

California Environmental Protection Agency  
AIR RESOURCES BOARD

Notice of Public Availability of Modified Text

NOTICE OF PUBLIC HEARING TO CONSIDER THE AMENDMENT AND ADOPTION OF  
REGULATIONS REGARDING STATIONARY SOURCE TEST METHODS

Public Hearing Date: September 26, 1996  
Public Availability Date: April 1, 1997  
Deadline for Public Comment: April 15, 1997

At a public hearing held September 26, 1996, the Air Resources Board (the "ARB" or "Board") considered the amendment of six existing test methods and the adoption of one new test method for determining emissions from nonvehicular, or stationary sources. The proposed regulatory action is described in the "Staff Report: Initial Statement of Reasons for a Proposed Public Hearing to Consider the Amendment and Adoption of Stationary Source Test Methods" released to the public on August 9, 1996.

At the hearing, the Board adopted Resolution 96-46 to amend and adopt the stationary source test methods, specifically amending Title 17, California Code of Regulations, Sections 94105, 94107, 94114, 94135, 94141, and 94143 and adopting Title 17, California Code of Regulations, Section 94161, and the incorporated test methods, Methods 5, 7, 100, 425, 429, 431, and 436, respectively. The Board also directed the Executive Officer to make minor modifications to the test methods for stationary sources, provided that the Executive Officer determines that such modifications are necessary. The Board resolution is appended to this notice as Attachment A.

In accordance with Section 11346.8 of the Government Code, the Board has directed the Executive Officer to adopt the new and amended stationary source test methods after making the modified language available for a period of at least fifteen (15) days. The Executive Officer was also directed to consider such written comments as may be submitted during the period, to make such modifications as may be appropriate in light of the comments received, and to present the test methods to the Board for further consideration if he determines that this is warranted.

By this notice, the modifications to the stationary source test methods are being made available for public comment prior to final action by the Board's Executive Officer. The modified text is appended to this notice as Attachment B.

Written comments must be submitted to the following address, no later than April 15, 1997, for consideration by the Executive Officer prior to final action:

Clerk of the Board  
Air Resources Board  
P.O. Box 2815  
Sacramento, CA 95812

The Executive Officer will consider only comments relating to the modifications which are described in this notice.

Attachments

ATTACHMENT A

State of California  
California Environmental Protection Agency  
AIR RESOURCES BOARD

Resolution 96-46

September 26, 1996

Agenda Item: 96-7-2

WHEREAS, Sections 39600 and 39601 of the Health and Safety Code authorize the Air Resources Board ("Board") to adopt standards, rules, and regulations and to do such acts as may be necessary for the proper execution of the powers and duties granted to, and imposed upon, the Board by law;

WHEREAS, Section 39607(d) of the Health and Safety Code requires the Board to adopt test procedures to measure compliance with its nonvehicular, or stationary source, emission standards and those of the air pollution control and air quality management districts ("districts");

WHEREAS, the Board's staff has identified improved test methods for six existing stationary source test methods, Methods 5, 7, 100, 425, 429, and 431, and has identified one new test method, Method 436;

WHEREAS, the Board's staff has proposed amendments to Sections 94105, 94107, 94114, 94135, 94141, and 94143, and has proposed adoption of Section 94161 of Title 17, California Code of Regulations, which incorporate by reference the identified improved and new stationary source test methods, Methods 5, 7, 100, 425, 429, 431, and 436, respectively;

WHEREAS, the proposed amendments and adoption are reasonable and necessary to achieve and maintain applicable ambient air quality standards;

WHEREAS, the California Environmental Quality Act and Board regulations require that no project having significant adverse environmental impacts be adopted as originally proposed if feasible alternatives or mitigation measures are available which would substantially reduce or avoid such impacts;

WHEREAS, a public hearing and other administrative proceedings have been held in accordance with the provisions of the Administrative Procedure Act (Government Code, Title 2, Division 3, Part 1, Chapter 3.5);

WHEREAS, the Board has considered the impact of the proposed regulatory action on the economy of the state; and

WHEREAS, the Board finds that:

Amendment and adoption of the provisions of Title 17, California Code of Regulations, as set forth in Attachment 1 hereto, and the incorporation of the proposed new and amended test methods for stationary sources as set forth in Attachment 2 hereto, are necessary and appropriate to satisfy the requirements of Sections 39601 and 39607(d) of the Health and Safety Code; and

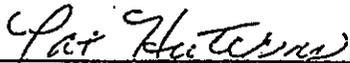
The actions approved herein will have no significant adverse environmental impacts, and will have no, or an insignificant, impact on California business enterprises; and

There is no alternative considered by the Board which would be more effective and less burdensome to public agencies, small businesses, or private persons or businesses, other than small businesses, than the proposed action.

NOW, THEREFORE, BE IT RESOLVED that the Board hereby approves the amendment of Title 17, California Code of Regulations, Sections 94105, 94107, 94114, 94135, 94141, and 94143 and the adoption of Title 17, California Code of Regulations, Section 94161, as set forth in Attachment 1 hereto, and the amendment and adoption of the incorporated test methods for stationary sources, Methods 5, 7, 100, 425, 429, 431, and 436, respectively, as set forth in Attachment 2, hereto.

BE IT FURTHER RESOLVED, that the Board directs the Executive Officer to make minor modifications to the test methods for stationary sources, provided that the Executive Officer determines that such modifications are necessary. The Executive Officer shall make such modifications available to the public for a period of 15 days, as required by Government Code Section 11346.8, shall consider such written comments as may be submitted during this period, shall make modifications as may be appropriate in light of the comments received, and shall present the modifications to the Board for further consideration if he determines this is warranted.

I hereby certify that the above is a true and correct copy of Resolution 96-46, as adopted by the Air Resources Board.

  
\_\_\_\_\_  
Pat Hutchens, Clerk of the Board

California Environmental Protection Agency  
AIR RESOURCES BOARD

Attachment B

STATIONARY SOURCE TEST METHODS

Proposed "Fifteen Day Changes" for

September 26, 1996 Public Hearing

Attached are the proposed modifications to the text of ARB Test Methods 5, 100, 425, 429, 431 and 436, as originally set forth in the Staff Report released on August 9, 1996. Only those pages or portions of the test method containing the proposed modifications are included. For Methods 100, 425, 429, 431 and 436, proposed additions to the original new and revised methods are noted by underline and proposed deletions are noted by ~~strikeout~~. For Method 5, proposed additions are noted by *italic* and proposed deletions are noted by ~~strikeout~~.

March 31, 1997

State of California  
California Environmental Protection Agency  
Air Resources Board

Method 5

Determination of Particulate Matter Emissions  
from Stationary Sources

Adopted: June 29, 1983  
Amended: March 28, 1986  
Amended: January 7, 1988  
Amended: \_\_\_\_\_

This document includes the text of Method 5, as proposed in the Staff Report released August 9, 1996. Proposed deletions were noted by ~~graphic screen~~ and proposed additions were noted by underline. Additional proposed modifications are indicated as follows:  
Proposed deletions are noted by ~~strikeout~~ and proposed additions are noted by *italic*.

0.5 g using a balance. This step may be conducted in the field.

"Acetone Blank" Container. Measure acetone in this container either volumetrically or gravimetrically. Transfer the acetone to a tared 250-ml beaker and evaporate to dryness at ambient temperature and pressure. Desiccate for 24 hours and weigh to a constant weight. Report the results to the nearest 0.1 mg.

Note - At the option of the tester, the contents of Container No. 2 as well as the acetone blank container may be evaporated at temperatures higher than ambient. If the evaporation is done at an elevated temperature, the temperature must be below the boiling point of the solvent; also, to prevent "bumping," the evaporation process must be closely supervised, and the contents of the beaker must be swirled occasionally to maintain an even temperature. Use extreme care, as acetone is highly flammable and has a low flash point.

#### 4.3.1 Impinger Catch and Extract

4.3.1.1 The impinger catch consists of the water and organic solvent<sup>2</sup> rinsings from the sample train connections between the filter and impingers, plus the impinger contents. ~~These are usually received in 1 to 4 one pint wide-mouth Mason jars~~

Field Blanks of water and methylene chloride described in 4.2.1 shall be analyzed for solids content by evaporation. The impinger catch and impinger catch extract residue weights shall be corrected based on these analyses and the total volume of each reagent used. Accordingly, determine the amount of water and solvent in the sample containers before proceeding. The methylene chloride used in the extraction shall also have a blank run on it similar to those run for the water and acetone. The methylene chloride extraction is to be corrected the same way the acetone rinse is.

The residues of the impinger catch solvent extract and impinger catch are to be weighed to a constant weight as defined earlier.

4.3.1.2 Combine the catch in a separatory funnel of suitable size. The Mason-jar sample container is to be rinsed with methylene chloride into the separatory funnel.

4.3.1.3 Extract the aqueous catch three times with 50 ml portions of methylene chloride ( $\text{CH}_2\text{Cl}_2$ ). Each time, extract for 30 seconds with vigorous shaking, then allow the layers to separate (which may sometimes take up to 15 minutes due to emulsion formation). Drain the  $\text{CH}_2\text{Cl}_2$  layers into a beaker of suitable size through a short stem funnel containing a cotton plug, to

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<sup>2</sup> Methylene Chloride ( $\text{CH}_2\text{Cl}_2$ ) unless the source being evaluated dictates otherwise, then an alternate solvent may be used subject to approval of the Executive Officer. ~~usually benzene is used~~

PROPOSED  
Appendix A of Method 5

Guidelines for Field Calculation of Target Values for  $D_n$  and  $\Delta H$

Section 4.1.5 of Method 5 requires that an isokinetic sampling rate be maintained during sampling, normally within +/-10% of the true isokinetic rate. No specific procedures are specified for adjustment of sampling rate. Rather the intent is that the departure from true isokinetic be calculated as specified by Section 6.11 after the completion of sampling. Some departure from true isokinetic is recognized as inevitable, in part because stack conditions during sampling including moisture content may vary and can not be anticipated completely or accommodated instantaneously.

The principle means of keeping sampling rates near true isokinetic are:

- (1) selection of an appropriate nozzle diameter  $D_n$
- (2) adjustment of console valves to keep  $\Delta H$  (orifice meter differential pressure in inches of water) at or near a calculated appropriate value.

Rapid and reliable calculation of target values for these parameters in the field is facilitated by use of nomographs, special slide rules or pre-programmed portable calculators or computers. Calculators and computers are becoming more popular for this purpose but the references cited in EPA Method 5 pertain only to the basis and use of nomographs originally developed by EPA. The purpose of this appendix is to present equations which can be programmed into a portable calculator or computer. Because different programming languages are used by or available on different calculators and computers it is impractical and beyond the scope of this appendix to present complete programs for the execution of these calculations.

Estimation of Orifice Differential Pressure from Pitot Pressure

$$\Delta H = [ 846.72 D_n^4 \Delta H_{@} C_p^2 (1 - B_{ws})^2 (M_d / M_s) (T_m / T_s) (P_s / P_m) ] \Delta p$$

Estimation of Ideal Nozzle Diameter

$$D_n = [ 0.035 Q_m P_m (1 - B_{ws}) / (T_m C_p (1 - B_{ws})) ]^{0.5} [ T_s M_s / (P_s \Delta p) ]^{0.25}$$

Nomenclature

The nomenclature for these equations is the same as as defined in Section 6.1 of Method 5 except that

$$P_m = \text{meter pressure} = P_{\text{barr}} + \Delta H / 13.6,$$

$$Q_m = \text{orifice meter flow rate} \\ = [ 0.9244 / \Delta H_{@} ]^{0.5} [ T_m \Delta H / (P_m M_m) ]^{0.5}$$

$$M_m = \text{molecular weight of metered gas stream, approximately the same as } M_d.$$

Equations are from the APTI Course 450 instructor's manual.

**State of California  
California Environmental Protection Agency  
Air Resources Board**

**Method 100**

**Procedures for Continuous Gaseous  
Emission Stack Sampling**

**Adopted: June 29, 1983  
Amended: \_\_\_\_\_**

This document includes the text of Method 100, as proposed in the Staff Report released August 9, 1996. Additional proposed modifications are indicated as follows:  
Proposed deletions are noted by ~~graph screen~~ and proposed additions are noted by underline.

5	SAMPLE COLLECTION .....	9
6	POST TEST PERFORMANCE CHECKS .....	9
6.1	ZERO AND CALIBRATION DRIFT .....	9
6.2	SAMPLING SYSTEM BIAS .....	10
7	CALCULATIONS .....	11
7.1	POLLUTANT CONCENTRATION .....	11
7.2	MASS EMISSION RATE .....	11
7.3	POLLUTANT CONCENTRATION FOR 12% CO <sub>2</sub> OR 3% O <sub>2</sub> .....	12
	TABLE 100.1 GAS ANALYZER SPECIFICATIONS .....	13
	FIGURE 100.1 METHOD 100 SAMPLE TRAIN ASSEMBLY .....	16
	APPENDIX 100.1 VERIFICATION OF GAS DILUTION SYSTEMS FOR FIELD INSTRUMENT CALIBRATIONS .....	AT

The analyzers shall be housed in a temperature-controlled, vibration-free environment.

### 2.2.2 Carbon Dioxide and Carbon Monoxide

Nondispersive infrared analyzers are acceptable.

### 2.2.3 Oxygen

A paramagnetic analyzer or an electrochemical (fuel cell) analyzer is acceptable.

### 2.2.4 Total Hydrocarbons

An analyzer using a flame ionization detector (FID) or a nondispersive infrared analyzer (NDIR) is acceptable. Propane or methane is usually used as a span gas. ~~Note~~ The hydrocarbon species should be characterized prior to the source test to determine that the detector will respond predictably to the organic compounds present. Compound-specific calibration curves must be determined for use of either the FID or the NDIR analyzer to measure specific organic compounds.

### 2.2.5 Oxides of Nitrogen

An analyzer using chemiluminescence is acceptable. The  $\text{NO}_2$  to  $\text{NO}$  converter must have at least a 90% efficiency in converting nitrogen dioxide ( $\text{NO}_2$ ) in the sample gas to nitric oxide ( $\text{NO}$ ). A  $\text{NO}_2$  to  $\text{NO}$  converter is not necessary if data are presented to demonstrate that the  $\text{NO}_2$  portion of the exhaust gas is less than 5 percent of the total  $\text{NO}_x$  concentration. A low temperature (maximum  $350^\circ\text{C}$ ) converter must be used when  $\text{NH}_3$  is present. A high temperature ( $650^\circ\text{C}$ ) stainless steel converter may be used when no  $\text{NH}_3$  is present.

If data are not available to demonstrate that the concentration of  $\text{NO}_2$  in the sample gas is less than 5% of the total  $\text{NO}_x$  concentration, a test of the efficiency of the  $\text{NO}_2$  converter must be conducted prior to each source test.

### 2.2.6 Sulfur Dioxide

An analyzer using infrared or ultraviolet absorption or fluorescence is acceptable.

### 2.2.7 Other Analyzers

An analyzer operating by measurement principles not listed in Table 100.1 may be used, if its performance meets the requirements of Table 100.1.

### 2.2.8 Data Acquisition System/Data Recorder

Provide a permanent record of gas analyzer data using a strip chart recorder. ~~A data logger or other electronic data acquisition system, if a data recorder is not~~

~~used. a real time hardcopy of test data must be provided upon request.~~ A data logger or other electronic data acquisition system may also be used. Any electronic data acquisition system must be capable of integration at a ten second interval. ~~Any data acquisition system~~ The strip chart, as well as the data acquisition system, must have a resolution of 0.5 percent of the analyzer range. Data reporting includes the following information: pollutant, source, analyzer range, date, time, zero offsets, person operating instruments, and any other pertinent data.

## **2.3 MEASUREMENT OF STACK FLOWRATE, MOISTURE, AND OTHER PARAMETERS**

### **2.3.1 Stack Gas Flowrate and Moisture Measurement**

Stack gas flowrate and moisture content can be determined using equipment specified by ARB Test Methods 1 through 4. Stack gas velocity can be determined from a pitot tube measurement as outlined by Methods 1 and 2. Two possible alternatives are:

- (1) A simultaneous traverse of stack gas concentration and velocity,
- (2) A pre and a post test velocity traverse. (Repeat the velocity traverse whenever aware of a change in process conditions which may affect emissions.)

Note: If the pitot tube and the sampling probe are used in combination in a testing assembly, care must be taken that any aerodynamic effects on the pitot tube are eliminated. Otherwise, the pitot tube must be calibrated with the other components of the test assembly in place. (See ARB Method 2, Section 4.1.1.)

Alternate methods of flowrate measurement, including consideration of fuel rate, combustion stoichiometry and oxygen concentration in the stack gas and applicable F-factors listed in 40 CFR Part 60 Appendix A, Method 19, must be approved by the Executive Officer of the Air Resources Board or his or her authorized representative.

### **2.3.2 Barometer**

A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg. shall be used.

### **2.3.3 Vacuum Gauge or Flowmeter**

Use a vacuum gauge or a flowmeter for leak check of the sampling train.

### 3 CALIBRATION GASES

#### 3.1 Calibration Gases

The calibration gases must be certified according to EPA Traceability Protocol<sup>1</sup>. Alternately the calibration gases must be certified to an analytical accuracy of  $\pm 2$  percent, traceable to a reference material approved by the National Institute of Standards and Technology (NIST), and recertified annually.

Multi-component gas mixtures certified according to EPA Protocol are acceptable. Multi-component gas mixtures which meet the following requirements are also acceptable: the concentration of each component gas must be certified to an analytical accuracy of  $\pm 2$  percent, each component must be traceable to a NIST standard, and the mixture must be recertified semi-annually.

A permeation tube may be used as a calibration standard in place of the calibration gas, provided the following requirements of EPA Method 16 (CFR 60 Appendix A) are met for use of permeation tubes: Section 5.5 for the calibration system, Section 6.5 for the calibration gases, Sections 8.2 and 8.3 on pretest calibration, and Sections 10.2 and 10.3 on post test calibration.

For each pollutant to be measured, use the following three calibration gases:

##### 3.1.1 High-Range Gas

The concentration should be between 80 and 100 percent of the analyzer range.

##### 3.1.2 Mid-range Gas

The concentration should be between 40 and 60 percent of the analyzer range.

##### 3.1.3 Zero Gas

Purified air or, if appropriate, nitrogen with a contaminant concentration less than 0.25% of the analyzer range for the appropriate pollutant gas may be used.

#### 3.2 GAS DILUTION SYSTEM

An approved gas dilution system which meets the requirements of EPA Method 205, Verification of Gas Dilution Systems for Field Instrument Calibrations, CFR 40, Part 51, Appendix M, can may be used to provide low-level calibration gases from a high-level calibration gas. The calibration gas used with a gas dilution system must should be an EPA Protocol gas. Alternately the gas used with a diluter must be

<sup>1</sup> "EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards," EPA-600/R93/224, Revised September 1993.

certified to an analytical accuracy of  $\pm 1$  percent, NIST-traceable, and recertified annually. See Appendix 100.1 for the performance specifications of a gas dilution system. An approved gas dilution system which meets the requirements of EPA Method 205 may be used for all analyzer calibrations and sampling system bias checks.

## **4 ON-SITE PREPARATION FOR SAMPLING**

### **4.1 CLEANING/ASSEMBLY OF SAMPLE TRAIN**

The sample train may be cleaned prior to being transported to the field. When at the testing site, assemble the cleaned sample train as shown in Figure 100.1.

### **4.2 CALIBRATION OF CONTINUOUS ANALYZERS**

Allow analyzers to warm up according to manufacturer's instructions. Adjust system components to achieve the individual analyzer sampling rates recommended by the instrument manufacturer. Alternately introduce zero and calibration gases to the instruments and make all necessary adjustments to calibrate the analyzer and the data recorder.

Conduct the analyzer calibration error check by sequentially introducing the three calibration gases (high-range, mid-range and zero gas) and recording the analyzer response to each calibration gas. Make no adjustments to the sampling/analysis system except those necessary to achieve the proper calibration gas flowrate. The test run will be considered invalid if the analyzer calibration error for any calibration gas exceeds  $\pm 2$  percent of the range. If needed, take corrective action until acceptable performance is achieved.

