
**EMISSION MEASUREMENT TECHNICAL INFORMATION CENTER
CONDITIONAL TEST METHOD**

Prepared by Emission Measurement Branch
Technical Support Division, OAQPS, EPA

EMTIC CTM-012.WPF
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Determination of Metals Emissions from Stationary Sources

Note: This conditional method (CTM-012.WPF) replaces the EMTIC "Interim" test method for metals emissions from stationary sources (ITM-001). The current version of the method reflects the slated-to-be proposed "Method 29 - Determination of Metals Emissions from Stationary Sources" which will be proposed in conjunction with additional standards regulating municipal waste combustors. A copy of Method 29 (dated 6/30/93) is contained in Docket A-90-45, item II-B-12.

1. Applicability and Principle

1.1 Applicability. This method is applicable to the determination of total chromium (Cr), cadmium (Cd), arsenic (As), nickel (Ni), manganese (Mn), beryllium (Be), copper (Cu), zinc (Zn), lead (Pb), selenium (Se), phosphorus (P), thallium (Tl), silver (Ag), antimony (Sb), barium (Ba), and mercury (Hg) emissions from stationary sources. This method may also be used for determining particulate emissions when the prescribed procedures and precautions are followed. Changes in the procedures to further facilitate particulate determination may affect the front-half mercury determination.

1.2 Principle. A stack sample is withdrawn isokinetically from the source, with particulate emissions collected in the probe and on a heated filter and gaseous emissions collected in solutions of acidic hydrogen peroxide and acidic potassium permanganate. The recovered samples are digested, and

appropriate fractions are analyzed for mercury by cold vapor atomic absorption spectroscopy (CVAAS) and for Cr, Cd, Ni, Mn, Be, Cu, Zn, Pb, Se, P, Tl, Ag, Sb, Ba, and As by inductively coupled argon plasma emission spectroscopy (ICAP) or atomic absorption spectroscopy (AAS). Graphite furnace atomic absorption spectroscopy (GFAAS) is used for analysis of Sb, As, Pb, Se, and Tl if these elements require greater analytical sensitivity than can be obtained by ICAP. Additionally, if desired, the tester may use AAS for analysis of all metals if the resulting in-stack method detection limits meet the goal of the testing program.

2. Range, Sensitivity, 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 ($\mu\text{g/ml}$) range in the final analytical solution can be analyzed using this method. Samples containing greater than approximately 50 $\mu\text{g/ml}$ Cr, Pb, or As should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20 $\mu\text{g/ml}$ of Cd should be diluted to that level before analysis.

2.2 Analytical Sensitivity. ICAP analytical detection limits for the sample solutions (based on SW-846, Method 6010) are approximately as follows: Sb (32 ng/ml), As (53 ng/ml), Ba (2 ng/ml), Be (0.3 ng/ml), Cd (4 ng/ml), Cr (7 ng/ml), Cu (6 ng/ml), Pb (42 ng/ml), Mn (2 ng/ml), Ni (15 ng/ml),

P (75 ng/ml), Se (75 ng/ml), Ag (7 ng/ml), Tl (40 ng/ml), and Zn (2 ng/ml). The actual method detection limits are sample dependent and may vary as the sample matrix may affect the limits. The analytical detection limits for analysis by direct aspiration AAS (based on SW-846, Method 7000 series) are approximately as follows: Sb (200 ng/ml), As (2 ng/ml), Ba (100 ng/ml), Be (5 ng/ml), Cd (5 ng/ml), Cr (50 ng/ml), Cu (20 ng/ml), Pb (100 ng/ml), Mn (10 ng/ml), Ni (40 ng/ml), Se (2 ng/ml), Ag (10 ng/ml), Tl (100 ng/ml), and Zn (5 ng/ml). The detection limit for mercury by CVAAS is approximately 0.2 ng/ml. The use of GFAAS can give added sensitivity compared to direct aspiration AAS for the following metals: Sb (3 ng/ml), As (1 ng/ml), Be (0.2 ng/ml), Cd (0.1 ng/ml), Cr (1 ng/ml), Pb (1 ng/ml), Se (2 ng/ml), and Tl (1 ng/ml).

2.3 In-stack Detection Limit.

2.3.1 Using (1) the procedures described in this method, (2) the analytical detection limits described in the previous paragraph, (3) a volume of 300 ml (Fraction 1) for the front-half and 150 ml (Fraction 2A) for the back-half samples, and (4) a stack gas sample volume of 1.25 m³, the corresponding in-stack method detection limits are presented in Table 29-1 and calculated using Eq. 29-1.

$$A \times B/C = D$$

Eq. 29-1

where:

A = Analytical detection limit, $\mu\text{g/ml}$.

B = Volume of sample prior to aliquotting for analysis, ml.

C = Stack sample volume, dm^3 .

D = In-stack detection limit, $\mu\text{g/m}^3$.

Values in Table 29-1 are calculated for the front- and back-half and/or the total train.

2.3.2 To ensure optimum sensitivity in the measurements, the concentrations of target metals in the solutions are suggested to be at least ten times the analytical detection limits. Under certain conditions, and with greater care in the analytical procedure, this concentration can be as low as approximately three times the analytical detection limit. In all cases, on at least one sample (run) in the source test and for each metal analyzed, repetitive analyses, method of standard additions (MSA), serial dilution, or matrix spike addition, etc., shall be used to establish the quality of the data.

2.3.3 Actual in-stack method detection limits will be determined based on actual source sampling parameters and analytical results as described above. If required, the method in-stack detection limits can be made more sensitive than those shown in Table 29-1 for a specific test by using one or more of the following options:

2.3.4 A 1-hour sampling run may collect a stack gas sampling volume of about 1.25 m^3 . If the sampling time is

Table 29-1. In-stack method detection limits.

Front-half	Back-half	Back-half	Fractions	
	Fraction 1	Fraction 2	"Hg, only"	
Metal	Probe and Filter	Impingers 1-3	Impingers 4-6	Total Train
Antimony	7.7 (0.7)*	3.8 (0.4)*		11.5 (1.1)*
Arsenic	12.7 (0.3)*	6.4 (0.1)*		19.1 (0.4)*
Barium	0.5	0.3		0.8
Beryllium	0.07 (0.05)*	0.04 (0.03)*		0.11 (0.08)*
Cadmium	1.0 (0.02)*	0.5 (0.01)*		1.5 (0.03)*
Chromium	1.7 (0.2)*	0.8 (0.1)*		2.5 (0.3)*
Copper	1.4	0.7		2.1
Lead	10.1 (0.2)*	5.0 (0.1)*		15.1 (0.3)*
Manganese	0.5 (0.2)*	0.2 (0.1)*		0.7 (0.3)*
Mercury	0.6**	3.0**	2.0**	5.6**
Nickel	3.6	1.8		5.4
Phosphorus	18	9		27
Selenium	18 (0.5)*	9 (0.3)*		27 (0.8)*
Silver	1.7	0.9		2.6
Thallium	9.6 (0.2)*	4.8 (0.1)*		14.4 (0.3)*
Zinc	0.5	0.3		0.8

() * Detection limit when analyzed by GFAAS.

** Detection limit when analyzed by CVAAS, estimated for back-Half and total Train.

Note: Actual method in-stack detection limits will be determined based on actual source sampling parameters and analytical results as described earlier in this section.

increased and 5 m³ are collected, the in-stack method detection limits would be one fourth the values shown in Table 29-1 (with this change, the method is four times more sensitive than a 1-hour run. Larger sample volumes (longer runs) would make it even more sensitive.

2.3.5 The in-stack detection limits assume that all of the sample is digested (except the aliquot for mercury) and the final liquid volumes for analysis are 300 ml (Fraction 1) for the front-half and 150 ml (Fraction 2A) for the back-half sample. If the front-half volume is reduced from 300 to 30 ml, the front-half in-stack detection limits would be one tenth the values shown above (ten times more sensitive). If the back-half volume is reduced from 150 to 25 ml, the in-stack detection limits would be one sixth the above values. Matrix effect checks are necessary on sample analyses and typically are of greater significance for samples that have been concentrated to less than the normal original sample volume. Reduction to a volume of less than 25 ml may not allow redissolving of the residue and may increase interference by other compounds.

