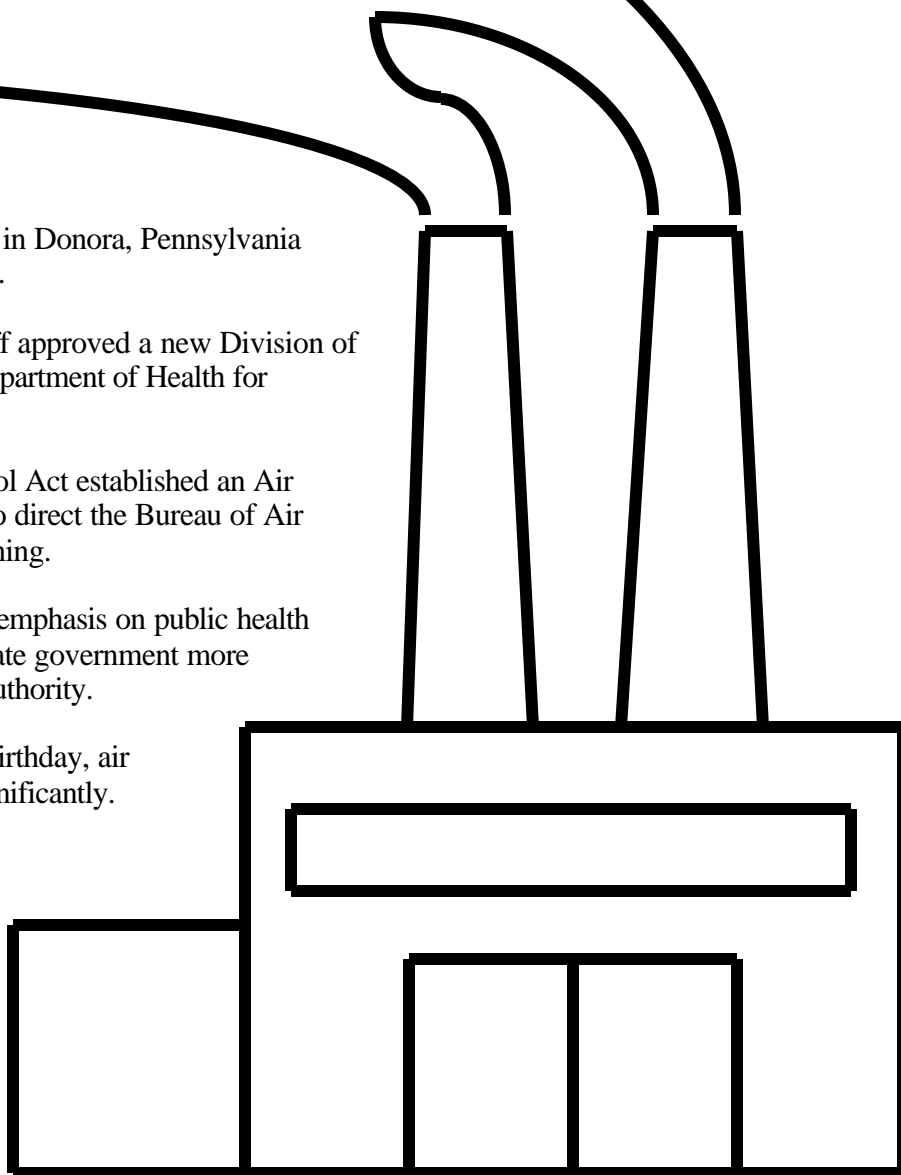


*New Millenium  
Edition*

*Source Testing Manual  
Revision 3.3  
November 2000*

- Oct. 1948 -- Twenty people died in Donora, Pennsylvania from industrial smog.
- Dec. 1948 -- Governor James Duff approved a new Division of Air Quality in the Department of Health for research.
- 1960 -- The Air Pollution Control Act established an Air Pollution Commission to direct the Bureau of Air Pollution Control's planning.
- 1968 -- Legislation put primary emphasis on public health and welfare and gave state government more powerful enforcement authority.
- 1998 -- By the program's 50th birthday, air quality had improved significantly.



Commonwealth of Pennsylvania  
Department of Environmental Protection  
Bureau of Air Quality  
Division of Source Testing & Monitoring  
Source Testing Section

## **Source Testing Manual (Revision 3.3)**

**DOCUMENT NUMBER:** 274-0300-002

**TITLE:** Source Testing Manual (Revision 3.3)

**EFFECTIVE DATE:** November 11, 2000

**AUTHORITY:** 25 Pa. Code §139.3(b)

**POLICY:** The Department will periodically update and publish a supplement to 25 Pa. Code Chapter 139, Sampling and Testing, entitled the Source Testing Manual.

**PURPOSE:** The purpose of this document is to provide detailed information on source test methods, procedures and guidance for the reporting of emissions to the Department.

**APPLICABILITY:** This guidance document applies to anyone conducting source tests at stationary sources or submitting the resultant source test data to the Department.

**DISCLAIMER:** The policies and procedures outlined in this guidance document are intended to supplement existing requirements. Nothing in the policies and procedures shall affect regulatory requirements. The policies and procedures herein are not an adjudication or a regulation. There is no intent on the part of DEP to give the rules in these policies that weight or deference. This document establishes the framework, within which DEP will exercise its administrative discretion in the future. DEP reserves the discretion to deviate from this policy statement if circumstances warrant.

**PAGE LENGTH:** 38 (including the cover and standard elements page)

**LOCATION:** Volume 2, Tab 19

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# Source Testing Manual (Revision 3.3)

## 1. Introduction

Source testing is to be conducted whenever specified by a plan approval, operating permit, consent agreement, et cetera. A detailed knowledge of the operation of the source(s) and any associated air pollution control devices, a thorough understanding of the test method(s) and any limitations, and knowledge of all applicable testing or operating requirements is essential. This manual is intended to clarify the Department's existing regulatory requirements by providing guidance on how to conduct stationary source testing and report the results. This manual does not provide detailed systematic instructions relative to sampling, recovery, or analysis. This information can be found in the promulgated reference methods. More stringent requirements in state and federal regulations, plan approvals, or operating permits supercede the requirements herein. When feasible, the regulated community should be encouraged to make an appraisal of possible changes that could be made to reduce, if not prevent, pollution.

Questions regarding stationary source testing should be directed to:

Pennsylvania Department of Environmental Protection  
Bureau of Air Quality  
Division of Source Testing and Monitoring  
Source Testing Section  
400 Market Street, R.C.S.O.B. (12<sup>th</sup> Floor)  
Harrisburg, PA 17105-8468  
(717) 787-6547

Information pertaining to continuous emission monitoring systems (CEMS) can be found in the Department's Continuous Source Monitoring Manual that can be obtained by writing to:

Pennsylvania Department of Environmental Protection  
Bureau of Air Quality  
Division of Source Testing and Monitoring  
Continuous Emission Monitoring Testing Section  
400 Market Street, R.C.S.O.B. (12<sup>th</sup> Floor)  
Harrisburg, PA 17105-8468  
(717) 787-6547

### 1.1. Organization

This manual is divided into four sections: (1) Introduction, (2) General Requirements, (3) Specific Requirements, and (4) References. Section 1 provides general information about this manual, including web site information and definitions; Section 2 provides requirements that are applicable to testing for all pollutants; Section 3 provides requirements for specific pollutants; and Section 4 lists pertinent references.

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### **1.2. Web Site Information**

The Source Testing Section's web site can be found at the following URL address:

<http://www.dep.state.pa.us/dep/deputate/airwaste/aq/source/sts.htm>. This web site can be used to:

- view important notices, such as pending changes to regulations or guidance documents,
- download the Source Testing Manual or other guidance documents,
- add a name to the mailing list, and
- access other web sites relating to testing to (1) download EPA (OAQPS and OSW) test methods, (2) download a list of testing firms, (3) check on the availability of audit samples, and (4) view other information and guidance.

### **1.3. Definitions**

The terminology used in all submissions to the Department must conform to the definitions in this section or those in 25 Pa. Code §121.1.

#### **1.3.1. Particulate Matter (PM)**

Material, except uncombined water, that is, or has been, airborne and exists as a solid or liquid at 68°F and 29.92 inches Hg.

##### **1.3.1.1. Total Particulate**

The sum of the filterable particulate, as defined in §1.3.1.2 of this manual, and the condensable particulate matter, as defined in §1.3.1.3 of this manual.

##### **1.3.1.2. Filterable (In-Stack) Particulate**

Particulate matter as measured by EPA Method 5 or an equivalent method.

##### **1.3.1.3. Condensable Particulate Matter (CPM)**

The sum of the condensable organic particulate and the condensable inorganic particulate as determined by EPA Method 202 or an equivalent method.

##### **1.3.1.4. Total PM-10**

The sum of the filterable PM-10, as defined in §1.3.1.5 of this manual, and the condensable PM-10, as defined in §1.3.1.6 of this manual.

##### **1.3.1.5. Filterable (In-Stack) PM-10**

Particulate matter with an aerodynamic diameter of  $\leq 10$  micrometers ( $\mu\text{m}$ ) as measured by EPA Method 201, EPA Method 201A, or an equivalent method.

##### **1.3.1.6. Condensable PM-10**

Particulate matter with an aerodynamic diameter of  $\leq 10$  micrometers ( $\mu\text{m}$ ) that forms after entering the atmosphere. There is no reference method for condensable PM-10.

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### **1.3.2. Detection Limit**

#### **1.3.2.1. In-Stack Detection Limit (ISDL)**

The product of the method detection limit and the quantity of analyte, divided by the volume of stack gas sampled. The ISDL is determined in accordance with EMC Guideline Document 038 (Description of In-Stack Detection Limit). Compliance cannot be determined if the ISDL exceeds the emission standard.

#### **1.3.2.2. Method Detection Limit (MDL)**

The minimum concentration or amount of a substance that an analytical method can reliably distinguish from zero. To determine the MDL, analyze a series of at least seven blank samples. The MDL is determined by multiplying the standard deviation of the replicate samples by three.

#### **1.3.2.3. Practical Limit of Quantification (PLQ)**

The minimum concentration or amount of a substance that an analytical method can measure with a specified degree of confidence. To determine the PLQ, analyze a series of at least seven blank samples. The PLQ is determined by multiplying the standard deviation of the replicate samples by ten.

### **1.3.3. Organic Compounds**

#### **1.3.3.1. Volatile Organic Compounds (VOCs)**

An organic compound that participates in atmospheric photochemical reactions; that is, an organic compound other than those that the Administrator of the EPA designates as having negligible photochemical reactivity. The exempted compounds are listed in 40 CFR §51.100(s)(1).

#### **1.3.3.2. Semivolatile Organic Compounds (SVOCs)**

The subset of all volatile organic compounds with boiling points of 300-600°F or vapor pressures= $10^{-1}$  mm Hg as collected by EPA SW-846 Method 0010 and analyzed by EPA SW-846 Method 8270D, or equivalent methods.