### **4.3 PRETEST LEAK CHECK**

Perform a leak check on the vacuum side of the assembly at the maximum pump vacuum. Correct any leaks found and repeat the leak check and correction procedure until no leak is detected.

### **4.4 SAMPLE SYSTEM BIAS CHECK**

A pretest sampling system bias check is required for each gas analyzer.

Perform the sampling system bias check by alternately introducing at the probe the zero gas and either the high-range or mid-range calibration gas, whichever calibration gas is closest in concentration to the sample gas. Record the gas concentrations displayed by the analyzer. During the sampling system bias check operate the system at the normal sampling rate and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rate. Determine the sampling system response time.

If the difference between the gas concentrations for the analyzer calibration error check and the sample system bias check exceeds  $\pm 5\%$  of the range for either the zero or upscale calibration gas, the bias check is invalid. If needed, take corrective action before repeating the sample system bias check. If the analyzer is adjusted, repeat the analyzer calibration error check before repeating the bias check.

#### 4.5 DETERMINATION OF SAMPLING TRAVERSE POINTS

Select gas sampling traverse points according to the guidelines given in ARB Methods 1 and 2 for velocity traverses. Multipoint gas sampling must be performed unless data are available to demonstrate that the mean pollutant concentration is less than 10% different from that at any single point.

### 5 SAMPLE COLLECTION

Insert the sample probe assembly into the stack and block off the remainder of the sample port opening. Set the probe at the predetermined position and begin data acquisition. If a traverse is required, the sampling time at each traverse point is constant. Sample for at least the sampling system response time plus one minute, allowing enough time for the system to be flushed and the instruments to respond fully. Move probe to next position and repeat. Continue until the stack has been fully traversed.

A test shall include at least three sample runs. Each sample run shall be the length of time specified in the applicable emission limit regulation. As a minimum, the sampling time must be such that the emission test is conducted during representative operating conditions of the source. For a sample run ~~test duration~~ exceeding two hours, conduct sampling system bias checks every two hours. Record performance check data. As necessary, back flush through the probe to prevent particulate build-up on the probe filter. Periodically check the sample conditioner and remove condensate as needed.

If adjustments to the sampling train are necessary during the sample run, conduct a system bias check before any adjustments are made. After any adjustments are made to the analyzer, the analyzer calibration error check shall be conducted. After all adjustments are made to the sampling system, the sampling system bias check shall be performed prior to continuation of the test run.

### 6 POST TEST PERFORMANCE CHECKS

At the end of the sample run, conduct a sampling system bias check for all analyzers. Perform the sampling system bias check by alternately introducing the zero gas and the calibration gas at the probe. During the sampling system check operate the system at the normal sampling rate and make no adjustments to the measurement system other than those necessary to achieve proper calibration gas flow rates through the sampling system to the gas analyzer.

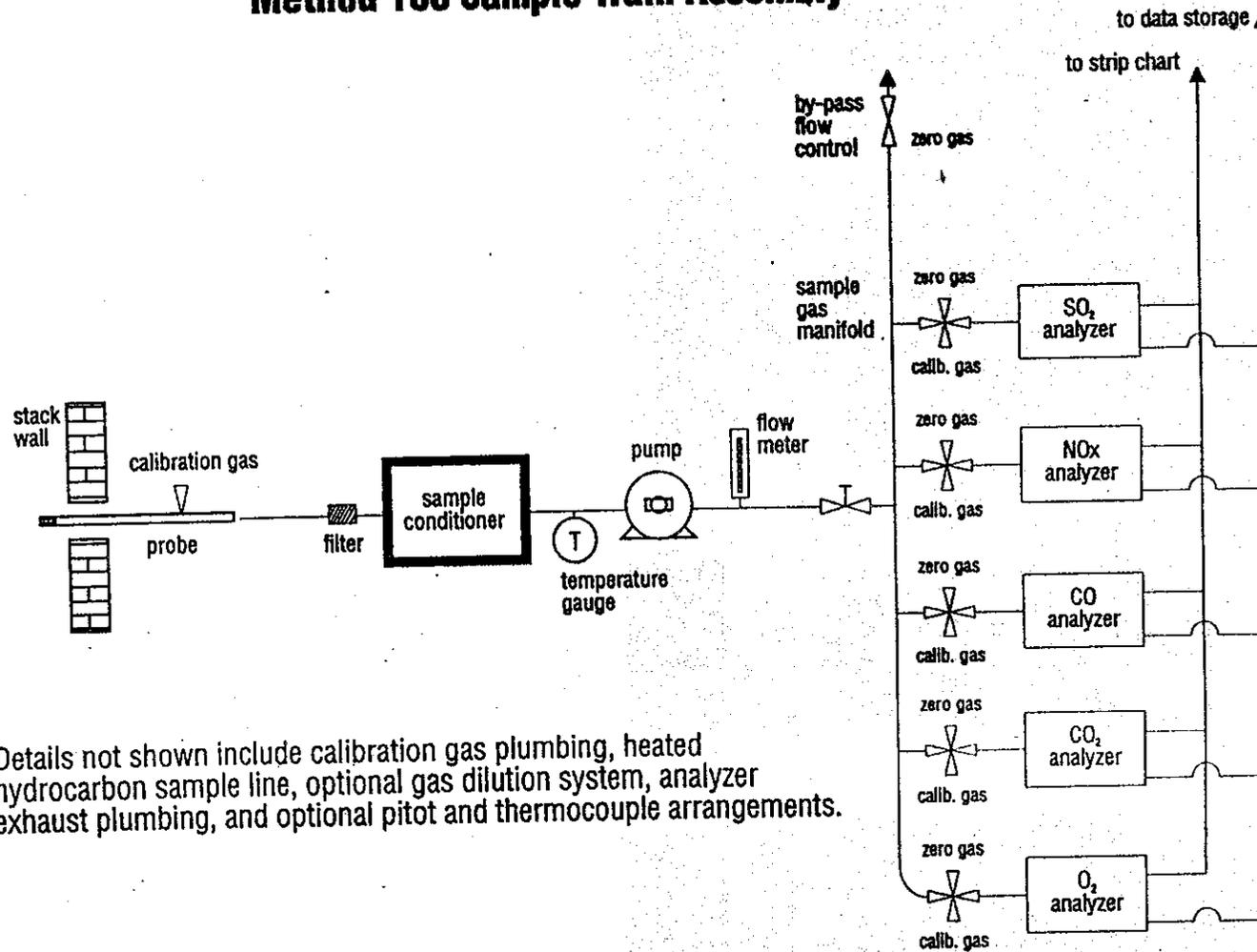
**Table 100.1 (page 2 of 3)  
Gas Analyzer Specifications**

	SULFUR DIOXIDE	OXIDES OF NITROGEN	CARBON MONOXIDE	CARBON DIOXIDE	HYDROCARBONS	OXYGEN
Repeatability, % of range <sup>3</sup>	1%	1%	1%	1%	1%	1%
Zero Drift after 24 hours of unadjusted continuous operation, % range	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%
Span Drift after 24 hours of unadjusted continuous operation, % range	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%	< ± 1%
Interference of a component other than the target component measured by the gas analyzer, % of range	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %	< ± 5 %
Analyzer response to temperature variation <sup>4</sup>	✓	✓	✓	✓	✓	✓

<sup>3</sup> ~~1%~~ 1% of the analyzer range is the maximum absolute difference between replicate results which may be expected with a probability of 95%.

<sup>4</sup> When sampling zero or span gas, the analyzer response shall not change more than ± 2% of range when the ambient temperature changes ± 10°C from 25°C.

**FIGURE 100.1**  
**Method 100 Sample Train Assembly**



\* Details not shown include calibration gas plumbing, heated hydrocarbon sample line, optional gas dilution system, analyzer exhaust plumbing, and optional pitot and thermocouple arrangements.

## Appendix 100.1

### Verification of Gas Dilution Systems for Field Instrument Calibrations

#### 1 INTRODUCTION

##### 1.1 Applicability

A gas dilution system satisfying the requirements of this Appendix may be used in place of multiple calibration gases for all field calibrations required in ARB Method 100.

##### 1.2 Principle

A gas dilution system produces a variety of known concentrations of calibration gases through controlled dilution of a known high-level calibration gas with a dilution gas. Performance of the gas dilution system is verified in the field by using a gas analyzer which has been previously calibrated.

##### 1.3 Alternative Method

U.S. EPA Method 205, Verification of Gas Dilution Systems for Field Instrument Calibrations, CFR 40, Part 51, Appendix M, is an acceptable alternative method for gas dilution system calibration.

#### 2 DEFINITIONS

##### 2.1 Dilution Device

The mass flow controller, critical orifice, capillary tubes, positive displacement pump or any other component which is used to achieve the correct gas dilution.

#### 3 SPECIFICATIONS

##### 3.1 Gas Dilution System

The gas dilution system shall produce calibration gas mixtures which have measured values within  $\pm 2\%$  of the predicted values. The predicted values are calculated based on the certified concentration of the calibration gas and the gas flow rates or dilution ratios through the gas dilution system.

##### 3.2 Annual Certification Procedure

The gas dilution system shall be calibrated prior to initial use in the field, after repair or maintenance, and once every twelve months with NIST-traceable primary flow standards with an uncertainty of 0.25 percent. A label shall be affixed at all times to

the gas dilution system listing the date of the most recent calibration, the due date for the next calibration, and the person or manufacturer who carried out the calibration. A copy of the most recent recalibration documentation shall be made available upon request.

### 3.3 Mass Flow Controller Systems

The accuracy of mass flow controllers diminishes at low flow rates. Therefore, a mass flow controller shall be operated above ten percent (10%) of the mass flow controller capacity.

### 3.4 Gases

#### 3.4.1 High-Level Calibration Gas

U.S. EPA Protocol gases or NIST-traceable standard gases certified to  $\pm 1\%$  analytical accuracy are required for the high-level calibration gas. (Safety Warning: Some high concentration gases may require special placarding regarding flammability or other hazards.)

#### 3.4.2 Mid-Level Calibration Gas

A U.S. EPA Protocol gas or a NIST traceable standard gas certified to  $\pm 1\%$  analytical accuracy shall be used as an independent check of the dilution system. The undiluted mid-level calibration gas shall be within 10 percent of one of the dilution levels tested in Section 4.3.

#### 3.4.3 Dilution Gases

Nitrogen or purified air, if appropriate, with a concentration of less than 0.25% of the range of the appropriate gas analyzer.

## 4 FIELD EVALUATION OF THE GAS DILUTION SYSTEM

The gas dilution system shall be evaluated at the test site with a gas analyzer calibrated according to Section 4.2 of ARB Method 100. The calibration gas used to calibrate the gas analyzer shall be a U.S. EPA Protocol gas or a NIST-traceable gas certified to  $\pm 1\%$  analytical accuracy.

4.1 Prepare the gas dilution system according to the manufacturer's instructions. Using the high-level calibration gas, prepare dilutions according to the following procedures:

(1) For each variable flow device, such as a mass flow controller or capillary tube gas divider, prepare two dilutions within the range of the dilution device.

(2) For each dilution device used to make one dilution, such as a critical orifice or a positive displacement pump, prepare one dilution.

4.2 Calculate the predicted concentration of each of the above dilutions based on the flow rates through the gas dilution system or the dilution ratios and the certified concentration of the high-level calibration gas.

4.3 Introduce each of the dilutions from Section 4.1 into the gas analyzer one at a time and determine the instrument response for each of the dilutions.

4.4 For each dilution level, calculate the difference between the concentration measured by the analyzer and the predicted concentration calculated in Section 4.2. The difference shall be within  $\pm 2\%$  of the range of the gas analyzer.

4.5 Introduce the mid-level calibration gas directly into the analyzer, bypassing the gas dilution system. The difference between the certified concentration of the mid-level calibration gas and the instrument response shall be within  $\pm 2\%$  of the range of the gas analyzer.

#### 5 USE OF FIELD-VERIFIED GAS DILUTION SYSTEM

If the gas dilution system meets the criteria listed in Section 4, the gas dilution system may be used throughout that field test. If the gas dilution system fails any of the criteria listed in Section 4 and the tester corrects the problem with the gas dilution system, the procedure in Section 4 must be repeated in its entirety and all the criteria in Section 4 must be met in order for the gas dilution system to be utilized in the test.

**State of California  
California Environmental Protection Agency  
Air Resources Board**

**Method 425**

**Determination of Total Chromium and Hexavalent Chromium  
Emissions from Stationary Sources**

**Adopted: January 22, 1987  
Amended: September 12, 1990  
Amended: \_\_\_\_\_**

This document includes the text of Method 425, as proposed in the Staff Report released August 9, 1996. Additional proposed modifications are indicated as follows:

Proposed deletions are noted by ~~graph screen~~ and proposed additions are noted by underline.

## 2.4 Limit of Detection

The limit of detection (LOD) is a limit of the performance of the analytical procedures below which quantitative results must not be reported. The LOD is based on the absolute value of the x-intercept of the calibration plot for absorbance versus concentration adjusted by three times the standard deviation of the absorbance for a mid-point concentration.

## 2.5 Reporting Limit

The reporting limit (RL) is a limit of the performance of the entire test method below which quantitative mass analyses must not be reported for a given sample run. The RL is based on the minimum analyte mass that must be collected in the sampling train to allow detection by the laboratory according to the requirements of this method. Such mass is the product of the LOD and the liquid volume used to collect the analyte in the sampling train.

## 2.6 Source Reporting Limit

The source reporting limit (SRL) is a limit of the performance of the entire test method below which quantitative emission results must not be reported.

# 3 PRE-TEST PROTOCOL

## 3.1 Responsibilities of the End User and Tester

### 3.1.1 The End User

Before testing may begin, the end user of the test results must specify the source target concentration to be determined by this method using the guidelines of § 3.2.1.

The end user shall approve the pre-test protocol after reviewing the document and determining that the minimum requirements for the pre-test protocol (§ 3.2) have been met.

### 3.1.2 The Tester

The tester shall have primary responsibility for the performance of the test method, and shall co-ordinate the efforts of the sampling and analytical groups.

The tester shall plan the test based on the information provided by the end user and the tester's calculations of target source testing parameters.

The tester shall be responsible for selection of an analyst qualified for use of the method. The tester shall make that decision based on information supplied by the analyst.

### 3.5.5 Planned Sampling Time (PST)

The planned sampling time (PST) is calculated using Equation 425-7.

$$PST = MST \times F \quad 425-7$$

Where:

PST = planned sampling time, hours  
MST = minimum sampling time, hours  
F = safety factor for detection ( $F \geq 1$ )

### 3.5.6 Pre-Test Calculation of Source Reporting Limit (SRL)

Before the test proceeds, the end user and the tester shall agree on a preliminary estimate of the reporting limit for emissions of Cr6 from the source. Notice that the SRL is higher than the STC if F is less than one in which case it is unsafe to assume that Cr6 will be detected at the STC.

Equation 425-4 shall be used to calculate the SRL.

$$SRL = \frac{RL}{PSV} \quad 425-8$$

Where:

SRL = source concentration reporting limit, ng/dscm  
RL = analytical mass reporting limit, ng  
PSV = planned sampling volume, dscm

## 4 BIASES AND INTERFERENCES

### 4.1 Sample Instability

Chromium is subject to changes in valence state during the time between sampling and ~~analysis~~ recovery hold time. Take all reasonable precautions, some of which are required in various sections of this method, to minimize all influences which may change the valence states of chromium in each sample. Factors which influence such changes are hold time, pH, and other chemical species.

Recovery of trains shall take place within 24 hours of sampling. Storage between recovery and analysis shall be at or below 4C and shall be limited to two weeks.

### 4.2 Cr6 IC-C Interferences

A high ionic concentration in the sample may overload the chromatographic column, altering the retention time and/or the shape of the chromate peak. Anionic species such as molybdate or vanadate which will react with the 1,5 diphenylcarbazide post-column reagent to form a colored product absorbing at

Based on the procedures given in the "Pre-Test Protocol," an LOD as low as 0.5 ng/mL has been observed; this is not a default value as achievement of such low levels depends upon the skill of the analytical team.

## 5.2 Cr6 M-C Sensitivity

Based on the procedures given in the "Pre-Test Protocol," an LOD as low as 4.0 ng/mL has been observed; this is not a default value as achievement of such low levels depends upon the skill of the analytical team.

## 5.3 Cr GF-AA Sensitivity

EPA Method 306, Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations, reports a value of 1.0 ng/mL, based on method 7191 of SW-846. For some sample matrices, the Cr GF-AA sensitivity can be lower than the Cr6 IC-C sensitivity.

# 6 RANGE

## 6.1 Cr6 IC-C Range

Using sample loops of 10 uL to 250 uL, the linear range of this procedure without dilution or concentration of the sample is approximately 0.5 ng Cr6/mL to 40 µg Cr6/mL.

## 6.2 Cr6 M-C Range

A straight line response curve was obtained in the range 0.5 µg Cr6 /50 mL to 3.0 µg Cr6 /50 mL (10 to 60 ng/mL). The range can be expanded to 0.5 to 50 µg/mL, provided that the residuals are less than 10%. For a minimum analytical accuracy of  $100 \pm 10$  percent, the lower limit of the range is 2 µg/100mL. The upper limit can be extended by appropriate dilution or by using a smaller cell path length after recalibration for the smaller cell.

## 6.3 Cr GF-AA Range

EPA Method 306, Determination of Chromium Emissions from Decorative and Hard Chromium Electroplating and Anodizing Operations, reports an optimum range of 5 to 100 ng/mL, based on method 7191 of SW-846. For some sample matrices, the Cr GF-AA range can be broader than the Cr6 IC-C range.

# 7 EQUIPMENT

All surfaces which may come in contact with sample shall be glass, quartz, Teflon, or other similarly non-metallic (stainless steel may be a source of chromium contamination) inert material.

9.3.1 Batch of 0.1N NaOH Solution

See "PREPARATION OF REAGENTS."

9.3.2 Water

All water used in this procedure shall, at minimum, conform to the specifications of American Society for Testing and Materials (ASTM) Type II reagent water as specified in ASTM Test Procedure D 1193. Use of ASTM Type I reagent water shall be an acceptable alternative.

9.3.3 Eluent

Dissolve 33 g of ammonium sulfate in water in a 1 L Class A volumetric flask. Add 6.5 mL of 29% ammonium hydroxide and make to volume. The concentration of the prepared eluent is 250 mM  $(\text{NH}_4)_2\text{SO}_4$  and 100 mM  $\text{NH}_4\text{OH}$ .

9.3.4 Post-Column Reagent

Dissolve 0.5 g of 1,5 diphenylcarbazide in 100 mL of glass distilled HPLC grade methanol. Add to approximately 500 mL of degassed or nitrogen purged or helium purged water containing 28 mL of 96-98% sulfuric acid, and make to 1 L with degassed or nitrogen purged or helium purged water. High purity sulfuric acid such as EM Science Suprapur grade or JT Baker Ultrex grade is recommended. The stability of the post-column reagent is enhanced by preparing it in a nitrogen atmosphere, pressurizing the reagent reservoir with nitrogen, and shielding it from light.

9.3.5 Cr6 Stock Solution

Prepare a standard solution containing 1000  $\mu\text{g}$  Cr6 /mL as a solution of potassium dichromate in water. Use analytical reagent grade  $\text{K}_2\text{Cr}_2\text{O}_7$  which has been dried at 105° C for at least one hour. Dissolve 2.8289 g of the dried  $\text{K}_2\text{Cr}_2\text{O}_7$  in water in a class A volumetric flask and make to volume with water. Alternatively, obtain a chromate standard solution in water prepared specifically for use in ion chromatography.

Storage shall be at or below 4°C and shall be limited to four weeks.

9.3.6 Regenerant Solution for the DIONEX MPIC-NG1 Guard Column (or equivalent)

In this application, the DIONEX MPIC-NG1 guard column (or equivalent) is used to trap organic compounds which could adversely affect the anion chromatographic columns. The trapped organic compounds shall be flushed from the column periodically using a 70-90% solution of acetonitrile or methanol in water.

