

NATIONAL COUNCIL FOR AIR AND STREAM IMPROVEMENT

## REVIEW OF AIR EMISSION SOURCE TEST METHODS USED IN CANADA

TECHNICAL BULLETIN NO. 987 JULY 2011

by

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### **PRESIDENT'S NOTE**

Forest products companies frequently undertake stack emissions testing to meet permit or regulatory requirements or to evaluate the effectiveness of a given emission control technology or process change. Source test methods accepted by Canadian provinces may or may not be equivalent across jurisdictions, and may or may not be based on standard methods published by Environment Canada or the US Environmental Protection Agency. In addition, given that regulatory standards are inextricably linked with listed source test methods specified for compliance, the sampling and analytical components of these methods must be understood when comparing regulatory requirements across jurisdictions and/or across a company's various facilities.

This report provides a synthesis and comparative review of over 70 air emission source test methods accepted by provincial jurisdictions across Canada. The synthesis covers methods pertaining to sample acquisition as well as those developed for the measurement of relevant substances (or group of substances) emitted from stationary sources at forest products manufacturing facilities. The substances for which methods have been summarized include particulate matter (total and fine), nitrogen oxides, sulphur dioxide, volatile organic compounds, total reduced sulphur compounds, dioxins and furans, chlorine dioxide, mercury, carbon monoxide, and sulphuric acid.

This report will be of use in preparing for compliance testing, as well as in comparing or assessing the applicability of different source test methods to a given facility. The report will also be relevant in discussions regarding the extent to which a given test method is capable of measuring low-level releases, as it also provides perspective on current method detection capabilities.

Km Johne

Ronald A. Yeske

July 2011



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## NOTE DU PRÉSIDENT

Les sociétés de produits forestiers effectuent souvent la caractérisation de leurs émissions à la cheminée afin de se conformer à des exigences règlementaires ou à des conditions dans un permis, ou afin d'évaluer l'efficacité d'une technologie de contrôle des émissions ou d'un changement dans le procédé. Les méthodes d'essai à la source qu'acceptent les provinces canadiennes peuvent être équivalentes d'une juridiction à l'autre, mais peuvent aussi être différentes. De plus, leur contenu peut s'inspirer des méthodes d'essai publiées par Environnement Canada ou l'Agence américaine de protection de l'environnement (EPA) ou peut provenir d'autres sources. Compte tenu que les normes règlementaires sont étroitement liées aux méthodes d'essai à la source exigées par les provinces, il faut donc bien comprendre la partie sur l'échantillonnage et la partie sur l'analyse des échantillons de ces méthodes lorsqu'on compare les exigences règlementaires entre les juridictions et/ou entre les installations d'une même société.

Le présent rapport est une synthèse et une analyse comparative de plus de 70 méthodes d'essai à la source acceptées par les différentes provinces canadiennes pour les émissions atmosphériques. Cette synthèse couvre les méthodes sur le prélèvement des échantillons. Elle couvre également les méthodes destinées à la mesure de substances (ou groupe de substances) particulières émises par des sources stationnaires dans des installations de fabrication de produits forestiers, soit les particules (totales et fines), les oxydes d'azote, le dioxyde de soufre, les composés organiques volatils, les composés de soufre réduit total, les dioxines et les furannes, le dioxyde de chlore, le mercure, le monoxyde de carbone et l'acide sulfurique.

Le présent rapport peut être utile pour se préparer aux essais de conformité ou pour comparer ou évaluer l'applicabilité des différentes méthodes d'essais à la source dans une installation donnée. Il sera également utile dans les discussions pour déterminer dans quelle mesure une méthode d'essai donnée peut mesurer des substances émises en faibles concentrations, car il aborde également la question de capacité de détection des méthodes actuelles.

Rom Johne

Ronald A. Yeske Juillet 2011

#### **REVIEW OF AIR EMISSION SOURCE TEST METHODS USED IN CANADA**

#### TECHNICAL BULLETIN NO. 987 JULY 2011

#### ABSTRACT

This report synthesizes and compares nearly 70 extractive air emission source test methods approved by provincial jurisdictions across Canada. The synthesis includes a summary of essential concepts regarding extractive source testing and a review of methods pertaining to the sampling of exhaust gas streams as well as to the measurement of air emissions relevant to the Canadian forest products industry. These substances are particulate matter (total PM,  $PM_{2.5}$  and  $PM_{10}$ ), nitrogen oxides ( $NO_x$ ), sulphur dioxide ( $SO_2$ ), volatile organic compounds (VOCs), total reduced sulphur (TRS), dioxins and furans, chlorine dioxide ( $ClO_2$ ), mercury (Hg), carbon monoxide (CO), and sulphuric acid (H<sub>2</sub>SO<sub>4</sub>). Each substance is discussed in terms of predominant sources at forest products manufacturing facilities and the test methods to measure that substance. The report includes conceptual schematics and/or tables to help the reader easily identify similarities and/or differences between methods. A summary table listing all the extractive test methods approved by each province, as well as hyperlinks to the respective full method write-ups, is provided at the end of the report.

#### **KEYWORDS**

air emission, analytical method, ClO<sub>2</sub>, CO, dioxins, furans, H<sub>2</sub>SO<sub>4</sub>, Hg, NO<sub>x</sub>, PM, PM<sub>2.5</sub>, PM<sub>10</sub>, pulp and paper, RSC, SO<sub>2</sub>, source testing, stack sampling, stack testing, standard method, sulfur, sulphur, test method, TRS, VOC, wood products

#### **RELATED NCASI PUBLICATIONS**

Technical Bulletin No. 956 (September 2008). *Emissions of reduced sulfur compounds and methane from kraft mill wastewater treatment plants*.

Technical Bulletin No. 952 (August 2008). Formation, release and control of reduced sulphur compounds from kraft pulp and paper facilities.

Special Report No. 07-08 (October 2007). *Review of available technologies for control of air quality parameters relevant to pulp and paper and wood products facilities in Canada.* 

Technical Bulletin No. 921 (August 2006). *Laboratory evaluation of a modified method 25A VOC sampling system*.

Technical Bulletin No. 851 (September 2002). *Literature review of emissions of mercury from fossil fuel and biomass combustion and emerging control technologies.* 

Special Report No. 02-04 (May 2002). *Review of EPA regulations and guidance related to VOC emissions.* 

Technical Bulletin No. 774 (January 1999). Volatile organic compound emissions from wood products manufacturing facilities, part VII - test methods, quality assurance/quality control procedures and data analysis protocol.

Special Report No. 95-10 (October 1995). A laboratory study of moisture effects on EPA Method 25A VOC measurements.

Special Report No. 91-07 (June 1991). *Measurement and quality assurance procedures for determining chloroform, chlorine, and chlorine dioxide releases from pulp bleach plants.* 

Technical Bulletin No. 520 (April 1987). *Optimization and evaluation of an impinger capture method for measuring chlorine and chlorine dioxide in pulp bleach plant vents.* 

Technical Bulletin No. 504 (September 1986). A survey of emissions from dryer exhausts in the wood panelboard.

Technical Bulletin No. 503 (September 1986). Formaldehyde, phenol, and total gaseous non-methane organic compound emissions from flakeboard and oriented-strand board press vents.

Technical Bulletin No. 493 (June 1986). A survey of formaldehyde and total gaseous non-methane organic compound emissions from particleboard press vents.

Technical Bulletin No. 455 (April 1985). Volatile organic carbon emissions from wood residue fired power boilers in the Southeast.

Special Report No. 08-01 (May 2008). Wood products air quality technical information document.

Technical Bulletin No. 405 (August 1983). A study of organic compound emission from veneer dryers and means for their control.

Atmospheric Quality Technical Bulletin No. 106 (April 1980). A study of SOx measurement procedures and their use at kraft recovery furnaces.

## REVUE DES MÉTHODES D'ESSAI À LA SOURCE UTILISÉES AU CANADA POUR LES ÉMISSIONS ATMOSPHÉRIQUES

## BULLETIN TECHNIQUE N<sup>O</sup> 987 JUILLET 2011

#### RÉSUMÉ

Le présent rapport est une synthèse et une analyse comparative de plus de 70 méthodes d'essai par extraction à la source approuvées par les différentes provinces canadiennes pour les émissions atmosphériques. Il contient un résumé des concepts essentiels associés aux essais par extraction à la source et une analyse des méthodes s'appliquant à l'échantillonnage des gaz de combustion et à la mesure de substances émises à l'atmosphère qui sont pertinentes à l'industrie canadienne des produits forestiers. Ces substances sont les particules (particules totales, PM<sub>2.5</sub> et PM<sub>10</sub>), les oxydes d'azote (NO<sub>x</sub>), le dioxyde de soufre (SO<sub>2</sub>), les composés organiques volatils (COV), le soufre réduit total (SRT), les dioxines et les furannes, le dioxyde de chlore (ClO<sub>2</sub>), le mercure (Hg), le monoxyde de carbone (CO) et l'acide sulfurique (H<sub>2</sub>SO<sub>4</sub>). Dans le rapport, on examine chaque substance en fonction des méthodes d'essai pour mesurer la substance. Le rapport contient des schémas conceptuels et/ou des tableaux pour aider le lecteur à facilement reconnaître les similarités et/ou les différences entre les méthodes. Il contient également un tableau sommaire qui fait la liste de toutes les méthodes d'essai par extraction approuvées par chaque province et fournit des hyperliens menant au texte complet de chaque méthode.

#### **MOTS-CLÉS**

caractérisation à la cheminée, caractérisation à la source, ClO<sub>2</sub>, CO, composés de soufre réduit, COV, dioxines, échantillonnage à la cheminée, émissions atmosphériques, furannes, H<sub>2</sub>SO<sub>4</sub>, Hg, méthode analytique, méthode d'essai, NO<sub>x</sub>, particules, pâtes et papiers, PM<sub>2.5</sub>, PM<sub>10</sub>, produits du bois, SO<sub>2</sub>, soufre, SRT

#### **AUTRES PUBLICATIONS DE NCASI**

Bulletin technique n° 956 (septembre 2008). Émissions de composés de soufre réduit et de méthane des systèmes de traitement des effluents de fabriques kraft.

Bulletin technique n° 952 (août 2008). *Formation, rejet et contrôle des composés de soufre réduit des fabriques de pâtes et papiers kraft.* 

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Bulletin technique n° 921 (août 2006). *Laboratory evaluation of a modified method 25A VOC sampling system*.

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Rapport spécial nº 02-04 (mai 2002). *Review of EPA regulations and guidance related to VOC emissions*.

Bulletin technique n° 774 (janvier 1999). Volatile organic compound emissions from wood products manufacturing facilities, part VII - test methods, quality assurance/quality control procedures and data analysis protocol.

Rapport spécial n° 95-10 (octobre 1995). A laboratory study of moisture effects on EPA Method 25A VOC measurements.

Rapport spécial n° 91-07 (juin 1991). *Measurement and quality assurance procedures for determining chloroform, chlorine, and chlorine dioxide releases from pulp bleach plants.* 

Bulletin technique n<sup>o</sup> 520 (avril 1987). *Optimization and evaluation of an impinger capture method for measuring chlorine and chlorine dioxide in pulp bleach plant vents.* 

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Bulletin technique n° 503 (septembre 1986). *Formaldehyde, phenol, and total gaseous non-methane organic compound emissions from flakeboard and oriented-strand board press vents.* 

Bulletin technique n<sup>o</sup> 493 (juin 1986). A survey of formaldehyde and total gaseous non-methane organic compound emissions from particleboard press vents.

Bulletin technique n° 455 (avril 1985). Volatile organic carbon emissions from wood residue fired power boilers in the Southeast.

Rapport spécial nº 08-01 (mai 2008). Wood products air quality technical information document.

Bulletin technique n° 405 (août 1983). A study of organic compound emission from veneer dryers and means for their control.

Bulletin technique sur la qualité de l'air n° 106 (avril 1980). A study of SOx measurement procedures and their use at kraft recovery furnaces.

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## **REVIEW OF AIR EMISSION SOURCE TEST METHODS USED IN CANADA**

#### 1.0 INTRODUCTION

#### 1.1 Background

As companies in Canada are faced with meeting existing air permit requirements or current regulations, they may be asked to undertake stack sampling using a variety of different source test methods. More broadly, source testing is also used to evaluate the effectiveness and efficiency of a given emission control technology, to develop regulatory standards and emission factors, and to assess the effect of process modifications or operating changes on air emissions (Harrison 1999; Franek and DeRose 2003; Baukal 2004; NARSTO 2005).

Different provincial jurisdictions approve source test methods that may or may not be equivalent to one another, or to a reference or standard method [e.g., that of Environment Canada or the US Environmental Protection Agency (USEPA)]. Furthermore, analytical results for mills from different provinces may be erroneously compared without knowledge as to which method has been used, or whether the different methods used are comparable or suitable for the complex forest products air matrices. Finally, analytical results may be inadvertently taken at face value, without consideration of the test method's detection and quantitation limits.

In this context, both the sampling and the analytical aspects of source test methods are important in comparing regulatory requirements across jurisdictions, making comparisons across a company's various facilities, and in the context of developing regulatory policy.

#### **1.2** Scope of the Review

Source testing consists of extracting representative samples of stack gases, conditioning them if needed, and analyzing the samples for the substance of concern. This report begins by outlining the principles of extractive source testing, including essential concepts associated with sampling and chemical analysis. This is followed by a synthesis and comparison of extractive source test methods approved by provincial jurisdictions across Canada. In-situ, or continuous emission monitoring systems (CEMS), are not discussed. The synthesis covers methods pertaining to the determination of sampling flow rate as well as methods for the measurement of substances emitted from stationary sources. The substances (or substance groups) included in this report are considered by Environment Canada and the forest products industry (FPI) as being the most relevant source emissions at Canadian pulp and paper and wood products facilities, at this time (NCASI 2007; 2008a):

- Particulate matter (PM), including total PM, PM<sub>10</sub>, PM<sub>2.5</sub>, and condensable PM
- Nitrogen oxides (NO<sub>x</sub>)
- Sulphur dioxide (SO<sub>2</sub>)
- Volatile organic compounds (VOCs), including total and speciated VOC
- Total reduced sulphur (TRS)
- Dioxins and furans (D/F)
- Chlorine dioxide (ClO<sub>2</sub>)
- Mercury (Hg)
- Carbon monoxide (CO)

• Sulphuric acid (H<sub>2</sub>SO<sub>4</sub>)

For each substance or substance group, this report discusses the predominant emission sources at forest products manufacturing facilities, the test methods approved by each provincial jurisdiction, and the most relevant sampling and analytical features of each method. Each substance section is completed with conceptual schematics to allow for quick method comparison.

In general, methods compiled by this review are classified into principal and alternative. Principal methods comprise USEPA methods of widespread use in the US and/or widely approved by Canadian jurisdictions, as well as reference methods developed by Environment Canada. Alternative methods include USEPA methods occasionally used in the US and approved in some Canadian provinces, as well as methods issued or developed by provincial or state agencies, or developed by NCASI. Methods that are not approved by any Canadian province, but considered relevant to the FPI are briefly summarized where appropriate.

A summary table listing all the extractive test methods approved in each province as well as hyperlinks to the respective full method write-ups is provided in Section 15. It should be noted that all methods listed are as published and available in May 2011. The reader is cautioned to refer to this report only for general comparative and informational purposes, and to use the current published method for undertaking any stack testing and/or related analyses.

### A Note on the Use of Qualifiers for Comparison Purposes

The following qualifiers are used within the text of this report to compare two test methods.

- *Identical* means "exactly the same".
- *Equivalent* means "equal in principle". This qualifier is typically applied to methods using, in essence, the same sampling configuration/procedures and analytical techniques. In particular, the applicability criteria of the methods compared, i.e., type of emission source and substances measured (both in number and type), must also be the same.
- *Similar* means "showing resemblance in qualities, characteristics, or appearance". This qualifier is applied to specific elements of the methods under comparison. When relevant components or characteristics of the sampling train configuration, sample collection/recovery procedures, or analytical techniques used are different or nonexistent, they are pointed out in the text descriptions.

#### **1.3** Information Sources

The Air Quality Research Division of Environment Canada and the air testing departments of most provincial agencies were contacted to obtain source test manuals/guidelines/codes that were not readily accessible through the internet. These documents are shown in Table 1. They typically provide a list of source test methods approved by the provincial authority. In the case of Nova Scotia and Ontario, a full list of methods was obtained directly from representatives of the respective Ministries of the Environment.

Two USEPA Emission Measurement Center websites were consulted to obtain full method write-ups: <u>http://www.epa.gov/ttn/emc/tmethods.html</u> [for methods promulgated in the US Code of Federal Regulations as well as for alternative (ALT), historic conditional (CTM), and other test methods (OTM)] and <u>http://www.epa.gov/osw/hazard/testmethods/index.htm</u> (for SW-846 methods).

The *NCASI Methods Manual* was also consulted. This manual contains a compilation of methods for substances and/or source types for which no rigorously tested or validated (standard) government methods are available.

Province	Guideline/Code					
Alberta	Alberta Stack Sampling Code (1995), Methods Manual for Chemical Analysis of Atmospheric Pollutants (1993)					
British Columbia	British Columbia Field Sampling Manual (2003)					
Manitoba	Interim Stack Sampling Performance Protocol, Version 1.0 (1996)					
New Brunswick	Guidance Document for Source Testing (2003)					
Newfoundland & Labrador	Procedural Guide for Source Emission Testing (2004)					
Nova Scotia	Nova Scotia does not have a published stack testing guide. Methods are approved on a case-by-case basis through submission of a pre-test plan within the context of an operating approval. The province uses either EC or USEPA. Where standard methods are not considered applicable, NCASI or National Institute for Occupational Safety and Health (NIOSH) methods are accepted					
Ontario	Ontario Source Testing Code, Version 2 (1991) (for stack gas parameters and particulate matter only). Depending on the target substance and emission source, Ontario approves USEPA, EC, NCASI, and California Air Resources Board (CARB) methods					
Quebec	Sampling Guide for Environmental Analysis: Booklet 4 – Sampling of Atmospheric Emissions from Stationary Sources (2009)					
Saskatchewan	Air Monitoring Directive for Saskatchewan (2007). This directive has limited information on source methods approved in Saskatchewan. In general, operating permits outline specific stack testing requirements for a facility. Both EC and USEPA methods are considered acceptable by the Ministry					

### 2.0 PRINCIPLES OF EXTRACTIVE SOURCE TESTING

The equipment used for extracting, conditioning, and collecting the gas sample from the main gas stream is called the sampling train. Source testing involves the use of the sampling train to assess the contents of the gas stream under specific process conditions.

In general, the accuracy and reliability of a test method primarily depends on the representativeness of the gas sample extracted from the stationary source, the correct mechanical operation and calibration of the sampling train, the selectivity of the physical/chemical principle used for sample collection, and the sensitivity of the analytical method used on the collected sample. This section briefly discusses the steps typically involved in extractive source testing<sup>1</sup>:

- Acquisition of a representative gas sample containing the target substance
- Conditioning of the gas sample

<sup>&</sup>lt;sup>1</sup> These are also the primary steps taken into account in the schematic method syntheses presented at the end of each substance section.

- For indirect extractive methods:
  - o Collection of the target substance using solid or liquid media
  - Recovery of the collected sample
- Analysis of the sample

Essentially, the gas sample is pumped by suction from the main stream through a nozzle and probe<sup>2</sup> into the collection section of the sampling train. The collected sample is subsequently analyzed for the desired substance. Indirect extractive methods also include, following the sample pump, a dry gas meter (DGM) and an orifice plate. The DGM measures the volume of the gas sample<sup>3</sup> withdrawn for analysis, while the pressure drop measured across the orifice is used to calculate the sample flow rate.

### 2.1 Acquisition of the Gas Sample

The selection of a source test method depends on the physical state, at source conditions, of the targeted substance. Sampling gaseous substances is generally less involved than sampling particulate matter<sup>4</sup>, which typically requires special nozzle designs as well as specific methods to determine sampling locations and flow rates to ensure the collection of a representative sample. For both gaseous and particulate sampling, the nozzle and the probe must be constructed of materials that will not react with the gas stream (e.g., glass), and sampling must be conducted at a time and over a sufficient time period to account for temporal variability in the exhaust gas stream (Pfafflin and Ziegler 2006).

### 2.1.1 Sampling of Particulate Matter

A representative gas sample should contain the same number and size distribution of particles per unit volume as the main gas stream and must be extracted at a location that is free of unusual flow patterns (e.g., cyclonic flow or stratified flow) and sufficiently far away from flow disturbances (e.g., elbows, bends, fans, etc.). In addition, sampling must be carried out for a short time at each of multiple (traverse) points across the duct cross-section.

The design of the nozzle has also an effect on the representativeness of the gas collected. The opening of the nozzle is designed with sharply tapered edges and the nozzle itself is shaped to minimize deposition of particulates on the inside walls as the stream turns 90° (Pfafflin and Ziegler 2006).

Another essential feature associated with extracting representative samples from particulate-laden gas stream is *isokinetic sampling*. Isokinetic sampling is defined by USEPA as "sampling in which the linear velocity of the gas entering the sampling nozzle is equal to that of the undisturbed gas stream sample point" [US CFR 40, Part 60]. The exhaust gas stream velocity in the vicinity of the probe is determined from the pressure exerted by the flowing gas stream, which is measured by a pitot tube. The exhaust gas flow rate is subsequently calculated at reference conditions<sup>5</sup> from stack pressure and temperature measurements, and the moisture content and molecular weight of the gas stream. Isokinetic conditions are obtained by selecting an appropriate nozzle size and adjusting the sample

<sup>&</sup>lt;sup>2</sup> A typical probe for sampling particulate-laden gas stream consists of a hollow tube with the front end (nozzle) directed into the gas stream.

<sup>&</sup>lt;sup>3</sup> The volume of the gas sample is used to determine the concentration of the targeted substance in the gas stream.

<sup>&</sup>lt;sup>4</sup> Small liquid droplets and/or solid particles.

<sup>&</sup>lt;sup>5</sup> Gas sample volumes and flow rates are typically expressed at reference or standard conditions. Reference conditions used by Canadian methods are: T=25°C and P=760 mmHg. Standard conditions used by USEPA and NCASI methods: T=20°C and P=760 mmHg.

flow rate<sup>6</sup> to that determined from the pitot tube measurements. The exhaust gas flow rate is also used to calculate emission rates of the substance being measured.

Standard test methods are typically used for the determination of sampling location; traverse points; stack gas velocity, moisture, and molecular weight; and sampling volumetric flow rate (see Section 3).

## 2.1.2 Sampling of Gaseous Substances

Gaseous substances are significantly better mixed across the stack than particulate matter, and thus are typically subject to less restrictive considerations regarding nozzle/probe design, sampling location, traverse points and, sometimes, isokinetic sampling. In many cases, it suffices that the sample be extracted at the centroid of the stack cross-section. The exhaust gas flow rate is determined using the same procedures specified for particulate matter sampling.

## 2.2 Sample Conditioning

When sampling some gaseous substances, a filter<sup>7</sup> may be used to prevent particulate matter from clogging up the sample line and/or entering the collection section of the sampling train. Depending on the targeted gaseous substance, the filter's content may be recovered and saved for analysis.

Many test methods specify that the gas sample be maintained above the dew point to prevent vapours in the stream from condensing on the walls of the probe until they reach the water knockout unit (Baukal 2004).

### 2.3 Sample Collection

Once the gas sample has been suitably conditioned, the targeted substance is separated from the gas sample and collected using one or more physical or chemical techniques. Particulate matter is typically captured through filtration, impingement, and centrifugal force. Gaseous substances are most efficiently collected via physical or chemical absorption, adsorption, condensation, or grab sampling.

## 2.3.1 Filtration

Particulate matter is captured on filters, which are often heated and located out of the stack. When applicable, most methods specify the use of glass fibre filters without organic binders. The filter holder is typically made of borosilicate glass (Pyrex) with clamps to seal the filter between the two halves of the holder (Pfafflin and Ziegler 2006).

#### 2.3.2 Impingement

This technique involves the use of impingers and/or cascade impactors. Standard impingers are sealed glass flasks that possess a ground glass joint with a small tip, through which the gas is forced, and an impaction surface near the bottom on which the particles will tend to collect (Harrison 1999). The impingers used for collecting particulate matter are operated with the tip and impaction surface under liquid. Some impingers use an attached impaction disk, while others use the bottom of the flask as the impaction surface. Impingers also collect substances in condensable concentrations or in materials that can be readily retained by physical absorption or reactions with a liquid (Zhang 2007). (See *absorption* below.)

<sup>&</sup>lt;sup>6</sup> The sample flow rate can be manipulated by adjusting either the sample pump suction rate or a control valve.

<sup>&</sup>lt;sup>7</sup> Either a plug of glass wool at the probe inlet or an out-of-the-stack heated filter.

Cascade impactors use the aerodynamic impaction properties of particles to separate the particulate matter into different size fractions through use of sequential jets and collection surfaces (impactor plates) (Harrison 1999; Hocking 2005). As the sampled gas flows into the first stage of large jets (holes), large particles strike the impactor plate and remain stuck there, while smaller particles with less momentum are diverted away from the impactor plate and move on to the next stage. The jets in each successive stage are smaller than those in the preceding plate, thereby forcing the gas to move at higher velocities as it proceeds further into the cascade impactor. As the gas velocity increases, smaller particles are imparted enough kinetic energy to impinge on the impactor plates, and stick there. The result of this sequential impingement is that the collected particles are roughly classified by size.

