effective date by publishing a subsequent document that will withdraw the final action. All public comments received will then be addressed in a subsequent final rule based on the separate proposed rule. The EPA will not institute a second comment period on this action. Any parties interested in commenting on this action should do so at this time. If no such comments are received, the public is advised that this action will be effective June 24, 1996.

Under section 307(b)(1) of the Clean Air Act (CAA), 42 U.S.C. 7607(b)(1), petitions for judicial review of this action must be filed in the United States Court of Appeals for the appropriate circuit by June 24, 1996. Filing a petition for reconsideration by the Administrator of this final rule does not affect the finality of this rule for purposes of judicial review nor does it extend the time within which a petition for judicial review may be filed, and shall not postpone the effectiveness of such rule or action. This action may not be challenged later in proceedings to enforce its requirements. (See section 307(b)(2) of the CAA, 42 U.S.C. 7607(b)(2).)

This action has been classified as a Table 3 action for signature by the Regional Administrator under the procedures published in the Federal Register on January 19, 1989 (54 FR 2214–2225), as revised by a July 10, 1995 memorandum from Mary Nichols, Assistant Administrator for Air and Radiation. The Office of Management and Budget (OMB) has exempted this regulatory action from E.O. 12866 review.

Nothing in this action shall be construed as permitting or allowing or establishing a precedent for any future request for a revision to any state implementation plan. Each request for revision to the state implementation plan shall be considered separately in light of specific technical, economic, and environmental factors and in relation to relevant statutory and regulatory requirements.

Under the Regulatory Flexibility Act, 5 U.S.C. 600 *et seq.*, EPA must prepare a regulatory flexibility analysis assessing the impact of any proposed or final rule on small entities. 5 U.S.C. 603 and 604. Alternatively, EPA may certify that the rule will not have a significant impact on a substantial number of small entities. Small entities include small businesses, small not-for-profit enterprises, and government entities with jurisdiction over populations of less than 50,000.

SIP approvals under section 110 and subchapter I, part D of the CAA do not create any new requirements, but simply approve requirements that the State is already imposing. Therefore, because the Federal SIP-approval does not impose any new requirements, I certify that it does not have a significant impact on any small entities affected. Moreover, due to the nature of the Federal-state relationship under the CAA, preparation of a regulatory flexibility analysis would constitute Federal inquiry into the economic reasonableness of state action. The CAA forbids EPA to base its actions concerning SIPs on such grounds. *Union Electric Co.* v. *U.S. E.P.A.*, 427 U.S. 246, 256–66 (S.Ct. 1976); 42 U.S.C. section 7410(a)(2) and 7410(k)(3).

Unfunded Mandates

Under Sections 202, 203, and 205 of the Unfunded Mandates Reform Act of 1995 (''Unfunded Mandates Act''), signed into law on March 22, 1995, EPA must undertake various actions in association with proposed or final rules that include a Federal mandate that may result in estimated costs of $100 million or more to the private sector, or to State, local, or tribal governments in the aggregate.

Through submission of this state implementation plan or plan revision, the State and any affected local or tribal governments have elected to adopt the program provided for under Section 110 of the CAA. These rules may bind State, local and tribal governments to perform certain actions and also require the private sector to perform certain duties. EPA has examined whether the rules being approved by this action will impose no new requirements, since such sources are already subject to these regulations under State law. Accordingly, no additional costs to State, local, or tribal governments, or to the private sector, result from this action, and therefore there will be no significant impact on a substantial number of small entities.

List of Subjects in 40 CFR Part 52

Environmental protection, Air pollution control, Hydrocarbons, Incorporation by reference, Intergovernmental relations, Nitrogen dioxide, Ozone, Reporting and recordkeeping requirements.

Dated: January 29, 1996.

Phyllis P. Harris,

Acting Regional Administrator.

Part 52 of chapter I, title 40, *Code of Federal Regulations,* is amended as follows:

PART 52—[AMENDED]

1. The authority citation for part 52 continues to read as follows:

Authority: 42 U.S.C. 7401–7671q.

Subpart K—Florida

2. Section 52.520, is amended by adding paragraph (c)(94) to read as follows:

§ 52.520 Identification of plan.

* * * * *

(c) * * *

(94) Revisions to the Florida SIP regarding perchloroethylene dry cleaning facilities submitted on April 24, 1995.

(i) Incorporation by reference.

Sections 62–210.200(17) and (48)(c); 62–210.300(2)(b) and (4); 62–296.200(58); and 62–296.412 of the F.A.C., effective April 18, 1995.

(ii) Other material. None.

[FR Doc. 96–10127 Filed 4–24–96; 8:45 am]

BILLING CODE 6560–50–P

40 CFR Parts 60 and 61

[AD–FRL 5407–4]

Standards of Performance for New Stationary Sources National Emission Standards for Hazardous Air Pollutants Addition of Method 29 to Appendix A of Part 60 and Amendments to Method 101A of Appendix B of Part 61

AGENCY: Environmental Protection Agency (EPA).

ACTION: Final rule.

SUMMARY: This rule adds Method 29, ''Determination of Metals Emissions from Stationary Sources,'' to Appendix A of Part 60, and makes amendments to Method 101A of Appendix B of Part 61. Method 29 is being added so that it can be used to determine cadmium, lead, and mercury emissions from municipal waste combustors (MWC) under subpart Ea of part 60. The amendments to Method 101A of appendix B of part 61 are to expand that method's applicability, and to revise procedures for handling and analyzing samples collected by the sampling train.

EFFECTIVE DATE: April 25, 1996.

Incorporation by Reference. The incorporation by reference of certain publications listed in the regulation is approved by the Director of the Office of the Federal Register April 25, 1996.

ADDRESSES: *Docket.* Docket No. A–94–28, containing materials relevant to this rulemaking, is available for public inspection and copying between 8:30 a.m. and Noon, and 1:30 and 3:30 p.m.,

Monday through Friday, at EPA's Air And Docket Section, Room M1500, First Floor, Waterside Mall, Gallery 1, 401 M Street, S.W., Washington, D.C. 20460. A reasonable fee may be charged for copying.

FOR FURTHER INFORMATION CONTACT: William Grimley at (919) 541–1065, Source Characterization Group B (MD–19), Emissions, Monitoring, and Analysis Division, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina 27711.

SUPPLEMENTARY INFORMATION:

I. The Rulemaking

Under Subparts Ca and Ea, the EPA promulgated guidelines and standards to regulate mercury, cadmium, and lead emissions from MWC's which were published in the Federal Register on December 19, 1995 (see 60 FR 65382). Method 29 is being promulgated for addition to Appendix A of 40 CFR Part 60 and will serve as the compliance test method for mercury, cadmium, and lead. Amendments to Method 101A of Appendix B of Part 61 are being promulgated to provide consistency with Method 29. These regulations were proposed on September 20, 1994 (see 59 FR 48259).

II. Public Participation

The opportunity to hold a public hearing on October 20, 1994 at 10 a.m. was present in the proposal notice, but no one wanted to make an oral presentation. The public comment period was from September 21, 1994 to November 21, 1994.

III. Significant Comments and Changes to the Proposed Rulemaking

One comment letter was received from the proposed rulemaking. The comments and responses are summarized in this preamble.

The first comment dealt with the analytical detection limits stated in Method 29. The commenter believes the detection limits are unrealistically low, and represent values achievable only under ideal conditions. The commenter concludes by saying that the method should state that it is the analyst's responsibility to determine the actual detection limit achieved.

The detection limits stated in Method 29 are those listed in the *SW–846* methods manual, and EPA believes they are reasonable ones for use in this application of *SW–846* analytical methods. However, Method 29 as proposed is clear in its discussion of the application of quality assurance procedures to document the quality of the data actually produced, and is also clear in the description of the procedure to be used to establish the actual detection limits achieved during the measurement of emissions.

The second comment addressed the point that dilution is likely to be effective in avoiding the analytical problem of spectral interference only if the analyte is present at a much greater concentration than the interferant. The commenter then suggests that Method 29 be revised to say that the effective way to adjust for spectral interference is by making background corrections or overlap corrections.

The EPA agrees with this comment, and Section 2.5 of the Method has been revised to permit these corrective techniques.

The third comment addressed the use of an alumina torch in the inductively coupled argon plasma (ICAP) emission spectroscopy procedure. The commenter believes that few ICAP users have this capability, and that an alternative technique for dealing with hydrogen fluoride could be suggested in the Method.

The EPA notes that the use of an alumina torch in this procedure has been described in related methodology for several years and is commercially available and is in use by many analysts. The alternative procedure suggested in the comment may be suitable if the detection limits needed in the particular emission measurement situation can be met.

The fourth comment addressed the required purity of the nickel nitrate used to produce the nickel nitrate matrix modifier. The commenter suggests that commercial nickel nitrate may contain small amounts of impurities.

The EPA is not aware of instances where commercial nickel nitrate that would be purchased for this purpose would contain objectionable amounts of impurities, however the Method has been revised to permit other nickel compounds of suitable purity to be used.

The fifth and final comment made a general statement concerning the length and complexity of the Method, with the commenter suggesting that the EPA should attempt to streamline and simplify the Method in order to make it less costly and easier to use.

The EPA recognizes the need to simplify methods to reduce costs, and believes that to meet the needed quality of the data to be generated by Method 29, that the best possible effort has been made.

IV. Administrative Requirements

A. Docket

The docket is an organized and complete file of all the information submitted to or otherwise considered by the EPA in the development of this final rulemaking. The principal purposes of the docket are: (1) to allow interested parties to identify and locate documents so that they can effectively participate in the rulemaking process, and (2) to serve as the record in case of judicial review (except for interagency review materials) [Section 307(d)(7)(A)].

B. Office of Management and Budget Review

1. Paperwork Reduction Act

This rule does not contain any information collection requirements subject to the Office of Management and Budget (OMB) review under the Paperwork Reduction Act, 44 U.S.C. 3501 *et seq.*

2. Executive Order 12866 Review

Under Executive Order 12866 (58 FR 51735, October 4, 1993), the EPA must determine whether the regulatory action is ''significant'' and therefore subject to the OMB review and the requirements of the Executive Order. The Order defines ''significant'' regulatory action as one that is likely to lead to a rule that may:

1. Have an annual effect on the economy of $100 million or more, or adversely affect in a material way the economy, a sector of the economy, productivity, competition, jobs, the environment, public health or safety, or State, local or tribal governments or communities;

2. Create a serious inconsistency or otherwise interfere with an action taken or planned by another agency;

3. Materially alter the budgetary impact of entitlements, grants, users fees, or loan programs or the rights and obligations of recipients thereof; or

4. Raise novel legal or policy issues arising out of legal mandates, the President's priorities, or the principles set forth in the Executive Order.

Pursuant to the terms of Executive Order 12866, the EPA does not consider this action to be significant because it does not involve any of the above mentioned items.

D. Unfunded Mandates Act

Section 202 of the Unfunded Mandates Reform Act of 1995 (''Unfunded Mandates Act'') (signed into law on March 22, 1995) requires that the Agency prepare a budgetary impact statement before promulgating a rule that includes a Federal mandate

that may result in expenditure by State, local, and tribal governments, in aggregate, or by the private sector of $100 million or more in any one year. Section 204 requires the Agency to establish a plan for obtaining input from and informing, educating, and advising any small governments that may be significantly or uniquely affected by the rule.

Under section 205 of the Unfunded Mandates Act, the Agency must identify and consider a reasonable number of regulatory alternatives before promulgating a rule for which a budgetary impact statement must be prepared. The agency must select from those alternatives the least costly, most cost-effective, or least burdensome alternative that achieves the objectives of the rule, unless the Agency explains why this alternative is not selected or the selection of this alternative is inconsistent with law.

Because this rule is estimated to result in the expenditure by State, local, and tribal governments or the private sector of less than $100 million in any one year, the Agency has not prepared a budgetary impact statement or specifically addressed the selection of the least costly, most cost-effective, or least burdensome alternative. Because small governments will not be significantly or uniquely affected by this rule, the Agency is not required to develop a plan with regard to small governments.

E. Regulatory Flexibility Act Compliance

Pursuant to the provisions of 5 U.S.C. 601 *et seq*., I hereby certify that this final rule will not have an economic impact on small entities because no additional costs will be incurred.

List of Subjects in 40 CFR Parts 60 and 61

Environmental protection, Air pollution control, Arsenic, Asbestos, Beryllium, Cadmium, Lead, Hazardous materials, Incorporation by reference, Intergovernmental relations, Mercury, Municipal waste combustors, Reporting and recordkeeping requirements, Sewage sludge incineration.

Statutory Authority. The statutory authority for this final rule is provided by sections 101, 111, 112, 114, 116, 129, and 301 of the Clean Air Act, as amended; 42 U.S.C., 7401, 7411, 7412, 7414, 7416, 7429, and 7601.

Dated: January 18, 1996.

Carol M. Browner,

Administrator.

40 CFR parts 60 and 61 are amended as follows:

PART 60—[AMENDED]

1. The authority citation for part 60 continues to read as follows:

Authority: 42 U.S.C. 7401, 7411, 7412, 7414, 7416, and 7601.