9.4 Cr6 M-C Analytical Reagents

Inject a series of Cr6 calibration standards which brackets the sample concentrations. Also, use a zero standard. Typically, 4 to 6 calibration standards will be sufficient to establish the calibration curve. The recommended procedure is to inject one series of calibration standards before the samples, to establish that the system is working properly and has reached equilibrium so that a linear response is attained. A second set of calibration standards is injected at the end of the analytical run to confirm constancy of response throughout the run. If the peak areas or peak heights of the two sets of calibration standards differs by more than 5% the run shall usually be repeated. If any drift in response which may have occurred is within acceptable limits, use the concentration and response values of the two sets of calibration standards to establish a calibration curve which is used to quantitate the Cr6 concentration in the samples.

Inject a check standard prior to the tenth run of the instrument since its last calibration run.

#### 11.4 Cr6 M-C Analytical Calibration Procedure

- (1) Calibrate the wavelength scale of the spectrophotometer every 6 months. The calibration may be accomplished by using an energy source with an intense line emission such as a mercury lamp, or by using a series of glass filters spanning the measuring range of the spectrophotometer. Calibration materials are available commercially and from the National Institute of Standards and Technology. Specific details on the use of such materials shall be supplied by the vendor; general information about calibration techniques can be obtained from general reference books on analytical chemistry. The wavelength scale of the spectrophotometer shall read correctly within  $\pm 5$  nm at all calibration points; otherwise, the spectrophotometer shall be repaired and recalibrated. Once the wavelength scale of the spectrophotometer is in proper calibration, use 540 nm as the optimum wavelength for the measurement of the absorbance of the standards and samples.
- (2) Alternatively, a scanning procedure may be employed to determine the proper measuring wavelength. If the instrument is a double-beam spectrophotometer, scan the spectrum between 530 and 550 nm using a 50  $\mu$ g Cr6 standard solution in the sample cell and a reagent blank solution in the reference cell. If a peak does not occur, the spectrophotometer is malfunctioning and shall be repaired. When a peak is obtained within the 530 to 550 nm range, the wavelength at which this peak occurs shall be the optimum wavelength for the measurement of absorbance of both the standards and the samples. For a single-beam spectrophotometer, follow the scanning procedure described above, except that the reagent blank and standard solutions shall be scanned separately. The optimum wavelength shall be the wavelength at which the maximum differences in absorbance between the standard and the reagent blank occurs.
- (3) Either (1) run a series of 4 to 6 chromium calibration standards and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) if matrix effects require the method of standard additions (see 17.2.1), plot added concentration versus absorbance.

- (4) Freshly make up each standard for Cr6 in a separate 50 mL volumetric flask starting with 35 mL of the same batch of NaOH solution reserved for its sample set. Then add an appropriate amount of Cr6 to each calibration standard, starting with none for the zero standard. Then add 6N sulfuric acid and diphenylcarbazide solution in the same manner as in sample preparation.
- (5) Inject a check standard prior to the tenth run of the instrument since its last calibration run.

#### 11.5 Cr GF-AA Analytical Calibration Procedure

- (1) Calibration standards for total chromium shall start with 1% v/v HNO<sub>3</sub> with no chromium for the reagent blank with appropriate increases in total chromium concentration in the other calibration standards. The calibration standards shall be prepared following the steps outlined for sample preparation in the analytical procedures.
- (2) Check standards shall be prepared in the same manner as calibration standards. Check standards shall be prepared separately and independently from the calibration standards and shall serve to protect against errors in the preparation of the calibration standards.
- (3) Either (1) run a series of chromium standards and reagent blanks and construct a calibration curve by plotting the concentrations of the standards against the absorbances or (2) if matrix effects require the method of standard additions (see 17.2.1), plot added concentration versus absorbance. For instruments that read directly in concentration, set the curve corrector to read out the proper concentration.
- (4) Re-run the lowest calibration standard after approximately every 10 sample injections. Standards are run in part to monitor the life and performance of the graphite tube. Lack of reproducibility or a significant change in the signal for the standards indicates that the tube shall be replaced.
- (5) Duplicates, spiked samples, and check standards shall be routinely analyzed. This requirement is further specified in the quality assurance/quality control procedures.
- (6) Calculate Cr concentrations (1) from a calibration curve, or (2) by the method of standard additions, or (3) directly from the instrument's concentration readout. All dilution or concentration factors shall be taken into account. ~~Concentrations reported for multiphased or wet samples shall be appropriately qualified (e.g., 5 µg/g dry weight).~~
- (7) Calibration curves shall be composed of a minimum of a reagent blank and three total chromium standards. A calibration curve shall be made for every batch of samples, unless check standards remain within 10% of the last calibration curve.

For each preparation, transfer 35 mL of solution to a 100 mL beaker, adjust the pH to  $1.0 \pm 0.2$  with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide solution, dilute to volume with water in a 50 mL volumetric flask, and let color develop for 10 minutes.

#### 15.1.2 Hexavalent Chromium Sample Preparation

For each preparation, transfer 35 mL of solution to a 100 mL beaker, adjust the pH to  $1.0 \pm 0.2$  with 6N sulfuric acid, add 1.0 mL of diphenylcarbazide solution, dilute to volume with water in a 50 mL volumetric flask, and let color develop for 10 minutes. (This leaves at least 15 mL of sample split for further analyses. The total volume of sample split shall be known at this point.)

### 15.2 M-C Analysis

- (1) ~~The analyst shall filter the preparation for clarity at this point.~~ Filtration shall be an option for the analyst at this point, depending on the turbidity of the prepared sample. Medium retention filter paper shall be used. The filter paper shall be pre-wetted with a few mL of reagent blank and sample preparation. This will prime the filter so that it won't absorb color complex.
- (2) Transfer a portion of the filtered preparation into a 5 cm absorption cell.
- (3) Measure the absorbance at the optimum wavelength of 540 nm.
- (4) Subtract the sample blank absorbance reading to obtain a net reading.
- (5) If the absorbance reading of a sample preparation exceeds the calibration range, dilute with reagent blank or re-measure using less of the sample preparation. (There shall be about 15 mL remaining at this point.)

## 16 Cr GF-AA ANALYTICAL PROCEDURES

### 16.1 Cr GF-AA Preparation

#### 16.1.1 Cr Reagent Blank Preparation

For total chromium, the reagent blank is an aliquot of 1%  $\text{HNO}_3$ .

#### 16.1.2 Cr Sample Preparation

In a beaker, add 10 ml of concentrated nitric acid to the sample aliquot taken for analysis. Cover the beaker with a digestion coverglass. Place the beaker on a hot plate and reflux the sample down to near dryness. Add another 5 mL nitric acid to complete digestion. Reflux the sample volume down to near dryness.

Wash down the beaker walls and digestion cover with distilled water and filter the sample to remove silicates and other insoluble material that could

If instrument blank values are not automatically taken and subtracted by the instrument, report these calculations based on net values, and report all instrument blank values, too.

These are zero standards.

See below for determination of net values.

#### 19.1.2 Cr6 M-C Analytical Calculations

Report these calculations based on net values using Equation 425-11. Report all instrument blank values, too.

Net Value = Sample Train Component Value - Instrument Zero Blank Value 425-11

#### 19.2 Total Cr in the Sample Train (mCr)

Calculate and report mCr, the total  $\mu\text{g}$  of chromium in the sample train. This can be obtained from the calibration curve or from the method of standard additions. Note that mCr is the sum of the masses of total chromium analyses performed on all sample portions. Also take into account the necessary dilutions when calculating out mCr.

Calculations shall include only sample portions which have values above the LOD.

Do not subtract the LOD from the sample train values.

Report these calculations based on net values, and report all instrument blank values, too.

See above for determination of net values.

#### 19.3 Method 5 Testing Parameters

Except where otherwise noted in this method, follow the procedures of ARB Method 5 to determine:

(1) Standard Volume of Gas Sample  $\equiv$  (Vsample)

Typical units for Vsample are dry standard cubic meters, dscm.

(2) Isokinetic Variation

(3) Standard Volumetric Flow Rate of Stack Gas  $\equiv$  (Qstack)

Typical units for Qstack are dry standard cubic meters per hour, dscm/hour.

#### 19.4 Cr6 Mass Emission Concentration $\equiv$ Cr6 MEC

Calculate and report the Cr6 mass emission concentration in the stack gas, dry basis, corrected to standard conditions, using Equation 425-12:

### 21.3 Total Chromium Determination by Flame Atomic Absorption Spectroscopy

For high total chromium concentrations which are within the detection range of flame atomic absorption spectroscopy, this analytical method may be used instead of the furnace type method specified in these pages. This option applies only to the analysis of total chromium. The remainder of the test method shall be performed as specified.

### 21.4 Other Methods

Alternative test methods may be used provided that they are equivalent to Method 425 and approved in writing by the Executive Officer of the California Air Resources Board. The ARB Executive Officer may require the submittal of test data or other information to demonstrate equivalency.

## 22 REFERENCES

(1) US. Environmental Protection Agency/Office of Solid Waste, Washington, D.C., "Test Methods for Evaluating Solid Waste, Physical/Chemical Methods," Method 7191 SW-846 (1986), Third Edition.

(2) (1) EPA Method 5, Determination of Particulate Emissions from Stationary Sources, CFR 40, Part 60, Appendix A.

(3) (2) (Draft) Laboratory and Field Evaluations of Methodology for Determining Hexavalent Chromium Emissions from Stationary Sources; Prepared by: Anna C. Carver, Entropy Environmentalists, Inc., Research Triangle Park, NC 27709; EPA Contract No. 68-02-4550; Prepared for: Dr. Joseph E. Knoll, United States Environmental Protection Agency, Quality Assurance Division, Research Triangle Park, North Carolina 27711, UNDATED.

## 23 FIGURES

The following figures summarize features of this method:

Figure 1.  
Sample Collection and Recovery for Hexavalent and Total Chromium

Figure 2.  
Hexavalent Chromium Analysis

Figure 3.  
Total Chromium Analysis

**State of California  
California Environmental Protection Agency  
Air Resources Board**

**Method 429**

**Determination of Polycyclic Aromatic Hydrocarbon (PAH)  
Emissions from Stationary Sources**

**Adopted: September 12, 1989  
Amended: \_\_\_\_\_**

This document includes the text of Method 429, as proposed in the Staff Report released August 9, 1996. Additional proposed modifications are indicated as follows:  
Proposed deletions are noted by ~~graphic screen~~ and proposed additions are noted by underline.

## 4. SAMPLING APPARATUS, MATERIALS AND REAGENTS

### 4.1 SAMPLING APPARATUS

The sampling train components listed below are required. All surfaces which may come in contact with the sample or recovery solvents shall be of quartz, borosilicate glass or Teflon. The tester may use an alternative to the required sampling apparatus only if, after review by the Executive Officer, it is deemed equivalent for the purposes of this test method.

Mention of trade names or specific products does not constitute endorsement by the California Air Resources Board. In all cases, equivalent items from other suppliers may be used.

A schematic of the sampling train is shown in Figure 2. The train consists of nozzle, probe, heated particulate filter, condenser, and sorbent module followed by three impingers and a silica gel drying cartridge. An in-stack filter may not be used because at the in-stack temperatures the filter material must be of a material other than the Teflon required by the method. A cyclone or similar device in the heated filter box may be used for sources emitting a large amount of particulate matter.

For sources with a high moisture content, a water trap may be placed between the heated filter and the sorbent module. Additional impingers may also be placed after the sorbent module. If any of these options are used, details must be provided in the test report. The train may be constructed by adaptation of an ARB Method 5 train. Descriptions of the train components are contained in the following sections.

#### 4.1.1 Probe Nozzle

Quartz, or borosilicate glass with sharp, tapered leading edge. The angle of taper shall be 30° and the taper shall be on the outside to preserve a constant internal diameter. The probe nozzle shall be of the button-hook or elbow design, unless otherwise approved by the Executive Officer.

A range of sizes suitable for isokinetic sampling should be available, e.g., 0.32 to 1.27 cm (1/8 to 1/2 in.) - or larger if higher volume sampling trains are used - inside diameter (ID) nozzles in increments of 0.16 cm (1/16 in.). Each nozzle shall be calibrated according to the procedures outlined in Section 5.1 of ARB method 5.

#### 4.1.2 Probe

The probe ~~should~~ must be lined or made of Teflon, quartz, or borosilicate glass. ~~The liner or probe is to provide an inert surface for the PAH in the stack gas.~~ Other inert materials may be used only if they have been approved by the Executive Officer. The liner or probe extends past the retaining nut into the stack. A temperature-controlled jacket provides protection of the liner or probe. The liner shall be equipped with a connecting fitting that is capable of forming a leak-free, vacuum tight connection without the use of sealing greases.

#### 4.1.3 Preseparator

A cyclone, a high capacity impactor or other device may be used if necessary to remove the majority of the particles before the gas stream is filtered. This catch must be used for any subsequent analysis. The device shall be constructed of quartz or borosilicate glass. Other inert materials may be used subject to approval by the Executive Officer.

#### 4.1.4 Filter Holder

The filter holder shall be constructed of borosilicate glass, with a Teflon frit or Teflon coated wire support and glass-to-glass seal or Teflon gasket. The holder design shall provide a positive seal against leakage from the outside or around the filter. The holder shall be attached immediately at the outlet of the probe, cyclone, or nozzle depending on the configuration used.

Whenever "O" ring seals are used, they shall be of Teflon or Teflon coated material. Other inert holder and gasket materials may be used subject to approval by the Executive Officer.

#### 4.1.5 Sample Transfer Line

The sample transfer line shall be Teflon (1/4 in. O.D. x 1/32 in. wall) with connecting fittings that are capable of forming leak-free, vacuum tight connections without using sealing greases. The line should be as short as possible.

#### 4.1.6 Condenser

The condenser shall be constructed of borosilicate glass and shall be designed to allow the cooling of the gas stream to at least 20°C before it enters the sorbent module. Design for the normal range of stack gas conditions is shown in Figure 3.

#### 4.1.7 Sorbent Module

The sorbent module shall be made of glass with connecting fittings that are able to form leak-free, vacuum tight seals without the use of sealant greases (Figure 3). The vertical resin trap is preceded by a coil-type condenser, also oriented vertically, with circulating cold water. Gas entering the sorbent module must have been cooled to 20 °C (68°F) or less. The gas temperature shall be monitored by a thermocouple placed either at the inlet or exit of the sorbent trap. The sorbent bed must be firmly packed and secured in place to prevent settling or channeling during sample collection. Ground glass caps (or equivalent) must be provided to seal the sorbent-filled trap both prior to and following sampling. All sorbent modules must be maintained in the vertical position during sampling.

#### 4.1.8 Impinger Train

Connect three or more impingers in series with ground glass fittings able to form leak-free, vacuum tight seals without sealant greases. Whenever "O" ring seals are used, they shall be of Teflon or Teflon coated material. All impingers shall be of the Greenburg-Smith design modified by replacing the tip with a 1.3 cm (1/2 in.) I.D. glass tube extending to 1.3 cm (1/2 in.) from the bottom of the flask.

The first impinger may be oversized for sampling high moisture streams. The first and second impingers shall contain 100 mL of 3 mM sodium bicarbonate ( $\text{NaHCO}_3$ ) and 2.4 mM sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) (Section 4.2.5). This is intended to neutralize any acids that might form in the impingers. The third impinger shall be empty. Silica gel shall be added to the fourth impinger. A thermometer which measures temperatures to within  $1^\circ\text{C}$  ( $2^\circ\text{F}$ ), shall be placed at the outlet of the third impinger.

#### 4.1.9 Silica Gel Cartridge

This may be used instead of a fourth impinger. It shall be sized to hold 200 to 300 gm of silica gel.

#### 4.1.10 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe extension to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of ARB Method 5. When the pitot tube occurs with other sampling components as part of an assembly, the arrangements must meet the specifications required by Section 4.1.1 of ARB Method 2. Interference-free arrangements are illustrated in Figures 2-6 through 2-8 of ARB Method 2 for Type S pitot tubes having external tubing diameters between 0.48 and 0.95 cm (3/16 and 3/8 in.).

Source-sampling assemblies that do not meet these minimum spacing requirements (or the equivalent of these requirements) may be used only if the pitot tube coefficients of such assemblies have been determined by calibration procedures approved by the Executive Officer.

#### 4.1.11 Differential Pressure Gauge

Two inclined manometers or equivalent devices, as described in Section 2.2 of ARB Method 2. One manometer shall be used for velocity head ( $\Delta P$ ) readings and the other for orifice differential pressure readings.

#### 4.1.12 Metering System

Vacuum gauge, leak-free pump, thermometers accurate to within  $3^\circ\text{C}$  ( $5.4^\circ\text{F}$ ), dry gas meter capable of measuring volume to within 2 percent, and related equipment, as shown in Figure 2. Other metering systems must meet the requirements stated in Section 2.1.8 of ARB Method 5.

#### 4.1.13 Barometer

Mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within 2.5 mm Hg (0.1 in. Hg). In many cases, the barometric reading may be obtained from a nearby national weather service station, in which case the station value (which is the absolute barometric pressure) shall be requested and an adjustment for elevation differences between the weather station and sampling point shall be applied at a rate of minus 2.5 mm Hg (0.1 in. Hg) per 30 m (100 ft) elevation increase or vice versa for elevation decrease.

#### 4.1.14 Gas Density Determination Equipment

Temperature sensor and pressure gauge, as described in Section 2.3 and 2.4 of Method 2, and gas analyzer, if necessary, as described in Method 3. The preferred configuration and alternative arrangements of the temperature sensor shall be the same as those described in Section 2.1.10 of ARB Method 5.

#### 4.1.15 Filter Heating System

The heating system must be capable of maintaining a temperature around the filter holder during sampling of  $(120 \pm 14^{\circ}\text{C})$  ( $248 \pm 25^{\circ}\text{F}$ ). A temperature gauge capable of measuring temperature to within  $3^{\circ}\text{C}$  ( $5.4^{\circ}\text{F}$ ) shall be installed so that the temperature around the filter holder can be regulated and monitored during sampling.

#### 4.1.16 Balance

To weigh the impingers and silica gel cartridge to within 0.5 g.

### 4.2 SAMPLING MATERIALS AND REAGENTS

#### 4.2.1 Filters

The filters shall be Teflon coated glass fiber filters without organic binders, or Teflon membrane filters, and shall exhibit at least 99.95 percent efficiency (0.05 percent penetration) on 0.3 micron dioctyl phthalate smoke particles. The filter efficiency test shall be conducted in accordance with ASTM standard Method D 2986-71 (Reapproved 1978). Test data from the supplier's quality control program are sufficient for this purpose. Record the manufacturer's lot number.

##### 4.2.1.1 Contamination Check of Filter

The tester must have the filters cleaned by the analyst and checked for contamination prior to use in the field. The contamination check must confirm that there are no PAH contaminants present that will interfere with the analysis of the sample PAHs of interest at the target reporting limits. The analyst must record the date the filter was cleaned.

The filters shall be cleaned in batches not to exceed 50 filters. To clean the filters, shake for one hour in methylene chloride in a glass dish that has been cleaned according to Section 6.2. After extraction, remove the filters and dry them under a clean N<sub>2</sub> stream. Analyze one filter using the same extraction, clean-up and analysis procedures to be used for the field samples (Sections 6.5.1.2, 6.6, and 7.5).

$$\text{Blank value per filter} = \frac{\text{Total mass (ng) of analyte}}{\text{No. filters extracted}} \quad 429-8$$

The acceptance criteria for filter cleanliness depends on 1) the method reporting limit, 2) the expected field sample volume and 3) the desired reporting limit for the sampled emissions stream. Filters with PAH levels equal to or greater than the target reporting limit for the analyte(s) of concern shall be rejected for field use.

If the filter does not pass the contamination check, re-extract the batch and analyze a clean filter from the re-extracted batch. Repeat the re-extraction and analysis until an acceptably low background level is achieved. Store the remainder tightly wrapped in clean hexane-rinsed aluminum foil as described in Section 4.3.3.

