C_{12}$-2,3,7,8-TCDD. Retention times are required for all chromatograms, but scan numbers are optional. These parameters should be printed next to the appropriate peak.

11.4.2 The integrated ion currents detected for m/z 257, 320, and 322 must maximize simultaneously. If there are peaks that will affect the maximization or quantitation of peaks of interest, attempts should be made to narrow the scan window to eliminate the interfering peaks. This should be reported on a separate chromatogram.

11.4.3 The integrated ion current for each analyte and surrogate compound ion (m/z 257, 320, 322 and 328) must be at least 2.5 times background noise and must not have saturated the detector; internal standard ions (m/z 332 and 334) must be at least 10 times background and must not have saturated the detector.

11.4.4 Relative abundance of m/z 257 to m/z 322 should be $\geq$ 20% and $\leq$ 45%.

11.4.5 Abundance of integrated ion counts detected for m/z 320 must be $\geq$ 67% and $\leq$ 87% of integrated ion counts detected for m/z 322.

11.5 Column Chromatography Procedure for Difficult Samples -- Use the following procedure for extracts previously subjected to the column chromatography procedures in Section 11.2, but found by GC/MS analysis to contain interfering components.

11.5.1 Mix 3.6 grams of Carbopack C (or equivalent) with 16.4 grams of Celite 545^R (or equivalent) in a 40-mL vial and activate by heating in an oven at 130°C for 6 hours. Store in a desiccator. CAUTION: Check each new batch of mixed Carbopack/Celite^R to ensure TCDD recovery of $\geq$ 50%. Subject the low level concentration calibration solution to this procedure and measure the quantity of labeled and unlabeled 2,3,7,8-TCDD.

11.5.2 Insert a small plug of glass wool into a disposable pipet approximately 15 cm long by 7 mm O.D. Apply suction with a vacuum aspirator attached to the pointed end of the pipet, and add the Carbopack/Celite^R mixture until a 2 cm column is obtained.

11.5.3 Pre-elute the column with:

11.5.3.1 2 mL of toluene

11.5.3.2 1 mL of a mixture of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.5.3.3 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.5.3.4 2 mL of hexane

11.5.4 While the column is still wet with hexane, add the sample extract. Elute the column with the following sequence of solvents and discard eluents.

11.5.4.1 2 mL of hexane

11.5.4.2 1 mL of 50% (by volume) cyclohexane and 50% methylene chloride

11.5.4.3 1 mL of 75% (by volume) methylene chloride, 20% methanol and 5% benzene

11.5.5 Elute with 2 mL of toluene and collect the eluent, which contains the TCDD.

11.5.6 Store the sample extract until just before GC/MS analysis.

12. CALCULATIONS

12.1 Concentration

12.1.1 Concentration when a linear response factor was obtained:

12.1.1.1 Calculate the concentration of 2,3,7,8-TCDD using the formula:

$$C_x = \frac{A_x \cdot Q_{is}}{A_{ii} \cdot RF \cdot W}$$

where C_x = 2,3,7,8-TCDD concentration in micrograms per kilogram

A_x = the sum of integrated ion abundance detected for m/z 320 and 322

A_{is} = the sum of integrated ion abundances detected for m/z 332 and 334 (characteristic ions of $^{13}C_{12}$-2,3,7,8-TCDD, the internal standard)

Q_{is} = quantity (in nanograms) of $^{13}C_{12}$-2,3,7,8-TCDD added to the sample before extraction

RF = calculated mean response factor for unlabeled 2,3,7,8-TCDD relative to $^{13}C_{12}$-2,3,7,8-TCDD

W = weight (in grams) of wet soil or sediment sample.

APP[illegible]DIX III

1.7.1.2 Immediately after weighing the sample for extraction, weigh 5-10 g of the sediment into a tared crucible. Determine the percent moisture by drying overnight at 105°C. Allow to cool in a desiccator before weighing. Concentrations of individual analytes will be reported relative to the dry weight of sediment.

$$\frac{\text{gm of sample} - \text{gm of dry sample}}{\text{gm of sample}} \times 100 = \%\ \text{moisture}$$

APPENDIX IV

Tetra-Octa CDD/CDF Scan Quantitation Protocol and Analytical Standards

- Minimal Requirements for Bidders

Analytical Standards

- 2378 TCDD, $^{13}C_{12}$, $^{37}Cl_4$
- 2378 TCDF
- Mixture of TCDD isomers to verify column resolution*
- OCDD, $^{13}C_{12}$-OCDD
- Mix of Penta CDD/CDF, Hexa CDD/CDF, Hepta CDD/CDF to establish RT windows for spiking

Quantitation

Quantitate:

TCDD, TCDF, Penta CDD, Penta CDF, Hexa CDD, Hexa CDF

against $^{13}C_{12}$-2378-TCDD

(Quantitate TCDF, Penta CDF, and Hexa CDF against $^{13}C_{12}$-TCDF, if available)

Quantitate:

Hepta CDD, Hepta CDF, OCDD, OCDF against $^{13}C_{12}$-OCDD

Qualify data as "estimated" concentrations with tentative identifications unless you have access to pure isomer standards (i.e., all 38 TCDF isomers, etc.)

*Column resolution should meet Dioxin IFB WA86-K357 criteria; i.e., 25 percent valley or lower between 2,3,7,8-TCDD and it's nearest neighbor in SIC display (Appendix VII).

APPENDIX V

DELIVERABLES REQUIRED FOR GC/MS DIOXIN/FURAN ANALYSIS

A. SAMPLE PREPARATION AND METHOD DOCUMENTATION

(1) "Cookbook" style step-by-step method including instrument/conditions, type and source of reagents.

(2) Analyst bench records describing dilutions, weighings and any unusual occurrences during prep, extraction or clean up.

(3) Calculations and method used in determination of percent lipids and percent solids (where applicable).

B. DIOXIN/FURAN QUANTITATION AND IDENTIFICATION DOCUMENTATION

(1) Detailed explanation of the quantitation and identification procedure used for all isomer classes and specific isomers.

(2) List of criteria for positive identification of 2,3,7,8-TCDD and 2,3,7,8-TCDF.

(3) Example calculations of response ratios, sample results and detection limits.

(4) Simultaneous display/offset SICs and peak areas of native, $^{13}C_{12}$- and $^{37}Cl_4$-2,3,7,8-TCDD in all samples and QC, including blanks.

(5) Simultaneous display/offset SICs and peak areas of ions monitored for each PCDD/PCDF class.

(7) List of exact ion masses for each isomer/class, current and historical response factors and retention times for positive ID.

(8) Simultaneous display/offset SICs to check for polychlorinated diphenylethers which may co-elute with the furans.

(9) Simultaneous display/offset SICs of M/Z 257, 259 in samples with positive 2, 3, 7, 8-TCDD content.

(10) Simultaneous display/offset SICs and peak areas of ions monitored, for all standards used, for each PCDD/PCDF class. Include a listing of response ratios, ion ratios and amount of each standard used.

APPENDIX VI

CASE # ______________

PCDD/PCDF Concentration (PPT) as Dry Weight

ISOMER OR HOMOLOG	DATE:	ALIQUOT WT. (g)	DATE:	ALIQUOT WT. (g)	PRECISION AS RPD	PRECISION LIMITS	COMMENTS
	Samp.#		Samp.#				
2,3,7,8-TCDF							
^{37}Cl-2,3,7,8-TCDF % Recovery							
ng ^{37}Cl-2,3,7,8-TCDF Added							
Total TCDFs							
Total Penta CDFs							
Total Hexa CDFs							
Total Hepta CDFs							
OCDF							
- - - - - - - - - -	- - - - -	- - - - -	- - - - -	- - - - -	- - - - -	- - - - -	- - - - -
2,3,7,8-TCDD							
^{37}Cl-2,3,7,8-TCDD % Recovery							
ng ^{37}Cl-2,3,7,8-TCDD Added							
Total Tetra CDDs							
Total Penta CDDs							
124679 & 124689 H_6CDD							
123679 & 123689 H_6CDD							
123469 H_6CDD							
123478 H_6CDD							
123678 H_6CDD							
123467 & 123789 H_6CDD							
Total H_6CDDs							
^{37}Cl-123478 H_7CDD % Recovery							
ng ^{37}Cl-1232478 H_7CDD Added							
1234679 H_7CDD							
1234678 H_7CDD							
TOTAL H_7CDD							
OCDD							
^{37}Cl-OCDD %Recovery							
ng ^{37}Cl-OCDD Added							

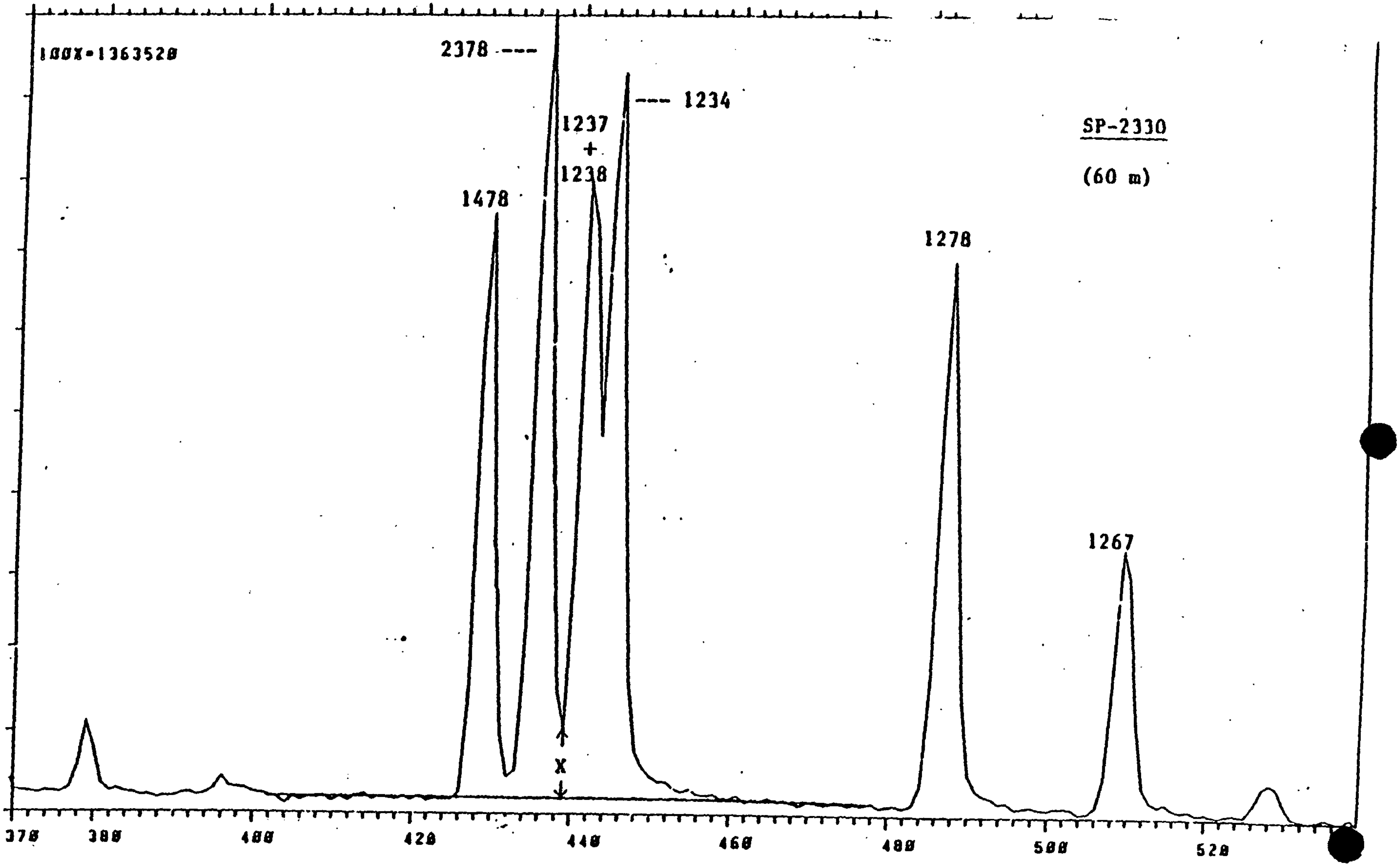

Figure 2. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 60-m SP-2330 fused silica capillary column and conditions listed in Table 1.

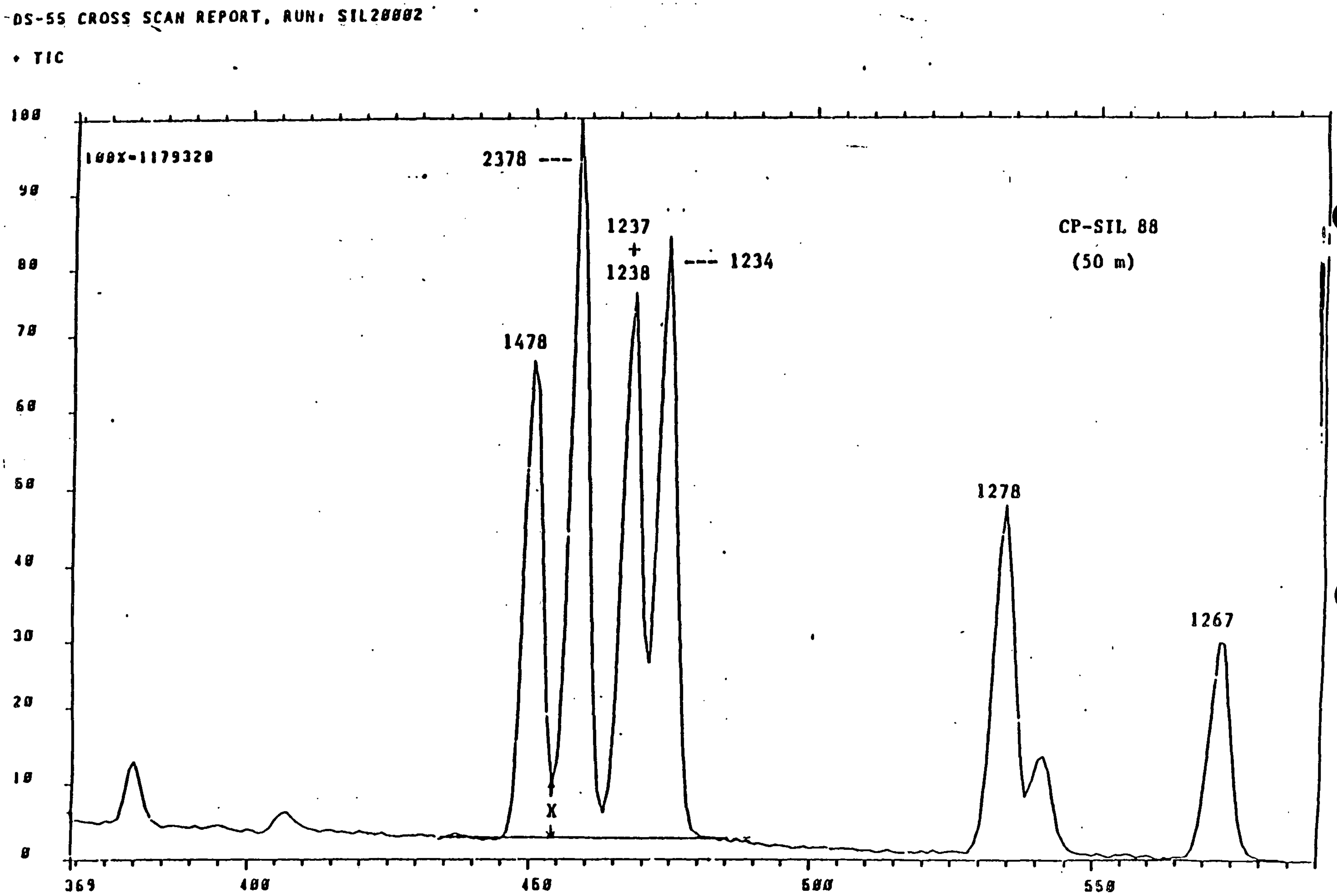

Figure 3. Selected ion current profile for m/z 320 and 322 produced by MS analysis of performance check solution using a 50-m CP-SIL 88 fused silica capillary column and conditions listed in Table 1.

Attachment H-11
PARTICLE-SIZE ANALYSIS OF SOILS

Method: American Society for Testing Materials
D422-63 (1972)

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☐ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American
B. Regional Representative: Dennis Wesolowski
C. Telephone Number: (312) 886-1971
D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Soil samples analyzed for particle - size distribution and atterberg limits.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

   Analyzed 12 soil samples for the parameters listed above.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

   Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6. Approximate number of days results required after lab receipt of samples: __________

Laboratory should report results within 30 days of receipt of samples.

7. Analytical protocol required (attach copy if other than a protocol currently used in this program):

Particle Size Analysis of Soils, ASTM Method D422

8. Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):

Use only the method specified above. Obtain approval of CPMS, CRL, prior to use of any other method. Rewrite SAS request to reflect new methodology.

9. Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.

Submit all raw data including container tare weights. Report results as percent finer than the specified particle diameter and present data in the form of a grain- size distribution curve on a semilogarithmic chart with percent finer by weight plotted on the arithmetic scale and grain size plotted on the logarithmic scale.

10. Other (use additional sheets or attach supplementary information, as needed):

11. Name of sampling/shipping contact: ____________________

Phone: ____________________

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services.

I. DATA REQUIREMENTS

Parameter	**Detection Limit**	**Precision Desired (±% or Conc.)**
Percentage Finer Than	Not Applicable	

II. QUALITY CONTROL REQUIREMENTS

Audits Required	**Frequency of Audits**	**Limits* (±% or Conc.)**
Lab Duplicate	2 for sets< 10 1 per 10 for sets > 10	10% passing

III. *Action Required if Limits are Exceeded:

Reanalyze contact Chuck Elly at the Region V CRL

Designation: D 422 – 63 (Reapproved 1972)$^{\epsilon 1}$

Standard Method for
PARTICLE-SIZE ANALYSIS OF SOILS[1]

This standard is issued under the fixed designation D 422; 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—Section 2 was added editorially and subsequent sections renumbered in July 1984.

1. Scope

1.1 This method covers the quantitative determination of the distribution of particle sizes in soils. The distribution of particle sizes larger than 75 µm (retained on the No. 200 sieve) is determined by sieving, while the distribution of particle sizes smaller than 75 µm is determined by a sedimentation process, using a hydrometer to secure the necessary data (Notes 1 and 2).

Note 1—Separation may be made on the No. 4 (4.75-mm), No. 40 (425-µm), or No. 200 (75-µm) sieve instead of the No. 10. For whatever sieve used, the size shall be indicated in the report.

Note 2—Two types of dispersion devices are provided: (*1*) a high-speed mechanical stirrer, and (*2*) air dispersion. Extensive investigations indicate that air-dispersion devices produce a more positive dispersion of plastic soils below the 20-µm size and appreciably less degradation on all sizes when used with sandy soils. Because of the definite advantages favoring air dispersion, its use is recommended. The results from the two types of devices differ in magnitude, depending upon soil type, leading to marked differences in particle size distribution, especially for sizes finer than 20 µm.

2. Applicable Documents

2.1 *ASTM Standards:*

D421 Method for Dry Preparation of Soil Samples for Particle-Size Analysis and Determination of Soil Constants[2]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[3]

E 100 Specification for ASTM Hydrometers[4]

3. Apparatus

3.1 *Balances*—A balance sensitive to 0.01 g for weighing the material passing a No. 10 (2.00-mm) sieve, and a balance sensitive to 0.1 % of the mass of the sample to be weighed for weighing the material retained on a No. 10 sieve.

3.2 *Stirring Apparatus*—Either apparatus A or B may be used.