## 2.3.3 Centrifugal Force

This principle is put to use when sampling gas streams with significant particulate matter content. The equipment used is a cyclone typically located following the sampling probe and preceding the filter. The use of cyclones is typically optional in most Canadian methods, and rarely specified in USEPA methods.

## 2.3.4 Absorption

Gaseous substances can be collected either by dissolving the gas sample in a liquid medium or by chemical reaction with a liquid absorbent. Absorption typically takes place in standard impingers, but also in gas bubblers. Bubblers are similar to impingers with the exception of having a fritted tip that breaks the gas sample into smaller bubbles, thereby increasing the contact area between the gas sample and the impinger liquid.

## 2.3.5 Adsorption

Through the adsorption principle, gas molecules become bound to the surface of a solid called the adsorbent. Sorbent tubes are used to capture target substances. There are two types of sorbing materials: *thermally desorbed media* and *solvent extracted media* (Zhang 2007). The former include Tenax and carbonized polymers, while the latter include Amberlite XAD-2, activated carbon, and Tenax. Other materials used as adsorbents include silica gel (for moisture removal) and alumina.

## 2.3.6 Condensation

The gas sample can also be cooled to temperatures below the boiling point of the target substance to condense it. Given that this will freeze the water vapour present in the gas sample, methods typically specify using a first trap of large volume designed to collect water followed by a second trap at a sufficiently low temperature to collect the targeted substance (Harrison 1999).

## 2.3.7 Grab Sampling

Samples may be simply collected in impermeable containers (e.g., Tedlar or Teflon bags) and returned to the laboratory for analysis. Bags are filled by evacuating the rigid air-tight box holding the bags.

## 2.4 Recovery of Collected Sample

The contents of each relevant component of the front half of the sampling train, filter (if applicable), and back half of the sampling train<sup>8</sup> are carefully recovered in sealed containers. Gaseous substances

<sup>&</sup>lt;sup>8</sup> The front half of the sampling train consists of the nozzle, probe, cyclone (if specified), and front half of the filter holder. The back half of the sampling train includes the back half of the filter holder and all the collection equipment that follows, including connecting glassware.

that have been captured by sorbent traps are either thermally desorbed or the solvent is extracted from the adsorbent prior to analysis.

#### 2.5 Sample Analysis

This step depends on the substance measured. The quantitative determination of gaseous substances relies on wet chemical techniques and instrumental analysis. A common wet chemical technique specified in various test methods is *titrimetry* or *volumetric analysis* in which a liquid reagent (titrant) of a known concentration is used to react with a solution of the analyte<sup>9</sup> whose concentration is not known. The titrant is added with a calibrated burette until the titration is complete (endpoint), which is determined by a (colour) indicator. Given that both the concentration and the exact volume of titrant consumed at the endpoint are known, the number of moles of titrant can be calculated. The number of moles of the analyte present in the sample is then determined from the chemical equation relating the titrant to the analyte.

Instrumental analysis involves the quantitative determination of analytes using devices capable of measuring physical manifestations of chemical species and chemical reactions (Manahan 2001). The instrumental techniques specified in the test methods reviewed in this report are primarily based on:

- (a) The absorption or emission of electromagnetic radiation
  - Atomic absorption spectroscopy (AAS)
  - Nondispersive infrared detectors (NDIR)
  - Ultraviolet-visible (UV) spectroscopy
- (b) The separation of small quantities of analytes
  - Gas chromatography (GC)
  - High-performance liquid chromatography (HPLC)
  - Ion chromatography (IC)
- (c) The detection of ions, the spectrum of light, or changes in thermal conductivity produced by analytes
  - Mass spectrometry (MS)
  - Conductivity detection (CD)
  - Flame ionization detection (FID)
  - Nitrogen-phosphorus detection (NPD)
  - Mass selective detection (MSD)

Test methods for filterable PM rely on gravimetric techniques, which quantitatively determine the analyte based on the mass of a solid collected. Filterable PM recovered from filters is desiccated and weighed, while liquids containing particles are typically evaporated to dryness, desiccated, and weighed. Condensable PM can be determined through a combination of gravimetric and titrating procedures (see Figure 2).

<sup>&</sup>lt;sup>9</sup> The substance that is determined in an analytical procedure.

#### A Note on Common Laboratory Techniques

The following common laboratory techniques are often mentioned in this report when describing the analytical component of source test methods: filtration, concentration, digestion, and extraction. The purpose of each of these basic techniques is presented below. The reader can consult Zhang (2007) and Manahan (2001) for more details on these or other routinely used laboratory techniques.

- (a) *Filtration* is used to remove (collect) materials from a liquid or air matrix in which the materials are suspended. The filter media can be ashless quantitative filter papers (e.g., Whatman) or membrane filters (e.g., Gelman). Filtration can be carried out through gravity or suction using a water aspirator or a vacuum pump.
- (b) Concentration is used to remove excess solvent from the mixture of analyte and solvent so that the concentration of analytes will be sufficiently high to be detected. Concentration equipment typically used includes Kuderna-Danish (K-D) evaporative concentrators or rotary evaporators (rotavap).
- (c) Digestion procedures dissolve metals that can be put into solution by using liquid oxidizing agents such as sulphuric acid (H<sub>2</sub>SO<sub>4</sub>), nitric acid (HNO<sub>3</sub>), perchloric acid (HClO<sub>4</sub>), or hydrochloric acid (HCl). If the decomposition of silicates is needed, hydrogen fluoride (HF) is used. The typical procedure involves mixing the sample with a concentrated acid, placing the sample in a digestion vessel, and heating. After digestion is complete, the sample is cooled, solids are filtered, and the liquid remaining is analyzed using an instrumental technique.
- (d) Extraction methods use the different solubility of substances in different solvents to selectively remove a solute from a mixture. Extraction is typically used as a sample preparation technique to concentrate trace organic compounds. Two classical extraction procedures are the liquid–liquid extraction with a separatory funnel for liquid samples, and Soxhlet extraction for solid samples using an extraction solvent (e.g., benzene, toluene).

#### 2.6 A Note on Detection and Quantitation Limits of Source Test Methods

All measurements have associated with them random errors which cause replicate measurements to vary. It is well documented that with most methods the magnitude of the random error decreases as the value of the measured parameter increases. Thus, at high concentrations, random errors do not affect the measured values significantly. However, as the measured value decreases, the potential contribution of the random error to the measured value increases. This in turn decreases confidence in the measured value until the point where it cannot be distinguished from random error. Faced with the need to determine whether or not a substance is present in a sample, and if present what its true level is, analysts use two important concepts: *limit of detection* and *limit of quantitation*. In general, the detection limit of an analytical method for a substance of interest is defined as the lowest concentration of the substance that can be distinguished from a blank. The quantitation limit of a method for a substance is defined as the smallest concentration of the substance which can be measured with a known accuracy.

Quantitation limits of test methods have great significance when measuring very low concentrations of pollutants. In practice, no reported value below a method's quantitation limit should be treated as a real value but should only be treated as a measurement below the method quantitation limit.

Since the issue of establishing quantitation limits has primarily been addressed by analytical chemists, they have proposed a number of procedures for determining analytical method detection and quantitation limits (Coleman, Auses, and Grams 1997; Corley 2003; Currie 1999; Voigtman 2008). In 2004, USEPA conducted a detailed review of analytical method detection and quantitation

approaches (USEPA 2004). In its simplest form, the detection limit of an analytical method is determined by conducting seven replicate analyses of a very low level sample and multiplying the resulting standard deviation by 3.14. The quantitation limit, which is also defined as the minimum level of the test method, is then calculated by multiplying the detection limit by 3.18 (USEPA 2004, pp. 5-35).

While this procedure for determining the detection and quantitation limits is adequate for analytical methods, source emission test methods have two other components, namely source sampling and sample recovery, prior to sample analysis. Thus, any procedure for determining the detection and quantitation limits of source emission test methods needs to include procedures to account for the random errors associated with sampling and sample recovery in addition to evaluating random errors associated with sample analysis. Additionally, since a large number of testing companies and analytical laboratories are involved in source emission testing and analysis, the variability in their performance needs to be considered when establishing test method quantitation limits.

Given the possibilities of introducing random errors during the sampling, sample recovery, and sample analysis steps in an air emission testing method, the appropriate methodology for establishing the detection and quantitation limits of a test method would consist of three steps: a) simultaneous sampling using multiple sampling trains and sampling teams on sources operating at very low emission rates; b) sample recovery by each team consistent with its practice; and b) sample analysis by different analytical laboratories which analyze the samples as a part of their routine analytical practice and not as a special study project. The data obtained from such studies would allow the calculation of method standard deviations and the estimation of the method quantitation limit using appropriate statistics for the source under study. It is only when such studies are carried out at many different sources using different testing and analytical laboratories that a good understanding of the method quantitation limit can be achieved.

#### 3.0 STANDARD METHODS PERTAINING TO SAMPLE ACQUISITION

The USEPA and Environment Canada methods summarized below are indispensable for the determination of the volumetric flow rate at which sampling must be carried out, and thus provide supportive and necessary information to perform most of the methods reviewed in this report. The provinces of Ontario and Alberta have published equivalent methods.

#### 3.1 Sample Location and Traverse Points

EPA Method 1 – Sample and Velocity Traverses for Stationary Sources and Environment Canada EPS 1/RM/8, Method A – Determination of Sampling Site and Traverse Points define procedures to determine where to sample in the stack of a stationary source in order to get a true measure of stack gas flow rate or a representative sample for particulate matter. The cross-section of the stack is mathematically divided into a number of equal areas, and then a sample point is located within each of these equal areas. An ideal sampling site on the stack is at a point at a height equivalent to at least eight stack diameters downstream and two diameters upstream of any flow disturbance, such as a bend or change in stack diameter. The method cannot be used when a) flow is cyclonic or swirling, b) a stack is smaller than about 0.30 m in diameter, or c) the measurement site is less than two stack or duct diameters downstream or less than a half diameter upstream from a flow disturbance.

#### 3.2 Stack Gas Velocity and Volumetric Flow Rate

EPA Method 2 – Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S pitot tube) and Environment Canada EPS 1/RM/8, Method B – Determination of Stack Gas Velocity and Volumetric Flow Rate define procedures and equipment to measure the stack gas velocity and flow rate. Both methods help ensure that an isokinetic sampling rate is used for sample collection and refer

to an S-type or standard pitot tube for measurements. There is a historical conditional test method (CTM-19) that addresses velocity and flow rate determinations in stacks with cyclonic flow.

### 3.3 Gas Molecular Weight

EPA Method 3 – *Gas Analysis for Determining Dry Molecular Weight* and Environment Canada EPS 1/RM/8, Method C – *Determination of Molecular Weight by Gas Analysis* determine the dry molecular weight of the exhaust gas stream, which is a parameter needed in the calculation of stack gas velocity. The method essentially determines the carbon dioxide (CO<sub>2</sub>) and oxygen (O<sub>2</sub>) concentrations in the gas stream. The USEPA technique uses either single-point grab sampling, single-point integrated sampling. The EC method specifies only integrated and grab sampling. Integrated samples are collected in Tedlar, Myrex, or Teflon leak-proof bags. The sample is typically analyzed using an Orsat or a Fyrite analyzer, but the EC method also allows the use of a gas chromatograph, or calibrated continuous gas analyzers.

## 3.4 Gas Moisture Content

The moisture content of the gas stream is used in the calculation of its volumetric flow rate through the stack. EPA Method 4 - Determination of Moisture Content in Stack Gases contains two procedures. One is a reference test method to use when accurate determinations of moisture are needed, such as for setting isokinetic sampling rates prior to a sampling run. The second procedure is an approximation method. The reference test method consists of sampling a known volume of source gas at a constant rate from multiple traverse points across the stack. The moisture in the gas is condensed out of the gas stream and measured. The approximation method is similar, but samples a smaller volume of gas. Other approximation methods are allowed, such as using wet bulb-dry bulb temperatures. The EPA Method 4 reference procedure is included as part of EPA Method 5. Environment Canada EPS 1/RM/8, Method D – Determination of Moisture Content is equivalent to the EPA approximation method.

## 4.0 PARTICULATE MATTER (PM)

## 4.1 Sources of PM at Forest Products Manufacturing Facilities

Particulate matter (PM) consists of microscopic solid and fine liquid droplets that remain suspended in the air for any length of time (Baukal 2004; EC 2010). PM may be released directly into the atmosphere or formed secondarily in the atmosphere from precursors as a result of physical or chemical transformations (EC 2010).

Three fractions of particulate matter are reported under the National Pollutant Release Inventory (NPRI): total particulate matter (TPM), PM<sub>10</sub>, and PM<sub>2.5</sub>. TPM refers to particulate of a size fraction less than 100 microns while PM<sub>10</sub> and PM<sub>2.5</sub> refer to particulate below 10 and 2.5 microns, respectively. PM<sub>2.5</sub> may be further segregated into filterable and condensable particulate fractions. Filterable particulate matter refers to the material that is directly emitted by a source as a solid or liquid at stack conditions and captured on the filter of a stack test train (US *Federal Register* Vol. 67, No. 111, June 10, 2002). Condensable particulate matter is material that is vapour phase at stack conditions, but which condenses and/or reacts upon cooling and dilution in the ambient air to form solid or liquid PM immediately after discharge from the stack (US *Federal Register* Vol. 67, No. 111, June 10, 2002). From a sample collection perspective, the condensable fraction refers to components that exist as gas when they pass through the front half of the sampling system (probe, filter and/or cyclones) but condense and are captured in the back half of the sampling train (typically, chilled impingers).

The following are the primary source emissions of PM at forest products manufacturing facilities.

- Dryers and presses at wood products plants
- Combustion devices burning fossil fuels (e.g., heavy and light fuel oils, or coal) and wood and/or wood residues
- Kraft Mills: Thermal oxidizers, DCE recovery furnaces, NDCE recovery furnaces, lime kilns, smelt dissolving tanks, lime slakers, paper machine vents
- Non-Kraft Mills: Sulphite recovery furnaces, semi-chemical liquor combustors, semichemical recovery furnaces
- Chip and bark cyclones

### 4.2 Source Test Methods for PM Approved Across Canada

Seventeen source test methods have been identified as having been approved by provincial authorities for measuring PM. Provinces allow the use of at least two methods. Table 2 shows the list of approved source test methods for each Canadian province. This list suggests that EPA Method 5 – *Determination of Particulate Matter Emissions from Stationary Sources* or equivalent, and EC Method EPS 1/RM/8 – *Measurement of Releases of Particulate from Stationary Sources* are the methods most commonly approved in Canada for measuring total PM from stationary sources at forest products manufacturing facilities. Finer PM is primarily measured by EPA Methods 201 and 201A. Condensable particulate emission testing is only addressed by some provinces, with EPA Method 202 being the preferred choice.

#### 4.3 Principal USEPA and Environment Canada Standard Methods Used at Forest Products Manufacturing Facilities

#### 4.3.1 EPA Method 5: Determination of Particulate Matter Emissions from Stationary Sources

The most common method for particulate matter sampling is EPA Method 5. In this method, the stack gas is withdrawn isokinetically from the source and passed through a filter maintained at  $120\pm14^{\circ}$ C. The PM mass, which includes any material that collects on the filter and the interior surfaces of the components upstream of the filter, is determined gravimetrically after the removal of uncombined water<sup>10</sup>. The sampling train primarily consists of the following components:

- (a) A heated probe of sufficient length to traverse an appropriate number of sample points. The sample collection rate is adjusted at each traverse point so that the velocity of the sampled gas through the nozzle matches the stack gas velocity at that point (i.e., isokinetic sampling).
- (b) A heated out-of-stack particulate filter and a sample line from the probe that must be maintained at 120±14°C to prevent condensation and plugging.
- (c) A set of four chilled impingers. The first two impingers contain water and collect most of the condensables. The third impinger is left empty and the fourth impinger contains silica gel to collect residual water vapour.

<sup>&</sup>lt;sup>10</sup> The term *uncombined water* means visible mist or condensed water vapor.

	Provinces										
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan		
Exclusively	Total I	PM									
Alberta Stack Sampling Code: Method 5 - Determination of particulate emissions from stationary sources U.S. EPA 5: Determination of particulate matter emissions from stationary sources	X	X	X		X		X		X		
U.S. EPA 5B: Determination of nonsulfuric acid particulate matter emissions from stationary sources			X				Х				
<b>U.S. EPA 5D:</b> Determination of particulate matter emissions from positive pressure fabric filters		Х	Х				Х				
<b>U.S. EPA 17:</b> Determination of particulate matter emissions from stationary sources		Х	Х								
U.S. EPA CTM 003: Determination of particulate matter (modified high volume sampling procedure)		Х									
Method for measuring particulate emissions from stationary sources with cyclonic flow pattern		Х									
State of Oregon Source Sampling Manual - Method 8: Sampling particulate emissions from stationary sources (high volume method)		х									
Environment Canada EPS 1/RM/8 (Method E): Measurement of releases of particulate from stationary sources	Х	Х	Х	Х		Х	Х	Х			
Ontario Source Testing Code - Method 5: Determination of particulate emissions from stationary sources							Х		Х		
Saskatchewan Environment Standard Reference Methods for Source Testing, APC-31: Measurement of emissions of particulates from stationary sources									Х		
Total PM and/o	r PM <sub>10</sub>	/ PM <sub>2.5</sub>		1			1		1		
<b>U.S. EPA 201:</b> Determination of PM <sub>10</sub> and PM <sub>2.5</sub> emissions (exhaust gas recycle procedure)		Х	Х	Х							
<b>U.S. EPA 201A:</b> Determination of PM <sub>10</sub> and PM <sub>2.5</sub> emissions (constant sampling rate procedure)		Х	Х		Х		Х	Х			
<b>Ontario Source Testing Code</b> – ( <b>Draft</b> ) <b>Method ON-7:</b> Determination of size distribution of particulate matter from stationary sources							Х				
Total PM and/or Condensable PM											
Alberta Stack Sampling Code: Method 5A (AEP) - Determination of condensable particulate emissions from stationary sources	х										
<b>U.S. EPA 202:</b> Determination of condensable particulate emissions from stationary sources		Х	Х				Х				
State of Oregon Source Sampling Manual - Method 7: Sampling condensable emissions from stationary sources		Х									

 Table 2
 Source Test Methods Approved by Provincial Authorities to Measure Particulate Matter

The gas sample is drawn through the sampling train using a vacuum pump. The particulate matter is primarily collected on the filter and its mass is determined gravimetrically after desiccation. The probe and nozzle are cleaned with acetone, and the material collected in the probe is also weighed after desiccation and is considered part of the sample. The particulate mass collected in the filter and probe/nozzle wash is commonly referred to as the front-half catch of EPA Method 5.

EPA Method 5 does not explicitly specify applicability limitations; however, some equivalent methods do [see summaries of EPS Method 1/RM/8 (E) and Ontario Method 5]. Several of these

limitations are, nonetheless, discussed in EPA Methods 1 through 4, which are all incorporated by reference in the full write-up of EPA Method 5.

# **4.3.2** EC Method EPS 1/RM/8 (E): Measurement of Releases of Particulate from Stationary Sources

This method is comprised of five components – Methods A, B, C, D, and E. Methods A-D are similar to EPA Methods 1-4. Method E is equivalent to EPA Method 5; however, Method E requires a pretest leak check of the sampling train (not mandatory in EPA Method 5) and does not allow for any flow rate corrections due to leakage.

EC states that the direct application of the procedures specified in Method E may be limited by sample locations less than two stack diameters downstream or less than 0.5 stack diameter upstream of a flow disturbance; duct cross-sectional areas less than 0.071 m<sup>2</sup>; supersaturated gas streams with entrained liquid droplets; gas stream flow rates less than 3 m/s or greater than 30 m/s; excessively high stack gas temperature; gas streams containing corrosive components; cyclonic flow patterns within the gas stream; or rapid fluctuations in velocity, particulate loading, and/or temperature of the gas stream.

### 4.3.3 EPA Method 17: Determination of Particulate Matter Emissions from Stationary Sources

The sampling train of EPA Method 17 is similar to that of EPA Method 5. In particular, the sampling nozzle and the impinger set configuration of both methods are identical; however, Method 17 uses an in-stack filter and the probe extension used after the filter is not heated<sup>11</sup>. This configuration makes sample recovery much easier, as the probe is not considered part of the sample. Both Methods 5 and 17 collect and measure material that condenses at or above the filter temperature. Both methods are considered to measure total filterable particulate matter concentrations; the difference is that Method 5 has a set filter temperature of  $120^{\circ}C$  ( $\pm 14^{\circ}C$ ), while Method 17 measures material that is condensed at the stack temperature. EPA states that Method 17 can be used if particulate emissions are expected to be independent of stack temperature under normal source operating conditions; however, the method cannot be used on gas streams saturated with water vapour or if water droplets are present. Method 17 is easier than Method 5 to use in the field because it requires less equipment. For some sources, USEPA requires a correction to the PM concentration measured by Method 17.

# **4.3.4** EPA Method 201A: Determination of PM<sub>10</sub> and PM<sub>2.5</sub> Emissions (Constant Sampling Rate Procedure)

This method is applicable to the measurement of PM emissions equal to or less than aerodynamic equivalent diameters (AED<sup>12</sup>) of 10 (PM<sub>10</sub>) and 2.5 microns (PM<sub>2.5</sub>) from stationary sources. In this method, the gas sample is extracted at a constant flow rate through in-stack cyclones, which separate PM greater than PM<sub>10</sub> and PM<sub>2.5</sub>. An in-stack glass fibre filter is used to collect the PM<sub>2.5</sub> fraction. Particulate matter is determined gravimetrically after removal of uncombined water.

The particle sizing devices are two cyclones followed by a final in-stack filter. A cyclone will only provide information on the emissions of particles larger and smaller than the cut point (the size at which it separates particles) of the cyclone, in this case 10 and 2.5 microns. The filter is followed by a set of impingers (an optional heated probe can be installed between the filter and the first impinger), and metering and gas density determination systems arranged in identical manner to EPA Methods 5 or 17.

<sup>&</sup>lt;sup>11</sup> Flexible tubing may be used between the probe extension and first impinger.

<sup>&</sup>lt;sup>12</sup> An AED is a particle diameter as measured by aerodynamic forces.

The particle sizing device must be operated at a constant flow rate in order for the particle size cut points to remain constant during the sample run. This makes the collection of an isokinetic sample a problem. Method 201A uses a constant flow rate and is allowed a wider range of isokinetic error than that specified in EPA Method 5 or 17. Since the main focus of Method 201A is measuring particles less than 10 and 2.5 microns, the additional isokinetic error is acceptable. Small particles are less affected by isokinetic error than are large particles. Total filterable PM can be approximated by summing the results for particulate matter larger and smaller than 10 microns, but this is less accurate than Method 5 or 17 because of the increased isokinetic error and a higher detection limit associated with the measurement of large particles. The duration of the sampling period for this test needs to be adjusted so that sufficient PM mass is collected to meet desired accuracy. This issue was addressed in detail in NCASI (2002c).

EPA Method 201A is unsuitable for use on stack gases that are saturated with moisture, or where there are entrained water droplets.

## Note on EPA Method CTM 39: Measurement of $PM_{2.5}$ and $PM_{10}$ Emissions by Dilution Sampling (Constant Sampling Rate Procedures)

CTM 39 includes a Method 201A PM<sub>10</sub> cyclone followed by a PM<sub>2.5</sub> cyclone. Stack gas is extracted at isokinetic rate conditions through the sampling nozzle and the two cyclones. Following the PM<sub>2.5</sub> cyclone, the gas sample is diluted with filtered air and cooled to 29°C to allow the formation of condensed PM. The diluted cooled gas is then passed through a glass fibre filter to capture the remaining particles (i.e., those with AED less than 2.5 microns plus particles formed by condensation). EPA states the method is most applicable to sources with gas temperatures between 35 and 425°C. The method is capable of measuring source emissions of PM<sub>10</sub> and PM<sub>2.5</sub>. USEPA believes the method can be applied to industrial boilers and sources at reconstituted wood products plants, i.e., particleboard, MDF, OSB, hardboard, and fibreboard. Nonetheless, the (dilution tunnel) method used for diluting the gas sample requires relatively large equipment and significant cost for its application. Thus, it is essentially a research tool rather than a test method suitable for routine stack test measurements. Recognizing this limitation in application of the dilution method, USEPA is currently working to reduce the size of the sampling train as well as simplifying it.

CTM 39 is a new method and, to NCASI's knowledge, has not yet been approved in Canada for routine testing.

## **4.3.5** EPA Method 202 (as Promulgated in 1991): Determination of Condensable Particulate Emissions from Stationary Sources

EPA Method 202 is intended to measure particulate matter that condenses after passing through a filter in the front half of a sampling train. This method may be used in conjunction with EPA Methods 201, 201A or 17 if the probes are glass or Teflon-lined. Using Method 202 in conjunction with Method 201, 201A or 17, only the impinger train configuration and analysis aspects are addressed with this method; the sample train operation and front end recovery and analysis are to be conducted according to Method 201, 201A or 17. A heated EPA Method 5 out-of-stack filter may be used instead of the in-stack filter to determine condensable emissions from wet sources.