Record the date of the last cleaning of the filters and the date of the PAH analysis, and prepare a laboratory report of the analytical results that includes all of the information required by Section 10.2.

The tester shall obtain this laboratory report with the date of cleaning of the filters, and the date of the filter contamination check from the analyst, and report them in the source test protocol and the test report as required by Sections 10.1 and 10.3.

#### 4.2.2 Amberlite XAD-2 Resin

The XAD-2 resin must be purchased precleaned and then cleaned again as described below before use in the sampling train.

##### 4.2.2.1 Cleaning XAD-2 Resin

This procedure must be carried out in a ~~glass~~ Soxhlet extractor which will hold enough XAD-2 for several sorbent traps, method blanks and QC samples. Use an all glass thimble containing an extra coarse frit for extraction of the XAD-2. The frit is recessed 10 to 15 mm above a crenelated ring at the bottom of the thimble to facilitate drainage. The resin must be carefully retained in the extractor cup with a glass wool plug and stainless steel screen to prevent floating on the methylene chloride.

Clean the resin by two sequential 24 hour Soxhlet extractions with methylene chloride. Replace with fresh methylene chloride after the first 24 hour period.

The adsorbent must be used within twenty one (21) days of cleaning. If the adsorbent is not used within 21 days, it must be re-checked for contamination before use.

#### 4.2.3 Silica Gel

Indicating type, 6 to 16 mesh. If previously used, dry at 175°C (350°F) for 2 hours. New silica gel may be used as received. Alternatively, other desiccants (equivalent or better) may be used, subject to approval by the Executive Officer.

#### 4.2.4 Reagent Water

Deionized, then glass-distilled, and stored in hexane- and methylene chloride-rinsed glass containers with TFE-lined screw caps.

#### 4.2.5 Impinger Solution

Sodium bicarbonate 3 mM, and sodium carbonate 2.4 mM. Dissolve 1.0081 g sodium bicarbonate (NaHCO<sub>3</sub>) and 1.0176 g of sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>) in reagent water (4.2.4), and dilute to 4 liters.

#### 4.2.6 Crushed Ice

Place crushed ice in the water bath around the impingers.

#### 4.2.7 Glass Wool

Cleaned by sequential rinsing in three aliquots of hexane, dried in a 110 °C oven, and stored in a hexane-washed glass jar with TFE-lined screw cap. Clean by methylene chloride soxhlet extraction for 16 hours. Air dry in a clean container in a clean hood. Store in methylene chloride washed glass jar with TFE-lined screw cap.

#### 4.2.8 Chromic Acid Cleaning Solution

Dissolve 200 g of sodium dichromate in 15 mL of reagent water, and then carefully add 400 mL of concentrated sulfuric acid.

### 4.3 PRE-TEST PREPARATION

The positive identification and quantitation of PAH in an emissions test of stationary sources are strongly dependent on the integrity of the samples received and the precision and accuracy of all analytical procedures employed. The QA procedures described in Sections 4.3.7 and 8 are to be used to monitor the performance of the sampling methods, identify problems, and take corrective action.

#### 4.4.4 Train Operation

No smoking is allowed.

##### 4.4.4.1 Sampling Train

During the sampling run maintain a sampling rate within 10 percent of true isokinetic, unless otherwise specified or approved by the Executive Officer. The actual sampling rate must be at or above the VSR (Equation 429-4) to collect the target sample mass in the estimated sampling time. If the target sampling rate cannot be achieved, adjust the planned sampling time to achieve the target sample volume (PSV).

For each run, record the data required on the sample data sheet shown in Figure 5. The operator must record the dry gas meter reading at the beginning of the test, at the beginning and end of each sampling time increment, when changes in flow rates are made, before and after each leak-check, and when sampling is halted.

Record other readings required by Figure 5 at least once at each sample point during each time increment and additional readings when significant changes (20 percent variation in velocity head readings) necessitate additional adjustments in flow rate.

Level and zero the manometer. Because the manometer level and zero may drift due to vibrations and temperature changes, make periodic checks during the traverse.

Clean the portholes prior to the test run to minimize the chance of sampling the deposited material. To begin sampling, remove the nozzle cap and verify that the pitot tube and probe extension are properly positioned. Position the nozzle at the first traverse point with the tip pointing directly into the gas stream.

Immediately start the pump and adjust the flow to isokinetic conditions. Nomographs are available, which aid in the rapid adjustment of the isokinetic sampling rate without excessive computations. These nomographs are designed for use when the Type S pitot tube coefficient ( $C_p$ ) is  $0.85 \pm 0.02$ , and the stack gas equivalent density (dry molecular weight) ( $M_d$ ) is equal to  $29 \pm 4$ . APTD-0576 (Reference 11.7) details the procedure for using the nomographs. If  $C_p$  and  $M_d$  are outside the above stated ranges, do not use the nomographs unless appropriate steps (see Reference 11.8) are taken to compensate for the deviations.

When the stack is under significant negative pressure (height of impinger stem), take care to close the coarse adjust valve before inserting the probe extension assembly into the stack to prevent water from being forced backward. If necessary, the pump may be turned on with the coarse adjust valve closed.

When the probe is in position, block off the openings around the probe and porthole to prevent unrepresentative dilution of the gas stream.

#### 4.6 ISOKINETIC CRITERIA

If 90 percent  $< I < 110$  percent, the isokinetic results are acceptable. If there is a bias to the results because  $I < 90$  percent or  $I > 110$  percent, then the results must be rejected and the test repeated, unless the test results are accepted by the Executive Officer.

### 5 SAMPLE RECOVERY

#### 5.1 SAMPLE RECOVERY APPARATUS

##### 5.1.1 Probe Nozzle Brush

~~Inert bristle brush with stainless steel wire handle.~~ Teflon brush with Teflon handle. The brush shall be properly sized and shaped to brush out the probe nozzle.

##### 5.1.2 Wash Bottles

Teflon wash bottles are required; Teflon FEP<sup>®</sup>.

##### 5.1.3 Glass Sample Storage Containers

Precleaned narrow mouth amber glass bottles, 500 mL or 1000 mL. Screw cap liners shall be Teflon.

##### 5.1.4 Filter Storage Containers

Sealed filter holder or precleaned, wide-mouth amber glass containers with Teflon-lined screw caps.

##### 5.1.5 Balance

To measure condensed water to within 0.5 g.

##### 5.1.6 Silica Gel Storage Containers

Air tight metal containers to store silica gel.

##### 5.1.7 Funnel and Rubber Policeman

To aid in transfer of silica gel to container; not necessary if silica gel is weighed in the field.

##### 5.1.8 Funnel

To aid in sample recovery. Glass or Teflon<sup>®</sup> must be used.

##### 5.1.9 Ground Glass Caps or Hexane Rinsed Aluminum Foil

### 5.3.6 Sample Container No. 4 (Impinger contents)

Wipe off the outside of each of the first three impingers to remove excess water and other material. Weigh the impingers and contents to the nearest  $\pm 0.5$  g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the silica gel (Section 5.3.8) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6). Pour the impinger catch directly into Container No. 4. Mark the liquid level.

### 5.3.7 Sample Container No. 5 (Impinger rinses)

Rinse each impinger sequentially three times with acetone, hexane, and methylene chloride and pour rinses into Container No. 5. Mark the liquid level. These rinses may be combined with the previously weighed impinger contents in Container No. 4.

### 5.3.8 Weighing Silica Gel

Weigh the spent silica gel to the nearest 0.5 g using a balance. Record the weight. Calculate and then record the weight of liquid collected during sampling. Use this weight and the weight of liquid collected in the impingers (Section 5.3.6) to calculate the moisture content of the effluent gas (Sections 4.5.5 and 4.5.6).

## 5.4 SAMPLE PRESERVATION AND HANDLING

From the time of collection to extraction, maintain all samples (Sections 5.3.1 to 5.3.7) at 4°C or lower and protect from light. All samples must be extracted as soon as practically feasible, but within 21 days of collection; and all extracts must be analyzed as soon as practically feasible, but within 40 days of extraction. Success in meeting the holding time requirement will depend on pre-test planning by the tester and the laboratory.

## 6 ANALYTICAL PREPARATION

This method is restricted to use only by or under the supervision of analysts experienced in the use of capillary column gas chromatography/mass spectrometry and skilled in the interpretation of mass spectra. Each analyst must demonstrate the ability to generate acceptable results with this method using the procedures described in Sections 7.3, 8.2.6, and 8.3.1.

### 6.1 SAFETY

The toxicity or carcinogenicity of each reagent used in this method has not been precisely defined. Nevertheless, each chemical compound should be treated as a potential health hazard and exposure to these chemicals must be reduced to the lowest possible level by whatever means available. The laboratory is responsible for maintaining a current file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data ~~handling~~ sheets should also be made available to all personnel involved in the

The signal of each analyte in the initial and ongoing laboratory control samples must be at least 10 times that of the background.

Acceptable accuracy is a percent recovery between 50 and 150 percent. Acceptable precision for the initial LCS samples is a relative standard deviation (RSD) of 30 percent or less.

Acceptable precision for the ongoing analysis of duplicate samples is a relative percent difference of 50 percent or less.

If the RSD for the initial demonstration exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.

If the RPD for any ongoing duplicate analyses exceeds the precision limit, or any calculated recovery falls outside the range for accuracy, the laboratory performance for that analyte is unacceptable.

Beginning with Section 8.1.3.1, repeat the test for those analytes that failed to meet the performance criteria. Repeated failure, however, will confirm a general problem with the measurement system. If this occurs, locate and correct the source of the problem and repeat the test for all compounds of interest beginning with Section 8.1.3.1 for the initial analysis and Section 8.3.1.2 for the ongoing analysis.

### 8.3 ESTIMATION OF THE METHOD DETECTION LIMIT (MDL) AND PRACTICAL QUANTITATION LIMIT (PQL)

#### 8.3.1 Initial Estimate of MDL and PQL

The analyst shall prepare a batch of XAD-2 resin as described in Sections 4.2.2.1 to 4.2.2.3, then check for contamination as required by Section 4.2.2.4. Identify those PAH analytes present at background levels that are too high for the MDL determination. Use the procedure of Appendix A to calculate MDLs for the remaining target PAH compounds. ~~A suggested initial spike level for the MDL determination is 5 times~~ The analyst may use any of the five approaches described in Appendix A(A1.1) to estimate an initial spike level for the MDL determination. One of the suggested approaches is based on a theoretical method quantitation limit (TMQL) estimated according to Equation 429-16:

$$TMQL = C \times \frac{V}{P} \times 100 \times 2 \quad 429-16$$

Where:

- C = the concentration of the PAH in the lowest concentration calibration standard used in the initial calibration, (ng/ $\mu$ L)
- V = the final extract volume, ( $\mu$ L)
- P = the assumed percent recovery (50%) of the internal standard
- 2 = a factor to account for the fact that the final extract volume (V) contains one half of the analyte in the sample. The other half is archived.

FIGURE 9

EXAMPLE OF PRE-TEST CALCULATIONS FOR PAH EMISSIONS TEST

					PST = 6 hours PSV = 180 dscf	
	PQL (ng/sample)	STC (ng/dscm)	MSV (dscf)	MST (hours)	F	SRL (ng/dscm)
Naphthalene	2400	<1500	>56.5	>1.89	NA	471
2-Methylnaphthalene	330	NA	NA	NA	NA	64.7
Acenaphthylene	5.0	180	0.98	0.03	183	0.98
Acenaphthene	5.0	6	29.4	0.98	6	0.98
Fluorene <sup>1</sup>	83	<6	>489	>16.3	NA	16.3
Phenanthrene	110	120	32.4	1.08	6	21.6
Anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Fluoranthene	5.0	46	3.8	0.13	47	0.98
Pyrene	5.0	46	3.8	0.13	47	0.98
Benzo(a)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Chrysene	5.0	42	4.2	0.14	43	0.98
Benzo(b)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(k)fluoranthene	5.0	50	3.5	0.12	51	0.98
Benzo(e)pyrene	5.0	NA	NA	NA	NA	0.98
Benzo(a)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Perylene	5.0	NA	NA	NA	NA	0.98
Indeno(1,2,3-c,d)pyrene	5.0	<6	>29.4	>0.98	NA	0.98
Dibenzo(a,h)anthracene	5.0	<6	>29.4	>0.98	NA	0.98
Benzo(g,h,i)perylene	5.0	<6	>29.4	>0.98	NA	0.98
Average Volumetric Sampling Rate (VSR) = 0.5 dscfm = 30 dscf/hr						

- PQL = Practical quantitation limit for analyte (based on pre-test analysis of XAD-2 resin)
- STC = Source target concentration for analyte. (From previous emissions test. Samples were analyzed by HRGC/LRMS).
- MSV = Minimum sample volume required to collect detectable levels of target analyte.  
(MSV = PQL ÷ STC) Equation 429-1
- MST = Minimum sample time required to collect detectable levels of target analyte at VSR.  
(MST = MSV ÷ VSR) Equation 429-2
- PST = Planned sampling time (6 hours chosen as the longest practical sampling time for the planned emissions test)
- PSV = Planned sample volume (PSV = PST × VSR) Equation 429-4
- F = Safety factor (> 1) that allows for deviation from ideal sampling and analytical conditions. (F = PSV ÷ MSV) Equation 429-5
- SRL = Source reporting limit if the target analyte cannot be detected with the planned test parameters. (SRL = PQL ÷ PSV) Equation 429-7
- NA This calculation is not applicable either because there is no STC value available or the STC is a detection limit.

<sup>1</sup> PSV is lower than the MSV. Therefore, the analyte is not expected to be detected if it is present at the target concentrations. It will only be detected if the actual concentration is ~~lower~~ higher than the indicated SRL.

**State of California  
California Environmental Protection Agency  
Air Resources Board**

**Method 431**

**Determination of Ethylene Oxide  
Emissions from Stationary Sources**

**Adopted September 12, 1989  
Amended: \_\_\_\_\_**

This document includes text of Method 431, as proposed in the Staff Report released August 9, 1996. Additional proposed modifications are indicated as follows:

Proposed deletions are noted by ~~graphic screen~~ and proposed additions are noted by underline.

## REAGENTS:

1. Ethylene oxide in compressed gas cylinders at levels bracketing the sample concentrations. Sterilant diluent gas may be included in the gas mixtures at levels expected in the emission matrix.
2. Helium, 99.999%, and FID grade hydrogen and air.
3. Air, purified, to be used for dilutions, blank preparation, and standard preparation.

## EQUIPMENT:

1. Gas chromatograph, flame ionization detector, integrator, and columns.
2. Sample loops .50, 1.0, and 2.0 cc.

**\*\* SPECIAL PRECAUTIONS:** Ethylene Oxide is a potential carcinogen. Work should be performed in a well ventilated fume hood. For specific regulatory requirements refer to the California Labor Code, Part 10, Section 9020; Title 8, California Code of Regulations, Section 5220.

## CALIBRATION AND QUALITY CONTROL:

Refer to Appendix E for multipoint and daily calibration and quality control procedures. Refer to Appendix E for calibration procedures specific to the direct-interface gas chromatography.

## LIST OF APPENDICES:

- Appendix A: Testing Procedures for Sterilizers with Catalytic Oxidation or Hydrolytic Scrubber Type Control Units
- Appendix B: Procedures for Estimating Mass of EtO at the Control Unit Inlet
- Appendix C: Testing Procedures for Aeration Chambers
- Appendix D: Documentation of the Probe Position at the Inlet of Catalytic Oxidation Units
- Appendix E: Calibration and Quality Control Procedures
- Appendix F: Calculations
- Appendix G: Reporting Requirements
- Appendix H: Method Limitations
- Appendix I: Tedlar Bag Sampling and Quality Control Procedures
- Appendix J: Definitions
- Appendix K: Testing Procedures for Sterilizers with Joslyn Recovery Type Control Units

APPENDIX A  
TESTING PROCEDURES FOR STERILIZERS WITH  
CATALYTIC OXIDATION OR HYDROLYTIC SCRUBBER  
TYPE CONTROL UNITS

The following procedures shall be used to determine the efficiency of catalytic oxidation and hydrolytic scrubber types of control devices used in controlling emissions from an ethylene oxide sterilizer. The following aspects of the ethylene oxide compliance test are discussed below in this Appendix:

- Stack gas moisture determination.
- Stack gas volumetric flow rate determination.
- Determination of ethylene oxide concentration.

The procedures described herein are used to provide control unit inlet and outlet mass or concentration values to be used in calculating a control efficiency, as specified in the Ethylene Oxide Airborne Toxic Control Measure for Sterilizers and Aerators (17 CCR, Section 93108). As described below, stack gas moisture and volumetric flow rate determination may not be required for many control unit configurations. In such cases the control efficiency will be based solely on the concentration reduction across the control device.

#### **Stack Gas Moisture**

For catalytic oxidation units, the atmospheric moisture dominates the resulting average moisture from the sterilization chamber humidification process and of the moisture created by the destruction of EtO. This is due to the fact that ambient air is used in great excess (normally >100:1) to dilute the chamber sterilant gas before passing across the catalyst bed. Thus the "stack" gas moisture content may be assumed to be the same as that of the ambient air. The wet/dry bulb method may be used for determination of the ambient moisture content.

For hydrolytic scrubber units, the outlet gas may be assumed to be saturated with moisture (i.e., the temperature of the outlet stream must be obtained for the calculation).

If volumetric flow measurements are required, measure At the discretion of the Source Test Protocol reviewer the moisture content of the exhaust gas may be measured using ARB Method 4 during the evacuation and wash stages of at least one cycle (out of the three).

#### **Stack Gas Flow Rate**

If volumetric flow measurements are required, measure the volumetric flow rate of the control device exhaust continuously during the evacuation and wash cycles using the procedures found in ARB test methods 2, 2A or EPA Method 2C or 2D, as appropriate. Following are the recommended procedures for flow rate measurements for hydrolytic scrubber and catalytic oxidation type control devices.

Hydrolytic scrubber type control units: ARB Method 2A is required for measuring flow rates from hydrolytic scrubber type control units. It may be necessary to have multiple meters available in order to cover the expected range of flow rates. To calculate the molecular

weight of the gas, assume that the composition of the sterilant gas is delivered unchanged from the chamber to the control unit and that the balance of the control unit emission gas is sterilant balance gas (if any) plus the measured moisture content. If there is any dilution of the sterilant gas though, the diluent gas concentration will have to be measured along with the concentration of EtO in the gas streams for volumetric flow to be calculated correctly. Record the flow rate at 1 minute intervals throughout the test cycle, taking the first reading within 15 seconds after time zero. Time zero is defined as the moment when the pressure in the sterilizer is released. (The purpose here is to measure flow rates concurrently with the bag samples or on-site GC). Correct the flow to standard conditions (68°F and 1 atm) and determine flow rate in units of standard cubic feet per minute for the run as outlined in the test methods listed in this paragraph.

Catalytic oxidation type control units: Volumetric flow measurements may not be necessary for compliance testing of catalytic oxidation control units. In those systems that meet the following criteria the destruction efficiency calculation can be based solely on the EtO concentration measurements (not applicable where the inlet estimation technique is used).

1. no dilution between inlet and outlet sampling locations,
2. identical flow at inlet and outlet sampling locations, and
3. constant flow throughout the duration of the compliance test.

However, volumetric flow measurements may be required by the Districts in order to determine yearly mass emissions for inventory or facility risk assessment purposes. In those cases the following procedures shall be followed. Note that flow measurements need only be obtained at one of the sampling locations, either inlet or outlet, if the above conditions are met.