2. Section 60.17 is amended by revising paragraph (a)(22) and by adding paragraphs (i) and (j) to read as follows:

§ 60.17 Incorporations by reference.

* * * * *

(a) * * *

(22) ASTM D 1193–77, Standard Specification for Reagent Water, for appendix A to part 60, Method 6, par. 3.1.1; Method 7, par. 3.2.2; Method 7C, par. 3.1.1; Method 7D, par. 3.1.1; Method 8, par. 3.1.3; Method 12, par. 4.1.3; Method 25D, par. 3.2.2.4; Method 26A, par. 3.1.1; Method 29, pars. 4.2.2., 4.4.2., and 4.5.6.

* * * * *

(i) Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,'' EPA Publication SW–846 Third Edition (November 1986), as amended by Updates I (July, 1992), II (September 1994), IIA (August, 1993), and IIB (January, 1995). Test Method are incorporated by reference for appendix A to part 60, Method 29, pars. 2.2.1; 2.3.1; 2.5; 3.3.12.1; 3.3.12.2; 3.3.13; 3.3.14; 5.4.3; 6.2; 6.3; 7.2.1; 7.2.3; and Table 29–2. The Third Edition of SW–846 and Updates I, II, IIA, and IIB (document number 955–001–00000–1) are available from the Superintendent of Documents, U.S. Government Printing Office, Washington, DC 20402, (202) 512–1800. Copies may be obtained from the Library of the U.S. Environmental Protection Agency, 401 M Street, SW., Washington, DC 20460.

(j) Standard Methods for the Examination of Water and Wastewater, 16th edition, 1985. Method 303F Determination of Mercury by the Cold Vapor Technique. This document may be obtained from the American Public Health Association, 1015 18th Street, NW., Washington, DC 20036, and is incorporated by reference for Method 29, pars 5.4.3; 6.3; and 7.2.3 of appendix A to part 60.

3. In part 60, by adding method 29 to appendix A to read as follows:

Appendix A—Test Methods

* * * * *

Method 29—Determination of Metals Emissions from Stationary Sources

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (T1), and zinc (Zn) emissions from stationary sources. This method may be used to determine particulate emissions in addition to the metals emissions if the prescribed procedures and precautions are followed.

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

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

2. Range, Detection Limits, Precision, and Interferences

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

2.2 Analytical Detection Limits. (Note: See section 2.3 for the description of in-stack detection limits.)

2.2.1 ICAP analytical detection limits for the sample solutions (based on Method 6010 in EPA Publication SW–846, Third Edition (November 1986) including updates I, II, IIA, and IIB, as incorporated by reference in § 60.17(i)) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Co (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml), P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). ICP–MS analytical detection limits (based on based on Method 6020 in EPA Publication SW–846, Third Edition (November 1986) as incorporated by reference in § 60.17(i)) are lower generally by a factor of ten or more. Be is lower by a factor

of three. The actual sample analytical detection limits are sample dependent and may vary due to the sample matrix.

2.2.2 The analytical detection limits for analysis by direct aspiration AAS are approximately as follow: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Co (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml).

2.2.3 The detection limit for Hg by CVAAS (on the resultant volume of the *disgestion* of the aliquots taken for Hg analyses) can be approximately 0.02 to 0.2ng/ml, depending upon the type of CVAAS analytical instrument used.

2.2.4 The use of GFAAS can enhance the detection limits compared to direct aspiration AAS as follows: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Co (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and T1 (ng/ml).

2.3 *In-stack Detection Limits.*

2.3.1 For test planning purposes in-stack detection limits can be developed by using the following information (1) the procedures described in this method, (2) the analytical detection limits described in Section 2.2 and in EPA Publication SW–846, Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i), (3) the normal volumes of 300 ml (Analytical Fraction 1) for the front-half and 150 ml (Analytical Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m^3. The resultant in-stack method detection limits for the above set of conditions are presented in Table 29–1 and were calculated by using Eq. 29–1.

$$A \times B/C = D \qquad \text{Eq. 29–1}$$

Where:

A=Analytical detectin limit, µg/ml.
B=Liquid volume of digested sample prior to aliquotting for analysis, Ml.
C=Stack sample gas volume, dsm^3.
D=In-stack detection limit, $\mu g/m^3$.

TABLE 29–1.—IN-STACK METHOD DETECTION LIMITS ($\mu g/m^3$) FOR THE FRONT-HALF, THE BACK-HALF, AND THE TOTAL SAMPLING TRAIN USING ICAP AND AAS

Metal	Front-half: Probe and filter	Back-half: Impingers 1–3	Back-half: Impingers (4–6) [a]	Total train:
Antimony	[1] 7.7 (0.7)	[1] 3.8 (0.4)		[1] 11.5 (1.1)
Arsenic	[1] 12.7 (0.3)	[1] 6.4 (0.1)		[1] 19.1 (0.4)
Barium	0.5	0.3		0.8
Beryllium	[1] 0.07 (0.05)	[1] 0.04 (0.03)		[1] 0.11 (0.08)
Cadmium	[1] 1.0 (0.02)	[1] 0.5 (0.01)		[1] 1.5 (0.03)
Chromium	[1] 1.7 (0.2)	[1] 0.8 (0.1)		[1] 2.5 (0.3)
Cobalt	[1] 1.7 (0.2)	[1] 0.8 (0.1)		[1] 2.5 (0.3)
Copper	1.4	0.7		2.1
Lead	[1] 10.1 (0.2)	[1] 5.0 (0.1)		[1] 15.1 (0.3)
Manganese	[1] 0.5 (0.2)	[1] 0.2 (0.1)		[1] 0.7 (0.3)
Mercury	[2] 0.06	[2] 0.3	[2] 0.2	[2] 0.56
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	[1] 18 (0.5)	[1] 9 (0.3)		[1] 27 (0.8)
Silver	1.7	0.9		2.6
Thallium	[1] 9.6 (0.2)	[1] 4.8 (0.1)		[1] 14.4 (0.3)
Zinc	0.5	0.3		0.8

[a] Mercury analysis only.
[1] Detection limit when analyzed by GFAAS.
[2] Detection limit when analyzed by CVAAS, estimated for Back-Half and Total Train. See Sections 2.2 and 5.4.3.
Note: Actual method in-stack detection limits may vary from these values, as described in Section 2.3.3.

2.3.2 To ensure optimum precision/resolution in the analyses, the target concentrations of metals in the analytical solutions should be at least ten times their respective analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, these concentrations can be as low as approximately three times the respective analytical detection limits without seriously impairing the precision of the analyses. On at least one sample run in the source test, and for each metal analyzed, perform either repetitive analyses, Method of Standard Additions, serial dilution, or matrix spike addition, etc., to document the quality of the data.

2.3.3 Actual in-stack method detection limits are based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be improved over those shown in Table 29–1 for a specific test by either increasing the sampled stack gas volume, reducing the total volume of the digested samples, improving the analytical detection limits, or any combination of the three. For extremely low levels of *Hg only*, the aliquot size selected for digestion and analysis can be increased to as much as 10 ml, thus improving the in-stack detection limit by a factor of ten compared to a 1 ml aliquot size.

2.3.3.1 A nominal one hour sampling run will collect a stack gas sampling volume of about 1.25 m^3. If the sampling time is increased to four hours and 5 m^3 are collected, the in-stack method detection limits would be improved by a factor of four compared to the values shown in Table 29–1.

2.3.3.2 The in-stack detection limits assume that all of the sample is digested and the final liquid volumes for analysis are the normal values of 300 ml for Analytical Fraction 1, and 150 ml for Analytical Fraction 2A. If the volume of Analytical Fraction 1 is reduced from 300 to 30 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of ten. If the volume of Analytical Fraction 2A is reduced from 150 to 25 ml, the in-stack detection limits for that fraction of the sample would be improved by a factor of six. Matrix effect checks are necessary on sample analyses and typically are of much greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction of Analytical Fractions 1 and 2A to volumes of less than 30 and 25 ml, respectively, could interfere with the redissolving of the residue and could increase interference by other compounds to an intolerable level.

2.3.3.3 When both of the modifications described in Sections 2.3.3.1 and 2.3.3.2 are used simultaneously on one sample, the resultant improvements are multiplicative. For example, an increase in stack gas volume by a factor of four and a reduction in the total liquid sample digested volume of both Analytical Fractions 1 and 2A by a factor of six would result in an improvement by a factor of twenty-four of the in-stack method detection limit.

2.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test performed at

a sewage sludge incinerator were found to be as follows: Sb (12.7 percent), As (13.5 percent), Ba (20.6 percent), Cd (11.5 percent), Cr (11.2 percent), Cu (11.5 percent), Pb (11.6 percent), P (14.6 percent), Se (15.3 percent), Tl (12.3 percent), and Zn (11.8 percent). The precision for Ni was 7.7 percent for another test conducted at a source simulator. Be, Mn, and Ag were not detected in the tests. However, based on the analytical detection limits of the ICAP for these metals, their precisions could be similar to those for the other metals when detected at similar levels.

2.5 Interferences. Iron (Fe) can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Aluminum (Al) can be a spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the analytical sample, but such dilution raises the in-stack detection limits. Background and overlap corrections may be used to adjust for spectral interferences. Refer to Method 6010 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i) the other analytical methods used for details on potential interferences to this method. For all GFAAS analyses, use matrix modifiers to limit interferences, and matrix match all standards.

3. Apparatus

3.1 Sampling. A schematic of the sampling train is shown in Figure 29–1. It has general similarities to the Method 5 train.

BILLING 6560–50–M

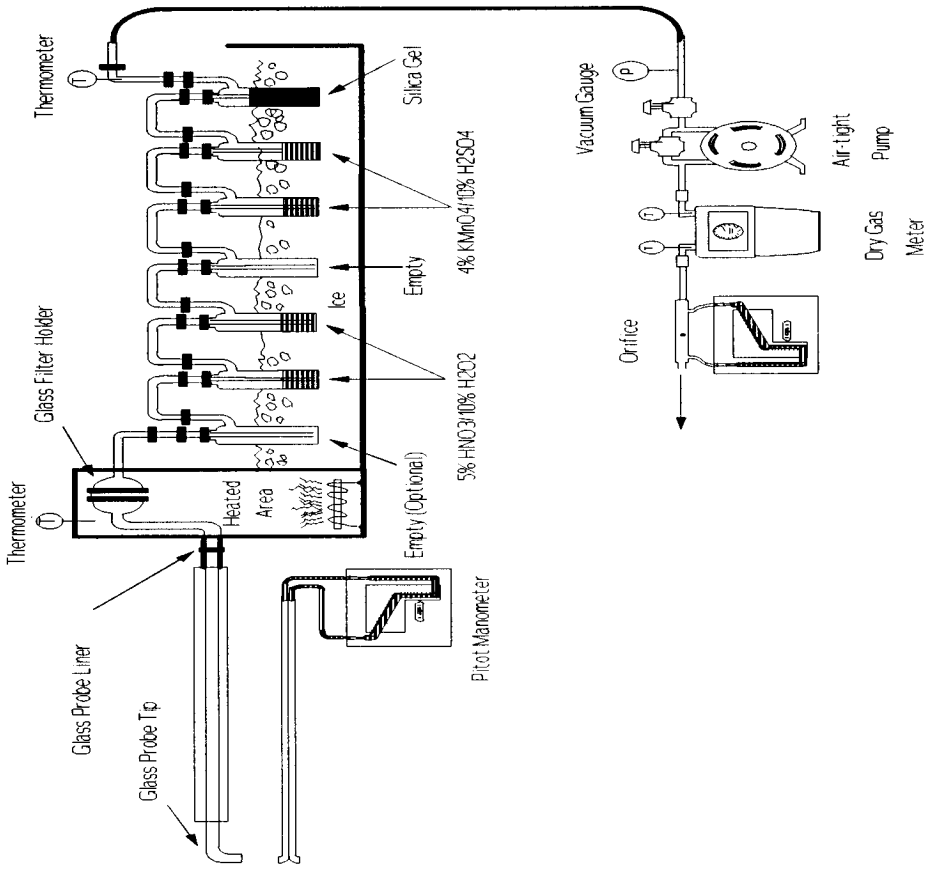

Figure 29-1. Sampling train.

BILLING 6560–50–C

3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2, except that glass nozzles are required unless alternate tips are constructed of materials that are free from contamination and will not interfere with the sample. If a probe tip other than glass is used, no correction to the sample test results to compensate for the nozzle's effect on the sample is allowed. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended instead of metal fittings to prevent contamination. If one chooses to do so, a single glass piece consisting of a combined probe tip and probe liner may be used.

3.1.2 Pitot Tube and Differential Pressure Gauge. Same as Method 2, Sections 2.1 and 2.2, respectively.

3.1.3 Filter Holder. Glass, same as Method 5, Section 2.1.5, except use a Teflon filter support or other non-metallic, non-contaminating support in place of the glass frit.