2.3.6 When both of the above modifications are used simultaneously on one sample, the resultant improvements are multiplicative. For example, where stack gas volume is increased by a factor of five and the total liquid sample digested volume of both the front- and back-halves is reduced by a factor of six, the in-stack method detection limit is reduced by a factor of thirty (the method is thirty times more sensitive). Conversely,

reducing stack sample volume and increasing sample liquid volume will increase in-stack detection limits (the method would then be less sensitive). The front-half and back-half samples (Fractions 1A and 2A) can be combined proportionally (see Section 1.2) prior to analysis. The resultant liquid volume (excluding the mercury fractions, which must be analyzed separately) is recorded. Combining the sample in this manner does not allow the point of capture in the train to be determined. The in-stack method detection limit then becomes a single value for all metals except mercury (due to exclusion of the mercury fraction). This discussion assumes no blank correction. Blank corrections are discussed later in this method.

2.4 Precision. The precision (relative standard deviation) for each metal detected in a method development test at a sewage sludge incinerator are 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. Beryllium, Mn, and Ag were not detected in the tests; however, based on the analytical sensitivity of the ICAP for these metals, it is assumed that their precisions should be similar to those for the other metals when detected at similar levels.

2.5 Interferences. Iron can be a spectral interference during the analysis of As, Cr, and Cd by ICAP. Al can be a

spectral interference during the analysis of As and Pb by ICAP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit (in-stack detection limit). Refer to Method 6010 of Citation 1 of the Bibliography or the other analytical methods used for details on potential interferences to this method. The analyst must eliminate or reduce interferences to acceptable levels. For all GFAAS analyses, matrix modifiers should be used to limit interferences, and standards should be matrix matched.

3. Apparatus

3.1 Sampling Train. A schematic of the sampling train is shown in Figure 29-1. It is similar to the Method 5 train and consists of the following components.

3.1.1 Probe Nozzle (Probe Tip) and Borosilicate or Quartz Glass Probe Liner. Same as Method 5, Sections 2.1.1 and 2.1.2, 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 may be made to compensate for its effect on the sample. Probe fittings of plastic such as Teflon, polypropylene, etc. are recommended over metal fittings to prevent contamination; further, if desired, a single glass piece consisting of a combined probe tip and probe liner may be used, but such a single glass piece is not a requirement of this methodology)

12a

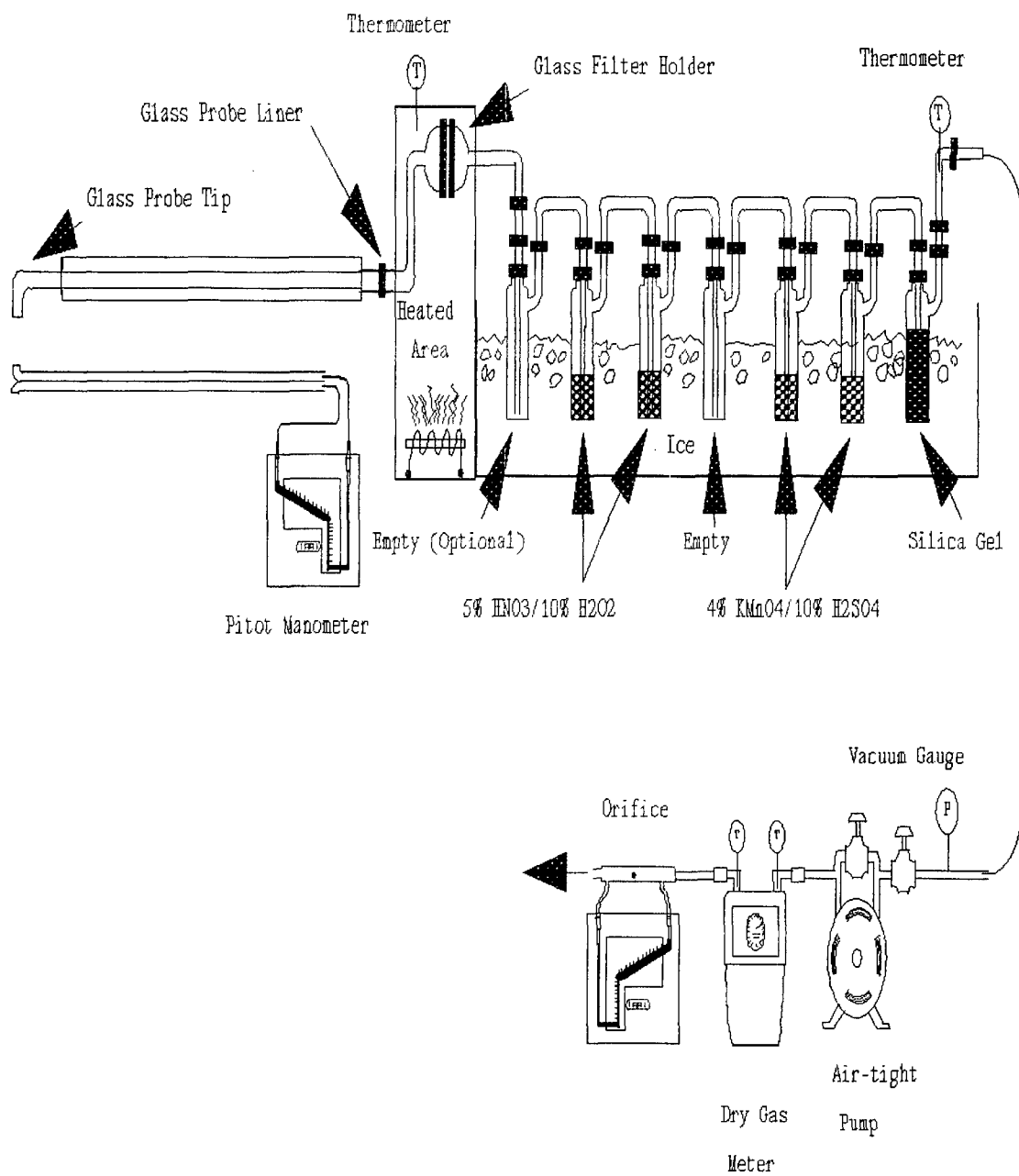


Figure 29-1. Sampling train.

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 a Teflon filter support or other non-metallic, non-contaminating support must be used in place of the glass frit.

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

3.1.5 Condenser. The following system shall be used for condensing and collecting gaseous metals and determining the moisture content of the stack gas. The condensing system should consist of four to seven impingers connected in series with leak-free ground glass fittings or other leak-free, non-contaminating fittings. The first impinger is optional and is recommended as a moisture trap. The second impinger (or the first $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) shall be as described for the first impinger in Method 5. The third impinger (or second $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger) shall be the Greenburg Smith impinger with the standard tip described as the second impinger in Method 5, Section 2.1.7. All other impingers are the same as the first $\text{HNO}_3/\text{H}_2\text{O}_2$ impinger previously described. A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. If mercury analysis is not to be performed, the potassium

permanganate impingers and the empty impinger preceding them are removed.

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

3.1.7 Teflon Tape. For capping openings and sealing connections, 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. For quantitative recovery of materials collected in the front-half of the sampling train. A description of acceptable all-Teflon component brushes or swabs are to be included in EPA's Emission Measurement Technical Information Center (EMTIC) files.

3.2.2 Sample Storage Containers. Glass bottles with Teflon-lined caps which are non-reactive to the oxidizing solutions, with capacities of 1000- and 500-ml shall be used for KMnO_4 -containing samples and blanks. Polyethylene bottles may be used for other sample types.