CARB Method 2 (type S pitot tube) should be used to determine stack gas velocity and volumetric flow rate of stacks greater than 12 inches in diameter. Testing stacks/ducts having cross-sectional diameters less than 12 inches and equal to or greater than four inches, must be conducted according to United States Environmental Protection Agency (USEPA) Stationary Source Sampling Methods 1A and 2C. The differential pressure gauge used to measure velocity head ( $\Delta P$ ) must meet the requirements of ARB Method 2, Section 2.2 (also USEPA Method 2, Section 2.2). Pitot tube dimensions and specifications must be demonstrated to meet the requirements of ARB Method 2, Sections 2.7 and 4.2 (also USEPA Method 2, Sections 2.7 and 4.2). The source test reports must (1) include reasonably accurate as-installed drawings of the stack from the sterilizer to the point of emission, and (2) identify sampling locations, including dimensions, for each facility. Volumetric flow measurements will be conducted in the following manner: 1. A complete velocity traverse of the exhaust duct will be conducted in a manner consistent with applicable ARB or USEPA reference methods for flow determinations. 2. An average velocity pressure will be calculated from the individual pressure measurements made at each velocity traverse point as specified in the ARB/EPA reference method. 3. A traverse point, where the measured velocity pressure corresponds to the calculated average pressure, will be used to make single point pressure measurements during direct sampling and analysis of EtO emission. 4. Velocity pressure measurements will be made concurrently with each

## Measurement Methods

The mass of ethylene oxide delivered to the control unit inlet during an aeration cycle and the mass of ethylene oxide emitted from the control unit outlet during a sterilization or aeration cycle must be determined by using one of the following sampling/analysis procedures and the calculations found in Appendix F. For catalytic oxidation control units, if the mass of EtO at the inlet is measured rather than estimated, testers must report documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and ambient make-up). This documentation may be obtained by following the steps outlined in Appendix D.

Tedlar bag sampling/analysis procedure: The Tedlar bag sampling procedure specified in Appendix I may be used to collect samples of sterilizer/aerator and control unit exhaust gas for subsequent analysis by GC/FID. The sampling quality assurance procedures detailed in Appendix I must be followed. In addition, the following procedures must be followed.

If Option 1, Inlet Estimation, is used then the entire 1st evacuation and wash period must be monitored for EtO emissions at the outlet of a control system. Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

If Option 2, Inlet Measurement, is performed then the inlet and outlet monitoring will be conducted simultaneously. ~~For cat-ox control units, integrated bag samples will be taken for at least the duration of the entire first evacuation. For acid scrubber control systems, integrated bag samples will be taken during the 1st evacuation and for the duration of any additional evacuation/wash periods (up to the point where aeration begins).~~ Sampling will be initiated for the first evacuation when the pressure in the sterilizer is released.

ARB staff recommends that one of the test personnel monitor the sterilizer chamber pressure during the run and communicate, with walkie-talkies, the sampling start and stop times to the sampling test crew.

Excess EtO shall be bubbled through a sulfuric acid (1 N solution) impinger before discharge, or alternatively can be routed back into the control unit inlet gas stream. Ensure that the excess sample gas which has passed through the acid filled impinger is discharged to a safe location and will not imperil test personnel.

The Tedlar bag samples must be analyzed within 24 hours (of the sample stop time) by the procedures listed herein. The mass of EtO associated with each bag sampling interval is calculated as outlined in Appendix F.

Repeat the procedures three times (three cycles). The arithmetic average percent efficiency (see Appendix F: Calculations) of the three runs shall determine the overall efficiency of the control device.

Direct Interface Sampling Analysis: As an alternative to the Tedlar bag sampling procedure described above, a gas chromatograph (with FID or PID) interfaced directly to the emission source may be used to continuously monitor ethylene oxide concentration at the outlet (and inlet) of the control device. For catalytic oxidation type control units, this procedure shall

## APPENDIX B

### PROCEDURES FOR ESTIMATING MASS OF ETO AT THE INLET

The amount of ethylene oxide, in pounds, loaded into the sterilizer shall be determined by one of the following three procedures. These estimation procedures are valid only if there are no significant leaks or loss of EtO before the control unit. These estimation procedures shall be performed using an empty sterilization chamber. A short exposure stage, e.g., manually aborted, should be used to minimize leak and chamber losses. For those sterilization systems where sterilant gas is also added as "make-up" during the exposure stage, the cycle shall be aborted and the chamber exhausted before such "make-up". These estimation procedures may not be used with sterilization systems using water ring sealed pumps for evacuation of the chamber.

1) For small sterilizer operations using disposable sterilant cartridges, weigh the cartridge to the nearest .5 gram before and after use. Multiply the total mass of gas charged by the weight percent ethylene oxide present in the sterilant mixture. Alternatively, if the cartridge supplier has certified the weight of EtO contained in the cartridge then this weight may be used for the estimation calculation. Or,

2) Weighing the ethylene oxide gas cylinder(s) used to charge the sterilizer before and after charging. Record these weights to the nearest 0.1 lb. Multiply the total mass of gas charged by the weight percent ethylene oxide present in the gas. Or,

3) Calculating the mass based on the conditions of the chamber immediately after it has been charged and using the following equation. A calibrated differential pressure gauge shall be used to monitor the chamber pressure.

$$W_c = \frac{MW \times M \times P \times V}{R \times T}$$

where:

- $W_c$  = weight of ethylene oxide charged to the chamber, in pounds (grams)
- $MW$  = Molecular weight of ethylene oxide, 44.05 lb/mol (gr/gr-mole)
- $M$  = mole fraction of ethylene oxide
- $P$  = chamber pressure, psia (atm)
- $V$  = chamber volume, ft<sup>3</sup> (L)
- $R$  = gas constant, 10.73 (psia\*ft<sup>3</sup>)/(mol\*R) ((.08205 L\*atm)/(g-mole\*K))
- $T$  = temperature, R (K)
- $S$  = standard conditions are 68°F (°R or °K) and 1 atm.

## APPENDIX C

### TESTING PROCEDURES FOR AERATION ROOMS

The following procedures shall be used to determine the efficiency of a control device used to control ethylene oxide emissions from an aeration room. An aeration room is defined as any facility used for the dissipation of ethylene oxide residue from equipment previously sterilized in a sterilizer. The procedures are identical to those used to test sterilization chamber/control units (Appendix A) with the exception of the following.

The test shall be performed by placing a normal load of previously-sterilized equipment into the aeration room. The exposure stage ~~should not~~ cannot be shortened or aborted.

The measurement procedures in Appendix A shall be used to determine the volumetric flow rate and EtO concentration at the inlet and outlet of the control device. (The inlet estimation technique cannot be used.)

If using the direct GC sampling and analysis procedure, sample and analyze a slipstream of the outlet concentration of EtO once every 3 minutes continuously for 1 hour.

The emissions test shall be conducted in the hour immediately following the loading of the aeration room. The test shall consist of one aeration cycle run. The test engineer and/or test administrator shall insure that the aeration room is being tested under normal operating conditions and equipment load. These conditions shall be documented and reported with the final test results.

Testers must have documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and make-up air). Procedures for insuring the correct probe position are listed in Appendix D. This documentation shall be reported along with the test final results.

## APPENDIX D

### DOCUMENTATION OF INLET PROBE POSITION FOR CATALYTIC OXIDATION UNITS

For catalytic oxidation control units, if the mass of EtO at the inlet is measured rather than estimated, testers must report documented evidence that the inlet probe is placed such that the sampled gases are completely mixed (i.e., chamber exhaust and ambient make-up). This documentation may be obtained by the following steps:

1. Install the sampling probe in the control unit inlet.
2. During a sterilizer chamber evacuation monitor the volumetric flow rate of the chamber exhaust (e.g., before dilution in the control unit) and control unit exhaust. Also measure the concentration of ethylene oxide (or diluent gas) in the chamber exhaust (e.g., before dilution in the control unit) and at the control unit inlet (e.g., after dilution in the control unit). The expected concentration of EtO at the control unit inlet (at a given time) can be calculated by the following equation (note that the concentration and flow measurements must be taken simultaneously):

$$C_i = (Q_c / Q_{cu}) \times C_e$$

where:

- $C_i$  = EtO (or diluent gas) concentration expected at the control unit inlet.
- $Q_c$  = volumetric flow rate of the chamber exhaust
- $Q_{cu}$  = volumetric flow rate at the control unit inlet
- $C_e$  = EtO (or diluent gas) concentration measured in the chamber exhaust

3. The concentration of ethylene oxide measured at the control unit inlet must be within 10% of  $C_i$  for the probe to be documented as correctly positioned.

Alternatively, the correct placement of the control unit inlet probe may be documented as follows:

1. Install the sampling probe in the control unit inlet.
2. During a sterilizer chamber evacuation monitor the volumetric flow rate of the control unit exhaust. Also monitor the concentration of ethylene oxide, using the procedures outlined below, at the control unit inlet (e.g., after dilution in the control unit). Monitor both the flow rate and EtO concentration for the duration of the sterilization chamber exhaust (first evacuation and following washes).
3. Calculate the total amount of EtO delivered to the control unit. These calculations are outlined in Appendix F.

## 4.1 Multipoint calibration

- 4.1.1 Standards are analyzed at least three times at four different concentrations. The concentration levels should be five times the limit of detection on the low end, approximately midway in the linear response range of the method, and near the high concentration end of the linear response limit. Results of the multipoint analyses must be documented and shall include data on intercept, slope, correlation of fit, relative standard deviations, range of concentrations tested, response factor and limit of detection calculations.
- 4.1.2 Option 1, Least Squares Fit. The least squares analysis of the data should produce a correlation coefficient of at least 0.99. Blank values shall not be subtracted from the raw data and the origin (0.0, 0.0) will not be used in the calculations. If the intercept deviates significantly from zero, the analysis must be reviewed for possible system contamination or other problems.
- 4.1.3 Standard deviations of the GC responses (area counts) are calculated at each level of the multipoint and must be comparable to those published for the method included in the analytical report.
- 4.1.4 Option 2, Response Factor. For each calibration target compound, calculate the pooled mean response factor (RF) from the set of four multipoint levels. Calculate the standard deviation and the percent relative standard deviation. The laboratory must demonstrate that RF values over the working range for the target compounds are constant. The percent relative standard deviations of the mean RF's must not exceed 15%. The equation for calculating the pooled mean response factor is listed below.

$$Rf_{\text{pooled}} = (RF_{1a} + RF_{1b} + RF_{1c} + RF_{2a} + \dots + RF_{4b} + RF_{4c}) / 12$$

where 1a through 4c represent the individual response factors calculated from the 12 multipoint runs.

- 4.1.5 Analytical Limits of Detection (LOD) must be calculated. The LOD for each method must be calculated by the following equation:

$$LOD = |A| + 3S$$

where

A is the least squares x-intercept, in units of ppmV, calculated from the multipoint data (section 4.1.1).

S is the standard deviation of replicate determinations of the lowest standard, in units of ppmV, calculated from the multipoint data by the following equation:

$$S \equiv (Y - b) / m$$

Where

Y  $\equiv$  the standard deviation of the GC response, in area counts, of replicate determinations of the lowest standard.

b  $\equiv$  the least squares Y intercept

m  $\equiv$  the least squares slope

At least 3 replicates are required. The lowest standard must be run at 1 to 5 times the estimated detection limit. If data is not available in the concentration range near the detection limit, S may be estimated by:

$$S = \text{RSD} \times A$$

where RSD is the relative deviation of the lowest standard analyzed.

4.1.6 The Limit of Quantitation (LOQ) must be calculated by the following equation:

$$\text{LOQ} = 3.3 \times \text{LOD}$$

No analysis results will be reported below the LOQ.

## 5. ROUTINE CALIBRATION PROCEDURE

Routine users of the method, i.e. daily, will use one of the following options for calibrations and result calculations. Compound concentrations used in the calibration curves must bracket levels found in stationary source emission samples. Peak area integration, and not peak height, must be used for determination of instrument response.

### 5.1 Option 1, Least Squares Fit

A least squares fit, i.e. as determined with the initial multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every eight ten hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration as a check. The GC response must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The GC responses are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

## 5.2 Option 2, Response Factor

The average response factors, i.e. as determined with the multipoint calibration, must be used for sample quantitative calculations. A calibration check must be performed every ~~eight~~ ten hours, or every ten sample analyses, whichever is more frequent. Use the midpoint calibration (see section 4.1) as a check. The measured RFs must be within 10% of the mean values established in the multipoint calibration or a new calibration curve must be prepared. The response factors are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

For non-routine users of the method, i.e. 1 test per month or less, calibration involves generation of at least a 3 point curve during each analysis day and a midpoint calibration check after every 10 samples. Either linear regression or mean response factor calculations can be used. The initial performance evaluation is still required.

## 6. ROUTINE QUALITY CONTROL

### 6.1 Laboratory Blanks

A laboratory method blank is a volume of ultra high purity gas carried through the entire analytical scheme. The gas used for blank runs should be certified by the gas supplier or laboratory to contain less than the analytical limit of detection (LOD) of the analytes of interest. The laboratory blank volume must be equal to the sample volumes being processed. Laboratory blanks are analyzed each shift before the analysis of samples may proceed. A blank is also analyzed after the analysis of a sample containing components with concentrations greater than the most concentrated standard used. The laboratory blank results will be reported along with raw sample data in final reports. Sample results should not be corrected for blank contribution. Note that a field blank analysis may be used in place of the laboratory blank. However, if the results of the field blank are greater than LOQ, a laboratory blank will be run to isolate the source of contamination.

### 6.2 Laboratory Replicate Samples

Replicates serve to measure the precision of an analysis. Ten percent of all samples, or at least one sample per batch, will be analyzed in duplicate to indicate reproducibility of the analysis and to monitor such conditions as instrument drift. The precision ( $|Ave. - X_i|/Ave.$ ) x 100) of duplicate analyses must fall within predetermined limits, i.e. 3 x RSD as established during the initial performance evaluation.

### 6.3 Calibration Check Sample

The midpoint standard used in multipoint calibrations must be analyzed every eight hours, or every ten samples, whichever is more frequent, to check instrument performance. The GC response of all analytes must be within 10 % of the mean

values established in the multipoint calibration or a new calibration curve must be generated. The GC responses are recorded and inspected to check for trends which indicate the degradation of standards or instrument performance.

#### 6.4 Performance Evaluation Samples

To demonstrate data quality, performance evaluation samples may be analyzed periodically. At the discretion of the Executive Officer, periodic analysis of performance evaluation samples may be required. If analysis of performance evaluation samples is required by the Executive Officer, the analyses shall be conducted in the following manner. The performance evaluation material shall be used to evaluate both sampling and analytical systems. Performance evaluation samples shall be analyzed at a frequency dependent on how often the method is used. If the method is used on a daily basis, the performance evaluation sample must be analyzed twice a month. If the method is used less frequently, the performance evaluation sample must be analyzed once a month or whenever the method is used (whichever is less). A value of  $\pm 10\%$  of the stated concentration of the performance evaluation sample must be recovered for the analyte of interest. The results of these analyses must also be recorded and placed on permanent file for at least three years and shall be made available to the Executive Officer upon request. All performance evaluation samples will be labeled with an expiration date and may be re-certified by the vendor if they contain sufficient volume (i.e. greater than 60% residual).

#### 6.5 Qualitative Analysis Criteria

The retention time of the target compound must be within 0.06 RRT units of the standard RRT.

#### 6.6 Quantitation Criteria

The column resolution criteria of 20% valley (as measured from the baseline to valley minimum) between a target compound and an interfering compound must be achieved before any quantitation can be allowed. When a compound interferes with the target compound and the degree of the interferences exceeds the column resolution criteria the compound can still be quantified if the following criteria is met. Set the reporting limit for the lowest amount that can be quantified high enough such that the interfering compound accounts for less than 10% of the area of the target compound.

### 7. ANALYTICAL REPORTING REQUIREMENTS

Each report of analyses shall be in the following format and will include the following information. Refer to Appendix F for result calculations format.

- 7.1 Complete identification of the samples analyzed (sample numbers and source). Pertinent information should be submitted to the analytical laboratory via a chain of custody record.

- 7.2 Date of submittal of the sample, date and time of GC analysis. The latter should appear on each chromatogram included with the report.
- 7.3 The raw and calculated data which are reported for the actual samples will also be reported for the duplicate analyses, laboratory and field blank analyses, the field spike sample analyses, and any other QA or performance evaluation samples analyzed in conjunction with the actual sample set(s).
- 7.4 The calibration data, including average response factors calculated from the calibration procedure described in Section 5. Include the relative standard deviation, and data showing that the midpoint response factors have been verified at least once during each  $\approx$  10-hour period of operation or with each separate set of samples analyzed.
- 7.5 All relevant data used to define the reporting limit will be reported. This will include parameters such as sampling volumes, sample injection volume, chromatographic interferences, and Tedlar bag contamination levels. In no case will results be reported below the established reporting limit. Test reports should include a table summarizing reporting limits (per sample) including a description of causes of variation.

## 8. DIRECT SAMPLING CALIBRATION AND QUALITY CONTROL PROCEDURES

Due to the nature of direct sampling routine calibration procedures are somewhat different. The sequence of in-field calibration, QC, and sample runs listed below is recommended when performing on-site analyses.

1. Run a 3 point calibration (triplicate runs at three levels) bracketing the expected sample concentration before each compliance test. The calibration curve prepared from the averages shall be used for quantitation of the cycle samples as well as determination of the limit of quantitation.
2. Run a field blank, through the entire sampling train, using zero air (ambient air normally can be used for this purpose for ethylene oxide sampling).
3. Run a field spike, through the entire sampling train, using the calibration standard closest to the sample concentrations. The spike gas introduced at the transfer line inlet should be at ambient pressure.
4. Analyze the field samples.
5. Run standard checks after sample analyses are complete for each cycle test. Standard check results must be within 10% of the pretest average values.

## APPENDIX G

### REPORTING REQUIREMENTS

The following outline of reporting requirements is meant to be used as a general guide for EtO source test report reviewing purposes.

**Sterilizer:** manufacturer and model number, volume of the chamber, the type of sterilant gas used, the type of materials sterilized, a cycle process diagram, e.g., a plot of chamber pressure vs. time including footnotes regarding start and stop points of cycle stages and including a detailed explanation of the evacuation flow discharge path (water and vapor) during all stages of the cycle. If pressure/volume calculations are used to determine the weight of EtO charged to the chamber then chamber pressure sensor calibration data shall be included in the report.

**Control Unit:** type of chamber evacuation pumps used, type of control unit, manufacturer and model number, the size or capacity of the control unit, the operating temperature, a diagram of the control unit and sampling locations. If monitoring is conducted at the inlet of a catalytic oxidation unit then the test report shall include documentation of the correct positioning of the inlet sampling probe.

**Test Data:** plots of volumetric flow rate versus time (the reviewer should determine whether integrated sampling is appropriate), results of moisture determinations, a plot of the multipoint calibrations used for quantitative calculations, calculations for limit of detection and reporting limits, tables of raw data, final results, and all chromatograms (refer to Appendix E, section 7 of this document for more detailed "Analytical Reporting Requirements"). If the direct GC approach is used then plots of EtO concentration vs. time should be included in the report along with the integrated total mass emission result.

**Quality Control:** The test report shall include complete identification of the samples analyzed (sample numbers and source), date of submittal of the sample, date and time of GC analysis. The raw and calculated data which are reported for the actual samples will also be reported for the duplicate analyses, laboratory and field blank analyses, the field spike sample analyses, and any other QA or performance evaluation samples analyzed in conjunction with the actual sample set(s).

## APPENDIX H

### METHOD LIMITATIONS

Alternative sampling and analytical methodologies that are demonstrated to be substantially equivalent may be used if approved by the Executive Officer. The term Executive Officer as used in this document shall mean the Executive Officer of the Air Resources Board or his or her authorized representative. The Executive Officer may require the submission of test data or other information showing that the alternate method is equivalent to Method 431. Any modifications to the sampling and analytical procedures described must also be approved in writing by the Executive Officer.

#### Tedlar Bag Sampling

Tedlar bag samples must be analyzed within 24 hours of end of the sampling period.

Tedlar bags with fittings other than those listed may not be suitable for EtO sampling. The appropriate recovery and stability tests should be conducted before using other fitting types (especially for bags with stainless steel fittings).

CARB staff have not conducted bag stability studies for EtO in dilute-acid hydrolytic scrubber emissions.

The integrated Tedlar bag sampling procedure is not applicable for testing of sources where both the emission gas volumetric flow rate and target compound concentration are variable. The test engineer and/or the reviewing agency will determine whether integrated sampling is appropriate.