#### **1.3.3.3. Total Organic Compounds (TOCs)**

The sum of all volatile organic compounds and all exempted compounds listed in 40 CFR §51.100(s)(1).

#### **1.3.3.4. Total Hydrocarbons (THCs)**

The subset of total organic compounds containing only carbon and hydrogen.

#### **1.3.3.5. Total Non-Methane Organic Compounds (TNMOCs)**

The sum of all volatile organic compounds and all exempted compounds listed in 40 CFR §51.100(s)(1), except methane.

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### **1.3.3.6. Total Non-Methane/Non-Ethane Organic Compounds (TNM/NEOCs)**

The sum of all volatile organic compounds and all exempted compounds listed in 40 CFR §51.100(s)(1), except methane and ethane.

### **1.3.3.7. Polycyclic Organic Matter**

Organic compounds with more than one benzene ring, and which have a boiling point =100°C.

### **1.3.3.8. Hazardous Air Pollutants (HAPs)**

Those compounds listed in §112(b) of the Clean Air Act Amendments of 1990, as amended by the Administrator of the EPA.

## **1.3.4. Other**

### **1.3.4.1. Reference Method (RM)**

A test method promulgated by the EPA for use in determining compliance with an air emission standard or for determining rule applicability.

### **1.3.4.2. Equivalent Method**

A test method that has been proven by an EPA Method 301 validation study to yield results equivalent to those produced by a reference method for a particular source category or a test method that has been approved by the EPA for use in determining compliance with an air emission standard or for determining rule applicability. In the latter case, a copy of the approval letter from the EPA must be provided.

### **1.3.4.3. Response Factor (RF)**

The response of 1 ppm of a reference compound to 1 ppm of a measured compound. The response factor can be determined in accordance with the procedures in EPA Method 204A, 204F, or an equivalent method.

### **1.3.4.4. Instrumental Analyzer**

An analyzer that is not permanently installed at a facility and is used to continuously monitor pollutant concentrations for short time periods (such as three 1-hour test runs).

### **1.3.4.5. Continuous Emission Monitor (CEM)**

An analyzer that is permanently installed at a facility and is used to continuously monitor pollutant concentrations for extended time periods (8760 hours per year, e.g.).

## **2. General Requirements**

### **2.1. Submittals and Approval**

The Department requires two copies of all procedural protocols, source test reports, and correspondence with the Department regarding testing. Both copies should be submitted to the

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Department's Regional Office with jurisdiction over the source(s). If EPA notification is required, a third copy should be sent directly to them. All submittals, including any addendums and revisions, should clearly indicate the recipients to whom copies have been sent. Submissions that do not contain all of the information required by §§2.1.1 (Pretest Procedural Protocols) or 2.1.2 (Source Test Reports) of this manual will not be reviewed for acceptability. Upon receipt of an incomplete submission, the Department will send a deficiency notice stating that the submission is unacceptable to the Department. Copies of this notice will be distributed to the source owner/operator, the testing firm, and the Department's Regional Office. Sanctions may be imposed against those who repeatedly submit incomplete procedural protocols or source test reports.

In accordance with Section 13.1 of the Air Pollution Control Act (35 P.S. §4013.2), the source owner/operator must show cause that information submitted to the Department should be considered confidential and protected from disclosure to the public. The Department will not, however, consider any emissions data confidential information. Each page that contains proprietary information should be clearly marked so that it may be removed from the submittal and stored in a secure area. Only those pages that are stamped "confidential" will be separated. The introductory paragraph for each submittal should indicate (1) if the submittal contains confidential information and (2) the page(s) on which the confidential material (if any) can be found.

### **2.1.1. Pretest Procedural Protocols**

Procedural protocols must be submitted for approval only when mandated by a plan approval, operating permit, or consent agreement. However, submission of a protocol is strongly recommended in all cases to alleviate potential problems and to avoid misinterpretation of the Department's testing requirements. Procedural protocols must be received at least 30 days prior to testing to ensure adequate time for review. The Department's Regional Office, with jurisdiction over the source(s) to be tested, must be notified of the anticipated testing schedule at least 15 days in advance of the start of testing so that a Department observer may be present. Failure to provide adequate notification could lead to rejection of all test results. When testing of a source is required on a recurring basis, a single procedural protocol may be submitted for approval; thereafter, a letter referencing the previously approved procedural protocol is sufficient. If modifications are made to the process(es), or if an applicable section of this manual has been revised since approval, a new protocol must be submitted for approval. Each page of the protocol must be numbered sequentially. The source owner/operator, the testing firm, and the Department's Regional Office will be notified each time that additional information is required. The following information must be included in all pretest procedural submittals.

- 2.1.1.1. The source owner/operator's name, mailing address, contact person (including their job title), and telephone number.



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- 2.1.1.2. The testing firm's name, mailing address, contact person (including their job title), and telephone number.
- 2.1.1.3. The analytical laboratory's name, mailing address, contact person (including their job title), and telephone number.
- 2.1.1.4. A detailed description of each source and any associated air pollution control devices. Include the name of the manufacturer(s), the model number(s), and the Department ID(s).
- 2.1.1.5. A simple block diagram showing: (1) each source, (2) any associated air pollution control devices, (3) all fans and their rated capacities, (4) all raw material flows, and (5) all effluent flows. Do not include engineering drawings.
- 2.1.1.6. A copy of all correspondence, and a written synopsis of all conversations, with the Department regarding the test program.
- 2.1.1.7. The current plan approval or operating permit number(s) for each source to be tested and the issuance date(s).
- 2.1.1.8. The specific objective(s) of the test program such as: (1) compliance with a plan approval or operating permit limit or condition, (2) rule applicability determination (RACT, Title V, et cetera), (3) emission reduction credits, or (4) "periodic monitoring". Note that approval will be dependent on the objective(s). The test results may not be acceptable for other (unspecified) objectives.
- 2.1.1.9. A statement signed by the on-site supervisor for the test team and a representative of the source owner/operator certifying that "to the best of their knowledge" the state and federal regulations, operating permits, or plan approvals applicable to each source or control device to be tested have been reviewed and that all testing requirements therein have been incorporated into the test plan.
- 2.1.1.10. The rated capacity and maximum normal operating conditions (MNOC) for each source and the conditions at which each source and any associated air pollution control devices will be operated during the testing. The rated capacity is typically specified in the Plan Approval Application.
- 2.1.1.11. A list of all process parameters to be recorded during testing to verify that each source is operating at the levels specified in §2.1.1.10 of this manual and that all associated air pollution control devices are operating normally.
- 2.1.1.12. A summary table for each source indicating the pollutants, sampling and analytical procedures (including the method number and date of revision), and all variations to the proposed methods. Unless a variation to the method is proposed, the Department will assume that the testing will follow the reference method, verbatim.

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- 2.1.1.13. A dimensioned diagram showing each testing location, the stack (or duct) dimensions and area, and the distances to the nearest upstream and downstream flow disturbances.
- 2.1.1.14. A table (for each sampling location) indicating the number, configuration, and identification (i.e. A and B) of sampling ports, and the number of traverse points per port.
- 2.1.1.15. A detailed description of the proposed sample collection, recovery (including storage conditions and method of transport), and analytical procedures. If an EPA reference method is to be used without deviation, a copy of the procedure should not be included. However, a copy of other sampling or analytical methods (NIOSH, e.g.) must be provided, even if no deviations are proposed.
- 2.1.1.16. The formulas to be used for all calculations used in data reduction. Note: in some cases, simply referring to the reference method may not be adequate. For instance, the reporting of VOC emissions is not adequately addressed by the reference methods.
- 2.1.1.17. Examples of field data sheets (including chain-of-custody) and field/laboratory calibration sheets.

### **2.1.2. Source Test Reports**

The Department requires at least 60 days to complete its review of source test reports. Additional time may be required if (1) the report is incomplete, poorly organized, or contains numerous errors, (2) the testing program is complex, or (3) the backlog of reviews is substantial. Each page of the report (including the appendices) should be numbered sequentially. Reports that do not contain all of the following information will not be reviewed for acceptability. The source owner/operator, the testing firm, and the Department's Regional Office will be notified each time that additional information is required. The following information must be included in all source test reports:

- 2.1.2.1. All information required in §§2.1.1.1-2.1.1.8 of this manual.
- 2.1.2.2. A detailed description of the actual sample collection, recovery (including storage conditions and method of transport), and analytical procedures. If an EPA reference method was used without deviation, a copy of the procedure should not be included. However, a copy of other sampling or analytical methods (NIOSH, e.g.) must be provided, even if no deviations are proposed.
- 2.1.2.3. A list of all deviations from the approved pretest procedural protocol and problems associated with the sampling, recovery, analysis, or source/control device operation.
- 2.1.2.4. A summary table that includes: (1) the run number, (2) the test date, (3) the volumetric flow rate, (4) the emission concentration, (5) the emission rate in lbs./hour and the units of any applicable emission standard(s), and (6) all applicable standard(s).

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- 2.1.2.5. A summary table of all process parameters (including the units) recorded during the actual testing period to verify that each source was operating at the levels specified in the approved procedural protocol and that all associated air pollution control devices were operating normally.
- 2.1.2.6. A statement signed by the on-site supervisor of the test team and a source owner/operator representative certifying that “to the best of their knowledge” the source test report has been checked for completeness, and that the results presented therein are accurate, error-free, legible, and representative of the actual emissions measured during testing.
- 2.1.2.7. A chain-of-custody record verifying the integrity of the samples.
- 2.1.2.8. The dates and results of the most recent calibrations for pitot tubes, thermocouples, dry gas meters, rotometers, orifices, and any other equipment used which requires periodic calibration. The actual calibration procedures must only be supplied upon request by the Department.
- 2.1.2.9. The results of each audit sample, including the audit sample number, the date(s) of analysis, the name of the analyst(s), and the name of the analytical laboratory.
- 2.1.2.10. All raw field data obtained during the testing and calibration data after the field program.
- 2.1.2.11. All analytical data and calibration data after the field program. As an option, only the calibration curves and sample chromatograms for one of the test runs per pollutant per source must be provided. The remainder of the analytical data must be retained for five years after submittal of the test report and supplied to the Department upon request.
  - 2.1.2.11.1. A statement signed by the laboratory manager certifying that “to the best of their knowledge” the analytical data has been checked for completeness, and that the results presented are accurate, error-free, legible, and have been conducted in accordance with the methods in the approved protocol. A detailed summary of all deviations from the approved methods or problems with the analyses is mandatory.
  - 2.1.2.11.2. Type of instrument(s) and/or detector(s) used, including the manufacturer’s name, the model number, and the range.
  - 2.1.2.11.3. Calibration gas certification sheets including the name, range, type, and vendor.
  - 2.1.2.11.4. Instrument calibration curves with specific instrument ranges.
  - 2.1.2.11.5. Chromatographic data
    - 2.1.2.11.5.1. Chromatograms (must be scaled so that the largest target peak is full scale).
    - 2.1.2.11.5.2. Identity of all target peaks.

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2.1.2.11.5.3. Retention times and peak areas/heights.