Condensable particulate matter (CPM) is collected in the impinger portion of an EPA Method 17 type sampling train. The impinger contents are immediately purged with nitrogen after the test to remove dissolved sulphur dioxide gases, and then transferred to a sample bottle. Each impinger and the connecting glassware, including the probe extension, are rinsed with water. The water rinse is recovered and added to the same sample bottle. Then, the impingers and the connecting glassware, including the probe extension are rinsed with MeCl<sub>2</sub>. These rinses are saved in a different sample bottle. The content of both sample bottles are added together in a separatory funnel. The organic

fraction is separated from the aqueous phase by multiple extractions with methylene chlorine. The organic extract is evaporated at ambient temperature and pressure in a laboratory hood, desiccated, and weighted. The aqueous phase is evaporated to near dryness in the oven, air-dried at ambient temperature, and weighted. The total weight of both fractions represents the CPM.

Note that the multiple options with respect to operation of the sampling train and collection and analysis of samples make comparison of results between sources inappropriate unless it is known that both tests were conducted identically. In sources that use ammonia injection as a control technique for hydrogen chloride (HCl), the ammonia interferes by reacting with HCl in the gas stream to form ammonium chloride (NH<sub>4</sub>Cl), which would be measured as CPM. Therefore, the sample may be analyzed for chloride and the equivalent amount of  $NH_4Cl$  can be subtracted from the CPM weight. USEPA also recognizes that stack gases with several hundred ppm of SO<sub>2</sub> may cause artefact sulphates to be formed in the impingers even after the recommended impinger purging, and these sulphates would be included in the condensable PM sample, imparting a positive bias in the CPM emission estimate. To minimize this impact, a change to the sampling method has been promulgated (see note below).

#### Note on EPA Method 202 (as Promulgated in 2010): Dry Impinger Method for Determining Condensable Particulate Emissions from Stationary Sources

EPA Method 202 is intended to measure particulate matter that condenses after passing through a filter in the front half of a sampling train. This method may be used in conjunction with EPA Methods 201, 201A, or 17 if the probes are glass or Teflon-lined. Using Method 202 in conjunction with Method 201, 201A, or 17, only the impinger train configuration and analysis aspects are addressed with this method; the sample train operation and front end recovery and analysis are conducted according to Method 201, 201A, or 17. A heated EPA Method 5 out-of-stack filter may be used instead of the in-stack filter to determine condensable emissions from wet sources.

The new Method 202 eliminates the first two wet impingers used in the old Method 202 where artefact sulphate was formed when  $SO_2$  gas was retained in the impinger liquid. These impingers are replaced with a water-jacketed condenser followed by a drop-out impinger or bottle, followed by a second impinger, and an ambient temperature membrane filter, all of which start out dry. This method is not required to measure total primary PM (filterable condensable) if the source temperature never exceeds  $30^{\circ}C$ .

To NCASI's knowledge, the new Method 202 has not yet been applied in Canada.

#### 4.4 Alternative Source Test Methods

# **4.4.1** EPA Method 5B: Determination of Nonsulfuric Acid Particulate Matter Emissions from Stationary Sources

EPA Method 5B is intended to measure particulate matter emissions from boilers that use wet flue gas desulphurization systems for  $SO_2$  removal. Method 5B is very similar to Method 5 except that in Method 5B the filter temperature is specified as 160°C and all collected material is heated at 160°C for six hours prior to weighing to volatilize any condensed sulphuric acid that may have been collected. Accordingly, Method 5B procedures minimize the likelihood that sulphuric acid mist will be improperly measured as sulphate particulate matter.

## **4.4.2** EPA Method 5D: Determination of Particulate Matter Emissions from Positive Pressure Fabric Filters

EPA Method 5D is intended to identify appropriate alternate measurement sites and location of traverse points for sampling emissions from positive pressure fabric filters. Guidance is also provided

to determine the velocity of exhaust gases from these emission control devices. EPA states that this method should be consulted if a source using fabric filters does not meet the criteria for stack length and minimal flow disturbances specified in Method 1 (e.g., certain short stacks, fabric filters equipped with roof monitors). The equipment requirements for the sampling train, sample recovery, and analysis are identical to those specified in EPA Method 5.

# **4.4.3** Ontario Source Testing Code Method 5: Determination of Particulate Emissions from Stationary Sources

This method is equivalent to EC Method EPS 1/RM/8 (E). The Ontario Source Testing Code specifically indicates that EPA Method 5 is not applicable to measuring PM in gas streams a) containing significant concentrations of one or more substances with a dew point greater than 120°C, or b) from non-continuous processes.

# **4.4.4** EPA Method CTM 003: Determination of Particulate Matter (Modified High Volume Sampling Procedure)

This method is applicable for the determination of total PM from positive pressure baghouses and other sources that have low concentrations of PM, low humidity, and noncorrosive gases. The sampling train for this method is similar to that specified in EPA Method 5, except that no impingers are part of the configuration. There are also a few differences in the nozzle, probe, filter holder, and metering system. For instance, the probe, nozzle, and filter holder are made of aluminum, as opposed to stainless steel or glass, and neither the probe nor the filter need to be heated. Also, the metering system uses a blower to pull the gas sample through the train. Sample recovery concerns only the filter and the acetone rinses from the front half of the sampling train, while sample analysis is equivalent to that specified in EPA Method 5.

# **4.4.5** State of Oregon Source Sampling Manual - Method 8: Sampling Particulate Emissions from Stationary Sources (High Volume Method)

This method is applicable to stationary sources whose primary emissions are solid particulate. It is primarily intended to measure total PM from wood product handling cyclone and baghouse exhaust systems. The sampling train for this method is very similar to that specified in EPA Method CTM 003, with the exception of minor differences in the metering system, such as the absence of a dry gas meter in Oregon Method 8. Sample recovery and analysis are equivalent to those specified in EPA Method CTM 003.

## **4.4.6** Saskatchewan Environment Standard Reference Methods for Source Testing, APC-31: Measurement of Emissions of Particulates from Stationary Sources

This method is equivalent to EC Method EPS 1/RM/8 (E).

## **4.4.7** Alberta Stack Sampling Code Method 5 - Determination of Particulate Emissions from Stationary Sources

This method is equivalent to EPA Method 5.

#### 4.4.8 British Columbia Field Sampling Manual – Appendix 12: Method for Measuring Particulate Emissions from Stationary Sources with Cyclonic Flow Pattern

This method must be used in conjunction with EPA Methods 1 to 5 to determine the concentration of particulate material in gas streams with cyclonic flow pattern. Prior to considering using this method, the provincial authority requests that the tester evaluate the possibility of eliminating cyclonic flow patterns at the sampling location by relocating the sampling port, installing flow straighteners, or extending the stack.

The method specifies the isokinetic withdrawal of the source gas from a number of sampling or traverse points. At each traverse point, the nozzle is canted directly into the flow at a predetermined rotational angle where the maximum gas velocity occurs. The isokinetic sampling rate is based on the actual stack gas velocity. The particulate sample is collected in the nozzle, probe, cyclone (if used) and filter, all maintained within a temperature range required by EPA Method 5. The particulate weight is determined gravimetrically after removal of uncombined water.

This method is similar to that specified in EPA Method 5, except that the BC method requires that a preliminary determination of the velocity and rotational angle at each traverse point be conducted. This pre-sampling procedure is described in the method's write up.

## **4.4.9** EPA Method 201: Determination of PM<sub>10</sub> Emissions (Exhaust Gas Recycle Procedure)

Like EPA Method 201A, Method 201 is designed to measure filterable particulate matter that has an AED of less than 10 microns, and is unsuitable for use on stack gases that are saturated with respect to moisture, or where there are entrained water droplets.

EPA Methods 201 and 201A are similar in that a sizing device (a cyclone)<sup>13</sup> is used to separate PM greater than  $PM_{10}$ , and an in-stack filter is used to collect the fine fraction; however, Method 201 uses a special sampling train which recycles a clean, dried portion of the gas sample at stack temperature back into the nozzle. This allows the flow rate through the nozzle to be adjusted to meet isokinetic conditions, while the total flow through the sizing device remains constant. Sample recovery and analysis are identical to those specified in EPA Method 201A.

Method 201 is more complex and the equipment is more expensive than Method 201A.

## **4.4.10** Ontario Source Testing Code – (Draft) Method ON-7: Determination of Size Distribution of Particulate Matter from Stationary Sources

Method ON-7 is intended to determine the size distribution of particulate matter in a gas stream withdrawn from a stack under isokinetic conditions. Particulate matter is segregated by size via a cascade impactor, and determined gravimetrically. This method has been adapted by the Ontario Ministry of Environment (OMOE) from the State of California's Air Resources Board - Method 501: Determination of Size Distribution of Particulate Matter from Stationary Sources.

The sampling train of Method ON-7 is similar to that specified in EPA Method 5 (or equivalent) for total PM, except that Method ON-7 uses a right-angle nozzle (as opposed to a curved one) and a cascade impactor is installed between the nozzle and the heated probe.

This method may be used as a screening tool for the determination of  $PM_{10}$  and  $PM_{2.5}$  while conducting standard sampling for total suspended particulate matter (EPA Method 5 or equivalent). The mass fraction obtained from the cascade impactor sampling is multiplied by the total emissions.

Particulate matter is recovered from the impactor's plate inserts and the out-of-stack glass fibre filter, the acetone rinses from washing the probe liner all through the front half of the filter holder, and the impinger water. Similar to EPA Method 201A, PM collected by each collection plate insert and the filter is desiccated and weighed (for size distribution determination), while the solvent rinses and impinger water are evaporated to dryness and the respective residues are desiccated and weighed.

Method ON-7 is applicable to gas sources with a particulate mass concentration range of 0.00001 to  $100 \text{ g/m}^3$  (based on a pressure range between 125 to 500 mm of water gauge); a temperature range

<sup>&</sup>lt;sup>13</sup> EPA Method 201 does not specify a cascade impactor as an alternative.

between 0 and 450°C; and a velocity between 3.0 and 30 m/s. This method is not applicable to high temperature, moisture saturated gas streams or fibrous material.

# **4.4.11** Alberta Stack Sampling Code: Method 5A (AEP) - Determination of Condensable Particulate Emissions from Stationary Sources

This method is similar to EPA Method 202, except that Alberta Method 5A refers to Alberta Method 5, as opposed to EPA Method 17, for details regarding specific sampling, recovery, or analytical procedures.

# **4.4.12** State of Oregon Source Sampling Manual - Method 7: Sampling Condensable Emissions from Stationary Sources

Oregon Method 7 is intended to measure total PM, including condensable gases. It is primarily used on wood dryers where condensable organics are present, e.g., veneer dryer exhausts. In particular, the sampling train is similar to that specified in EPA Method 5 except that a heated out-of-the-stack filter is optional and an unheated glass fibre filter is placed between the third and fourth impinger. The recovery procedure is similar to that specified in EPA Method 5, but also includes a) the contents of the first three impingers and associated water rinses; b) acetone rinses of all sample exposed glassware between the front filter holder (if used) and the fourth impinger; and c) the rear filter. The analysis of the front half catch of the sampling train is carried out as specified in EPA Method 5. The impinger sample is transferred to a separatory funnel, and the organic fraction is extracted with methylene chloride, evaporated to dryness, and weighed. The remaining aqueous fraction and the acetone rinses are separately evaporated, desiccated, and weighed. The rear filter is desiccated and weighed. Total PM (including condensable PM) is determined by summing weights from the front half PM catch, the impingers, the acetone rinses, and the rear filter.

Oregon Method 7 does not specify nitrogen purge of impingers to remove dissolved  $SO_2$ , and thus it may yield high-biased results (due to sulphate formation in the impingers) when used on gas sources with significant  $SO_2$  concentrations.

## 4.5 Synthesis of Test Methods for PM

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure PM. The intent is to help the reader pin down the most important similarities and/or differences between the methods that use similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagram.

PM methods reviewed in this section do not involve continuous sampling and measurement; i.e., sample recovery and analysis are performed off-line. In general, filterable PM can be segregated by size using cyclones or cascade impactors, and is primarily captured by glass fibre filters. Condensable PM is primarily captured by a liquid medium. Particulate is typically determined gravimetrically, with the exception of the new EPA Method 202, where condensable PM is captured primarily on an ambient temperature membrane filter.

#### 4.5.1 Total PM Methods

The schematic comparison between these methods is shown in Figure 1.

## 4.5.2 PM<sub>2.5</sub>, PM<sub>10</sub> and CPM Methods

These methods are summarized in Figure 2. They can also be used to determine total PM.

Gas		 Sample Line	 			
Sample	Acquisition	Filterable PM	Condensable PM	Vacuum Line	Sample Recovery	Analysis
Methods						
U.S. EPA 5: Determination of particulate matter emissions from stationary sources British Columbia Field Sampling Manual — Appendix 12: Method for measuring particulate emissions from stationary sources with stationary sources with stationary sources with cyclonic flow pattern Alberta Stack Sampling, Code Method 5: Determination of particulate emissions from stationary sources Environment Canada EPS 1/R/M8 (Method E): Measurement of releases of particulate from stationary sources Saskatchewan Environment Standard Reference Methods for Source Testing, APC-31: Measurement of emissions of particulates from stationary sources Ontario Source Testing, Code Method 5: Determination of particulate emissions from stationary sources U.S. EPA 5B: Determination of particulate matter emissions from stationary sources U.S. EPA 5D: Determination of particulate matter emissions from positive pressure fabric filters	Stainless steel or quartz rozzle of button-hook or elbow design, and with a sharp, tapered leading edge. Probe liner of borosilicate or quartz glass equipped with heating system kept at @ 120 ± 14°C (EPA Method 58 1/RM/8 and Saskatchewan Method APC-31 specify that probe liner is encased in stainless steel tube	Out-of-stack glass fibre filter without organic binder in a borosilicate glass filter holder and heated @ 120 ± 14°C (EPA Method 5B specifies 160 ± 14°C (EPA Method 5B specifies 160 ± 14°C, Method APC-31, and Ontario Method 5 specify optional use of a heated cyclone between probe and filter	Four impingers connected in series placed in ice bath (1st and 2nd impinger contain deiopnized water, 3rd impinger is empty, 4th impinger contains silica gel)		Filter is removed from filter holder for analysis. Probe and front half of sampling train are washed with acetone or deionized water (Oregon Method 8 specifies also methanol as an alternative). Acetone rinses are recovered for analysis. If applicable, contents of first three impingers may be recovered for analysis	Filter sample is desiccated with calcium sulphate (or oven dried) and weighed. Solvent rinses (and, if applicable, impinger water) are evaporated to dryness and residue is desiccated and weighed. Filterable total PM is the sum of desiccated residue from filter and solvent rinses. (Method 5B specifies that both filter and solvent rinses. (Method 5B specifies that both filter and solvent specifies that both filter and solvent rinses. (Method 5B specifies that both filter and solvent rinses. (Method 5B specifies that both filter and solvent rinse samples must be oven dried at 160 ± 5°C for six hours prior to weighing)
U.S. EPA 17: Determination of particulate matter emissions from stationary sources	Stainless steel or quartz nozzle of button-hook or elbow design, and with a sharp, tapered leading edge. Rigid probe extension	In-stack glass fibre filter				
U.S. EPA CTM 003: Determination of particulate matter (modified high volume sampling procedure) State of Oregon Source Sampling Manual - Method 8: Sampling particulate emissions (high volume method)	Nozzle with sharp, tapered leading edge, and of elbow design, Probe and nozzle made of seamless tubing. No heating needed. EPA CTM 003 specifies a nozzle and probe made of aluminum. Oregon Method 8 does not specify type of metal for nozzle and probe, but indicates that probe should be as short as possible	Out-of-stack glass fibre filter without organic binder in an air-tight filter holder (EPA Method CTM 003 specifies a filter holder made of aluminum). No heating system required	Not applicable			

Figure 1 Total PM Methods

Gas													
Sample	Acquisition	Filterable PM	Condensable PM		Sample Recovery	Analysis							
Methods													
U.S. EPA 201A: Determination of fitterable PM <sub>10</sub> and PM <sub>2.5</sub> emissions (constant sampling rate procedure)	Stainless steel nozzle with a sharp, tapered leading edge (EPA 202, Oregon 7, and Alberta 5A allow use of glass nozzle of button-hook or elbowu design). Heated probe is optional in EPA 201 Adds a heated stainless steel recycle attachment welded directly on the side of the nozzle. Probe extension in EPA 201 and sa heated stainless steel recycle attachment welded directly on the side of the nozzle. Probe extension in EPA 202 and Alberta 5A must be glass-lined or Teflon. Oregon Method 7 specifies a probe liner of borosilicate or quartz glass equipped with heating system kept at @ 120 ± 14°C	Stainless steel nozzle with a sharp, tapered leading edge (EPA 202, Oregon 7, and Alberta 5A allow use of glass nozzle of button-hook or elbow design). Heated probe is optional in EPA 2014. EPA 2014 adds a heated stainless steel recycle attachment welded directly on the side of the nozzle. Probe extension in EPA 2024 and Alberta 5A must be glass-lined or Teflon. Oregon Method 7 specifies a probe liner of homsilicate or quartz	Stainless steel nozzle with a sharp, tapered leading edge (EPA 202, Oregon 7, and Alberta 5A allow use	Stainless steel nozzle with a sharp, tapered leading edge (EPA 202, Oregon 7, and Alberta 5A allow use	Stainless steel nozzle with a sharp, tapered leading edge (EPA 202, Oregon 7, and Alberta 5A allow use	Stainless steel nozzle with a sharp, tapered leading edge (EPA 202, Oregon 7, and Alberta 5A allow use	Stainless steel nozzle with a sharp, tapered leading edge (EPA 202, Oregon 7, and Alberta 5A allow use			Stainless steel sizing devices followed by in-stack un-heated filter. For the sizing device, EPA 201 specifies a cyclone and EPA 2014 also allows the use of alternative sizing devices that meet the requirements in "Development and Laboratory	Stainless steel       Up to four distinct samples m         Sizing devices       PM2.5 cyclones are used.         followed by in-stack       Container No. 2 is rins.         followed by in-stack       PM.0 cyclone grit cup and bo         un-heated filter. For       PM.0 cyclone grit cup and bo         the sizing device,       up to, but on including the tu         a cyclone and EPA       the rinse of the interior of the fuelse starting         a cyclone and EPA       the use of         alternative sizing       interior of the font-half of th         PM10 cyclone exit tube starting       interior of the font-half of th         relevices that meet       the filter Actional or on used. If both PM10 cyclon         "Development and       and PM-cyclone size ruses	Up to four distinct samples may be generated if both $PM_{10}$ and $PM_{2.5}$ cyclones are used. <b>Container No. 1</b> is the front-half filter. <b>Container No. 2</b> is rinse of the nozzle interior, interior of the $PM_{10}$ cyclone grit cup and body up to, but not including the turn around cup. <b>Container No. 3</b> is the rinse of the interior of the $PM_{10}$ cyclone exit tube starting with the turn around cup and the interior of the front-half of the filter holder if the $PM_{10}$ cyclone is the only one used. If both $PM_{10}$ and $PM_{2.5}$ cyclones are used	Filter sample is desiccated and weighed. Solvent rinses are evaporated to dryness and residue is desiccated and weighed. Filterable PM <sub>10</sub> sample: Filter weight gain plus dry residue weight from Container No. 3 if the PM <sub>10</sub> cyclone is the only one used. If both cyclones are used the filterable PM <sub>10</sub> sample also includes the dry residue weight from Container No. 4. Filterable PM <sub>25</sub> sample: Filter weight from Container No. 4. Filterable PM sample: Filter weight from Container No. 4.
U.S. EPA 201: Determination of filterable PM <sub>10</sub> emissions (exhaust gas recycle procedure)								Evaluation of a Pre- stage Cyclone System", EPA- 600/7-78-008, EPA Method 201A, Section 6.1.2.2 (2010)			Interior of the exit tube of the $PM_{10}$ cyclone starting with the tum around cup, the interior of the $PM_{25}$ cyclone grit cup and body up to but not including the exit tube. <b>Container No. 4</b> is the rise of the interior of the PM <sub>25</sub> cyclone exit tube and interior of the front-half of the filter holder.	weight from Containers Nos. 2 and 3 if the PM <sub>10</sub> cyclone is the only one used. If both cyclones are used the fitterable PM sample also includes the dry residue weight from Container No. 4. <b>NOTE</b> : Determination of filterable PM requires meeting tighter isokinetic limits of 90 to 110 percent.	
U.S. EPA 202: Determination of condensible particulate emissions from stationary sources.			In-stack glass fibre filter	Method 202 as promulagted in 1991 uses four impingers, first three contain de- ionized water, fourth contains silica gel, filter between second and third impinger optional. Method 202 as promultaged in 2010 uses water-jacketed condenser with dropout, followed by empty impinger and polymer filter. All components start out dry.		Impinger contents are purged with nitrogen after the test (optional for Alberta Method 5A and EPA Method 202 as promulgated in 1991). Filter is removed from filter holder for analysis, <b>Container No. 4</b> : The contents of first three impingers and associated water rinses are recovered for analysis. <b>Container No. 5</b> : Rinses from washing impingers with methylene chloride are recovered for analysis (Alberta Method 5A and EPA Method 202 as promul-gated in 1991). EPA	Filter is desiccated and weighed (Alberta Method SA and EPA Method 202 as promulgated in 1991). Filter is extracted with water and hexane (EPA Method 202 as promulgated in 2011) and extracts combined with respective samples. Water samples are extracted with methylene chloride (Alberta Method 5A and EPA Method 202 as promulgated in 1991) or hexane (EPA Method 202 as promulgated in 2010). Water samples are titrated with NH <sub>4</sub> OH (optional for Methods 5A and						
Alberta Stack Sampling Code - Method 5A (AEP): Determination of condensible particulate emissions from stationary sources					2010 Container No. 1: The contents of the sampling train between the filter in the front-half plus water rinses of these components are recovered for analysis. Container No. 2: An acetone and two hexare rinses of these same components are recovered for analysis.	202) evaporated, desiccated and weighed. Dry residue weights of water samples are adjusted for amount of NH <sub>4</sub> OH retained. Organic solvent rinses and extractions are evaporated to dryness, desiccated and weighed. Total CPM is determined by summing the organic and inorganic CPM.							
State of Oregon Source Sampling Manual - Method 7: Sampling condensible emissions from stationary sources		Out-of-stack glass fibre filter heated @ 120 ± 14°C (Optional in Oregon Method 7)	Four impingers connected in series placed in ice bath (1st and 2nd impinger contain deionized water, 3rd impinger is empty, 4th impinger contains silica gel). Oregon Method 7 specifies an unheated glass fibre filter between the third and fourth impingers		Front-half of sampling train is recovered as specified in EPA Method 5. In addition the following samples are recovered: (a) contents of first three impingers and associated water rinses; (b) acetone rinses of all sample-exposed glassware between front filter holder and fourth impinger; and (c) rear filter	Front-half catch of sampling train analyzed as per EPA 5. Organic fraction of impinger contents is extracted with methylene chloride, evaporated, and weighed. Remaining aqueous fraction and acetone rinses are separately evaporated, desiccated, and weighed. Rear filter is desiccated and weighed. Total PM (including condensible PM) is determined gravimetrically from front-half PM catch, impingers, acetone rinses, and rear filter							
Ontario Source Testing Code – (Draft) Method ON-7: Determination of size distribution of particulate matter from stationary sources	Right-angle nozzle. Heated probe capable of maintaining T @ 120°C	Cascade impactor followed by an out- of-stack glass fibre fitter without organic binder and heated @ 120°C			Impactor's plate inserts and filter are recovered for analysis. Probe liner and front half of filter holder are washed with acetone, and rinse is recovered for analysis. Water from three first impingers is recovered for analysis	Impactor plate inserts and filter are desiccated and weighed. Solvent rinses and impinger water are evaporated to dryness and respective residues are desiccated and weighed							

Figure 2 Methods Measuring  $PM_{2.5}$ ,  $PM_{10}$ , and CPM

National Council for Air and Stream Improvement
### 5.0 NITROGEN OXIDES (NO<sub>X</sub>)

#### 5.1 Sources of NO<sub>x</sub> at Forest Products Manufacturing Facilities

Nitrogen oxides are predominantly generated during fuel combustion. Approximately 90–95% of the  $NO_x$  compounds are nitric oxide (NO) with the remainder being primarily nitrogen dioxide (NO<sub>2</sub>) (NCASI 2007; Harrison 1999; Pfafflin and Ziegler 2006).

Nitrogen oxides can be categorized as either fuel NO<sub>x</sub> or thermal NO<sub>x</sub>. Fuel NO<sub>x</sub> compounds are formed during combustion by the direct oxidation of organonitrogen compounds<sup>14</sup> contained in fuels like fossil oils, coal, wood residues, spent pulping liquor, secondary sludge, deinking sludge, and certain non-condensable gases containing ammonia (Baukal 2004; NCASI 2007). Available literature suggests that the fuel NO<sub>x</sub> mechanism is the predominant pathway of NO<sub>x</sub> formation in wood-fired boilers and wood-derived spent liquor-fired furnaces (NCASI 2007). Thermal NO<sub>x</sub> compounds are formed in the high temperature, post-flame region of a combustion system by the thermal fixation of molecular nitrogen found in combustion air (NCASI 2007; Peirce, Weiner, and Vesilind 1998; Pfafflin and Ziegler 2006):

$$N_2 + O_2 \leftrightarrow 2 \text{ NO}$$
  
2 NO +  $O_2 \leftrightarrow 2 \text{ NO}_2$ 

The following are the primary air emission sources of nitrogen oxides at pulp and paper and wood products mills:

- Industrial boilers and fluidized bed combustors burning nitrogen-containing fuels
- Kraft recovery furnaces
- Lime kilns burning nitrogen-containing fuels, and kraft mill non-condensable gases

#### 5.2 Source Test Methods for NO<sub>x</sub> Approved Across Canada

Ten source test methods have been identified as having been approved by provincial authorities for measuring nitrogen oxides at forest products manufacturing facilities. Most provinces allow the use of two or more methods, with the exception of Newfoundland and Labrador and Nova Scotia, which generally approve the use of only one method. Table 3 shows the list of approved source test methods for each Canadian province. This list suggests that EPA Method 7E – *Determination of NO<sub>x</sub> Emissions from Stationary Sources (Instrumental Analyzer Procedure)* is the method most commonly approved in Canada for measuring NO<sub>x</sub> from stationary sources at forest products manufacturing facilities.