3.2.1 Apparatus A shall consist of a mechanically operated stirring device in which a suitably mounted electric motor turns a vertical shaft at a speed of not less than 10 000 rpm without load. The shaft shall be equipped with a replaceable stirring paddle made of metal, plastic, or hard rubber, as shown in Fig. 1. The shaft shall be of such length that the stirring paddle will operate not less than ¾ in. (19.0 mm) nor more than 1½ in. (38.1 mm) above the bottom of the dispersion cup. A special dispersion cup conforming to either of the designs shown in Fig. 2 shall be provided to hold the sample while it is being dispersed.

3.2.2 Apparatus B shall consist of an air-jet dispersion cup[5] (Note 3) conforming to the general details shown in Fig. 3 (Notes 4 and 5).

Note 3—The amount of air required by an air-jet dispersion cup is of the order of 2 ft^3/min; some small air compressors are not capable of supplying sufficient air to operate a cup.

Note 4—Another air-type dispersion device, known as a dispersion tube, developed by Chu and Davidson at Iowa State College, has been shown to give

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[1] This method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity, and Density Characteristics of Soils.

Current edition approved Nov. 21, 1963. Originally published 1935. Replaces D 422 – 62.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

[4] *Annual Book of ASTM Standards*, Vol 14.01.

[5] Detailed working drawings for this cup are available at a nominal cost from the American Society for Testing and Materials, 1916 Race St., Philadelphia, PA 19103. Order Adjunct No. 12-404220-00.

results equivalent to those secured by the air-jet dispersion cups. When it is used, soaking of the sample can be done in the sedimentation cylinder, thus eliminating the need for transferring the slurry. When the air-dispersion tube is used, it shall be so indicated in the report.

NOTE 5—Water may condense in air lines when not in use. This water must be removed, either by using a water trap on the air line, or by blowing the water out of the line before using any of the air for dispersion purposes.

3.3 *Hydrometer*—An ASTM hydrometer, graduated to read in either specific gravity of the suspension or grams per litre of suspension, and conforming to the requirements for hydrometers 151H or 152H in Specifications E 100. Dimensions of both hydrometers are the same, the scale being the only item of difference.

3.4 *Sedimentation Cylinder*—A glass cylinder essentially 18 in. (457 mm) in height and 2½ in. (63.5 mm) in diameter, and marked for a volume of 1000 mL. The inside diameter shall be such that the 1000-mL mark is 36 ± 2 cm from the bottom on the inside.

3.5 *Thermometer*—A thermometer accurate to 1°F (0.5°C).

3.6 *Sieves*—A series of sieves, of square-mesh woven-wire cloth, conforming to the requirements of Specification E 11. A full set of sieves includes the following (Note 6):

3-in. (75-mm)
2-in. (50-mm)
1½-in. (37.5-mm)
1-in. (25.0-mm)
¾-in. (19.0-mm)
⅜-in. (9.5-mm)
No. 4 (4.75-mm)
No. 10 (2.00-mm)
No. 20 (850-μm)
No. 40 (425-μm)
No. 60 (250-μm)
No. 140 (106-μm)
No. 200 (75-μm)

NOTE 6—A set of sieves giving uniform spacing of points for the graph, as required in Section 17, may be used if desired. This set consists of the following sieves:

3-in. (75-mm)
1½-in. (37.5-mm)
¾-in. (19.0-mm)
⅜-in. (9.5-mm)
No. 4 (4.75-mm)
No. 8 (2.36-mm)
No. 16 (1.18-mm)
No. 30 (600-μm)
No. 50 (300-μm)
No. 100 (150-μm)
No. 200 (75-μm)

3.7 *Water Bath or Constant-Temperature Room*—A water bath or constant-temperature room for maintaining the soil suspension at a constant temperature during the hydrometer analysis. A satisfactory water tank is an insulated tank that maintains the temperature of the suspension at a convenient constant temperature at or near 68°F (20°C). Such a device is illustrated in Fig. 4. In cases where the work is performed in a room at an automatically controlled constant temperature, the water bath is not necessary.

3.8 *Beaker*—A beaker of 250-mL capacity.

3.9 *Timing Device*—A watch or clock with a second hand.

4. Dispersing Agent

4.1 A solution of sodium hexametaphosphate (sometimes called sodium metaphosphate) shall be used in distilled or demineralized water, at the rate of 40 g of sodium hexametaphosphate/litre of solution (Note 7).

NOTE 7—Solutions of this salt, if acidic, slowly revert or hydrolyze back to the orthophosphate form with a resultant decrease in dispersive action. Solutions should be prepared frequently (at least once a month) or adjusted to pH of 8 or 9 by means of sodium carbonate. Bottles containing solutions should have the date of preparation marked on them.

4.2 All water used shall be either distilled or demineralized water. The water for a hydrometer test shall be brought to the temperature that is expected to prevail during the hydrometer test. For example, if the sedimentation cylinder is to be placed in the water bath, the distilled or demineralized water to be used shall be brought to the temperature of the controlled water bath: or, if the sedimentation cylinder is used in a room with controlled temperature, the water for the test shall be at the temperature of the room. The basic temperature for the hydrometer test is 68°F (20°C). Small variations of temperature do not introduce differences that are of practical significance and do not prevent the use of corrections derived as prescribed.

5. Test Sample

5.1 Prepare the test sample for mechanical analysis as outlined in Method D 421. During the preparation procedure the sample is divided into two portions. One portion contains only particles retained on the No. 10 (2.00-mm) sieve while the other portion contains only particles passing the No. 10 sieve. The mass of air-dried soil selected for purpose of tests, as prescribed in Method D 421, shall be sufficient to yield quantities for mechanical analysis as follows:

5.1.1 The size of the portion retained on the No. 10 sieve shall depend on the maximum size of particle, according to the following schedule:

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
⅜ (9.5)	500
¾ (19.0)	1000

Nominal Diameter of Largest Particles, in. (mm)	Approximate Minimum Mass of Portion, g
1 (25.4)	2000
1½ (38.1)	3000
2 (50.8)	4000
3 (76.2)	5000

5.1.2 The size of the portion passing the No. 10 sieve shall be approximately 115 g for sandy soils and approximately 65 g for silt and clay soils.

5.2 Provision is made in Section 5 of Method D 421 for weighing of the air-dry soil selected for purpose of tests, the separation of the soil on the No. 10 sieve by dry-sieving and washing, and the weighing of the washed and dried fraction retained on the No. 10 sieve. From these two masses the percentages retained and passing the No. 10 sieve can be calculated in accordance with 12.1.

NOTE 8—A check on the mass values and the thoroughness of pulverization of the clods may be secured by weighing the portion passing the No. 10 sieve and adding this value to the mass of the washed and oven-dried portion retained on the No. 10 sieve.

SIEVE ANALYSIS OF PORTION RETAINED ON NO. 10 (2.00-mm) SIEVE

6. Procedure

6.1 Separate the portion retained on the No. 10 (2.00-mm) sieve into a series of fractions using the 3-in. (75-mm), 2-in. (50-mm), 1½-in. (37.5-mm), 1-in. (25.0-mm), ¾-in. (19.0-mm), ⅜-in. (9.5-mm), No. 4 (4.75-mm), and No. 10 sieves, or as many as may be needed depending on the sample, or upon the specifications for the material under test.

6.2 Conduct the sieving operation by means of a lateral and vertical motion of the sieve, accompanied by a jarring action in order to keep the sample moving continuously over the surface of the sieve. In no case turn or manipulate fragments in the sample through the sieve by hand. Continue sieving until not more than 1 mass % of the residue on a sieve passes that sieve during 1 min of sieving. When mechanical sieving is used, test the thoroughness of sieving by using the hand method of sieving as described above.

6.3 Determine the mass of each fraction on a balance conforming to the requirements of 3.1. At the end of weighing, the sum of the masses retained on all the sieves used should equal closely the original mass of the quantity sieved.

HYDROMETER AND SIEVE ANALYSIS OF PORTION PASSING THE NO. 10 (2.00-mm) SIEVE

7. Determination of Composite Correction for Hydrometer Reading

7.1 Equations for percentages of soil remaining in suspension, as given in 14.3, are based on the use of distilled or demineralized water. A dispersing agent is used in the water, however, and the specific gravity of the resulting liquid is appreciably greater than that of distilled or demineralized water.

7.1.1 Both soil hydrometers are calibrated at 68°F (20°C), and variations in temperature from this standard temperature produce inaccuracies in the actual hydrometer readings. The amount of the inaccuracy increases as the variation from the standard temperature increases.

7.1.2 Hydrometers are graduated by the manufacturer to be read at the bottom of the meniscus formed by the liquid on the stem. Since it is not possible to secure readings of soil suspensions at the bottom of the meniscus, readings must be taken at the top and a correction applied.

7.1.3 The net amount of the corrections for the three items enumerated is designated as the composite correction, and may be determined experimentally.

7.2 For convenience, a graph or table of composite corrections for a series of 1° temperature differences for the range of expected test temperatures may be prepared and used as needed. Measurement of the composite corrections may be made at two temperatures spanning the range of expected test temperatures, and corrections for the intermediate temperatures calculated assuming a straight-line relationship between the two observed values.

7.3 Prepare 1000 mL of liquid composed of distilled or demineralized water and dispersing agent in the same proportion as will prevail in the sedimentation (hydrometer) test. Place the liquid in a sedimentation cylinder and the cylinder in the constant-temperature water bath, set for one of the two temperatures to be used. When the temperature of the liquid becomes constant, insert the hydrometer, and, after a short interval to permit the hydrometer to come to the temperature of the liquid, read the hydrometer at the top of the meniscus formed on the stem. For hydrometer 151H the composite correction is the difference between this reading and one; for hydrometer 152H it is the difference between the reading and zero. Bring the liquid and the hydrometer to the other temperature to be used, and secure the composite correction as before.

8. Hygroscopic Moisture

8.1 When the sample is weighed for the hydrometer test, weigh out an auxiliary portion of from 10 to 15 g in a small metal or glass container, dry the sample to a constant mass in an oven at 230 ± 9°F (110 ± 5°C), and weigh again. Record the masses.

9. Dispersion of Soil Sample

9.1 When the soil is mostly of the clay and silt sizes, weigh out a sample of air-dry soil of approximately 50 g. When the soil is mostly sand the sample should be approximately 100 g.

9.2 Place the sample in the 250-mL beaker and cover with 125 mL of sodium hexametaphosphate solution (40 g/l). Stir until the soil is thoroughly wetted. Allow to soak for at least 16 h.

9.3 At the end of the soaking period, disperse the sample further, using either stirring apparatus A or B. If stirring apparatus A is used, transfer the soil - water slurry from the beaker into the special dispersion cup shown in Fig. 2, washing any residue from the beaker into the cup with distilled or demineralized water (Note 9). Add distilled or demineralized water, if necessary, so that the cup is more than half full. Stir for a period of 1 min.

NOTE 9—A large size syringe is a convenient device for handling the water in the washing operation. Other devices include the wash-water bottle and a hose with nozzle connected to a pressurized distilled water tank.

9.4 If stirring apparatus B (Fig. 3) is used, remove the cover cap and connect the cup to a compressed air supply by means of a rubber hose. A air gage must be on the line between the cup and the control valve. Open the control valve so that the gage indicates 1 psi (7 kPa) pressure (Note 10). Transfer the soil - water slurry from the beaker to the air-jet dispersion cup by washing with distilled or demineralized water. Add distilled or demineralized water, if necessary, so that the total volume in the cup is 250 mL, but no more.

NOTE 10—The initial air pressure of 1 psi is required to prevent the soil - water mixture from entering the air-jet chamber when the mixture is transferred to the dispersion cup.

9.5 Place the cover cap on the cup and open the air control valve until the gage pressure is 20 psi (140 kPa). Disperse the soil according to the following schedule:

Plasticity Index	Dispersion Period, min
Under 5	5
6 to 20	10
Over 20	15

Soils containing large percentages of mica need be dispersed for only 1 min. After the dispersion period, reduce the gage pressure to 1 psi preparatory to transfer of soil - water slurry to the sedimentation cylinder.

10. Hydrometer Test

10.1 Immediately after dispersion, transfer the soil - water slurry to the glass sedimentation cylinder, and add distilled or demineralized water until the total volume is 1000 mL.

10.2 Using the palm of the hand over the open end of the cylinder (or a rubber stopper in the open end), turn the cylinder upside down and back for a period of 1 min to complete the agitation of the slurry (Note 11). At the end of 1 min set the cylinder in a convenient location and take hydrometer readings at the following intervals of time (measured from the beginning of sedimentation), or as many as may be needed, depending on the sample or the specification for the material under test: 2, 5, 15, 30, 60, 250, and 1440 min. If the controlled water bath is used, the sedimentation cylinder should be placed in the bath between the 2- and 5-min readings.

NOTE 11—The number of turns during this minute should be approximately 60, counting the turn upside down and back as two turns. Any soil remaining in the bottom of the cylinder during the first few turns should be loosened by vigorous shaking of the cylinder while it is in the inverted position.

10.3 When it is desired to take a hydrometer reading, carefully insert the hydrometer about 20 to 25 s before the reading is due to approximately the depth it will have when the reading is taken. As soon as the reading is taken, carefully remove the hydrometer and place it with a spinning motion in a graduate of clean distilled or demineralized water.

NOTE 12—It is important to remove the hydrometer immediately after each reading. Readings shall be taken at the top of the meniscus formed by the suspension around the stem, since it is not possible to secure readings at the bottom of the meniscus.

10.4 After each reading, take the temperature of the suspension by inserting the thermometer into the suspension.

11. Sieve Analysis

11.1 After taking the final hydrometer reading, transfer the suspension to a No. 200 (75-µm) sieve and wash with tap water until the wash water is clear. Transfer the material on the No. 200 sieve to a suitable container, dry in an oven at 230 ± 9°F (110 ± 5°C) and make a sieve analysis of the portion retained, using as many sieves as desired, or required for the material, or upon the specification of the material under test.

CALCULATIONS AND REPORT

12. Sieve Analysis Values for the Portion Coarser than the No. 10 (2.00-mm) Sieve

12.1 Calculate the percentage passing the No. 10 sieve by dividing the mass passing the No. 10 sieve by the mass of soil originally split on the No. 10 sieve, and multiplying the result by 100. To obtain the mass passing the No. 10 sieve, subtract the mass retained on the No. 10 sieve from the original mass.

12.2 To secure the total mass of soil passing the No. 4 (4.75-mm) sieve, add to the mass of the material passing the No. 10 sieve the mass of the fraction passing the No. 4 sieve and retained on the No. 10 sieve. To secure the total mass of soil passing the ⅜-in. (9.5-mm) sieve, add to the total mass of soil passing the No. 4 sieve, the mass of the fraction passing the ⅜-in. sieve and retained on the No. 4 sieve. For the remaining sieves, continue the calculations in the same manner.

12.3 To determine the total percentage passing for each sieve, divide the total mass passing (see 12.2) by the total mass of sample and multiply the result by 100.

13. Hygroscopic Moisture Correction Factor

13.1 The hydroscopic moisture correction factor is the ratio between the mass of the oven-dried sample and the air-dry mass before drying. It is a number less than one, except when there is no hygroscopic moisture.

14. Percentages of Soil in Suspension

14.1 Calculate the oven-dry mass of soil used in the hydrometer analysis by multiplying the air-dry mass by the hygroscopic moisture correction factor.

14.2 Calculate the mass of a total sample represented by the mass of soil used in the hydrometer test, by dividing the oven-dry mass used by the percentage passing the No. 10 (2.00-mm) sieve, and multiplying the result by 100. This value is the weight W in the equation for percentage remaining in suspension.

14.3 The percentage of soil remaining in suspension at the level at which the hydrometer is measuring the density of the suspension may be calculated as follows (Note 13): For hydrometer 151H:

$$P = [(100\,000/W) \times G/(G - G_1)](R - G_1)$$

NOTE 13—The bracketed portion of the equation for hydrometer 151H is constant for a series of readings and may be calculated first and then multiplied by the portion in the parentheses.

For hydrometer 152H:

$$P = (Ra/W') \times 100$$

where:

a = correction faction to be applied to the reading of hydrometer 152H. (Values shown on the scale are computed using a specific gravity of 2.65. Correction factors are given in Table 1),

P = percentage of soil remaining in suspension at the level at which the hydrometer measures the density of the suspension,

R = hydrometer reading with composite correction applied (Section 7),

W' = oven-dry mass of soil in a total test sample represented by mass of soil dispersed (see 14.2), g,

G = specific gravity of the soil particles, and

G_1 = specific gravity of the liquid in which soil particles are suspended. Use numerical value of one in both instances in the equation. In the first instance any possible variation produces no significant effect, and in the second instance, the composite correction for R is based on a value of one for G_1.

15. Diameter of Soil Particles

15.1 The diameter of a particle corresponding to the percentage indicated by a given hydrometer reading shall be calculated according to Stokes' law (Note 14), on the basis that a particle of this diameter was at the surface of the suspension at the beginning of sedimentation and had settled to the level at which the hydrometer is measuring the density of the suspension. According to Stokes' law:

$$D = \sqrt{[30n/980(G - G_1)] \times L/T}$$

where:

D = diameter of particle, mm,

n = coefficient of viscosity of the suspending medium (in this case water) in poises (varies with changes in temperature of the suspending medium),

L = distance from the surface of the suspension to the level at which the density of the suspension is being measured, cm. (For a given hydrometer and sedimentation cylinder, values vary according to the hydrometer readings. This distance is known as effective depth (Table 2)),

T = interval of time from beginning of sedimentation to the taking of the reading, min,

G = specific gravity of soil particles, and

G_1 = specific gravity (relative density) of suspending medium (value may be used as 1.000 for all practical purposes).

NOTE 14—Since Stokes' law considers the terminal velocity of a single sphere falling in an infinity of liquid, the sizes calculated represent the diameter of spheres that would fall at the same rate as the soil particles.

15.2 For convenience in calculations the above equation may be written as follows:

$$D = K\sqrt{L/T}$$

where:

K = constant depending on the temperature of the suspension and the specific gravity of the soil particles. Values of K for a range of temperatures and specific gravities are given in Table 3. The value of K does not change for a series of readings constituting a test, while values of L and T do vary.

15.3 Values of D may be computed with sufficient accuracy, using an ordinary 10-in. slide rule.

NOTE 15—The value of L is divided by T using the A- and B-scales, the square root being indicated on the D-scale. Without ascertaining the value of the square root it may be multiplied by K, using either the C- or CI-scale.

16. Sieve Analysis Values for Portion Finer than No. 10 (2.00-mm) Sieve

16.1 Calculation of percentages passing the various sieves used in sieving the portion of the sample from the hydrometer test involves several steps. The first step is to calculate the mass of the fraction that would have been retained on the No. 10 sieve had it not been removed. This mass is equal to the total percentage retained on the No. 10 sieve (100 minus total percentage passing) times the mass of the total sample represented by the mass of soil used (as calculated in 14.2), and the result divided by 100.

16.2 Calculate next the total mass passing the No. 200 sieve. Add together the fractional masses retained on all the sieves, including the No. 10 sieve, and subtract this sum from the mass of the total sample (as calculated in 14.2).

16.3 Calculate next the total masses passing each of the other sieves, in a manner similar to that given in 12.2.

16.4 Calculate last the total percentages passing by dividing the total mass passing (as calculated in 16.3) by the total mass of sample (as calculated in 14.2), and multiply the result by 100.

17. Graph

17.1 When the hydrometer analysis is performed, a graph of the test results shall be made, plotting the diameters of the particles on a logarithmic scale as the abscissa and the percentages smaller than the corresponding diameters to an arithmetic scale as the ordinate. When the hydrometer analysis is not made on a portion of the soil, the preparation of the graph is optional, since values may be secured directly from tabulated data.