2.1.2.11.5.4. Amount of material introduced to the analyzer (for spiked compounds).

2.1.2.11.5.5. Attenuation.

2.1.2.11.5.6. Integration time table.

2.1.2.11.6. Strip charts

All strip charts must be legible, clearly annotated, and must clearly distinguish the concentration trace for each pollutant. The use of colored copies or highlighters is strongly recommended. Strip charts should not be used for data reduction if the measured pollutant concentration is highly variable.

2.1.2.11.6.1. The start/stop of each run, the test data, and the run identifier.

2.1.2.11.6.2. The introduction point of calibration gases.

2.1.2.11.6.3. The calibration gas concentrations.

2.1.2.11.6.4. The “zero” point concentration and the concentration at full scale (span) for each pollutant.

2.1.2.11.6.5. The chart speed.

2.1.2.11.6.6. The point(s) at which changes are made to the span or chart speed.

2.1.2.11.7. Data logger printouts

2.1.2.11.8. QA summary for all field activities

2.1.2.11.8.1. For instrumental analyzers, a Table(s) similar to those provided in Figures 6C-3, 6C-4, and 6C-5 of EPA Method 6C must be provided.

2.1.2.11.8.2. For laboratory instrumentation, a table must be provided for all QA checks (spikes, recovery studies, breakthrough determinations, etc.).

2.1.2.11.9. All laboratory calculations and summary of results.

2.1.2.11.10. All other pertinent information used to calculate the laboratory results.

2.1.2.12. A complete set of sample calculations for one run of each pollutant test. This sample should show all the formulas and input values used to calculate the emissions from the raw data.

2.1.2.13. All other pertinent information used to calculate the emission results.

### **2.2. Detection Limits**

A reasonable attempt must be made to obtain results that are greater than the method detection limit. There are several ways to potentially increase the pollutant concentration above the detection limit, including (1) increasing the sample volume, (2) concentrating the sample, and (3) using high-sensitivity

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analytical techniques. If appropriate steps are not taken, the results that are below the detection limit could be considered unacceptable. If the result for a sample is less than the analytical detection limit, despite reasonable efforts to obtain detectable results, the detection limit shall be utilized in the source emission calculations, except for EPA Methods 23 and 29. For reagent blank values less than the analytical detection limit, a value of zero shall be used. The procedures for PCDDs/PCDFs with values below the detection limit are specified immediately after §9.9 of EPA Method 23. These procedures may also be used for PAHs. For heavy metals, use the following guidelines:

- (1) If all of the fractions are above the detection limit, use the reported values. For example, 10 mg As (FH) and 1 mg As (BH) = 11 mg As (total).
- (2) If one or more fractions, but not all, are below the detection limits, use the detectable values only. For example, 10 mg As (FH) and <1 mg As (BH) = 10 mg As (total).
- (3) If all fractions are below the detection limit, use the detection limits. For example, <10 mg As (FH) and <1 mg As (BH) = <11 mg As (total).

### 2.3. Reagent Blanks

All chemical reagents must be analyzed for contamination, preferably before use in the field. The sample results may be corrected for minor contamination. The maximum allowable blank correction is 0.001% of the reagent weight used, unless specified otherwise by the method. EPA Method 5, for instance, limits the blank correction to 0.001% of the weight of acetone used for recovery of the sample train.

### 2.4. Sampling Times and Volumes

A test program shall consist of three test runs per pollutant with minimum sampling times and volumes greater than or equal to those specified in Table 1 or those stipulated in state/federal requirements, if they are more stringent. The minimum sampling times listed in Table 1 do not apply for variable processes (e.g. batch operations). In these cases, sampling during an entire batch cycle may be necessary. Sample volumes less than those stipulated in Table 1 are acceptable provided the results for all sample fractions are above the detection limit.

Table 1: Minimum Sampling Times and Volumes for Isokinetic Sampling

EPA Method	Time (min.)	Volume (dscf)
5	60	50
23	240	144
29	120	72
306	120	72
0010 (SW-846)	240	144
0061 (SW-846)	90	54
All Others	60	36

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### 2.5. Audit Samples

Audit samples are required when available. The list of available audit materials can be found at <http://www.epa.gov/ttn/emc/email.html#audit>. Do not request the audit materials directly from the EPA. At least 30 days prior to testing, submit a written request for audit samples to:

Pennsylvania Department of Environmental Protection  
Bureau of Air Quality  
Division of Source Testing and Monitoring  
Quality Assurance Unit  
400 Market Street, R.C.S.O.B. (12<sup>th</sup> Floor)  
Harrisburg, PA 17105-8468

The request must include the name and address of the source owner/operator, the source(s), the anticipated test date, the pollutant(s), the test method(s), the expected stack concentration(s), and the mailing address to which the audit is to be delivered, including the company name, contact person (including their job title), the contact's telephone number, and any special instructions. The audit(s) shall be analyzed concurrently with the test samples using the same instrumentation and analysis procedures.

### 2.6. Leak Checks

Immediately following every sampling run and prior to any change in sampling train components, a leak check of the entire sampling train must be conducted. Pitot tube leak checks are also required. Pretest and midtest leak checks are recommended, but not mandatory. For isokinetic sampling, the leakage rate at the highest vacuum during the run must not exceed the lesser of 0.02 cfm or 4% of the average sampling rate. For constant rate sampling, the leakage rate at the highest vacuum must not exceed 2% of the sampling rate. If the leakage rate does not meet these criteria, the run shall be voided. No correction of the sample volume is permitted except as noted hereafter. The measured leakage rate and vacuum for all leak checks (mandatory or voluntary) must be reported in the test report. All leak checks must be conducted as specified in the approved test method.

If the emission rate, corrected for leakage, is  $\geq 20\%$  of the emission standard, the Department may allow correction of the sample volume. The following steps must be followed.

1. The emissions should be presented both with and without the correction of the sample volume.
2. The test run should be "flagged," indicating that it is invalid, but that it might be an acceptable indicator of compliance, after correction for the leakage rate.
3. The Department will evaluate the claim, on a case-by-case basis, using the following criteria:
  - the reason for the excessive leakage (if known),
  - the measured leakage rate versus the allowable leakage rate,
  - the average vacuum during testing versus that during the leakage rate determination, and

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- the number of test runs in the series that have leakage rates in excess of the allowable.

### 2.7. Combined Sampling Trains

The Department allows for the combined collection of particulate and the following compounds: sulfur dioxide/sulfur trioxide (EPA Method 8), hydrogen halides/halogens (EPA Method 26A), heavy metals (EPA Method 29), and condensable particulate matter (EPA Method 202). Dioxins, furans, PCBs, PAHs, and SVOCs may, in some instances, be collected in a single sampling train. Modifications to the collection, recovery, and analysis procedures may be necessary.

### 2.8. Collection Efficiency

In accordance with 25 Pa. Code §§139.12(1) and 139.14(b)(1), sampling trains shall achieve a collection efficiency of  $\geq 95\%$ . Collection efficiency is a function of (1) the concentration of the reagent, (2) the temperature, and (3) the residence time. The collection efficiency for the reference methods has not been evaluated at a wide range of source categories. If a “wet chemical” collection technique is being employed, the last impinger containing reagent must be analyzed separately from the other impingers. If sorbent tubes are being employed, the last section of the sorbent tube must be analyzed separately. If the catch in the last impinger or sorbent tube section is  $>10\%$  of the total catch, the run shall be voided. Exceptions include sampling methods for heavy metals, POHCs, dioxins/furans, PCBs, and PAHs. For EPA SW-846 Methods 0030 and 0031, the last section of the sorbent tube must contain  $\geq 30\%$  for a valid run.

#### Example 1

An EPA Method 26A sampling train for HCl uses two impingers containing acidic solution for collection of the HCl and two impingers containing basic solution for the collection of  $\text{Cl}_2$ . Each impinger containing acidic solution must be analyzed separately. If determination of the  $\text{Cl}_2$  emissions is also desired, each impinger containing basic solution must be analyzed separately.

#### Example 2

An EPA Method 18 sampling train for a specific HAP uses three dual section sorbent tubes. Analysis must be conducted on the first five sections (combined) and the last (sixth) section.

### 2.9. Gas Dilution Systems

Gas dilution systems meeting the requirements of EPA Method 205 may be utilized for field instrument calibrations. Dilution Interface sampling for organic compounds is also allowed provided the testing is conducted in accordance with EPA Method 18.

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### **2.10. Portable Analyzers**

Electrochemical cells are not acceptable for compliance determinations; however, they may be used for NO<sub>x</sub> and CO testing to verify continued compliance. The analyzer must be operated in accordance with the manufacturer's specifications and calibrated over an appropriate range with a certified gas standard with accuracy within  $\pm 2\%$  of the tag value.

### **2.11. F Factors**

The Department will allow the use of the average F Factors published in EPA Method 19, Table 19-1, for sources firing anthracite coal, bituminous coal, lignite coal, oil, natural gas, propane gas, or butane gas. At sources firing all other types of fuel, a composite fuel sample must be collected during each sampling run and the F Factor must be derived from the fuel analysis. Fuel samples must be collected and analyzed by the procedures discussed in §3.4 (Fuel Samples) of this manual.

### **2.12. Calibration, Maintenance, and Quality Assurance**

Reliable, accurate equipment is fundamental to quality source testing. During sampling, there are many separate measurements where bias fluctuations can significantly affect the final test results. An effective quality assurance program will minimize the effect of these equipment-related variables. The Department will not accept the results of a source test unless it has the assurance that appropriate equipment calibrations have been conducted. Prior to and after testing, equipment calibration and routine maintenance must be performed in accordance with the requirements specified in the Quality Assurance Handbook for Air Pollution Measurement Systems.

#### **2.12.1. Calibration Gases**

All calibration gases must be prepared in accordance with the EPA Traceability Protocol for Assay and Certification of Gaseous Calibration Standards. If EPA Traceability Protocol gases cannot be obtained due to a lack of NIST standards, certified gas standards with an accuracy of  $\pm 2\%$  or better must be used. Documentation from the gas supplier must be provided to verify that the certified concentration was valid at the time of testing. Tests conducted with any expired calibration gases must be voided. Alternatively, the expired gases may be reanalyzed and the recertification value shall be used.

#### **2.12.2. Interference Response Checks**

Interference checks are required by EPA Methods 6C, 7E, and 20. These checks are mandatory and must be conducted in accordance with the test method. The results of the interference checks must be provided in the source test report.



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### 3. Specific Requirements

This section contains information regarding reference methods that are generally acceptable to the Department. Source specific factors or method limitations may make these methods unacceptable. The most recently promulgated (or finalized) version of a method must always be employed. This requirement takes precedence over the “year of revision” listed for the ASTM Methods throughout this manual. EPA OAQPS methods can be obtained at the following URL address:

<http://www.epa.gov/ttn/emc/tmethods.html> and EPA OSW methods can be found at:

<http://www.epa.gov/epaoswer/hazwaste/test/sw846.htm>. Reference methods should be used whenever possible. Use of an equivalent method is acceptable. The acceptability of other methods (NIOSH, OSHA, NCASI, OSW EPA SW-846, et cetera) that have not been proven equivalent will be evaluated by the Department on a case-by-case basis. Anyone proposing a methodology not listed in this manual “shall have the burden of proof to demonstrate that the test methods, procedures, and guidance accurately characterize the emissions from the source” per 25 Pa. Code §139.5(f). Sampling locations must be selected in accordance with EPA Method 1 or 1A. If cyclonic flow exists, as determined by §2.4 of EPA Method 1, one of the three recommendations discussed in EMC Guideline Document 008 (Particulate Sampling in Cyclonic Flow) must be followed.