<sup>&</sup>lt;sup>14</sup> A compound containing at least one carbon-nitrogen bond.

				I	rovince	s			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
<b>Alberta Stack Sampling Code: Method 7</b> - Determination of NO <sub>x</sub> emissions from stationary sources	Х								
Alberta Stack Sampling Code: Method 7A - Determination of NO <sub>x</sub> emissions from stationary sources (ion chromatographic method)	х								
Alberta Stack Sampling Code: Method 7C - Determination of NO <sub>x</sub> emissions from stationary sources (alkaline-permanganate/colorimetric method)	Х								
<b>U.S. EPA 7:</b> Determination of NO <sub>x</sub> emissions from stationary sources		Х	Х	Х			Х		Х
<b>U.S. EPA 7A:</b> Determination of NO <sub>x</sub> emissions from stationary sources (ion chromatographic method)		Х		Х			Х		Х
<b>U.S. EPA 7C:</b> Determination of NO <sub>x</sub> emissions from stationary sources (alkaline permanganate/colorimetric method)		Х		Х			Х		Х
<b>U.S. EPA 7D:</b> Determination of NO <sub>x</sub> emissions from stationary sources (alkaline permanganate/ion chromatographic method)		Х		Х			Х		Х
<b>U.S. EPA 7E:</b> Determination of NO <sub>x</sub> emissions from stationary sources (instrumental analyzer procedure)		Х		Х	Х		Х	Х	Х
Environment Canada EPS 1/RM/15: Reference method for the monitoring of gaseous emissions from fossil fuel-fired boilers			Х	Х		Х	Х		Х
<b>Environment Canada EPS 1-AP-77-3:</b> Measurement of releases of NO <sub>x</sub> emissions from stationary sources								Х	

 Table 3
 Source Test Methods Approved by Provincial Authorities to Measure Nitrogen Oxides

#### 5.3 Principal USEPA and Environment Canada Standard Methods Used at Forest Products Manufacturing Facilities

### 5.3.1 EPA Method 7E – Determination of NO<sub>x</sub> Emissions from Stationary Sources (Instrumental Analyzer Procedure)

EPA Method 7E, an instrumental analyzer procedure, is the most commonly used method for measuring  $NO_x$  emissions and is probably the easiest and most accurate. Although this method requires more equipment, it has the advantage of giving real-time information.

In this method, the gas is continuously sampled from the stack and conveyed to a chemiluminescent analyzer for  $NO_x$  (NO and  $NO_2$ ) determination. A measurement system likely to meet the requirements specified in the method consists of the following essential components:

- (a) A probe of sufficient length to traverse an appropriate number of sample points.
- (b) A particulate filter and a sample line from the probe that must be heated to prevent condensation prior to the sample conditioning equipment or the analyzer.
- (c) A condenser or dryer device to remove moisture continuously from the gas sample.
- (d) A sample pump to pull the gas through the system at a flow rate sufficient to minimize the response time of the measurement system.

- (e) A calibration gas manifold to allow the introduction of a calibration gas<sup>15</sup> directly to the analyzer and/or into the measurement system (at the probe).
- (f) A gas sample manifold to divert a portion of the sample to the analyzer.
- (g) A NO<sub>x</sub> analyzer that operates on the principle of chemiluminescence. This principle is based on the reaction of NO with ozone to form  $NO_2$  and a photon of light, which is measured with a photomultiplier (Pfafflin and Ziegler 2006; Khandpur 2006):

$$NO + O_3 \rightarrow NO_2 + O_2$$
  
 $NO_2 \rightarrow NO_2 + hv$  (photon)

The response of the analyzer is proportional to the NO<sub>x</sub> concentration in the sample.

The method specifies a procedure to conduct an interference test on the gas analyzer prior to its initial use in the field. Potential interferents include carbon dioxide, water vapour, ammonia, methane, sulphur dioxide, hydrochloric acid, or carbon monoxide.

The analytical range must be selected such that the  $NO_x$  emission limit required for the source is not less than 30% of the instrument span.

#### 5.3.2 EPA Method 7 – Determination of NO<sub>x</sub> Emissions from Stationary Sources

EPA Method 7 uses a wet chemical technique. A grab sample of stack gas is drawn into an evacuated flask containing a dilute absorbing solution of sulphuric acid and hydrogen peroxide. Colorimetric analysis of the solution for NO and  $NO_2$  is done with the phenoldisulphonic acid procedure.

The grab sampling train consists of the following essential components:

- (a) A probe, equipped with a heating system, if necessary, to prevent water condensation and a filter to remove particulate matter.
- (b) A collection flask containing a solution of sulphuric acid and hydrogen peroxide to absorb NO<sub>2</sub>. Oxygen from the source is required for NO oxidation to NO<sub>2</sub>. If the gas being sampled contains insufficient oxygen, the method establishes steps to introduce oxygen into the flask. The chemical reactions that occur during sampling absorption are

$$2 \text{ NO}(g) + O_2 \rightarrow 2 \text{ NO}_2$$
  
NO + H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  NO<sub>2</sub> + H<sub>2</sub>O  
2 NO<sub>2</sub> + H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  2 HNO<sub>3</sub> (USEPA 1988)

After the sampling run is complete, the flask must sit for a minimum of 16 hours to maximize NO oxidation. The pH of the liquid is adjusted to between 9 and 12 and then transferred to a volumetric flask and diluted. An aliquot of this solution is transferred to an evaporating dish and evaporated to dryness. A phenoldisulphonic acid (PDA) solution is added to the dried residue along with distilled water and a few drops of concentrated sulphuric acid. The solution is heated for three minutes followed by the addition of water. The resulting solution is adjusted to pH = 10 with ammonium hydroxide, filtered (if necessary), transferred to another volumetric flask, and diluted. The contents of the flask are mixed thoroughly. In an alkaline environment, the tri-ammonium salt of nitrophenol disulphonic acid produced from the reaction between the nitrate ion and PDA develops a yellow colour whose absorbance is measured by a calibrated spectrophotometer (Goel 2007; Khandpur

<sup>&</sup>lt;sup>15</sup> Calibration gas must be NO in nitrogen gas.

2006). The  $NO_x$  concentration (as  $NO_2$ ) is determined based on the measured absorbance and the sample volume corrected for standard conditions.

This method has an interference from sulphur dioxide when present at concentrations above 2,000 ppmv. The analytical range of the method has been determined to be  $2-400 \text{ mg NO}_x$  (as NO<sub>2</sub>)/dscm.

# **5.3.3** EC Method EPS 1-AP-77-3 – Measurement of Releases of NO<sub>x</sub> Emissions from Stationary Sources

This method is equivalent to EPA Method 7.

## **5.3.4** EC Method EPS 1/RM/15 – Reference Method for the Monitoring of Gaseous Emissions from Fossil Fuel-Fired Boilers

This method is applicable to the measurement of emissions of nitrogen oxides (NO species), sulphur dioxide (SO<sub>2</sub>), and carbon monoxide (CO) contained in the flue gases from the combustion of fossil fuels used to generate hot water or steam.

The sampling system consists essentially of a probe connected to a portable calibrated analyzer<sup>16</sup>. The gas sample is extracted from a single point in the exhaust gas from the stack being tested. The water vapour is removed from the sample, and the resulting concentrations of SO<sub>2</sub>, NO, CO and oxygen are measured using species-specific sensors. Portable packages range from single species systems designed for very short sampling to those which can operate continuously for long time periods and measure multiple gaseous compounds. The method also has a procedure to check for interference between each of the measured compounds (SO<sub>2</sub>, NO, and CO). Unlike EPA Method 7E, this method does not use a heated filter to remove particulate matter prior to the analyzer. The analytical range of the method has been determined to be 0-1,250 mg NO<sub>x</sub> (as NO)/dscm.

### 5.4 Alternative Source Test Methods

# 5.4.1 EPA Method 7A – Determination of NO<sub>x</sub> Emissions from Stationary Sources (Ion Chromatographic Method)

The sample collection and recovery for this method are identical to those specified in EPA Method 7. The analytical component, on the other hand, is different in that Method 7A does not use the colorimetric phenoldisulphonic acid procedure, but instead ion chromatography<sup>17</sup> to measure the nitrate resulting from the oxidation of NO and NO<sub>2</sub>. Biased results have been observed when sampling under conditions of sulphur dioxide concentrations above 2,000 ppmv.

The analytical range of the method has been determined to be  $125-1,250 \text{ mg NO}_x$  (as NO<sub>2</sub>)/dscm.

# 5.4.2 EPA Method 7C – Determination of NO<sub>x</sub> Emissions from Stationary Sources (Alkaline Permanganate/Colorimetric Method)

In this method, a gas sample is passed through impingers containing an alkaline solution of potassium permanganate. The captured NO and  $NO_2$  are oxidized to  $NO_2^-$  and  $NO_3^-$  by the permanganate and the  $NO_3^-$  is reduced by cadmium to  $NO_2^-$ . The total  $NO_2^-$  concentration is determined using a

<sup>&</sup>lt;sup>16</sup> Ambient air and NO in nitrogen gas are used as the zero and span gas, respectively, to calibrate the analyzer for measuring NO.

<sup>&</sup>lt;sup>17</sup> Ion exchange chromatography retains analyte atoms or molecules (in this case the nitrate ion) on a column based on ionic interactions between the ions in the sample and those situated in a stationary phase packed into the column. As a mobile phase runs continuously through the column, the absorbed target ions begin to separate (elute) from the stationary phase. The concentration of eluted ionic species in the solution exiting the column can be detected by conductivity (Small 1989; Bruckner 2009).

spectrophotometer. The sampling train for this method is similar to that specified in EPA Method 6, except for a few aspects such as the use of larger impingers and a lower gas flow rate, or the measurement of carbon dioxide during the run. Possible interferents are sulphur dioxide, and in particular, ammonia. Accordingly, the method may not be applicable to plants using ammonia injection to control  $NO_x$  emissions, unless results are corrected. The method includes a procedure to account for the ammonia interference.

The lower detectable limit of this method is 13 mg  $NO_x$  (as  $NO_2$ )/dscm when sampling at 500 mL/min for one hour. Under these conditions, the method has been found to collect up to 1,782 mg  $NO_x$  (as  $NO_2$ )/dscm.

# **5.4.3** EPA Method 7D – Determination of NO<sub>x</sub> Emissions from Stationary Sources (Alkaline Permanganate/Ion Chromatographic Method)

In this method, the stack gas is passed through impingers containing an alkaline solution of potassium permanganate. The captured NO and NO<sub>2</sub> are oxidized to NO<sub>3</sub><sup>-</sup> by the permanganate, and the NO<sub>3</sub><sup>-</sup> is analyzed by ion chromatography. The sampling train and recovery sample procedure for this method are identical to those specified in EPA Method 7C. Possible interferents are identical to those specified in EPA Method 7C.

The lower detectable limit and the upper limits are the same as those specified in EPA Method 7C.

## **5.4.4** Alberta Stack Sampling Code Method 7 - Determination of NO<sub>x</sub> Emissions from Stationary Sources

This method is equivalent to EPA Method 7.

## 5.4.5 Alberta Stack Sampling Code Method 7A - Determination of NO<sub>x</sub> Emissions from Stationary Sources (Ion Chromatographic Method)

This method is equivalent to EPA Method 7A.

# **5.4.6** Alberta Stack Sampling Code Method 7C - Determination of NO<sub>x</sub> Emissions from Stationary Sources (Alkaline Permanganate/Colorimetric Method)

This method is equivalent to EPA Method 7C.

### 5.5 Synthesis of Test Methods for NO<sub>x</sub>

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure  $NO_x$ . The intent is to help the reader pin down the most important similarities and/or differences between methods using similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagram.

### 5.5.1 Direct Sampling Methods

These methods involve on-line chemical analysis of the gas sample, i.e., as soon as it is withdrawn from the stack. The schematic comparison between these methods is shown in Figure 3.

### 5.5.2 Indirect Sampling Methods

In these methods, the sampling and measurement of  $NO_x$  are not performed continuously, i.e., sample recovery and analysis are carried out off-line. These methods use a liquid medium to capture the  $NO_x$  from the gas sample and are illustrated in Figure 4.

Gas San	nple Line (EPA 7E	Teflon, heated abov	e dew point; EPS	1/RM/15: Material r	not specified. Unhea	ated)	
Sample	Acquisition		Conditioning		Pump		Analysis
L						_!	
Methods							
U.S. EPA 7E: Determination of NOx emissions from stationary sources (instrumental analyzer procedure)	Stainless steel (Method 7E specifies glass as		In-stack or heated out-of-stack filter made of material that is non reactive to gas sampled. For dry basis measurements a condenser or dryer is required to remove moisture		Pump constructed of any material that is non reactive to gas sampled		Sample is analyzed for NO <sub>x</sub> using the principle of chemilumines- cence
Environment Canada EPS 1/RW/15: Reference method for the monitoring of gaseous emissions from fossil fuel-fired boilers	alternative) tubing probe of sufficient length to traverse sample points		No particulate filter is used. A mechanical trap and/or desiccants must be used to remove condensed water. Chemical absorbents may be used within the system to remove interfering species of gases		N.A.		Species-specific sensors capable of detecting and quantifying concentrations of NO, SO <sub>2</sub> , CO, and O <sub>2</sub> in the gas sample

Figure 3 Direct NO<sub>x</sub> Methods

Gas			Sample Line											
Sample	Acquisition		Conditioning		Collection	$\rightarrow$	Vacuum Line		Sample Recovery	Analysis				
Methods														
U.S. EPA 7: Determination of NOx emissions from stationary sources										Sample is diluted. An aliquot of sample is concentrated. A phenoldisulphonic acid (PDA) solution is added to dried residue. Deionized water and few drops of				
Alberta Stack Sampling Code: Method 7 - Determination of NOx emissions from stationary sources									Contents of flask are recovered for analysis.	concentrated sulphuric acid are added to this solution, which is then heated, diluted, and adjusted to a pH=10. The resulting solution is filtered, if necessary, diluted again, and mixed thoroughly. The absorbance of the final solution is measured by a				
Environment Canada EPS 1-AP-77-3: Measurement of releases of NOx emissions from stationary sources			A plug of glass wool filter at the probe inlet to remove particulate matter (EPA and Alberta Methods specify a heated out-of-stack filter as alternative)		A collection glass flask containing a solution of sulphuric acid and hydrogen peroxide				Flask is rinsed with deionized water, and rinse are added to recovered sample (EPA and Alberta Methods 7 as well as EPS Method 1-AP-77- 3 specify addition of sodium hydroxide to	spectrophotometer at optimum wavelength (EPA and Alberta Methods 7: 410 nm; EPS Method: 450 nm). NO <sub>x</sub> concentration (as NO <sub>2</sub> ) is function of this absorbance				
U.S. EPA 7A: Determination of NOx emissions from stationary sources (ion chromatographic method)									adjust pH of the sample)	Sample is diluted and injected into an ion chromatograph/conductivity detector (IC/CD) system to				
Alberta Stack Sampling Code: Method 7A - Determination of NOx emissions from stationary sources (ion chromatographic method)	Borosilicate glass tubing probe sufficiently heated to prevent water condensation (EPA and Alberta Methods specify stainless steel or Teflon as													
U.S. EPA 7C: Determination of NOx emissions from stationary sources (alkaline permanganate/colorimetr ic method)	alternative material)									Recovered sample is diluted. An aliquot of the sample is prepared for cadium reduction by adjusting its pH to 0.7; heating the resulting solution; mixing it with oxalic acid; cooling it down; adjusting it to a pH=11.7-12; and filtering it. An aliquot of filtrate is mixed with an				
Alberta Stack Sampling Code: Method 7C - Determination of NOx emissions from stationary sources (alkaline- permanganate/colorimetr ic method)					Three impingers connected in series and containing a solution of potasium permanganate and sodium hydroxide			a	Contents of impingers are recovered for analysis. Impingers are rinsed with deionized water, and rinses are added to the recovered sample	EDTA solution and the whole passed through a cadmium reduction column. The cadmium-reduced solution is mixed with solutions of sulphanilamide and NEDA, and the absorbance of the resulting solution is measured with a spectrophotometer. NO <sub>x</sub> concentration (as NO <sub>2</sub> ) is function of this absorbance				
U.S. EPA 7D: Determination of NOx emissions from stationary sources (alkaline permanganate/ion chromatographic method)										Sample preparation must start 36 hrs after recovery. A hydrogen peroxide solution is added to an aliquot of the sample until color of solution is removed. Solution is filtered and filtrate is diluted and analyzed by ion chromatography				

Figure 4 Indirect NO<sub>x</sub> Methods

#### 6.0 SULPHUR DIOXIDE (SO<sub>2</sub>)

#### 6.1 Sources of SO<sub>2</sub> at Forest Products Manufacturing Facilities

Sulphur is a constituent of most types and grades of fuels and by-products burned in industrial boilers. Coal, petroleum coke, heavy fuel oils, tire-derived fuel (TDF), and spent pulping liquors, such as kraft black liquor, may have significant sulphur contents (NCASI 2007). Natural gas and propane, as well as wood and biomass-derived fuel, typically contain little sulphur (ibid.).

Almost all of the sulphur present in a fuel is oxidized to form sulphur dioxide (SO<sub>2</sub>) during combustion at high temperatures:

$$S+O_2 \rightarrow SO_2$$

A second oxidation step, however, can also occur to form sulphur trioxide (SO<sub>3</sub>):

$$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$$

At high temperatures (e.g., during combustion) the chemical equilibrium favours the production of  $SO_2$ , while at ambient temperatures the opposite is true (Baukal 2004).

The following are the primary air emission sources of sulphur dioxide at pulp & paper and wood products facilities:

- Boilers burning sulphur-containing fuels (e.g., residual oil, light fuel oil) or by-products (e.g., black liquor)
- Kraft recovery furnaces
- Lime kilns burning sulphur-containing fuels, and kraft mill non-condensable gases (NCGs) or stripper off-gases (SOGs)
- Thermal oxidizers burning kraft mill NCGs or SOGs
- Digester and blow tank area vents in acid sulphite pulping

#### 6.2 Source Test Methods for SO<sub>2</sub> Approved Across Canada

Eight source test methods have been identified as having been approved by provincial authorities for measuring sulphur dioxide at forest products manufacturing facilities. Most provinces allow the use of two or more methods, with the exception of Alberta, Nova Scotia, and Newfoundland and Labrador which generally approve the use of only one method. Table 4 shows the list of approved source test methods for each Canadian province. This list suggests that EPA Method 6C – *Determination of Sulphur Dioxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)* is the method most commonly approved in Canada for measuring SO<sub>2</sub> from stationary sources at forest products manufacturing facilities.

				I	Province	s			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
Alberta Stack Sampling Code: Method 8 - Determination of sulphuric acid mist and SO <sub>2</sub> emissions from stationary sources	х								
<b>U.S. EPA 6:</b> Determination of SO <sub>2</sub> emissions from stationary sources		Х	Х	Х			Х		Х
<b>U.S. EPA 6A:</b> Determination of SO <sub>2</sub> , moisture, and carbon dioxide from fossil fuel combustion sources		Х		х			Х		Х
<b>U.S. EPA 6B:</b> Determination of SO <sub>2</sub> and carbon dioxide daily average emissions from fossil fuel combustion sources				Х			Х		Х
<b>U.S. EPA 6C:</b> Determination of SO <sub>2</sub> emissions from stationary sources (instrumental analyzer procedure)		Х		Х	Х		Х	Х	Х
<b>U.S. EPA 8:</b> Determination of sulphuric acid and SO <sub>2</sub> emissions from stationary sources		Х	Х					Х	
Environment Canada EPS 1/RM/15: Reference method for the monitoring of gaseous emissions from fossil fuel-fired boilers			Х	Х		Х	Х		Х
<b>Environment Canada EPS 1-AP-74-3</b> : Measurement of releases of SO <sub>2</sub> from stationary sources								Х	

Table 4 Source Test Methods Approved by Provincial Authorities to Measure Sulphur Dioxide

#### 6.3 Principal USEPA and Environment Canada Standard Methods Used at Forest Products Manufacturing Facilities

## 6.3.1 EPA Method 6C – Determination of SO<sub>2</sub> Emissions from Stationary Sources (Instrumental Analyzer Procedure)

EPA Method 6C is the most commonly used method to measure  $SO_2$  from industrial combustion processes (Baukal 2004). In this method, the emitted gas is continuously sampled from the stationary source and conveyed to an instrumental analyzer that measures  $SO_2$  concentrations. A measurement system likely to meet the requirements specified in the method consists of the following essential components:

- (a) A probe of sufficient length to traverse an appropriate number of sample points.
- (b) A particulate filter and a sample line from the probe that must be heated to prevent condensation prior to the sample conditioning equipment or the analyzer.
- (c) A condenser or dryer device to remove moisture continuously from the gas sample.
- (d) A sample pump to pull the gas through the system at a flow rate sufficient to minimize the response time of the measurement system.
- (e) A calibration gas manifold to allow the introduction of calibration gases<sup>18</sup> directly to the analyzer and/or into the measurement system (at the probe).
- (f) A gas sample manifold to divert a portion of the sample to the analyzer.
- (g) An SO<sub>2</sub> analyzer which can use ultraviolet, non-dispersive infrared, or fluorescence techniques.

<sup>&</sup>lt;sup>18</sup> Examples of calibration gases are e.g., SO<sub>2</sub> in nitrogen or SO<sub>2</sub> in air.

This method has an interference from ammonia, which may be present in boiler stack gases where ammonia or urea is used to reduce nitrogen oxide emissions. There is a procedure in the method to reduce this interference.

The analytical range must be selected such that the  $SO_2$  emission limit required for the source is not less than 30% of the instrument span.

#### 6.3.2 EPA Method 6 – Determination of SO<sub>2</sub> Emissions from Stationary Sources

The gas sample is extracted from the sampling point in the stack using a sampling train, which consists of the following primary components:

- (a) A probe, equipped with a heating system to prevent water condensation and a filter to remove particulate matter, including sulphuric acid mist.
- (b) One midget bubbler containing a solution of isopropanol (80% v/v) with glass wool packed in the top. The isopropanol solution and the glass wool collect SO<sub>3</sub> and sulphuric acid mist carryover.
- (c) A set of three midget impingers connected in series with the midget bubbler. The first two impingers contain a solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 3% v/v), while the final impinger is dry. Sulphur dioxide is efficiently trapped when a solution of hydrogen peroxide in water is used (Hocking 2005):

$$\begin{split} &SO_2 + H_2O \rightarrow H_2SO_3 \\ &H_2SO_3 + H_2O_2 \rightarrow H_2SO_4 + H_2O \end{split}$$

(d) A drying tube packed with silica gel to dry the gas sample.

After the sampling run is complete, a post-test leak check must be conducted, and the contents of the midget impingers transferred to a volumetric flask for analysis. The sample is diluted with water followed by an addition of pure isopropanol and a few drops of thorin indicator. The solution is titrated with a barium perchlorate standard solution (colorimetric reagent). The volume of titrant used serves to calculate the final sulphuric acid concentration obtained in the capture solution (second chemical reaction above). The  $H_2SO_4$  concentration is then used together with the measured gas volume to calculate the sulphur dioxide concentration originally present in the gas sample.

This method has an interference from ammonia, which may be present in boiler stack gases where ammonia or urea is used to reduce nitrogen oxide emissions. There is a procedure in the method to reduce this interference.

The minimum detectable limit of the method has been determined at  $3.4 \text{ mg SO}_2/\text{dscm}$ . Theoretical calculations indicate that the upper concentration limit in a 20 litre gas sample is about 93,300 mg SO<sub>2</sub>/dscm.

#### 6.3.3 EC Method EPS 1-AP-74-3 – Measurement of Releases of SO<sub>2</sub> from Stationary Sources

This method is equivalent to EPA Method 6, except for a few aspects.

- (a) The analytical range of the method is  $13.1-5,240 \text{ mg SO}_2/\text{dscm}$ .
- (b) Preparation of the barium perchlorate standard for sample analysis.
- (c) Use of an additional titration indicator (methylene blue).

# 6.3.4 EC Method EPS 1/RM/15 – Reference Method for the Monitoring Of Gaseous Emissions from Fossil Fuel-Fired Boilers

This method is applicable to the measurement of emissions of  $SO_2$ , nitrogen oxides (NO<sub>x</sub>), and carbon monoxide (CO) contained in the flue gases from the combustion of fossil fuels used to generate hot water or steam, i.e., from boilers.

The sampling system consists essentially of a probe connected to a portable calibrated analyzer<sup>19</sup>. The gas sample is extracted from a single point in the exhaust gas from the boiler being tested<sup>20</sup>. The water vapour is removed from the sample, and the resulting concentrations of SO<sub>2</sub>, NO, CO, and oxygen (O<sub>2</sub>) are measured using species-specific sensors. Portable packages range from single species systems designed for very short sampling to those which can operate continuously for long time periods, and measure multiple gaseous compounds. This method does not use a filter to remove particulate matter prior to the analyzer. Accordingly, for sources where other particulate matter containing sulphur is present, the particulate may be a major interferent. The method also has a procedure to check for interference between each of the measured compounds (SO<sub>2</sub>, NO, and CO).