3.1.4 Filter Heating System. Same as Method 5, Section 2.1.6.

3.1.5 Condenser. Use the following system for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system shall consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. Use the first impinger as a moisture trap. The second impinger (which is the first HNO_3/H_2O_2 impinger) shall be identical to the first impinger in Method 5. The third impinger (which is the second HNO_3/H_2O_2 impinger) shall be a Greenburg Smith impinger with the standard tip as described for the second impinger in Method 5, Section 2.1.7. The fourth (empty) impinger and the fifth and sixth (both acidified $KMnO_4$) impingers are the same as the first impinger in Method 5. Place a thermometer capable of measuring to within 1°C (2°F) at the outlet of the last impinger. If no Hg analysis is planned, then the fourth, fifth, and sixth impingers are not used.

3.1.6 Metering System, Barometer, and Gas Density Determination Equipment. Same as Method 5, Sections 2.1.8 through 2.1.10, respectively.

3.1.7 Teflon Tape. For capping openings and sealing connections, if necessary, on the sampling train.

3.2. Sample Recovery. Same as Method 5, Sections 2.2.1 through 2.2.8 (Probe-Liner and Probe-Nozzle Brushes or Swabs, Wash Bottles, Sample Storage Containers, Petri Dishes, Glass Graduated Cylinder, Plastic Storage Containers, Funnel and Rubber Policeman, and Glass Funnel), respectively, with the following exceptions and additions:

3.2.1 Non-metallic Probe-Liner and Probe-Nozzle Brushes or Swabs. Use non-metallic probe-liner and probe-nozzle brushes or swabs for quantitative recovery of materials collected in the front-half of the sampling train.

3.2.2 Sample Storage Containers. Use glass bottles (see the *Precaution:* in Section 4.3.2 of this Method) with Teflon-lined caps that are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml, for storage of acidified $KMnO_4$-containing samples and blanks. Glass or polyethylene bottles may be used for other sample types.

3.2.3 Graduated Cylinder. Glass or equivalent.

3.2.4 Funnel. Glass or equivalent.

3.2.5 Labels. For identifying samples.

3.2.6 Polypropylene Tweezers and/or Plastic Gloves. For recovery of the filter from the sampling train filter holder.

3.3 Sample Preparation and Analysis.

3.3.1 Volumetric Flasks, 100-ml, 250-ml, and 100-ml. For preparation of standards and sample dilutions.

3.3.2 Graduated Cylinders. For preparation of reagents.

3.3.3 Parr[R] Bombs or Microwave Pressure Relief Vessels with Capping Station (CEM Corporation model or equivalent). For sample digestion.

3.3.4 Beakers and Watch Glasses. 250-ml beakers, with watch glass covers, for sample digestion.

3.3.5 Ring Stands and Clamps. For securing equipment such as filtration apparatus.

3.3.6 Filter Funnels. For holding filter paper.

3.3.7 Disposable Pasteur Pipets and Bulbs.

3.3.8 Volumetric Pipets.

3.3.9 Analytical Balance. Accurate to within .01 mg.

3.3.10 Microwave or Conventional Oven. For heating samples at fixed power levels or temperatures, respectively.

3.3.11 Hot Plates.

3.3.12 Atomic Absorption Spectrometer (AAS). Equipped with a background corrector.

3.3.12.1 Graphite Furnace Attachment. With Sb, As, Cd, Co, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7201 (Co), 7421 (Pb), 7740 (Se), and 7841 (Tl) in EPA publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i).

3.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL, an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp shall be capable of raising the temperature at the quartz cell by 10°C above ambient, so that no condensation forms on the wall of the quartz cell. Same as Method 6020 in EPA publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i). See Note No. 2: Section 5.4.3 for other acceptable approaches for analysis of Hg in which analytical detection limits of 0.002 ng/ml were obtained.

3.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in EPA publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i).

3.3.14 Inductively Coupled Plasma-Mass Spectrometer. Same as EPA Method 6020 in EPA publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i).

4. Reagents

4.1 Unless otherwise indicated, it is intended that all reagents conform to the specifications established by the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Otherwise, use the best available grade.

4.2 Sampling Reagents.

4.2.1 Sample Filters. Without organic binders. The filters shall contain less than 1.3 μg/in.^{2} of each of the metals to be measured. Analytical results provided by filter manufacturers stating metals content of the filters are acceptable. However, if no such results are available, analyze filter blanks for each target metal prior to emission testing. Quartz fiber filters meeting these requirements are recommended. However, if glass fiber filters become available which meet these requirements, they may be used. Filter efficiencies and unreactiveness to sulfur dioxide (SO_2) or sulfur trioxide (SO_3) shall be as described in Section 3.1.1 of Method 5.

4.2.2 Water. To conform to ASTM Specification D1193–77, Type II (incorporated by reference—See § 60.17). If necessary, analyze the water for all target metals prior to field use. All target metals should be less than 1 ng/ml.

4.2.3 Nitric Acid (HNO_3). Concentrated. Baker Instra-analyzed or equivalent.

4.2.4 Hydrochloric Acid (HCL). Concentrated. Baker Instra-analyzed or equivalent.

4.2.5 Hydrogen Peroxide (H_2O_2), 30 Percent (V/V).

4.2.6 Potassium Permanganate ($KMnO_4$).

4.2.7 Sulfuric Acid (H_2SO_4). Concentrated.

4.2.8 Silica Gel and Crushed Ice. Same as Method 5, Sections 3.1.2 and 3.1.4, respectively.

4.3 Pretest Preparation of Sampling Reagents.

4.3.1 HNO_3/H_2O_2 Absorbing Solution, 5 Percent HNO_3/10 Percent H_2O_2. Add carefully with stirring 50 ml of concentrated HNO_3 to a 1000-ml volumeric flask containing approximately 500 ml of water, and then add carefully with stirring 333 ml of 30 percent H_2O_2. Dilute to volume with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.3.2 Acidic $KMnO_4$ Absorbing Solution, 4 Percent $KMnO_4$ (W/V), 10 Percent H_2SO_4 (V/V). Prepare fresh daily. Mix carefully, with stirring, 100 ml of concentrated H_2SO_4 into approximately 800 ml of water, and add water with stirring to make a volume of 1 liter: this solution is 10 percent H_2SO_4 (V/V). Dissolve, with stirring, 40 g of $KMnO_4$ into 10 percent H_2SO_4 (V/V) and add 10 percent H_2SO_4 (V/V) with stirring to make a volume of 1 liter. Prepare and store in glass bottles to prevent degradation. This reagent shall contain less than 2 ng/ml of Hg.
Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541

filter paper. Also, due to the potential reaction of the potassium permanganate with the acid, there could be pressure buildup in the solution storage bottle. Therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosion potentials. Venting is required, but not in a manner that will allow contamination of the solution. A No. 70–72 hole drilled in the container cap and Teflon liner has been used.

4.3.3 HNO_3, 0.1 N. Add with stirring 6.3 ml of concentrated HNO_3 (70 percent) to a flask containing approximately 900 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.3.4 HCl, 8 N. Carefully add with stirring 690 ml of concentrated HCl to a flask containing 250 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of Hg.

4.4 Glassware Cleaning Reagents.

4.4.1 HNO_3, Concentrated. Fisher ACS grade or equivalent.

4.4.2 Water. To conform to ASTM Specification D1193–77, Type II (incorporated by reference—See § 60.17).

4.4.3 HNO_3, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO_3 to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.5 Sample Digestion and Analysis Reagents.

The metals standards, except Hg, may also be made from solid chemicals as described in Citation 3 of the Bibliography. Refer to Citations 1, 2, or 5 of the Bibliography for additional information on Hg standards. The 1000 µg/ml Hg stock solution standard may be made according to Section 6.2.5 of Method 101A.

4.5.1 HCL, Concentrated.

4.5.2 Hydrofluoric Acid (HF), Concentrated.

4.5.3 HNO_3, Concentrated. Baker Instra-analyzed or equivalent.

4.5.4 HNO_3, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO_3 to 100 ml of water. Dilute to 250 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.5.5 HNO_3, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO_3 to 800 ml of water. Dilute to 1000 ml with water. Mix well. This reagent shall contain less than 2 ng/ml of each target metal.

4.5.6 Water. To conform to ASTM Specification D1193–77, Type II (incorporated by reference—See § 60.17).

4.5.7 Hydroxylamine Hydrochloride and Sodium Chloride Solution. See Citation 2 of the Bibliography for preparation.

4.5.8 Stannous Chloride. See Citation 2 of the Bibliography for preparation.

4.5.9 $KMnO_4$, 5 Percent (W/V). See Citation 2 of the Bibliography for preparation.

4.5.10 H_2SO_4, Concentrated.

4.5.11 Potassium Persulfate, 5 Percent (W/V). See Citation 2 of the Bibliography for preparation.

4.5.12 Nickel Nitrate, Ni $(NO_3)_2$ $6H_2O$.

4.5.13 Lanthanum Oxide, La_2O_3.

4.5.14 Hg Standard (AAS Grade), 1000 µg/ml.

4.5.15 Pb Standard (AAS Grade), 1000 µg/ml.

4.5.16 As Standard (AAS Grade), 1000 µg/ml.

4.5.17 Cd Standard (AAS Grade), 1000 µg/ml.

4.5.18 Cr Standard (AAS Grade), 1000 µg/ml.

4.5.19 Sb Standard (AAS Grade), 1000 µg/ml.

4.5.20 Ba Standard (AAS Grade), 1000 µg/ml.

4.5.21 Be Standard (AAS Grade), 1000 µg/ml.

4.5.22 Co Standard (AAS Grade), 1000 µg/ml.

4.5.23 Cu Standard (AAS Grade), 1000 µg/ml.

4.5.24 Mn Standard (AAS Grade), 1000 µg/ml.

4.5.25 Ni Standard (AAS Grade), 1000 µg/ml.

4.5.26 P Standard (AAS Grade), 1000 µg/ml.

4.5.27 Se Standard (AAS Grade), 1000 µg/ml.

4.5.28 Ag Standard (AAS Grade), 1000 µg/ml.

4.5.29 Tl Standard (AAS Grade), 1000 µg/ml.

4.5.30 Zn Standard (AAS Grade), 1000 µg/ml.

4.5.31 Al Standard (AAS Grade), 1000 µg/ml.

4.5.32 Fe Standard (AAS Grade), 1000 µg/ml.

4.5.33 Hg Standards and Quality Control Samples. Prepare fresh weekly a 10 µg/ml intermediate Hg standard by adding 5 ml of 1000 µg/ml Hg stock solution prepared according to Method 101A to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working Hg standard solution fresh daily: add 5 ml of the 10 µg/ml intermediate standard to a 250-ml volumetric flask, and dilute to 250 ml with 5 ml of 4 percent $KMnO_4$, 5 ml of 15 percent HNO_3, and then water. Mix well. Use at least five separate aliquots of the working Hg standard solution and a blank to prepare the standard curve. These aliquots and blank shall contain 0.0, 1.0, 2.0, 3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng Hg, respectively. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until in the calibration range.

4.5.34 ICAP Standards and Quality Control Samples. Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn.
II	Ba, Co, Cu, Fe.
III	Al, Cr, Ni.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS—Continued

Solution	Elements
IV	Ag, P, Sb, Tl.

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO_3. A minimum of one standard and a blank can be used to form each calibration curve. However, prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve. Suggested standard levels are 25 µg/ml for Al, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks. For ICP–MS, follow Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i).

4.5.35 GFAAS Standards. Sb, As, Cd, Co, Pb, Se, and Tl. Prepare a 10 µg/ml standard by adding 1 ml of 1000 µg/ml standard to a 100-ml volumetric flask. Dilute with stirring to 100 ml with 10 percent HNO_3. For GFAAS, matrix match the standards. Prepare a 100 ng/ml standard by adding 1 ml of the 10 µg/ml standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Prepare other standards by diluting the 100 ng/ml standards. Use at least five standards to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Prepare quality control samples by making a separate 10 µg/ml standard and diluting until it is in the range of the samples. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.5.36 Matrix Modifiers.

4.5.36.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of Ni $(NO_3)_2 \bullet 6H_2O$ or other nickel compound suitable for preparation of this matrix modifier in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

4.5.36.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of 1 percent nickel nitrate solution to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

4.5.36.3 Lanthanum. Carefully dissolve 0.5864 g of La_2O_3 in 10 ml of concentrated HNO_3, and dilute the solution by adding it with stirring to approximately 50 ml of water. Dilute to 100 ml with water, and mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

4.5.37 Whatman 40 and 541 Filter Papers (or equivalent). For filtration of digested samples.

5. Procedure

5.1 Sampling. The complexity of this method is such that, to obtain reliable results,

both testers and analysts must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment and procedures; analytical calculations; reporting; and the specific procedural descriptions throughout this method.

5.1.1 Pretest Preparation. Follow the same general procedure given in Method 5, Section 4.1.1, except that, unless particulate emissions are to be determined, the filter need not be desiccated or weighed. First, rinse all sampling train glassware with hot tap water and then wash in hot soapy water. Next, rinse glassware three times with tap water, followed by three additional rinses with water. Then soak all glassware in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinse three times with water, rinse a final time with acetone, and allow to air dry. Cover all glassware openings where contamination can occur until the sampling train is assembled for sampling.