#### 3.1. Inorganic Compounds

##### 3.1.1. Particulate Matter (PM)

###### 3.1.1.1. Total Particulate

Total particulate, as defined in §1.3.1.1 of this manual, shall be determined in accordance with the reference methods in §§3.1.1.2 and 3.1.1.3 of this manual.

###### 3.1.1.2. Filterable (In-Stack) Particulate

The reference methods for the isokinetic determination of filterable particulate, as defined in §1.3.1.2 of this manual, are EPA Methods 5, 5A, 5B, 5D, 5E, 5F, 5G, and 5H. Method 5 is preferred (unless another reference method is applicable). Particulate is captured in the front-half of the sampling train and on the filter. Analysis is gravimetric.

###### 3.1.1.3. Condensable Particulate Matter (CPM)

The reference method for the determination of condensable particulate matter, as defined in §1.3.1.3 of this manual, is EPA Method 202. Both the organic and inorganic fractions must be determined. Sources emitting “oily mists” (potato chip fryers and cold rolling mills, for instance) must use EPA Method 202 modified as follows.

**Sample Collection:** Add an empty, high-volume, modified impinger in front of the first two regular impingers to account for high temperature and moisture. The extra impinger will provide capacity for

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collecting most of the water while cooling the sample gas. The tester should load 350-400 g of 6-16 mesh, indicating silica gel in the last impinger. In addition, the tester should place sufficient ice around the impingers to maintain the temperature of the gas exiting the last impinger at  $\approx 68^{\circ}\text{F}$ .

**Sample Recovery:** Measure and recover the impinger contents as specified; making sure that most of the water is removed. Afterward, rinse the impinger glassware in triplicate with acetone (soluble w/water) and place in a separate container (4A). Following the acetone rinse, rinse the impinger glassware in triplicate with methylene chloride and place in container No. 5 as specified in the method. Collect an acetone blank (6A) equivalent to the amount used during the rinsing of the impingers. In addition, the tester should observe the silica gel color to estimate the percentage that is spent and include this information in the test report.

**Sample Analysis:** Perform analysis on sample fractions as specified in the method. For the acetone fraction (4A), the sample should be placed in a beaker and the acetone allowed to evaporate for 24-48 hours using a hood air sweep. The 4A fraction is then added with the water/methylene chloride fractions prior to the extraction step. Rinse the 4A beaker in triplicate with methylene chloride and add the rinses along with the water/methylene chloride fractions prior to the extraction step. The analyst may incur difficulty in obtaining a "constant weight" if there are considerable amounts of oil in the extracted samples. For the acetone blank (6A), place the sample fraction in a beaker and evaporate as specified for fraction 4A. Afterward, rinse the beaker in triplicate with methylene chloride and add these rinses to the methylene chloride blank (7) prior to the organic fraction weight determination.

### 3.1.1.4. Total PM-10

Total PM-10, as defined in §1.3.1.4 of this manual, shall be determined in accordance with the reference methods in §§3.1.1.5 and 3.1.1.6 of this manual. When determining the PM-10 contribution to ambient levels, such as for emission inventory purposes, the total PM-10 emissions must be determined. If the plan approval, operating permit, or applicable rule (a NSPS Subpart, e.g.) does not specify whether testing is to be conducted for filterable PM-10 or total PM-10 (condensable and filterable), the total PM-10 emissions must be determined.

### 3.1.1.5. Filterable (In-Stack) PM-10

The reference methods for the determination of filterable PM-10, as defined in §1.3.1.5 of this manual, are EPA Methods 201(exhaust gas recycle) and 201A (constant rate). EPA Methods 201 and 201A cannot be used when water droplets are present in the effluent (when it is at or near saturation). The recommended alternative is EPA Method 5 (per EMC Technical Information Document 009).

### 3.1.1.6. Condensable PM-10

There is no reference method for condensable PM-10, as defined in §1.3.1.6 of this manual. EPA Method 202 is acceptable, but the condensable PM-10 results will probably be biased high.

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### 3.1.2. Sulfur Compounds

#### 3.1.2.1. Sulfur Dioxide ( $\text{SO}_2$ )

The reference methods for the non-isokinetic determination of sulfur dioxide are EPA Methods 6, 6A, 6B, 6C, and 8. Methods 6, 6C, and 8 are preferred (when applicable). Methods 6 and 8 collect the sulfur dioxide in the same manner. The sulfur dioxide is converted to sulfate ion ( $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$ ) in the impingers containing peroxide (3%  $\text{H}_2\text{O}_2$ ). Carryover of solution from the first impinger (IPA) into the following impingers ( $\text{H}_2\text{O}_2$ ) could cause a positive bias. Ion chromatography is the preferred analytical technique. Titration may only be used if the requirements of §2.2 (Detection Limits) of this manual can be met. EPA Method 6C is an instrumental procedure using either an ultraviolet (UV), non-dispersive infrared (NDIR), or fluorescence analyzer. All  $\text{SO}_2$  emissions must be reported as  $\text{SO}_2$  (molecular weight of 64.06).

#### 3.1.2.2. Sulfur Oxides ( $\text{SO}_x$ )

The reference method for the isokinetic determination of sulfur oxides is EPA Method 8.  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  are captured as  $\text{SO}_4^{2-}$  in the front-half train rinses, the filter, and the first impinger, containing an aqueous solution of isopropanol (80% IPA). Sulfur dioxide is converted to sulfate ion ( $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$ ) in the impingers containing a solution of peroxide (3%  $\text{H}_2\text{O}_2$ ). Particulate sulfate salts ( $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ , etc.) will cause a positive bias. Carryover of solution from the first impinger (IPA) into the following impingers ( $\text{H}_2\text{O}_2$ ) could cause a negative bias. Ion chromatography is the preferred analytical technique. Titration may only be used if the requirements of §2.2 (Detection Limits) of this manual can be met. All  $\text{SO}_x$  emissions must be reported as  $\text{SO}_2$  (molecular weight of 64.06).

#### 3.1.2.3. Sulfur Trioxide and Sulfuric Acid Mist ( $\text{SO}_3/\text{H}_2\text{SO}_4$ )

The reference method for the isokinetic determination of sulfur trioxide and sulfuric acid mist is EPA Method 8.  $\text{SO}_3$  and  $\text{H}_2\text{SO}_4$  are captured as  $\text{SO}_4^{2-}$  in the front-half train rinses, the filter, and the first impinger, containing an aqueous solution of isopropanol (80% IPA). Particulate sulfate salts ( $\text{Na}_2\text{SO}_4$ ,  $\text{CaSO}_4$ , etc.) will cause a positive bias. Carryover of solution from the first impinger (IPA) into the following impingers ( $\text{H}_2\text{O}_2$ ) could cause a negative bias. The maximum holding time for samples is 14 days at 4°C. Ion chromatography is the preferred analytical technique. Titration may only be used if the requirements of §2.2 (Detection Limits) of this manual can be met. NCASI Method 8A is an acceptable alternative at kraft recovery furnaces. All  $\text{SO}_3$  emissions must be reported as  $\text{SO}_3$  (molecular weight of 80.06). All  $\text{H}_2\text{SO}_4$  emissions must be reported as  $\text{H}_2\text{SO}_4$  (molecular weight of 98.07).

#### 3.1.2.4. Hydrogen Sulfide ( $\text{H}_2\text{S}$ )

The reference methods for the non-isokinetic determination of hydrogen sulfide are EPA Methods 11 and 16. In Method 11, hydrogen sulfide is converted to sulfide ion ( $\text{H}_2\text{S} \rightarrow \text{S}^{2-}$ ) in the midjet impingers containing cadmium sulfate ( $\text{CdSO}_4$ ). Analysis is iodometric. In Method 16, the effluent is introduced

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directly into a gas chromatograph with a flame photometric detector (GC/FPD).  $\text{H}_2\text{S}$  can be differentiated from other sulfur compounds by the gas chromatograph. Particulate, moisture, and sulfur dioxide are removed prior to analysis by a filter and a citrate buffer scrubber. All  $\text{H}_2\text{S}$  emissions must be reported as  $\text{H}_2\text{S}$  (molecular weight of 34.08).

### 3.1.2.5. Total Reduced Sulfur (TRS)

The reference methods for the non-isokinetic determination of total reduced sulfur are EPA Methods 16, 16A, and 16B. In Method 16, the effluent is introduced directly into a gas chromatograph with a flame photometric detector (GC/FPD). Particulate, moisture, and sulfur dioxide are removed prior to analysis by a filter and a citrate buffer scrubber. In Method 16A, particulate, moisture, and sulfur dioxide are removed by a filter and a citrate buffer scrubber, the TRS compounds are then oxidized in a tube furnace ( $\text{H}_2\text{S} \rightarrow \text{SO}_2$ ), and collected in a peroxide solution (3%  $\text{H}_2\text{O}_2$ ) as sulfate ion ( $\text{SO}_2 \rightarrow \text{SO}_4^{2-}$ ). Ion chromatography is the preferred analytical technique. Titration may only be used if the detection limit requirements (§2.2 of this manual) are met. In Method 16B, particulate, moisture, and sulfur dioxide are removed by a filter and a citrate buffer scrubber, the TRS compounds are then oxidized in a tube furnace ( $\text{H}_2\text{S} \rightarrow \text{SO}_2$ ), and then analyzed directly by a gas chromatograph with a flame photometric detector (GC/FPD).

### 3.1.3. Nitrogen Compounds

#### 3.1.3.1. Nitrogen Dioxide ( $\text{NO}_2$ )

Some chemiluminescent analyzers can be used for the determination of nitrogen dioxide. EPA Methods 7E and 20 should be used with these analyzers for the non-isokinetic determination of nitrogen dioxide emissions by subtracting the nitric oxide concentration from the total concentration of nitrogen oxides ( $\text{NO}_2 = \text{NO}_x - \text{NO}$ ). All  $\text{NO}_2$  emissions must be reported as  $\text{NO}_2$  (molecular weight of 46.01).

#### 3.1.3.2. Nitrogen Oxides ( $\text{NO}_x$ )

The reference methods for the non-isokinetic determination of  $\text{NO}_x$  include EPA Methods 7, 7A, 7B, 7C, 7D, 7E, and 20. Methods 7D, 7E, and 20 are preferred (when applicable). In Method 7D, nitrogen dioxide ( $\text{NO}_2$ ) and nitric oxide ( $\text{NO}$ ) are converted to nitrate ion ( $\text{NO}_2 + \text{NO} \rightarrow \text{NO}_3^-$ ) in the impingers containing a basic potassium permanganate solution (4%  $\text{KMnO}_4$ ). Analysis is by ion chromatography. Methods 7E and 20 specify the use of a chemiluminescent analyzer. All  $\text{NO}_x$  emissions must be reported as  $\text{NO}_2$  (molecular weight of 46.01).