The analytical range of the method is  $0-5,240 \text{ mg SO}_2/\text{dscm}$ .

#### 6.4 Alternative Source Test Methods

## 6.4.1 EPA Method 6A – Determination of SO<sub>2</sub>, Moisture, and Carbon Dioxide from Fossil Fuel Combustion Sources

The sampling train and measurement techniques for this method are similar to those specified in EPA Method 6, except for a few aspects.

- (a) The vessel train consists of two midget bubblers and two midget impingers, with the bubblers located at both ends of the vessel train to remove SO<sub>3</sub> and sulphuric acid mist (first bubbler) and moisture (second bubbler, containing anhydrous calcium sulphate).
- (b) Instead of the drying tube packed with silica gel specified in EPA Method 6, there is a CO<sub>2</sub> absorber tube containing sodium hydroxide-coated silica.

Moisture and CO<sub>2</sub> concentration are calculated gravimetrically, i.e., by weighing the vessel train and the CO<sub>2</sub> absorber prior to and after sampling.

# **6.4.2** EPA Method 6B – Determination of SO<sub>2</sub> and Carbon Dioxide Daily Average Emissions from Fossil Fuel Combustion Sources

In this method, a gas sample is intermittently extracted from the sampling point in the stack, typically over a 24-hr time period. The sampling train and measurement technique for this method are similar to those specified in EPA Method 6A, except for a few aspects.

- (a) The isopropanol bubbler is not used, although an empty bubbler for the collection of liquid droplets may be included in the sampling train.
- (b) An industrial timer switch is used to cycle the pump on for at least 12 evenly spaced periods of at least two minutes each to allow for intermittent sampling.

<sup>&</sup>lt;sup>19</sup> Ambient air and  $SO_2$  in nitrogen are used as the zero and span gas, respectively, to calibrate the analyzer for measuring  $SO_2$ .

<sup>&</sup>lt;sup>20</sup> A check for gas stratification must be performed.

## 6.4.3 EPA Method 8 – Determination of Sulphuric Acid and SO<sub>2</sub> Emissions from Stationary Sources

Although this method can measure  $SO_2$  emissions, it is primarily used to measure sulphuric acid mist. Details of this method are discussed in Section 13.3. In general, this method is similar to EPA Method 6 except that the sulphuric acid captured by the isopropanol solution is also measured by the barium-thorin titration method. Also, four full-size impingers are used instead of the two midget impingers and two midget bubblers used by Method 6. Typically, EPA Method 8 does not use a heated filter between the probe and the isopropanol impinger to remove particulate matter; instead, a non-heated filter is installed between the isopropanol impinger and the first hydrogen peroxide impinger to capture any sulphuric acid carry over. Accordingly, for sources where other particulate matter containing sulphur is present, the particulate is a major interferent. Other possible interfering agents are fluorides, free ammonia, and dimethyl aniline.

The minimum detectable limit of the method is 1.2 mg SO<sub>2</sub>/dscm. Theoretical calculations indicate that the upper concentration limit for SO<sub>2</sub> in a 1-cubic meter gas sample is about 12,000 mg SO<sub>2</sub>/m<sup>3</sup> (standard conditions).

#### 6.4.4 Alberta Stack Sampling Code Method 8 – Determination of Sulphuric Acid and SO<sub>2</sub> Emissions from Stationary Sources

This method is equivalent to EPA Method 8.

### 6.5 Synthesis of Test Methods for SO<sub>2</sub>

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure SO<sub>2</sub>. The intent is to help the reader pin down the most important similarities and/or differences between methods using similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagram.

### 6.5.1 Direct Sampling Methods

These methods involve on-line chemical analysis of the gas sample, i.e., as soon as it is withdrawn from the stack. The schematic comparison between these methods is shown in Figure 5.

### 6.5.2 Indirect Sampling Methods

In these methods, the sampling and measurement of  $SO_2$  are not performed continuously, i.e., sample recovery and analysis are carried out off-line. These methods use a liquid medium to catch the  $SO_2$  from the gas sample and are illustrated in Figure 6.

Gas Sam	ple Line (EPA 6C:	Teflon, heated abo	ve dew point; EPS	1/RM/15: Material r	not specified. Unhe	ated)	
Sample	Acquisition		Conditioning		Pump		Analysis
						i	
Methods							
<u>U.S. EPA 6C:</u> Determination of SO <sub>2</sub> emissions from stationary sources (instrumental analyzer procedure)	Stainless steel (Method 6C specifies glass as		In-stack or heated out-of-stack filter made of material that is non reactive to gas sampled. For dry basis measurements a condenser or dryer is required to remove moisture		Pump constructed of any material that is non reactive to gas sampled		Ultraviolet, non- dispersive infrared, fluorescence, or other detection principle to constinuously measure SO <sub>2</sub>
Environment Canada EPS 1/RM/15: Reference method for the monitoring of gaseous emissions from fossil fuel-fired boilers	alternative) tubing probe of sufficient length to traverse sample points		No particulate filter is used. A mechanical trap and/or desiccants must be used to remove condensed water. Chemical absorbents may be used within the system to remove interfering species of gases		N.A.		Species-specific sensors capable of detecting and quantifying concentrations of NO, SO <sub>2</sub> , CO, and O <sub>2</sub> in the gas sample

Figure 5 Direct SO<sub>2</sub> Methods

			Sample Line						
Gas Sample	Acquisition		Conditioning		Collection	Vacuum	-	Sample	Apolyzia
	Acquisition		Conditioning		Collection	Line	ľ	Recovery	Analysis
	1	1	1						!
Methods									
U.S. EPA 6: Determination of SO <sub>2</sub> emissions from stationary sources	Borosilicate glass or stainless steel tubing probe with heating system to prevent water condensation		In-stack quartz or pyrex wool, or heated out-of-stack glass fibre filter		One midget bubbler containing isopropanol with glass wool packed in the top, followed by three midget impingers connected in series and placed in ice bath (first two impingers contain hydrogen peroxide solution, 3rd impinger is empty). A silica gel drying tube is placed after impingers				
U.S. EPA 6A: Determination of SO <sub>2</sub> , moisture, and carbon dioxide from fossil fuel combustion sources	Borosilicate glass or stainless steel tubing probe with heating system maintained at 20°C above source temperature but < 120°C		Filter may be within sampling probe or be a separate heated glass fibre unit maintained at 20°C above source temperature but < 120°C		Two midget impingers and two midget bubblers (one located before first impinger and the other after second impinger). Set-up for first bubbler and impingers same as specified by EPA Method 6. Last bubbler contains anhydrous calcium sulphate. All vessels are placed in ice bath. A CO <sub>2</sub> absorber packed with sodium hydroxide- coated silica is placed after last bubbler			Contents of impingers are recovered for analysis. Impingers and connecting tubes are rinsed with deionized water, and rinses are added to sample recovered from impingers	
U.S. EPA 6B: Determination of SO <sub>2</sub> and carbon dioxide daily average emissions from fossil fuel combustion sources	Heated glass tubing probe		Similar to EPA Method 6A except that temperature at the filter must be maintained between 20 and 120°C		Similar to EPA Method 6A except that first bubbler is not included		impingers		Isopropanol and few drops of thorin indicator (EC Method EPS 1-AP-74-3 uses also methylene blue) are added to an aliquot of
Environment Canada EPS 1-AP-74-3: Measurement of releases of SO <sub>2</sub> from stationary sources	Pyrex sampling probe encased in stainless steel tubing with heating system capable of maintaining exit gas temperature in excess of acid dewpoint or 120°C (whichever is greater)		Fine quartz or pyrex wool plug at the probe inlet		Similar to EPA Method 6A except that slightly smaller bubblers and impingers are used				sample solution. Solution is titrated with barium perchlorate to a pink endpoint. SO <sub>2</sub> concentration is calculated from the volume of titrant used
U.S. EPA 8: Determination of suploruic acid and SO <sub>2</sub> emissions from stationary sources Alberta Stack Sampling <u>Code: Method 8 -</u> Determination of Sulphuric acid mist and SO <sub>2</sub> emissions from stationary sources	Glass probe nozzle of button-book or elbow design with a sharp, tapered leading edge. Borosilicate or quartz glass probe liner @ 120 ± 14°C		Glass fibre filter without organic binder, Filter must be unheated and placed between 1st and 2nd impingers.		Four full size impingers connected in series and placed in ice bath (1st impinger contains isopropanol solution, 2nd and 3rd impingers contain hydrogen peroxide solution, 4th impinger contains silica gel)			Contents of 2nd and 3rd impingers are collected together with deionized water rinses from connecting glassware between filter and 4th impinger for analysis of SO <sub>2</sub> (see analysis step). Content of first impinger is recovered for analysis of H <sub>2</sub> SO <sub>4</sub> (not included in this table)	

Figure 6 Indirect SO<sub>2</sub> Methods

National Council for Air and Stream Improvement

### 7.0 VOLATILE ORGANIC COMPOUNDS (VOCS)

### 7.1 Sources of VOCs at Forest Products Manufacturing Facilities

In Canada, the Guide for Reporting to the National Pollutant Release Inventory (NPRI) (EC 2010) defines VOCs as "an aggregate grouping of more than 1,000 organic substances that readily volatilize and undergo photochemical reactions in the atmosphere which contribute to the formation of secondary particulate matter (PM) and ground-level ozone". The Canadian Environmental Protection Act (CEPA) provides a list of over 40 compounds that are specifically exempted from consideration as VOCs. Methane, for example, is not considered as a VOC.

According to USEPA (40 CFR Part 51 Section 51.100), "VOC means any compound of carbon, excluding carbon monoxide, carbon dioxide, carbonic acid, metallic carbides or carbonates, and ammonium carbonate, which participates in atmospheric photochemical reactions". This includes any such organic compound other than those that have been determined to have negligible photochemical reactivity including methane, ethane, acetone, and a host of chlorinated organics including methylene chloride, 1,1,1-trichloroethane and tetrachloroethylene, but excluding chloroform.

At forest products manufacturing facilities, VOCs are typically formed as a result of the breakdown of lignocellulosic materials in wood, under elevated temperatures and pressures (NCASI 2007). VOCs are also directly contributed through chemical additives, adhesives, and combustion devices for certain processes. Process type, operating conditions, type of emission control device, moisture content and wood species of the raw wood material all affect VOC emissions. The forest products industry emits a broad range of volatile organic compounds including terpenes, short chain alcohols and aldehydes (e.g., ethanol, methanol, acetaldehyde, and formaldehyde), short chain organic acids (e.g., formic and acetic acid), and aromatic compounds (e.g., benzene).

VOCs are present in many pulping and downstream process streams, as well as wood products plant process vents and stack gases. The following are the primary air emission sources of VOCs at forest products manufacturing facilities:

- Kraft process: chip bins, uncontrolled batch digester relief, tall oil and turpentine recovery systems, pulp deckers, brown stock washers, oxygen delignification and bleaching plants, uncontrolled NCGs from multiple effect evaporators, and black liquor oxidation tank vents.
- Groundwood and thermomechanical pulping.
- Sulphite pulp mill digesters.
- Washing systems at sulphite and semi-chemical pulp mills.
- Paper machines and pulp dryers.
- Dryers, presses, and lumber kilns at wood products facilities.
- Combustion sources such as recovery furnaces, lime kilns and boilers.

### 7.2 Source Test Methods for VOC Approved Across Canada

Fifteen source test methods have been identified as having been approved by provincial authorities for measuring both total and individual VOCs. Most provinces allow the use of two or more methods. Table 5 shows the list of approved source test methods for each Canadian province. This list suggests that EPA Method 25A – *Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer* is the method most commonly approved in Canada for measuring total VOCs from stationary sources at forest products manufacturing facilities. For individual VOCs, jurisdictions

accept two or more methods depending on the number and type of VOC species, emission source, and process tested.

				Ι	Province	s			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
For total	VOCs								
Alberta Stack Sampling Code: Method 25 - Determination of total gaseous non-methane organic emissions as carbon	х					ĩed			ied
<b>U.S. EPA 25:</b> Determination of total gaseous non-methane organic emissions as carbon		х	х			specif			specif
<b>U.S. EPA 25A:</b> Determination of total gaseous organic concentration using a flame ionization analyzer		х	х	х	Х	Not		Х	Not
For individu	al VOC	Ċs							
Alberta Stack Sampling Code: Method 18 - Measurement of gaseous organic compound emissions by gas chromatography	Х								
<b>U.S. EPA 18:</b> Measurement of gaseous organic compound emissions by gas chromatography		Х	Х				Х	Х	
<b>U.S. EPA 308:</b> Procedure for determination of methanol emission from stationary sources							Х		
U.S. EPA SW-846 - Method 0010: Modified method 5 sampling train (semi-volatiles)			Х		Х				
U.S. EPA SW-846 - Method 0011: Sampling for selected aldehyde and ketone emissions from stationary sources		Х	Х						
U.S. EPA SW-846 - Method 0030: Volatile organic sampling train		Х	Х		Х	pe	Х	Х	pe
U.S. EPA SW-846 - Method 0207: A method for measuring isocyanates in stationary source emissions			Х			pecifia	Х		pecifia
NCASI Method CI/WP-98.01: Chilled impinger method for use at wood products mills to measure formaldehyde, methanol, and phenol		х				Not s	Х		Not s
NCASI Method CI/SG/PULP-94.02: Chilled impinger/silica gel test method at pulp mill sources for methanol, acetone, acetaldehyde, methyl ethyl ketone and formaldehyde							Х		
NCASI Method IM/CAN/WP-99.02: Impinger/canister source sampling method for selected HAPs at wood products facilities							Х		
NCASI Method ISS/FP A105.01: Impinger source sampling method for aldehydes, ketones, and polar compounds							Х		
Environment Canada EPS 1/RM/2: Measurement of releases of selected semi-volatile organic compounds from stationary sources	X	Х	Х	Х				Х	

 
 Table 5
 Source Test Methods Approved by Provincial Authorities to Measure Volatile Organic Compounds

#### 7.3 Standard Methods Used at Forest Products Manufacturing Facilities for Measuring Total VOCs

There are two main approaches for measuring "all" VOCs that are released in stack emissions, one being a) total VOCs as measured by EPA Methods 25A and 25, or equivalent, on an "as carbon" or "as propane" basis; or b) the sum of all individual VOCs identified by appropriate measurement methods where each VOC is added on an "as compound" (full molecular mass) basis. Given that not all wood-origin VOCs have yet been identified, nor measured, both USEPA and Environment Canada have considered use of EPA Method 25A to be a consistent, repeatable approach for reporting on "total VOC" emissions for the time being. Ongoing research by NCASI will ultimately lead to the

ability to undertake more comprehensive reporting of total VOCs (as compounds) using alternative methods or approaches in the future.

Extensive background on Methods 25 and 25A can be found in NCASI Special Report 02-04 (NCASI 2002a), which also discusses US EPA guidance relative to use of the methods and the reporting of VOC emissions.

Environment Canada reference method EPS 1/RM/2, although approved by most provinces, has limited use for testing VOCs as it is primarily designed to measure polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons. Other individual VOC methods, such as those specified in USEPA publication SW-846 or developed by NCASI, are also accepted by some provincial authorities, but only on a case-by-case basis.

Table 6 shows a matrix of individual VOCs relevant to the forest products industry and the appropriate test methods that can be used to measure these compounds.

Compound (Boiling Point)			EPA	Methods	5		Canadiar	n Methods	NCASI Methods						
	18	308	0010	SW-	-846	0207	Alberta EC CI 18 1/RM/2 98		CI/WP 98.01	CI/SG/ PULP 94.02	IM/CAN /WP 99.02	ISS/FP A105.01			
Acetaldehyde (20.2°C)	X	500	0010	X	0020	0207	X		70.01	X	X	X			
Acetophenone (202°C)	х		Х	Х			Х	Х							
Acetone (56.5°C)	х			Х	Х		Х			Х	Х	Х			
Acrolein (53°C)	Х				Х		Х				Х	Х			
<b>Formaldehyde</b> (-21°C)				Х					Х	Х	Х	Х			
Isophorone (215°C)	Х		Х	Х			Х	Х							
Methanol (64.7°C)	Х	Х					Х		Х	Х	Х	Х			
Methyl Ethyl Ketone (MEK) (79.6°C)	х				Х		Х			Х	х	Х			
Methyl Isobutyl Ketone (117-118°C)	x		х	Х			Х	Х			Х	Х			
Methylene Diphenyl Isocyanate (MDI) (314°C)			х			Х		Х							
Phenol (182°C)	Х		Х				Х	Х	Х		Х	Х			
<b>Propionaldehyde</b> (46-50°C)	Х			Х	Х		Х				Х	Х			
Terpenes	1	1	1	1	1	1	1	I	1	I	1				
<b>α-pinene</b> (155-156°C)	Х		Х		Х		Х	Х			Х				
<b>β-pinene</b> (164-165°C)	х		Х		Х		Х	Х			Х				
<b>3-carene</b> (170°C)	X		Х		Х		Х	Х			Х				
<b>p-cymene</b> (177°C)	X		Х		Х		Х	Х			Х				
Limonene (176°C)	Х		Х		Х		Х	Х			Х				

 Table 6
 Forest Products Industry-Relevant VOCs and Individual VOC Test Methods

#### 7.3.1 EPA Method 18 – Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

In this method, the major organic components of a gas mixture are separated by gas chromatography (GC) and individually quantified by a detector based on flame ionization (FID), photoionization, electron capture, or other appropriate principles. Prior to the actual sampling, pre-survey sampling is necessary to determine the VOCs present and their approximate concentration.

The GC column must be operated under conditions that result in good resolution and rapid analysis time for the organic compounds of interest. When a compound separated by the column passes through the detector, the response shows a peak; the time from when the mixed sample was injected to the time the peak occurs is known as *retention time* (Pfafflin and Ziegler 2006). During the pre-survey sample analysis, the retention times of each separated component are compared with those of known compounds under identical analytical conditions. This allows the analyst to identity and quantify the approximate concentrations<sup>21</sup> of the organic emission components beforehand. This information is then used to prepare or purchase commercially available standard mixtures to calibrate the GC. Finally, the analyst assesses the need for sample conditioning, e.g., sample dilution to avoid detector saturation, or filtration to eliminate particulate matter. Specifically, the method offers four sampling configurations depending on the physical layout of the site or the source conditions:

- (a) Integrated bag sampling: In this configuration, a Teflon or Tedlar bag is placed in a rigid airtight container then filled with the gas sample by evacuating the container. This configuration eliminates the possibility of contamination or absorption by a sample pump. The bag's contents are analyzed chromatographically.
- (b) Direct interface sampling: In this configuration, the sample is sucked directly through a heated gas sample loop, and then injected onto the GC column. This configuration eliminates the possibility of adsorption, loss due to reactivity, or contamination by the bags.
- (c) Dilution interface sampling: This configuration is suitable for sources containing a high concentration of organic materials that may require dilution prior to analysis to prevent saturating the GC detector. Stack gases are diluted by a factor of either 10:1 or 100:1 by adding nitrogen or clean dry air.
- (d) Adsorption tube procedure: The adsorbent (e.g., charcoal) is selected based on the chemicals present in the stack gas. In this configuration, a known volume of gas is drawn through the tube, and then the tube is sent for analysis. At the laboratory, the adsorbent is extracted with a suitable solvent, which is then analyzed chromatographically.

Method 18 can be used to sample a broad range of organic compounds, but it is rarely used to sample multiple compounds from the same source. The method complexity, requirement to make or purchase multiple standards for each tested compound, and the need to know the target analytes and their expected concentrations prior to performing sampling prevent this method from being widely used as a VOC speciation tool. It is widely used in the forest products industry for methane measurement and is well suited for that purpose. Method 18 should not be used for compounds that a) are polymeric (high molecular weight), b) can polymerize before analysis, or c) have very low vapour pressures at stack or instrument conditions.

<sup>&</sup>lt;sup>21</sup> The concentration of a given compound is quantified by comparing its response peak height with that of known concentrations of the compound in question.

The lower range of this method is determined by the sampling system, while the upper limit is governed by GC detector saturation, column overloading, or the condensation of higher boiling compounds.

Method 18 is commonly used to measure methane, occasionally used for other compounds, and rarely used for measurement of multiple compounds.

# 7.3.2 EPA Method 25 – Determination of Total Gaseous Non-Methane Organic Emissions as Carbon

This method is for measurement of total gaseous non-methane organics (TGNMOs) as carbon in source emissions. The gas sample is extracted from the stack using a sampling train, which consists of the following main components:

- (a) A probe, equipped with a heating system to prevent water condensation and a heated filter to remove particulate matter.
- (b) A chilled condensate trap to collect the heavier organic compounds.
- (c) An evacuated sample tank.

The evacuated sample tank withdraws the gas sample from the stack at a constant rate through the heated filter and the condensate trap, and collects the lighter (non-condensable) organic compounds. After sampling is completed, the TGNMOs are determined by independently analyzing the condensate trap and sample tank fractions and combining the analytical results. The analysis is carried out by a semicontinuous GC/FID analyzer, also known as a NMO (non-methane organics) analyzer, equipped with an oxidation catalyst and reduction catalyst.

Prior to analysis, the condensable NMOs collected in condensate trap fraction are oxidized to  $CO_2$ , which is collected in an intermediate collection vessel. The  $CO_2$  in the vessel is then injected into the NMO analyzer. In the analyzer, the  $CO_2$  is catalytically reduced to  $CH_4$ , and quantified as  $CH_4$  by the FID.

The contents of the sample tank are injected into the analyzer, but only the NMO portion is quantified. The NMOs are separated from the other gases in the sample (CO,  $CO_2$ , and  $CH_4$ ) by being retained on the GC column. The NMOs are then back flushed off the column and oxidized to  $CO_2$ , reduced to  $CH_4$ , and quantified as such by the FID.

The measured concentrations of NMOs in the condensate trap and sample tank are summed and expressed in terms of carbon equivalents (e.g., ppm C).

When carbon dioxide and water vapour are present together in the stack, they can produce a positive bias in the sample. The magnitude of the bias depends on the concentrations of carbon dioxide and water vapour. EPA recommends calculation procedures to assess the significance of this bias. Organic particulate matter in the condensate trap could also introduce positive bias in the analysis, and hence the need for a particulate filter.

EPA has indicated that Method 25 should not be used if the NMO concentration is less than 50 ppmv. No upper limit has been established.

The advantage to Method 25 is that all NMO compounds are measured equally (as methane) on a percarbon basis. The main drawback of the method is that accurate results can only be obtained with extensive quality assurance and control measures. It is also difficult to sample and analyze high moisture sources because the moisture tends to plug the chilled trap and also complicates the oxidation of the NMOs to carbon dioxide. NCASI experience with using EPA Methods 25 on a number of wood products sources can be found in (NCASI 1983, 1985, 1986a, 1986b, 1986c). Alberta Stack Sampling Code Method 25 (Determination of total gaseous non-methane organic emissions as carbon) is equivalent to EPA Method 25.

# 7.3.3 EPA Method 25A – Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer

This method is for the measurement of total gaseous organic concentration of vapours consisting primarily of alkanes, alkenes and/or arenes (aromatic hydrocarbons). The concentration is based on the response of a flame ionization analyzer (FIA) and expressed in terms of propane (or other appropriate organic calibration gas) or in terms of carbon. Because of the relative ease of use of this method, it is widely used to measure total VOC at forest products sources.

A typical measurement system for this method essentially consists of the following components:

- (a) A probe to extract the gas sample from the center of the stack.
- (b) A heated sample line to prevent condensation.
- (c) A heated particulate glass fibre filter.
- (d) A heated flame ionization analyzer to measure the organic compounds present in the gas sample.

In general, the organic compounds combusted in the FIA produce a potential that is proportional to the number of carbon atoms in the molecule. For example, a molecule of propane (three carbon atoms) provides approximately three times the response of a molecule of methane (one carbon). The FIA can be thought of as a *carbon counter* that quantifies the number of carbon atoms sent to the FIA. For the forest products industry the convention has been to report VOC results as carbon equivalents.

EPA Method 25A has known limitations. Not all carbon atoms provide the same ionization potential (response) in the FIA. Carbon atoms bonded either to carbon or hydrogen will provide the best response, while those part of a carbonyl (-C=O) or carboxyl (-COOH) group or bonded to a hydroxyl group (OH) will have their responses diminished. Thus, the response of the FIA to organic compounds on a per-carbon basis for non-oxidized carbons is approximately 100%, but its response to oxidized carbon is less than 100%. For example, the response to carbon dioxide is nil. The response to formaldehyde, a significant emission from many wood products plant sources, is close to zero; while the response factor for methanol is about 65–75%. An FIA will respond fully to methane, which is not considered a VOC. There is also a problem with high moisture sources and high boiling point organics, present as a gas in the stack, may condense in the Method 25A sample system if the system is below stack temperatures. High moisture sources, such as TMP refiners and lumber kilns, can adversely affect VOC measurements in two ways: a) by overloading sampling systems with inadequate heaters, thus causing condensation; and b) by creating bias in the FIA measurements. Work conducted by NCASI indicates that bias increases with increasing moisture levels (NCASI 1995).