5.1.2 Preliminary Determinations. Same as Method 5, Section 4.1.2.

5.1.3 Preparation of Sampling Train.

5.1.3.1 Set up the sampling train as shown in Figure 29–1. Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the HNO_3/H_2O_2 solution (Section 4.3.1. of this method) in each of the second and third impingers as shown in Figure 29–1. Placee 100 ml of the acidic $KMnO_4$ absorbing solution (Section 4.3.2 of this method) in each of the fifth and sixth impingers as shown in Figure 29–1, and transfer approximately 200 to 300 g of pre-weighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to final train assembly.

5.1.3.2 Based on the specific source sampling conditions, the use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml.

5.1.3.3 If Hg analysis will not be performed, the fourth, fifth, and sixth impingers as shown in Figure 29–1 are not required.

5.1.3.4 To insure leak-free sampling train connections and to prevent possible sample contamination problems, use Teflon tape or other non-contaminating material instead of silicone grease.

Precaution: Exercise extreme care to prevent contamination within the train. Prevent the acidic $KMnO_4$ from contacting any glassware that contains sample material to be analyzed for Mn. Prevent acidic H_2O_2 from mixing with the acidic $KMnO_4$.

5.1.4 Leak-Check Procedures. Follow the leak-check procedures given in Method 5, Section 4.1.4.1 (Pretest Leak-Check), Section 4.1.4.2 (Leak-Checks During the Sample Run), and Section 4.1.4.3 (Post-Test Leak-Checks).

5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. When sampling for Hg, use a procedure analagous to that described in Section 7.1.1 of Method 101A, 40 CFR Part 61, Appendix B, if necessary to maintain the desired color in the last acidified permanganate impinger. For each run, record the data required on a data sheet such as the one shown in Figure 5–2 of Method 5.

5.1.6 Calculation of Percent Isokinetic. Same as Method 5, Section 4.1.6.

5.2 Sample Recovery.

5.2.1 Begin cleanup procedures as soon as the probe is removed from the stack at the end of a sampling period. The probe should be allowed to cool prior to sample recovery. When it can be safely handled, wipe off all external particulate matter near the tip of the probe nozzle and place a rinsed, non-contaminating cap over the probe nozzle to prevent losing or gaining particulate matter. Do not cap the probe tip tightly while the sampling train is cooling; a vacuum can form in the filter holder with the undesired result of drawing liquid from the impingers onto the filter.

5.2.2 Before moving the sampling train to the cleanup site, remove the probe from the sampling train and cap the open outlet. Be careful not to lose any condensate that might be present. Cap the filter inlet where the probe was fastened. Remove the umbilical cord from the last impinger and cap the impinger. Cap the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

5.2.3 Alternatively, the following procedure may be used to disassemble the train before the probe and filter holder/oven are completely cooled: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

5.2.4 Transfer the probe and filter-impinger assembly to a cleanup area that is clean and protected from the wind and other potential causes of contamination or loss of sample. Inspect the train before and during disassembly and note any abnormal conditions. Take special precautions to assure that all the items necessary for recovery do not contaminate the samples. The sample is recovered and treated as follows (see schematic in Figures 29–2a and 29–2b):

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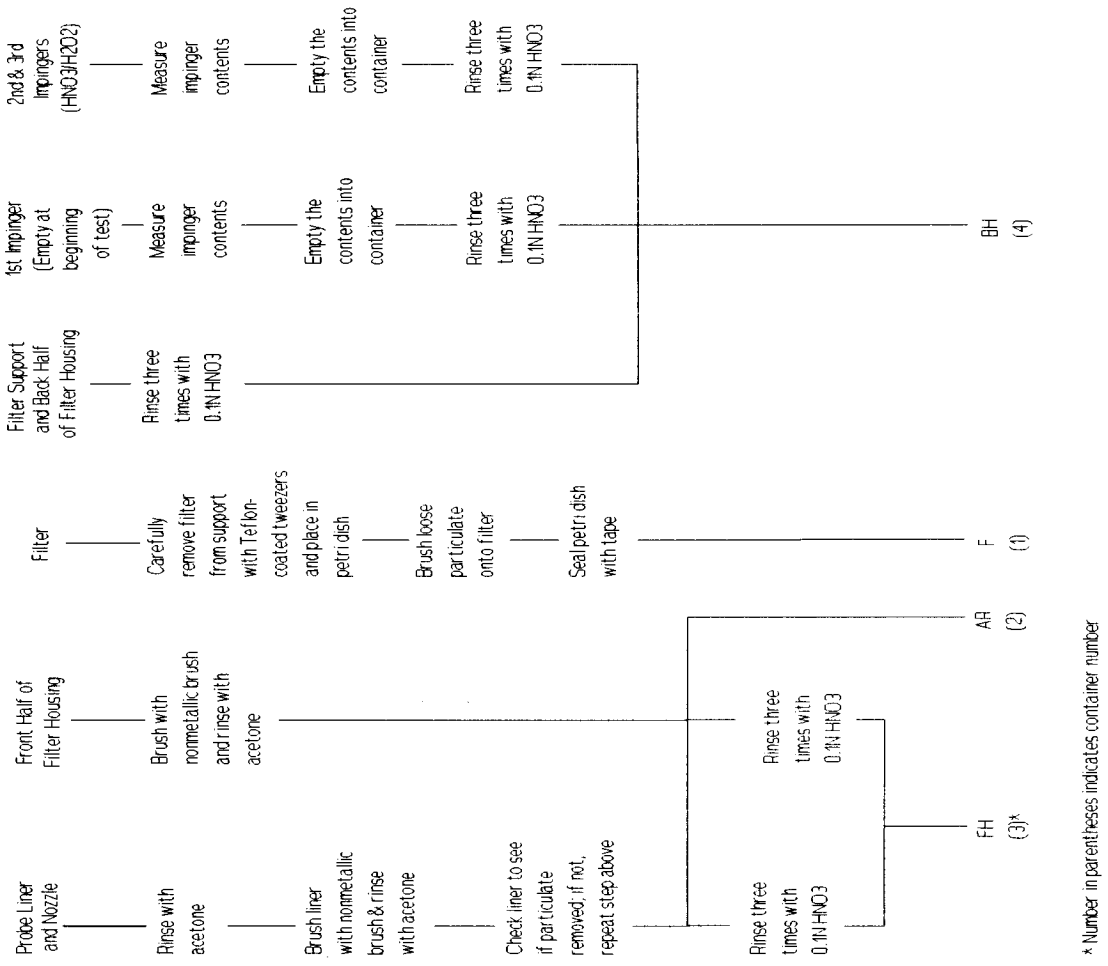

Figure 29-2a. Sample recovery scheme.

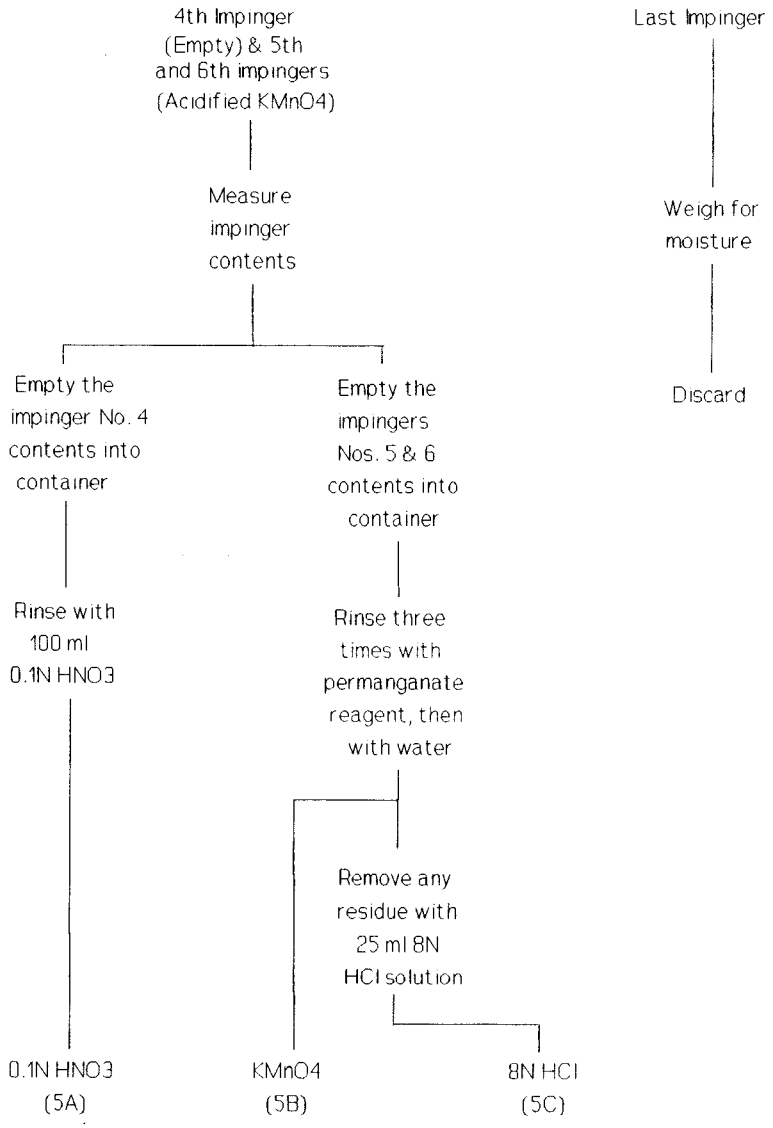

Figure 29-2b. Sample recovery scheme.

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5.2.5 Container No. 1 (Sample Filter). Carefully remove the filter from the filter holder and place it in its labeled petri dish container. To handle the filter, use either acid-washed polypropylene or Teflon coated tweezers or clean, disposable surgical gloves rinsed with water and dried. If it is necessary to fold the filter, make certain the particulate cake is inside the fold. Carefully transfer the filter and any particulate matter or filter fibers that adhere to the filter holder gasket to the petri dish by using a dry (acid-cleaned) nylon bristle brush. Do not use any metal-containing materials when recovering this train. Seal the labeled petri dish.

5.2.6 Container No. 2. (Acetone Rinse). Perform this procedure only if a determination of particulate emissions is to be made. Quantitatively recover particulate matter and any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with a total of 100 ml of acetone, while simultaneously taking great care to see that no dust on the outside of the probe or other surfaces gets in the sample. The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

5.2.6.1 Carefully remove the probe nozzle, and clean the inside surface by rinsing with acetone from a wash bottle while brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, then make a final rinse of the inside surface with acetone.

5.2.6.2 Brush and rinse the sample exposed inside parts of the probe fitting with acetone in a similar way until no visible particles remain. Rinse the probe liner with acetone by tilting and rotating the probe while squirting acetone into its upper end so that all inside surfaces will be wetted with acetone. Allow the acetone to drain from the lower end into the sample container. A funnel may be used to aid in transferring liquid washings to the container. Follow the acetone rinse with a non-metallic probe brush. Hold the probe in an inclined position, squirt acetone into the upper end as the probe brush is being pushed with a twisting action three times through the probe. Hold a sample container underneath the lower end of the probe, and catch any acetone and particulate matter which is brushed through the probe until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

5.2.6.3 It is recommended that two people clean the probe to minimize sample losses. Between sampling runs, keep brushes clean and protected from contamination. Clean the inside of the front-half of the filter holder by rubbing the surfaces with a non-metallic brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid so that acetone will not leak out when shipped to the laboratory. Mark the height of the fluid level to determine whether or not leakage occurred during transport. Clearly label the container to identify its contents.

5.2.7 Container No. 3 (Probe Rinse). Keep the probe assembly clean and free from contamination during the probe rinse. Rinse the probe nozzle and fitting, probe liner, and front-half of the filter holder thoroughly with a total of 100 ml of 0.1 N HNO_3, and place the wash into a sample storage container.

(Note: The use of a total of exactly 100 ml is necessary for the subsequent blank correction procedures.)

Perform the rinses as applicable and generally as described in Method 12, Section 5.2.2. Record the volume of the rinses. Mark the height of the fluid level on the outside of the storage container and use this mark to determine if leakage occurs during transport. Seal the container, and clearly label the contents. Finally, rinse the nozzle, probe liner, and front-half of the filter holder with water followed by acetone, and discard these rinses.

5.2.8 Container No. 4 (Impingers 1 through 3, Moisture Knockout Impinger, when used, HNO_3/H_2O_2 Impingers Contents and Rinses). Due to the potentially large quantity of liquid involved, the tester may place the impinger solutions from impingers 1 through 3 in more than one container, if necessary. Measure the liquid in the first three impingers to within 0.5 ml using a graduated cylinder. Record the volume. This information is required to calculate the moisture content of the sampled flue gas. Clean each of the first three impingers, the filter support, the back half of the filter housing, and connecting glassware by thoroughly rinsing with 100 ml of 0.1 N HNO_3 using the procedure as applicable in Method 12, Section 5.2.4.

(Note: The use of exactly 100 ml of 0.1 N HNO_3 rinse is necessary for the subsequent blank correction procedures. Combine the rinses and impinger solutions, measure and record the final total volume. Mark the height of the fluid level, seal the container, and clearly label the contents.)