#### 3.1.3.3. Ammonia ( $\text{NH}_3$ )

The reference method for the isokinetic determination of ammonia emissions is EPA Method 206 (draft). Collection is accomplished with an EPA Method 17-type train (in-stack filter) composed entirely of glass or Teflon. The entire train up to the first impinger is heated to 5°F above the stack temperature. The impingers contain acidic media (0.1N  $\text{H}_2\text{SO}_4$ ) that converts ammonia to ammonium ion ( $\text{NH}_3 \rightarrow \text{NH}_4^+$ ). Analysis is by ion chromatography. Use of an EPA Method 5-type train (heated

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filter box) is not recommended due to the potential for alteration in the  $\text{NH}_3/\text{NH}_4^+$  equilibrium. Positive or negative error of unknown magnitude may be introduced by this phenomenon. All  $\text{NH}_3$  emissions must be reported as  $\text{NH}_3$  (molecular weight of 17.03).

### 3.1.4. Carbon Monoxide (CO)

The reference methods for the non-isokinetic determination of carbon monoxide are EPA Methods 10, 10A, and 10B. In Method 10, sampling of the CO is continuous with a silica gel and ascarite trap for moisture and carbon dioxide removal, respectively. Certification by the manufacturer that the instrumental analyzer is free from  $\text{CO}_2$  interference is sufficient without the use of silica gel and ascarite. Analysis is by a non-dispersive infrared analyzer (NDIR). In Methods 10A and B, the CO is collected in a Tedlar bag after removal of sulfur and nitrogen oxides with an alkaline permanganate trap. Analysis is by spectrophotometry (Method 10A); or by gas chromatography, a reduction catalyst, and flame ionization detection (GC/FID) (Method 10B). All CO emissions must be reported as CO (molecular weight of 28.01).

### 3.1.5. Halogenated Compounds

#### 3.1.5.1. Chlorine Dioxide ( $\text{ClO}_2$ )

An acceptable method for the non-isokinetic determination of chlorine dioxide emissions from Pulp Mill Bleach Plants was proposed by the National Council of the Paper Industry for Air and Stream Improvement (NCASI). It is entitled Determination of Chlorine and Chlorine Dioxide in Pulp Mill Bleach Plant Vents. Important NCASI references are listed in §4 (References) of this manual. The chlorine dioxide is converted to chloride ion and water ( $\text{ClO}_2 + \text{Cl}^- + \text{H}_2\text{O}$ ) in the impingers that contain a neutral solution of potassium iodide (KI) buffered to ~ pH 7 with potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) and sodium hydroxide (NaOH). Ion chromatography is the preferred analytical technique. Titration may only be used if the requirements of §2.2 (Detection Limits) of this manual can be met. All  $\text{ClO}_2$  emissions must be reported as  $\text{ClO}_2$  (molecular weight of 67.45).

#### 3.1.5.2. Hydrogen Halides (HF, HCl, HBr)

The reference methods for the determination of hydrogen halides are EPA Methods 26 (constant rate) and 26A (isokinetic). Chloride salts ( $\text{NaCl}$ ,  $\text{CaCl}_2$ , etc.) will cause a positive bias. The hydrogen halides are collected in a sample train composed entirely of glass or Teflon. The probe and filter holder (up to the inlet of the first impinger) must be heated to the greater of  $36^\circ\text{F}$  above stack temperature or  $248^\circ\text{F}$ . The impingers contain acidic media ( $0.1\text{N H}_2\text{SO}_4$ ) in which halogens are not soluble. EPA Method 26A must be utilized at all sources where water droplets are present in the effluent due to the highly soluble nature of the halides. EPA Method 26A is also recommended for sampling periods greater than one hour to avoid depletion of the impinger solution. Analysis of the impinger solution for both reference methods is by ion chromatography. EPA Method 321 (draft) using Fourier Transform Infrared (FTIR) analysis is acceptable at Portland cement kilns. All hydrogen halides must be reported

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as the particular hydrogen halide (molecular weight of 20.01 for HF, 36.46 for HCl, and 80.91 for HBr).

### 3.1.5.3. Halogens (F<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>)

The reference methods for the determination of halogens are EPA Methods 26 (constant rate) and 26A (isokinetic). The halogens are collected in impingers containing basic media (0.1N NaOH) that causes the halogens to dissociate into the respective halide anions (F<sup>-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>). Dissociation may not be complete unless sodium thiosulfate (NaS<sub>2</sub>O<sub>3</sub>) is added per the method. Addition of too much NaS<sub>2</sub>O<sub>3</sub> will result in a high detection limit. Proper addition of NaS<sub>2</sub>O<sub>3</sub> is discussed in detail in the April 1996 edition of the Riley Report (Insight into EPA's Test Methods for Hydrogen Chloride (HCl) and Chlorine (Cl<sub>2</sub>). The acidic solution specified in the reference methods is necessary, even if determination of hydrogen halides is not desired, but the contents may be discarded. An empty impinger between the acidic and basic impinger solutions is recommended to avoid carryover and the resultant positive bias. An EPA Method 26A train is recommended for sampling periods greater than one hour to avoid depletion of the impinger solution. Analysis of the impinger solution for both reference methods is by ion chromatography. An acceptable method for the non-isokinetic determination of chlorine emissions from Pulp Mill Bleach Plants was proposed by the National Council of the Paper Industry for Air and Stream Improvement (NCASI). It is entitled Determination of Chlorine and Chlorine Dioxide in Pulp Mill Bleach Plant Vents. Important NCASI references are listed in §4 (References). The chlorine is converted to chloride ion (Cl<sub>2</sub> → 2 Cl<sup>-</sup>). Ion chromatography is the preferred analytical technique. Titration may only be used if the requirements of §2.2 (Detection Limits) of this manual can be met. All halogens must be reported as the particular halogen (molecular weight of 38.00 for F<sub>2</sub>, 70.91 for Cl<sub>2</sub>, and 159.81 for Br<sub>2</sub>).

### 3.1.6. Heavy Metals

#### 3.1.6.1. Multiple Metals

The reference method for the isokinetic determination of multiple metals is EPA Method 29. This method may be used for antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), total chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), mercury (Hg), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (Tl), and zinc (Zn). If the objective of the testing is to ascertain the emissions of a particular metal, an approved method specific to that metal, such as EPA Method 101/101A for Hg or EPA Method 12 for Pb, should be used. For a detailed discussion about EPA Methods 29 and 101A including guidance pertaining to blank corrections, see the October 1996 edition of the Riley Report (Measurement of Trace Metals; Especially Mercury).

#### 3.1.6.2. Hexavalent Chromium (Cr<sup>+6</sup>)

The reference method for the isokinetic collection of hexavalent chromium is EPA SW-846 Method 0061. Following each sampling run or prior to the addition of OH<sup>-</sup>, the pH of the solution in the first impinger must be checked and recorded on the field data sheet for each run. The pH should also be

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checked during port changes. The pH must be  $\approx 8.5$  for a valid test. The maximum holding time for samples to be analyzed for hexavalent chromium is 14 days at 4°C. Analysis of the impinger solution is by ion chromatography and post column reaction (IC/PCR) per EPA SW-846 Method 7199. Determination of  $\text{Cr}^{+6}$  emissions from chromium electroplating and anodizing operations may be conducted in accordance with the procedures discussed in EPA Method 306.

### 3.1.6.3. Total Chromium

The reference methods for the determination of chromium emissions from chromium electroplating and anodizing operations are EPA Methods 306 (isokinetic) and 306A (constant rate). California Air Resources Board (CARB) Method 425 is an acceptable alternative. At other sources, EPA Method 29 must be used. EPA Method 306 must be employed unless the effluent is at ambient moisture, air, and temperature. In both methods, the chromium is collected in the impingers (mason jars for Method 306A) that contain an alkaline solution (0.1N NaOH or  $\text{NaHCO}_3$ ). The maximum holding time for samples to be analyzed for total chromium is 60 days at ambient temperature whereas the maximum holding time for samples to be analyzed for hexavalent chromium is 14 days at 4°C. When analyzing samples for  $\text{Cr}^{+6}$  using IC/PCR, the pH of the impinger solution must be checked and recorded following sampling and prior to analysis. For a valid test, the pH must be  $\approx 8.5$  for sodium hydroxide (NaOH) or  $\approx 8.0$  for sodium bicarbonate ( $\text{NaHCO}_3$ ). The pH should also be checked during port changes. The preferred analytical technique is graphite furnace atomic absorption spectroscopy (GFAAS). Ion chromatography with post column reaction (IC/PCR) or inductively coupled argon plasma emission spectrometry (ICAP) may only be used if the requirements of §2.2 (Detection Limits) of this manual are met.

## 3.2. Organic Compounds

### 3.2.1. Volatile Organic Compounds (VOCs)

Testing for volatile organic compounds is often confusing for a variety of reasons. It is important to recognize that:

- (1) the state and federal regulations are based on VOC emissions (not TOC or TNMOC),
- (2) the terms TOC, TNMOC, and VOC are often erroneously applied interchangeably,
- (3) there is no straightforward way to measure the VOC emissions since there is no way to separate compounds by photoreactivity (or vapor pressure).
- (4) All of the reference methods for organic compounds have inherent limitations that restrict their applicability.

#### 3.2.1.1. Test Method Selection

Before selecting a test method for the determination of the VOC emissions, one must consider several factors including:

- (1) the chemical composition of the VOCs being emitted,

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- (2) the expected concentration range of the VOCs,
- (3) the chemical properties (boiling point, reactivity, solubility) of the VOCs,
- (4) the characteristics of the effluent (temperature, moisture, %CO<sub>2</sub>),
- (5) the advantages and disadvantages of the various test methods, and
- (6) the state and federal testing requirements.

When proposing a test method for VOCs, a discussion involving all of these factors must be included in the pretest procedural submission to justify the method. The chemical composition is important because EPA Method 18 should not be employed if the target constituents of the effluent are unknown. EPA Method 25 may not be adequate when the effluent contains chlorinated organics. The flame ionization analyzer used in EPA Method 25A, although it is good for hydrocarbons, has a diminished response to compounds containing electronegative atoms (N, O, F, P, S, Cl, Se, and Br). The response to formaldehyde, for instance, is essentially zero! The expected concentration, based on usage records or prior testing, is important for several reasons. At low concentrations (<50 ppm as C), EPA Method 25 generally produces erroneous results due to the errors associated with sample manipulation (oxidation, reduction, backflushing, et cetera). Above 100,000 ppm (as C), EPA Method 25B (NDIR) or sample dilution is necessary. The expected concentration is also valuable in the selection of calibration gases and establishment of the instrument span. Knowledge of the chemical properties of the VOCs helps one select an appropriate temperature for the sample collection system, system bias check gas for EPA Method 25A, and the best collection technique for EPA Method 18. The characteristics of the effluent also impact the collection technique for EPA Method 18. Charcoal adsorption tubes, for instance, may not be used if the moisture content exceeds 3%. The first four factors can be used in conjunction with each method's limitations to justify a method. In addition, the advantages of a method can be used to choose between two reference methods. Lastly, and perhaps most importantly, the purpose of the testing as specified in the state and federal regulations greatly impacts the test program. If an NSPS Subpart, applicable to the source to be tested, specifies a test method, that method must be used. Similarly, if the state operating permit specifies testing for VOCs, do not propose a THC or TNMOC test method unless a detailed justification is provided. In most cases, one of the predominant reference methods (EPA Methods 18, 25, and 25A) should be chosen.