18. Report

18.1 The report shall include the following:

18.1.1 Maximum size of particles,

18.1.2 Percentage passing (or retained on) each sieve, which may be tabulated or presented by plotting on a graph (Note 16),

18.1.3 Description of sand and gravel particles:

18.1.3.1 Shape—rounded or angular,

18.1.3.2 Hardness—hard and durable, soft, or weathered and friable,

18.1.4 Specific gravity, if unusually high or low,

18.1.5 Any difficulty in dispersing the fraction passing the No. 10 (2.00-mm) sieve, indicating any change in type and amount of dispersing agent, and

18.1.6 The dispersion device used and the length of the dispersion period.

Note 16—This tabulation of graph represents the gradation of the sample tested. If particles larger than those contained in the sample were removed before testing, the report shall so state giving the amount and maximum size.

18.2 For materials tested for compliance with definite specifications, the fractions called for in such specifications shall be reported. The fractions smaller than the No. 10 sieve shall be read from the graph.

18.3 For materials for which compliance with definite specifications is not indicated and when the soil is composed almost entirely of particles passing the No. 4 (4.75-mm) sieve, the results read from the graph may be reported as follows:

(*1*) Gravel, passing 3-in. and retained on No. 4 sieve ..... %
(*2*) Sand, passing No. 4 sieve and retained on No. 200 sieve ..... %
  (*a*) Coarse sand, passing No. 4 sieve and retained on No. 10 sieve ..... %
  (*b*) Medium sand, passing No. 10 sieve and retained on No. 40 sieve ..... %
  (*c*) Fine sand, passing No. 40 sieve and retained on No. 200 sieve ..... %
(*3*) Silt size, 0.074 to 0.005 mm ..... %
(*4*) Clay size, smaller than 0.005 mm ..... %
  Colloids, smaller than 0.001 mm ..... %

18.4 For materials for which compliance with definite specifications is not indicated and when the soil contains material retained on the No. 4 sieve sufficient to require a sieve analysis on that portion, the results may be reported as follows (Note 17):

SIEVE ANALYSIS

Sieve Size	Percentage Passing
3-in.	....
2-in.	....
1½-in.	....
1-in.	....
¾-in.	....
⅜-in.	....
No. 4 (4.75-mm)	....
No. 10 (2.00-mm)	....
No. 40 (425-μm)	....
No. 200 (75-μm)	....
HYDROMETER ANALYSIS	
0.074 mm	....
0.005 mm	....
0.001 mm	....

Note 17—No. 8 (2.36-mm) and No. 50 (300-μm) sieves may be substituted for No. 10 and No. 40 sieves.

TABLE 1 Values of Correction Factor, α, for Different Specific Gravities of Soil Particles[A]

Specific Gravity	Correction Factor[A]
2.95	0.94
2.90	0.95
2.85	0.96
2.80	0.97
2.75	0.98
2.70	0.99
2.65	1.00
2.60	1.01
2.55	1.02
2.50	1.03
2.45	1.05

[A] For use in equation for percentage of soil remaining in suspension when using Hydrometer 152H.

TABLE 2 Values of Effective Depth Based on Hydrometer and Sedimentation Cylinder of Specified Sizes[A]

Hydrometer 151H		Hydrometer 152H			
Actual Hydrometer Reading	Effective Depth, L cm	Actual Hydrometer Reading	Effective Depth, L cm	Actual Hydrometer Reading	Effective Depth, L cm
1.000	16.3	0	16.3	31	11.2
1.001	16.0	1	16.1	32	11.1
1.002	15.8	2	16.0	33	10.9
1.003	15.5	3	15.8	34	10.7
1.004	15.2	4	15.6	35	10.6
1.005	15.0	5	15.5		
1.006	14.7	6	15.3	36	10.4
1.007	14.4	7	15.2	37	10.2
1.008	14.2	8	15.0	38	10.1
1.009	13.9	9	14.8	39	9.9
1.010	13.7	10	14.7	40	9.7
1.011	13.4	11	14.5	41	9.6
1.012	13.1	12	14.3	42	9.4
1.013	12.9	13	14.2	43	9.2
1.014	12.6	14	14.0	44	9.1
1.015	12.3	15	13.8	45	8.9
1.016	12.1	16	13.7	46	8.8
1.017	11.8	17	13.5	47	8.6
1.018	11.5	18	13.3	48	8.4
1.019	11.3	19	13.2	49	8.3
1.020	11.0	20	13.0	50	8.1
1.021	10.7	21	12.9	51	7.9
1.022	10.5	22	12.7	52	7.8
1.023	10.2	23	12.5	53	7.6
1.024	10.0	24	12.4	54	7.4
1.025	9.7	25	12.2	55	7.3
1.026	9.4	26	12.0	56	7.1
1.027	9.2	27	11.9	57	7.0
1.028	8.9	28	11.7	58	6.8
1.029	8.6	29	11.5	59	6.6
1.030	8.4	30	11.4	60	6.5
1.031	8.1				
1.032	7.8				
1.033	7.6				
1.034	7.3				
1.035	7.0				
1.036	6.8				
1.037	6.5				
1.038	6.2				

[A] Values of effective depth are calculated from the equation:

$$L = L_1 + \tfrac{1}{2}\left[L_2 - (V_B/A)\right]$$

where:

L = effective depth, cm,

L_1 = distance along the stem of the hydrometer from the top of the bulb to the mark for a hydrometer reading, cm,

L_2 = overall length of the hydrometer bulb, cm,

V_B = volume of hydrometer bulb, cm^3, and

A = cross-sectional area of sedimentation cylinder, cm^2

Values used in calculating the values in Table 2 are as follows:

For both hydrometers, 151H and 152H:

L_2 = 14.0 cm

V_B = 67.0 cm^3

A = 27.8 cm^2

For hydrometer 151H:

L_1 = 10.5 cm for a reading of 1.000

= 2.3 cm for a reading of 1.031

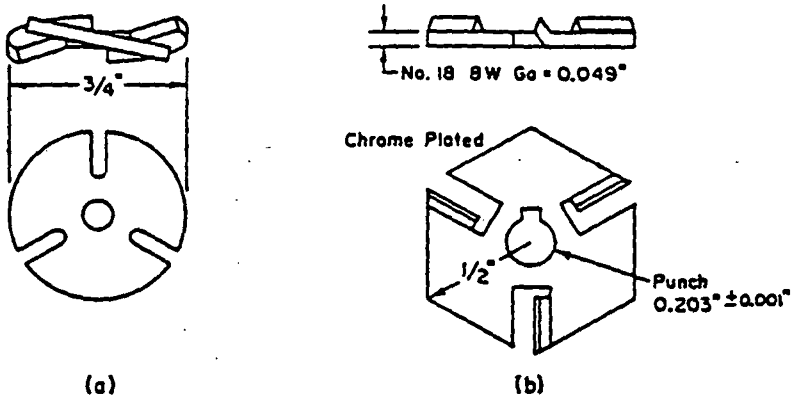
For hydrometer 152H:

L_1 = 10.5 cm for a reading of 0 g/litre

= 2.3 cm for a reading of 50 g/litre

TABLE 3 Values of *K* for Use in Equation for Computing Diameter of Particle in Hydrometer Analysis

Temperature, °C	Specific Gravity of Soil Particles								
	2.45	2.50	2.55	2.60	2.65	2.70	2.75	2.80	2.85
16	0.01510	0.01505	0.01481	0.01457	0.01435	0.01414	0.01394	0.01374	0.01356
17	0.01511	0.01486	0.01462	0.01439	0.01417	0.01396	0.01376	0.01356	0.01338
18	0.01492	0.01467	0.01443	0.01421	0.01399	0.01378	0.01359	0.01339	0.01321
19	0.01474	0.01449	0.01425	0.01403	0.01382	0.01361	0.01342	0.1323	0.01305
20	0.01456	0.01431	0.01408	0.01386	0.01365	0.01344	0.01325	0.01307	0.01289
21	0.01438	0.01414	0.01391	0.01369	0.01348	0.01328	0.01309	0.01291	0.01273
22	0.01421	0.01397	0.01374	0.01353	0.01332	0.01312	0.01294	0.01276	0.01258
23	0.01404	0.01381	0.01358	0.01337	0.01317	0.01297	0.01279	0.01261	0.01243
24	0.01388	0.01365	0.01342	0.01321	0.01301	0.01282	0.01264	0.01246	0.01229
25	0.01372	0.01349	0.01327	0.01306	0.01286	0.01267	0.01249	0.01232	0.01215
26	0.01357	0.01334	0.01312	0.01291	0.01272	0.01253	0.01235	0.01218	0.01201
27	0.01342	0.01319	0.01297	0.01277	0.01258	0.01239	0.01221	0.01204	0.01188
28	0.01327	0.01304	0.01283	0.01264	0.01244	0.01255	0.01208	0.01191	0.01175
29	0.01312	0.01290	0.01269	0.01249	0.01230	0.01212	0.01195	0.01178	0.01162
30	0.01298	0.01276	0.01256	0.01236	0.01217	0.01199	0.01182	0.01165	0.01149

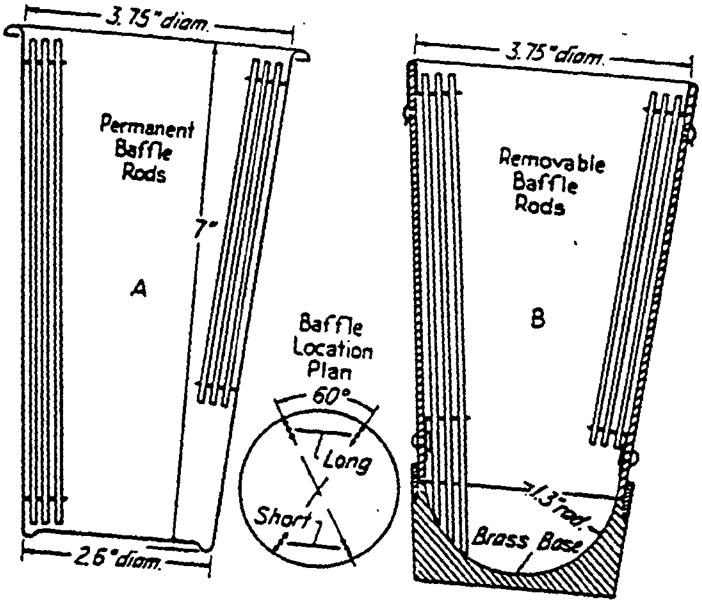


(a) (b)

Metric Equivalents

in.	0.001	0.049	0.203	½	¾
mm	0.03	1.24	5.16	12.7	19.0

FIG. 1 Detail of Stirring Paddles



Metric Equivalents

in.	1.3	2.6	3.75
mm	33	66	95.2

FIG. 2 Dispersion Cups of Apparatus

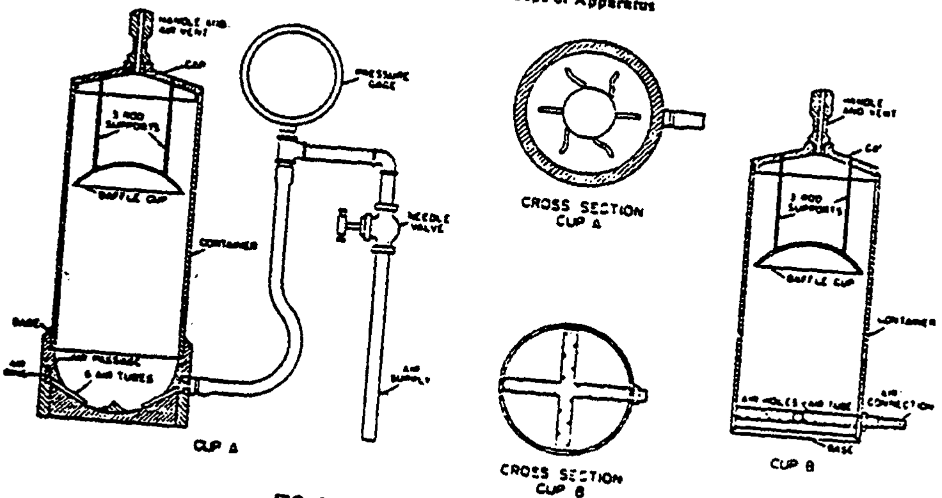
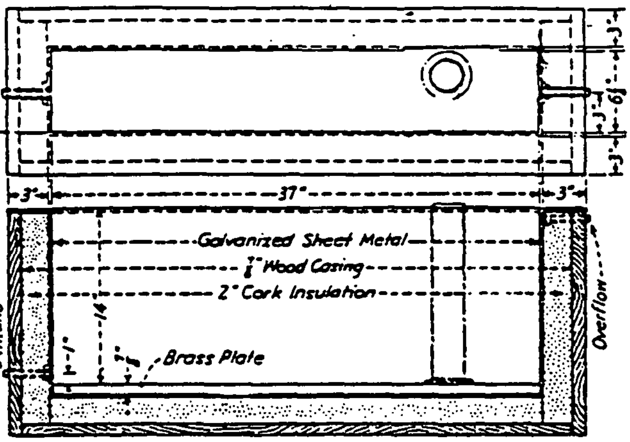


FIG. 3 Air-Jet Dispersion Cups of Apparatus B



Metric Equivalents

in.	⅞	1	3	6¼	14	37
mm	22.2	25.4	76.2	158.2	356	940

FIG. 4 Insulated Water Bath

Attachment H-12
LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX OF SOILS (ATTERBERG LIMITS)

Method: American Society for Testing Methods D4318-84

U.S. Environmental Protection Agency
HWI Sample Management Office
P.O. Box 818, Alexandria, Virginia 22313
PHONE: (703) 557-2490 or FTS-557-2490

SAS Number

SPECIAL ANALYTICAL SERVICES
Regional Request

☐ Regional Transmittal ☐ Telephone Request

A. EPA Region and Site Name: Region V, Moss American

B. Regional Representative: Dennis Wesolowski

C. Telephone Number: (312) 886-1971

D. Date of Request:

Please provide below a description of your request for Special Analytical Services under the Uncontrolled Hazardous Waste Dumpsite Program. In order to most efficiently obtain laboratory capability for your request, please address the following considerations, if applicable. Incomplete or erroneous information may result in delay in the processing of your request. Please continue response on additional sheets, or attach supplementary information as needed.

1. General description of analytical service requested: Soil samples analyzed for particle - size distribution and atterberg limits.

2. Definition and number of work units involved (specify whether whole samples or fractions; whether organics or inorganics; whether aqueous or soil and sediments; and whether low, medium, or high concentration):

   Analyzed 12 soil samples for the parameters listed above.

3. Purpose of analysis (specify whether Superfund (Remedial or Enforcement), RCRA, NPDES, etc.):

   Superfund, Enforcement

4. Estimated date(s) of collection:

5. Estimated date(s) and method of shipment: Daily by overnight carrier

6. **Approximate number of days results required after lab receipt of samples:** ________

Laboratory should report results within 30 days of receipt of samples.

7. **Analytical protocol required (attach copy if other than a protocol currently used in this program):**

Liquid Limit Plastic Limit, and Plasticity index, Plastic Limit, and Natural Water

Content of Soils ASTM D-4318

8. **Special technical instructions (if outside protocol requirements, specify compound names, CAS numbers, detection limits, etc.):**

Liquid Limit using the Multipoint Method.

Use only the method specified above. Obtain approval of CPMS, CRL, prior to use of any

other method. Rewrite SAS request to reflect new methodology.

9. **Analytical results required (if known, specify format for data sheets, QA/QC reports, Chain-of-Custody documentation, etc.). If not completed, format of results will be left to program discretion.**

Report all raw date. Results reported as percent water content.

10. **Other (use additional sheets or attach supplementary information, as needed):**

11. **Name of sampling/shipping contact:** ________

Phone: ________

Please return this request to the Sample Management Office as soon as possible to expedite processing of your request for special analytical services. Should

I. DATA REQUIREMENTS

Parameter	Detection Limit	Precision Desired (±% or Conc.)
Liquid Limit	Not Applicable	
Plastic Limit	Not Applicable	
Natural Water Content	Not Applicable	

II. QUALITY CONTROL REQUIREMENTS

Audits Required	Frequency of Audits	Limits* (±% or Conc.)
Lab Duplicate	2 for sets < 10 1 per 10 for sets > 10	20%

III. *Action Required if Limits are Exceeded:

Reanalyze contact Chuck Elly at Region V CRL

Designation: D 4318 – 84

Standard Test Method for
LIQUID LIMIT, PLASTIC LIMIT, AND PLASTICITY INDEX OF SOILS[1]

This standard is issued under the fixed designation D 4318; 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 liquid limit, plastic limit, and the plasticity index of soils as defined in Section 3.

1.1.1 Two procedures for preparing test specimens and two procedures for performing the liquid limit are provided as follows:

- *A* Multipoint test using a wet preparation procedure, described in Sections 10.1, 11, and 12.
- *B* Multipoint test using a dry preparation procedure, described in Sections 10.2, 11, and 12.
- *C* One-point test using a wet preparation procedure, described in Sections 13, 14, and 15.
- *D* One-point test using a dry preparation procedure, described in Sections 13, 14, and 15.

The procedure to be used shall be specified by the requesting authority. If no procedure is specified, Procedure A shall be used.

NOTE 1—Prior to the adoption of this test method, a curved grooving tool was specified as part of the apparatus for performing the liquid limit test. The curved tool is not considered to be as accurate as the flat tool described in 6.2 since it does not control the depth of the soil in the liquid limit cup. However, there are some data which indicate that typically the liquid limit is slightly increased when the flat tool is used instead of the curved tool.

1.1.2 The plastic limit test procedure is described in Sections 16, 17, and 18. The plastic limit test is performed on material prepared for the liquid limit test. In effect, there are two procedures for preparing test specimens for the plastic limit test.

1.1.3 The procedure for calculating the plasticity index is given in Section 19.

1.2 The liquid limit and plastic limit of soils (along with the shrinkage limit) are often collectively referred to as the Atterberg limits in recognition of their formation by Swedish soil scientist, A. Atterberg. These limits distinguish the boundaries of the several consistency states of plastic soils.

1.3 As used in this test method, soil is any natural aggregation of mineral or organic materials, mixtures of such materials, or artificial mixtures of aggregates and natural mineral and organic particles.

1.4 The multipoint liquid limit procedure is somewhat more time consuming than the one-point procedure when both are performed by experienced operators. However, the one-point procedure requires the operator to judge when the test specimen is approximately at its liquid limit. In cases where this is not done reliably, the multipoint procedure is as fast as the one-point procedure and provides additional precision due to the information obtained from additional trials. It is particularly recommended that the multipoint procedure be used by inexperienced operators.

1.5 The correlations on which the calculations of the one-point procedure are based may not be valid for certain soils, such as organic soils or soils from a marine environment. The liquid

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[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.03 on Texture, Plasticity and Density Characteristics of Soils.

Current edition approved Oct. 26, 1984. Published December 1984. Originally published as D 4318 – 83. Last previous edition D 4318 – $83^{\epsilon1}$.

limit of these soils should therefore be determined by the multipoint procedure (Procedure A).

1.6 The liquid and plastic limits of many soils that have been allowed to dry before testing may be considerably different from values obtained on undried samples. If the liquid and plastic limits of soils are used to correlate or estimate the engineering behavior of soils in their natural moist state, samples should not be permitted to dry before testing unless data on dried samples are specifically desired.