3.2.3 Graduated Cylinder. Glass or equivalent.

3.2.4 Funnel. Glass or equivalent.

3.2.5 Labels. For 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. For the analysis, the following equipment is needed:

3.3.1 Volumetric Flasks, 100-ml, 250-ml, and 1000-ml. For preparation of standards and sample 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).

3.3.4 Beakers and Watch Glasses. 250-ml beakers for sample digestion with watch glasses to cover the tops.

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

3.3.6 Filter Funnels. For holding filter paper.

3.3.7 Disposable Pasteur Pipets and Bulbs.

3.3.8 Volumetric Pipets.

3.3.9 Analytical Balance. Accurate to within 0.1 mg.

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

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, Pb, Se, and Tl hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as Bibliography Citation 1 Methods 7041 (Sb), 7060 (As), 7131 (Cd), 7421 (Pb), 7740 (Se), and 7841 (Tl).

3.3.12.2 Cold Vapor Mercury Attachment. With a mercury HCL or EDL. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10°C such that no condensation forms on the wall of the quartz cell. Same as Method 7470 in Citation 2 of the Bibliography.

3.3.13 Inductively Coupled Argon Plasma Spectrometer. With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010 in Citation 1 of the Bibliography.

4. Reagents

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

4.2 Sampling. The reagents used in sampling are as follows:

4.2.1 Filters. The filters shall contain less than 1.3 $\mu\text{g}/\text{in.}^2$ of each of the metals to be measured. Analytical results provided by filter manufacturers are acceptable. However, if no such results are available, filter blanks must be analyzed for each target metal prior to emission testing. Quartz or glass fiber filters without organic binders shall be used. The filters should exhibit at least 99.95 percent efficiency

(<0.05 percent penetration) on 0.3- μ dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM Standard Method D2986-71 (incorporated by reference). For particulate determination in sources containing sulfur dioxide (SO₂) or sulfur trioxide (SO₃), the filter material must be of a type that is unreactive to SO₂ or SO₃, as described in Method 5. Quartz fiber filters meeting these requirements are recommended.

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

4.2.3 Nitric Acid. Concentrated. Baker Instra-analyzed or equivalent.

4.2.4 Hydrochloric Acid. Concentrated. Baker Instra-analyzed or equivalent.

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

4.2.6 Potassium Permanganate.

4.2.7 Sulfuric Acid. 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 Nitric Acid (HNO₃)/Hydrogen Peroxide (H₂O₂) Absorbing Solution, 5 Percent HNO₃/10 Percent H₂O₂. Add carefully with stirring 50 ml of concentrated HNO₃ to a 1000-ml volumetric flask containing approximately 500 ml of water, and then add carefully

with stirring 333 ml of 30 percent H_2O_2 . Dilute to volume with water. Mix well. The reagent shall contain less than 2 ng/ml of each target metal.

4.3.2 Acidic Potassium Permanganate (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: this is the acidic potassium permanganate absorbing solution. Prepare and store in glass bottles to prevent degradation. The reagent shall contain less than 2 ng/ml of Hg.

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

4.3.3 Nitric Acid, 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. The reagent shall contain less than 2 ng/ml of each target metal.

4.3.4 Hydrochloric Acid (HCl), 8 N. Make the desired volume of 8N HCl in the following proportions. 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. The reagent shall contain less than 2 ng/ml of Hg.

4.4 Glassware Cleaning Reagents.

4.4.1 Nitric Acid, Concentrated. Fisher ACS grade or equivalent.

4.4.2 Water. To conform to ASTM Specifications D1193-77, Type II.

4.4.3 Nitric Acid, 10 Percent (V/V). Add with stirring 500 ml of concentrated HNO₃ to a flask containing approximately 4000 ml of water. Dilute to 5000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.5 Sample Digestion and Analysis Reagents.

4.5.1 Hydrochloric Acid, Concentrated.

4.5.2 Hydrofluoric Acid, Concentrated.

4.5.3 Nitric Acid, Concentrated. Baker Instra-analyzed or equivalent.

4.5.4 Nitric Acid, 50 Percent (V/V). Add with stirring 125 ml of concentrated HNO₃ to 100 ml of water. Dilute to 250 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.5.5 Nitric Acid, 5 Percent (V/V). Add with stirring 50 ml of concentrated HNO₃ to 800 ml of water. Dilute to 1000 ml with water. Mix well. Reagent shall contain less than 2 ng/ml of each target metal.

4.5.6 Water. To conform to ASTM Specifications D1193-77, Type II.

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

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

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

4.5.10 Sulfuric Acid, Concentrated.

4.5.11 Nitric Acid, 50 Percent (V/V).

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

4.5.13 Nickel Nitrate, Ni(NO₃)₂·6H₂O.

4.5.14 Lanthanum Oxide, La₂O₃.

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

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

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

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

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

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

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

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

- 4.5.23 Cu Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.24 Mn Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.25 Ni Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.26 P Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.27 Se Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.28 Ag Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.29 Tl Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.30 Zn Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.31 Al Standard (AAS Grade), 1000 $\mu\text{g/ml}$.
- 4.5.32 Fe Standard (AAS Grade), 1000 $\mu\text{g/ml}$.

4.5.33 The metals standards may also be made from solid chemicals as described in Citation 3 of the Bibliography. Citations 1, 2, or 4 of the Bibliography should be referred to for additional information on mercury standards.

4.5.34 Mercury Standards and Quality Control Samples. Prepare fresh weekly a 10 $\mu\text{g/ml}$ intermediate mercury standard by adding 5 ml of 1000 $\mu\text{g/ml}$ mercury stock solution to a 500-ml volumetric flask; dilute with stirring to 500 ml by first carefully adding 20 ml of 15 percent HNO_3 and then adding water to the 500-ml volume. Mix well. Prepare a 200 ng/ml working mercury standard solution fresh daily: add 5 ml of the 10 $\mu\text{g/ml}$ 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. At least six separate aliquots of the working mercury standard solution should be used to prepare the standard curve. These aliquots should contain 0.0, 1.0, 2.0,

3.0, 4.0, and 5.0 ml of the working standard solution containing 0, 200, 400, 600, 800, and 1000 ng mercury, respectively. Quality control samples should be prepared by making a separate 10 µg/ml standard and diluting until in the range of the calibration.

4.5.35 ICAP Standards and Quality Control Samples.

Calibration standards for ICAP analysis can be combined into four different mixed standard solutions as shown below.

MIXED STANDARD SOLUTIONS FOR ICAP ANALYSIS

<u>Solution</u>	<u>Elements</u>
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Cu, Fe
III	Al, Cr, Ni
IV	Ag, P, Sb, Tl

Prepare these standards by combining and diluting the appropriate volumes of the 1000 µg/ml solutions with 5 percent HNO₃. A minimum of one standard and a blank can be used to form each calibration curve. However, a separate quality control sample spiked with known amounts of the target metals in quantities in the mid-range of the calibration curve should be prepared. Suggested standard levels are 25 µg/ml for AL, Cr and Pb, 15 µg/ml for Fe, and 10 µg/ml for the remaining elements. Prepare any standards containing less than 1 µg/ml of metal on a daily basis. Standards containing greater than 1 µg/ml of metal should be stable for a minimum of 1 to 2 weeks.

4.5.36 Graphite Furnace AAS Standards. Sb, As, Cd, 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 graphite furnace AAS, the standards must be matrix matched. Prepare a 100 ng/ml standard by adding 1 ml of the 10 $\mu\text{g/ml}$ standard to a 100-ml volumetric flask, and dilute to 100 ml with the appropriate matrix solution. Other standards should be prepared by diluting the 100 ng/ml standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/ml. Quality control samples should be prepared by making a separate 10 $\mu\text{g/ml}$ standard and diluting until it is in the range of the samples. Any standards containing less than 1 $\mu\text{g/ml}$ of metal should be prepared on a daily basis. Standards containing greater than 1 $\mu\text{g/ml}$ of metal should be stable for a minimum of 1 to 2 weeks.