### Example 1

Source: Coal-fired boiler

Control: Cyclone

- Factors:
- (1) The chemical composition of the VOCs being emitted is unknown.
  - (2) The expected concentration of VOCs will be low (<50 ppm as C).
  - (3) The chemical properties are unknown.
  - (4) The duct temperature is ~300°F, the effluent moisture is ~3%, and the CO<sub>2</sub> concentration is ~6%.



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(5) Because the chemical composition and properties of the VOCs are unknown, EPA Method 18 (alone) is not an option. EPA Method 25 is excluded because the VOC concentration will probably be <50 ppm as C. There should not be any problems associated with the use of EPA Method 25A at this source and it provides real-time data.

(6) Determine the VOC emissions to demonstrate compliance.

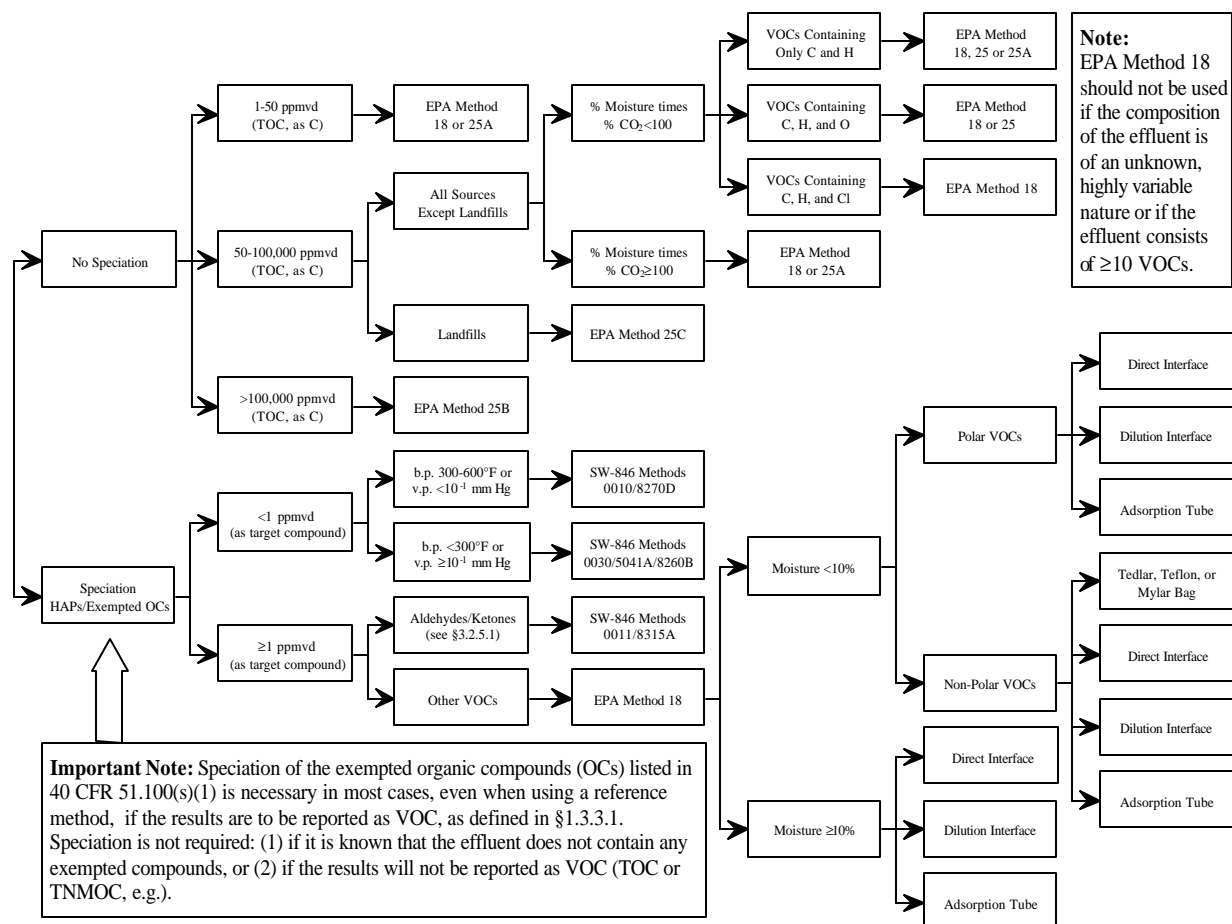
Test Method: Use EPA Method 25A and EPA Method 18 (tedlar bag sample; GC/FID analysis) for determination of the exempted compounds (only methane and ethane are likely). Use propane to calibrate the analyzer and for the system bias checks. The recovery study (§7.6.2 of EPA Method 18) is not required for methane or ethane provided the bag shows no visible deflation and the sample is analyzed within 48 hours.

Alternative: Use EPA Method 25A only and report the TOC emissions instead of the VOC emissions (written approval from the Department is necessary). This is less expensive and the concentration of the exempted compounds will probably not affect the compliance status. Use propane to calibrate the analyzer and for the system bias checks. One drawback is that the TOC results could not be used to determine the emission reduction credits.

A general scheme for the selection of a VOC test method is provided on the following page. This scheme, if used properly, can be used to select an appropriate sampling technique. The selection scheme does not address all of the limitations for a given reference method nor does it list all of the possibilities.

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### General Scheme for the Selection of a VOC Reference Method



#### 3.2.1.2. Sampling and Analysis

All sampling must be conducted in accordance with an approved test method. Specific information regarding the three reference methods for organic compounds is presented hereafter.

##### 3.2.1.2.1. EPA Method 18

In order to effectively employ EPA Method 18, a thorough knowledge of factors 1-4 of §3.2.1.1 of this manual is essential. A presurvey and presurvey sampling, as discussed in §5 of the method, should be conducted. The collection method (15 L Tedlar Bag, e.g.) and analytical technique (GC/FID, e.g.) must be specified in all submissions. All sample analyses must be conducted within 48 hours of collection. When conducting the recovery study for bag sampling outlined in §7.6.2 of the method, the spike must remain in the bag for the same duration that the collected sample was in the bag. The recovery study is mandatory. When a VOC sample is collected in a bag, the bag must be shielded from sunlight (UV rays) at all times. All tubing used in the sampling train should be made of Teflon. Tygon

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tubing is not acceptable. Aluminized Mylar bags are recommended for low concentration bag sampling because of the lower permeation rate.

### 3.2.1.2.2. EPA Method 25

EPA Method 25 has several potential limitations. When the effluent contains high moisture and CO<sub>2</sub>, a high bias is likely. As the water freezes in the trap, CO<sub>2</sub> is entrapped prematurely. The CO<sub>2</sub> (upon reduction to methane) is then erroneously counted as a VOC. To avoid this problem, it is recommended that an ice water-cooled trap be added prior to that cooled by dry ice. Another problem is the relatively high, method detection limit, 50 ppm as C. Thorough cleaning of the trap and Summa canister is critical to attaining this level. To achieve a lower in-stack detection limit, increase the sample volume to 6 liters. The presence of chlorinated organics could result in “poisoning” of the oxidation catalyst and therefore this method is not recommended if the presence of chlorinated organics is suspected.

### 3.2.1.2.3. EPA Method 25A

Calibrations for EPA Method 25A should be done using EPA Traceability Protocol gas standards, preferably propane, although a gas equivalent to the effluent with respect to molecular weight could also be used. The entire sampling system prior to the flame ionization analyzer (FIA) must be heated to the higher of 248±25°F (120±14°C) or stack temperature. Heating above 400°F is not required. A system bias check is required and is performed by introducing the bias check standard directly into the flame ionization analyzer (FIA) and then through the entire sampling system, excluding the probe. If the results agree within 5%, the bias check is acceptable, otherwise the test data (since the last valid bias check) is invalid. The bias check standard must be representative of the effluent as a whole with regards to boiling point, water solubility, and chemical reactivity. If the composition of the effluent is unknown, propane may be used for the system bias check. Propane may be used for the bias check at the following sources: incinerators, boilers, asphalt plants, cement plants, and resource recovery facilities. Propane may not be used for the system bias check at the following sources: bakeries (using yeast), ethylene oxide sterilizers, chemical manufacturing facilities, surface coating operations, and graphic arts operations.

### Selecting a System Bias Check Gas Standard

- (1) Estimate what inks and/or coatings are to be used during the testing. This can be done based on the expected job(s) during the proposed testing or based on historical usage.
- (2) Using the MSDS sheets and the following equation, calculate the boiling point for each ink or coating.

$$\sum_i (x_i)(bp_i)$$

where:  $x_i$  is the mole fraction of component  $i$  and  $bp_i$  is the boiling point of component  $i$ .

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- (3) Determine the relative solubility in water based on polarity and/or a reference (such as The Merck Index).
- (4) If >1 ink and/or coating is to be used, estimate the relative usage of each and determine the boiling point for the mixture of inks and/or coatings by (a) multiplying the relative usage by the boiling point for the ink or coating (from step 2 above) and (b) summing the values.
- (5) The bias check gas should contain a component with a boiling point within 10% of the highest boiling point for any VOC in the ink and/or coating, a component with similar water solubility, and a component with similar reactivity. A two-component blend is necessary if the effluent contains water soluble VOCs and the highest boiling compound in the effluent is not water soluble (not polar). The concentration of the bias check gas should be similar to the expected concentration at the sampling location.

### 3.2.1.3. Reporting of Emissions

The test report should clearly indicate how the emissions have been reported (ppmvd as propane, for example). The pretest procedural protocol, if submitted, should also specify in detail how the emissions will be reported. Strict conformance with the definitions in §1.3 of this manual is critical! The Department requires all emissions to be reported in ppmvd (parts per million, by volume, dry basis) and lbs./hour as outlined in one of the following four scenarios. In the absence of data to prove otherwise, the Department will assume that the composition of the effluent before and after a control device is the same. Subject to written approval by the Department, the emissions of TOC or TNMOC may be reported in lieu of reporting the VOC emissions.