### Note on NCASI Modified Method 25A

NCASI has developed and evaluated modifications to EPA Method 25A that substantially reduce the above mentioned limitations when the method is used to measure total VOC emissions from moisture-laden sources found at wood products plants (NCASI 2006). The modification to Method 25A consists of inserting a chilled impinger in the sampling line prior to the FIA to remove moisture from the gas stream and to capture water-soluble VOCs, many of which have diminished responses. The total VOC (measured as carbon) concentration is obtained by adding the organic carbon present

in VOCs captured in the impinger to the organic carbon present in the gas stream that passed through the impinger into the FIA. The performance of this modified method has been evaluated for methanol, phenol, formaldehyde, propionaldehyde, acetaldehyde, acrolein, hexanal, acetic acid, formic acid, and alpha-pinene, as well as for seven different mixtures of these compounds in gas streams with varying levels of moisture. The recovery of organic carbon was above 90% for the modified Method 25A in all cases, compared to the 37–90% recovery range for the standard Method 25A sampling system, demonstrating this modification is potentially capable of overcoming many of the problems with the standard Method 25A when applied to wood products sources.

# 7.3.4 EC Method EPS 1/RM/2 – Measurement of Releases of Selected Semi-Volatile Organic Compounds from Stationary Sources

This method involves isokinetic sampling of a stack gas using traverses, and is intended to measure semi-volatile organic compounds with boiling points greater than 100°C that are associated with particulate matter, including polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, polycyclic aromatic hydrocarbons, and PCBs. The sampling train consists of the following essential components:

- (a) A probe, equipped with a heating system to prevent water condensation. The gas is extracted from a minimum number of traverse points.
- (b) A heated filter to remove particulate matter. An optional cyclone can be installed after the probe and prior to the filter to collect large particles.
- (c) An organic sampling module consisting of a gas-condensing coil (to remove moisture), a sorbent trap containing a polymeric resin, Amberlite XAD-2, (to collect gaseous semi-volatile organic compounds not captured by the filter), and a condensate trap to prevent bubbling and carryover of condensate into the impingers.
- (d) Three impingers connected in series contained in an ice bath. The first impinger contains ethylene glycol, the second remains empty, and the third impinger contains silica gel.

Samples recovered for analysis include the filter and the sorbent resin trap, as well as solvent rinses from specific components of the sampling train: a) hexane/acetone rinse from sampling train's front half (nozzle, probe, cyclone, and front half of filter holder); b) contents of the condensate trap and first impinger, and associated water rinse; c) hexane/acetone rinse from back half of filter holder and condenser; and d) hexane/acetone rinse from sampling train's back-half glassware (i.e., from back-half filter through the impinger train (ethylene glycol), excluding the sorbent resin trap). The recovered PCBs, dioxins and furans amounts are analyzed chromatographically as per EC Method EPS-1/RM/3 (see section on dioxins and furans).

### 7.4 Source Test Methods for Individual VOC Determination

### 7.4.1 EPA SW-846 Methods

These methods can be found in the EPA publication SW-846, *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, which is the official guidance document of analytical and sampling methods that have been evaluated and approved for use in complying with the US Resource Conservation and Recovery Act (RCRA). RCRA is the primary regulation governing the disposal of solid and hazardous waste in the United States. Hence, strictly speaking, these test methods are not applicable to other source types; however, some of these methods have occasionally been used in the US wood products industry to sample for VOCs like formaldehyde.

British Columbia, Manitoba, Newfoundland & Labrador, Ontario and Quebec approve, on a case-bycase basis, the use of some SW-846 methods to measure individual VOCs.

#### 7.4.1.1 Method 0010 – Modified Method 5 Sampling Train (Semi-Volatiles)

The method is applicable to the determination of semi-volatile principal organic hazardous compounds (POHCs) from incineration systems. In this method, the gas sample is withdrawn from the stack at an isokinetic sampling rate and is collected in a multi-component sampling train, which includes a high-efficiency glass- or quartz-fibre filter, a packed bed of porous polymeric adsorbent resin (Amberlite XAD-2), and a set of impingers. The filter is used to collect organic-laden particulate materials and the porous polymeric resin to adsorb semi-volatile organic species (compounds with boiling points >100°C).

The equipment and operation of this sampling train are similar to that of EC method EPS 1/RM/2, except for the impinger set configuration<sup>22</sup> and the solvent used for sample recovery<sup>23</sup>.

The semi-volatile compounds captured by the filter and adsorbent resin are simultaneously recovered using a continuous extractor, and are concentrated for analysis. The contents of the condensate trap and impingers (if required), and solvent rinses from sampling train are extracted separately using separatory funnels and concentrated for analysis. All extracts are analyzed by GC/mass spectrometry (MS). The method suggests the pre-screening of the sample extracts by gas chromatography/flame ionization detection (GC/FID) or with electron capture (GC/ECD).

Nitrogen oxides  $(NO_x)$  and moisture are possible interferents in the determination of certain watersoluble compounds (e.g., phenol), as some of these tend to react with  $NO_x$  in the presence of moisture. Other issues that could result in biased results include: the stability of the compounds in methylene chloride (sample recovery solvent); the formation of water-soluble organic salts on the resin in the presence of moisture; and the solvent extraction efficiency of water-soluble compounds from aqueous media.

## **7.4.1.2** Method 0011 – Sampling for Selected Aldehyde and Ketone Emissions from Stationary Sources

The method can be applied to determine formaldehyde, acetaldehyde, acetophenone, isophorone, and propionaldehyde. The applicability of the method can be extended to measure other aldehydes and ketones, with the exception of quinine, acrolein, methyl ethyl ketone (MEK), and methyl isobutyl ketone.

The method consists of isokinetically withdrawing the gas sample from an emission source using a sampling train adapted from EPA Method 5 (see section on particulate matter). The pollutants are collected in aqueous acidic 2,4-dinitrophenylhydrazine (DNPH). The formaldehyde and other aldehydes and ketones present in the emissions react with the DNPH to form a stable hydrazone derivative, which is then extracted, solvent-exchanged, concentrated, and analyzed by high performance liquid chromatography (HPLC) or other appropriate technique. The DNPH reagent preparation and handling requirements of the method are difficult.

In terms of interferences, the compound 2,4-dinitroaniline, a decomposition product of DNPH, can coelute with the formaldehyde dinitrophenylhydrazone. Other compounds that may interfere with the analysis of formaldehyde include acetone, dimethylolurea, hexamethylenetetramine, paraformaldehyde. Tolualdehyde is also an interferent as it coelutes with acetophenone. Also, high

<sup>&</sup>lt;sup>22</sup> Method 0010 specifies the use of four impingers, with the first two containing water, the third typically left empty (unless HCl is present in the gas stream, in which case a caustic solution is also added), and the fourth containing silica gel.

<sup>&</sup>lt;sup>23</sup> A methylene chloride/methanol mixture is used for the probe wash instead of the acetone/hexane mixture specified in EC Method 1/RM/2.

levels of nitrogen dioxide  $(NO_2)$  can interfere by consuming all of the DNPH reagent. There is evidence to suggest that the acidic, reactive DNPH solution can disassociate formaldehyde bound to urea or phenol. Due to this, wood products facilities sometimes request permission to use a filter to prevent resin-laden wood particles from entering the impingers.

The detection limits for an 849 L-sample over an hour of sampling may be as low as 10 ppbv for acetophenone and isophorone, 60 ppbv for propionaldehyde, 40 ppbv for acetaldehyde, and 90 ppbv for formaldehyde.

### 7.4.1.3 Method 0030 – Volatile Organic Sampling Train

This method is accepted in British Columbia, Manitoba, Newfoundland and Labrador, Ontario, and Quebec. The method is applicable to the determination of volatile POHCs in the stack gas effluent of hazardous waste incinerators. Volatile POHCs are those compounds with boiling points less than 100°C. This method has been validated for many organic compounds boiling between 30°C and 100°C, and successfully used for some compounds boiling higher than 100°C.

In this method, a sample of gas containing volatile POHCs is withdrawn from the center of the stack at a constant flow rate, using a heated probe and a volatile organic sampling train (VOST). In this sampling configuration, the gas stream is cooled and the volatile POHCs are collected on a pair of sorbent resin traps. The liquid condensate is collected in an impinger placed between the two resin traps. The first resin trap contains 2,6-diphenylene oxide polymer (Tenax) and the second trap contains Tenax and petroleum-based charcoal. The traps are heated to desorb the compounds which are then analyzed by GC/MS.

Water-soluble compounds may not be purged from the condensate completely and therefore should not be analyzed using this method. Interferences arise typically from background contamination of the sorbent traps prior to or after use in sample collection.

Laboratory development data have demonstrated a range of 0.1 to  $100 \ \mu g/m^3$  for selected volatile POHCs collected on a pair of sorbent traps using a total sample volume of 20 L or less. This method requires extensive quality assurance and control.

### 7.4.1.4 Method 0207 – A Method for Measuring Isocyanates in Stationary Source Emissions

This method is accepted in Manitoba and Ontario and is applicable to the collection and analysis of isocyanate compounds from emissions associated with manufacturing process. With respect to its applicability to forest products process sources, the method has been specifically evaluated to measure methylene diphenyl isocyanate (MDI) from pressed board production processes.

The method consists of isokinetically withdrawing the gas sample from an emission source using a sampling train that primary consists of a heated probe and six impingers. The first three impingers contain a derivatizing reagent (1-(2-pyridyl) piperazine) in toluene, the forth impinger is left empty, and the fifth and sixth impingers contain, respectively, activated charcoal and silica gel. After the sampling is completed, the impinger contents are concentrated to dryness under vacuum, brought to volume with acetonitrile and analyzed by high pressure liquid chromatography (HPLC) for individual isocyanates of interest.

Interferences could arise from the competition between alcohols and the derivatizing agent for reacting with an isocyanate, or from other compounds coeluting with one or more of the derivatized isocyanates.

A detection limit of  $112 \text{ ng/m}^3$  has been estimated for MDI based on a sample volume of  $1 \text{ m}^3$  and a 10-mL sample extraction volume.

## 7.4.2 EPA Method 308 – Procedure for Determination of Methanol Emissions from Stationary Sources

This method is accepted in Ontario and is used extensively in the US pulp and paper industry. In this method, a gas sample is extracted from the stack using an unheated probe. The sampling train is completed with a midget impinger placed in an ice bath, an adsorbent tube, a pump, and a dry gas meter. The gas is collected in deionized distilled water (impinger) and adsorbed on silica gel (adsorbent tube). The methanol in the water fraction is analyzed by GC/FID. The fraction adsorbed on silica gel is extracted with an aqueous solution of n-propanol and is also analyzed by GC/FID.

### 7.4.3 NCASI Methods

These methods are available in the *NCASI Methods Manual*, and can be downloaded from <u>http://www.ncasi.org/publications/TOC/Default.aspx?ID=6</u>.

## 7.4.3.1 CI/WP-98.01 – Chilled Impinger Method for Use at Wood Products Mills to Measure Formaldehyde, Methanol, and Phenol

This method is accepted in British Columbia and Ontario, and is commonly used in the US wood products industry. In this method, the source gas is drawn through a heated probe and heated filter into two midget impingers containing chilled, organic-free water. Formaldehyde, methanol, and phenol are absorbed in the water. At the completion of a sampling run, an aliquot of the impinger contents is injected into a gas chromatograph equipped with a FID for quantitation of methanol and phenol. The formaldehyde concentration in the impinger solution is determined using the acetylacetone procedure. This procedure involves the reaction of acetylacetone with formaldehyde to produce a coloured derivative which is measured by colorimetric analysis.

This method has been validated according to EPA Method 301 criteria for rotary and tube dryers, and for presses where either urea-formaldehyde or phenol formaldehyde resins are used. Validation studies have determined that three samples must be taken at each location to obtain representative stack concentrations of the three compounds (formaldehyde, methanol, and phenol).

#### 7.4.3.2 CI/SG/PULP-94.02 – Chilled Impinger/Silica Gel Test Method at Pulp Mill Sources for Methanol, Acetone, Acetaldehyde, Methyl Ethyl Ketone and Formaldehyde

This method is accepted in Ontario. The method has been validated according to the requirements specified in EPA Method 301. The method has been found to be applicable for the measurement of methanol and acetone in pulp mill emissions from recovery furnaces, bleach plant scrubbers, smelt dissolving tank vents, and brownstock washer vents; acetaldehyde in pulp mill emissions from recovery furnaces, smelt dissolving tank vents, and brownstock washer vents; methyl ethyl ketone (MEK) in pulp mill emissions from recovery furnaces, bleach plant scrubbers, and smelt dissolving tank vents; and the measurement of formaldehyde in pulp mill emissions from bleach plant scrubbers, smelt dissolving tank vents; and the measurement of formaldehyde in pulp mill emissions from bleach plant scrubbers, smelt dissolving tank vents, and brownstock washer vents.

The method involves collection of an air sample by drawing it through a midget impinger which is filled with water, and then through two, 2-section silica gel sorbent tubes. The impinger is kept in an ice water bath during sampling to enhance collection efficiency. The impinger catch is analyzed for methanol, acetone, acetaldehyde and MEK by GC/FID. The silica gel sorbent is desorbed with a 3% (v/v) solution of n-propanol. The desorbate is injected directly into the GC/FID for analysis of methanol, acetone, acetaldehyde and MEK. Formaldehyde is quantified from an aliquot of the impinger solution using the acetylacetone derivatization/spectrophotometric analysis method.

Interferences with the formaldehyde analysis can be caused by the presence of  $SO_2$  in the source gas. This is the reason that this method is not valid for the analysis of formaldehyde in recovery furnace source gas.

# Note on NCASI Method CI/SG/PULP-94.03 – Chilled Impinger Test Method for Use on Pulp Mill Sources to Quantify Methanol Emissions

This method has been approved as an alternative method for use on pulp and paper mill sources, regulated under title 40 of the US Code of Federal Regulations (CFR) Part 63, when the analyte of interest is only methanol. In particular, the method has been found to be applicable for the measurement of methanol in emissions from recovery furnaces, bleach plant scrubbers, smelt dissolving tank vents, and brownstock washer vents.

The method involves collection of an air sample by drawing it through midget impingers. Unlike NCASI Method CI/SG/PULP-94.02, this method does not use silica gel sorbent tubes. The impinger catch is analyzed for methanol by direct injection into a gas chromatograph equipped with a flame ionization detector.

Studies on method precision indicate that at least three samples must be taken at each location in order to obtain a representative stack concentration.

### 7.4.3.3 NCASI Method IM/CAN/WP-99.02 – Impinger/Canister Source Sampling Method for Selected HAPs at Wood Products Facilities

This method is accepted in Ontario and is commonly used in the US wood products industry. In this method, the source gas is drawn through a heated probe and heated filter into three midget impingers containing chilled, organic free water. After the third impinger, the source gas passes through a second filter and then into an evacuated stainless steel canister. The impinger contents are analyzed for acetaldehyde, acrolein, methanol, phenol, methyl ethyl ketone, methyl isobutyl ketone, and propionaldehyde using a GC/FID. The formaldehyde concentration in the impinger solution is determined colorimetrically using the acetylacetone procedure. For analysis of the canister contents, gas is withdrawn from the canister and cryogenically concentrated, and then injected into a gas chromatograph equipped with a mass selective detector for analysis of acetaldehyde, plus selected compounds that are not soluble in water such as styrene, toluene, and xylenes. The canister contents can also be analyzed for terpenes, including  $\alpha$ -pinene,  $\beta$ -pinene, 3-carene, p-cymene, and limonene with a gas chromatograph/flame ionization detector (GC/FID). Total hydrocarbon concentrations can also be determined with the GC/FID. This method is not applicable for any emission source that has a moisture content greater than 60% v/v.

This is a self-validating method (by spiking and recovering specific compounds) and thus, it has not been validated according to EPA Method 301 criteria. However, NCASI has made extensive use of the method on wood products sources, and to a lesser degree on pulp and paper sources, with reasonable results for a number of compounds of significance to the sector (NCASI 1999).

### 7.4.3.4 ISS/FP A105.01 – Impinger Source Sampling Method for Aldehydes, Ketones, and Polar Compounds

This method is accepted in Ontario and is occasionally used in the US wood products industry. The method is capable of quantifying stack gas concentrations of methanol, phenol, acetaldehyde, acrolein, formaldehyde, and propionaldehyde. The field sampling equipment is similar to the equipment used for NCASI Method CI/WP-98.01. The gas sample passes through three chilled aqueous impingers containing an o-benzylhydroxylamine (BHA) solution. The carbonyl group of aldehyde compounds reacts with the amine group of BHA forming aldehyde oximes and splitting off

water. The two alcohols are captured in the water and unaffected by the BHA. The aldehyde oximes have limited water solubility and form an emulsion in the bubbling impingers. The impingers and impinger contents are washed with hexane to extract the oximes. An aliquot of the hexane solution is introduced into a gas chromatograph with a nitrogen-phosphorous detector (GC/NPD) for quantification of the aldehydes. The alcohols are determined by direct aqueous injection into a GC with a flame ionization detector (GC/FID).

This method has not been field validated via EPA Method 301 and is considered a self-validating method. Method precision and accuracy are demonstrated on each source for each compound by conducting train spikes, run spikes, duplicate sample runs, and other procedures.

This method should not be used on sources where entrained water droplets are present unless it is used in an isokinetic manner. There is potential, within the source ducts or stacks, for alcohols and aldehydes to concentrate in water droplets. Failure to capture a representative amount of water droplets can bias the results. Theoretically, isokinetic sampling will capture a representative portion of the water droplets. This method may be used isokinetically if all QA/QC procedures are conducted and all QA/QC criteria are met.

### 7.4.4 Alberta Stack Sampling Code Method 18 – Measurement of Gaseous Organic Compound Emissions by Gas Chromatography

This method is equivalent to EPA Method 18.

### 7.5 OTM 26 – Interim VOC Measurement Protocol for the Wood Products Industry

Although this protocol is not currently accepted in Canada, it is now commonly used to measure total VOC at wood products plants in the US as an alternative to EPA Method 25A. It can be considered to be a calculation approach, rather than a "measurement method" *per se*, given that it leverages measurements gathered using two other EPA test methods.

As mentioned earlier, EPA Method 25A does not measure formaldehyde (as part of the aggregate VOC) and only partially measures the carbon in methanol. Thus, Method 25A substantially undermeasures these two compounds as part of the aggregate VOC. Method 25A also significantly undermeasures both the amount of carbon and the total mass of most volatile oxygenated organic compounds (e.g. alcohols, aldehydes, and organic acids).

Regulatory agencies in the US and Canada would like for VOC to be reported on a full mass basis. In order to do so accurately, all the individual compounds in a gas stream would have to be accurately measured individually, and then the sum of those compounds would provide a VOC value that represents the total mass of the emissions. While this might be practical for a process unit that emits only a few organic compounds, it is not practical for wood products processes where dozens, perhaps hundreds, of organic compounds are emitted. To temporarily resolve this issue for wood products plants in the US, EPA and the wood products industry agreed upon an interim VOC measurement and reporting protocol that provides a reasonable approximation of the total mass of VOC with a reasonably simple sampling procedure. The protocol is named EPA Method OTM 26 and is titled *Interim VOC Measurement Protocol for the Wood Products Industry*. OTM 26 is available on EPA's measurement method website (http://www.epa.gov/ttn/emc/prelim/otm26.pdf). The protocol is somewhat flexible and allows a number of procedures and exceptions.

OTM 26 calls for total VOC to be measured by Method 25A and reported as propane. Methanol and formaldehyde are measured separately and added to the VOC as propane value on a full mass basis. Methane, acetone, and other organic compounds that are listed non-VOCs (i.e. specifically exempted from the US VOC definition), may be measured separately and subtracted from the total (as propane). Sixty-five percent of the methanol that is measured separately may also be subtracted from the total

(as propane). This avoids double-counting of methanol, given that about 65% of the carbon in methanol is measured by the FID.

The VOC values reported via the protocol represent an estimate of the total mass of VOC emitted. EPA has worked with NCASI and industry representatives to develop the basic protocol. Theoretically, the protocol provides a good estimate of total mass. The fact that EPA has temporarily "signed off" on the use of the protocol provides sufficient credibility for most users and regulatory agencies to be comfortable with applying this method in their jurisdiction. Note that at this point, NCASI's research efforts have confirmed applicability of this protocol to wood products sources using softwoods, only. Initial results for hardwood do not show as effective a correlation between OTM 26 and total VOCs as compounds, and pulp and paper facility sources have yet to be analyzed for the potential applicability of OTM 26.

### 7.6 Synthesis of Test Methods for VOC

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure VOCs. The intent is to help the reader pin down the most important similarities and/or differences between methods using similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagram.

### 7.6.1 Direct Sampling Methods

These methods involve on-line chemical analysis of the gas sample, i.e., as soon as it is withdrawn from the stack. The schematic comparison between these methods is shown in Figure 7.

### 7.6.2 Indirect Sampling Methods

In these methods, the sampling and measurement of the volatile organic compound(s) of interest are not performed continuously, i.e., sample recovery and analysis are conducted off-line.

Methods in this subsection are segregated according to the way the source gas is captured by the sampling train. Methods using a solid medium or a combination of solid and liquid media to catch VOCs from the gas sample are illustrated in Figure 8. Methods using liquids as their primary collection media are illustrated in Figure 9.

Methods that specify, as part of their sampling train, the use of gas collection devices, such as sample tanks or canisters, are also incorporated in Figure 9, given that a portion of the gas sample is captured by liquid media. In both Figure 8 and Figure 9, the main collection devices such as impingers, sorbent traps, sample tanks or canisters are underlined and in bold-face type.



Figure 7 Direct VOC Methods

_		 Sample Line	 				
Gas Sample	Acquisition	Conditioning	Collection	 Vacuum Line	P	Sample Recovery	Analysis
Methods							
Environment Canada EPS 1/RM2: Measurement of releases of selected semi-volatile organic compounds from stationary sources	Stainless steel or quartz probe nozzle with button-hook design and sharp, tapered leading edge. Borosilicate glass, quartz, or Teflon liner, encased in a stainless steel tube @ 120 ± 14°C	An optional cyclone to remove large particles. A quartz fibre filter @ 120 ± 14°C	A gas condensing coil @ <20°C, followed by an <u>Amberlite XAD-2</u> (sorbent) tube; a <u>condensate trap</u> and three <u>impingers</u> in series (1st impinger contains ethylene glycol, 2nd is empty, 3rd contains silica gel)			Filter and sorbent tube are removed from sampling train for analysis. Contents of condensate trap and 1st impinger are recovered for analysis. Entire sampling train (except for filter and sorbent tube) is rinsed with acetone/hexane, and rinses are also recovered for analysis	The semi-volatile compounds captured by the filter and adsorbert resin are recovered using a Soxhlet extractor, and are concentrated for analysis.
U.S. EPA SW-846 - <u>Method 0010</u> : Modified method 5 sampling train (semi-volatiles)	Stainless steel or glass probe nozie with button-hook or elbow design and sharp, tapered leading edge. Borosilicate or quartz glass probe liner @ 120 ± 14°C	Glass or quartz fibre filter without organic binder. Filter heating system maintained @ 120 ± 14°C	A gas condensing coll @ <20°C, followed by an <u>Amberlite XAD-2</u> (sorbent) tube @ 17 ± 3°C, a <u>condensate</u> trap, and four impingers in series (1st) and 2nd impingers contain water, 3rd is empty, and 4th contains silica gel)			Filter and sorbent tube are removed from sampling train for analysis. Contents of condensate trap and first three impingers are recovered for analysis. Entire sampling train (except for filter and sorbent tube) is rinsed with methanol/methylene chloride, and rinses are also recovered for analysis	The contents of condensate trap and impinger(s), and sampling train inses are extracted separately using separatory funnels and concentrated for analysis. All extracts are analyzed by GC/mass spectrometry (MS)
U.S. EPA SW-846 - Method 0030: Volatile organic sampling train (VOST)	Borosilicate or quartz glass liner, encased in a stainless steel tube @ > 130°C. Isokinetic sampling not a requirement	In-stack glass wool particulate filter	The collection system consists of a condenser followed by a <u>resin trap</u> (cartridge packed with Tenax), a condenser trap, a second condenser, a <u>second</u> condenser, a <u>second</u> packed with Tenax and petroleum-based charcoal), an empty impinger, and a silica gel drying tube			Sorbent cartridges are removed from sampling train for analysis	Cartridges are heated to desorb the compounds captured, which are then analyzed by GC/MS. Cartridges may be analyzed separately or combined
NCASI Method CI/SG/PULP-94.02: Chilled impinger/silica gel test method at pulp mill sources for methanol, acetone, acetaldehyde, methyl ethyl ketone and formaldehyde	Probe is made from Teflon tubing or stainless steel, which is then attached to first impinger. No probe heating system is specified in the method	Not applicable	Two midget <u>impingers</u> connected in series followed by two 2- section <u>silida gel</u> <u>sorbent tubes</u> . Both impingers contain deionized water. All impinger train connectors should be glass and/or Teflon			Contents of impinger(s) and silica gel tube(s) are recovered for analysis	Siliga gel samples are desorbed with an n-propanol solution. Desorbate and impinger solutions are analyzed, separately, by GC/FID. Analysis is made for methanol, acetone, acetaldehyde, and MEK. Formaldehyde is quantified from an aliquot of the impinger sample by adding to it acetylacetone reagent and measuring the absorbance of resulting solution with a spectrophotometer
U.S. EPA 308: Procedure for determination of methanol emission from stationary sources	Unheated Teflon probe	Not applicable	One midget <u>impinger</u> containing deionized water, followed by a <u>silica gel tube</u>				Siliga gel sample is desorbed with an n-propanol solution. Desorbate and impinger sample are analyzed, separately, by GC/FID for methanol