4.5.37 Matrix Modifiers.

4.5.37.1 Nickel Nitrate, 1 Percent (V/V). Dissolve 4.956 g of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in approximately 50 ml of water in a 100-ml volumetric flask. Dilute to 100 ml with water.

4.5.37.2 Nickel Nitrate, 0.1 Percent (V/V). Dilute 10 ml of the 1 percent nickel nitrate solution from Section 4.5.37.1 above to 100 ml with water. Inject an equal amount of sample and this modifier into the graphite furnace during AAS analysis for As.

4.5.37.3 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 AAS analysis for Pb.

4.5.38 Whatman 541 Filter Paper (or equivalent). For filtration of digested samples.

5. Procedure

5.1 Sampling. The complexity of this method is such that, to obtain reliable results, testers and analysts should be trained and experienced with the test procedures, including source sampling, reagent preparation and handling, sample handling, safety equipment, analytical calculations, reporting, and specific 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. All sampling train glassware should first be rinsed with hot tap water and then washed in hot soapy water. Next, glassware should be rinsed three times with tap water, followed by three additional rinses with water. All glassware should then be soaked in a 10 percent (V/V) nitric acid solution for a minimum of 4 hours, rinsed three times with water, rinsed a final time with acetone, and allowed to air dry. All glassware openings where contamination can occur should be covered until the sampling train is assembled 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 Follow the same general procedures given in Method 5, Section 4.1.3, except place 100 ml of the $\text{HNO}_3/\text{H}_2\text{O}_2$ solution (Section 4.2.1) in each of the two impingers as shown in Figure 29-1 (normally the second and third impingers). Place 100 ml of the acidic KMnO_4 absorbing solution (Section 4.2.2) in each of the two impingers as shown in Figure 29-1, and transfer approximately 200 to 300 g of preweighed silica gel from its container to the last impinger. Alternatively, the silica gel may be weighed directly in the impinger just prior to train assembly.

5.1.3.2 Several options are available to the tester based on the sampling requirements and conditions. The use of an empty first impinger can be eliminated if the moisture to be collected in the impingers will be less than approximately 100 ml. If necessary, use as applicable to this methodology the procedure described in Section 7.1.1 of Method 101A, 40 CFR Part 61, Appendix B, to maintain the desired color in the last permanganate impinger.

5.1.3.3 Retain for reagent blanks volumes of the $\text{HNO}_3/\text{H}_2\text{O}_2$ solution per Section 5.2.16 of this method and of the acidic KMnO_4 solution per Section 5.2.17. These reagent blanks should be labeled and analyzed as described in Section 7. Set up the sampling train as shown in Figure 29-1. If mercury analysis is not desired, delete the empty impinger and the two permanganate impingers following the $\text{HNO}_3/\text{H}_2\text{O}_2$ impingers. If necessary to

ensure leak-free sampling train connections, Teflon tape or other non-contaminating material should be used instead of silicone grease to prevent contamination. Precaution: Extreme care should be taken to prevent contamination within the train. Prevent the mercury collection reagent (acidic KMnO_4) from contacting any glassware of the train which is washed and analyzed for Mn. Prevent H_2O_2 from mixing with the acidic KMnO_4 .

5.1.3.4 Mercury emissions can be measured, alternatively, in a separate train using EPA Method 101A with the modifications for processing the permanganate containers as described in the precaution in Section 4.3.2 and the note in Section 5.2.11 of this method). This alternative method is applicable for measurement of mercury emissions, and it may be of special interest to sources which must measure both mercury and manganese emissions.

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

5.1.5 Sampling Train Operation. Follow the procedures given in Method 5, Section 4.1.5. For each run, record the data required on a data sheet such as the one shown in Figure 5-2 of Method 5.

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

5.2 Sample Recovery.

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 may 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 off the filter holder outlet and impinger inlet. Use non-contaminating caps, whether ground-glass stoppers, plastic caps, serum caps, or Teflon tape to close these openings.

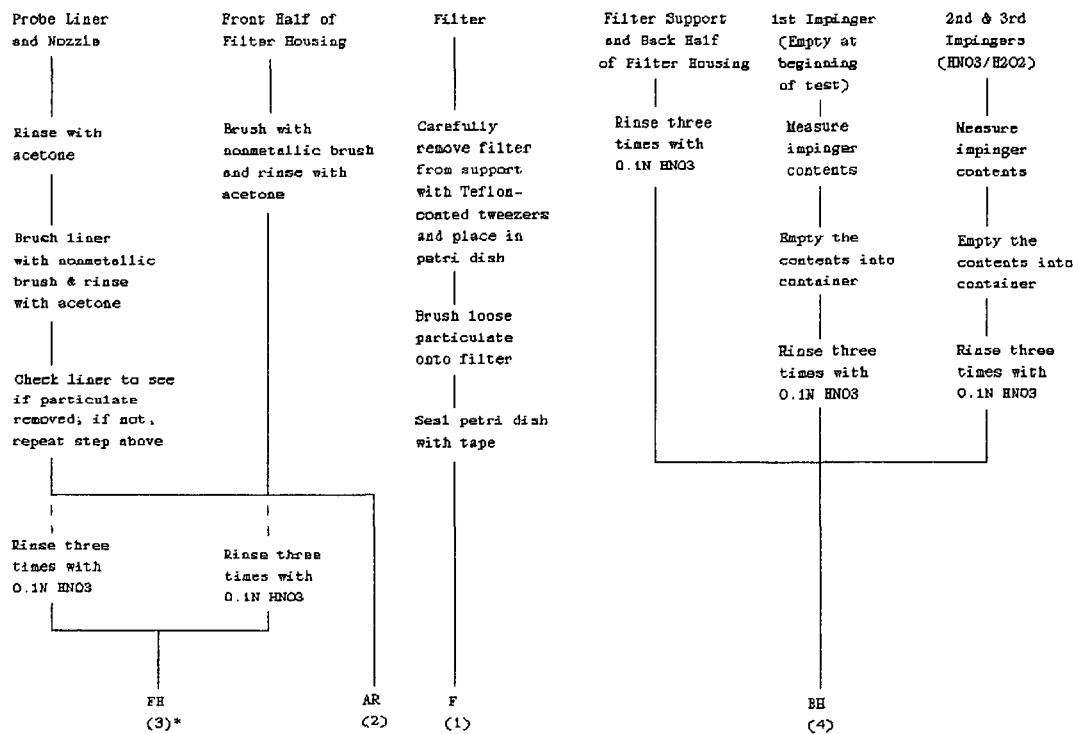
5.2.3 Alternatively, the train can be disassembled before the probe and filter holder/oven are completely cooled if this procedure is followed: Initially disconnect the filter holder outlet/impinger inlet and loosely cap the open ends. Then disconnect the probe from the filter holder or cyclone inlet and loosely cap the open ends. Cap the probe tip and remove the umbilical cord as previously described.

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. The sample is recovered and treated as follows (see schematic in Figures 29-2a and 29-2b). Assure that all items necessary for recovery of the sample do not contaminate it.

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

5.2.6 Container No. 2 (Acetone Rinse). **NOTE:** Perform this section only if determination of particulate emissions are desired in addition to metals emissions. Ensuring that dust on the outside of the probe or other exterior surfaces does not get into the sample, quantitatively recover particulate matter and

28a



* Number in parentheses indicates container number

Figure 29-2a. Sample recovery scheme.