Ethylene oxide may decay if exposed to sunlight. Thus, Tedlar bag samples and standards should be protected from sunlight exposure.

Sampling with Tedlar bags must be planned carefully so that the entire emission curve is monitored. To provide documentation that the sampling is representative of the emission curve, it is strongly recommended that a continuous monitor (e.g., FID) be used along with the bag at the control unit inlet. Sampling times could then be modified as necessary to account for shifts in emissions.

#### On-Site GC

At many hospitals, the control unit is not accessible from parking areas (i.e., with 150 foot heated lines to a parked GC-van). Thus, the GC, gas cylinders and associated support equipment must be physically moved to a location near the control unit, which may prove inconvenient. Also, adequate power may be difficult to get at some facilities. Many testers feel that on-site GC is more expensive and more difficult than container sampling. In addition to the equipment required, performance of on-site GC requires that an experienced chemist be involved in the field operations.

### Inlet Estimation

The inlet estimation procedure assumes that there is no loss of EtO to the chamber, chamber contents, transfer plumbing or pumps and that there are no leaks before the control unit.

Use of the inlet estimation technique assumes that the composition of the sterilant gas is accurately defined and consistent in individual cylinders/cartridges. Thus, at the discretion of the District, a sample from the gas cylinder(s) used during the test ~~should~~ may be analyzed to verify the exact sterilant gas composition for the inlet estimation.

Accurate estimates rely on accurate volume measurements and calibrated pressure gauges. Thus, manufacturer's chamber volume specifications should always be double checked and system pressure monitoring devices should be evaluated for accuracy.

Some sterilization systems add sterilant gas as needed to the chamber during the exposure stage because the chamber pressure may decrease slightly after initial pressurization. This addition of make-up gas would, if significant, invalidate the inlet estimation calculation since with existing systems it would be quite difficult to estimate the amount of make-up gas added. To minimize this source of error, when using the inlet estimation technique, the test should be conducted with an empty chamber and the exposure stage should be aborted after no more than 10 minutes.

Since the estimation technique can only be used for empty chamber tests, an exposed chamber load will not be available if subsequent aeration tests are to be performed. There must be an exposed load in the aerator for a valid test. Thus, an additional sterilization cycle with unaborted exposure stage would have to be run to provide the materials to be aerated. Furthermore, the inlet EtO concentrations must be physically measured with Tedlar bags or direct GC for aeration tests since estimation is not possible. Thus, where aeration tests must be conducted in addition to sterilizer tests, inlet estimation may not provide any time or cost benefit.

The inlet estimation technique should not be used with sterilization systems using water ring seal pumps, either flow through or recirculating.

### Acid Scrubber

The stability of ethylene oxide in hydrolytic scrubber unit emission matrix, in Tedlar bags, has not yet been demonstrated (by ARB staff). Stability studies for ethylene oxide in this matrix should be conducted and results reviewed by the ARB before compliance tests are performed using this method; included in the test report.

This method allows the option to measure inlet concentrations (e.g., with bag sampling or by direct GC) instead of using the estimation technique outlined in Appendix B. However, the concentration of EtO at the inlet of hydrolytic scrubber units will be approximately 27% and 100% by volume for systems using 12/88 and 100% EtO sterilant gases, respectively. Due to the safety concerns associated with the high inlet EtO concentrations, it is

- 5.2 Assemble the sampling train at the sampling site as shown in Figure 1.
- 5.3 Leak check the sample train. To start the leak check, connect the sample line to the bag, making sure the valve on the bag is closed. Place the bag in the rigid container and close as if for sampling. Turn on the vacuum pump until a reading of 15 inches H<sub>2</sub>O is maintained. Make sure that the probe line is not plugged and that the ON/OFF valve is open. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before the leak check continues. Turn the pump off, break the vacuum on the rigid container and open the mininert valve on the Tedlar bag. Place the bag back in the container and close as if for sampling. Plug (leak tight) the end of the probe. Turn on the vacuum pump and adjust until a reading of 15 inches H<sub>2</sub>O is maintained. If a leak greater than 5% of the sampling flow rate is found, then the problem must be located and fixed before sampling continues. If impingers are used, extreme care must be used when applying and removing the vacuum to avoid carry over of the liquids in the impingers.
- 5.4 Break the vacuum on the rigid container. Unplug the end of the probe and place the end of the probe in the stack away from the walls. Care should be taken to avoid dilution of the stack gas sample with ambient air by sealing the open port area around the probe, especially in stacks with negative static pressure.
- 5.5 Make sure the sampling train is configured correctly, the valve on the sample bag is open and the ON/OFF valve is closed. Turn the vacuum pump on and adjust until a reading of 15 inches H<sub>2</sub>O is maintained. Begin sampling by opening the ON/OFF valve. Record the sample start time on the field data sheet.
- 5.6 Monitor the container vacuum and sample flow rate and adjust as necessary. After sampling for the planned interval, close the ON/OFF valve noting the time on the field data sheet. Bags should be filled no more than half full. If condensation occurs, discard sample and resample as per 5.1.1.
- 5.7 After sample purge is complete, close the ON/OFF valve, turn the pump off, break the vacuum on the rigid container and close the mininert valve on the bag.
- 5.8 Attach a label to each Tedlar bag sample (and impinger if used) containing the following information:

Job #  
Date  
Time  
Sample/Run #  
Plant Name  
Sample Location  
Log #  
Initials of Sampler Operator

## APPENDIX K

### TESTING PROCEDURES FOR STERILIZERS WITH JOSLYN RECOVERY TYPE CONTROL UNITS

Identified points of EtO emission from Joslyn system include:

1. Recovery compressor "burps" which are routed to an acid scrubber. These burps are short-duration (e.g., 3 seconds) recovery compressor pressure relief emissions which occur on an irregular basis (infrequent according to manufacturer). Recovery compressor "burps" are routed to an acid scrubber. These burps would only occur while the recovery compressor is in operation during sterilizer exhaust stage (i.e., the recovery compressor is not in operation during the detoxification-B and preconditioning stages). For the purpose of occupational safety, the composition of the emission from these burps should be assumed to be the same as the 12/88 sterilant mixture and appropriate precautions are taken.
2. An oil-sealed pump is used to evacuate the sterilization chamber during the primary exhaust and detox-A stages. The oil is held in an oil/water separator where oil and water intermingle. Moisture from the chamber collects in the separator and is discharged from the pump several times per cycle. Volume of the discharge would normally be approximately 2 liters and normally has EtO concentrations in excess of 5000 mg/liter. The Joslyn system was modified to attempt to abate this waterborne EtO emission. The EtO-contaminated water collected during the exhaust and detox-A stages is transferred to a "heater" for hydrolysis followed by transfer to the heated sterilizer chamber water jacket, which is discharged to the floor drain.
3. A water ring seal pump is used to evacuate the chamber during the preconditioning and the detox-B stages. The pump working fluid (water) is discharged to the floor drain and vapors are discharged to a floor drain vent. The aeration stage (the manufacturer calls this stage "detoxification-B") discharges of EtO must be controlled/compliance tested at those facilities permitted for use over 600 pounds of EtO per year (as per the statewide ATCM) or as dictated by the District Rule.

The following general test procedures are recommended:

#### Sterilization Exhaust

1. Use of the inlet estimation technique, as described in Appendix B, to calculate the mass of EtO delivered to the inlet of the recovery/control system.
2. Capture the total exhaust from the acid scrubber with a small volume Tedlar bag. Do not manually induce a compressor emission. This testing must be conducted in such a manner that no back pressure and/or leaks are produced in the acid scrubber. If the system does not offgas during testing then the district may ask the facility to provide an engineering estimate (worst plausible case calculations) of mass of EtO emitted from the acid scrubber.

This emission estimate could be used in calculating the system control efficiency.

3. Follow the Tedlar bag sampling and analytical quality control procedures described in Appendix I. In particular, follow the Initial Performance Demonstration, Routine Calibration Procedures and Routine Quality Control Procedures.
4. Collect and analyze water samples from the outlet of the heated sterilization chamber water jacket.
5. Run three cycles with the sterilization chamber empty and average the results.

#### Aeration Exhaust

1. Use the measurement methods described in Appendix A to determine the mass of EtO delivered to the inlet of, and emitted from, the aeration exhaust control system. Do not abort or shorten the exposure stage.
2. Use the volumetric flow measurement procedure appropriate for the facility's stack diameter, configuration and flow characteristics.
3. Collect and analyze the water discharge of the control system associated with the water ring seal pump during the detoxification (aeration) stage.
4. Run one cycle with a normal load in the aeration chamber.

**State of California  
California Environmental Protection Agency  
Air Resources Board**

**Proposed**

**Method 436**

**Determination of Multiple Metals  
Emissions from Stationary Sources**

**Adopted: \_\_\_\_\_**

It is proposed that the content of ARB Method 436, Determination of Multiple Metals Emissions from Stationary Sources, be adopted as shown in the following text.

Proposed deletions are noted by ~~graphic text~~, proposed additions are noted by underline.

The reporting limit (RL) is a limit for each metal at or below which data must not be reported. It is based on the minimum analyte mass that must be collected in the sampling train to allow detection during routine laboratory operation within the precision established by the MDL determination. The RL will be calculated as 5 times the MDL for those metals not detected in pre-test reagent blanks. The RL for detected metals will be calculated as 5 times the pre-test reagent blank detection level.

## 2 RANGE, PRECISION, METHOD DETECTION LIMIT, REPORTING LIMIT AND INTERFERENCES

### 2.1 ANALYTICAL RANGE

For the analyses described in this methodology and for similar analyses the ICPAES response is linear over several orders of magnitude. Samples containing metal concentrations in the nanograms per milliliter (ng/ml) to micrograms per milliliter ( $\mu\text{g/ml}$ ) range in the final analytical solution can be analyzed using this technique. Samples containing greater than approximately 50  $\mu\text{g/ml}$  of chromium, lead, or arsenic should be diluted to that level or lower for final analysis. Samples containing greater than approximately 20  $\mu\text{g/ml}$  of cadmium should be diluted to that level before analysis.

### 2.2 METHOD PRECISION

The precision (relative standard deviation) for each metal detected in an EPA method development test at a sewage sludge incinerator, are as follows: Sb (12.7%), As (13.5%), Ba (20.6%), Cd (11.5%), Cr (11.2%), Cu (11.5%), Pb (11.6%), P (14.6%), Se (15.3%), Tl (12.3%), and Zn (11.8%). The precision for nickel was 7.7% for another test conducted at a source simulator. Beryllium, manganese and silver were not detected in the tests; however, based on the analytical sensitivity of the ICP for these metals, it is assumed that their precisions should be similar to those for the other metals, when detected at similar levels.

### 2.3 METHOD DETECTION LIMIT (MDL)

Method detection limits for the target metals using the various analytical techniques referenced in this method are estimated in Table 1. The MDLs shown in Table 1 assume complete digestion and a final sample volume of 300 ml. For example, if the sample fraction volume is reduced from 300 ml to 30 ml, the MDL for that fraction is improved by a factor of ten. Actual MDLs are sample dependent and will vary based on the final sample volume, the sample matrix and the skill of the analyst.

ICPAES method 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), 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). ICPMS method analytical detection limits shown in Table 1 are estimated MDL's and generally based on SW-846, Method

5020) are lower generally by a factor of ten or more. Be is lower by a factor of three. The actual sample method analytical detection limits are sample dependent and may vary due to the sample matrix.

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), 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).

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

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

## 2.4 REPORTING LIMIT (RL)

The tester shall calculate the reporting limits (RLs) for the target metals. This value will be 5 times the MDL determined for the pre-test blank contamination checks or 5 times the field blank sample results if no pre-test analyses are performed. If the field blank analytical results yield unacceptable RLs, then the field reagent blanks may be analyzed to calculate RLs.

The RL is a required parameter for pre-test minimum sample volume and minimum sample time determination. Therefore, when no pre-test contamination checks are performed, the minimum RL for each target metal shall be estimated as 5 times the MDL shown in Table 1 or 5 times the MDL estimated by the laboratory performing sample analysis.

### Note:

If reagent blanks are not analyzed prior to testing, the RLs are calculated as 5 times the MDL or detection level, whichever is greater, determined for the field blank sample train. If the field blank detection levels yield unacceptable RLs, then the RLs may be established by analysis of the field reagent blank samples.

## 2.5 INTERFERENCES

### 2.5.1 ICP

Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Background

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

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), 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).

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

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

## 2.4 REPORTING LIMIT (RL)

The tester shall calculate the reporting limits (RLs) for the target metals. This value will be 5 times the MDL determined for the pre-test blank contamination checks or 5 times the field blank sample results if no pre-test analyses are performed. If the field blank analytical results yield unacceptable RLs, then the field reagent blanks may be analyzed to calculate RLs.

The RL is a required parameter for pre-test minimum sample volume and minimum sample time determination. Therefore, when no pre-test contamination checks are performed, the minimum RL for each target metal shall be estimated as 5 times the MDL shown in Table 1 or 5 times the MDL estimated by the laboratory performing sample analysis.

### Note:

If reagent blanks are not analyzed prior to testing, the RLs are calculated as 5 times the MDL or detection level, whichever is greater, determined for the field blank sample train. If the field blank detection levels yield unacceptable RLs, then the RLs may be established by analysis of the field reagent blank samples.

## 2.5 INTERFERENCES

### 2.5.1 ICP

Iron can be a spectral interference during the analysis of arsenic, chromium, and cadmium by ICP. Aluminum can be a spectral interference during the analysis of arsenic and lead by ICP. Generally, these interferences can be reduced by diluting the sample, but this increases the method detection limit. Background and overlap corrections may be used to adjust for spectral interferences. Refer

first impinger is used as a water knockout, it shall be of the Greenburg-Smith design modified to have either a short or long stem, appropriately sized for the expected moisture catch and installed empty. The second impinger ~~for the first HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> impinger~~ shall be of the Greenburg-Smith design modified to have a long stem as described for the first impinger in ARB Method 5, Section 2.1.7 and contain 100 ml of 5% HNO<sub>3</sub>/10% H<sub>2</sub>O<sub>2</sub> solution (Section 4.3.1). The third impinger (or the impinger used as the second HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> impinger) shall be of the Greenburg-Smith design with the standard tip as described for the second impinger in ARB Method 5, Paragraph 2.1.7 and contain 100 ml of 5% HNO<sub>3</sub>/10% H<sub>2</sub>O<sub>2</sub> solution (Section 4.3.1).

The fourth impinger shall be installed empty and shall be of the Greenburg-Smith design modified to have a short stem. The function of the fourth impinger is to prevent commingling of the solution in the second and third impingers with the solution in the fifth and sixth impingers. The fifth and sixth impingers shall be of the Greenburg-Smith design modified to have a long stem and shall each contain 100 ml ~~a known quantity~~ of acidic potassium permanganate (4% KMnO<sub>4</sub>/10% H<sub>2</sub>SO<sub>4</sub>) solution (Section 4.3.3). A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knock out impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

In summary, the optional first impinger is empty, the second and third shall each contain 100 ml ~~known quantities~~ of a nitric acid/hydrogen peroxide solution (5% HNO<sub>3</sub>/10% H<sub>2</sub>O<sub>2</sub>, Section 4.3.1), the fourth shall be empty, the fifth and sixth shall each contain 100 ml ~~a known quantity~~ of acidic potassium permanganate solution (4% KMnO<sub>4</sub>/10% H<sub>2</sub>SO<sub>4</sub>, Section 4.3.3). A thermometer capable of measuring to within 1°C (2°F) shall be placed at the outlet of the last impinger. When the water knock out (first) impinger is not needed, it is removed from the train and the other impingers remain the same. If mercury analysis is not needed, the potassium permanganate impingers and the empty impinger preceding them are removed.

#### 4.1.7 Silica Gel Cartridge

A silica gel cartridge or impinger shall be placed at the exit of the sixth (last) impinger. The silica gel may be contained in an impinger in the ice bath or an external cartridge if desired. The cartridge or impinger shall contain 200 to 300 grams of silica gel or equivalent desiccant for use in determining stack gas moisture and to prevent damage to the metering system.

#### 4.1.8 Pitot Tube

Type S, as described in Section 2.1 of ARB Method 2 or other devices approved by the Executive Officer. The pitot tube shall be attached to the probe to allow constant monitoring of the stack gas velocity as required by Section 2.1.3 of

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 should be analyzed for each target metal prior to emission testing. Quartz fiber or glass fiber filters without organic binders such as the Pallflex 2500QAT-UP shall be used. However, if glass fiber filters which meet these requirements become available, they may be used. The filters should exhibit at least 99.95 percent efficiency ( $<0.05$  percent penetration) on 0.3 micron dioctyl phthalate smoke particles.

#### 4.2.2 Water

Deionized, distilled. Water conforming to ASTM Specification D1193-77, Type II (incorporated by reference) is recommended. If necessary, analyze the water required that the water be analyzed for all target metals prior to field use (see Sections 7.1 through 7.3). All target metal concentrations shall 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

Thirty Percent (V/V).

#### 4.2.6 Potassium Permanganate

#### 4.2.7 Sulfuric Acid

Concentrated.

#### 4.2.8 Silica Gel and Crushed Ice

Same as ARB Method 5, Sections 3.1.2 and 3.1.4 respectively.

### 4.3 SAMPLING REAGENT PREPARATION

#### 4.3.1 Nitric Acid ( $\text{HNO}_3$ )/Hydrogen Peroxide ( $\text{H}_2\text{O}_2$ ) Absorbing Solution, 5 Percent $\text{HNO}_3$ /10 Percent $\text{H}_2\text{O}_2$

Add carefully with stirring 50 ml of concentrated  $\text{HNO}_3$  to a 1000-ml volumetric flask or graduated cylinder containing approximately 500 ml of water, and then add 333 ml of 30 percent  $\text{H}_2\text{O}_2$ . Dilute to volume with water. Mix well. The

- 4.5.31 TI Standard (AAS Grade), 1000 ug/ml
- 4.5.32 V Standard (AAS Grade), 1000 ug/ml
- 4.5.33 Zn Standard (AAS Grade), 1000 ug/ml
- 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 (see EPA SW-846 Method 7470A, Section 5.9 for preparation) to a 500 mL volumetric flask; dilute to 500 mL by first adding 20 mL of 15 percent  $\text{HNO}_3$  and then adding water to the 500 mL volume. 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 5 percent (w/v)  $\text{KMnO}_4$  (Section 4.5.9), 5 mL of 15 percent  $\text{HNO}_3$ , and then water.

Use at least five separate aliquots of the working mercury standard solution and a blank to prepare the standard curve in the linear range of the instrument. 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  $\mu\text{g/mL}$  standard and diluting until in the calibration range.

4.5.35 ICP Standards and Quality Control Samples

Calibration standards for ICP analysis can be combined into four different mixed standard solutions as follows:

MIXED STANDARD SOLUTIONS FOR ICP ANALYSIS	
Solution	Elements
I	As, Be, Cd, Mn, Pb, Se, Zn
II	Ba, Co, Cu, Fe,
III	Al, Cr, Ni
IV	Ag, P, Sb, TI

Prepare these standards by combining and diluting the appropriate volumes of the 1000  $\mu\text{g/mL}$  solutions with 5 percent nitric acid. Use a minimum of one standard and a blank to form each calibration curve. Also prepare a separate quality control sample spiked with known amounts of the target metals in quantities in the midrange of the calibration curve. Suggested standard levels are 25  $\mu\text{g/mL}$  for Al, Cr and Pb, 15  $\mu\text{g/mL}$  for Fe, and 10  $\mu\text{g/mL}$  for the remaining elements. Standards containing less than 1  $\mu\text{g/mL}$  of metal should be

prepared daily. Standards containing greater than 1  $\mu\text{g}/\text{mL}$  of metal are typically stable for a minimum of 1 to 2 weeks. For ICPMS, follow Method 6020 in SW-846.