1.7 The composition and concentration of soluble salts in a soil affect the values of the liquid and plastic limits as well as the water content values of soils (see Method D 2216). Special consideration should therefore be given to soils from a marine environment or other sources where high soluble salt concentrations may be present. The degree to which the salts present in these soils are diluted or concentrated must be given consideration if meaningful results are to be obtained.

1.8 Since the tests described herein are performed only on that portion of a soil which passes the 425-μm (No. 40) sieve, the relative contribution of this portion of the soil to the properties of the sample as a whole must be considered when using these tests to evaluate the properties of a soil.

1.9 The values stated in acceptable metric units are to be regarded as the standard. The values given in parentheses are for information only.

1.10 *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. Applicable Documents

2.1 *ASTM Standards:*

C 702 Methods for Reducing Field Samples of Aggregate to Testing Size[2]

D 75 Practice for Sampling Aggregates[3]

D 420 Recommended Practice for Investigating and Sampling Soil and Rock for Engineering Purposes[4]

D 653 Terms and Symbols Relating to Soil and Rock Mechanics[4]

D 1241 Specification for Materials for Soil-Aggregate Subbase, Base, and Surface Courses[4]

D 2216 Method for Laboratory Determination of Water (Moisture) Content of Soil, Rock, and Soil-Aggregate Mixtures[4]

D 2240 Test Method for Rubber Property—Durometer Hardness[5]

D 2487 Test Method for Classification of Soils for Engineering Purposes[4]

D 2488 Practice for Description and Identification of Soils (Visual-Manual Procedure)[4]

D 3282 Practice for Classification of Soils and Soil-Aggregate Mixtures for Highway Construction Purposes[4]

E 11 Specification for Wire-Cloth Sieves for Testing Purposes[4]

E 319 Methods of Testing Single-Arm Balances[6]

E 898 Method of Testing Top-Loading, Direct-Reading Laboratory Scales and Balances[6]

3. Definitions

3.1 *Atterberg limits*—originally, seven "limits of consistency" of fine-grained soils were defined by Albert Atterberg. In current engineering usage, the term usually refers only to the liquid limit, plastic limit, and in some references, the shrinkage limit.

3.2 *consistency*—the relative ease with which a soil can be deformed.

3.3 *liquid limit (LL)*—the water content, in percent, of a soil at the arbitrarily defined boundary between the liquid and plastic states. This water content is defined as the water content at which a pat of soil placed in a standard cup and cut by a groove of standard dimensions will flow together at the base of the groove for a distance of 13 mm (½ in.) when subjected to 25 shocks from the cup being dropped 10 mm in a standard liquid limit apparatus operated at a rate of 2 shocks per second.

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[2] *Annual Book of ASTM Standards*, Vol 04.02.

[3] *Annual Book of ASTM Standards*, Vols 04.02, 04.03, and 04.08.

[4] *Annual Book of ASTM Standards*, Vol 04.08.

[5] *Annual Book of ASTM Standards*, Vol 09.01.

[6] *Annual Book of ASTM Standards*, Vol 14.02.

NOTE 2—The undrained shear strength of soil at the liquid limit is considered to be 2 ±0.2 kPa (0.28 psi).

3.4 *plastic limit (PL)*—the water content, in percent, of a soil at the boundary between the plastic and brittle states. The water content at this boundary is the water content at which a soil can no longer be deformed by rolling into 3.2 mm (⅛ in.) in diameter threads without crumbling.

3.5 *plastic soil*—a soil which has a range of water content over which it exhibits plasticity and which will retain its shape on drying.

3.6 *plasticity index (PI)*—the range of water content over which a soil behaves plastically. Numerically, it is the difference between the liquid limit and the plastic limit.

3.7 *liquidity index*—the ratio, expressed as a percentage, of (*1*) the natural water content of a soil minus its plastic limit, to (*2*) its plasticity index.

3.8 *activity number (A)*—the ratio of (*1*) the plasticity index of a soil to (*2*) the percent by weight of particles having an equivalent diameter smaller than 0.002 mm.

4. Summary of Method

4.1 The sample is processed to remove any material retained on a 425-μm (No. 40) sieve. The liquid limit is determined by performing trials in which a portion of the sample is spread in a brass cup, divided in two by a grooving tool, and then allowed to flow together from the shocks caused by repeatedly dropping the cup in a standard mechanical device. The multipoint liquid limit, Procedures A and B, requires three or more trials over a range of water contents to be performed and the data from the trials plotted or calculated to make a relationship from which the liquid limit is determined. The one-point liquid limit, Procedures C and D, uses the data from two trials at one water content multiplied by a correction factor to determine the liquid limit.

4.2 The plastic limit is determined by alternately pressing together and rolling into a 3.2 mm (⅛ in.) diameter thread a small portion of plastic soil until its water content is reduced to a point at which the thread crumbles and is no longer able to be pressed together and rerolled. The water content of the soil at this stage is reported as the plastic limit.

4.3 The plasticity index is calculated as the difference between the liquid limit and the plastic limit.

5. Significance and Use

5.1 This test method is used as an integral part of several engineering classification systems to characterize the fine-grained fractions of soils (see Test Method D 2487 and Practice D 3282) and to specify the fine-grained fraction of construction materials (see Specification D 1241). The liquid limit, plastic limit, and plasticity index of soils are also used extensively, either individually or together with other soil properties to correlate with engineering behavior such as compressibility, permeability, compactibility, shrink-swell, and shear strength.

5.2 The liquid and plastic limits of a soil can be used with the natural water content of the soil to express its relative consistency or liquidity index and can be used with the percentage finer than 2-μm size to determine its activity number.

5.3 The one-point liquid limit procedure is frequently used for routine classification purposes. When greater precision is required, as when used for the acceptance of a material or for correlation with other test data, the multipoint procedure should be used.

5.4 These methods are sometimes used to evaluate the weathering characteristics of clay-shale materials. When subjected to repeated wetting and drying cycles, the liquid limits of these materials tend to increase. The amount of increase is considered to be a measure of a shale's susceptibility to weathering.

5.5 The liquid limit of a soil containing substantial amounts of organic matter decreases dramatically when the soil is oven-dried before testing. Comparison of the liquid limit of a sample before and after oven-drying can therefore be used as a qualitative measure of organic matter content of a soil.

6. Apparatus

6.1 *Liquid Limit Device*—A mechanical device consisting of a brass cup suspended from a carriage designed to control its drop onto a hard rubber base. A drawing showing the essential features of the device and the critical dimensions is given in Fig. 1. The design of the device may vary provided that the essential functions are preserved. The device may be operated either by a hand crank or by an electric motor.

6.1.1 *Base*—The base shall be hard rubber having a D Durometer hardness of 80 to 90, and a resilience such that an 8-mm (5/16-in.) diameter polished steel ball, when dropped from a height of 25 cm (9.84 in.) will have an average rebound of at least 80 % but no more than 90 %. The tests shall be conducted on the finished base with feet attached.

6.1.2 *Feet*—The base shall be supported by rubber feet designed to provide isolation of the base from the work surface and having an A Durometer hardness no greater than 60 as measured on the finished feet attached to the base.

6.1.3 *Cup*—The cup shall be brass and have a weight, including cup hanger, of 185 to 215 g.

6.1.4 *Cam*—The cam shall raise the cup smoothly and continuously to its maximum height, over a distance of at least 180° of cam rotation. The preferred cam motion is a uniformly accelerated lift curve. The design of the cam and follower combination shall be such that there is no upward or downward velocity of the cup when the cam follower leaves the cam.

NOTE 3—The cam and follower design in Fig. 1 is for uniformly accelerated (parabolic) motion after contact and assures that the cup has no velocity at drop off. Other cam designs also provide this feature and may be used. However, if the cam-follower lift pattern is not known, zero velocity at drop off can be assured by carefully filing or machining the cam and follower so that the cup height remains constant over the last 20 to 45° of cam rotation.

6.1.5 *Carriage*—The cup carriage shall be constructed in a way that allows convenient but secure adjustment of the height of drop of the cup to 10 mm (0.394 in.). The cup hanger shall be attached to the carriage by means of a pin which allows removal of the cup and cup hanger for cleaning and inspection.

6.1.6 *Optional Motor Drive*—As an alternative to the hand crank shown in Fig. 1, the device may be equipped with a motor to turn the cam. Such a motor must turn the cam at 2 ±0.1 revolutions per second, and must be isolated from the rest of the device by rubber mounts or in some other way that prevents vibration from the motor being transmitted to the rest of the apparatus. It must be equipped with an ON-OFF switch and a means of conveniently positioning the cam for height of drop adjustments. The results obtained using a motor-driven device must not differ from those obtained using a manually operated device.

6.2 *Flat Grooving Tool*—A grooving tool having dimensions shown in Fig. 2. The tool shall be made of plastic or noncorroding metal. The design of the tool may vary as long as the essential dimensions are maintained. The tool may, but need not, incorporate the gage for adjusting the height of drop of the liquid limit device.

6.3 *Gage*—A metal gage block for adjusting the height of drop of the cup, having the dimensions shown in Fig. 3. The design of the tool may vary provided the gage will rest securely on the base without being susceptible to rocking, and the edge which contacts the cup during adjustment is straight, at least 10 mm (3/8 in.) wide, and without bevel or radius.

6.4 *Containers*—Small corrosion-resistant containers with snug-fitting lids for water content specimens. Aluminum or stainless steel cans 2.5 cm (1 in.) high by 5 cm (2 in.) in diameter are appropriate.

6.5 *Balance*—A balance readable to at least 0.01 g and having an accuracy of 0.03 g within three standard deviations within the range of use. Within any 15-g range, a difference between readings shall be accurate within 0.01 g (Notes 4 and 5).

NOTE 4—See Methods E 898 and E 319 for an explanation of terms relating to balance performance.

NOTE 5—For frequent use, a top-loading type balance with automatic load indication, readable to 0.01 g, and having an index of precision (standard deviation) of 0.003 or better is most suitable for this method. However, nonautomatic indicating equal-arm analytical balances and some small equal arm top pan balances having readabilities and sensitivities of 0.002 g or better provide the required accuracy when used with a weight set of ASTM Class 4 (National Bureau of Standards Class P) or better. Ordinary commercial and classroom type balances such as beam balances are not suitable for this method.

6.6 *Storage Container*—A container in which to store the prepared soil specimen that will not contaminate the specimen in any way, and which prevents moisture loss. A porcelain, glass, or plastic dish about 11.4 cm (4½ in.) in diameter and a plastic bag large enough to enclose the dish and be folded over is adequate.

6.7 *Ground Glass Plate*—A ground glass plate at least 30 cm (12 in.) square by 1 cm (3/8 in.) thick for mixing soil and rolling plastic limit threads.

6.8 *Spatula*—A spatula or pill knife having a blade about 2 cm (¾ in.) wide by about 10 cm (4 in.) long. In addition, a spatula having a blade about 2.5 cm (1 in.) wide and 15 cm (6 in.) long has been found useful for initial mixing of samples.

6.9 *Sieve*—A 20.3 cm (8 in.) diameter, 425-µm (No. 40) sieve conforming to the requirements of Specification E 11 and having a rim at least 5 cm (2 in.) above the mesh. A 2-mm (No. 10) sieve meeting the same requirements may also be needed.

6.10 *Wash Bottle*, or similar container for adding controlled amounts of water to soil and washing fines from coarse particles.

6.11 *Drying Oven*—A thermostatically controlled oven, preferably of the forced-draft type, capable of continuously maintaining a temperature of 110 ± 5°C throughout the drying chamber. The oven shall be equipped with a thermometer of suitable range and accuracy for monitoring oven temperature.

6.12 *Washing Pan*—A round, flat-bottomed pan at least 7.6 cm (3 in.) deep, slightly larger at the bottom than a 20.3-cm (8-in.) diameter sieve.

6.13 *Rod* (optional)—A metal or plastic rod or tube 3.2 mm (⅛ in.) in diameter and about 10 cm (4 in.) long for judging the size of plastic limit threads.

7. Materials

7.1 A supply of distilled or demineralized water.

8. Sampling

8.1 Samples may be taken from any location that satisfies testing needs. However, Methods C 702, and Practice D 75, and Recommended Practice D 420 should be used as guides for selecting and preserving samples from various types of sampling operations. Samples which will be prepared using the wet preparation procedure, 10.1, must be kept at their natural water content prior to preparation.

8.2 Where sampling operations have preserved the natural stratification of a sample, the various strata must be kept separated and tests performed on the particular stratum of interest with as little contamination as possible from other strata. Where a mixture of materials will be used in construction, combine the various components in such proportions that the resultant sample represents the actual construction case.

8.3 Where data from this test method are to be used for correlation with other laboratory or field test data, use the same material as used for these tests where possible.

8.4 Obtain a representative portion from the total sample sufficient to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve. Free flowing samples may be reduced by the methods of quartering or splitting. Cohesive samples shall be mixed thoroughly in a pan with a spatula, or scoop and a representative portion scooped from the total mass by making one or more sweeps with a scoop through the mixed mass.

9. Calibration of Apparatus

9.1 *Inspection of Wear:*

9.1.1 *Liquid Limit Device*—Determine that the liquid limit device is clean and in good working order. The following specific points should be checked:

9.1.1.1 *Wear of Base*—The spot on the base where the cup makes contact should be worn no greater than 10 mm (⅜ in.) in diameter. If the wear spot is greater than this, the base can be machined to remove the worn spot provided the resurfacing does not make the base thinner than specified in 6.1 and the other dimensional relationships are maintained.

9.1.1.2 *Wear of Cup*—The cup must be replaced when the grooving tool has worn a depression in the cup 0.1 mm (0.004 in.) deep or when the edge of the cup has been reduced to half its original thickness. Verify that the cup is firmly attached to the cup hanger.

9.1.1.3 *Wear of Cup Hanger*—Verify that the cup hanger pivot does not bind and is not worn to an extent that allows more than 3-mm (⅛-in.) side-to-side movement of the lowest point on the rim.

9.1.1.4 *Wear of Cam*—The cam shall not be worn to an extent that the cup drops before the cup hanger (cam follower) loses contact with the cam.

9.1.2 *Grooving Tools*—Inspect grooving tools for wear on a frequent and regular basis. The rapidity of wear depends on the material from which the tool is made and the types of soils being tested. Sandy soils cause rapid wear of grooving tools; therefore, when testing these materials, tools should be inspected more frequently than for other soils. Any tool with a tip width greater than 2.1 mm must not be used. The depth of the tip of the grooving tool must be 7.9 to 8.1 mm.

NOTE 6—The width of the tip of grooving tools is conveniently checked using a pocket-sized measuring magnifier equipped with a millimetre scale. Magnifiers of this type are available from most laboratory supply companies. The depth of the tip of grooving tools can be checked using the depth measuring feature of vernier calipers.

9.2 *Adjustment of Height of Drop*—Adjust the height of drop of the cup so that the point on the cup that comes in contact with the base rises to a height of 10 ±0.2 mm. See Fig. 4 for proper location of the gage relative to the cup during adjustment.

NOTE 7—A convenient procedure for adjusting the height of drop is as follows: place a piece of masking tape across the outside bottom of the cup parallel with the axis of the cup hanger pivot. The edge of the tape away from the cup hanger should bisect the spot on the cup that contacts the base. For new cups, placing a piece of carbon paper on the base and allowing the cup to drop several times will mark the contact spot. Attach the cup to the device and turn the crank until the cup is raised to its maximum height. Slide the height gage under the cup from the front, and observe whether the gage contacts the cup or the tape. See Fig. 4. If the tape and cup are both contacted, the height of drop is approximately correct. If not, adjust the cup until simultaneous contact is made. Check adjustment by turning the crank at 2 revolutions per second while holding the gage in position against the tape and cup. If a ringing or clicking sound is heard without the cup rising from the gage, the adjustment is correct. If no ringing is heard or if the cup rises from the gage, readjust the height of drop. If the cup rocks on the gage during this checking operation, the cam follower pivot is excessively worn and the worn parts should be replaced. Always remove tape after completion of adjustment operation.

MULTIPOINT LIQUID LIMIT—PROCEDURES A AND B

10. Preparation of Test Specimens

10.1 *Wet Preparation*—Except where the dry method of specimen preparation is specified (10.2), prepare specimens for test as described in the following sections.

10.1.1 *Samples Passing the 425-μm (No. 40) Sieve*—When by visual and manual procedures it is determined that the sample has little or no material retained on a 425-μm (No. 40) sieve, prepare a specimen of 150 to 200 g by mixing thoroughly with distilled or demineralized water on the glass plate using the spatula. If desired, soak soil in a storage dish with small amount of water to soften the soil before the start of mixing. Adjust the water content of the soil to bring it to a consistency that would require 25 to 35 blows of the liquid limit device to close the groove (Note 8). If, during mixing, a small percentage of material is encountered that would be retained on a 425-μm (No. 40) sieve, remove these particles by hand, if possible. If it is impractical to remove the coarser material by hand, remove small percentages (less than about 15 %) of coarser material by working the specimen through a 425-μm (No. 40) sieve using a piece of rubber sheeting, rubber stopper, or other convenient device provided the operation does not distort the sieve or degrade material that would be retained if the washing method described in 10.1.2 were used. If larger percentages of coarse material are encountered during mixing, or it is considered impractical to remove the coarser material by the methods just described, wash the sample as described in 10.1.2. When the coarse particles found during mixing are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-μm (No. 40) sieve, but remove by hand or by washing. Place the mixed soil in the storage dish, cover to prevent loss of moisture, and allow to stand for at least 16 h (overnight). After the standing period and immediately before starting the test, thoroughly remix the soil.

NOTE 8—The time taken to adequately mix a soil will vary greatly, depending on the plasticity and initial water content. Initial mixing times of more than 30 — in may be needed for stiff, fat clays.

10.1.2 *Samples Containing Material Retained on a 425-μm (No. 40) Sieve:*

10.1.2.1 Select a sufficient quantity of soil at natural water content to provide 150 to 200 g of material passing the 425-μm (No. 40) sieve. Place in a pan or dish and add sufficient water to cover the soil. Allow to soak until all lumps have softened and the fines no longer adhere to the surfaces of the corase particles (Note 9).

NOTE 9—In some cases, the cations of salts present in tap water will exchange with the natural cations in the soil and significantly alter the test results should tap water be used in the soaking and washing operations. Unless it is known that such cations are not present in the tap water, distilled or demineralized water should be used. As a general rule, water containing more than 100 mg/L of dissolved solids should not be used for washing operations.

10.1.2.2 When the sample contains a large percentage of material retained on the 425-μm

(No. 40) sieve, perform the following washing operation in increments, washing no more than 0.5 kg (1 lb) of material at one time. Place the 425-µm (No. 40) sieve in the bottom of the clean pan. Pour the soil water mixture onto the sieve. If gravel or coarse sand particles are present, rinse as many of these as possible with small quantities of water from a wash bottle, and discard. Alternatively, pour the soil water mixture over a 2-mm (No. 10) sieve nested atop the 425-µm (No. 40) sieve, rinse the fine material through and remove the 2-mm (No. 10) sieve. After washing and removing as much of the coarser material as possible, add sufficient water to the pan to bring the level to about 13 mm (½ in.) above the surface of the 425-µm (No. 40) sieve. Agitate the slurry by stirring with the fingers while raising and lowering the sieve in the pan and swirling the suspension so that fine material is washed from the coarser particles. Disaggregate fine soil lumps that have not slaked by gently rubbing them over the sieve with the fingertips. Complete the washing operation by raising the sieve above the water surface and rinsing the material retained with a small amount of clean water. Discard material retained on the 425-µm (No. 40) sieve.