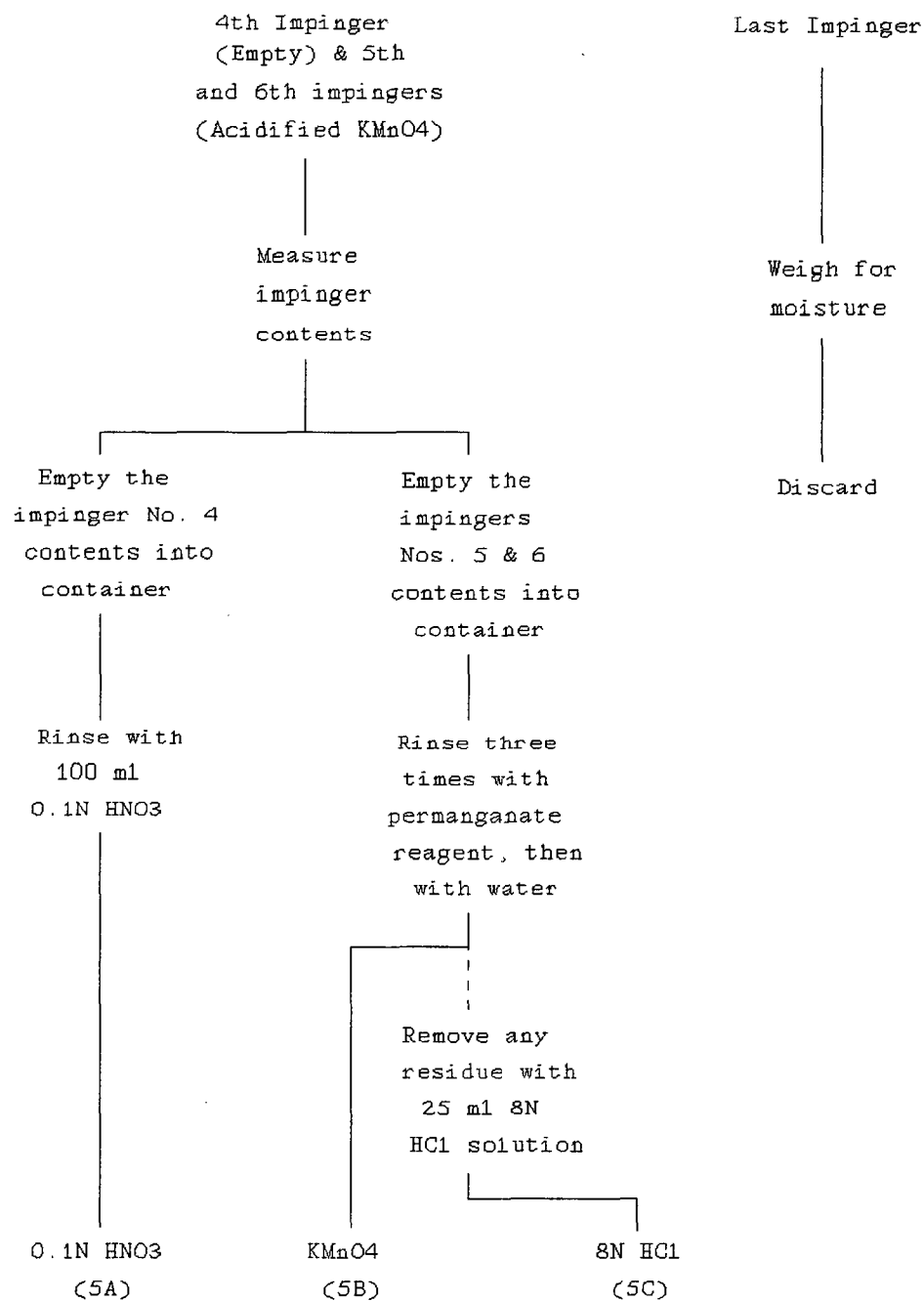


Figure 29-2b. Sample recovery scheme.

28b

any condensate from the probe nozzle, probe fitting, probe liner, and front half of the filter holder by washing these components with 100 ml of acetone and placing the wash in a glass container.

NOTE: The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Distilled water may be used instead of acetone when approved by the Administrator and shall be used when specified by the Administrator; in these cases, save a water blank and follow the Administrator's directions on analysis.

Perform the acetone rinse as follows: Carefully remove the probe nozzle and clean the inside surface by rinsing with acetone from a wash bottle and brushing with a non-metallic brush. Brush until the acetone rinse shows no visible particles, after which make a final rinse of the inside surface with acetone.

5.2.7 Brush and rinse the sample exposed inside parts of the 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 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

three times or more until no visible particulate matter is carried out with the acetone or until none remains in the probe liner on visual inspection. Rinse the brush with acetone, and quantitatively collect these washings in the sample container. After the brushing, make a final acetone rinse of the probe as described above.

5.2.8 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 nylon bristle brush and rinsing with acetone. Rinse each surface three times or more if needed to remove visible particulate. Make a final rinse of the brush and filter holder. After all acetone washings and particulate matter have been collected in the sample container, tighten the lid 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. Label the container clearly to identify its contents.

5.2.9 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 100 ml of 0.1 N HNO_3 , and place the wash into a sample storage container. **NOTE:** The use of exactly 100 ml is necessary for the subsequent blank correction procedures. Perform the rinses as applicable

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

5.2.10 Container No. 4 (Impingers 1 through 3, $\text{HNO}_3/\text{H}_2\text{O}_2$ Impingers and Moisture Knockout Impinger, when used, 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. 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 volume. Mark the height of the fluid level, seal the container, and clearly label the contents.

5.2.11 Container Nos. 5A (0.1 N HNO_3), 5B ($\text{KMnO}_4/\text{H}_2\text{SO}_4$ absorbing solution), and 5C (8 N HCl rinse and dilution). Pour

all the liquid, if any, from the impinger which was empty at the start of the run and which immediately precedes the two permanganate impingers (normally impinger No. 4) 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 Sample Container No. 5A. Rinse the impinger (No. 4) with 100 ml of 0.1 N HNO₃ and place this into Container No. 5A.

5.2.12 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 KMnO₄ solution into Container No. 5B. Using 100 ml total of fresh acidified KMnO₄ solution, rinse the two permanganate impingers and connecting glass a minimum of three times. Pour the rinses into Container No. 5B, carefully assuring transfer of all loose precipitated materials from the two impingers. 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 all loose precipitated material, if any. Mark the height of the fluid level, and clearly label the contents. Note the precaution in Section 4.3.2. **NOTE:** Due to the potential reaction of KMnO₄ with acid, there may 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.

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

5.2.14 Container No. 6 (Silica Gel). Note the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. Transfer the silica gel from its impinger to its original container and seal. The tester may use a funnel to pour the silica gel and a rubber policeman to remove the silica gel from the impinger. The small amount of particles that may adhere to the impinger wall need not be removed. Do not use water or other liquids to transfer the silica gel since weight gained in the silica gel impinger is used

for moisture calculations. Alternatively, if a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g.

5.2.15 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 labeled container for use in the front-half field reagent blank. Seal the container.

5.2.16 Container No. 8A (0.1 N HNO₃ Blank). At least once during each field test, place 300 ml of the 0.1 N HNO₃ solution used in the sample recovery process into a labeled container for use in the front-half and back-half field reagent blanks. Seal the container.

5.2.17 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 labeled Container No. 8B. Seal the container.

5.2.18 Container No. 9 (5 Percent HNO₃/10 Percent H₂O₂ Blank). At least once during each field test, place 200 ml of the 5 Percent HNO₃/10 Percent H₂O₂ solution used as the nitric acid impinger reagent into a labeled container for use in the back-half field reagent blank. Seal the container.

5.2.19 Container No. 10 (Acidified KMnO₄ Blank). At least once during each field test, place 100 ml of the acidified KMnO₄ solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back-half field

reagent blank for mercury analysis. Prepare the container as described in Section 5.2.11. See the note in Section 5.2.12.