Figure 8 Indirect VOC Methods Using Solid Media or a Combination of Solid and Liquid Media for Sample Collection

Gas			Sample Line	 						
Sample	Acquisition		Conditioning	Collection	$\rightarrow$	Vacuum Line	ľ	Sample Recovery	Analysis	
Methods										
U.S. EPA 25: Determination of total gaseous non-methane organic emissions as carbon Alberta Stack Sampling Code: Method 25 - Determination of total gaseous non-methane organic emissions as carbon	Probe nozzle is of elbow desing and attached to front end of probe, which consists of a stainless steel tubing @ > 129°C, wrapped with high temperature heating tape, and covered with glass covered aluminum foil		Glass or quartz fibre filter without organic binder. Filter heating system maintained @ 121 ± 3°C	The condensible organic fraction is captured in a <u>stainless</u> <u>steel condensate trap</u> packed with coarse quartz wool. The trap is placed in dry ice. Noncondensible compounds are captured in a <u>stainless</u> <u>steel or aluminum</u> <u>sample tank</u>				Condensible organic fraction from the condensate trap is heated and catalytically oxidized to CO <sub>2</sub> CO <sub>2</sub> is recovered for analysis	Organic gases in the sample tank are separated from CO, CO <sub>2</sub> , and CH <sub>4</sub> by a gas cromatograph (GC) and are subsequently oxidized to CO <sub>2</sub> . This CO <sub>2</sub> and that from the condensate trap are reduced to CH <sub>4</sub> and as such quantified by an flame ionization detector (FID)	
U.S. EPA SW-846 - Method 0011: Sampling for selected aldehyde and ketone emissions from stationary sources	Quartz glass probe nozzle with button- hook or elbow design and sharp, tapered leading edge. Borosilicate or quartz glass probe liner @ 120 ± 14°C		Not applicable	Minimum of five <u>impingers</u> in series placed in ice bath. First three impingers contain 2,4- dinitrophenylhydrazine (DNPH) reagent, 4th impinger is empty, 5th contains silica gel				Contents of first three impingers are recovered for analysis. Impingers are rinsed with methylene chloride and water, and rinses are added to sample recovered from impingers	Recovered sample is extracted, solvent- exchanged, concentrated, and analyzed typically by high performance liquid chromatography (HPLC)	
NCASI Method CI/WP- 98.01: Chilled impinger method for use at wood products mills to measure formaldehyde, methanol, and phenol				Two midget <b>impingers</b> , placed in ice bath and connected in series to the end of the teffon line exiting the heated filter box. Both impingers contain deionized water. All impinger train connectors should be glass and/or Teflon				Contents of both impingers are recovered for analysis	An aliquot of impinger catch is analyzed for methanol and phenol by GC/FID. Formaldehyde is quantified as per NCASI method CI/SG/PULP-94.02 (See previous Figure)	
NCASI Method ISS/FP A105.01: Impinger source sampling method for aldehydes, ketones, and polar compounds	Probe made of stainless steel tubing (Methods 98.01 and A105.01 specifies Teflon as alternative) maintained @ 121 ± 14°C. Methods 98.01 and 99.02		Teflon filter (Method 98.01 specifies glass fibre as alternative) contained in heated box @ 121 ± 14°C. Filter housing & connections made of stainless steel (Method 98.01	Teflon filter (Method 98.01 specifies glass fibre as alternative) contained in heated box @ 121 ± 14°C. Filter housing & connections made of stainless steel (Method 98.01	Three or more impingers (midget or large) placed in ice bath and connected in series. All impingers contain a solution of o- Benzylhydroxylamine (BHA). All impinger train connectors should be glass and/or Tefton. A condenser may be used prior to 1st impinger. An impinger containing silica gel may be used after three BHA impingers.				Contents of three impingers are recovered for analysis. Impingers are rinsed with deionized water and hexane, and rinses are added to sample recovered from impingers	Sample is extracted repeatedly with a separatory funnel and split into hexane and aqueous fractions. The hexane solution is analyzed for aldehydes oximes and ketone oximes using GC/hitrogen-phosphorous detection (NPD). The aqueous solution is analyzed for methanol, phenol and other polar compounds using GC/FID
NCASI Method IM/CANWP-99.02: Impinger/casister source sampling method for selected HAPs at wood products facilities	specify that probe must be placed near center of the stack		An unheated Teflon line conveys sample from back of heated filter box to 1st impinger	Three midget Impingers in series all containing deionized water. Source gas leaving 3rd impinger passes through a second filter and is evacuated into a stainless steel <u>canister</u>				Content of three impingers as well as that of canister are recovered for analysis	Impinger sample is analyzed for acetaldehyde, acrolein, methanol, phenol, MEK, MIK, & propionaldehyde using GC/FID. Formaldehyde in this sample is quantified as per NCASI method CI/SG/PULP 94.02 (See previous Figure). Canister sample is cryogenically concentrated and then analyzed via GC/mass selective detection (MSD) for acetaldehyde, acrolein, methanol, phenol, MEK, MIK, propionaldehyde, styrene, toluene and xylenes. GC/FID analysis of the canister sample can be used for measuring selected terpenes	
U.S. EPA SW-846 - Method 0207: A method for measuring isocyanates in stationary source emissions	Glass probe nozzle with button-hook or elbow design and sharp, tapered leading edge. Borosilicate or quartz glass probe liner @ 120 ± 14°C		Not applicable	Six <u>impingers</u> in series. First three impingers contain 1-(2-pyridyl) piperazine reagent in toluene, 4th impinger is empty, 5th impinger contains activated charcoal, 6th contains silica gel. A condenser is placed between outlet of 1st impinger and inlet of 2nd impinger				Contents of first four impingers are recovered for analysis. Probe, impingers 1-4, and condenser are rinsed with toluene/acctonitrile, and rinses are also recovered for analysis	Sample is concentrated to dryness under vacuum in a warm water bath, brought to volume with acetonitrile and analyzed by HPLC for selected isocyanates	

Figure 9 Indirect VOC Methods Using Liquid Media or a Combination of Liquid Media and Gas Containers for Sample Collection

### 8.0 TOTAL REDUCED SULPHUR (TRS)

### 8.1 Sources of TRS at Forest Products Manufacturing Facilities

Within the forest products industry, kraft pulp mills are the primary emitters of total reduced sulphur (TRS) (NCASI 2007). According to Environment Canada, in the case of pulp and paper mills, the following compounds are considered as TRS for reporting under NPRI: hydrogen sulphide (H<sub>2</sub>S), methyl mercaptan (CH<sub>3</sub>S-H), dimethyl sulphide (CH<sub>3</sub>-S-CH<sub>3</sub>), and dimethyl disulphide (CH<sub>3</sub>-S-CH<sub>3</sub>).

TRS is inadvertently generated in kraft pulp mills as a by-product from the use of sodium sulphide (Na<sub>2</sub>S) in kraft cooking. TRS can be found in the digester, evaporator, turpentine recovery, and chemical recovery areas. Non-condensable gases (NCG) from the above mentioned process areas contain large quantities of the four reduced sulphur compounds (RSCs). Additionally, these compounds are also present in process condensates collected from the various process areas. RSCs present in combined condensates may be released into the atmosphere when these condensates are reused on brownstock washers (BSWs), deckers, or in the causticizing area. In addition to RSCs formed during the kraft pulping and recovery process, RSCs are also formed and emitted during black liquor combustion in recovery furnaces, during black liquor oxidation at mills with recovery furnaces with direct contact evaporators, during lime mud calcining in lime kilns, and during smelt dissolution in smelt dissolving tanks. Kraft mill wastewater treatment plant sources primarily include primary settling ponds, clarifiers, and secondary treatment (e.g., aerated stabilization basins or activated sludge). The amount of TRS emitted from these units depends on condensate collection and stripping practices, and type of secondary treatment.

NCASI has summarized the work undertaken by various researchers on the formation mechanisms of reduced sulphur compounds during kraft pulping (NCASI 2008b). During kraft pulping, methyl mercaptan is produced first as a result of the reaction of hydrogen sulphide ions (HS<sup>-</sup>) with methoxyl groups (OCH<sub>3</sub>) present in the pulping liquor. Methyl mercaptan further reacts with methoxyl groups present in the lignin structure to form dimethyl sulphide. Cooking to a lower pH decreases the conversion of methyl mercaptan to dimethyl sulphide. Also, the generation of methyl mercaptan and dimethyl sulphide increases with temperature, sodium sulphide concentration, and duration of cooking (especially for hardwood cooks). Dimethyl disulphide is likely formed through the oxidation of methyl mercaptan when black liquor comes in contact with air. Hydrogen sulphide is formed when the sodium sulphide present in the black liquor dissociates via a two-step hydrolysis reaction sequence. This reaction is favoured at pH < 10. Accordingly, hydrogen sulphide is not formed during kraft cooking (high pH), but instead during brownstock washing or black liquor storage or evaporation (lower pH).

Reduced sulphur emissions from wastewater treatment plants result primarily from two mechanisms: *surface mass transfer* from the liquid phase (influent) to the air, and *mass generation* from treatment sediments (NCASI 2008c). Surface mass transfer is the main source of TRS emissions through volatilization when the effluent is exposed to ambient air (e.g., primary clarifiers and settling ponds), and through stripping when the effluent is subject to mechanical aeration (e.g., aerated stabilization basins). Surface emission rates depend on aeration characteristics, the basin's dimensions, atmospheric conditions, and concentration and diffusivity of TRS in the influent. The temperature and pH of the liquid phase are also important parameters affecting TRS surface emissions through their effect on the dissociation of hydrogen sulphide and methyl mercaptan in water. The mass generation mechanism involves the formation of methane, carbon monoxide and hydrogen sulphide as a result of the anaerobic activity occurring at the bottom of the treatment unit. The generated gas may bubble to the surface, creating a new pathway for emissions. This mechanism is most significant in anaerobic treatment units, with significant sludge accumulation that are prior to aerobic treatment (i.e. primary settling basins).

#### 8.2 Source Test Methods for TRS Approved Across Canada

Five source test methods have been identified as having been approved by provincial authorities for measuring TRS. Most provinces allow the use of at least one method, with the exception of Newfoundland and Labrador and Saskatchewan which specify none. Table 7 shows the list of approved source test methods for each Canadian province. This list suggests that EPA Method 16 – *Semicontinuous Determination of Sulfur Emissions from Stationary Sources* and EPA Method 16A – *Determination of Total Reduced Sulfur Emissions from Stationary Sources (Impinger Technique)* are the methods most commonly approved in Canada for measuring TRS from stationary sources at forest products manufacturing facilities.

				F	Province	es			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
Alberta Stack Sampling Code - Total reduced sulphur compounds from pulp and paper operations	Х								
<b>U.S. EPA 16:</b> Semicontinuous determination of sulfur emissions from stationary sources		Х	Х	Х	lied	Х	Х		lied
<b>U.S. EPA 16A:</b> Determination of total reduced sulfur emissions from stationary sources (impinger technique)		Х		х	specil	Х		Х	specil
<b>U.S. EPA 16B:</b> Determination of total reduced sulfur emissions from stationary sources (GC/FPD)		Х		Х	Not	Х			Not
Environment Canada EPS 1/RM/6: Total reduced sulphur compounds from pulp and paper operations			Х				Х		

 
 Table 7 Source Test Methods Approved by Provincial Authorities to Measure Total Reduced Sulphur

#### 8.3 Principal USEPA and Environment Canada Standard Methods Used at Forest Products Manufacturing Mills

## **8.3.1** EPA Method 16A: Determination of Total Reduced Sulfur Emissions from Stationary Sources (Impinger Technique)

EPA Method 16A is applicable for the determination of TRS emissions from recovery boilers, lime kilns, and smelt dissolving tanks at kraft pulp mills. The flue gas must contain at least 1% oxygen for complete oxidation of all TRS to SO<sub>2</sub>. This method first removes SO<sub>2</sub> from the gas sample, and then oxidizes the TRS present in the sample to SO<sub>2</sub>, which is collected in impingers and analyzed by the barium-thorin titration procedure specified in EPA Method 6.

The gas sample is extracted from the stack using a sampling train, which consists of the following primary components:

(a) A Teflon probe wrapped with heat-resistant tape and sheathed in stainless steel. A Teflon elbow (bored out) is attached to the inlet of the probe, and a piece of Teflon tubing is attached at the open end of the elbow to permit the opening of the probe to reduce the amount of particulate drawn into the sampling train. A heated Teflon particulate filter is installed after the probe.

- (b) A SO2-scrubber consisting of three impingers connected in series, with the first two impingers containing a citrate buffer24, and the last one left empty.
- (c) The scrubber is followed by a combustion tube with a furnace of sufficient size to enclose the combustion chamber of the combustion tube. TRS entering the combustion tube are thermally oxidized to SO<sub>2</sub>.
- (d) A set of three chilled midget impingers connected in series. The first two impingers contain a solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 3% v/v), while the final impinger is dry. Sulphur dioxide is efficiently trapped when a solution of hydrogen peroxide in water is used (Hocking 2005).
- (e) A drying tube packed, or alternatively a fourth midget impinger, with silica gel to dry the gas sample.

After the sampling run is complete, a post-test leak check is mandatory, and (for a 3-hour test run or three 1-hour test runs) a system performance check<sup>25</sup> must be conducted. The contents of the midget impingers are transferred to a volumetric flask and sent for analysis. Analysis of the sample is equivalent to that specified in EPA Method 6.

Reduced sulphur compounds other than the RSCs defined in Section 8.1 may be measured by EPA Method 16A. For example, carbonyl sulphide that may be present in a lime kiln exit gas, may be a positive interferent. Particulate matter (primarily calcium carbonate), if allowed to enter the SO<sub>2</sub>-scrubber and/or the midget impingers, can also cause biased results.

When sampling at 2 L/min, the minimum detectable limits of the method have been determined at 0.1 ppmv SO<sub>2</sub> for 3-hour test runs and 0.3 ppm for 1-hour test runs.

## Note on EPA Method 16C: Proposed Method for the Determination of Total Reduced Sulfur Emissions from Stationary Sources

EPA Method 16C is a second modification of Method 16A. Similar to Method 16A, Method 16C is based on scrubbing any SO<sub>2</sub> present in the stack gas with a citrate buffer and thermally oxidizing the RSCs to SO<sub>2</sub>. However, unlike Method 16A, in this modification, the resulting SO<sub>2</sub> is measured with a continuous SO<sub>2</sub> analyzer as prescribed in EPA Method 6C. This modification would simplify stack gas TRS emission testing as it would replace the wet chemistry of Method 16A or the more complex gas chromatographic analysis of Method 16B (see section on alternative methods) with a simpler to operate continuous SO<sub>2</sub> analyzer. To NCASI's knowledge, this EPA-proposed method is not currently applied in Canada.

## **8.3.2** EPA Method 16: Semicontinuous Determination of Sulfur Emissions from Stationary Sources

Similar to EPA Method 16A, Method 16 is applicable to recovery boilers, lime kilns, and smelt dissolving tanks at kraft pulp mills. This method conditions the gas sample (by removing particulate matter, moisture and SO<sub>2</sub>) and analyzes it for all four TRS compounds using gas chromatographic (GC) separation equipped with flame photometric detection (FPD).

<sup>&</sup>lt;sup>24</sup> The citrate buffer is an aqueous solution of potassium (or sodium) citrate and anhydrous citric acid, and pH-adjusted between 5.4–5.6.

 $<sup>^{25}</sup>$  A system performance check involves sampling a known concentration of H<sub>2</sub>S and comparing the analyzed concentration with the known concentration to determine the reduced sulphur recovery efficiency through the sampling train.

The gas sample is extracted from the stack using a sampling train, which consists of the following primary components:

- (a) A heated Teflon or Teflon-lined stainless steel probe with a deflector shield placed between the sample and the gas inlet holes to prevent clogging of the filter when sampling gas streams with high particulate matter content. An EPA Method 16A probe can also be used. A heated Teflon particulate filter is installed after the probe.
- (b) An SO<sub>2</sub>-scrubber identical to that specified in EPA Method 16A.

A diaphragm-type pump pulls the gas through the sampling train. The gas sample is diluted if it has high concentration of TRS, and then injected into the GC/FPD analyzer. The analyzer determines the concentration of each RSC. A sample run is composed of 16 individual analyses (injects) performed over a period of not less than three hours or more than six hours. The concentration of each RSC is the average concentration over the sample run.

Moisture condensation in the sample delivery system, the analytical column, or the FPD burner block can cause losses or interferences. These interferences are eliminated by heating the probe, filter box, and connections, and by maintaining the SO<sub>2</sub> scrubber in an ice water bath. Also, CO and CO<sub>2</sub> have substantial desensitizing effects on the FPD even after sample dilution. Alkali mist in the emissions of some control devices may result in low sample recoveries. This interference can be minimized by replacing the SO<sub>2</sub> scrubber contents after each run.

The analytical range for this method may extend from 0.1 to 100 ppmv using 10- to 0.1-mL sample volumes.

## **8.3.3** EC Method EPS 1/RM/6: Total Reduced Sulphur Compounds from Pulp and Paper Operations

This method specifies two alternative sampling procedures. In the first procedure, Bag Method S-1, the gas sample is withdrawn from a point at the centre of a stack using a Teflon probe encased in a rigid pipe packed with a particulate filter (quartz or glass wool) at the inlet end. From the probe, the gas travels through a heated Teflon line and is drawn through a chilled impinger containing concentrated phosphoric acid (85% v/v) to remove water vapour. The gas sample is finally collected in a Teflon or Tedlar bag. The second sampling procedure, Bottle Method S-2, is similar to the Bag Method with the exception of using a Teflon bottle (instead of a bag) as a collection device. In both procedures, the sample container is removed from the sampling train and analyzed within one hour of taking the sample. The gas sample is analyzed for each of the RSCs defined in Section 8.1 by GC/FPD.

For most sources, there should be no interference in the chromatographic separation of TRS. In case of presence of  $SO_2$  and/or carbonyl sulphide, samples may be analyzed for these compounds by using a separate chromatographic column.

The minimum detectable limit of the method has been determined at 1.41 mg  $H_2S/m^3$  (1 ppmv) using a 1-mL sample volume.

### 8.4 Alternative Source Test Methods

## **8.4.1** EPA Method 16B: Determination of Total Reduced Sulfur Emissions from Stationary Sources (GC/FPD)

The sampling train, up to the combustion tube and furnace, is identical to that of EPA Method 16A. The gas containing the oxidized RSCs is analyzed by GC/FPD. A post-test system performance check is mandatory as in EPA Method 16A. The chromatographic columns used in this method are identical to those used in EPA Method 16.

Interferences associated with Method 16A are also applicable to Method 16B, in addition to the fact that CO and  $CO_2$  in the gas stream may result in substantial desensitizing of the FPD.

Coupled with a GC using a 1-mL sample size, the maximum limit of the FPD for  $SO_2$  is approximately 10 ppmv. This limit can be, however, extended by diluting the gas sample before analysis or by reducing the sample aliquot size.

### 8.4.2 Alberta Stack Sampling Code - Total Reduced Sulphur Compounds from Pulp and Paper Operations

This method is equivalent to EC Method EPS 1/RM/6. The Albertan version specifies, in addition, the possibility of including a scrubbing step, immediately upstream of the phosphoric acid impinger (in the same way as specified in EPA Methods 16, 16A–C), as well as a pre-test leak check of the sample collection system.

### 8.5 Synthesis of Test Methods for TRS

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure TRS. The intent is to help the reader pin down the most important similarities and/or differences between methods using similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagram.

### 8.5.1 Direct Sampling Methods

These methods involve on-line chemical analysis of the gas sample, i.e., as soon as it is withdrawn from the stack. The schematic comparison between these methods is shown in Figure 10.

### 8.5.2 Indirect Sampling Methods

In these methods, the sampling and measurement of TRS are not performed continuously, i.e., sample recovery and analysis are carried out off-line. These methods are illustrated in Figure 11.
Gas [		Sample	Line (Teflon and ur	nheated)		-,	
Sample	Acquisition		Conditioning		Pump		Analysis
i						_ 1	
Methods	İ						
<u>U.S. EPA 16</u> ; Semicontinuous determination of sulfur emissions from stationary sources	Teflon-lined stainless steel probe (Method 16 specifies a		Heated out-of- stack Teflon filter (@ 120°C EPA 16; @ 121°C EPA 16B). SO <sub>2</sub> - scrubber (two first				Sample is analyzed for hydrogen sulphide, methyl mercaptan, dimethyl sulphide, and dimethyl disulphide by GC/FPD
U.S. EPA 16B: Determination of total reduced sulfur emissions from stationary sources (GC/FPD)	heated-probe) with a Teflon elbow nozzle directed away from the gas stream		impingers contain citrate buffer, last impinger left empty). EPA 16B specifies a combustion tube & furnace prior to pump		Teflon-coated diaphragm pump		Sample is analyzed for SO <sub>2</sub> (oxidized TRS) by GC/FPD

Figure 10 Direct TRS Methods



Figure 11 Indirect TRS Methods

### 9.0 POLYCHLORINATED DIBENZO P-DIOXINS AND POLYCHLORINATED DIBENZO FURANS (D/F)

#### 9.1 Sources of D/F at Forest Products Manufacturing Facilities

Polychlorinated dibenzo p-dioxins and polychlorinated dibenzo furans (D/Fs) are two families of highly stable compounds that are similar in chemical structure and biological properties, and that are usually found together in the environment (OMOE 1997). The chemical structure of dioxins is based on two benzene rings joined via two oxygen bridges, while in the case of furans the benzene rings are joined via a central furan ring (ATSDR 2006).

The number of chlorine atoms attached to a given dioxin or furan molecule can vary from one to eight, at any of eight locations. In total, there are 75 different chemical configurations (congeners) of dioxins and 135 of furans. Of the 210 possible congeners, a subset of seven dioxins and 10 furans having chlorine at the 2, 3, 7, and 8 positions (i.e., 2, 3, 7, 8-substituted) are generally considered to pose the greatest risk to human health (USEPA 2006).

D/Fs are formed through one of three mechanisms (NCASI 2007):

- Combination of chlorine radicals with hydrocarbons at elevated temperatures (prevalent in combustion environments)
- Condensation of chlorinated sodium phenolate structures, or
- Electrophilic substitution by chlorine of an unchlorinated precursor compound

The main source for dioxins and furans formation relevant to forest products manufacturing facilities relates to combustion, where chlorine radicals, if present, could combine with hydrocarbons at elevated temperatures. Examples of these sources are conical burners, beehive burners, boilers burning solid or liquid fossil fuel and/or wood residue (especially salt-laden bark), and kraft recovery furnaces.

## 9.2 Source Test Methods for D/F Approved Across Canada

Three source test methods have been identified as having been approved by provincial authorities for measuring D/Fs. Most provinces allow the use of at least one method, with the exception of Alberta and Saskatchewan which specify none. Table 8 shows the list of approved source test methods for each Canadian province. This list suggests that EC Method EPS 1/RM/2 – *Measurement of Releases of Selected Semi-Volatile Organic Compounds from Stationary Sources* is the method most commonly approved in Canada for measuring D/F from stationary sources at forest products manufacturing facilities.

				F	rovince	s			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
U.S. EPA 23: Determination of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans from municipal waste combustors	ied	Х	Х				Х		ïed
U.S. EPA SW-846 - Method 0023A: Sampling method for polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofuran emissions from stationary sources	ot specif				Х				lot specif
Environment Canada EPS 1/RM/2: Measurement of releases of selected semi-volatile organic compounds from stationary sources		Х	Х	Х		Х	Х	Х	Z

Table 8 Source Test Methods Approved by Provincial Authorities to Measure D/F

#### 9.3 USEPA and Environment Canada Standard Methods Used at Forest Products Manufacturing Facilities

#### 9.3.1 EC Method EPS 1/RM/2 – Measurement of Releases of Selected Semi-Volatile Organic Compounds from Stationary Sources

This method involves isokinetic sampling of a stack gas using traverses, and is intended to measure semi-volatile organic compounds with boiling points greater than 100°C that are associated with particulate matter, including polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans, polycyclic aromatic hydrocarbons, and PCBs. The sampling train consists of the following essential components:

- (a) A probe, equipped with a heating system to prevent water condensation. The gas is extracted from a minimum number of traverse points.
- (b) A heated filter to remove particulate matter. An optional cyclone can be installed after the probe and prior to the filter to collect large particles.
- (c) An organic sampling module consisting of a gas condensing coil (to remove moisture), a sorbent trap containing a polymeric resin, Amberlite XAD-2, (to collect gaseous semi-volatile organic compounds not captured by the filter), and a condensate trap to prevent bubbling and carryover of condensate into the impingers.
- (d) Three impingers connected in series contained in an ice bath. The first impinger contains ethylene glycol, the second remains empty, and the third impinger contains silica gel.

Samples recovered for analysis include the filter and the sorbent resin trap, as well as solvent rinses from specific components of the sampling train: a) hexane/acetone rinse from sampling train's front half (nozzle, probe, cyclone, and front half of filter holder); b) contents of the condensate trap and first impinger, and associated water rinse; c) hexane/acetone rinse from back half of filter holder and condenser; and d) hexane/acetone rinse from sampling train's back-half glassware (i.e., from back-half filter through the impinger train (ethylene glycol), excluding the sorbent resin trap). The recovered dioxins and furans amounts are analyzed chromatographically as per EC Method EPS-1/RM/3 (see below).