10.1.2.3 Reduce the water content of the material passing the 425-µm (No. 40) sieve until it approaches the liquid limit. Reduction of water content may be accomplished by one or a combination of the following methods: (*a*) exposing the air currents at ordinary room temperature, (*b*) exposing to warm air currents from a source such as an electric hair dryer, (*c*) filtering in a Buckner funnel or using filter candles, (*d*) decanting clear water from surface of suspension, or (*e*) draining in a colander or plaster of paris dish lined with high retentivity, high wet-strength filter paper.[7] If a plaster of paris dish is used, take care that the dish never becomes sufficiently saturated that it fails to actively absorb water into its surface. Thoroughly dry dishes between uses. During evaporation and cooling, stir the sample often enough to prevent overdrying of the fringes and soil pinnacles on the surface of the mixture. For soil samples containing soluble salts, use a method of water reduction such as *a* or *b* that will not eliminate the soluble salts from the test specimen.

10.1.2.4 Thoroughly mix the material passing the 425-µm (No. 40) sieve on the glass plate using the spatula. Adjust the water content of the mixture, if necessary, by adding small increments of distilled or demineralized water or by allowing the mixture to dry at room temperature while mixing on the glass plate. The soil should be at a water content that will result in closure of the groove in 25 to 35 blows. Return the mixed soil to the mixing dish, cover to prevent loss of moisture, and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, remix the soil thoroughly.

10.2 *Dry Preparation:*

10.2.1 Select sufficient soil to provide 150 to 200 g of material passing the 425-µm (No. 40) sieve after processing. Dry the sample at room temperature or in an oven at a temperature not exceeding 60°C until the soil clods will pulverize readily. Disaggregation is expedited if the sample is not allowed to completely dry. However, the soil should have a dry appearance when pulverized. Pulverize the sample in a mortar with a rubber tipped pestal or in some other way that does not cause breakdown of individual grains. When the coarse particles found during pulverization are concretions, shells, or other fragile particles, do not crush these particles to make them pass a 425-µm (No. 40) sieve, but remove by hand or other suitable means, such as washing.

10.2.2 Separate the sample on a 425-µm (No. 40) sieve, shaking the sieve by hand to assure thorough separation of the finer fraction. Return the material retained on the 425-µm (No. 40) sieve to the pulverizing apparatus and repeat the pulverizing and sieving operations as many times as necessary to assure that all finer material has been disaggregated and material retained on the 425-µm (No. 40) sieve consists only of individual sand or gravel grains.

10.2.3 Place material remaining on the 425-µm (No. 40) sieve after the final pulverizing operations in a dish and soak in a small amount of water. Stir the soil water mixture and pour over the 425-µm (No. 40) sieve, catching the water and any suspended fines in the washing pan. Pour this suspension into a dish containing the dry soil previously sieved through the 425-µm (No. 40) sieve. Discard material retained on the 425-µm (No. 40) sieve.

10.2.4 Adjust the water content as necessary by drying as described in 10.1.2.3 or by mixing on the glass plate, using the spatula while adding increments of distilled or demineralized water.

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[7] S and S 595 filter paper, available in 32-cm circles, has proven satisfactory.

until the soil is at a water content that will result in closure of the groove in 25 to 35 blows.

10.2.5 Put soil in the storage dish, cover to prevent loss of moisture and allow to stand for at least 16 h. After the standing period, and immediately before starting the test, thoroughly remix the soil (Note 8).

11. Procedure

11.1 Place a portion of the prepared soil in the cup of the liquid limit device at the point where the cup rests on the base, squeeze it down, and spread it into the cup to a depth of about 10 mm at its deepest point, tapering to form an approximately horizontal surface. Take care to eliminate air bubbles from the soil pat but form the pat with as few strokes as possible. Heap the unused soil on the glass plate and cover with the inverted storage dish or a wet towel.

11.2 Form a groove in the soil pat by drawing the tool, beveled edge forward, through the soil on a line joining the highest point to the lowest point on the rim of the cup. When cutting the groove, hold the grooving tool against the surface of the cup and draw in an arc, maintaining the tool perpendicular to the surface of the cup throughout its movement. See Fig. 5. In soils where a groove cannot be made in one stroke without tearing the soil, cut the groove with several strokes of the grooving tool. Alternatively, cut the groove to slightly less than required dimensions with a spatula and use the grooving tool to bring the groove to final dimensions. Exercise extreme care to prevent sliding the soil pat relative to the surface of the cup.

11.3 Verify that no crumbs of soil are present on the base or the underside of the cup. Lift and drop the cup by turning the crank at a rate of 1.9 to 2.1 drops per second until the two halves of the soil pat come in contact at the bottom of the groove along a distance of 13 mm (½ in.). See Fig. 6.

NOTE 10—Use the end of the grooving tool, Fig. 2, or a scale to verify that the groove has closed 13 mm (½ in.).

11.4 Verify that an air bubble has not caused premature closing of the groove by observing that both sides of the groove have flowed together with approximately the same shape. If a bubble has caused premature closing of the groove, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving operation and repeat 11.1 to 11.3. If the soil slides on the surface of the cup, repeat 11.1 through 11.3 at a higher water content. If, after several trials at successively higher water contents, the soil pat continues to slide in the cup or if the number of blows required to close the groove is always less than 25, record that the liquid limit could not be determined, and report the soil as nonplastic without performing the plastic limit test.

11.5 Record the number of drops, N, required to close the groove. Remove a slice of soil approximately the width of the spatula, extending from edge to edge of the soil cake at right angles to the groove and including that portion of the groove in which the soil flowed together, place in a weighed container, and cover.

11.6 Return the soil remaining in the cup to the glass plate. Wash and dry the cup and grooving tool and reattach the cup to the carriage in preparation for the next trial.

11.7 Remix the entire soil specimen on the glass plate adding distilled water to increase the water content of the soil and decrease the number of blows required to close the groove. Repeat 11.1 through 11.6 for at least two additional trials producing successively lower numbers of blows to close the groove. One of the trials shall be for a closure requiring 25 to 35 blows, one for closure between 20 and 30 blows, and one trial for a closure requiring 15 to 25 blows.

11.8 Determine the water content, W_N, of the soil specimen from each trial in accordance with Method D 2216. Make all weighings on the same balance. Initial weighings should be performed immediately after completion of the test. If the test is to be interrupted for more than about 15 min, the specimens already obtained should be weighed at the time of the interruption.

12. Calculations

12.1 Plot the relationship between the water content, W_N, and the corresponding number of drops, N, of the cup on a semilogarithmic graph with the water content as ordinates on the arithmetical scale, and the number of drops as abscissas on the logarithmic scale. Draw the best straight line through the three or more plotted points.

12.2 Take the water content corresponding to the intersection of the line with the 25-drop abscissa as the liquid limit of the soil. Computational methods may be substituted for the graphical method for fitting a straight line to the data and determining the liquid limit.

ONE-POINT LIQUID LIMIT—PROCEDURES C AND D

13. Preparation of Test Specimens

13.1 Prepare the specimen in the same manner as described in Section 10, except that at mixing, adjust the water content to a consistency requiring 20 to 30 drops of the liquid limit cup to close the groove.

14. Procedure

14.1 Proceed as described in 11.1 through 11.5 except that the number of blows required to close the groove shall be 20 to 30. If less than 20 or more than 30 blows are required, adjust the water content of the soil and repeat the procedure.

14.2 Immediately after removing a water content specimen as described in 11.5, reform the soil in the cup, adding a small amount of soil to make up for that lost in the grooving and water content sampling operations. Repeat 11.2 through 11.5, and, if the second closing of the groove requires the same number of drops or no more than two drops difference, secure another water content specimen. Otherwise, remix the entire specimen and repeat.

NOTE 11—Excessive drying or inadequate mixing will cause the number of blows to vary.

14.3 Determine water contents of specimens as described in 11.8.

15. Calculations

15.1 Determine the liquid limit for each water content specimen using one of the following equations:

$$LL = W_N\left(\frac{N}{25}\right)^{0.121} \quad \text{or}$$

$$LL = K(W_N)$$

where:

N = the number of blows causing closure of the groove at water content,

W_N = water content, and

K = a factor given in Table 1.

The liquid limit is the average of the two trial liquid limit values.

15.2 If the difference between the two trial liquid limit values is greater than one percentage point, repeat the test.

PLASTIC LIMIT

16. Preparation of Test Specimen

16.1 Select a 20-g portion of soil from the material prepared for the liquid limit test, either after the second mixing before the test, or from the soil remaining after completion of the test. Reduce the water content of the soil to a consistency at which it can be rolled without sticking to the hands by spreading and mixing continuously on the glass plate. The drying process may be accelerated by exposing the soil to the air current from an electric fan, or by blotting with paper that does not add any fiber to the soil, such as hard surface paper toweling or high wet strength filter paper.

17. Procedure

17.1 From the 20-g mass, select a portion of 1.5 to 2.0 g. Form the test specimen into an ellipsoidal mass. Roll this mass between the palm or fingers and the ground-glass plate with just sufficient pressure to roll the mass into a thread of uniform diameter throughout its length (Note 12). The thread shall be further deformed on each stroke so that its diameter is continuously reduced and its length extended until the diameter reaches 3.2 ±0.5 mm (0.125 ±.020 in.), taking no more than 2 min (Note 13). The amount of hand or finger pressure required will vary greatly, according to the soil. Fragile soils of low plasticity are best rolled under the outer edge of the palm or at the base of the thumb.

NOTE 12—A normal rate of rolling for most soils should be 80 to 90 strokes per minute, counting a stroke as one complete motion of the hand forward and back to the starting position. This rate of rolling may have to be decreased for very fragile soils.

NOTE 13—A 3.2-mm (⅛-in.) diameter rod or tube is useful for frequent comparison with the soil thread to ascertain when the thread has reached the proper diameter, especially for inexperienced operators.

17.1.1 When the diameter of the thread becomes 3.2 mm, break the thread into several pieces. Squeeze the pieces together, knead between the thumb and first finger of each hand, reform into an ellipsoidal mass, and reroll. Continue this alternate rolling to a thread 3.2 mm in diameter, gathering together, kneading and rerolling, until the thread crumbles under the pressure required for rolling and the soil can no longer be rolled into a 3.2-mm diameter thread (See Fig. 7). It has no significance if the thread breaks into threads of shorter length. Roll each of these shorter threads to 3.2 mm in diameter. The only requirement for continuing the test is that they are able to be reformed into an ellipsoidal mass and rolled out again. The operator shall at no time attempt to produce failure at exactly 3.2 mm diameter by allowing the thread to reach 3.2 mm, then reducing the rate of rolling or the hand pressure, or both, while continuing the rolling without further deformation until the thread falls apart. It is permissible, however, to reduce the total amount of deformation for feebly plastic soils by making the initial diameter of the ellipsoidal mass nearer to the required 3.2-mm final diameter. If crumbling occurs when the thread has a diameter greater than 3.2 mm, this shall be considered a satisfactory end point, provided the soil has been previously rolled into a thread 3.2 mm in diameter. Crumbling of the thread will manifest itself differently with the various types of soil. Some soils fall apart in numerous small aggregations of particles, others may form an outside tubular layer that starts splitting at both ends. The splitting progresses toward the middle, and finally, the thread falls apart in many small platy particles. Fat clay soils require much pressure to deform the thread, particularly as they approach the plastic limit. With these soils, the thread breaks into a series of barrel-shaped segments about 3.2 to 9.5 mm (⅛ to ⅜ in.) in length.

17.2 Gather the portions of the crumbled thread together and place in a weighed container. Immediately cover the container.

17.3 Select another 1.5 to 2.0 g portion of soil from the original 20-g specimen and repeat the operations described in 17.1 and 17.2 until the container has at least 6 g of soil.

17.4 Repeat 17.1 through 17.3 to make another container holding at least 6 g of soil. Determine the water content, in percent, of the soil contained in the containers in accordance with Method D 2216. Make all weighings on the same balance.

NOTE 14—The intent of performing two plastic limit trials is to verify the consistency of the test results. It is acceptable practice to perform only one plastic limit trial when the consistency in the test results can be confirmed by other means.

18. Calculations

18.1 Compute the average of the two water contents. If the difference between the two water contents is greater than two percentage points, repeat the test. The plastic limit is the average of the two water contents.

PLASTICITY INDEX

19. Calculations

19.1 Calculate the plasticity index as follows:

$$PI = LL - PL$$

where:

LL = the liquid limit.
PL = the plastic limit.

Both LL and PL are whole numbers. If either the liquid limit or plastic limit could not be determined, or if the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic, NP.

20. Report

20.1 Report the following information:

20.1.1 Sample identifying information,

20.1.2 Any special specimen selection process used, such as removal of sand lenses from undisturbed sample,

20.1.3 Report sample as airdried if the sample was airdried before or during preparation,

20.1.4 Liquid limit, plastic limit, and plasticity index to the nearest whole number and omitting the percent designation. If the liquid limit or plastic limit tests could not be performed, or if the plastic limit is equal to or greater than the liquid limit, report the soil as nonplastic, NP,

20.1.5 An estimate of the percentage of sample retained on the 425-μm (No. 40) sieve, and

20.1.6 Procedure by which liquid limit was performed, if it differs from the multipoint method.

21. Precision and Bias

21.1 No interlaboratory testing program has as yet been conducted using this test method to determine multilaboratory precision.

21.2 The within laboratory precision of the results of tests performed by different operators at one laboratory on two soils using Procedure A for the liquid limit is shown in Table 2.

TABLE 1 Factors for Obtaining Liquid Limit from Water Content and Number of Drops Causing Closure of Groove

N (Number of Drops)	K (Factor for Liquid Limit)
20	0.974
21	0.979
22	0.985
23	0.990
24	0.995
25	1.000
26	1.005
27	1.009
28	1.014
29	1.018
30	1.022

TABLE 2 Within Laboratory Precision for Liquid Limit

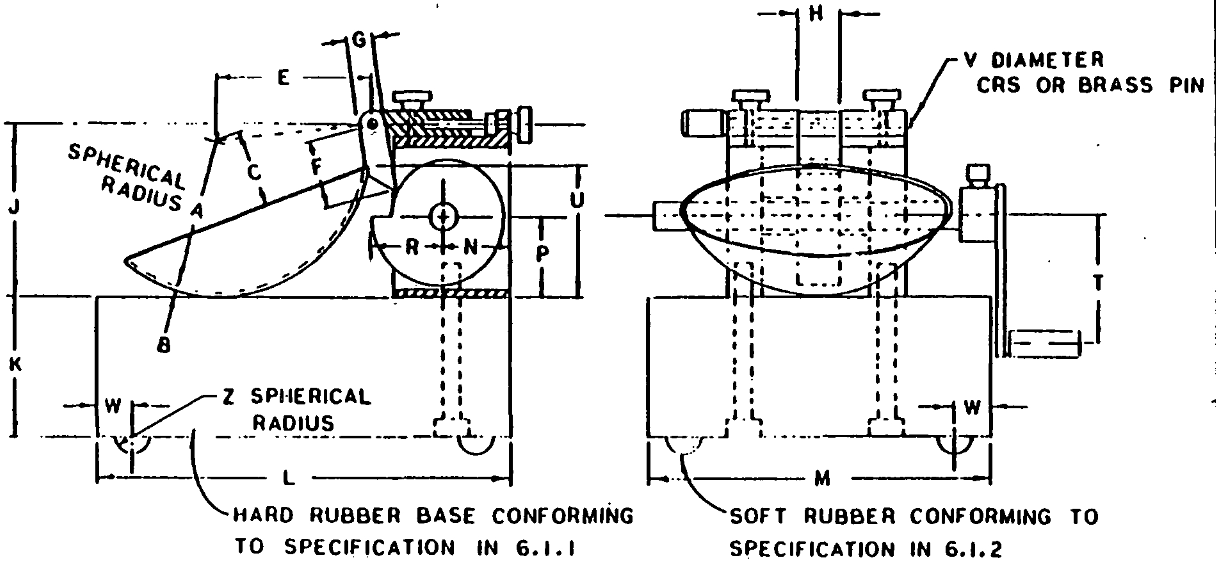
	Average Value, $\bar{x}$	Standard Deviation, s
Soil A:		
PL	21.9	1.07
LL	27.9	1.07
Soil B:		
PL	20.1	1.21
LL	32.6	0.98

DIMENSIONS

LETTER	A$^{\Delta}$	B$^{\Delta}$	C$^{\Delta}$	E$^{\Delta}$	F	G	H	J$^{\Delta}$	K$^{\Delta}$	L$^{\Delta}$	M$^{\Delta}$
MM	54 ± 0.5	2 ± 0.1	27 ± 0.5	56 ± 2.0	32	10	16	60 ± 1.0	50 ± 2.0	150 ± 2.0	125 ± 2.0

LETTER	N	P	R	T	U$^{\Delta}$	V	W	Z
MM	24	28	24	45	47 ± 1.0	3.8	13	6.5

$^{\Delta}$ ESSENTIAL DIMENSIONS



CAM ANGLE DEGREES	CAM RADIUS
0	0.742 R
30	0.753 R
60	0.764 R
90	0.773 R
120	0.784 R
150	0.796 R
180	0.818 R
210	0.854 R
240	0.901 R
270	0.945 R
300	0.974 R
330	0.995 R
360	1.000 R

FIG. 1 Hand-Operated Liquid Limit Device

DIMENSIONS

LETTER	A△	B△	C△	D△	E△	F△
MM	2 ± 0.1	11 ± 0.2	40 ± 0.5	8 ± 0.1	50 ± 0.5	2 ± 0.1
LETTER	G	H	J	K△	L△	N
MM	10 MINIMUM	13	60	10 ±0.05	60 DEG ± 1 DEG	20

△ *ESSENTIAL DIMENSIONS*

□ *BACK AT LEAST 15 MM FROM TIP*

NOTE : DIMENSION A SHOULD BE 1.9–2.0 AND DIMENSION D SHOULD BE 8.0–8.1 WHEN NEW TO ALLOW FOR ADEQUATE SERVICE LIFE

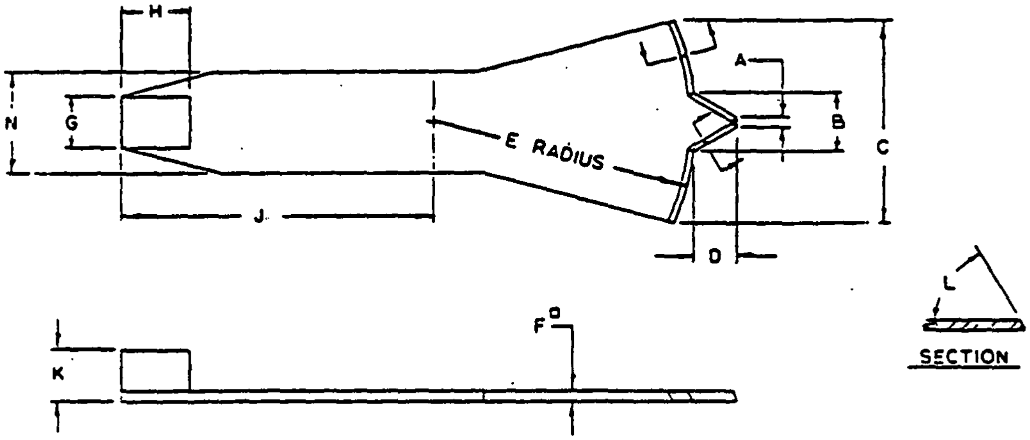
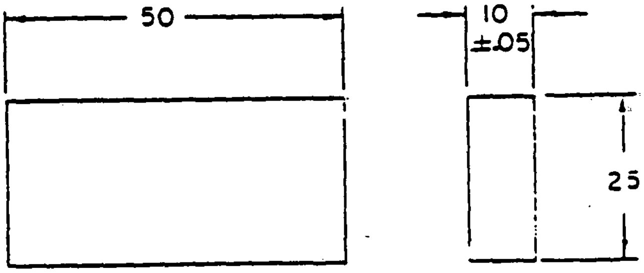