- (1) If a source is subject to a federal subpart (NSPS, NESHAPS, MACT, etc.) that specifies how to report the emissions, you must report the emissions in that manner. In addition, if a source would be subject to a federal subpart, but because of its size, date of construction, or other such factors, is exempt, the testing and reporting should still comply with the requirements of the subpart. Some of the source categories included under this scenario are bulk gasoline loading terminals, landfills, and ethylene oxide sterilizers.
- (2) If the VOC emissions are of an unknown, highly variable nature, the results shall be reported in terms of propane. Some of the sources included in this category are: incinerators, boilers; asphalt plants, cement plants, and resource recovery facilities.
- (3) If the composition of the effluent is known and a single VOC constitutes =75% (by volume) of the total emissions from a source, the emissions must be reported in terms of that compound. Some of the source categories included under this scenario are bakeries (using yeast) and synthetic organic chemical manufacturing industry (SOCMI) facilities.
- (4) If the composition of the effluent is known and a single VOC does not constitute =75% (by volume) of the total emissions from a source, the emissions must be reported in terms of a department-approved surrogate. Anticipated chemical usage for the source(s) during each test

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run should be used to select the surrogate. Some of the sources included in this category are: surface coating operations and graphic arts operations. As an alternative, if the primary intent of the testing is to determine the destruction efficiency of a control device, the results at both the inlet and the outlet should be reported as propane and the actual emissions (if needed) should be determined using the following equation, or a modified version that has been approved by the Department prior to testing.

$$\text{Emission Rate} = \{[(\text{Coating Usage})(\text{VOC Content})(1 - \text{DE})(\text{CE})] + [(\text{Coating Usage})(\text{VOC Content})(1 - \text{CE})]\}$$

### Sample Calculations

where:

RF:	the response factor, as defined in §1.3.4.3 of this manual
$\text{RRF}_{\text{C}_3\text{H}_8}$ :	the response factor of propane divided by the number of carbon atoms in propane.
$\text{RRF}_{\text{C}_2\text{H}_5\text{OH}}$ :	the response factor of ethanol divided by the number of carbon atoms in ethanol.
$K_{\text{M25A}}$ :	the carbon equivalent correction factor from EPA Method 25A, Equation 25A-1
ppmvw:	the parts of pollutant per million parts of air, by volume, on a wet basis
$\text{MW}_{\text{C}}$ :	the molecular weight of carbon, 12.01 lbs./lb.-mole
$\text{MW}_{\text{C}_2\text{H}_5\text{OH}}$ :	the molecular weight of ethanol, 46.07 lbs./lb.-mole
$B_{\text{ws}}$ :	the proportion of water vapor, by volume, in the effluent
$Q_{\text{sd}}$ :	the volumetric flow rate of the effluent in dscfh

### Example 1

Calculating the VOC mass emission rate from a source emitting mostly ethanol ( $\text{C}_2\text{H}_5\text{OH}$ ) using EPA Method 25A data in terms of propane...

$$\left( \frac{\left( \frac{\text{ppmvw as } \text{C}_3\text{H}_8}{(1 - B_{\text{ws}})} \right) (K_{\text{M25A}})(\text{MW}_{\text{C}})(Q_{\text{sd}})}{385.3 \times 10^6} \right) \left( \frac{\text{MW}_{\text{C}_2\text{H}_5\text{OH}}}{(\# \text{ C atoms } \text{C}_2\text{H}_5\text{OH})(\text{MW}_{\text{C}})} \right) \left( \frac{\text{RRF}_{\text{C}_3\text{H}_8}}{\text{RRF}_{\text{C}_2\text{H}_5\text{OH}}} \right) = \frac{\text{lbs } \text{C}_2\text{H}_5\text{OH}}{\text{hour}}$$

or

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$$\left( \frac{\left( \frac{\text{ppmvw as } C_3H_8}{(1 - B_{ws})} \right) (3)(12.01)(Q_{sd})}{385.3 \times 10^6} \right) \left( \frac{46.07}{(2)(12.01)} \left( \frac{1.00}{0.70} \right) \right) = \frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

### Example 2

Calculating the VOC mass emission rate from a source emitting mostly ethanol ( $C_2H_5OH$ ) using EPA Method 25 data in terms of carbon...

$$\left( \frac{\left( \frac{\text{ppmvw as } C}{(1 - B_{ws})} \right) (MW_C)(Q_{sd})}{385.3 \times 10^6} \right) \left( \frac{MW_{C_2H_5OH}}{(\# \text{ C atoms } C_2H_5OH)(MW_C)} \right) = \frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

or

$$\left( \frac{\left( \frac{\text{ppmvw as } C}{(1 - B_{ws})} \right) (12.01)(Q_{sd})}{385.3 \times 10^6} \right) \left( \frac{46.07}{(2)(12.01)} \right) = \frac{\text{lbs } C_2H_5OH}{\text{hour}}$$

#### 3.2.1.4. Capture Efficiency (CE)

There are several reference methods for the determination of the capture efficiency of a control device: EPA Methods 204, 204A, 204B, 204C, 204D, 204E, and 204F. All capture efficiency testing must be conducted in accordance with the reference method and any additional (or more stringent) requirements in EMC Guideline Documents 035 and 036.

#### 3.2.1.5. Coatings and Printing Inks

The reference method for the determination of the volatile matter content, water content, density, volume solids, and weight solids of all surface coatings or inks excluding publication rotogravure inks is EPA Method 24. The reference method for the determination of volatile matter content and density of publication rotogravure inks is EPA Method 24A. Analysis of the aforementioned coatings may also be conducted in accordance with the following methods (when applicable).

- ASTM D6053-96 (Standard Test Method for Determination of Volatile Organic Compound (VOC) Content of Electrical Insulating Varnishes).
- ASTM D2697-86 (1991) (Standard Test Method for Nonvolatile Matter in Clear or Pigmented Coatings).
- ASTM D6093-97 (Standard Test Method for Percent Volume Nonvolatile Matter in Clear or Pigmented Coatings Using a Helium Gas Pycnometer).

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- ASTM D3960-96 (Standard Practice for Determining Volatile Organic Compound Content of Paints and Related Coatings).
- EPA SW-846 Methods 5030B and 8260B.

### 3.2.2. Total Organic Compounds (TOCs)

There are several ways to determine the emissions of TOCs. Knowledge of the effluent composition and expected concentrations (as C) are necessary to determine which test method to use. If the effluent is known to consist primarily of alkanes, alkenes, and arenes (aromatics) with concentrations of 1-100,000 ppm, EPA Method 25A, which utilizes a flame ionization analyzer (FIA), may be used. For concentrations in excess of 100,000 ppm, EPA Method 25B, utilizing a non-dispersive infrared analyzer (NDIR), is preferred. If the effluent contains organic compounds other than alkanes, alkenes, and arenes, EPA Method 25A is not applicable. For instance, at wood products mills or wood-fired sources, formaldehyde may be emitted. EPA SW-846 Method 0011, or an equivalent method, must be used to account for the emissions of formaldehyde. If the composition of the effluent is known and there are only a few organic compounds, which can be easily separated by chromatography, EPA Method 18 could be employed by quantifying all of the organic compounds and summing the individual emission rates.

Determination of TOC emissions from cold rolling mills should utilize Alcoa Methods 1470-94 (Sampling Method for the Determination of Hydrocarbons Emissions from Cold Rolling Mills) and 1471-94 (Analysis Method for Determination of Hydrocarbon Emissions from Aluminum Rolling Mills). The sample train consists of a cyclone for particulate or "oil mist" removal and a two-section charcoal sorbent tube for capture of the volatile fraction. Analysis is by gas chromatography with flame ionization detection (GC/FID). A copy of this method is available from the Department upon request.

### 3.2.3. Total Non-Methane Organic Compounds (TNMOCs)

The reference method for the determination of the TNMOCs is EPA Method 25 that utilizes a gas chromatograph, oxidation and reduction catalysts and a flame ionization detector (GC/FID) for effluent with concentrations of 50-100,000 ppm. EPA Method 25A may be utilized in conjunction with EPA Method 18 for the determination of TNMOCs at concentrations <50 ppm as carbon. If this is done, the recovery study of the latter method is not required for methane. Alternatively, EPA Method 18 may be used alone at sources emitting <10 organic compounds. EPA Method 25C is the preferred method for the determination of TNMOCs in landfill gas.

### 3.2.4. Semivolatile Organic Compounds (SVOCs)

The reference method for the isokinetic collection of SVOCs is EPA SW-846 Method 0010. The train utilizes an all glass or Teflon train with a heated filter, a condenser, and an XAD-2 sorbent trap. It is critical that the trap be kept chilled to =68°F and wrapped in aluminum foil to prevent degradation of

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the sample. Furthermore, the trap must not be packed in the field due to the certainty of cross contamination. Analysis is by gas chromatography/mass spectrometry (GC/MS) per EPA SW-846 Method 8270D.



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### 3.2.5. Hazardous Air Pollutants (HAPs)

#### 3.2.5.1. Aldehydes and Ketones

The reference method for the isokinetic collection of formaldehyde, acetaldehyde, acetophenone, isophorone, and propionaldehyde is EPA SW-846 Method 0011 which utilizes an aqueous solution of 2,4-dinitrophenylhydrazine (2,4-DNPH) as a derivitizing agent to form the corresponding water-insoluble hydrazone. Analysis is by EPA SW-846 Method 8315A which utilizes high-pressure liquid chromatography and an UV detector (HPLC/UV). The possibility of extending the application of EPA SW-846 Method 0011 to other aldehydes and/or ketones will be evaluated by the Department on a case-by-case basis. This method is not applicable to quinone, acrolein, methyl ethyl ketone, or methyl isobutyl ketone. NCASI Method CI/WP-98.01 (Chilled Impinger Method for Use at Wood Products Mills to Measure Formaldehyde, Methanol, and Phenol) is an acceptable alternative for the non-isokinetic determination of formaldehyde at rotary dryers, MDF dryers, urea-formaldehyde presses, and phenol-formaldehyde presses. NCASI Method CI/SG/PULP-94.02 (Chilled Impinger / Silica Gel Tube Test Method at Pulp Mill Sources for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone, and Formaldehyde) is an acceptable alternative for the non-isokinetic determination of formaldehyde at brownstock washer hoods, bleach plant scrubbers, smelt dissolving tanks, and recovery furnaces. The reference methods for the determination of principal organic hazardous constituents are EPA SW-846 Methods 0030, 0031, and 0040.

#### 3.2.5.2. Hydrogen Cyanide (HCN)

Sampling for hydrogen cyanide utilizes an EPA Method 5-type train except that the impingers contain sodium hydroxide (0.1N NaOH). The hydrogen cyanide is converted to cyanide ion ( $\text{HCN} \rightarrow \text{CN}^-$ ) provided the pH=12. Following each sampling run or prior to the addition of OH<sup>-</sup>, the pH of the solution in the first impinger must be checked and recorded. The pH should also be checked during port changes. The pH must be maintained at =12 for the run to be valid. Analysis is by ion chromatography.