5.2.9 Container Nos. 5A (0.1 N HNO_3), *5B* ($KMnO_4/H_2SO_4$ absorbing solution), and 5C (8 N HCl rinse and dilution).

5.2.9.1 When sampling for Hg, pour all the liquid from the impinger (normally impinger No. 4) that immediately preceded the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place the liquid in Container No. 5A. Rinse the impinger with exactly 100 ml of 0.1 N HNO_3 and place this rinse in Container No. 5A.

5.2.9.2 Pour all the liquid from the two permanganate impingers into a graduated cylinder and measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Place this acidic $KMnO_4$ solution into Container No. 5B. Using a total of exactly 100 ml of fresh acidified $KMnO_4$ solution for all rinses (approximately 33 ml per rinse), rinse the two permanganate impingers and connecting glassware a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. Similarly, using 100 ml total of water, rinse the permanganate impingers and connecting glass a minimum of three times, and pour the rinses into Container 5B, carefully assuring transfer of any loose precipitated material. Mark the height of the fluid level, and clearly label the contents. Read the Precaution: in Section 4.3.2. *NOTE:* Due to the potential reaction of $KMnO_4$ with acid, pressure buildup can occur in the sample storage bottles. Do not fill these bottles completely and take precautions to relieve excess pressure. A No. 70–72 hole drilled in the container cap and Teflon liner has been used successfully.

5.2.9.3 If no visible deposits remain after the water rinse, no further rinse is necessary. However, if deposits remain on the impinger surfaces, wash them with 25 ml of 8 N HCl, and place the wash in a separate sample container labeled No. 5C containing 200 ml of water. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HC1 contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport.

5.2.10 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal it. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that might adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

5.2.11 Container No. 7 (Acetone Blank). If particulate emissions are to be determined, at least once during each field test, place a 100-ml portion of the acetone used in the sample recovery process into a container labeled No. 7. Seal the container.

5.2.12 Container No. 8A (0.1 N HNO_3 Blank). At least once during each field test, place 300 ml of the 0.1 N HNO_3 solution used in the sample recovery process into a container labeled No. 8A. Seal the container.

5.2.13 Container No. 8B (Water Blank). At least once during each field test, place 100 ml of the water used in the sample recovery process into a container labeled No. 8B. Seal the container.

5.2.14 Container No. 9 (5 Percent HNO_3/10 Percent H_2O_2 Blank). At least once during each field test, place 200 ml of the 5 Percent HNO_3/10 Percent H_2O_2 solution used as the nitric acid impinger reagent into a container labeled No. 9. Seal the container.

5.2.15 Container No. 10 (Acidified $KMnO_4$ Blank). At least once during each field test, place 100 ml of the acidified $KMnO_4$ solution used as the impinger solution and in the sample recovery process into a container labeled No. 10. Prepare the container as described in Section 5.2.9.2. Read the *Precaution:* in Section 4.3.2. and read the Note in Section 5.2.9.2.

5.2.16 Container No. 11 (8 N HCl Blank). At least once during each field test, place 200 ml of water into a sample container labeled No. 11. Then carefully add with stirring 25 ml of 8 N HCl. Mix well and seal the container.

5.2.17 Container No. 12 (Sample Filter Blank). Once during each field test, place into a petri dish labeled No. 12 three unused blank filters from the same lot as the sampling filters. Seal the petri dish.

5.3 *Sample Preparation.* Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 29–3.

5.3.1 *Container No. 1 (Sample Filter).*

5.3.1.1 If particulate emissions are being determined, first desiccate the filter and filter catch without added heat (do not heat the filters to speed the drying) and weigh to a constant weight as described in Section 4.3 of Method 5.

5.3.1.2 Following this procedure, or initially, if particulate emissions are not being determined in addition to metals analysis, divide the filter with its filter catch into portions containing approximately 0.5 g each. Place the pieces in the analyst's choice of either individual microwave pressure relief vessels or Parr^R Bombs. Add 6 ml of concentrated HNO_3 and 4 ml of concentrated HF to each vessel. For microwave heating, microwave the samples for approximately 12 to 15 minutes total heating time as follows: heat for 2 to 3 minutes, then turn off the microwave for 2 to 3 minutes, then heat for 2 to 3 minutes, etc., continue this alternation until the 12 to 15 minutes total heating time are completed (this procedure should comprise approximately 24 to 30 minutes at 600 watts). Microwave heating times are approximate and are dependent upon the number of samples being digested simultaneously. Sufficient heating is evidenced by sorbent reflux within the vessel. For conventional heating, heat the Parr^R Bombs at 140 °C (285 °F) for 6 hours. Then cool the samples to room temperature, and combine with the acid digested probe rinse as required in Section 5.3.3.

5.3.1.3 If the sampling train includes an optional glass cyclone in front of the filter, prepare and digest the cyclone catch by the procedures described in section 5.3.1.2 and then combine the digestate with the digested filter sample.

5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for 24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3.

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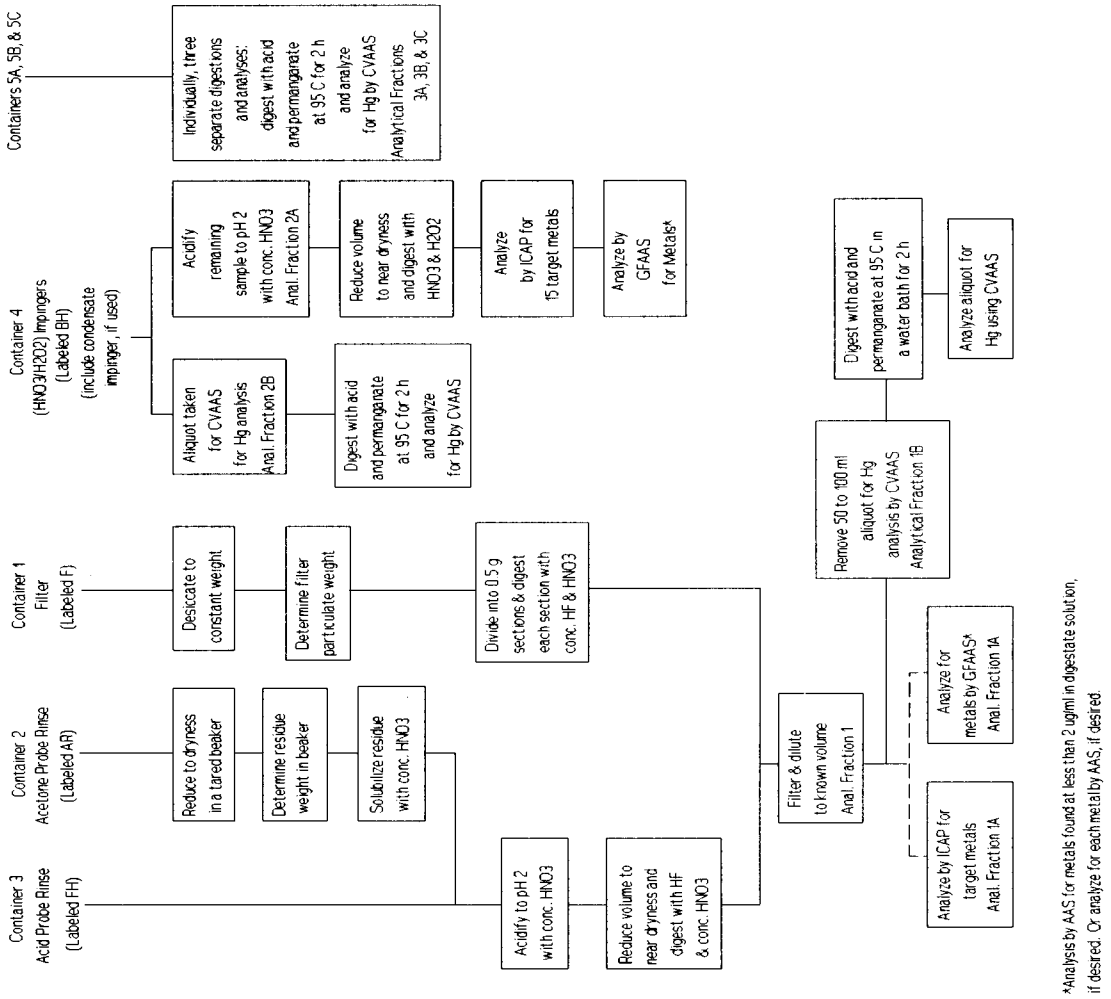

Figure 29-3. Sample preparation and analysis scheme.

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Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). Verify that the pH of this sample is 2 or lower. If it is not, acidify the sample by careful addition with stirring of concentrated HNO_3 to pH 2. Use water to rinse the sample into a beaker, and cover the beaker with a ribbed watch glass. Reduce the sample volume to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr[R] Bombs by quantitatively transferring the sample to the vessel or bomb, carefully adding the 6 ml of concentrated HNO_3, 4 ml of concentrated HF, and then continuing to follow the procedures described in Section 5.3.1.2. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1.2. The resultant combined sample is referred to as *''Sample Fraction 1''*. Filter the combined sample using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This diluted sample is *''Analytical Fraction 1''*. Measure and record the volume of Analytical Fraction 1 to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label as *''Analytical Fraction 1B''*. Label the remaining 250-ml portion as *''Analytical Fraction 1A''*. Analytical Fraction 1A is used for ICAP or AAS analysis for all desired metals except Hg. Analytical Fraction 1B is used for the determination of front-half Hg.

5.3.4 Container No. 4 (Impingers 1–3). Measure and record the total volume of this sample to within 0.5 ml and label it *''Sample Fraction 2''*. Remove a 75- to 100-ml aliquot for Hg analysis and label the aliquot *''Analytical Fraction 2B''*. Label the remaining portion of Container No. 4 as *''Sample Fraction 2A''*. Sample Fraction 2A defines the volume of Analytical Fraction 2A *prior* to digestion. All of Sample Fraction 2A is digested to produce *''Analytical Fraction 2A''*. Analytical Fraction 2A defines the volume of Sample Fraction 2A *after* its digestion and the volume of Analytical Fraction 2A is normally 150 ml. Analytical Fraction 2A is analyzed for all metals except Hg. Verify that the pH of Sample Fraction 2A is 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower Sample Fraction 2A to pH 2. Use water to rinse Sample Fraction 2A into a beaker and then cover the beaker with a ribbed watch glass. Reduce Sample Fraction 2A to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 5.3.4.1 or 5.3.4.2.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent HNO_3, and heat for 30 minutes on a hot plate to just below boiling. Add 10 ml of 3 percent H_2O_2 and heat for 10 more minutes. Add 50 ml of hot water, and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

5.3.4.2 Microwave Digestion Procedure. Add 10 ml of 50 percent HNO_3 and heat for 6 minutes total *heating* time in alternations of 1 to 2 minutes at 600 Watts followed by 1 to 2 minutes with no power, etc., similar to the procedure described in Section 5.3.1. Allow the sample to cool. Add 10 ml of 3 percent H_2O_2 and heat for 2 more minutes. Add 50 ml of hot water, and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 ml (or the appropriate volume for the expected metals concentrations) with water. This dilution produces Analytical Fraction 2A. Measure and record the volume to within 0.1 ml.

(Note: All microwave heating times given are approximate and are dependent upon the number of samples being digested at a time. Heating times as given above have been found acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by solvent reflux within the vessel.)

5.3.5 Container No. 5A (Impinger 4), Container Nos. 5B and 5C (Impingers 5 and 6). Keep the samples in Containers Nos. 5A, 5B, and 5C separate from each other. Measure and record the volume of 5A to within 0.5 ml. Label the contents of Container No. 5A to be Analytical Fraction 3A. To remove any brown MnO_2 precipitate from the contents of Container No. 5B, filter its contents through Whatman 40 filter paper into a 500 ml volumetric flask and dilute to volume with water. Save the filter for digestion of the brown MnO_2 precipitate. Label the 500 ml filtrate from Container No. 5B to be Analytical Fraction 3B. Analyze Analytical Fraction 3B for Hg within 48 hours of the filtration step. Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriately sized *vented* container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container No. 5C through a Whatman 40 filter into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 5B through a Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the Whatman 40 filter. Mark this combined 500-ml dilute HCl solution as Analytical Fraction 3C.

5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance.

5.4 Sample Analysis. For each sampling train sample run, seven individual analytical samples are generated; two for all desired metals except Hg, and five for Hg. A schematic identifying each sample container and the prescribed analytical preparation and analysis scheme is shown in Figure 29–3. The first two analytical samples, labeled Analytical Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Analytical Fraction 1A is for ICAP, ICP–MS or AAS analysis as described in Sections 5.4.1 and 5.4.2, respectively. Analytical Fraction 1B is for front-half Hg analysis as described in Section 5.4.3. The contents of the back-half of the train are used to prepare the third through seventh analytical samples. The third and fourth analytical samples, labeled Analytical Fractions 2A and 2B, contain the samples from the moisture removal impinger No. 1, if used, and $HNO_3H_2O_2$ impingers Nos. 2 and 3. Analytical Fraction 2A is for ICAP, ICP–MS or AAS analysis for target metals, except Hg. Analytical Fraction 2B is for analysis for Hg. The fifth through seventh analytical samples, labeled Analytical Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty impinger No. 4 and the $H_2SO_4/KMnO_4$ Impingers Nos. 5 and 6. These analytical samples are for analysis for Hg as described in Section 5.4.3. The total back-half Hg catch is determined from the sum of Analytical Fractions 2B, 3A, 3B, and 3C. Analytical Fractions 1A and 2A can be combined proportionally prior to analysis.