FIG. 2 Grooving Tool (Optional Height-of-Drop Gage Attached)



DIMENSIONS IN MILLIMETRES

FIG. 3 Height of Drop Gage

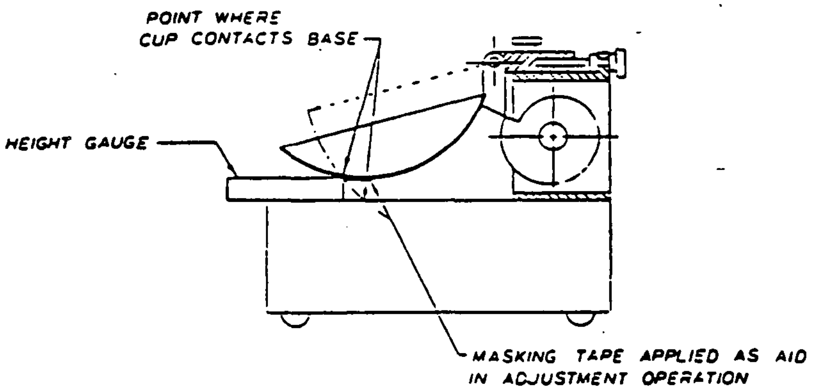


FIG. 4 Calibration for Height of Drop

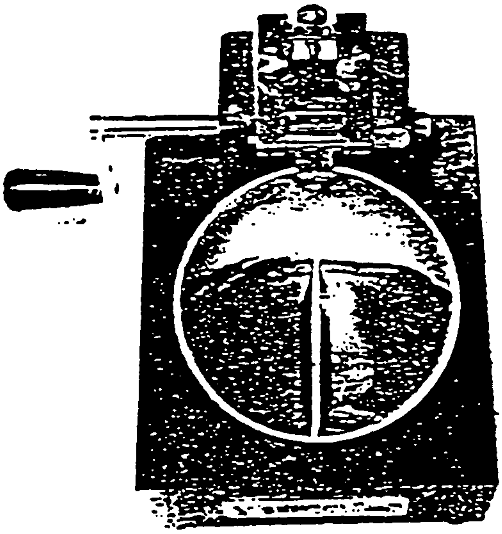


FIG. 5 Grooved Soil Pat in Liquid Limit Device

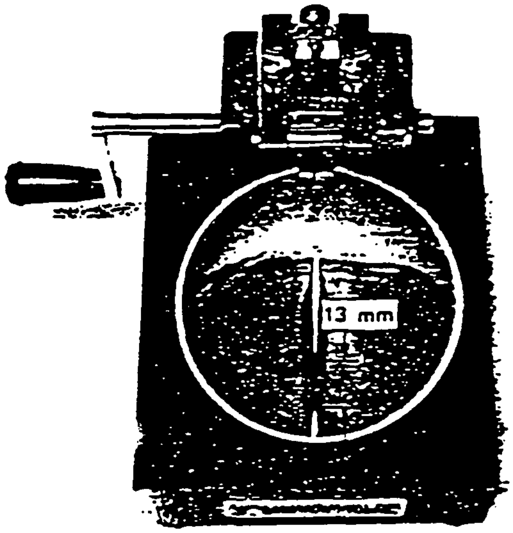


FIG. 6 Soil Pat After Groove Has Closed

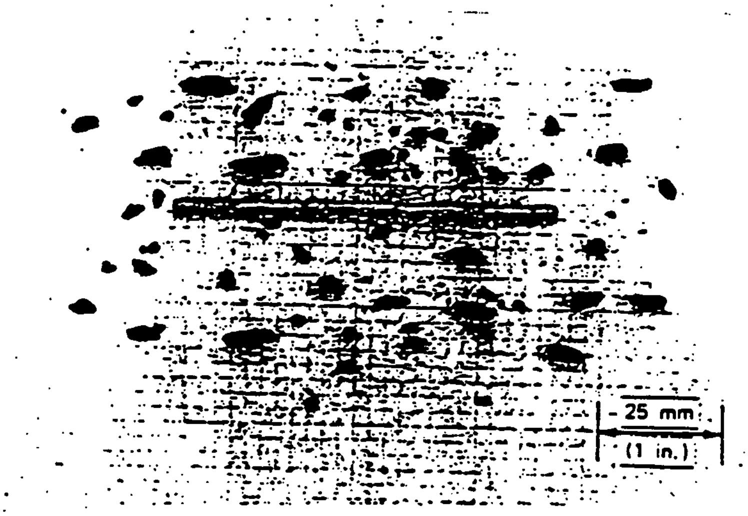


FIG. 7 Lean Clay Soil at the Plastic Limit

Appendix I
FIELD ANALYTICAL SERVICES

Attachment I-1: Specific Conductance
Attachment I-2: pH
Attachment I-3: Permeability (Slug Test)
Attachment I-4: Filtering of Water Samples
Attachment I-5: HNu Monitoring
Attachment I-6: OVA Monitoring

Attachment I-1
FIELD MEASUREMENT OF SPECIFIC CONDUCTANCE

Method: YSI Conductivity Meter Model 33

FIELD MEASUREMENT OF SPECIFIC CONDUCTANCE AND TEMPERATURE

l: Specific Conductance, umhos @ 25°C

ice: EPA 1979, Page 120.1, Standard Methods, 15th edition, pp 70-73

ion Limit: 1 umho/cm @ 25°C

um Range: 0.1 - 100,000 umhos/cm

Handling: Determine on-site or within 24 hours

ents and Apparatus:

Conductivity meter (YSI) and electrodes.

. Deionized water in squirt bottle.

3. Standard potassium chloride solution, 0.0100 N.

edure:

I Conductivity Meter

1. With mode switch at off position, check meter zero. If not zeroed, use meter screw and adjust to zero.

2. Plug probe into jack on side of meter.

3. Turn mode switch to red line, and turn red line knob until needle aligns with red line on dial. Change batteries if cannot be aligned.

4. Totally immerse probe in sample. Do not allow the probe to touch the sample container.

5. Turn mode switch to appropriate conductivity scale, X100, X10, or X1. Use a scale that will give a mid-range output on the meter.

6. Wait for needle to stabilize (about 15 sec.) and record conductivity multiplying by scale setting.

7. While gently agitating the probe, take sample temperature (°C) and record.

8. Rinse probe with deionized water.

9. Record specific conductivity (1st column) and temperature on F.O.S. sheet.

Notes:

1. Calculate conductivity using following formula:

$$G_{25} = \frac{G_T}{[1 + 0.02\ (T-25)]}$$

G_{25} = Conductivity at 25°C, umhos/cm

T = Temperature of sample, °C

G_T = Conductivity of sample at temperature T, umhos/cm

2. Report results for the standard solution with each data set.

3. Record on field sheet which meter and probe were used. Meter should be wiped clean as necessary.

4. After returning to lab, compare results with previous data. Report problems to lab personnel.

Reagent Preparation:

1. Stock Potassium Chloride Solution, 1.00 N: Dissolve 74.555 g. K Cl in Milli-Q water and dilute to 1,000 ml. in a volumetric flask.

2. Standard Potassium Chloride Solution, 0.0100N: Dilute to 10.0 mls. of stock solution to 1,000 mls. with Milli-Q water using a volumetric pipet and flask.

OPERATING INSTRUCTION
YSI MODEL 33
CONDUCTIVITY METER

TABLE OF CONTENTS

GENERAL DESCRIPTION

The YSI Model 33 and 33M S-C-T Meters are portable, battery powered, transistorized instruments designed to accurately measure salinity, conductivity and temperature. They use a probe consisting of a rugged, plastic conductivity cell and a precision YSI thermistor temperature sensor combined in a single unit.

Conductivity with the Model 33 is expressed as micromhos/centimeter (μmhos/cm); with the 33M, it's millisiemens/meter (mS/m). These are measurements of the electrical conductance the sample would show if measured between opposite faces of a 1cm cube. (Conversion information: 1 μmho/cm = 0.1 mS/m.) Salinity is the number of grams of salt/kilogram of sample (‰ = parts per thousand). This measurement assumes the sample contains a "standard" sea water salt mixture. The sample temperature is measured in degrees Celsius.

Salinity measurements are manually temperature compensated by direct dial. Conductivity measurements are not temperature compensated, however, a temperature function is provided on the instrument to aid with calculation of corrections. Also, when just temperature and conductivity are known it is possible to calculate salinity and when only temperature and salinity are known it is possible to calculate conductivity.

SPECIFICATIONS

Model 33 Conductivity

Ranges	0-500, 0-5,000, 0-50,000 μmhos/cm with YSI 3300 Series Probes (Note: The "μmho" designations on the meter are a shorthand form for "μmho/cm".)
Accuracy	±2.5% max. error at 500, 5,000 and 50,000 plus probe. ±3.0% max. error at 250, 2,500 and 25,000 plus probe See Error Section
Readability	2.5 μmhos/cm on 500 μmho/cm range 25 μmhos/cm on 5,000 μmho/cm range. 250 μmhos/cm on 50,000 μmho/cm range
Temperature Compensation	None

Model 33M Conductivity

Ranges:	0-50, 0-500, 0-5,000 mS/m with YSI 3300 Series Probes
Accuracy	±2.5% max. error at 50, 500 and 5,000 plus probe ±3.0% max. error at 25, 250 and 2,500 plus probe See Error Section
Readability	0.25 mS/m on 50 mS/m range 2.5 mS/m on 500 mS/m range 25.0 mS/m on 5,000 mS/m range
Temperature Compensation	None

Salinity

Range	0-40 ‰ in temperature range of -2 to +45°C
Accuracy	Above 4°C: ±0.9 ‰ at 40 ‰ and ±0.7 ‰ at 20 ‰ plus conductivity probe Below 4°C: ±1.1 ‰ at 40 ‰ and ±0.9 ‰ at 20 ‰ plus conductivity probe See Error Section
Readability	0.2 ‰ on 0-40 ‰ range
Temperature Compensation	Manual by direct dial from -2 to +45°C

Temperature	
Range	-2 to +50°C
Accuracy	±0.1°C at -2°C, ±0.6°C at 45°C plus probe See Error Section.
Readability	±0.15°C at -2°C to ±0.37°C at 45°C
Power Supply	Two D-size alkaline batteries. Eveready E95 or equivalent, provide approximately 200 hrs. of operation
Probe	YSI 3300 Series Conductivity/Temperature Probe Nominal Probe Constant: K = 5/cm
Accuracy	±2% of reading for conductivity and salinity Error of ±0.1°C at 0°C and ±0.3°C at 40°C
Instrument	
Ambient Range	Satisfactory operation -5 to +45°C. A maximum error of ±0.1% of the reading per °C change in instrument temperature can occur. This error is negligible if the instrument is readjusted to redline for each reading.

OPERATION PROCEDURE

1. Setup

(a) Adjust meter zero (if necessary) by turning the bakelite screw on the meter face so that the meter needle coincides with the zero on the conductivity scale.

(b) Calibrate the meter by turning the MODE control to REDLINE and adjusting the REDLINE control so the meter needle lines up with the redline on the meter face. If this cannot be accomplished, replace the batteries.

(c) Plug the probe into the probe jack on the side of the instrument.

(d) Put the probe in the solution to be measured. (See Probe Use.)

2. Temperature

Set the MODE control to TEMPERATURE. Read the temperature on the bottom scale of the meter in degrees Celsius. Allow time for the probe temperature to come to equilibrium with that of the water before reading.

3. Salinity

(a) Transfer the temperature reading from Step 2 to the °C scale on the instrument.

(b) Switch the MODE control to the SALINITY position and read salinity on the red 0-40 ‰ meter range.

(c) Depress the CELL TEST button. The meter reading should fall less than 2%. If greater, the probe is fouled and the measurement is in error. Clean the probe and re-measure.

4. Conductivity on Model 33 (Model 33M data are in parentheses.)

(a) Switch the MODE control to the X100 scale. If the reading is below 50 on the 0-500 range (5.0 on the 0-50 range) switch to the X10 scale. If the reading is still below 50 (5.0), switch to the X1 scale. Read the meter scale and multiply the reading appropriately. The answer is expressed in μmhos/cm (mS/m). Measurements are not temperature compensated.

Example:	Meter Reading	247 (24.7)
	Scale	X10
	Answer	2470 μmhos/cm (247.0 mS/m)

(b) When measuring on the X100 and X10 scales, depress the CELL TEST button. The meter reading should fall less than 2%; if greater, the probe is fouled and the measurement is in error. Clean the probe and re-measure.

NOTE: The CELL TEST does not function on the X1 scale.

5. Error

The maximum error in a reading can be calculated by using the graphs in the following sections.

(1) Temperature

The temperature scale is designed to give the minimum salinity error when the temperature readings are used to compensate salinity measurements.

Figure 1 shows total error for probe and instrument versus °C meter reading.

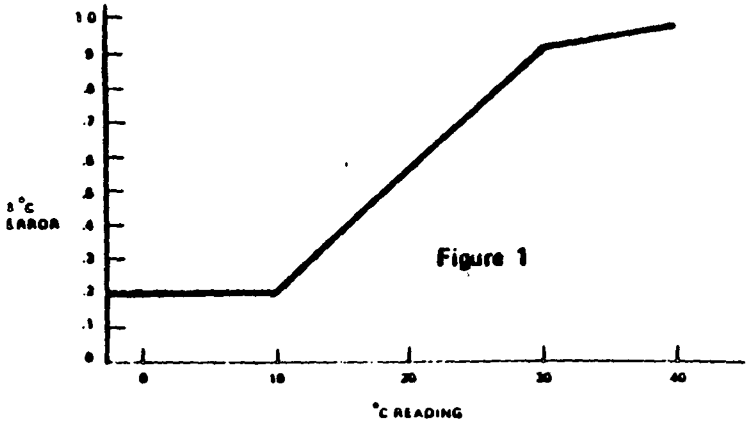


Figure 1

Example:	Meter Reading	15°C
	Total Error	0 4°C
	Accuracy	15°C ± 0 4°C for probe and instrument combined

(2) Conductivity on Model 33 (Model 33M data are in parentheses.)

Figure 2 shows the worst-case conductivity error as a function of the conductivity reading for the probe and instrument combined

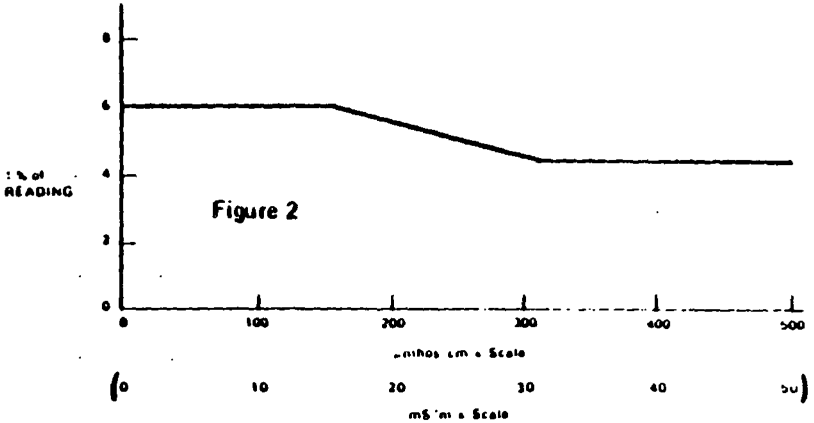
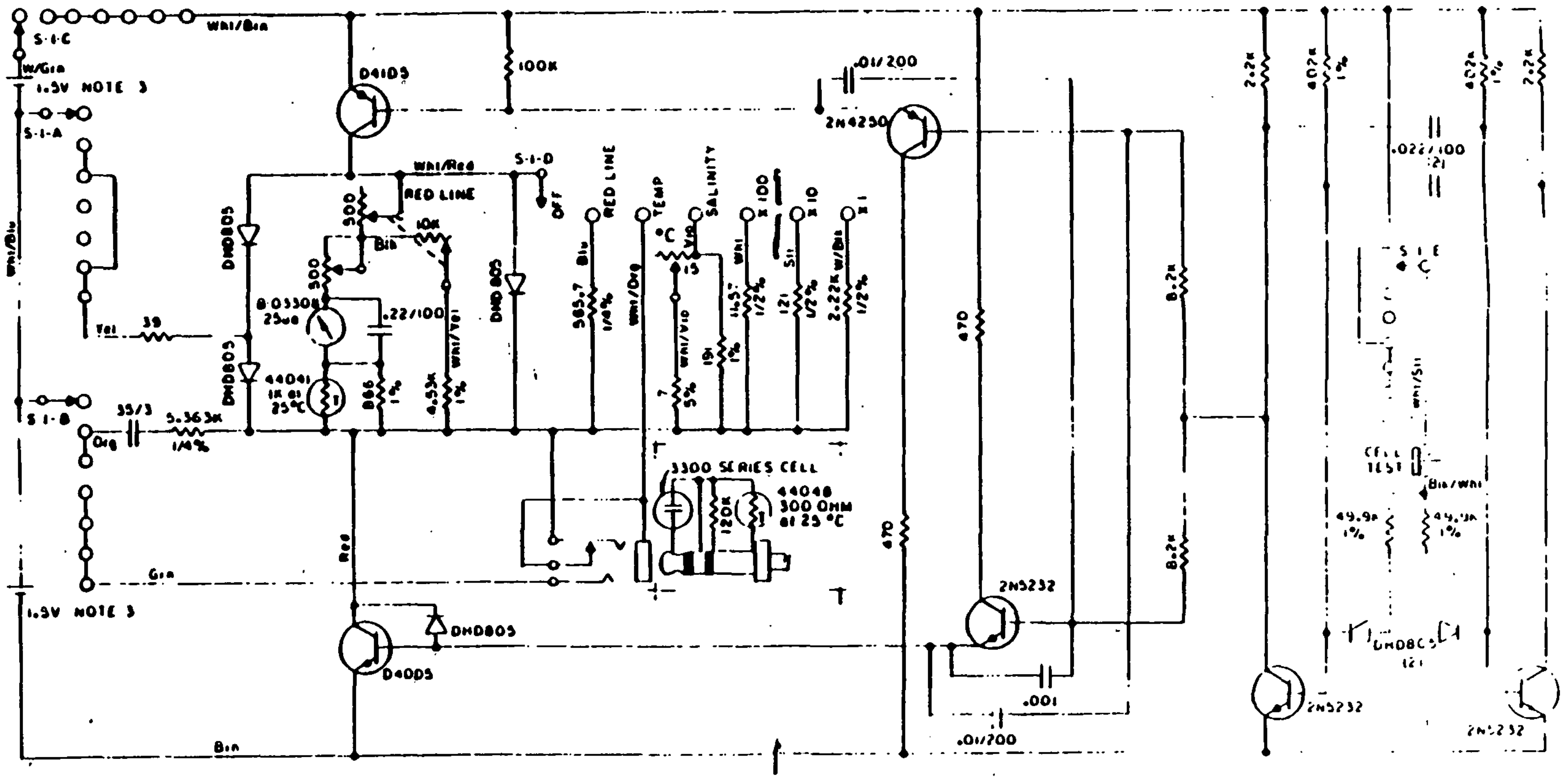


Figure 2

Example:	Meter Reading	360 µmhos/cm (36 mS/m)
	Scale	X10
	% Reading Error	± 4 5%
	Accuracy	3600 ± 162 µmhos/cm (360 ± 16 2 mS/m) for probe and instrument



YSI MODEL 33 AND 33M B-03321-E

NOTE

1. Resistance values in ohms, K=1,000 resistors are 1/4W, 10% unless otherwise specified
2. The values shown on the schematic may differ from those in the instrument, if so, either value can be used for replacement purposes
3. Battery is "D" size, alkaline only, Eveready E 95 or equal

CIRCUIT DESCRIPTION, MAINTENANCE AND CALIBRATION

1. Description

The circuit is composed of two parts; a multivibrator and switching transistors. The multivibrator produces a square waveform voltage. The square wave is applied to two switching transistors. They alternately apply two batteries of opposite polarity to the probe thus providing AC power which minimizes polarization effects. The meter is in series with one battery and measures the current from it. The current from the battery is proportional to the conductance of the cell. Salinity is measured in a special range conductivity circuit which includes a user-adjusted temperature compensator. In the temperature, redline and X1 positions the multivibrator operates at 100 Hz. In the salinity, X100 and X10 positions the multivibrator operates at 600 Hz and in these ranges pushing the CELL TEST button drops the frequency to 100 Hz allowing the operator to judge the degree of probe polarization.