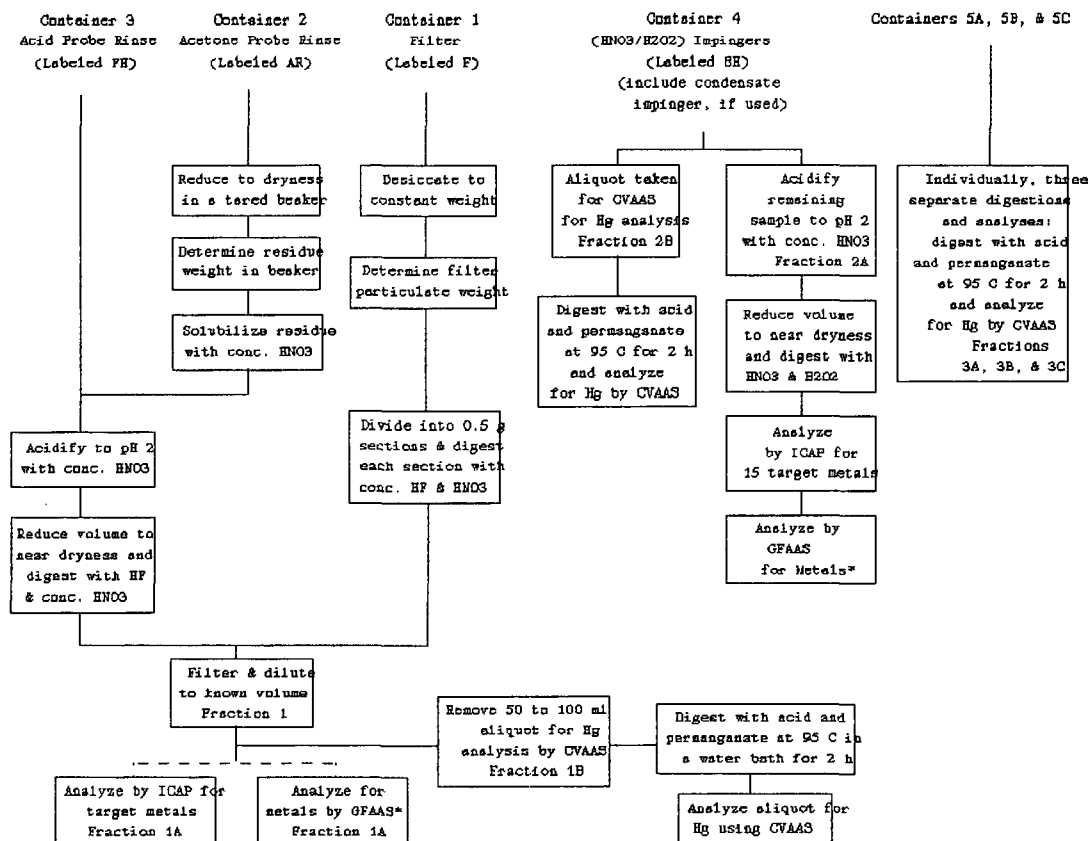
5.2.20 Container No. 11 (8 N HCl Blank). At least once during each field test, perform both of the following. Place 200 ml of water into a sample container. Pour 25 ml of 8 N HCl carefully with stirring into the container. Mix well and seal the container.

5.2.21 Container No. 12 (Filter Blank). Once during each field test, place three unused blank filters from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish. These will be used in the front-half field reagent blank.

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

5.3.1 Container No. 1 (Filter). If particulate emissions are being determined, desiccate the filter and filter catch without added heat and weigh to a constant weight as described in Section 4.3 of Method 5. For analysis of metals, divide the filter with its filter catch into portions containing approximately 0.5 g each and place into the analyst's choice of either individual microwave pressure relief vessels or Parr[®] Bombs. Add 6 ml of concentrated HNO₃ and 4 ml of concentrated HF

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*Analysis by AAS for metals found at less than 2 ug/ml in digestate solution, if desired. Or analyze for each metal by AAS, if desired.

Figure 29-3. Sample preparation and analysis scheme.

to each vessel. For microwave heating, microwave the sample vessels for approximately 12-15 minutes in intervals of 1 to 2 minutes at 600 Watts. For conventional heating, heat the Parr^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, below. **NOTES:**

5.3.1.1 Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Twelve to 15 minute heating times have been found to be acceptable for simultaneous digestion of up to 12 individual samples. Sufficient heating is evidenced by sorbent reflux within the vessel.

5.3.1.2 If the sampling train uses an optional cyclone, the cyclone catch should be prepared and digested using the same procedures described for the filters and combined with the digested filter samples.

5.3.2 Container No. 2 (Acetone Rinse). Note the level of liquid in the container and confirm on the analysis sheet whether or not leakage occurred during transport. If a noticeable amount of leakage has occurred, either void the sample or use methods, subject to the approval of the Administrator, to correct the final results. Measure the liquid in this container either volumetrically within 1 ml or gravimetrically within 0.5 g. Transfer the contents to an acid-cleaned, tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. If particulate emissions are being determined, desiccate for

24 hours without added heat, weigh to a constant weight according to the procedures described in Section 4.3 of Method 5, and report the results to the nearest 0.1 mg. Redissolve the residue with 10 ml of concentrated HNO_3 . Quantitatively combine the resultant sample, including all liquid and any particulate matter, with Container No. 3 before beginning Section 5.3.3.

5.3.3 Container No. 3 (Probe Rinse). The pH of this sample shall be 2 or lower. If the pH is higher, the sample should be acidified by careful addition with stirring of concentrated HNO_3 to pH 2. The sample should be rinsed into a beaker with water, and the beaker should be covered with a ribbed watch glass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Digest the sample in microwave vessels or Parr[®] 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. Then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 5.3.1. The resultant combined sample is referred to as Fraction 1 precursor. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 300 ml (or the appropriate volume for the expected metals concentration) with water. This dilution is Fraction 1. Measure and record the volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 50-ml aliquot and label

as Fraction 1B. Label the remaining 250-ml portion as Fraction 1A. Fraction 1A is used for ICAP or AAS analysis. Fraction 1B is used for the determination of front-half mercury.

5.3.4 Container No. 4 (Impingers 1-3). Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove a 75- to 100-ml aliquot for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 4 as aliquot Fraction 2A. Aliquot Fraction 2A defines the volume of 2A prior to digestion. All of aliquot Fraction 2A is digested to produce concentrated Fraction 2A. Concentrated Fraction 2A defines the volume of 2A after digestion and is normally 150 ml. Only concentrated Fraction 2A is analyzed for metals (except that it is not analyzed for mercury). The Fraction 2B aliquot should be prepared and analyzed for mercury as described in Section 5.4.3. Aliquot Fraction 2A shall have a pH of 2 or lower. If necessary, use concentrated HNO_3 by careful addition and stirring to lower aliquot Fraction 2A to pH 2. The sample should be rinsed into a beaker with water and the beaker covered with a ribbed watchglass. The sample volume should be reduced to approximately 20 ml by heating on a hot plate at a temperature just below boiling. Then follow either of the digestion procedures described in Sections 5.3.4.1 and 5.3.4.2, below.

5.3.4.1 Conventional Digestion Procedure. Add 30 ml of 50 percent 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 is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution 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 in intervals of 1 to 2 minutes at 600 Watts. 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 is concentrated Fraction 2A. Measure and record the volume of the Fraction 2A solution 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 Nos. 5A, 5B, and 5C (Impingers 4, 5, and 6). Keep these samples separate from each other and measure and record the volumes of 5A and 5B separately to within 0.5 ml. Dilute sample 5C to 500 ml with water. These samples 5A, 5B, and 5C are referred to respectively as Fractions 3A, 3B, and 3C. Follow the analysis procedures described in Section 5.4.3. Because the permanganate rinse and water rinse have the

capability to recover a high percentage of the mercury from the permanganate impingers, the amount of mercury in the HCl rinse (Fraction 3C) may be very small, possibly even insignificantly small. However, as instructed in this method, add the total of any mercury measured in and calculated for the HCl rinse (Fraction 3C) to that for Fractions 1B, 2B, 3A, and 3B for calculation of the total sample mercury concentration.