#### 4.5.36 Graphite Furnace AAS Standards for Antimony, Arsenic, Cadmium, Cobalt, Lead, Selenium, and Thallium

Prepare a 10  $\mu\text{g}/\text{mL}$  standard by adding 1 mL of 1000  $\mu\text{g}/\text{mL}$  standard to a 100 mL volumetric flask. Dilute to 100 mL with 10 percent nitric acid. For graphite furnace AAS, the standards must be matrix matched; e.g., if the samples contain 6 percent nitric acid and 4 percent hydrofluoric acid, the standards should also be made up with 6 percent nitric acid and 4 percent hydrofluoric acid. Prepare a 100 ng/mL standard by adding 1 mL of the 10  $\mu\text{g}/\text{mL}$  standard to a 100 mL volumetric flask and dilute to 100 mL with the appropriate matrix solution. Prepare other standards by dilution of the 100 ng/mL standards. At least five standards should be used to make up the standard curve. Suggested levels are 0, 10, 50, 75, and 100 ng/mL. Prepare quality control samples by making a separate 10  $\mu\text{g}/\text{mL}$  standard and diluting until it is in the range of the samples. Standards containing less than 1  $\mu\text{g}/\text{mL}$  of metal should be prepared daily. Standards containing greater than 1  $\mu\text{g}/\text{mL}$  of metal are typically 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, One tenth (0.1) Percent (V/V)

Dilute 10 mL of 1 percent nickel nitrate solution ([Section 4.5.37.1](#)) to 100 mL with water. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for As.

##### 4.5.37.3 Lanthanum

Carefully dissolve 0.5864 g of  $\text{La}_2\text{O}_3$  in 10 mL of concentrated  $\text{HNO}_3$  and dilute the solution by adding it with stirring to approximately 50 mL of water and then dilute to 100 mL with water. Mix well. Inject an equal amount of sample and this modifier into the graphite furnace during GFAAS analysis for Pb.

#### 4.5.38 Whatman 40 and 541 Filter Papers (or equivalent)

For filtration of digested samples.

**Corporation model or equivalent)**

For sample digestion.

**4.7.4 Beakers and Watchglasses**

250 mL beakers for sample digestion with watchglasses to cover the tops.

**4.7.5 Ring Stands and Clamps**

For securing equipment such as filtration apparatus.

**4.7.6 Filter Funnels**

For holding filter paper.

**4.7.7 Whatman 541 Filter Paper (or equivalent)**

For filtration of digested samples.

**4.7.8 Disposable Pasteur Pipets and Bulbs**

**4.7.9 Volumetric Pipets**

**4.7.10 Analytical Balance**

Accurate to within 0.1 mg.

**4.7.11 Microwave or Conventional Oven**

For heating samples at fixed power levels or temperatures.

**4.7.12 Hot Plates**

**4.7.13 Atomic Absorption Spectrometer (AAS)**

Equipped with a background corrector.

**4.7.13.1 Graphite Furnace Attachment**

With antimony, arsenic, cadmium, lead, selenium, thallium, and hollow cathode lamps (HCLs) or electrodeless discharge lamps (EDLs). Same as EPA SW846, Methods 7041 (antimony), 7060 (arsenic), 7131 (cadmium), 7421 (lead), 7740 (selenium), and 7841 (thallium). Pyrolytically-treated graphite platforms and tubes are recommended.

**4.7.13.2 Cold Vapor Mercury Attachment**

With a mercury hollow cathode lamp or electrodeless discharge lamp. The equipment needed for the cold vapor mercury attachment includes an air recirculation pump, a quartz cell, an aerator apparatus, and a heat lamp or desiccator tube. The heat lamp should be capable of raising the ambient temperature at the quartz cell by 10 °C such that no condensation forms on the wall of the quartz cell. Same as EPA SW846, Method 7470. See **Note No. 2**: Section 7.3 for other acceptable approaches for analysis of Hg in Which analytical detection limits of 0.02 µg Hg/ml were obtained.

#### **4.7.14 Inductively Coupled Plasma Spectrometer**

With either a direct or sequential reader and an alumina torch. Same as EPA Method 6010.

### **5 SAMPLE COLLECTION AND RECOVERY PROCEDURES**

The complexity of this method is such that, to obtain reliable results, tester and analyst must be trained and experienced with the test procedures, including source sampling; reagent preparation and handling; sample handling; safety equipment; analytical calculations; reporting and the specific procedural descriptions throughout this method.

#### **5.1 SAMPLING**

##### **5.1.1 Number of Sample Runs**

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

##### **5.1.2 Sample Train and Sample Recovery Apparatus Preparation**

Follow the same general procedure given in ARB Method 5, Section 4.1.1, except that the filter need not be desiccated or weighed. First rinse all sampling train glassware (including filter support), funnels, flasks, beakers and sample storage containers (if previously used) 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 and allow to air dry. Glassware may be dried in oven if desired. Cover all glassware openings where contamination can occur with a non-contaminating material (do not use aluminum foil) until the sampling train is assembled for sampling.

##### **5.1.3 Preliminary Determinations**

Same as ARB Method 5, Section 4.1.2.

##### **5.1.4 Sample Train Assembly**

Teflon tape or seals or other non-contaminating material should be used if necessary to ensure leak-free sampling train connections. The use of silicone grease is prohibited.

#### 5.1.6 Leak-Check Procedures

Follow the leak-check procedures given in ARB 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).

#### 5.1.7 Sampling Train Operation

Follow the procedures given in ARB 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 ARB Method 5.

**Note:** When sampling for Hg, the tester must take steps to maintain the desired color of the acidified permanganate solution in the last impinger, such as described in Section 7.1.1 of ARB Method 101A. Alternatively, the tester may replace the last impinger, as necessary, with an impinger containing 100 ml of fresh acidified permanganate solution to prevent discoloration. If additional permanganate solution is used during a sample run, it must be combined with the original permanganate solution during sample recovery.

#### 5.1.8 Field Blank Train

There shall be at least one field blank train for each series of three tests or fewer. For sources at which emissions are sampled at more than one sampling location, there shall be at least one blank train assembled at each location for each set of three tests or fewer.

~~Each source test must include at least one field blank train. Prepare and configure the blank train in a manner identical to the actual sampling trains. The field blank train shall be taken through all of the steps from preparation through leak check without actual sampling. Upon completion of the leak check, the entrance and exit of the blank train shall be sealed with non-contaminating material, and the blank train must remain in the test area for a length of time equivalent to an actual Method 4-36 sampling period.~~

Recover the field blank train in the same manner as described for stack samples in Section 5.2. Follow all subsequent sections for digestion, analysis and data reporting.

#### 5.1.9 Calculation of Percent Isokinetic

Same as ARB Method 5, Section 4.1.6.

### 5.2 SAMPLE RECOVERY

March 31, 1997

Proposed M-436 Page 25

#### 5.2.4 Container No. 4 (Impinger 4 - Middle knock-out)

Wipe off the outside of the impinger to remove excess water and other material. Record the weight of the fourth (previously empty) impinger or measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas. Quantitatively rinse the impinger with a measured volume of 0.1 N HNO<sub>3</sub>. Record the volume of rinse used. Add the rinse and impinger catch to a tared, labeled Container No. 4. Determine the pH of this sample. If the pH is greater than 2, acidify the sample with a measured volume of concentrated nitric acid to pH 2 or less.

Record the total rinse volume and concentrated nitric acid used for pH adjustment (when applicable). Seal the container and mark the fluid level. Record the final weight of the container or record the final volume of its contents.

#### 5.2.5 Containers Nos. 5A and 5B (Acidified Potassium Permanganate Solution and Rinses, Impingers No. 5 & 6)

Wipe off the outside of each impinger to remove excess water and other material. Record the weights of both the permanganate impingers (fifth and sixth) or measure the volume to within 0.5 ml. This information is required to calculate the moisture content of the sampled flue gas.

Combine Place the contents of impingers 5 and 6 into a labeled glass storage bottle identified as container 5A. Using measured volumes of fresh KMnO<sub>4</sub>, rinse impingers 5 and 6 and their its and connecting glassware a minimum of three times and pour the rinses into container 5A. Similarly, using measured volumes 50 ml total of water, rinse impingers 5 and 6 and their its connecting glassware a minimum of three times and pour the rinses into container 5A, carefully assuring transfer of any loose precipitated material. Record all rinse volumes and the final weight or final volume of container No. 5A. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.3.3 and properly seal the bottle and clearly label the contents.

Place the contents of impinger 6 into a labeled glass storage bottle identified as container 5B. Using measured volumes of fresh KMnO<sub>4</sub>, rinse impinger 6 and its and connecting glassware a minimum of three times and pour the rinses into container 5B. Using 50 ml total of water, rinse impinger 6 and its connecting glassware a minimum of three times and pour the rinses into container 5B, carefully assuring transfer of any loose precipitated material. Record all rinse volumes and the final weight or final volume of container No. 5B. Mark the height of the fluid level on the outside of the bottle to determine if leakage occurs during transport. See the following note and the Precaution in Paragraph 4.3.3 and properly seal the bottle and clearly label the contents.

Note: Due to the potential reaction of the potassium permanganate with the

acid, there may be pressure buildup in the sample storage bottles. These bottles should not be filled full and should be vented to relieve excess pressure. Venting is highly recommended. A No. 70-72 hole drilled in the container cap and Teflon liner has been found to allow adequate venting without loss of sample.

Do NOT rinse with 8 N HCl if no visible deposits remain after rinsing with the fresh  $\text{KMnO}_4$ .

#### **5.2.6 Container No. 6 (HCl Rinse)**

Examine impingers 5 and 6 for sample residue. If residue is observed, rinse these impingers with 25 mL of 8 N HCl. First, place 200 ml of water in the container. Then wash the impinger walls and stem with the HCl by turning the impinger on its side and rotating it so that the HCl contacts all inside surfaces. Use a total of only 25 ml of 8 N HCl for rinsing both permanganate impingers combined. Rinse the first impinger, then pour the actual rinse used for the first impinger into the second impinger for its rinse. Finally, pour the 25 ml of 8 N HCl rinse carefully into the container. Mark the height of the fluid level on the outside of the container to determine if leakage occurs during transport. Properly seal and label container No. 6.

#### **5.2.7 Container No. 7 (Silica Gel)**

Observe the color of the indicating silica gel to determine whether it has been completely spent and make a notation of its condition. If a balance is available in the field, record the weight of the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g. Alternatively, 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.

#### **5.2.8 Container No. 8 (0.1 N Nitric Acid Field Reagent Blank)**

At least once during each field test, place 100 mL of the 0.1 N nitric acid solution used in the sample recovery process into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

#### **5.2.9 Container No. 9 (5% Nitric Acid/10% Hydrogen Peroxide Field Reagent Blank)**

At least once during each field test, place 200 mL of 5% nitric acid/10% hydrogen peroxide solution used as the nitric acid impinger reagent into a labeled container for use as a field reagent blank. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

### 5.2.10 Container No. 10 (Acidified Potassium Permanganate Field Reagent Blank)

At least once during each field test place 100 mL of the acidified potassium permanganate solution used as the impinger solution and in the sample recovery process into a labeled container for use in the back half field reagent blank for mercury analysis. Seal the container and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

**Note:** This container should be vented, as described in Section 5.2.4, to relieve excess pressure.

### 5.2.11 Container No. 11 (8 N HCl Field Reagent Blank)

Collect only if HCl rinse described in Section 5.2.6 was conducted. At least once during each field test, place carefully and with stirring, 25 mL of the 8 N hydrochloric acid used to rinse the acidified potassium permanganate impingers into 200 mL water in a labeled container for use in the back half field reagent blank for mercury and make the appropriate entries in the reagent blank field data sheet shown in Figure 6.

### 5.2.12 Container No. 12 (Filter Blank)

Once during each field test, place an unused filter from the same lot as the sampling filters in a labeled petri dish. Seal the petri dish and make the appropriate entries in the reagent blank field data sheet shown in Figure 6. Store and transport on wet ice together with the sample filters. This will be used as the field reagent blank.

## 5.3 SAMPLE STORAGE

### 5.3.1 Filters

All filters shall be stored in their labelled petri dish away from possible contamination sources. Source filters should be separated from field and reagent blank filters to prevent cross contamination.

### 5.3.2 Liquid Samples

All liquid samples shall be stored in their respective labelled sample jars away from possible contamination sources. Source samples should be separated from field and reagent blank samples to prevent cross contamination. The tester should also consider separating the acidified  $\text{KMnO}_4$  samples due to their volatile nature.

## 6 ANALYTICAL PREPARATION

### 6.1 FIELD SAMPLES AND REAGENT BLANKS

Note the level of the liquid in each of the containers and determine if any sample was lost during shipment. If leakage has occurred, either void the sample or use methods, subject to the approval of the Executive Officer, to correct the final results. A diagram illustrating sample preparation and analysis procedures for each of the sample train components is shown in Figure 3. Record the data necessary to process, digest and prepare the sample containers for analysis using the data sheets supplied in Figure 7 through Figure 11.

#### 6.1.1 Container No. 1 (Filter)

Divide the filter with its filter catch into portions weighing approximately 0.5 g each. Place the filter pieces into the analyst's choice of either individual microwave pressure relief vessels or Parr<sup>R</sup> Bombs. Add 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid to each vessel. For microwave heating, microwave the sample vessels for approximately 12 to 15 minutes of total heating time at 600 watts in intervals 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). For conventional heating, heat the Parr<sup>R</sup> 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 5.3.2, below.

**Notes:** 1. Suggested microwave heating times are approximate and are dependent upon the number of samples being digested. Sufficient heating is evidenced by sorbent reflux within the vessel.

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

#### 6.1.2 Container No. 2 (Probe Rinse)

Determine the pH of this sample. If the pH is higher than 2, acidify the sample with concentrated nitric acid to pH 2 or lower within five (5) days of sample collection. Then Rinse the sample into a beaker with water and cover the beaker with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Digest the sample in microwave vessels or Parr<sup>R</sup> Bombs by carefully adding 6 mL of concentrated nitric acid and 4 mL of concentrated hydrofluoric acid and then continuing to follow the procedures described in Section 6.1.1; then combine the resultant sample directly with the acid digested portions of the filter prepared previously in Section 6.1.1. The resultant combined sample is referred to as Fraction 1. Filter the combined solution of the acid digested filter and probe rinse samples using Whatman 541 filter paper. Dilute to 150 mL (or the appropriate volume for the expected metals concentration) with water. Measure

and record the combined volume of the Fraction 1 solution to within 0.1 ml. Quantitatively remove a 15 mL aliquot (or 10% of the Fraction 1 volume) and label as Fraction 1B. Label the remaining 135 mL portion (or 90% of the Fraction 1 volume) as Fraction 1A. Analytical Fraction 1A is analyzed using ICP or AAS for all metals except Hg. Analytical Fraction 1B is analyzed using CVAAS for front half Hg.

### 6.1.3 Container No. 3 (Impingers 1-3)

Measure and record the total volume of this sample (Fraction 2) to within 0.5 ml. Remove an aliquot equal in volume to Analytical Fraction 1B for mercury analysis and label as Fraction 2B. Label the remaining portion of Container No. 3 as Fraction 2A. ~~Combine Analytical Fractions 1B and 2B to create Analytical Fraction B.~~

~~Determine the pH of Fraction 2A within five (5) days of sample collection. If necessary, acidify using concentrated nitric acid to pH 2 or lower.~~ Rinse the sample into a beaker with water and cover with a ribbed watchglass. Reduce the sample volume to approximately 20 mL by heating on a hot plate at a temperature just below boiling. Alternatively, the sample volumes may be reduced by heating the original sample containers covered by a ribbed watchglass on a hot plate. Then follow either of the digestion procedures described in Sections 6.1.3.1 and 6.1.3.2 below.

Fraction 2A is combined with Fraction 1A to form Analytical Fraction A and analyzed using ICP or AAS for all metals except Hg. Fraction 2B is combined with Fraction 1B to form Analytical Fraction B and analyzed using CVAAS to determine front half mercury.

#### 6.1.3.1 Conventional Digestion Procedure

Add 30 mL of 50 percent nitric acid and heat for 30 minutes on a hot plate to just below boiling. Add 10 mL of 3 percent hydrogen peroxide and heat for 10 more minutes. Add 50 mL of hot water and heat the sample for an additional 20 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

#### 6.1.3.2 Microwave Digestion Procedure

Add 10 mL of 50 percent nitric acid and heat for 6 minutes total heating time in alternating intervals 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 6.1.1. Allow the sample to cool. Add 10 mL of 3 percent hydrogen peroxide and heat for 2 more minutes. Add 50 mL of hot water and heat for an additional 5 minutes. Cool, filter the sample, and dilute to 150 mL (or the appropriate volume for the expected metals concentrations) with water.

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

**6.1.4 Container No. 4 (Impinger 4)**

Measure and record the volume of impinger 4 to within 0.5 ml and place in Container No. 4. Label the contents of container No. 4 as Analytical Fraction C. Analytical Fraction C will be separately analyzed for Hg using CVAAS.

**6.1.5 Container Nos. 5A and 6 5B (Impingers 5, 6 and HCl Rinse, If Necessary)**

Measure and record the volume of impinger 5 to within 0.5 ml and place in Container No. 5A. Measure and record the volume of impinger 6 to within 0.5 ml and place in Container No. 5B. Keep the samples in containers Nos. 5A and 5B separate from each other.

To remove any brown  $MnO_2$  precipitate from the contents of Container No. 5A, 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. 5A to be Analytical Fraction D. Analyze Analytical Fraction D 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. 6 5B 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. 5A 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 E. Analyze Analytical Fractions C, D and E according to the procedures in Section 7.3.

**6.1.6 Container No. 6 (HCl Rinse)**

This sample will exist only if the HCl rinse was necessary. Measure and record the total volume of this sample to within 0.5 ml. This sample is referred to as Fraction F. This sample is analyzed as described in Section 7.3.

**6.1.6 Container No. 7 (Silica Gel)**

March 31, 1997

Weigh the spent silica gel (or silica gel plus impinger or cartridge) to the nearest 0.5 g using a balance (this step may be conducted in the field).

#### 6.1.7 ~~8~~ Field Reagent Blanks

The field reagent blank samples in Container Numbers 8 through 12 produced previously in Sections 5.2.8 through 5.2.12, respectively, are used to correct sample values when authorized by the Executive Officer. These field reagent blanks shall be processed, digested, and analyzed as shown in Figure 4 and described as follows. Digest and process Container No. 12 contents per Section 5.3.1. Combine Container No. 8 with the contents of Container No. 9 and digest and process the resultant volume per Section 5.3.3. Combine the diluted digestates from Containers 8, 9 and 12. Use aliquots as Fractions A and B Blanks. Container No. 10 and Container No. 11 contents are Fraction C Blank and Fraction E Blank respectively. Analyze Fraction C and E Blanks (if applicable) per Section 7.3.

## 7 SAMPLE ANALYSIS

For each sampling train, four to ~~five~~ ~~six~~ individual samples are generated for analysis. Three to four of these samples are specific to mercury, the remaining sample is specific to all other target metals. A schematic identifying each sample and the prescribed sample preparation and analysis scheme is shown in Figure 3.

Fractions A and B consist of the digested samples for the train from the probe rinse through impinger 3. Fraction A is for ICPAES, ICPMS or AAS analysis as described in Sections 7.1 and/or 7.2. Fraction B is for determination of front half mercury as described in Section 7.3. Fraction C consists of the impinger contents and rinses from impinger 4 (middle knockout impinger). Fraction ~~D~~ consists of the impinger contents and rinses from permanganate Impingers 5 and 6. ~~Fraction D consists of the impinger contents and rinses from permanganate impinger 6 combined with the digested MnO<sub>2</sub> precipitate from impinger 5.~~ These samples are analyzed for mercury as described in Section 7.3.

Depending on the test, there may be a separate sample from ~~Impinger 4 (Fraction E)~~ and/or an HCl rinse of impingers 5 and 6 combined with the digested MnO<sub>2</sub> precipitate from Fraction D. ~~This~~ These samples should be analyzed for mercury and included in the total back half mercury catch. The total back half mercury catch is determined from the sum of Fraction C, Fraction D and ~~Fraction E~~ Fraction E. Report the analytical results on the Laboratory Analytical Results data sheet shown in Figure 12.