2. Maintenance

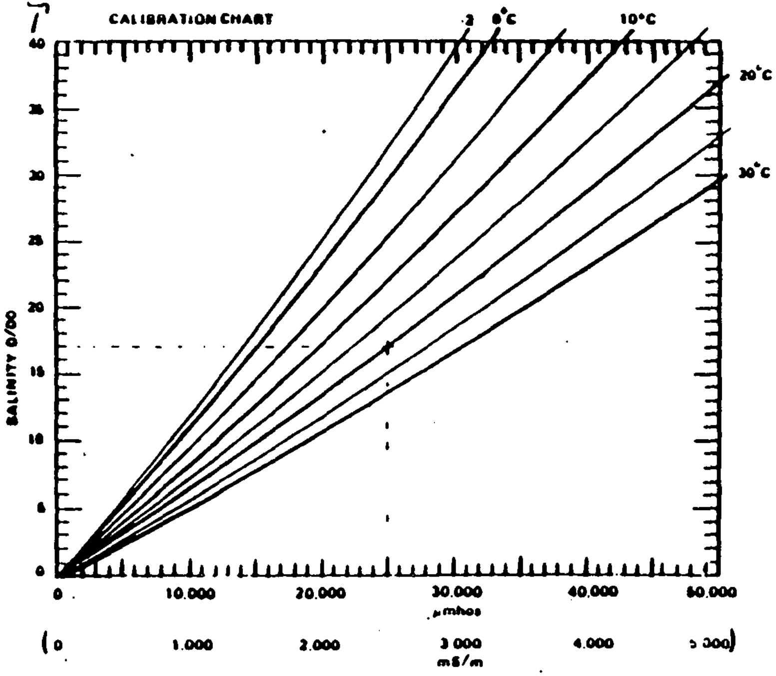
The only maintenance required is battery replacement. Two "D" size alkaline flashlight cells, such as Eveready E95 or equivalent, will provide 200 hrs. of operation. Accuracy will not be maintained if zinc-carbon "D" cells are used. Battery replacement is indicated when the redline adjustment cannot be accomplished.

Replace batteries every six months to reduce the danger of corrosion due to leaky batteries. To replace batteries, remove the six screws from the rear plate. The battery holders are color coded. The Positive (+ button) end must go on red.

3. Calibration of Model 33 (Model 33M data are in parentheses.)

It is possible for the temperature knob to become loose or slip from its normal position. In an emergency the dial can be re-positioned. It must be emphasized that this is an emergency procedure only, and that the instrument should be returned to the factory for proper recalibration at the earliest opportunity.

(a) Read the temperature and conductivity of the solution. Determine the salinity of the solution by running a line vertically on the graph from this conductance value until it intersects the appropriate °C line (interpolate as required for temperature between the given °C lines). From this intersection extend a



line horizontally to the edge of the graph. This determines the salinity for this sample.

Example: 25.000 μmhos/cm and 20°C gives a salinity of 17.
(Example: 2.500 mS/m and 20°C gives a salinity of 17.)

(b) Remove the °C knob, switch to SALINITY, and turn the control shaft until the meter needle indicates the salinity value determined in Step (a). In the example given, the value is 17.

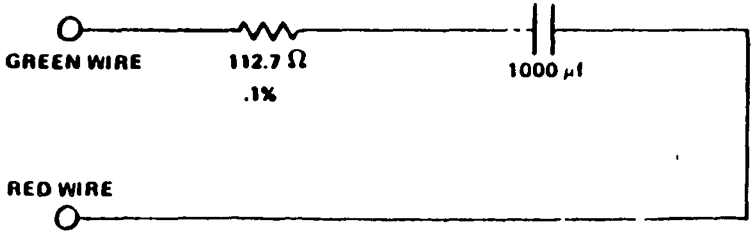
(c) Switch to TEMPERATURE. (Note: This temperature reading must be the same as Step (a); if not, begin again at Step (a).) Place the knob on the control shaft (without turning the control shaft) with the knob pointer at the same temperature as the meter reading and tighten both set screws securely.

At earliest opportunity recalibrate using the following procedure or return the instrument to factory for service.

(a) Set the instrument for a salinity measurement as normal.

(b) Substitute a 1000 μf capacitor and 112.7 ohm 0.1% tolerance resistor for the probe.

Connect the resistor and capacitor between the green wire and red wire on the jack connections inside the instrument.



(c) Turn the temperature dial until the meter reads redline

Now install the temperature knob with the arrow at 25°C This is a temporary calibration only Return the instrument to the factory for proper recalibration

PROBE

1. Description of YSI 3300 Series Conductivity/Temperature Probe

The YSI 3300 Series Conductivity Probes are designed for field use, embodying construction and design for rugged, accurate service

Each probe features a built-in cell constant of 5 0 (500 0/M) ±2%, a precision YSI thermistor temperature sensor of ±0.1°C accuracy at 0°C and ±0.3°C at 40°C and a low capacitance cable assembly terminating in a three therminal 0 25" dia. phone type connector.

The 3310 has a 10 ft cable and the 3311 is a 50 ft version Other lengths are available on special order

The probe has a rigid P V C body, platinized pure nickel electrodes, and a durable cable, providing resistance to a wide range of water-borne substances

2. Maintenance

(a) Cleaning

When the cell test indicates low readings the probable cause is dirty electrodes .Hard water deposits, oils and organic matter are the most likely contaminants

For convenient normal cleaning soak the electrodes for 5 minutes with a locally available bathroom tile cleaning preparation such as Dow Chemical "Bathroom Cleaner", Horizon Industries "Rally, Tile, Porcelain, and Chrome Cleaner" Johnson Wax "Envy, Instant Cleaner" or Lysol Brand "Basin, Tub Tile Cleaner"

For stronger cleaning a 5 minute soak in a solution made of 10 parts distilled water, 10 parts isopropyl alcohol and 1 part HCl can be used

Always rinse the probe after cleaning and before storage

CAUTION: Do not touch the electrodes inside the probe
Platinum black is soft and can be scraped off

If cleaning does not restore the probe performance, re platinizing is required.

(b) Re Platinizing

Equipment Required —

(1) YSI #3140 Platinizing Solution, 2 fl oz (3% platinum chloride dissolved in 0 025% lead acetate solution)

(2) YSI Model 33 or 33M S-C-T Meter.

(3) 50 ml glass breaker or equivalent bottle

(4) Distilled water

Procedure —

(1) Clean the probe as in Section (a) -- either method

(2) Place the cell in the beaker and add sufficient YSI #3140 solution to cover the electrodes Do not cover the top of the probe

(3) Plug the probe into the Model 33 or 33M, switch to the X100 scale to platinize the electrode Move the probe slightly to obtain the highest meter reading and continue platinizing for the approximate time shown below

Meter Reading		Time
µmhos/cm	mS/m	(minutes)
30,000	3,000	5
25,000	2,500	6
20,000	2,000	8
15,000	1,500	11
10,000	1,000	16

(4) After the elapsed time remove the probe and rinse in fresh water.

(5) Return the solution to its container. 2 oz. of solution should be sufficient for 50 treatments.

3. Probe Use

(a) Obstructions near the probe can disturb readings. At least two inches of clearance must be allowed from non-metallic underwater objects. Metallic objects such as piers or weights should be kept at least 6 inches from the probe.

(b) Weights are attached to the cable of the YSI 3310 and 3311 Probes. The YSI 3327 Weights are supplied in pairs with a total weight of 4 ounces per pair. Should it become necessary to add more weight to overcome water currents, we suggest limiting the total weight to two pounds (8 pairs). For weights in excess of two pounds use an independent suspension cable. In either case, weights must be kept at least 6 inches away from the probe.

(c) Gentle agitation by raising and lowering the probe several times during a measurement insures flow of specimen solution through the probe and improves the time response of the temperature sensor.

4. Cell Calibration & Standard Solutions

The YSI #3300 Series Cells are calibrated to absolute accuracy of ± 1.5% based on a standard solution. Since the literature on conductivity does not indicate a consistently accepted standardization method, we have chosen the 0.01 demal KCl solution method as determined by Jones and Bradshaw in 1937 as our standard. Recent textbooks, as well as the ASTM standards, concur with this choice.

The solution is prepared by diluting 0.745 grams of pure dry KCl with distilled water until the solution is 1 kilogram. The table below shows the values of conductivity this solution would have if the distilled water were non-conductive. However, since even high purity distilled water is slightly conductive, the measured conductivity will be higher by an amount equal to the water's conductivity.

Temperature °C	Conductivity µmhos/cm	Conductivity mS/m
15	1141.5	114.2
16	1167.5	116.8
17	1193.6	119.4
18	1219.9	122.0
19	1246.4	124.6
20	1273.0	127.3
21	1299.7	130.0
22	1326.6	132.7
23	1353.6	135.4
24	1380.8	138.1
25	1408.1	140.8
26	1436.5	143.7
27	1463.2	146.3
28	1490.9	149.1
29	1518.7	151.9
30	1546.7	154.7

The operator may use the standard solution and the table to check accuracy of a cell's constant or to determine an unknown constant. The formula is shown below.

$$K = \frac{R\,(C_1 + C_2)}{10^6} \quad \text{or} \quad \frac{R\,(S_1 + S_2)}{10^5}$$

where K = Cell constant
R = Measured resistance in Ω
C_1 = Conductivity in µmhos/cm
C_2 = Conductivity in µmhos/cm of the distilled water used to make solution

S_1 = Conductivity in mS/m
S_2 = Conductivity in mS/m of the distilled water used to make the solution.

R. C_1 and C_2, or S_1 and S_2, must either be determined at the same temperature or corrected to the same temperature to make the equation valid.

Note: For further information on conductivity and the above standard information, refer to ASTM Standards Part 23 — Standard Methods of Test for Electrical Conductivity, or Water and Industrial Waste Water — ASTM Designation D1125-64.

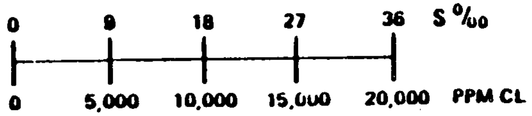
YSI MODEL 33 AND 33M USED WITH YSI 51A, 54 and 57 OXYGEN METERS

If the salinity measurement is to be used for salinity correction on the 51A, the reading should be converted to Chlorosity. The formula is:

$$\text{PPM Chlorosity} = \frac{\text{Salinity ‰} - 0.03}{1.8} \times 10^3$$

For these instruments the 0.03 can be neglected so the equation simplifies to:

$$\text{PPM Cl} = \frac{\text{SS ‰} \times 10^3}{1.8}$$



For salinity correction when using the Model 57 use the salinity reading direct from the Model 33 or 33M. No conversion is necessary.

Model 33 and 33M salinity readings taken in conjunction with Model 54 dissolved oxygen readings can be used to correct the Model 54 for salinity and to make post-measurement salinity corrections to dissolved oxygen data. Correction tables are available from the factory.

WARRANTY

All YSI products carry a one-year unconditional warranty on workmanship and parts, exclusive of batteries. Damage through accident, misuse, or tampering will be repaired at a nominal charge.

If you are experiencing difficulty with any YSI product, it may be returned to an authorized YSI dealer for repair, even if the warranty has expired. If you need factory assistance for any reason, contact

Service Department
Yellow Springs Instrument Co., Inc.
P.O. Box 279
Yellow Springs, Ohio U.S.A.
Phone: (513) 767-7241

Attachment I-2
FIELD MEASUREMENT OF pH

Method: Orion pH Meter Model 211

FIELD MEASUREMENT OF pH

Method: Electrometric

Reference: EPA 1979, Page 150.1

Sensitivity: 0.1 pH unit

Optimum Range: 1-12 pH units

Sample Handling: Determine on-site or within 6 hours.

Reagents and Apparatus:

1. pH meter (Orion Model 211 Mini pH meter).
2. Combination electrodes
3. Beakers or plastic cups.
4. pH buffer solutions, pH 4, 7, and 10.
5. Deionized water in squirt bottle.
6. All glassware soap and water washed, followed by two hot water rinses and two deionized water rinses.

Calibration:

1. Place electrode in pH7 buffer solution.
2. After allowing several minutes for meter to stabilize, turn calibration dial until a reading of 7.00 is obtained.
3. Rinse electrode with deionized water and place in pH4 or pH10 buffer solution.
4. Wait several minutes and then turn slope adjustment dial until a reading of 4.00 or 10.00 is obtained.
5. Rinse electrode with deionized water and place in pH7 buffer. If meter reading is not 7.00, follow Steps 2-5 again.

Procedure:

1. Calibrate meter using calibration procedure.
2. Pour the sample into a clean beaker or plastic cup.

3. Rinse electrode with deionized water between samples. Recheck calibration with pH7 buffer solution after every 5 samples.

4. Immerse electrode in solution. Make sure the white KCl junction on side of electrode is in the solution. The level of electrode solution should be one inch above sample to be measured.

Notes:

1. When calibrating the meter, use pH buffers 7 and 4 for samples with pH < 8, and buffers 7 and 10 for samples with pH ≥ 8. If meter will not read pH4 or 10, something may be wrong with the electrode. Return it to the lab with a note.

2. pH is a temperature dependent analysis. Therefore, temperatures of buffers and samples should be within about 2°C. For refrigerated or cool samples, use refrigerated buffers to calibrate meter.

3. Weak organic and inorganic salts and oil and grease are interferences in pH measurements. If oil and grease are visible, note on data sheet. Clean electrode with soap and water, followed by 10% HCl. Then recalibrate meter.

4. When not in use, the electrode should be stored in pH4 buffer.

5. Before going into the field:

   a) Check batteries;
   b) Do a quick calibration at pH7 and 4 to check electrode;
   c) Obtain fresh solutions.

6. Following field measurements:

   a) Report any problems;
   b) Compare with previous data;
   c) Clean all dirt off of meter and inside case;
   d) Make sure electrode is stored in pH4 buffer.

INSTRUCTION MANUAL

model 211
digital pH meter

ORION RESEARCH

contents

repair/service

For information on repair or replacement of this instrument, contact Orion Research toll-free. Ask for Customer Service.

ORION RESEARCH INCORPORATED
Customer Service
840 Memorial Drive
Cambridge, Massachusetts 02139 U.S.A.
800-225-1480 (Continental U.S.)
617-864-5400 (Massachusetts, Alaska, Hawaii, Canada)
Telex: 921466

Form IM211/3860

Printed in U S A

pecifications

package contents	model 211 digital pH meter, with model 910600 gel-filled unbreakable combination pH electrode, support rod, electrode holder, bottles for pH 7 buffer and distilled water, one packet pH 7 buffer powder, AC adapter, six 1.5 V batteries, and carrying case
range	0 to 14 pH
resolution	± .01 pH
temperature ompensation	manual (0 to 100°C)
isopotential point	pH 7 (fixed)
power requirement	six 1.5 V batteries; **battery life:** 3000 ten second intermittent measurements when line adapter is not used. **line adapter:** 110 or 220 V ± 20%, 50/60 Hz
dimensions	14 cm high x 9 cm wide x 4.5 cm deep
weight	0.4 kg

specifications subject to change without notice

notice of compliance

The Model 211 may generate radio frequency energy and if not installed and used properly, that is, in strict accordance with the manufacturer's instructions, may cause interference to radio and television reception. It has been type tested and found to comply with the limits for a Class B computing device in accordance with specifications in Subpart J of Part 15 of FCC Rules, which are designed to provide reasonable protection against such interference in a residential installation. However, there is no guarantee that interference will not occur in a particular installation. If the Model 211 does cause interference to radio or television reception, which can be determined by turning the unit off and on, the user is encouraged to try to correct the interference by one or more of the following measures:

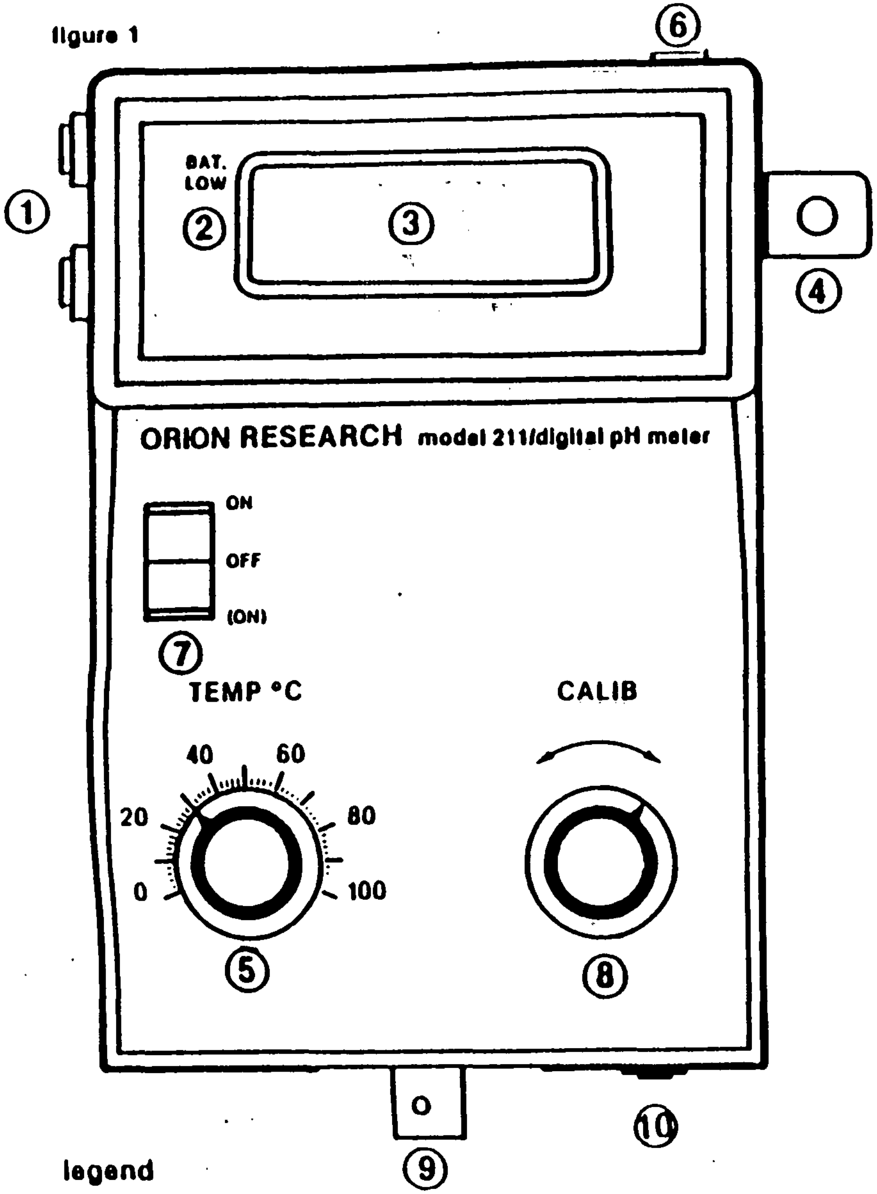
- reorient the receiving antenna
- relocate the Model 211 with respect to the receiver
- move the Model 211 away from the receiver
- plug the Model 211 into a different outlet so that the meter and receiver are on different branch circuits

If necessary, the user should consult the dealer or an experienced radio/television technician for additional suggestions. The user may find the following booklet prepared by the Federal Communications Commission helpful:

"How to Identify and Resolve Radio-TV Interference Problems"

This booklet is available from the U.S. Government Printing Office, Washington, DC 20402, Stock No. 004-000-00345-4.

figure 1



legend

1. strip chart recorder binding posts
2. BAT LOW
3. LC display
4. support rod clip
5. temperature indicator control
6. AC line adapter input
7. function control
8. calibration control
9. electrode connector
10. slope control

introduction

The Model 211 is a battery- or line-operated (110/220 V AC adapter) digital pH meter for field or laboratory use. The meter is complete with strip chart recorder binding posts and is supplied with an unbreakable, gel-filled combination pH electrode, one packet of pH 7 buffer powder, one bottle for pH 7 buffer, one bottle for distilled water, support rod, electrode holder, AC adapter, six 1.5 V batteries shorting plug, and carrying case.

instrument description

See figure 1.