5.3.6 Container No. 6 (Silica Gel). Weigh the spent silica gel (or silica gel plus impinger) to the nearest 0.5 g using a balance. (This step may be conducted in the field.)

5.4 Sample Analysis. For each sampling train, seven individual samples are generated for analysis. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 29-3. The first two samples, labeled Fractions 1A and 1B, consist of the digested samples from the front-half of the train. Fraction 1A is for ICAP or AAS analysis as described in Sections 5.4.1 and/or 5.4.2. Fraction 1B is for determination of front-half mercury as described in Section 5.4.3. The back-half of the train was used to prepare the third through seventh samples. The third and fourth samples, labeled Fractions 2A and 2B, contain the digested samples from the moisture knockout, if used, and $\text{HNO}_3/\text{H}_2\text{O}_2$ Impingers 1 through 3. Fraction 2A is for ICAP or AAS analysis. Fraction 2B will be analyzed for mercury. The fifth through seventh samples, labeled Fractions 3A, 3B, and 3C, consist of the impinger contents and rinses from the empty and permanganate

impingers 4, 5, and 6. These samples are analyzed for mercury as described in Section 5.4.3. The total back-half mercury catch is determined from the sum of Fraction 2B and Fractions 3A, 3B, and 3C.

5.4.1 ICAP Analysis. Fraction 1A and Fraction 2A are analyzed by ICAP using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICAP, and set up an analysis program as described in Method 6010 or Method 200.7. The quality control procedures described in Section 7.3.1 shall be followed.

Recommended wavelengths for use in the analysis are listed below.

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

The wavelengths listed are recommended because of their sensitivity and overall acceptance. Other wavelengths may be substituted if they can provide the needed sensitivity and are treated with the same corrective techniques for spectral interference. Initially, analyze all samples for the desired target metals (except mercury) plus iron and aluminum. If iron and aluminum are present, the sample may have to be diluted so

that each of these elements is at a concentration of less than 50 ppm to reduce their spectral interferences on arsenic, cadmium, chromium, and lead. **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 Graphite Furnace. If analysis of metals in Fraction 1A and Fraction 2A using graphite furnace or direct aspiration AAS is desired, Table 29-2 should be used to determine which techniques and methods should be applied for each target metal. Table 29-2 should also be consulted to determine possible interferences and techniques to be followed for their minimization. Calibrate the instrument according to Section 6.3 and follow the quality control procedures specified in Section 7.3.2.

Table 29-2. Applicable techniques, methods and minimization of interferences.

Metal	Technique	SW-846 Method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Fe	Aspiration	7380	248.3	Contamination	Great care taken to avoid contamination
Pb	Aspiration	7420	283.3	217.0 nm alternate	Background correction required
Pb	Furnace	7421	283.3	Poor recoveries	Matrix modifier, add 10 ul of phosphorus acid to 1 ml of prepared sample in sampler cup
Mn	Aspiration	7460	279.5	403.1 nm alternate	Background correction required
Ni	Aspiration	7520	232.0	352.4 nm alternate	Background correction required
				Fe, Co, and Cr	Matrix matching or nitrous-oxide/acetylene flame
				Nonlinear response	Sample dilution or use 352.3 nm line
Se	Furnace	7740	196.0	Volatility	Spike samples and reference materials and add nickel nitrate to minimize volatilization
				Adsorption & scattering	Background correction is required and Zeeman background correction can be useful
Ag	Aspiration	7760	328.1	Adsorption & scattering	Background correction is required
				AgCl insoluble	Avoid hydrochloric acid unless silver is in solution as a chloride complex
					Sample and standards monitored for aspiration rate
Tl	Aspiration	7840	276.8		Background correction is required
					Hydrochloric acid should not be used
Tl	Furnace	7841	276.8	Hydrochloric acid or chloride	Background correction is required
					Verify that losses are not occurring for volatilization by spiked samples or standard addition; Palladium is a suitable matrix modifier
Zn	Aspiration	7950	213.9	High Si, Cu, & P	Strontium removes Cu and phosphate
				Contamination	Great care taken to avoid contamination

Table 29-2 cont.

Metal	Technique	SW-846 Method No.	Wavelength (nm)	Interferences	
				Cause	Minimization
Sb	Aspiration	7040	217.6	1000 mg/ml Pb Ni, Cu, or acid	Use secondary wavelength of 231.1 nm; match sample & standards' acid concentra- tion or use nitrous oxide/acetylene flame
Sb	Furnace	7041	217.6	High Pb	Secondary wavelength or Zeeman correction
As	Furnace	7060	193.7	Arsenic volatilizes Alumina	Spiked samples and add nickel nitrate so- lution to digestates prior to analysis
Ba	Aspiration	7080	553.6	Calcium Barium ionization	Use Zeeman background correction 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
Cd	Furnace	7131	228.8	As above Excess chloride	As above Ammonium phosphate used as a matrix modifier
Cr	Aspiration	7190	357.9	Pipet tips Alkali metal	Use cadmium-free tips KCl ionization suppressant in samples and standards
Cr	Furnace	7191	357.9	200 mg/L Ca and P	Consult manufacturer's literature 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

5.4.3 Cold Vapor AAS Mercury Analysis. Fractions 1B, 2B, 3A, 3B, and 3C should be analyzed separately for mercury using CVAAS following the method outlined in EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470 or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Dilute separately, as described below, an aliquot sized from 1 ml to 10 ml of each original sample to 100 ml with water. Record the amount of the aliquot used for dilution to 100 ml. If no prior knowledge exists of the expected amount of mercury in the sample, a 5-ml aliquot is suggested for the first dilution to 100 ml and analysis. In determining the emission value for mercury, the size of the sample aliquot used for dilution and analysis is dependent upon its mercury content. The total amount of mercury in the aliquot shall be less than 1 μ g and within the range (zero to 1000 ng) of the calibration curve. Place each sample aliquot into a separate 300-ml BOD bottle, and add enough water to make a total volume of 100 ml. Then analyze the sample for mercury by adding to it sequentially the sample preparation solutions and performing the sample preparation and analysis as described in the procedures of SW-846 Method 7470 or Method 303F. If the reading maximums are off-scale (because mercury in the aliquot exceeded the calibration range), including the dilution of 1-ml aliquots of the original sample, then perform the following:

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 original sample is further diluted to 100 ml and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

6. Calibration

Maintain a laboratory log of all calibrations.

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

6.2 Inductively Coupled Argon Plasma Spectrometer Calibration. Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the manufacturer's recommended procedures using the above standards. The calibration should be checked once per hour. If the instrument does not reproduce the standard concentrations within 10 percent, the complete calibration procedures should be performed.

6.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses. Prepare the standards as outlined in Section 4.5 and use to calibrate the spectrometer. Calibration procedures are also outlined in the

EPA methods referred to in Table 29-2 and in SW-846 Method 7470 or Standard Methods for Water and Wastewater Method 303F (for mercury). Each standard curve should be run in duplicate and the mean values used to calculate the calibration line. The instrument should be recalibrated approximately once every 10 to 12 samples.