### 7.1 ICPAES AND ICPMS ANALYSIS

Analyze analytical fraction A by ICPAES using Method 6010 or Method 200.7 (40 CFR 136, Appendix C). Calibrate the ICP, and set up an analysis program as described in Method 6010 or Method 200.7. Follow the quality control procedures described in Section 9.4.1. Recommended wavelengths for analysis are as follows:

<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
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 ICPMS analysis by following Method 6020 in SW-846.

**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.

### 7.2 AAS by Direct Aspiration and/or Graphite Furnace

Analysis of metals in Fraction A using graphite furnace or direct aspiration AAS is often a preferred option. Use Table 2 to determine which techniques and methods should be applied for each target metal. Table 2 also lists possible interferences and ways to minimize these interferences. Calibrate the instrument according to Section 8.3 and follow the quality control procedures specified in Section 9.4.2.

### 7.3 Cold Vapor AAS Mercury Analysis

Analyze analytical fractions B, C, D (if applicable) and E (if applicable) separately for Hg using CVAAS following the method outlined in EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Analysis, 15th Edition, Method 303F, or, optionally using NOTE No. 2 at the end of this section. Set up the calibration curve (zero to 1000 ng) as described in SW-846 Method 7470, Section 4.5.34 of

this method or similar to Method 303F using 300-ml BOD bottles instead of Erlenmeyers. Perform the following for each Hg analysis. From each original sample, select and record an aliquot in the size range from 1 ml to 10 ml. Dilute the aliquot to 100 ml with water. If no prior knowledge of the expected amount of Hg in the sample exists, a 5 ml aliquot is suggested for the first dilution to 100 ml (see NOTE No. 1 at end of this Section). The total amount of Hg in the aliquot shall be less than 1  $\mu\text{g}$  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. Next add to it sequentially the sample digestion solutions and perform the sample preparation described in the procedures of SW-846 Method 7470 or Method 303F. (See NOTE No. 2 at the end of this Section). If the maximum readings are off-scale (because Hg in the aliquot exceeded the calibration range; including the situation where only a 1-ml aliquot of the original sample was digested), then dilute the original sample (or a portion of it) with 0.15 percent  $\text{HNO}_3$  (1.5 ml concentrated  $\text{HNO}_3$  per liter aqueous solution) so that when a 1- to 10-ml aliquot of the "0.15  $\text{HNO}_3$  percent dilution of the original sample" is digested and analyzed by the procedures described above, it will yield an analysis within the range of the calibration curve.

**NOTE No. 1:** When Hg levels in the sample fractions are below the RLs given in Table 1, select a 10 ml aliquot for digestion and analysis as described.

**NOTE No. 2:** Optionally, Hg can be analyzed by using the CVAAS analytical procedures given by some instrument manufacturer's directions. These include calibration and quality control procedures for the Leeman Model PS200, the Perkin Elmer 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 ~~Section 4.5.7~~ Section 4.5.7 (The Leeman, Perkin Elmer, and similar instruments described in this note add automatically the necessary stannous chloride solution during the automated analysis of Hg.); (2), Upon completion of the digestion described in (1), analyze the sample according to the instrument manufacturer's directions. This approach allows multiple (including duplicate) automated analyses of a digested sample aliquot.

## 8 CALIBRATION

Maintain a laboratory log of all calibrations.

### 8.1 Sampling Train Calibration

Calibrate the sampling train components according to the indicated sections of ARB 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).

## **8.2 Inductively Coupled Plasma Spectrometer Calibration**

Prepare standards as outlined in Section 4.5. Profile and calibrate the instrument according to the instrument manufacturer's recommended procedures using the above standards. Check the instrument calibration once per hour. If the instrument does not reproduce the concentrations of the standard within 10 percent, the complete calibration procedures should be performed. Perform ICPMS calibration by following Method 6020 in SW-846.

## **8.3 Atomic Absorption Spectrometer - Direct Aspiration, Graphite Furnace and Cold Vapor Mercury Analyses**

Prepare the standards as outlined in Section 4.5 and use them to calibrate the spectrometer. Calibration procedures are also outlined in the EPA methods referred to in Table 29-2 and in SW-846 Method 7470 or in Standard Methods for Water and Wastewater Method 303F (for Hg). Run each standard curve in duplicate and use the mean values to calculate the calibration line. Recalibrate the instrument approximately once every 10 to 12 samples.

# **9 QUALITY CONTROL**

## **9.1 PRE-TEST DETERMINATIONS (RECOMMENDED)**

Determine the linear range and minimum detectable and quantifiable limits of the analytical instrument selected for the respective target metals. Determine the reporting limit, minimum sample volume, planned sample volume and planned sample time according to Section 3 of this method.

## **9.2 FIELD REAGENT BLANKS (IF ANALYZED)**

Follow the steps in Figure 4 of this method.

### **9.2.1 Filter, Front and Back Half**

Combine one filter from the same lot as those used for sample collection (Container No. 12) with the reduced digestate from container 8. Combine 15 ml of this sample with a 15 ml aliquot from Container No. 9 and analyze for Hg. Combine the remainder of this sample with digested portion of Container No. 9 and analyze for multimetals.

### **9.2.2 Potassium Permanganate and Hydrochloric Acid**

Analyze the contents of Container No. 10 and Container No. 11 (if applicable) for Hg.

### **9.2.3 Reagent Water Check**

Analyze a minimum of triplicates of the water described in Section 4.2.2 ~~4.1.2~~ for concentrations of target metals. All target metal concentrations shall be less than 1 ng/ml.

### 9.3 SAMPLING

#### 9.3.1 Number of Sample Runs

The number of sampling runs must be sufficient to provide minimal statistical data and in no case shall be less than three (3).

#### 9.3.2 Blank Train

At least one blank train per field test shall be prepared, leak-checked and recovered in the field. The blank train shall be labelled and analyzed as if it were a sample train. The blank train results are used primarily for determining reporting limits (RL's) and as a check for on-site contamination. They also provide information regarding the magnitude of source emissions relative to background.

#### 9.3.3 Dedicated Impingers

Impingers should be coded for easy identification. Impingers used for potassium permanganate should not be used as nitric acid impingers for other tests to avoid contamination.

### 9.4 SAMPLE HANDLING

#### 9.4.1 Storage and Holding Times

Adjust the pH of ~~Store~~ all liquid samples in acid solutions to pH 2 or lower during sample recovery. ~~as soon as practicable after sampling~~. It is recommended that pH paper be used in the field after recovery of the sample train to verify pH 2 or lower condition. ~~Five days is the maximum time allowed between sampling and storage in pH 2 acid solutions~~. All liquid samples should be stored in a secure location immediately after sample train recovery.

Analyze appropriate sample fractions for mercury within 28 days of sample date. Analyze Fraction A for target metals other than mercury within sixty days ~~two months~~ of sampling date.

### 9.5 ANALYTICAL QC

Analytical QA/QC requirements for ICP and AA analysis are summarized in Figure 13.

#### 9.5.1 ICPAES and ICPMS Analysis

Follow the respective quality control descriptions in Section 8 of Methods 6010 and 6020 of SW-846. For the purposes of a three run test series, these requirements have been modified as follows: two instrument check standard runs, two calibration blank runs, one interference check sample at the beginning of the analysis (must be within 25% or analyze by standard addition), one quality control sample to check the accuracy of the calibration standards (must be within 25% of calibration), and one duplicate analysis (must be within 20% of average or repeat all analysis). All reagent blank values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

**9.5.2 Direct Aspiration and/or Graphite Furnace AAS Analysis for Antimony, Arsenic, Barium, Beryllium, Cadmium, Copper, Chromium, Lead, Nickel, Manganese, Mercury, Phosphorus, Selenium, Silver, Thallium, and Zinc**

Analyze all samples in duplicate. Perform a matrix spike on one 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. The results must be within 20 percent or the calibration repeated. All reagent blank values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

**9.5.3 Cold Vapor AAS Analysis for Mercury**

Analyze all samples in duplicate. Analyze a quality control sample to check the accuracy of the calibration standards (within 15% or repeat calibration). Perform a matrix spike on one sample from the nitric impinger portion (must be within 25% or samples must be analyzed by the method of standard additions). Additional information on quality control can be obtained from EPA SW-846 Method 7470 or in Standard Methods for Water and Wastewater Method 303F Fraction B blank, fraction C blank and fraction E blank (if applicable) values shall be reported with sample values to allow project engineer to calculate blank corrections, when appropriate, or Reporting Limits in instances when no pre-test analyses were performed or field blank analytical results in excess of the Method Detection Limit. Laboratories may make laboratory method blank corrections to sample data, but shall flag each sample value which received a laboratory method blank correction and report the magnitude of the correction applied.

method (laboratory) blank metals concentrations, calculate the total amount of each of the quantified metals collected in the sampling train as follows:

$$M_t = (M_A - M_{Ab}) \quad \text{Eq. 436-9}$$

where:

$M_t$  = Total mass of each metal (separately stated for each metal) collected in the sampling train,  $\mu\text{g}$ .

$M_{Ab}$  = Blank correction value for mass of metal detected in the Fraction A method (laboratory) blank,  $\mu\text{g}$ .

## 10.5 Hg IN SOURCE SAMPLE

### 10.5.1 Front-Half Hg; Analytical Fraction B

Calculate the amount of Hg collected in the filter and probe rinse combined with impingers 1 through 3 to form Analytical Fraction B of the sampling train by using Equation 436-10:

$$Hg_{fh} = \frac{Q_B}{V_B} (V_{soln,B}) \quad \text{Eq. 436-10}$$

where:

$Hg_{fh}$  = Total mass of Hg collected in Analytical Fraction B (filter, probe rinse and first three impingers of the sampling train),  $\mu\text{g}$ .

$Q_B$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL in the ALIQUOT of Analytical Fraction B analyzed. **NOTE:** For example, if a 10 ml aliquot of Analytical Fraction B is digested, but only 1 ml is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 10 ml aliquot for  $Q_B$ .

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

$V_B$  = Volume of aliquot of Analytical Fraction B analyzed, ml. **Note:** For example, if the 10 ml aliquot of Analytical Fraction B mentioned above was first diluted to 50 ml with 0.15 percent  $\text{HNO}_3$  as described in Section 5.4.3 to bring it into the proper analytical range, and then 1 ml of that 50-ml was digested according to Section 7.3 and analyzed,  $V_B$  would be 0.2 ml (10 ml/50 ml).

10.5.2 Back Half Hg; Analytical Fractions C, D and E

10.5.2.1 Calculate the amount of Hg collected in Analytical Fraction C (middle knockout impinger 4 ~~5~~), ~~and~~ Analytical Fraction D (impingers 5 and ~~6~~) and Analytical Fraction E (HCl rinse) by using Equation 436-11:

$$Hg_{C,D,E} = \frac{Q_{C,D,E}}{V_{C,D,E}} (V_{soln,C,D,E}) \quad \text{Eq. 436-11}$$

where:

$Hg_{C,D,E}$  = Total mass of Hg collected in Analytical Fraction C, D or E  $\mu\text{g}$ .

$Q_{C,D,E}$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL in the ALIQOT of Analytical Fraction C, D or E analyzed. **NOTE:** For example, if a 10 ml aliquot of Analytical Fraction C is digested, but only 5 ml is analyzed (according to Section 7.3 and its NOTES Nos. 1 and 2), then calculate and use the total amount of Hg in the 5 ml aliquot for  $Q_C$ .

$V_{soln,C,D,E}$  = Total volume of Analytical Fraction C, D or E, ml.

$V_{C,D,E}$  = Volume of Analytical Fraction C, D or E analyzed, ml. **Note:** For example, if the 10 ml aliquot of Analytical Fraction C mentioned above was first diluted to 100 ml with 0.15 percent  $\text{HNO}_3$  as described in Section 7.3 to bring it into the proper analytical range, and then 5 ml of that 100ml was digested and analyzed,  $V_C$  would be 0.1 ml (10 ml/100 ml).

~~10.5.2.2 Calculate each of the back-half Hg values for Analytical Fractions E (middle knockout impinger) and F (HCl rinse) by using Equation 436-12:~~

~~$$Hg_{E,F} = \frac{Q_{E,F}}{V_{E,F}} (V_{soln(E,F)}) \quad \text{Eq. 436-12}$$~~

~~where:~~

$Hg_{EF}$  = Total mass of Hg collected separately in Fraction E or F,  $\mu\text{g}$ .

$Q_{EF}$  = Quantity of Hg,  $\mu\text{g}$ , TOTAL, separately, in the ALIQUOT of Analytical Fraction E, or F analyzed (see previous notes in Sections 10.5.1 and 10.5.2 describing the quantity "Q" and calculate similarly).

$V_{EF}$  = Volume, separately, of Analytical Fraction E or F analyzed, ml (see previous notes in Sections 10.5.1 and 10.5.2, describing the quantity "V" and calculate similarly).

$V_{\text{solnt}(E)}$  = Total volume, separately, of Analytical Fraction E or F, ml.

10.5.2.23 Calculate the total amount of Hg collected in the back-half of the sampling train by using Equation 436-13:

$$Hg_{bh} = Hg_C + Hg_D + Hg_E + Hg_F \quad \text{Eq. 436-123}$$

where:

$Hg_{bh}$  = Total mass of Hg collected in the back-half of the sampling train,  $\mu\text{g}$ .

10.5.3 Total Train Hg Catch. Calculate the total amount of Hg collected in the sampling train by using Equation 436-14:

**Note:** Blank corrections may only be applied with the approval of the Executive Officer or his or her authorized representative.

$$Hg_t = (Hg_{fh} - Hg_{fhb}) + (Hg_{bh} - Hg_{bhb}) \quad \text{Eq. 436-134}$$

where:

$Hg_t$  = Total mass of Hg collected in the sampling train,  $\mu\text{g}$ .

$Hg_{fhb}$  = Blank correction value (if applicable) for mass of Hg detected in front half method blank,  $\mu\text{g}$ .

$Hg_{bhb}$  = Blank correction value (if applicable) for mass of Hg detected in back-half method blank,  $\mu\text{g}$ .

**Note:** If the total of the measured blank values ( $Hg_{fhb} + Hg_{bhb}$ ) is in the range of 0.0 to 0.6  $\mu\text{g}$ , then use the total to correct the sample value ( $Hg_{fh}$ ).

+  $Hg_{bh}$ ); if it exceeds  $0.6 \mu\text{g}$ , use the greater of I. or II:

I.  $0.6 \mu\text{g}$ .

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

## 10.6 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 436-15:

$$C_s = \frac{M_t}{V_{m(std)}} \quad \text{Eq. 436-14}$$

where:

$C_s$  = Concentration of a metal in the stack gas,  $\mu\text{g}/\text{dscm}$ .

$M_t$  = Total mass of that metal collected in the sampling train,  $\mu\text{g}$ ; (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.

## 10.7 ISOKINETIC VARIATION AND ACCEPTABLE RESULTS

Same as Method 5, Sections 6.11 and 6.12, respectively.

## 11 REPORTING REQUIREMENTS

At a minimum, any test report must include all of the calculations described in Section 10 and all of the sampling and laboratory data resulting from Section 5. Example forms for documenting field testing and laboratory work are provided as Figures 5 through 12. The quality assurance data required by Section 9 must be reported in detail (see Figure 13). This test report shall be maintained by the tester for the period of time required by the appropriate Air Pollution Control District (APCD) or Air Quality Management District (AQMD). ~~at least three years~~ For all tests required or requested by the local APCD/AQMD, ARB, U.S. EPA or other government agency, these records shall be made available to the Executive Officer upon request.

## 12 ALTERNATIVE TEST METHODS

Alternative test methods may be used provided that they are equivalent to Method

TABLE 1

MINIMUM DETECTION AND REPORTING QUANTITATION LIMITS (ug/sample)  
 USING ICP, GFAAS, DAAAS AND CVAAS  
 ASSUMING INSTRUMENT DETECTION LIMITS PUBLISHED IN EPA SW-846\*

ANALYTICAL METHOD	ICPAES		ICPMS		GFAAS		DAAAS		CVAAS	
	MDL	RL	MDL	RL	MDL	RL	MDL	RL	MDL	RL
METAL										
Aluminum (Al)	---	---	0.10	0.51	--	--	--	--	--	--
Antimony (Sb)	9.6	48	0.027	0.13	0.9	4.5	60.	300.	--	--
Arsenic (As)	16	80.	0.37	1.8	0.3	1.5	0.6	3	--	--
Barium (Ba)	0.6	3	0.009	0.043	--	--	30.0	150.	--	--
Beryllium (Be)	0.09	0.45	0.011	0.055	0.06	0.3	1.5	7.5	--	--
Cadmium (Cd)	1.2	6	0.002	0.010	0.03	0.15	1.5	7.5	--	--
Cobalt (Co)	2.1	10.5	0.001	0.005	0.3	1.5	15	75	--	--
Chromium (Cr)	2.1	10.5	0.26	1.3	0.3	1.5	15	75	--	--
Copper (Cu)	1.8	9	0.009	0.045	--	--	6.0	30.	--	--
Lead (Pb)	12.6	63	0.002	0.01	0.3	1.5	30.0	150.	--	--
Manganese (Mn)	0.6	3	0.005	0.023	--	--	3.0	15	--	--

Mercury (Hg)	--	--	---	---	--	--	--	--	0.06 <sup>@</sup>	0.3 <sup>@</sup>
Nickel (Ni)	4.5	22.5	0.014	0.070	--	--	12	60.	--	--
Phosphorous (P)	22.5	112.5	1.77	8.83	--	--	--	--	--	--
Selenium (Se)	22.5	112.5	0.19	0.95	0.6	3	0.6	3	--	--
Silver (Ag)	2.1	10.5	0.013	0.063	--	--	3.0	15	--	--
Thallium (Tl)	12	60.	0.16	0.79	0.3	1.5	30.0	150.	--	--
Vanadium (V)	---	---	0.83	4.1	--	--	--	--	--	--
Zinc (Zn)	0.6	3	0.027	0.14	--	--	1.5	7.5	--	--

\* assumes volume of sample from total train = 300 ml prior to aliquot for analysis

<sup>@</sup>assumes instrument detection limit of 0.2 ng Hg/ml

MDL - Minimum detection limit

RL - Reporting limit = MDL x 5

FIGURE 13

METHOD 436 MULTIPLE METALS  
ANALYTICAL QA/QC REQUIREMENTS

ICPAES: (EPA Method 6010)

REQUIREMENT	CRITERIA
2 instrument check standard runs	within 10% or repeat calibration
2 calibration blank runs	within 3 std. dev. of mean blank value or repeat calibration
1 interference check sample	within 25% of true value
1 quality control sample	within 25% of calibration curve
1 duplicate analysis	within 20% or repeat all analyses

AA: (EPA Method 7000 series)

REQUIREMENT	CRITERIA
Analyze all samples in duplicate	
1 sample matrix spike	within 25% or method of stand. add.
1 quality control sample	within 20% or repeat calibration

ICPMS: (EPA Method 6020)

REQUIREMENT	CRITERIA
Quality Control Sample	Mean Within 10% of True Value
Calibration Blank	Within 20% of the Analyte MDL
Laboratory Control Sample	One per 20 Samples
Calibration Blank Samples	Less than 3 Times Analyte IDL
Calibration Verification Samples	within 10% of calibration standards
Post Digestion Spike Sample	Within 25% of Spike Value
Interference Check Sample	Within 20% of True Value
Mass Calibration Check	Mass Within 0.1 AMU of True Value
Mass Resolution Check	Peak Width 0.9 AMU at 10% Height
Instrument Stability Check	RSD for 4 Replicates Within 5%
Duplicate Sample	RSD Less Than 20%

DEFINITIONS

**Instrument check standards:** prepared by combining compatible elements at concentrations equivalent to the midpoint of their respective calibration curves.

**Calibration blanks:** prepared by diluting 2 mL of (1:1) HNO<sub>3</sub> and 10 mL (1:1) HCl to 100 mL with Type II water.

**Interference check sample:** prepared to contain known concentrations of interfering elements that will provide an adequate test of correction factors.

**Quality control sample:** prepared in the same acid matrix as the calibration standards at approximately the calibration mid-point and in accordance with the instructions provided by the supplier.