5.4.1 ICAP and ICP–MS Analysis. Analyze Analytical Fractions 1A and 2A by ICAP using Method 6010 or Method 200.7 (40 CFR part 136, appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in Section 7.3.1. Recommended wavelengths for analysis are as follows:

Element	Wavelength (nm)
Aluminum	308.215
Antimony	206.833
Arsenic	193.696
Barium	455.403
Beryllium	313.042
Cadmium	226.502
Chromium	267.716
Cobalt	228.616
Copper	324.754
Iron	259.940
Lead	220.353
Manganese	257.610
Nickel	231.604
Phosphorous	214.914
Selenium	196.026
Silver	328.068
Thallium	190.864
Zinc	213.856

These wavelengths represent the best combination of specificity and potential detection limit. Other wavelengths may be substituted if they can provide the needed specificity and detection limit, and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the target metals (except Hg) plus Fe and Al. If Fe and Al are present, the sample might have to be diluted so that each of these elements is at a concentration of less than 50 ppm so as to reduce their spectral interferences on As, Cd, Cr, and Pb. Perform ICP–MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA, and IIB, as incorporated by reference in § 60.17(i).

(Note: When analyzing samples in a HF matrix, an alumina torch should be used;

since all front-half samples will contain HF, use an alumina torch.)

5.4.2. AAS by Direct Aspiration and/or GFAAS. If analysis of metals in Analytical Fractions 1A and 2A by using GFAAS or direct aspiration AAS is needed, use Table 29–2 to determine which techniques and procedures to apply for each target metal. Use Table 29–2, if necessary, to determine techniques for minimization of interferences. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

TABLE 29–2.—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS

Metal	Technique	SW–846 [1] method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination.
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required.
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 ul of phosphorus acid to 1 ml of prepared sample in sampler cup.
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required.
Ni	Aspiration	7520	232.0	352.4 nm alternate Fe, Co, and Cr.	Background correction required. Matrix matching or nitrous-oxide/acetylene flame.
				Nonlinear response	sample dilution or use 352.3 nm line.
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization.
				Adsorption & scatter	Background correction is required and Zeeman background correction can be useful.
Ag	Aspiration	7760	328.1	Adsorption & Scatter AgCl insoluble.	Background correction is required. Avoid Hydrochloric acid unless silver is in solution as a chloride complex Sample and standards monitored for aspiration rate.
Tl	Aspiration	7840	276.8		Background correction is required. Hydrochloric acid should not be used.
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required. Verify that losses are not occurring for volatization by spiked samples or standard addition; Palladium is a suitable matrix modifier.
Zn	Aspiration	7950	213.9	High Si, Cu, & P Contamination	Strontium removes Cu and phosphate, Great care taken to avoid contamination.
Sb	Aspiration	7040	217.6	1000 mg/ml Pb Ni, Cu, or acid	Use secondary wavelengths of 231.1.nm; match sample & standards acid concentration or use nitrous oxidefacetylene flame.
Sb	Furnace	7041	217.6	High Pb	Secondary Wavelength or Zeeman correction.
As	Furnace	7060	193.7	Arsenic volatilization Aluminum	Spiked samples and add nickel nitrate solution to digestates prior to analysis. Use Zeeman background correction.
Ba	Aspiration 7080	7080	553.6	Calcium Barium ionization	High hollow cathode current and narrow band set. 2 ml of KCl per 100 ml of sample.
Be	Aspiration	7090	234.9	500 ppm Al High Mg and Si	Add 0.1% fluoride. Use method of standard additions.
Be	Furnace	7091	234.9	Be in optical path	Optimize parameters to minimize effects.
Cd	Aspiration	7130	228.8	Absorption and light scattering	Background correction is required.

TABLE 29–2.—APPLICABLE TECHNIQUES, METHODS AND MINIMIZATION OF INTERFERENCE FOR AAS ANALYSIS—Continued

Metal	Technique	SW–846 [1] method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Cd	Furnace	7131	228.8	As above ..... Excess Chloride ..... Pipet tips	As above. Ammonium phosphate used as a matrix modifier. Use cadmiun-free tips.
Cr	Aspiration	7190	357.9	Akali metal	KCl ionization suppressant in samples and standards—Consult mfgs literature.
Co	Furnace	7201	240.7	Excess chloride	Use Method of Standard Additions.
Cr	Furnace	7191	357.9	200 mg/L Ca and P	All calcium nitrate for a known constant effect and to eliminate effect of phosphate.
Cu	Aspiration	7210	324.7	Absorption & scatter	Consult manufacturer's manual.

[1] Refer to EPA publication SW–846 Third Edition (November 1986) including updates I, II, IIA, and IIB, as incorporated by reference in § 60.17(i).

5.4.3 CVAAS Hg analysis. Analyze Analytical Fractions 1B, 2B, 3A, 3B, and 3C separately for Hg using CVAAS following the method outlined in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i) or in *Standard Methods for the Examination of Water and Wastewater,* 16th Edition, (1985), Method 303F, as incorporated by reference in § 60.17, or, optionally using *NOTE No. 2* in this section. Set up the calibration curve (zero to 1000 ng) as described in Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see *NOTE No. 1* in this Section). The total amount of Hg in the aliquot shall be less than 1 µg and within the range (zero to 1000 ng) of the calibration curve. Place the sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of Method 7470 or Method 303F. (See *NOTE No. 2* in this Section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent HNO_3 (1.5 ml concentrated HNO_3 per liter aqueous solution) so that when a 1- to 10-ml aliquot of the ''0.15 HNO_3 percent dilution of the original sample'' is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

Note No. 1 to Section 5.4.3. When Hg levels in the sample fractions are below the in-stack detection limit given in Table 29–1, select a 10 ml aliquot for digestion and analysis as described.

Note No. 2 to Section 5.4.3. Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer FIAS systems, and similar models, if available, of other instrument manufacturers. For digestion and analyses by these instruments, perform the following two steps:

(1) Digest the sample aliquot through the addition of the aqueous hydroxylamine hydrochloride/sodium chloride solution the same as described in this Section 5.4.3.: (*The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.)* and

(2) Upon completion of the digestion described in paragraph (1), of this note, analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

6. Calibration

Maintain a laboratory log of all calibrations.

6.1 Sampling Train Calibration. Calibrate the sampling train components according to the indicated sections of Method 5: Probe Nozzle (Section 5.1); Pitot Tube (Section 5.2); Metering System (Section 5.3); Probe Heater (Section 5.4); Temperature Gauges (Section 5.5); Leake-Check of the Metering System (Section 5.6); and Barometer (Section 5.7).

6.2 Industively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using those standards. Check the calibration once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, perform the complete calibration procedures. Perform ICP–MS analysis by following Method 6020 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i).

6.3 Atomic Absorption Spectrometer—Direct Aspiration AAS, GFAAS, and CVAAS analyses. Prepare the standards as outlined in Section 4.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29–2 and in Method 7470 in EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i) or in *Standard Methods for the Examination of Water and Wastewater,* 16th Edition, (1985), Method 303F (for Hg) as incorporated by reference in § 60.17. Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

7. Quality Control

7.1 Field Reagent Blanks, if analyzed. Perform the digestion and analysis of the blanks in Container Nos. 7 through 12 that were produced in Sections 5.2.11 through 5.2.17, respectively. For Hg field reagent blanks, use a 10 ml aliquot for digestion and analysis.

7.1.1 Digest and analyze one of the filters from Container No. 12 per Section 5.3.1, 100 ml from Container No. 7 per Section 5.3.2, and 100 ml from Container No. 8A per Section 5.3.3. This step produces blanks for Analytical Fractions 1A and 1B.

7.1.2 Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and analyze the resultant volume per Section 5.3.4. This step produces blanks for Analytical Fractions 2A and 2B.

7.1.3 Digest and analyze a 100-ml portion of Container No. 8A to produce a blank for Analytical Fraction 3A.

7.1.4 Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B to produce a blank for Analytical Fraction 3B. Filter the resultant 133 ml as described for Container No. 5B in Section 5.3.5, except do not dilute the 133ml. Analyze this blank for Hg within 48 hrs. of the filtration step, and use 400 ml as the blank volume when calculating the blank mass value. Use the

actual volumes of the other analytical blanks when calculating their mass values.

7.1.5 Digest the filter that was used to remove any brown MnO_2 precipitate from the blank for Analytical Fraction 3B by the same procedure as described in Section 5.3.5 for the similar sample filter. Filter the digestate and the contents of Container No. 11 through Whatman 40 paper into a 500-ml volumetric flask, and dilute to volume with water. These steps produce a blank for Analytical Fraction 3C.

7.1.6 Analyze the blanks for Analytical Fraction Blanks 1A and 2A per Section 5.4.1 and/or Section 5.4.2. Analyze the blanks for Analytical Fractions 1B, 2B, 3A, 3B, and 3C per Section 5.4.3. Analysis of the blank for Analytical Fraction 1A produces the front-half reagent blank correction values for the desired metals except for Hg; Analysis of the blank for Analytical Fraction 1B produces the front-half reagent blank correction value for Hg. Analysis of the blank for Analytical Fraction 2A produces the back-half reagent blank correction values for all of the desired metals except for Hg, while separate analyses of the blanks for Analytical Fractions 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for Hg.

7.2 Quality Control Samples. Analyze the following quality control samples.

7.2.1 ICAP and ICP–MS Analysis. Follow the respective quality control descriptions in Section 8 of Methods 6010 and 6020 of EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i). For the purposes of a source test that consists of three sample runs, modify those requirements to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (analyze by Method of Standard Additions unless within 25 percent), one quality control sample to check the accuracy of the calibration standards (required to be within 25 percent of calibration), and one duplicate analysis (required to be within 20 percent of average or repeat all analyses).

7.2.2. Direct Aspiration AAS and/or GFAAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Co, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. Analyze all samples in duplicate. Perform a matrix spike on at least one front-half sample and one back-half sample, or one combined sample. If recoveries of less than 75 percent or greater than 125 percent are obtained for the matrix spike, analyze each sample by the Method of Standard Additions. Analyze a quality control sample to check the accuracy of the calibration standards. If the results are not within 20 percent, repeat the calibration.

7.2.3 CVAAS Analysis for Hg. Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (if not within 15 percent, repeat calibration). Perform a matrix spike on one sample (if not within 25 percent, analyze all samples by the Method of Standard Additions). Additional information on quality control can be obtained from Method 7470 of EPA Publication SW–846 Third Edition (November 1986) including updates I, II, IIA and IIB, as incorporated by reference in § 60.17(i) or in *Standard Methods for the Examination of Water and Wastewater*, 16th Edition, (1985), Method 303F as incorporated by reference in § 60.17.

8. Calculations

8.1 Dry Gas Volume. Using the data from this test, calculate $V_{m(std)}$, the dry gas sample volume at standard conditions as outlined in Section 6.3 of Method 5.

8.2 Volume of Water Vapor and Moisture Content. Using the total volume of condensate collected during the source sampling, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5–2 and 5–3 of Method 5.

8.3 Stack Gas Velocity. Using the data from this test and Equation 2–9 of Method 2, calculate the average stack gas velocity.

8.4 Metals (Except Hg) in Source Sample.

8.4.1 Analytical Fraction 1A, Front-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Sample Fraction 1 of the sampling train using the following equation:

$$M_{fh}=C_{a1}\,F_d\,V_{soln,1} \qquad \text{Eq. 29–1}$$

where:

M_{fh}=Total mass of each metal (except Hg) collected in the front half of the sampling train (Sample Fraction 1), µg.

C_{a1}=Concentration of metal in Analytical Fraction 1A as read from the standard curve, µg/ml.

F_d=Dilution factor (F_d = the inverse of the fractional portion of the concentrated sample in the solution actually used in the instrument to produce the reading C_{a1}. For example, if a 2 ml aliquot of Analytical Fraction 1A is diluted to 10 ml to place it in the calibration range, F_d = 5).

$V_{soln,1}$=Total volume of digested sample solution (Analytical Fraction 1), ml.

8.4.1.1 If Analytical Fractions 1A and 2A are combined, use proportional aliquots. Then make appropriate changes in Equations 29–1 through 29–3 to reflect this approach.

8.4.2 Analytical Fraction 2A, Back-Half, Metals (except Hg). Calculate separately the amount of each metal collected in Fraction 2 of the sampling train using the following equation.

$$M_{bh}=C_{a2}\,F_a\,V_a \qquad \text{Eq. 29–2}$$

where:

M_{bh}=Total mass of each metal (except Hg) collected in the back-half of the sampling train (Sample Fraction 2), µg.