#### 3.2.5.3. Polycyclic Organic Matter

##### 3.2.5.3.1. Polychlorinated Dibenzo-p-Dioxins/Furans (PCDDs/PCDFs)

The reference method for the isokinetic collection of the various PCDD and PCDF congeners is EPA Method 23 that utilizes an XAD-2 sorbent trap. Recovery of the sampling train involves the use of an acetone/methylene chloride rinse followed by a toluene rinse. These rinses may be combined prior to analysis. Furthermore, the methylene chloride rinse is optional. Analysis is by high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS) as detailed in EPA SW-846 Method 8290A. Use of low-resolution mass spectrometry (EPA SW-846 Method 8280B) is not permitted unless the detection limit requirements (§2.2) of this manual are met.

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### **3.2.5.3.2. Polychlorinated Biphenyls (PCBs)**

The reference method for the isokinetic collection and recovery of PCBs is EPA SW-846 Method 0010. Analysis is performed by California Air Resources Board (CARB) Method 428 that utilizes high-resolution gas chromatography and high-resolution mass spectrometry (HRGC/HRMS).

### **3.2.5.3.3. Polycyclic Aromatic Hydrocarbons (PAHs)**

The reference method for the isokinetic collection and recovery of polycyclic aromatic hydrocarbons is EPA SW-846 Method 0010. Analysis is performed by EPA SW-846 Method 8270D that utilizes gas chromatography and low-resolution mass spectrometry (GC/LRMS). A high-resolution mass spectrometry technique is under development and upon validation it should be used instead of EPA SW-846 Method 8270D unless the detection limit requirements (§2.2) of this manual are met with LRMS.

## **3.3. Visible Emissions (Opacity)**

The standard reference methods for the determination of visible emissions are EPA Methods 9 and Alternative Method 1 (9A; lidar). Method 9 is preferred (when applicable). Opacity observations at coke oven batteries shall be conducted in accordance with the procedures in EPA Method 303 or 303A.

## **3.4. Fuel Samples**

### **3.4.1. General Collection Criteria**

- 3.4.1.1. The sample acquisition point(s) must be located as close to the point at which the fuel is burned and as far downstream of any process(es) which could alter the quality of the fuel (prior to combustion), as possible.
- 3.4.1.2. A sample should be collected from each fuel-input stream, unless sampling at one location will yield representative results.
- 3.4.1.3. Sampling should be conducted at a given location without discrimination based on the appearance of the material.
- 3.4.1.4. Samples should be collected from each location at intervals not to exceed 30 minutes.
- 3.4.1.5. Samples for a source collected over the period of one test run should be combined and analyzed as a single sample.

### **3.4.2. Fuel Specific Criteria**

Fuel analysis may be necessary to determine emission rates in terms of the heat input to the source. The heat input can be determined from the gross calorific value of the fuel and an ultimate analysis. Results

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must be reported on an “as received” basis. Any equivalent ASTM Method may be used in lieu of the methods specified in this section.

### **3.4.2.1. Coal and Coke**

#### **3.4.2.1.1. Collection**

Coal samples must be collected in accordance with ASTM Method D 2234-96 (Standard Practice for Collection of a Gross Sample of Coal). Prior to analysis, the coal samples shall be prepared in accordance with ASTM Method D 2013-86 (Standard Method of Preparing Coal Samples for Analysis). Coke samples shall be collected and prepared for analysis in accordance with ASTM Method D 346-90 (Practice for Collection and Preparation of Coke Samples for Laboratory Analysis). The recommended size for a composite sample is 1 gallon.

#### **3.4.2.1.2. Analysis**

##### **3.4.2.1.2.1. Gross Calorific Value (GCV)**

The GCV (Btu/lb.) shall be determined in accordance with ASTM Method D 2015-96 (Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter), ASTM Method D 1989-97 (Standard Test Method for Gross Calorific Value of Coal and Coke by Microprocessor Controlled Isoperibol Calorimeters), or ASTM Method D 3286-96 (Standard Test Method for Gross Calorific Value of Coal and Coke by Isoperibol Bomb Calorimeter).

##### **3.4.2.1.2.2. Carbon and Hydrogen Content**

The carbon and hydrogen content shall be determined in accordance with ASTM Method D 3178-89 (1993) (Standard Test Methods for Carbon and Hydrogen in the Analysis Sample of Coal and Coke) or ASTM Method D 5373-93 (1997) (Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke).

##### **3.4.2.1.2.3. Sulfur Content**

The sulfur content shall be determined in accordance with ASTM Method D 3177-89 (Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke) or D 4239-97 (Standard Test Method for Sulfur in the Analysis Sample of Coal and Coke Using High Temperature Tube Furnace Methods).

##### **3.4.2.1.2.4. Nitrogen Content**

The nitrogen content shall be determined in accordance with ASTM Method D 3179-89 (1993) (Standard Test Methods for Nitrogen in the Analysis Sample of Coal and Coke) or ASTM Method D 5373-93 (1997) (Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Laboratory Samples of Coal and Coke).

##### **3.4.2.1.2.5. Ash Content**

The percent ash shall be determined in accordance with ASTM Method D 3174-97 (Standard Test Method for Ash in the Analysis Sample of Coal and Coke from Coal) or ASTM Method D 5142-90

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(1994) (Standard Test Method for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures). When using the latter method, the instrumental results must be corrected or the instrument must be calibrated using samples of known proximate analysis, as discussed in §1 (Scope) of the method. ASTM Method D 5142-90 (1994) is “not applicable to thermogravimetric analyzers (TGA) utilizing microgram size samples”.

### 3.4.2.1.2.6. Oxygen Content

The percent oxygen shall be determined by difference per the following equation:

$$\%O = 100 - (\%C) - (\%H) - (\%S) - (\%N) - (\%Ash).$$

### 3.4.2.1.2.7. Moisture Content

The percent moisture shall be determined in accordance with ASTM Method D 3173-87 (1996) (Standard Test Method for Moisture in the Analysis Sample of Coal and Coke), ASTM Method D 5142-90 (1994) (Standard Test Method for the Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures), or ASTM Method D 2961-95a. When using ASTM Method D 5142-90 (1994), the instrumental results must be corrected or the instrument must be calibrated using samples of known proximate analysis, as discussed in §1 (Scope) of the method. ASTM Method D 5142-90 (1994) is “not applicable to thermogravimetric analyzers (TGA) utilizing microgram size samples”. Material subjected to ASTM Method D 2961-95a may not be used in the determination of other parameters.

### 3.4.2.2. Fuel Oil

#### 3.4.2.2.1. Collection

Fuel oil samples must be collected in accordance with ASTM Method D 4057-95 (Standard Practice for Manual Sampling of Petroleum and Petroleum Products) or ASTM Method D 4177-95 (Standard Practice for Automatic Sampling of Petroleum and Petroleum Products).

#### 3.4.2.2.2. Analysis

##### 3.4.2.2.2.1. Sulfur Content

The following ASTM methods are acceptable for the determination of the sulfur content: D 129-95 (Standard Test Methods for Sulfur in Petroleum Products: General Bomb Method), D 1266-91 (Standard Test Methods for Sulfur in Petroleum Products: Lamp Method), D 1552-95 (Standard Test Methods for Sulfur in Petroleum Products: High-Temperature Method), or D 2622-94 (Standard Test Methods for Sulfur in Petroleum Products by X-Ray Spectrometry).

### 3.4.2.3. Wood

#### 3.4.2.3.1. Collection

Wood samples must be collected in accordance with the procedures specified in §6.1 of ASTM Method E 871-82 (1987).

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### **3.4.2.3.2. Analysis**

#### **3.4.2.3.2.1. Gross Calorific Value (GCV)**

The GCV (Btu/lb.) shall be determined in accordance with ASTM Method E 711-87 (Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter).

#### **3.4.2.3.2.2. Carbon and Hydrogen Content**

The carbon and hydrogen content shall be determined in accordance with ASTM Method E 777-87 (1992) (Standard Test Method for Carbon and Hydrogen in the Analysis Sample of Refuse-Derived Fuel).

#### **3.4.2.3.2.3. Sulfur Content**

The sulfur content shall be determined in accordance with ASTM Method E 775-87 (Standard Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel).

#### **3.4.2.3.2.4. Nitrogen Content**

The nitrogen content shall be determined in accordance with ASTM Method E 778-87 (1992) (Standard Test Methods for Nitrogen in the Analysis Sample of Refuse-Derived Fuel).

#### **3.4.2.3.2.5. Ash Content**

The percent ash shall be determined in accordance with ASTM Method D 1102-84 (1995) (Standard Test Method for Ash in Wood).

#### **3.4.2.3.2.6. Oxygen Content**

The percent oxygen shall be determined by difference per the following equation:

$$\%O = 100 - (\%C) - (\%H) - (\%S) - (\%N) - (\%Ash).$$

#### **3.4.2.3.2.7. Moisture Content**

The percent moisture shall be determined in accordance with ASTM Method E 871-82 (1987) (Standard Method for Moisture Analysis of Particulate Wood Fuels).

### **3.4.2.4. Refuse-Derived Fuel (RDF)**

#### **3.4.2.4.1. Collection**

RDF samples must be collected in accordance with ASTM Method D 5115-90 (Standard Test Method for Collecting Gross Samples and Determining Fuel Quality of RDF. Prior to analysis, the sample(s) shall be prepared in accordance with ASTM Method E 829-94 (Standard Practice for Preparing Refuse-Derived Fuel (RDF) Laboratory Samples for Analysis).

#### **3.4.2.4.2. Analysis**

##### **3.4.2.4.2.1. Gross Calorific Value (GCV)**

The GCV (Btu/lb.) shall be determined in accordance with ASTM Method E 711-87 (Standard Test Method for Gross Calorific Value of Refuse-Derived Fuel by the Bomb Calorimeter).

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### **3.4.2.4.2.2. Carbon and Hydrogen Content**

The percent carbon and hydrogen shall be determined in accordance with ASTM Method E 777-87 (1992) (Standard Test Method for Carbon and Hydrogen in the Analysis Sample of Refuse-Derived Fuel).

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### 3.4.2.4.2.3. Sulfur Content

The percent sulfur shall be determined in accordance with ASTM Method E 775-87 (Standard Test Methods for Total Sulfur in the Analysis Sample of Refuse-Derived Fuel).

### 3.4.2.4.2.4. Nitrogen Content

The percent nitrogen shall be determined in accordance with ASTM Method E 778-87 (1992) (Standard Test Methods for Nitrogen in the Analysis Sample of Refuse-Derived Fuel).

### 3.4.2.4.2.5. Ash Content

The percent ash shall be determined in accordance with ASTM Method D 830-87 (Standard Test Method for Ash in the Analysis Sample of Refuse-Derived Fuel).

### 3.4.2.4.2.6. Oxygen Content

The percent oxygen shall be determined by difference per the following equation:

$$\%O = 100 - (\%C) - (\%H) - (\%S) - (\%N) - (\%Ash).$$

### 3.4.2.4.2.7. Moisture Content

The percent moisture shall be determined in accordance with ASTM Method E 790-87 (1996) (Standard Test Method for Residual Moisture in a Refuse-Derived Fuel Analysis Sample).

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