7. Quality Control

7.1 Sampling. Field Reagent Blanks. When analyzed, the blanks in Container Nos. 7 through 12 produced previously in Sections 5.2.14 through 5.2.19, respectively, shall be processed, digested, and analyzed as follows. Digest and process 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 produces Fraction Blanks 1A and 1B from Fraction Blank 1. [If desired, the other two filters may be digested separately according to Section 5.3.1, diluted separately to 300 ml each, and analyzed separately to produce a blank value for each of the two additional filters. If these analyses are performed, they will produce two additional values for each of Fraction Blanks 1A and 1B. The three Fraction Blank 1A values will be calculated as three values of $M_{f_{hb}}$ in Equation 3 of Section 8.4.3, then the three values shall be totalled and divided by 3 to become the value $M_{f_{hb}}$ to be used in computing M_t by Equation 3. Similarly, the three Fraction Blank 1B values will be calculated separately as three values, totalled, averaged, and used as the value for $Hg_{f_{hb}}$ in Equation 8 of

Section 8.5.3. The analyses of the two extra filters are optional and are not a requirement of this method, but if the analyses are performed, the results must be considered as described above.] Combine 100 ml of Container No. 8A with 200 ml from Container No. 9, and digest and process the resultant volume per Section 5.3.4. This produces concentrated Fraction Blanks 2A and 2B from Fraction Blank 2. A 100-ml portion of Container No. 8A is Fraction Blank 3A. Combine 100 ml from Container No. 10 with 33 ml from Container No. 8B. This produces Fraction Blank 3B (use 400 ml as the volume of Fraction Blank 3B when calculating the blank value. Use the actual volumes when calculating all the other blank values). Dilute 225 ml from Container No. 11 to 500 ml with water. This produces Fraction Blank 3C. Analyze Fraction Blank 1A and Fraction Blank 2A per Section 5.4.1 and/or 5.4.2. Analyze Fraction Blank 1B, Fraction Blank 2B, and Fraction Blanks 3A, 3B, and 3C per Section 5.4.3. The analysis of Fraction Blank 1A produces the front-half reagent blank correction values for the metals except for mercury; the analysis of Fraction Blank 1B produces the front-half reagent blank correction value for mercury. The analysis of concentrated Fraction Blank 2A produces the back-half reagent blank correction values for the metals except for mercury, while separate analyses of Fraction Blanks 2B, 3A, 3B, and 3C produce the back-half reagent blank correction value for mercury.

7.2 An attempt may be made to determine if the laboratory reagents used in Section 5.3 caused contamination. They should

be analyzed by the procedures in Section 5.4. The Administrator will determine whether or not the laboratory blank reagent values can be used in the calculation of the test results.

7.3 Quality Control Samples. The following quality control samples should be analyzed.

7.3.1 ICAP Analysis. Follow the quality control shown in Section 8 of Method 6010. For the purposes of a three run test series, these requirements have been modified to include the following: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25 percent or analyze by standard additions), one quality control sample to check the accuracy of the calibration standards (must be within 25 percent of calibration), and one duplicate analysis (must be within 10 percent of average or repeat all analyses).

7.3.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Sb, As, Ba, Be, Cd, Cu, Cr, Pb, Ni, Mn, Hg, P, Se, Ag, Tl, and Zn. All samples should be analyzed 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 additions. A quality control sample should be analyzed to check the accuracy of the calibration standards. The results must be within 10 percent or the calibration repeated.

7.3.3 Cold Vapor AAS Analysis for Mercury. All samples should be analyzed in duplicate. A quality control sample should be analyzed to check the accuracy of the calibration standards (within 15 percent or repeat calibration). Perform a matrix spike on one sample from the HNO₃ impinger portion (must be within 25 percent or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Method 303F.

8. Calculations

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

8.2 Volume of Water Vapor and Moisture Content. Using the data obtained from this test, calculate the volume of water vapor $V_{w(std)}$ and the moisture content B_{ws} of the stack gas. Use Equations 5-2 and 5-3 of Method 5.

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

8.4 Metals (Except Mercury) in Source Sample.

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

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

where:

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

C_{a1} = Concentration of metal in sample Fraction 1A as
read from the standard curve, $\mu\text{g/ml}$.

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, when
2 ml of Fraction 1A are diluted to 10 ml,
 $F_d = 5$).

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

NOTE: If Fractions 1A and 2A are combined, proportional aliquots
must be used. Appropriate changes must be made in Equations 29-1
to 29-3 to reflect this approach.

8.4.2 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.

$$M_{bh} = C_{a2} F_a V_a \quad \text{Eq. 29-2}$$

where:

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

C_{a2} = Concentration of metal in sample concentrated Fraction 2A as read from the standard curve, ($\mu\text{g/ml}$).

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

V_a = Total volume of digested sample solution (concentrated 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:

$$M_t = (M_{fh} - M_{fhh}) + (M_{bh} - M_{bhh}) \quad \text{Eq. 29-3}$$

where:

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

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

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

NOTE: If the measured blank value for the front half (m_{fhh}) is in the range 0.0 to A μg [where A μg equals the value determined by

multiplying $1.4 \mu\text{g}/\text{in.}^2$ times the actual area in in.^2 of the filter used in the emission sample], m_{fhh} may be used to correct the emission sample value (m_{fh}); if m_{fhh} exceeds $A \mu\text{g}$, the greater of the two following values may be used:

I. $A \mu\text{g}$, or

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

If the measured blank value for the back-half (m_{bhb}) is in the range 0.0 to $1 \mu\text{g}$, m_{bhb} may be used to correct the emission sample value (m_{bh}); if m_{bhb} exceeds $1 \mu\text{g}$, the greater of the two following values may be used: $1 \mu\text{g}$ or 5 percent of m_{bh} .

8.5 Mercury in Source Sample.

8.5.1 Fraction 1B, Front-Half, Mercury. Calculate the amount of mercury collected in the front-half, Fraction 1, of the sampling train using the following equation:

$$Hg_{fh} = \frac{Q_{fh}}{V_{f1B}} (V_{soln,1}) \quad \text{Eq. 29-4}$$

where:

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

Q_{fh} = Quantity of mercury in analyzed sample, μg .

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

V_{f1B} = Volume of Fraction 1B analyzed, ml. See the following Note.

Note: V_{f1B} is the actual amount of Fraction 1B analyzed. For example, if 1 ml of Fraction 1B were diluted to 100 ml to bring it into the proper analytical range, and 1 ml of the 100-ml dilution were analyzed, V_{f1B} would be 0.01.

8.5.2 Fractions 2B, 3A, 3B, and 3C, Back Half, Mercury. Calculate the amount of mercury collected in Fractions 2 using Equation 5 and in Fractions 3A, 3B, and 3C using Equation 6. Calculate the total amount of mercury collected in the back-half of the sampling train using Eq. 29-7.

$$Hg_{bh2} = \frac{Q_{bh2}}{V_{f2B}} (V_{soln,2}) \quad \text{Eq. 29-5}$$

where:

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

Q_{bh2} = Quantity of mercury in analyzed sample, μg .

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

V_{f2B} = Volume of Fraction 2B analyzed, ml (see the following note).

Note: V_{f2B} is the actual amount of Fraction 2B analyzed. For example, if 1 ml of Fraction 2B were diluted to 10 ml to bring it into the proper analytical range, and 5 ml of the 10-ml dilution was analyzed, V_{f2B} would be 0.5. Use Equation 6 to calculate separately the back-half mercury for Fractions 3A, then 3B, then 3C.

where:

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

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

$Q_{bh3(A,B,C)}$ = Quantity of mercury in separately analyzed samples, μg .

$V_{f3(A,B,C)}$ = Volume of Fraction 3A, 3B, or 3C analyzed, ml (see note in Sections 8.5.1 and 8.5.2, and calculate similarly).

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

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

where:

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

8.5.3 Total Train Mercury Catch. Calculate the total amount of mercury collected in the sampling train using Eq 29-8.

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

where:

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

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

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

Note: If the total of the measured blank values ($Hg_{fbb} + Hg_{bhb}$) is in the range of 0 to 6 μg , then the total may be used to correct the sample value ($Hg_{fth} + Hg_{bth}$); if it exceeds 6 μg , the greater of the following two values may be used: 6 μg or 5 percent of the sample value ($Hg_{fth} + Hg_{bth}$).

8.6 Metal Concentration in Stack Gas. Calculate each metal separately for the Cd, total Cr, As, Ni, Mn, Be, Cu, Pb, P, Tl, Ag, Ba, Zn, Se, Sb, and Hg concentrations in the stack gas (dry basis, adjusted to standard conditions) as follows:

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

where:

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

K_4 = 10^{-3} mg/ μg .

M_t = Total mass of each metal collected in the sampling train, μg ; (substitute Hg_t for M_t for the mercury 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

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