C_{a2}=Concentration of metal in Analytical Fraction 2A as read from the standard curve, (µg/ml).

F_a=Aliquot factor, volume of Sample Fraction 2 divided by volume of Sample Fraction 2A (*see Section 5.3.4.*)

V_a=Total volume of digested sample solution (Analytical Fraction 2A), ml (see Section 5.3.4.1 or 5.3.4.2, as applicable).

8.4.3 Total Train, Metals (except Hg). Calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t=(M_{fh}-M_{fhb})+(M_{bh}-M_{bhb}) \qquad \text{Eq. 29–3}$$

where:

M_t=Total mass of each metal (separately stated for each metal) collected in the sampling train, µg.

M_{fhb}=Blank correction value for mass of metal detected in front-half field reagent blank, µg.

M_{bhb}=Blank correction value for mass of metal detected in back-half field reagent blank, µg.

8.4.3.1 If the measured blank value for the front half (M_{fhb}) is in the range 0.0 to ''A'' µg [where ''A'' µg equals the value determined by multiplying 1.4 µg/in.^{2} times the actual area in in.^{2} of the sample filter], use M_{fhb} to correct the emission sample value (M_{fh}); if M_{fhb} exceeds ''A'' µg, use the greater of I or II:

I. ''A'' µg.

II. the lesser of (a) M_{fhb}, or (b) 5 percent of M_{fh}.

If the measured blank value for the black-half (M_{bhb}) is in the range 0.0 to 1 µg, use M_{bhb} to correct the emission sample value (M_{bh}); if M_{bhb}) exceeds 1 µg, use the greater of I or II:

I. 1 µg.

II. the lesser of (a) M_{bhb} or (b) 5 percent of M_{bh}.

8.5 Hg in Source Sample.

8.5.1 Analytical Fraction 1B; Front-Half Hg. Calculate the amount of Hg collected in the front-half, Sample Fraction 1, of the sampling train by using Equation 29–4:

$$Hg_{fh}=\frac{Q_{fh}}{V_{f1B}}\left(V_{soln,1}\right) \qquad \text{Eq. 29–4}$$

where:

Hg_{fh}=Total mass of Hg collected in the front-half of the sampling train (Sample Fraction 1), µg.

Q_{fh}=Quantity of Hg, µg, *TOTAL in the ALIQUOT of Analytical Fraction 1B selected for digestion and analysis.*

8.5.1.1 For example, if a 10 ml aliquot of Analytical Fraction 1B is taken and digested and analyzed (according to Section 5.4.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{fh}.

$V_{soln,1}$=Total volume of Analytical Fraction 1, ml.

V_{f1B}=Volume of aliquot of Analytical Fraction 1B analyzed, ml.

8.5.1.2 For example, if a 1 ml aliquot of Analytical Fraction 1B was diluted to 50 ml with 0.15 percent HNO_3 as described in Section 5.4.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml wa digested according to Section 5.4.3 and analyzed, V_{f1B} would be 0.02 ml.

8.5.2 Analytical Fractions 2B, 3A, 3B, and 3C; Back Half Hg.

8.5.2.1 Calculate the amount of Hg collected in Sample Fraction 2 by using Equation 29–5:

$$Hg_{bh2}=\frac{Q_{bh2}}{V_{f2B}}\left(V_{soln,2}\right) \qquad \text{Eq. 29–5}$$

where:

Hg_{bh2}=Total mass of Hg collected in Sample Fraction 2, µg.

Q_{bh2}=Quantity of Hg, µg, *TOTAL in the ALIQUOT of Analytical Fraction 2B selected for digestion and analysis.*

8.5.2.1.1 For example, if a 10 ml aliquot of Analytical Fraction 2B is taken and digested and analyzed (according to Section 5.4.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for Q_{bh2}.

$V_{soln,2}$=Total volume of Sample Fraction 2, ml.

V_{f2B}=Volume of Analytical Fraction 2B analyzed, ml.

8.5.2.1.2 For example, if 1 ml of Analytical Fraction 2B was diluted to 10 ml with 0.15 percent HNO_3 as described in Section 5.4.3 to bring it into the proper analytical range, and then 5 ml of that 10-ml was analyzed, V_{f2B} would be 0.5 ml.

8.5.2.2 Calculate each of the back-half Hg values for Analytical Fractions 3A, 3B, and 3C by using Equation 29–6:

$$Hg_{bh3(A,B,C)} = \frac{Q_{bh3(A,B,C)}}{V_{f3(A,B,C)}}\left(V_{soln,3(A,B,C)}\right) \quad \text{Eq. } 29-6$$

where:

$Hg_{bh3\ (A,B,C)}$=Total mass of Hg collected separately in Fraction 3A, 3B, or 3C, µg.

$Q_{bh3\ (A,B,C)}$=Quantity of Hg, µg, *TOTAL, separately, in the ALIQUOT of Analytical Fraction 3A, 3B, and 3C selected for digestion and analysis,* (see previous notes in Sections 8.5.1 and 8.5.2 describing the quantity ''Q'' and calculate similarly).

$V_{f3\ (A,B,C)}$=Volume, separately, of Analytical Fraction 3A, 3B, or 3C analyzed, ml (see previous notes in Sections 8.5.1 and 8.5.2, describing the quantity ''V'' and calculate similarly).

$V_{soln,\ 3\ (A,B,C)}$=Total volume, separately, of Analytical Fraction 3A, 3B, or 3C, ml.

8.5.2.3 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 29–7:

$$Hg_{bh}=Hg_{bh2}+Hg_{bh3A}+Hg_{bh3B}+Hg_{bh3C} \quad \text{Eq. } 29-7$$

where:

Hg_{bh}=Total mass of Hg collected in the back-half of the sampling train, µg.

8.5.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 29–8:

$$Hg_t=(Hg_{fh}-Hg_{fhb})+(Hg_{bh}-Hg_{bhb}) \quad \text{Eq. } 29-8$$

where:

Hg_t=Total mass of Hg collected in the sampling train, µg.

Hg_{fhb}=Blank correction value for mass of Hg detected in front-half field reagent blank, µg.

Hg_{bhb}=Blank correction value for mass of Hg detected in back-half field reagent blanks, µg.

8.5.4 If the total of the measured blank values ($Hg_{fhb}+Hg_{bhb}$) is in the range of 0.0 to 0.6 µg, then use the total to correct the sample value ($Hg_{fh}+Hg_{bh}$); if it exceeds 0.6 µg, use the greater of I. or II:

I. 0.6 µg.

II. the lesser of (a) ($Hg_{fhb}+Hg_{bhb}$), or (b) 5 percent of the sample value ($Hg_{fh}+Hg_{bh}$).

8.6 Individual Metal Concentrations in Stack Gas. Calculate the concentration of each metal in the stack gas (dry basis, adjusted to standard conditions) by using Equation 29–9:

$$C_s = \frac{K_4 M_t}{V_{m(std)}} \quad \text{Eq. } 29-9$$

C_s=Concentration of a metal in the stack gas, mg/dscm.

$K_4=10^{-3}$ mg/µg.

M_t=Total mass of that metal collected in the sampling train, µg; (substitute Hg_t for M_t for the Hg calculation).

$V_{m(std)}$=Volume of gas sample as measured by the dry gas meter, corrected to dry standard conditions, dscm.

8.7 Isokinetic Variation and Acceptable Results. Same as Method 5, Sections 6.11 and 6.12, respectively.

9. Bibliography

1. Method 303F in *Standard Methods for the Examination of Water Wastewater,* 16th Edition, 1985. Available from the American Pubic Health Association, 1015 18th Street NW., Washington, DC 20036.

2. EPA Methods 6010, 6020, 7000, 7041, 7060, 7131, 7421, 7470, 7740, and 7841, *Tesdt Methods for Evaluating Solid Waste: Physical/Chemical Methods.* SW–846, Third Edition, September 1986, with updates I, II, IIA and IIB. Office of Solid Waste and Emergency Response, U.S. Environmental Protection Agency, Washington, DC 20460.

3. EPA Method 200.7, *Code of Federal Regulations,* Title 40, Part 136, Appendix C. July 1, 1987.

4. EPA Methods 1 through 5, *Code of Federal Regulations,* Title 40, Part 60, Appendix A. July 1, 1991.

5. EPA Method 101A, *Code of Federal Regulations,* Title 40, Part 61, Appendix B. July 1, 1991.

PART 61—[AMENDED]

3. The authority citation for part 61 continues to read as follows:

Authority: 42 U.S.C. 7401, 7412, 7414, 7416, and 7601.

4. In part 61, Method 101A of appendix B, by revising the heading, Sections 6.1.5, 7.2.1, 7.2.3, 7.2.5, 7.3.1., 7.3.2, 7.3.3, and 9.2; and by adding sections 5.2.4 through 5.2.7, 6.1.7, 6.1.8, 7.2.1.1 through 7.2.1.3, 7.2.6, 9.2.1, 9.2.2 and reference 3 of item 10 bibliograph; and by adding text to the end of section 6.1.6 to read as follows:

Appendix B—Test Methods

* * * * *

Method 101A—Determination of Particulate and Gaseous Mercury Emissions From Stationary Sources

* * * * *

5.2.4 Atomic Absorption Spectrophotometer or Equivalent. Any atomic absorption unit with an open sample presentation area in which to mount the optical cell is suitable. Use those instrument settings recommended by the particular manufacturer. Instruments designed specifically for the measurement of mercury using the cold-vapor technique are commercially available and may be substituted for the atomic absorption spectrophotometer.

5.2.5 Optical Cell. Alternatively, a heat lamp mounted above the cell or a moisture trap installed upstream of the cell may be used.

5.2.6 Aeration Cell. Alternatively, aeration cells available with commercial cold vapor instrumentation may be used.

5.2.7 Aeration Gas Cylinder. Nitrogen, argon, or dry, Hg-free air, equipped with a single-stage regulator. Alternatively, aeration may be provided by a peristaltic metering pump. If a commercial cold vapor instrument is used, follow the manufacturer's recommendations.

* * * * *

6.1.5 Sulfuric Acid (H_2SO_4), 10 Percent (V/V). Carefully add and mix 100 ml of concentrated H_2SO_4 to 800 ml of deionized distilled water. Then, by adding deionized distilled water, mix and bring to a final volume of 1000 ml.

6.1.6 * * *

Precaution: To prevent autocatalytic decomposition of the permanganate solution, filter the solution through Whatman 541 filter paper. Also, due to the potential reaction of the potassium permanganate with the acid, there could be pressure buildup in the solution storage bottle; therefore these bottles shall not be fully filled and shall be vented to relieve excess pressure and prevent explosive potentials. Venting is required, but should not allow contamination of the solution; a No. 70–72 hole drilled in the container cap and Teflon liner has been used.

6.1.7 Hydrochloric Acid (HCL). Concentrated. Trace-metals grade is recommended. The Hg level shall be less than 3 ng/ml.

6.1.8 HCL, 8 N. Dilute 67 ml of concentrated HCl to 100 ml with water (slowly add the HCl to the water).

* * * * *

7.2.1 Container No. 1 (Impinger, Probe, and Filter Holder) and, if applicable, No. 1A (HCl rinse).

7.2.1.1 Using a graduated cylinder, measure the liquid in the first three

impingers to within 1 ml. Record the volume of liquid present (e.g., see Figure 5–3 of Method 5 in 40 CFR Part 60). This information is required to calculate the moisture content of the effluent gas. (Use only graduated cylinder and glass storage bottles that have been precleaned as in Section 7.1.2.) Place the contents of the first three impingers into a 1000-ml glass sample bottle labeled Container No. 1. See the *Precaution* in Section 6.1.6.

Note No. 1 to Section 7.2.1.1: Due to the potential reaction of $KMnO_4$ with acid, there could be pressure buildup in the sample storage bottles. These bottles shall not be filled completely and shall be vented to relieve excess pressure. A No. 70–72 hole drilled in the container cap and Teflon liner has been used successfully).

Note No. 2 to Section 7.2.1.1: If a filter is used in the sampling train, remove the filter from its holder as outlined under ''Container No. 3'' below.)

7.2.1.2 Taking care that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover the Hg (and any condensate) from the probe nozzle, probe fitting, probe liner, front half of the filter holder (if applicable), and impingers as follows: Rinse these components with a total of 250 to 400 ml of fresh acidified 4 percent $KMnO_4$ solution carefully assuring removal of all loose particulate matter from the impingers; add all washings to Container No. 1. See the *Precaution* in Section 6.1.6 and see the *Note No. 1* in Section 7.2.1.1. To remove any residual brown deposits on the glassware following the permanganate rinse, rinse with approximately 100 ml of water carefully assuring removal of all loose particulate matter from the impingers, and add this rinse to Container No. 1. If no visible deposits remain after this water rinse, do not rinse with 8 N HCl. However, if deposits do remain on the glassware after the water rinse, wash the impinger walls and stems with a total of only 25 ml of 8 N HCl as follows; turn and shake the impingers so that the 8 N HCl contacts all inside surfaces (wash the first impinger, then pour the wash from the first impinger into the second impinger, and finally pour the wash from the second into the third). DO NOT PLACE THE HCl WASH INTO THE ACIDIFIED PERMANGANATE SOLUTION. Place the HCl wash into a separate container labeled Container No. 1A as follows: place 150 ml of water in an empty sample container labeled Container No. 1A. Pour the HCl wash carefully, with stirring, into Container No. 1A. Rinse the impinger walls and stem with a total of 50 ml of water, and place this rinse into Container No. 1A.