1. **strip chart recorder binding posts:** black post is low (ground) and red post is high input side of recorder. See page 8.
2. **BAT LOW:** an arrow pointing towards BAT LOW appears on the display when battery requires replacement.
3. **LC display:** pH display over the range of 0 - 14 with ± .01 pH units resolution
4. **support rod clip:** holds steel rod used to mount electrode holder.
5. **temperature indicator control (TEMP °C):** compensates for variatio[illegible] electrode slope or temperature changes. Used in two-buffer calibration
6. **AC line adapter input:** jack used to insert AC line adapter. With AC line adapter operational, the internal battery is bypassed.
7. **function control:** rocker switch with three positions - ON, OFF and (ON) Depress (ON) for a momentary reading. The switch will return to OFF when released.
8. **calibration control (CALIB):** used to calibrate the meter with buffers of known pH.
9. **electrode connector:** accepts BNC connector from pH electrode.
10. **slope control:** screwdriver adjustment used to set second buffer in two-buffer calibration

instrument set-up

support rod

1. Insert steel support rod into the hole in the support rod clip on side of the meter.
2. Mount electrode holder on the rod by pinching to compress the spring. Release to hold in place.

power source

The Model 211 operates on six nonrechargeable 1.5 volt batteries or on 110 or 220 ± 20% V with an approved AC adapter (specify voltage when ordering). Low battery is indicated by the BAT LOW indicator on the display.

NOTE: Batteries are not rechargeable - use of line adapter whenever possible will prevent the unit's batteries from being discharged. If battery operation is desired, follow installation instructions under **battery replacement**.

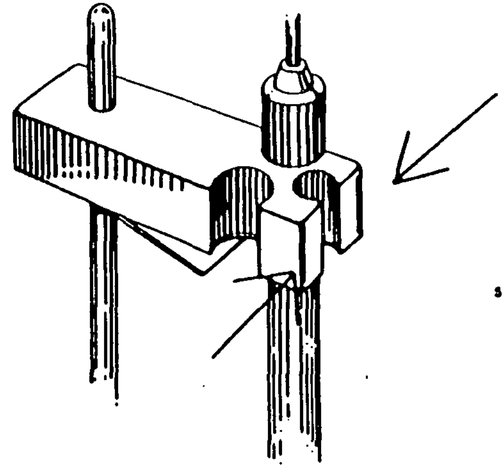
meter check-out

1. Install six AA batteries in the meter. Orient the (+) and (-) battery terminals to match the orientation shown in the battery compartment.
2. Depress ON button on the front panel. If the BAT. LOW indicator on the front display lights up, the batteries must be replaced.
3. If battery mode is not to be used, disregard steps 1 and 2. Insert pin end of appropriate AC line adapter into the meter, and the other end into the appropriate grounded AC line receptacle.
4. Attach BNC shorting plug to BNC input on the bottom side of the meter. Depress ON button on the front panel. Turn CALIB knob so display reads a steady 7.00. If this cannot be done consult ORION Technical Service.
5. Remove the shorting plug. Successful completion of steps 1-4 show the [illegible] is ready for use.

connecting electrode

1. Insert the BNC connector into the electrode jack on the bottom panel of the meter. Turn connector clockwise until it seats firmly.
2. Mount electrode in the electrode holder by spreading the electrode clip open and sliding the electrode into the holder so that the clip closes on electrode cap. See figure 2.
3. Follow **measurement procedures** to use the meter to measure pH.
4. Disconnnect electrode by turning connector counterclockwise until released from pin.

figure 2



squeeze as shown to insert electrode

measurement procedures

eneral measurement technique

emperature: All samples and buffers should be at the same temperature, as mall variations in temperature can cause errors in measurement. The slope of he pH electrode, the potential of the reference electrode, and the pH of the buf- er are temperature-dependent.

leaning electrodes: Electrode should be rinsed and shaken between measure- nents to remove drops and to prevent solution carryover.

tirring: Stir measured solutions moderately to obtain good contact between he glass bulb and the solution. Insert electrode to a depth of about 3 cm.

H measurements

ngle-buffer standardization
here maximum precision is not required)

OTE: For maximum accuracy it is recommended that a two-buffer calibration e performed once at the beginning of each day (see page 7). This procedure en- ures the correct setting of the slope control. Subsequent measurements during he day may be made using a single point calibration.

1. Place the electrode in a buffer solution whose pH is near the expected pH of the sample. Insert electrode to a depth of about 3 cm and stir moderately.
2. Set the temperature indicator control to the temperature of the buffer.
3. Set the function control to ON and allow the buffer reading to stabilize. Adjust the CALIB so that the display indicates the pH of the buffer at the solution temperature. See Table 1.
4. Remove the electrode from the buffer solution and rinse by stirring moderately in distilled water. Shake off excess drops of water.
5. Place electrode in the sample to a depth of about 3 cm and stir moderately. Set the function control to ON and allow the reading to stabilize. Record the steady pH reading.

two-buffer standardization
(where maximum precision is required)

1. Select two buffers to bracket the expected pH of the sample, with one buffer having a pH of 7.
2. Place the electrode in the pH 7 buffer to a depth of about 3 cm and stir moderately. Set the temperature indicator control to the temperature of the buffer. Set the function control to ON and allow the reading to stabilize. Turn CALIB until the display indicates the pH of the buffer at the solution temperature. See table 1.
3. Remove electrode from the first buffer and rinse by stirring moderately in distilled water. Shake off excess drops of water.
4. Place the electrode in the second buffer to a depth of about 3 cm and stir moderately. Set the function control to ON and adjust the slope control until the pH at the solution temperature is displayed. See Table 1.
5. Remove the electrode and rinse by stirring moderately in distilled water. Shake off excess drops of water.
6. Place the electrode in the sample to a depth of about 3 cm and stir moderately. Set the function control to ON and allow the reading to stabilize. Record the steady pH reading.

TABLE 1

TEMP (°C)	pH 7.00 Buffer	pH 4.01 Buffer	pH 10.01 Buffer
5	7.08	4.00	10.25
10	7.06	4.00	10.18
15	7.03	4.00	10.12
20	7.01	4.00	10.06
25	7.00	4.01	10.01
30	6.98	4.02	9.97
35	6.98	4.02	9.93
40	6.97	4.03	9.89
50	6.97	4.06	9.83
60	6.98	4.09	--

attery replacement

replace the batteries, remove the panel on the back of the meter. Be sure to serve the polarity marking when inserting new batteries.

ecorder output

e red and black binding posts at the side of the meter provide an output for ip chart recording of absolute mV independent of function mode. For orders with input impedance of 100 Kilohms or greater, the output is fixed to out 100 mV/pH. pH 14.00 output is 1.40 V. Lower impedance recorders may be ed but full-scale output is reduced.

Connect the lead from the high (input side of the recorder) to the red binding post and the lead from the low (ground) side to the black binding post.

Proceed according to directions in the strip chart recorder instruction manual.

pair and service

ION warranty covers failures due to manufacturer's workmanship or material ect from the date of purchase by the user. User should return the warranty d to ORION and retain proof of purchase. Warranty is void if product has been used, misused, or repairs attempted by unauthorized persons.

rranties herein are for products sold/installed for use only in the United States d Canada. For ORION products purchased for use in all other countries consult al in-country, authorized ORION sales agent/distributor for product warranty ormation.

eturn Authorization Number must be obtained from ORION Laboratory Products Customer Service before returning any product for in-warranty repair, lacement or credit.

o Lemon" Instrument Warranty

e instrument is covered by the ORION "No Lemon" warranty. If the instrument ils within twelve months from date of purchase for any reason other than use, the purchaser may elect to have it repaired or replaced at no charge. This arranty covers the original or replacement/repaired meter from date of original eter purchase; the warranty is not extended beyond the buyer's original warnty date.

accessories

815600	Ross™ epoxy body, bulb guard combination pH electrode
9104BN	Laboratory grade combination pH electrode (BNC connector)
910600	GX-series epoxy body, gel-filled combination electrode (BNC connector)
912600	GX-series epoxy body, gel-filled flask combination electrode (BNC connector)
913600	GX-series epoxy body, gel-filled flat surface combination pH electrode (BNC connector)
915600	RX-series refillable, epoxy body combination pH electrode (BNC connector)
9162BN	Combination pH electrode with rugged bulb (BNC connector)
9163BN	Combination pH electrode with needle shape (BNC connector)
910004	pH 4 buffer packets, box of 25 packets, each packet making 200 ml of buffer
910007	pH 7 buffer packets, box of 25 packets, each packet making 200 ml of buffer
910009	pH 9 buffer packets, box of 25 packets, each packet making 200 ml of buffer
910104	pH 4.01 buffer, 475 ml bottle
910107	pH 7.00 buffer, 475 ml bottle
910110	pH 10.01 buffer, 475 ml bottle
970899	Dissolved oxygen electrode
910002	Electrode holder
020030	Shorting plug
020120	110V AC line adapter
020121	220V AC line adapter

Attachment I-3
FIELD MEASUREMENT OF PERMEABILITY (SLUG TEST)

FIELD MEASUREMENT OF PERMEABILITY
(SLUG TEST)

INTRODUCTION

The objective is to determine hydraulic parameters (transmissivity, storativity, hydraulic conductivity) of the water-bearing strata. Single well aquifer tests are used because they may be conducted using a minimum of equipment, personnel, and time. They may also be done at many points within an aquifer and may be used to better plan a full scale pumping test.

PROCEDURES

Each slug test is conducted by measuring the static water level with an electric water level indicator, placing a pressure transducer (connected to a Hermit datalogger)[1], below the water level, lowering a 10.5 foot stainless steel slug bomb into the well above the static water level, starting the recorder, and submerging the bomb at least 10 feet below the static water level (or lowering it to the bottom of the well screen in wells with less than twenty feet of standing water). The change in water level back to the static level is recorded over a period of hours, using a logarithmic sampling mode on the datalogger.

The electric water level tape and transducers is wiped, first with methanol and then with deionized water as they are placed in the wells, to prevent cross-contamination between wells. New nylon rope (3/8-inch diameter) is used to lower the slug bombs into the wells. The slug bombs are decontaminated between uses by washing and rinsing with Liquinox soap and water, rinsing three times with methanol, and rinsing three times with deionized water. The slug bombs are then allowed to air-dry on steel supports and are covered with new sheet plastic.

DATA REDUCTION

The data accumulated during the slug tests are used to calculate hydraulic parameters using several published methods. Hydraulic conductivity is calculated for shallow, unconfined wells using the Bouwer and Rice method (1976). The NAVFAC method (1971) is used for comparison. Transmissivities and storativities for the deeper, confined wells are determined using the curve matching method described by Cooper, et al. (1967). For comparison, hydraulic conductivities are also calculated using the Hvorslev method (1951). All methods assume an infinite, homogenous, isotropic aquifer and an instantaneous change in head in the well.

The method described by Bouwer and Rice (1976) is based upon modifications to the Thiem equation, with the use of an analog model. A straight line is drawn through a semi-log plot of relative head versus time, and the hydraulic

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[1] Hermit Environmental Data Logger, Model SE1000B,
In-Situ, Inc., Laramie, Wyoming 82070.

conductivity is calculated using the slope of that line and the geometry of the well and aquifer. The formulation assumes that drawdown of the water table around the well is negligible, that flow in the capillary fringe may be ignored, and that well losses are negligible. It is applicable to completely or partially penetrating wells in unconfined aquifers, but may be used for confined aquifers that receive water from the upper confining layer.

In the NAVFAC method (1971), a straight line is also drawn through a semi-log plot of recovery data for unconfined aquifers. The method is based on the Hvorslev method. It assumes that the well is cased below the water table and the ratio of the screen length to the well radius (L/R) is greater than eight.

The Cooper, et al. (1967) formulation calculates the transmissivity of an aquifer by matching a plot of relative head (linear scale) versus time (logarithmic scale) to one of a set of type curves. The method assumes that the change in head after a known volume of water is injected or removed is instantaneous and that the well (non-flowing) is screened over the entire thickness of an artesian aquifer. It is directly applicable to fully penetrating screened wells in confined aquifers, but may be used to determine the transmissivity of the portion of an aquifer over which a partially penetrating well is screened, assuming no vertical flow occurs.

The Hvorslev method (1951) is based on a solution of the LaPlace equation and does not account for aquifer storage. A straight line is drawn through a semi-log plot of relative head versus time. The time that would be required for complete equalization of head difference if the original rate of inflow were maintained (defined as the basic time lag, T_0, and equal to the time when $H-h/H-H_0 = 0.37$) is used to calculate the hydraulic conductivity. The value of T_0 is measured graphically and the ratio of the piezometer length to radius is assumed to be greater than eight ($L/R>8$).

REFERENCES

Bouwer, H. and Rice, R.C., 1976. "A Slug Test for Determining Hydraulic Conductivity of Unconfined Aquifers with Completely or Partially Penetrating Wells", Water Resources Research, Vol. 12, No. 3, pp. 423-428.

Cooper, H.H., Bredehoeft, J.D., and Papadopulos, I.S., 1967. "Response of a Finite-Diameter Well to an Instantaneous Charge of Water", Water Resources Research, Vol. 3, No. 1, pp. 263-269.

Hvorslev, M.J., 1951. "Time Lag and Soil Permeability in Groundwater Observations", U.S. Army Corps of Engineers Waterways Exp. Sta. Bull. 36, Vicksburg, MA.

NAVFAC, DM-7, 1971. Design Manual - "Soil Mechanics, Foundations and Earth Structures", Department of the Navy, Naval Facilities Engineering Command.

Attachment I-4
FILTERING OF WATER SAMPLES

FIELD FILTERING

Reference: EPA 1979, Metals 5

Sample Handling: Filter as soon as possible after sample collection

Reagents and Apparatus:

1. 10% HCl solution in a squirt bottle and in a liter plastic bottle.
2. Milli-Q water
3. Plastic forceps
4. Millipore pressure filtration apparatus
5. 0.45 um. membrane filters (142 mm)
6. Glass fiber prefilters (124 mm)
7. 0.80 um. membrane filters (142 mm)
8. Compressed air
9. Pressure gauge

Procedure:

1. Using plastic forceps, place a 0.45 um. filter on top of blue grid.

2. Center the stainless steel cylinder on top of the filters, with the white gasket down.

3. Place a prefilter on top of membrane filter.

4. Place top onto cylinder rim. Screw handwheel bolts down until even and snug. Finish tightening with plastic wrench.

5. Attach end of PVC hosing to compressed air source.

6. Using squirt bottle, squirt about 10 to 25 mls. of 10% HCl into top opening.

7. Using the clamp, attach the hose adaptor to the top opening. Tighten clamp.

8. Place beaker under outlet.

9. Slowly increase pressure on compressed air tank. When liquid flows from outlet, lower pressure and bleed air from top plate vent valve until pressure gauge reads 10-15 PSI. Close valve and continue until flow stops. No leaks should be observed.

10. Shut off compressed air and open release valve.

11. Disconnect top clamp.

12. Rinse twice with Milli-Q water, following above procedure.

13. Place clean beaker or sample container under outlet.

14. Add sample, following above procedure, except that when flow of sample from outlet stops, increase pressure in increments of 10 PSI to 75 PSI and continue until flow stops.

15. After shutting off air and opening release valve, disconnect clamp and top plate and remove cylinder. Throw filters away.

16. Pour sample into a 100 ml. plastic bottle, label and preserve.

17. Run a Milli-Q blank every 10 to 20 samples.

Notes:

1. Samples with high sediment can be filtered through several membranes with increasing pore size and several prefilters. The 0.45 um. membrane filter should always be on the grid, and the coarsest filters on the top.

Reagent Preparation:

1. 10% HCl Solution: Add about 900 mls. of Milli-Q water to a one liter Erlenmeyer flask. Using a graduated cylinder, add 100 mls. concentrated HCL to the Milli-Q water while stirring.

Attachment I-5
HNu MONITORING

HNU MONITORING

1.0 Operation. For complete operating instructions, refer to the manufacturer's instruction manual.

2.0 Calibration. By analyzing a gas of known concentration, the HNu is easily calibrated. Benzene is typically used as the calibration gas. When calibrating an HNu, always remember to:

- Calibrate in the range to be tested.
- Deliver the calibration gas at ambient temperature ad pressure.
- Calibrate everyday.

Also:

- The calibration gas must be stable during the period of use.
- The calibration gas must be at concentration which reflects field sample concentrations.
- All gas cylinders must have proper regulators.

2.1 Calibration Procedure[1]. To calibrate an HNu:

1. Identify the probe by lamp label.
2. Connect the probe.
3. Affirm the ionization potential of the calibration gas.
4. Perform a battery check.
5. Zero the HNu
6. Sample calibration gas and adjust to proper reading.
7. Repeat steps 5 and 6.
8. If calibration cannot be achieved, the lamp must be cleaned.
9. Replace lamp if the lamp output is too low or if the lamp has failed.

To obtain more than a two point calibration, dilute the calibration gas to known concentrations and take additional readings.

*CAUTION: Handle gas cylinders with care.

3.0 HNu Monitoring Procedure at Moss/American

1. Sample soil.

2. Place soil sample in a glass jar, leaving ample headspace.

3. Cap jar and shake.

4. Uncap and sample headspace via HNu.

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[1] For a complete calibration procedure, see the manufacturer's instruction manual.

Attachment I-6
OVA MONITORING

OVA MONITORING

1.0 Operation. For complete operating instructions, refer to the manufacturers instruction manual.

2.0 Calibration. By analyzing a gas of known concentration, the OVA is easily calibrated. Methane in air is typically used as the calibration mixture, although the OVA can be calibrated to many other compounds.

Primary calibration of an OVA is performed at the factory.

2.1 Calibration Procedure'. To calibrate an OVA (in the field).

1. Zero the instrument.

2. Sample the calibration mixture and adjust to proper reading.

3. Next, set the calibration switch to a different range.

4. Sample another calibration mixture of different concentration and adjust to proper reading.

5. Zero the instrument.

*CAUTION: Handle gas cylinders with care.

3.0 OVA Monitoring Procedure at Moss/American

1. Sample soil.
2. Place soil sample in a glass jar, leaving ample headspace.
3. Cap jar and shake.
4. Uncap and sample headspace via OVA.

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[1] For a complete calibration procedure, see the manufacturers instruction manual.