7.2.1.3 After all washings have been collected in the sample containers, prepare as described above to prevent leakage during shipment to the laboratory. Mark the height of the fluid level to determine whether leakage occurs during transport. Label the containers to identify their contents clearly.

7.2.3 Container No, 3 (Filter). If a filter was used, carefully remove it from the filter holder, place it into a 100 ml glass sample container, and add 20 to 40 ml of acidified $KMnO_4$. If it is necessary to fold the filter, be sure that the particulate cake is inside the fold. Carefully transfer to the 100 ml sample bottle any particulate matter and filter fibers that might adhere to the filter holder gasket by using a dry Nylon bristle brush and a sharp edged blade. See the *Precaution* in Section 6.1.6 and see the *Note No. 1* in Section 7.2.1.1. Label the container to clearly identify its contents. Mark the height of the fluid level to determine whether leakage occurs during transport.

* * * * *

7.2.5 Container No, 5 (Absorbing Solution Blank). For a blank, place 500 ml of acidified absorbing solution in a 1000 ml sample bottle. See the *Precaution* in Section 6.1.6 and see the *Note No. 1* in Section 7.2.1.1.

7.2.6 Container No. 6 (HCl rinse blank). For a blank, place 200 ml of water in a 1000-ml sample bottle, and add 25 ml of 8 N HCl carefully with stirring. Seal the container. Only one blank sample per 3 runs is required.

* * * * *

7.3.1 Containers No. 3 and No. 4 (Filter and Filter Blank). If a filter is used, place the contents, including the filter, of Containers No. 3 and 4 in separate 250-ml beakers, and heat the beakers on a steam bath until most of the liquid has evaporated. Do not take to dryness. Add 20 ml of concentrated HNO_3 to the beakers, cover them with a watch glass, and heat on a hot plate at 70 °C for 2 hours. Remove from the hot plate. Filter the solution from digestion of the Container No. 3 contents through Whatman No. 40 filter paper, and save the filtrate for addition to the Container No. 1 filtrate as described in Section 7.3.2. Discard the filter. Filter the solution from the digestion of the Container No. 4 contents through Whatman No. 40 filter paper, and save the filtrate for addition to Container No. 5 filtrate as described in Section 7.3.3. Discard the filter.

7.3.2 Container No. 1 (Impingers, Probe, and Filter Holder) and, if applicable, No. 1A (HCl rinse). Filter the contents of Container No. 1 through Whatman 40 filter paper into a 1-liter volumetric flask to remove the brown MnO_2 precipitate. Save the filter for digestion of the brown MnO_2 precipitate. Add the sample filtrate from Container No. 3 to the 1-liter volumetric flask, and dilute to volume with water. If the combined filtrates are greater than 1000 ml, determine the volume to the nearest ml and make the appropriate corrections for blank subtractions. Mix thoroughly. Mark the combined filtrates as ANALYSIS SAMPLE No. A.1. and analyze for Hg within 48 hr of the filtration step (Note: Do not confuse ANALYSIS SAMPLE No. A.1. with the contents of field Sample Container No. 1A which contains the 8 N HCl wash). Place the saved filter, which was used to remove the brown MnO_2 precipitate, into an appropriate sized *vented* container, which will allow release of any gases including chlorine formed when the filter is digested. In a laboratory hood which will remove any gas produced by the digestion of the MnO_2, add 25 ml of 8 N HCl to the filter and allow to digest for a minimum of 24 hours at room temperature. Filter the contents of Container 1A through Whatman 40 paper into a 500-ml volumetric flask. Then filter the result of the digestion of the brown MnO_2 from Container No. 1 through Whatman 40 filter into the same 500-ml volumetric flask, and dilute and mix well to volume with water. Discard the filter. Mark this combined 500-ml dilute solution as ANALYSIS SAMPLE No. HCL A.2., and analyze for Hg.

7.3.3 Container No. 5 (Absorbing Solution Blank) and No. 6 (HCl Rinse Blank). Prepare the contents of Container No. 5 for analysis by the same procedure used for Container No. 1 as described in Section 7.3.2. Add the filter blank filtrate from Container No. 4 to the 1-liter volumetric flask, and dilute to volume. Mix thoroughly. Mark this as ANALYSIS SAMPLE No. A.1. BLANK, and analyze for Hg within 48 hours of the filtration step. Digest any brown precipitate remaining on the filter from the filtration of Container No. 5 by the same procedure as described in Section 7.3.2. Filter the contents of Container No. 6 by the same procedure as described in Section 7.3.2, and combine in the 500-ml volumetric flask with the filtrate from the digested blank MnO_2 precipitate. Mark this resultant 500-ml combined dilute solution as ANALYSIS SAMPLE No. HCl A.2 blank. (Note: When analyzing samples A.1 blank and HCl A.2 blank, always begin with 10-ml aliquots. This applies specifically to blank samples.)

* * * * *

9. * * *

9.2 Total Mercury. For each source sample, correct the average maximum absorbance of the two consecutive samples whose peak heights agree within 3 percent of their average for the contribution of the blank. Then calculate the total Hg content in µg in each sample. Correct for any dilutions made to bring the sample into the working range of the spectrophotometer.

$$m_{(HC1)Hg} = \left[\frac{\left[C_{(HC1)Hg} \; D.F._{(HC1)Hg} \right]}{S} - \frac{\left[C_{(HC1\,blk)Hg} \; D.F._{(HC1\,blk)Hg} \right]}{S_{blk}} \right] V_{f(HC1)} \left(10^{-3} \right) \quad \text{Eq. 101A} - 1$$

where:

$m_{(HCl)\ Hg}$=Total blank corrected µg of Hg in HCl rinse and HCl digestate of filter sample

$C_{(HCl)\ Hg}$=Total ng of Hg analyzed in the aliquot from the 500-ml ANALYSIS SAMPLE No. HCl A.2.

$C_{(HCl\ blk)\ Hg}$=Total ng of Hg analyzed in aliquot of the 500-ml ANALYSIS SAMPLE No. HCl A.2 blank.

$D.F._{(HCl)\ Hg}$=Dilution factor for the HCl-digested Hg-containing solution, ANALYSIS SAMPLE No. ''HCl A.2.'' This dilution factor applies only to the dilution steps, if necessary, of the 500 ml of the original sample volume [$V_{f\ (HCl)}$] of ''HCl A.2'' because the original volume has been factored out in the equation along with the sample aliquot (S). In Eq. 101A–1, the sample aliquot, S, is digested according to Sections 7.4, 8.1, and 8.2 and the Hg from this digestion is introduced directly into the aeration cell for analysis. A dilution factor is required only if it is necessary to bring the sample into the analytical instrument's calibration range. If no dilution is necessary, then $D.F._{(HCl)\ Hg}$ equals 1.0.

D.F. (HCl blk)Hg=Dilution factor for the HCl-digested Hg-containing solution, ANALYSIS SAMPLE No. ''HCl A.2 blank.'' (Refer to sample No. ''HCl A.2'' dilution factor information above.)

$V_{f(HCl)}$=Solution volume of original sample, 500 ml for the HCl samples diluted as described in Section 7.3.

10^{-3}=Conversion factor µg/ng.

S=Aliquot volume of sample: digested according to Sections 7.4, 8.1, 8.2 and the Hg from this digestion is introduced directly into the aeration cell for analysis, ml.

S_{blk}=Aliquot volume of blank: digested according to Sections 7.4, 8.1, and 8.2 and the Hg from this digestion is introduced directly into the aeration cell for analysis, ml.

9.2.1 The maximum allowable blank subtraction for the Hg in the HCl washes is the lesser of the two following values: (1) the actual blank measured value (ANALYSIS SAMPLE NO. HCl A.2 blank), or (2) 5% of the Hg content in the combined HCl rinse and digested sample (ANALYSIS SAMPLE No. HCl A.2).

$$m_{(fltr)Hg} = \left[\frac{\left[C_{(fltr)Hg}\ D.F._{(fltr)Hg}\ V_{f(fltr)} \right]}{S_{(fltr)}} - \frac{\left[C_{(fltr\ blk)Hg}\ D.F._{(fltr\ blk)Hg}\ V_{f(fltr\ blk)} \right]}{S_{(fltr\ blk)}} \right] \left(10^{-3} \right) \quad \text{Eq. 101A – 2}$$

where:

$m_{(fltr)Hg}$=Total blank corrected µg of Hg in $KMnO_4$ filtrate and HNO_3 digestion of filter sample.

$C_{(fltr)Hg}$=Total ng of Hg in aliquot of $KMnO_4$ filtrate and HNO_3 digestion of filter analyzed (aliquot of ANALYSIS SAMPLE No. A.1).

$C_{(fltr\ blk)Hg}$=Total ng of Hg analyzed in aliquot of $KMnO_4$ blank and HNO_3 digestion of blank filter (aliquot of ANALYSIS SAMPLE No. A.1 blank).

$V_{f(fltr)}$=Solution volume of original sample, normally 100 ml for samples diluted as described in Section 7.3.

$V_{f(blk)}$=Solution volume of blank sample, 1000 ml for samples diluted as described in Section 7.3.

$D.F._{(fltr)Hg}$=Dilution factors, if necessary for ANALYSIS SAMPLE No. A.1, calculated similarly to those above for the (HC1) Hg samples.

$D.F._{(fltr\ blk)Hg}$=Dilution factors, if necessary for ANALYSIS SAMPLE No. A.1 blank, calculated similarly to those above for the (HCl blk)Hg samples.

9.2.2 The maximum allowable blank subtraction for the HCl is the lesser of the two following values: (1) the actual blank measured value (ANALYSIS SAMPLE No. ''A.1 blank''), or (2) 5% of the Hg content in the filtrate (ANALYSIS SAMPLE No. ''A.1'').

$$m_{Hg} = m_{(HC1)Hg} + m_{(fltr)Hg} \qquad \text{Eq. 101A–3}$$

where:

m_{Hg}=Total blank corrected Hg content in each sample, µg.

$m_{(HC1)Hg}$=Total blank corrected µg of Hg in HCl rinse and HCl digestate of filter sample.

$M_{(fltr)Hg}$=Total blank corrected µg of Hg in $KMnO_4$ filtrate and HNO_3 digestion of filter sample.

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10. * * *

3. Wilshire, Frank W., J.E. Knoll, T.E. Ward, and M.R. Midgett. Reliability Study of the U.S. EPA's Method 101A—Determiantion of Particulate and Gaseous Mercury Emissions U.S. Environmental Protection Agency, Research Triangle Park, NC. Report No. 600/D–31/219 AREAL 367, NTIS Acc No. PB91–23361.

* * * * *

5. In Appendix B to part 61, Method 101A is amended by revising the second and last sentences of section 7.1.1 and by revising the last two sentences of the first paragraph of section 7.1.2 to read as follows:

Appendix B to Part 61—Test Methods

* * * * *

Method 101A Determination of Particulate and Gaseous Mercury Emissions From Sewage Sludge Incinerators Meth. 101A

* * * * *

7.1.1 * * * In this method, highly oxidizable matter could make it impossible to sample for the required minimum time.* * * In cases where an excess of water condensation is encountered, collect two runs to make one sample, or add an extra impinger in front of the first impinger (also containing acidified $KMnO_4$ solution).

7.2.1 * * * In this method, clean all the glass components (a hood is recommended) by rinsing with 50 percent HNO_3, tap water, 8 N HCl, tap water, and finally deionized distilled water. Then place 50 ml of the acidified 4 percent $KMnO_4$ absorbing solution in the first impinger and 100 ml in each of the second and third impingers.

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[FR Doc. 96–9834 Filed 4–24–96; 8:45 am]

BILLING CODE 6560–50–M

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40 CFR Part 63

[FRL–5458–7]

State of Tennessee Request for Approval of Section 112(l) Authority

AGENCY: Environmental Protection Agency (EPA).

ACTION: Direct final rule.

SUMMARY: State of Tennessee has applied for approval of its Rule No. 1200–3–11–.08, Emission Standards for Emissions of Radionuclides Other Than Radon From Department of Energy Facilities; and also Rule No. 1200–3–11–.17, National Emission Standard for Radon Emissions From Department of Energy Facilities, under section 112(l) of the Clean Air Act (CAA) as amended November 15, 1990. The Environmental Protection Agency (EPA) has reviewed the State of Tennessee's submittal and has made the decision that the State of Tennessee's Rule No. 1200–3–11–.08 and Rule No. 1200–3–11–.17, satisfies all of the requirements necessary to qualify as a complete submittal. Thus, the EPA intends to take comment on whether the State of Tennessee's Rule No. 1200–3–11–.08 and Rule No. 1200–