### Note on Environment Canada EPS 1/RM/3: Method for the Analysis of Polychlorinated Dibenzop-Dioxins (PCDD), Polychlorinated Dibenzofurans (PCDF) and Polychlorinated Biphenyls (PCB) in samples from the incineration of PCB waste

This method analyzes the samples collected by EC Method EPS 1/RM/2. The filter's particulate content is treated with a solution of HCl, filtered, and air-dried prior to extraction. The treated solid is Soxhlet extracted with benzene for 20 hours; the filtrate is extracted with dichloromethane, and the extract is desiccated.

The front-half acetone/hexane rinse is concentrated and desiccated. The desiccated front-half rinse is added to the filtrate (dichloromethane) extract, and both are combined with the Soxhlet extract. The resulting solution is concentrated, solvent exchanged to hexane, and desiccated (Extract 1).

The sorbent resin requires no chemical pretreatment and is also Soxhlet extracted with benzene for 20 hours.

The combined condensate/ethylene glycol rinse is acidified and extracted with dichloromethane and desiccated.

The back-half holder/condenser and the back-half glassware acetone/hexane rinses are separately concentrated and desiccated. The desiccated back-half glassware rinse is combined with the desiccated condensate/ethylene glycol extract, and the resulting solution is concentrated, and solvent exchanged to hexane (Extract 2). The desiccated back-half holder/condenser rinse is combined with the sorbent resin extract, and the resulting solution is concentrated, solvent exchanged to hexane, and desiccated (Extract 3).

Extracts 1–3 are separately passed through a series of two cleanup columns which remove, by reaction and selective adsorption, the bulk of the organic matrix co-extracted with target compounds and separate PCBs from the D/F fraction<sup>26</sup>. The D/F fraction is concentrated to a small volume and screened<sup>27</sup> for PCDD/PCDF analytes by column gas chromatography coupled with electron capture detection (GC/EC). Quantitative analysis of D/F s is performed with a gas chromatograph coupled with a mass spectrometer (GC/MS).

## **9.3.2** USEPA 23: Determination of Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofurans from Municipal Waste Combustors

The sampling train of this method is similar to that specified in EC Method EPS 1/RM/2 with the following primary variations:

- EPA 23 specifies nickel as an alternative material for the sampling nozzle.
- The collection train in EPA 23 consists of five impingers and is prepared as follows: the first and fourth impingers are empty (the first one acts as a condensate trap such as that specified

<sup>&</sup>lt;sup>26</sup> Concentrated raw extracts are added to the first column (acid/base silica gel) and eluted with 2% v/v dichloromethane in hexane. The eluate (effluent) from this column is concentrated and solvent exchanged to hexane. The concentrated eluate is transferred, along with hexane, into the second (alumina) column. This column is eluted first with a solution of 2% v/v dichloromethane in hexane to extract the fraction containing the PCBs (discarded), and then with a solution of 50% v/v dichloromethane in hexane to extract the D/F fraction. The use of a third chromatographic (carbon) column is contemplated in case there is a need for further clean up (no details are provided in the method).

<sup>&</sup>lt;sup>27</sup> The primary objective of a screening analysis is to determine the presence of one or more analytes in a sample.

in EPS 1/RM/2), the second and third impingers contain water, and the fifth impinger contains silica gel.

In terms of sample recovery, EPA Method 23 also recovers the material captured by the filter and the sorbent resin trap; however, unlike EPS 1/RM/2, there are only two rinse samples recovered.

- The material deposited in the front half of the sampling train, back half of filter holder, condenser, and connecting line between the filter and the condenser is recovered by rinsing with acetone. In addition, the probe, the condenser, and the connecting line between filter and condenser are rinsed with dichloromethane. All these rinses are collected in one container (Sample 1).
- After collecting Sample 1, the probe, the condenser, and the connecting line between the filter and the condenser are rinsed with toluene. This rinse is collected in a separate container (Sample 2).

Sample 1 is evaporated to dryness and the residue, together with the filter contents and the sorbent resin, is Soxhlet extracted with toluene for 16 hours. The extract is concentrated (Extract 1). Sample 2 is concentrated and mixed with toluene. The resulting solution is evaporated to near dryness (Extract 2).

Extracts are separately passed through a series of three cleanup columns which remove, by reaction and selective adsorption, the bulk of the organic matrix co-extracted with target compounds and separate PCBs from the D/F fraction<sup>28</sup>. The D/F fraction is concentrated to a small volume, and screened and quantitatively analyzed with gas chromatographic columns coupled with a mass spectrometer (GC/MS).

# **9.3.3** EPA SW-846 - Method 0023A: Sampling Method for Polychlorinated Dibenzo-p-Dioxins and Polychlorinated Dibenzofuran Emissions from Stationary Sources

The sampling train of this method is similar to that specified in EC Method EPS 1/R/2 except that the two impingers after the condensate trap contained deionized water (instead of ethylene glycol and an empty impinger). The sample recovery procedure is similar to that specified in EPA Method 23 except that

- the entire front half of the sampling train is sequentially rinsed with acetone, dichloromethane, and toluene, with the rinses collected in one container (Sample 1) and
- the acetone/dichloromethane/toluene rinses from the back half of the filter holder, the condenser, and the connecting line between filter are collected in a separate container (Sample 2).

The analytical procedure requires Sample 1 to be concentrated and combined with the filter sample, and Sample 2 to be concentrated and combined with the sorbent resin sample. Each combined sample

<sup>&</sup>lt;sup>28</sup> Concentrated raw extracts are added to the first column (acid/base silica gel) and eluted with hexane. The eluate from this column is concentrated. The concentrated eluate is transferred into the second (alumina) column. This column is eluted first with a solution of 0.5% v/v dichloromethane in hexane to extract the fraction containing the PCBs (discarded), and then with a solution of 35% v/v dichloromethane in hexane to extract the D/F fraction. The eluate containing the D/F fraction is concentrated to a small volume, diluted in hexane, and transferred to a carbon/celite column which is then sequentially eluted with solutions of 50% v/v dichloromethane in hexane and 50% v/v benzene in ethyl acetate. Eluates are discarded. The column is then inverted and eluted in the reverse direction with toluene. The resulting eluate is concentrated and contains the cleaned up D/F fraction.

is extracted, cleaned up, and analyzed separately, following the same procedure: Soxhlet extraction with toluene for 16 hours; concentration to a small volume; cleanup through three chromatographic columns<sup>29</sup>; and screening and quantitative analyses with a high resolution gas chromatographic column coupled with a high resolution mass spectrometer (HRGC/HRMS).

### 9.4 Synthesis of Test Methods for D/F

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure D/Fs. The intent is to help the reader pin down the most important similarities and/or differences between methods using similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagrams.

D/F methods reviewed in this section do not involve continuous sampling and measurement; i.e., sample recovery and analysis are performed off-line. In general, after samples are recovered, they are solvent extracted, cleaned up, and quantified by GC/MS. The schematic comparison between these methods is shown in Figure 12. Differences are primarily associated with the way samples are recovered and prepared for analysis (see Figures 13-15).

<sup>&</sup>lt;sup>29</sup> This cleanup procedure is similar to that specified in EPA Method 23 with the following variations: a) the alumina column is eluted first with hexane and then with a 60% v/v dichloromethane in hexane; and b) the first elution of the carbon/celite column is performed sequentially with solutions of 50% v/v dichloromethane in cyclohexane and dichloromethane/methanol/toluene (75:20:5% v/v).

Gas		 Sample Line	 					
Sample	Acquisition	Conditioning	Collection	<b></b> ,	Vacuum Line	P	Sample Recovery	Analysis
Methods								
Environment Canada EPS 1/RM2: Measurement of releases of selected semi-volatile organic compounds from stationary sources							Filter and sorbent tube are removed from sampling train for analysis. Recovery of solvent rinses varies with method. <u>EPS</u> <u>1/RM/2:</u> (a) hexane/acetone rinse from sampling train's front-half (nozzle, probe, cyclone, and front-half of filter holder); (b) hexane/acetone rinse	See Analytical Summary Diagram (A)
U.S. EPA 23: Determination of polychlorinated dibenzo- p-dioxins and polychlorinated dibenzofurans from municipal waste combustors	Borosilicate or quartz glass nozzle with button-hook design and sharp, tapered leading edge. Alternative nozzle materials include nickel (EPA 23), nickel alloys (EPA 23 and EPS 1/RM/2), and stainless steel (EPS 1/RM/2).	Optional cyclone prior to filter to remove large particles. A quartz fibre filter with no	A gas condensing coil followed by an Amberite XAD-2 (sorbent) tube, a condensate trap (which is specified as an empty impinger in EPA 23 and SW-846 0023A) and a set of <u>impingers</u> in series and placed in an ice bath. Impinger configuration and preparation varies with methods. EPS 1/RM/2				from back-half of filter holder and condenser; (c) hexane/acetone rinse from sampling train's back-half glassware, excluding the sorbent resin trap); and (d) content of condensate trap and 1st impinger, plus associated water rinse. <u>EPA 23</u> : (a) acetone rinse from front-half of sampling train, back- half of filter holder,	See Analytical Summary Diagram (B)
U.S. EPA SW-846 - Method 0023A: Sampling method for polychlorinated dibenzo- p-dioxins and polychlorinated dibenzofuran emissions from stationary sources	uartz glacate of guartz glacate of the neated @ 120 ± 14°C (Teflon is also specified as alternative material in EPS 1/RM/2 specifies liner can be encased in a stainless steel tube	organic binders @ 120 ± 14°C	1st impinger contains ethylene glycol, 2nd is empty, 3rd contains silica gel. <u>EPA 23</u> : 1st and 2nd impingers contain water, 3rd is empty, and 4th contains silica gel. <u>SW-846</u> <u>0023A</u> : 1st and 2nd impingers contain water, 3rd contains silica gel				connecting line connecting line between filter and condenser + dichloromethane rinse from probe, condenser, and connecting line between filter and condenser, (b) toluene rinse from probe, condenser, and condenser, and condenser, and condenser, and condenser, and condenser, and condenser, styl-2446 <u>EPA 00234</u> ; (a) Rinse from washing front-half of sampling train sequentially with acetone, dichloromethane and toluene; (b) Rinse from back-half of filter holder, condenser, and condenser (same three solvents)	See Analytical Summary Diagram (C)

Figure 12 D/F Methods



Figure 13 Analytical Summary Diagram A – Method EPS 1/RM/2

National Council for Air and Stream Improvement



Figure 14 Analytical Summary Diagram B – EPA Method 23



Figure 15 Analytical Summary Diagram C – EPA SW-846 Method 0023A

## **10.0 CHLORINE DIOXIDE (CLO<sub>2</sub>)**

#### **10.1** Sources of ClO<sub>2</sub> at Forest Products Manufacturing Facilities

Bleaching is an integral part of pulp manufacturing processes associated with white paper, newsprint, diapers, coloured printing papers, magazines, food and beverage containers, etc. The use of chlorine dioxide as a bleaching agent has become prevalent in the US and Canada with the advent of elemental chlorine free (ECF) bleaching sequences for chemical pulps. Since residual lignin cannot be removed from pulp using a single chemical, bleaching is typically accomplished using multiple chemicals (chlorine dioxide, peroxide, oxygen, ozone, hypochlorite etc.) with intermediate extraction (with alkali) and washing stages where spent chemicals and reaction products are removed from the pulp. Additionally, as ClO<sub>2</sub> solutions are unstable, the ClO<sub>2</sub> used for pulp bleaching is produced using onsite generators. For mills that generate ClO<sub>2</sub> on-site, the product ClO<sub>2</sub> gas is diluted to about 10% by volume in air and then absorbed in chilled water in a packed absorption tower to form a ClO<sub>2</sub> solution, which is then used for pulp bleaching (Singh 1979).

The primary sources of ClO<sub>2</sub> at bleached pulp mills are

- bleaching tower vents;
- washer vents and filtrate tank vents;
- ClO<sub>2</sub> generators/absorbers; and
- ClO<sub>2</sub> storage tanks.

### **10.2** Source Test Methods for ClO<sub>2</sub> Approved Across Canada

Three source test methods have been identified as having been approved by provincial authorities for measuring ClO<sub>2</sub>, in addition to chlorine (Cl<sub>2</sub>). Only Alberta, British Columbia, New Brunswick, Nova Scotia, and Ontario have a test method approved for this purpose. Table 9 shows the list of approved methods for each Canadian province. This list suggests that *NCASI Method for the Determination of Chlorine and Chlorine Dioxide in Pulp Mill Bleach Plant Vents* is one of the most commonly approved methods in Canada for measuring ClO<sub>2</sub> from stationary sources at forest products manufacturing facilities.

				F	rovince	s			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
Alberta Stack Sampling Code: Method for measuring chlorine and chlorine dioxide gaseous emissions	Х		1		1				I
<b>EPA 40CFR63.457 – Subpart S – National emission</b> <b>standards for hazardous air pollutants from the pulp and</b> <b>paper industry:</b> Test Methods And Procedures (paragraphs (b)(5)(ii)(A) through (b)(5)(ii)(K))		х	lot specified		lot specified			Vot specified	Not specified
<b>NCASI method</b> for the determination of chlorine and chlorine dioxide in pulp mill bleach plant vents				X **		X **	X *	Z	Z

 Table 9
 Source Test Methods Approved by Provincial Authorities to Measure Chlorine Dioxide

\* Provincial authority references (NCASI 1987); \*\* Provincial authority references (NCASI 1991)

### 10.3 Methods Used at Forest Products Manufacturing Facilities

#### 10.3.1 NCASI Method for the Determination of Chlorine and Chlorine Dioxide in Pulp Mill Bleach Plant Vents

In this method, a gas sample is extracted from a vent of a bleach plant process or a chlorine dioxide generator and passed through impingers containing a buffered (neutral) potassium iodide (KI) solution. The analytical determination of iodine (I<sub>2</sub>) formed at neutral and acidic pH permits the quantitative measurement of both  $Cl_2$  and  $ClO_2$ . This method has proven to be effective when the concentrations of  $Cl_2$  and  $ClO_2$  are close to the same order of magnitude in the gas stream being sampled<sup>30</sup>.

The gas sample is extracted from the stack using a sampling train consisting of the following primary components:

- (a) An opaque Teflon sampling line (a separate probe is not required) inserted into the stack in such a way as to not entrain liquid condensation from the vent gases. The sampling line is connected to a set of impingers and should be as short as possible.
- (b) Impinger set consisting of three midget impingers assembled in series with Teflon or glass connectors. The impinger train must be shielded from light. The first two impingers contain a 2% v/v KI solution, while the last one contains silica gel. When the gas enters in contact with the neutral impinger solution, both Cl<sub>2</sub> and ClO<sub>2</sub> react with the iodide ions (Γ) and form I<sub>2</sub>, as well as chlorite (ClO<sub>2</sub><sup>-</sup>) and chloride (Cl<sup>-</sup>) (NCASI 1987):

$$Cl_2 + 2I^- \rightarrow I_2 + 2Cl^-$$
$$ClO_2 + I^- \rightarrow \frac{1}{2}I_2 + ClO_2^-$$

- (c) A Teflon filter follows the impingers
- (d) A critical orifice followed by a vacuum pump that pulls the gas through the sampling train.

After the sampling run is complete<sup>31</sup>, the sampling line is rinsed with deionized water into the first impinger, and the contents of the first two midget impingers are transferred to a volumetric flask for analysis.

The sample solution is titrated with sodium thiosulphate  $(Na_2S_2O_3)$  until the solution becomes colorless (first endpoint). This volume relates to the total I<sub>2</sub> formed determined after neutral titration. After the first endpoint, the solution is acidified with a sulphuric acid solution (10% v/v). Under acidic conditions, the  $ClO_2^-$  present in the solution oxidizes I to I<sub>2</sub> (NCASI 1987):

$$\text{ClO}_2^- + 4\text{H}_3\text{O}^+ + 4\text{I}^- \rightarrow 2\text{I}_2 + 6\text{H}_2\text{O} + \text{Cl}^-$$

Titration is continued until the contents of the flask are again colorless (second endpoint). As the above equation shows, the volume of the second endpoint relates to the additional  $I_2$  formed as a result of chlorite reduction after acid titration. The chlorine dioxide concentration is calculated based on the difference of equivalents of  $I_2$  determined under acidic and neutral conditions.

Sulphur dioxide and hydrogen peroxide are known interferents for  $Cl_2$  determination. Sulphur dioxide reduces formed  $I_2$  back to  $I^-$  in the capture solution, and thus, it may become a negative interference<sup>32</sup>.

<sup>&</sup>lt;sup>30</sup> The precision of the chlorine analysis will decrease as the ratio  $ClO_2/Cl_2$  decreases.

<sup>&</sup>lt;sup>31</sup> The duration of the test run is approximately 60 minutes or shorter, i.e., as soon as the colour in the second impinger turns from a pale yellow to a medium yellow ( $I_2$  formation).

Hydrogen peroxide reacts with I<sup> $\cdot$ </sup> to form I<sub>2</sub> (as does Cl<sub>2</sub>) and thus can cause positive interference. Also, sunlight can cause photochemical degradation of ClO<sub>2</sub>, but this interference is overcome by shielding the sampling train from light.

## **10.3.2** EPA 40CFR63.457 – Subpart S – National Emission Standards for Hazardous Air Pollutants from the Pulp and Paper Industry: Test Methods and Procedures (Paragraphs (b)(5)(ii)(A) through (b)(5)(ii)(K))

This method is equivalent to the NCASI method specified above.

# **10.3.3** Alberta Stack Sampling Code: Method for Measuring Chlorine and Chlorine Dioxide Gaseous Emissions

This method is equivalent to the NCASI method specified above. A few minor modifications include the absence of a Teflon filter following the impingers and the use of a separate heated probe attached to the sampling line.

## 11.0 MERCURY (Hg)

## 11.1 Sources of Hg at Forest Products Manufacturing Facilities

Most anthropogenic mercury emissions result from combustion of waste fuels and coal in stationary sources. Mercury in combustors can exist in elemental, ionic, and particulate forms. Virtually all of the mercury released during combustion exists in the vapour phase as elemental mercury at temperatures greater than 1000°C (Richardson and Chang 2003). As the gases cool while leaving the combustion zone, some of this elemental mercury reacts to form chlorides, oxides, and sulphates. The ultimate split between elemental and ionic forms of mercury is a function of fuel properties, combustion conditions, flue gas composition, and the size distribution/characteristics of the fly ash (Benson 2004; NCASI 2002b). In addition, the time/temperature profile associated with the transfer of flue gases from the combustion zone to the pollution control device also has an impact on mercury speciation (NCASI 2002b).

Mercury is present in a variety of fuels commonly used in Canadian forest products industry boilers, including heavy and light fuel oils, natural gas, wood residues, wastewater treatment plant residuals, deinking residuals, old corrugated container (OCC) rejects, mixed waste paper, tire-derived fuel (TDF), and petroleum coke. Mercury is also present in spent pulping liquors that are burned in recovery furnaces. Among fossil fuels, Hg content in coal is significantly higher than those in fuel oil and natural gas.

## 11.2 Source Test Methods for Hg Approved Across Canada

Only two test methods have been identified as having been approved by provincial authorities for measuring Hg from forest products industry sources. Table 10 shows the list of approved source test methods for each Canadian province. This list suggests that EPA Method 29 – *Determination of Metals Emissions from Stationary Sources* is a commonly approved method in Canada for measuring Hg from stationary sources at forest products manufacturing facilities.

<sup>&</sup>lt;sup>32</sup> The method proposes the possibility of using a chromium trioxide impregnated filter to capture SO<sub>2</sub> (NCASI 1987).

				F	rovince	s			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
U.S. EPA 29: Determination of metals emissions from stationary sources	cified		Х	х	х	cified	Х	х	cified
<b>U.S. EPA 101A:</b> Determination of particulate and gaseous mercury emissions from sewage sludge incinerators	Not spe	Х				Not spe			Not spe

Table 10 Source Test Methods Approved by Provincial Authorities to Measure Mercury

## **11.3** Methods Used at Forest Products Manufacturing Facilities

#### 11.3.1 EPA Method 29: Determination of Metals Emissions from Stationary Sources

In addition to Hg emissions, EPA Method 29 is applicable to the determination of antimony (Sb), arsenic (As), barium (Ba), beryllium (Be), cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), lead (Pb), manganese (Mn), nickel (Ni), phosphorus (P), selenium (Se), silver (Ag), thallium (Tl) and zinc (Zn) emissions. This method may also be used to determine particulate emissions if the prescribed procedures and precautions are followed.

Method 29 uses a filter and a series of impingers for sample collection, and cold vapour atomic absorption spectroscopy (CVAAS) for analysis of total Hg. The gas sample is extracted isokinetically from the stack using a sampling train, which consists of the following primary components:

- (a) A probe connected to a heated out-of-stack filter.
- (b) A condensing system to collect gaseous metals and moisture, and consisting of seven chilled impingers connected in series: The first and fourth impingers are left empty; the second and third impingers contain a HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> (5%/10% v/v) absorbing solution; the fifth and sixth impingers contain a KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> (4%/10% v/v) absorbing solution; and the seventh impinger contains silica gel.

A vacuum pump pulls the gas through the sampling train, and Hg is captured on the filter and in the impinger solutions. The nitric acid solutions collect the various forms of oxidized Hg, but do not typically collect the elemental form<sup>33</sup>. The permanganate solution oxidizes the elemental Hg and retains it (in oxidized form) in solution (Kramlich and Sliger 2000). Leak checks are performed prior to and after the test run. Samples recovered for analysis are the following:

- (a) Sample 1: Particulate filter.
- (b) Sample 2: Rinse from washing the front half of the sampling train with acetone.
- (c) Sample 3: Rinse from washing the front half of the sampling train with a nitric acid solution.

 $<sup>^{33}</sup>$  It has been reported in the literature that some of the elemental Hg present in the source gas may be captured in the HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> absorbing solution specified in Method 29 (Laudal 1999).

- (d) Sample 4: Contents of the first three impingers together with rinse from washing these impingers, the filter support, the back half of the filter holder, and connecting glassware with a nitric acid solution.
- (e) Sample 5: Contents of fourth impinger together with rinse from washing that impinger with a solution of nitric acid.
- (f) Sample 6: Contents of fifth and sixth impingers together with rinse from washing these impingers and connecting glassware with an acidified permanganate solution, and then with water.
- (g) Sample 7: If, after the water rinse, visible deposits still remain on the surface of the fifth and/or sixth impingers, these impingers are washed with a solution of hydrochloric acid and water, and the rinse is collected.

Sample 1 is desiccated, weighed, digested with concentrated hydrofluoric acid and nitric acid. Sample 2 is evaporated to dryness, and the resulting residue weighed, dissolved in concentrated nitric acid, and combined with Sample 3. The resultant sample is acidified to pH=2 with concentrated nitric acid (if necessary), evaporated to near dryness, digested with concentrated hydrofluoric acid and nitric acid, and combined with the acid digested Sample 1. The resultant combined sample is filtered and water diluted, and used for the determination of front half Hg (Analytical Sample 1).

An aliquot of Sample 4 is used for the determination of Hg captured in the  $HNO_3/H_2O_2$  absorbing solution (Analytical Sample 2). An aliquot of Sample 5 is used for the determination of Hg captured in the rinse from the fourth (initially empty) impinger (Analytical Sample 3). Sample 6 is filtered and the filtrate is used for the determination of Hg captured in the  $KMnO_4/H_2SO_4$  absorbing solution (Analytical Sample 4). The precipitate is digested with hydrochloric acid and filtered, and the resulting filtrate is combined with that generated from filtering Sample 7. The resultant solution (Analytical Sample 5) is used for the determination of Hg that may still be present in the  $MnO_2$ precipitate formed in the permanganate impingers. Analytical Samples 2 through 5 contain back half Hg.

All analytical samples are separately digested with acid and potassium permanganate at 95°C for two hours to dissolve inorganics and to remove organic constituents that may create analytical interferences, and then analyzed for Hg by CVAAS. The total train Hg catch is calculated by summing individual Hg determinations.

Depending on the CVAAS analytical instrument used, the analytical detection limit for Hg (on the resultant volume of the digestion of aliquots taken for analysis) can vary between 0.02 and 0.2 ng/mL. The primary disadvantage with Method 29 is that it is a time-consuming process.

## Note on Ontario Hydro Mercury Speciation Method (ASTM D6784 - 02(2008) Standard Test Method for Elemental, Oxidized, Particle-Bound and Total Mercury in Flue Gas Generated from Coal-Fired Stationary Sources)

The Ontario Hydro method provides Hg speciation measurement data for coal-fired boilers. This method was developed by researchers at Ontario Hydro Technologies in 1994, with the primary objective of overcoming the apparent limitation of EPA Method 29 to selectively capture oxidized Hg. The Ontario Hydro method attempts to selectively capture  $Hg^{2+}$  by substituting three impingers containing aqueous potassium chloride (KCl) solutions for one impinger containing the HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> absorbing solution. The method also specifies an additional permanganate impinger and no empty impingers as part of the sampling train. Recovered samples primarily include the particulate filter as well as the contents of the KCl, HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>, and KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> impingers. All samples are digested and analyzed by CVAAS or fluorescence spectroscopy (CVAFS). The fraction captured by the KCl

solution is reported as  $Hg^{2+}$ , while the sum of the Hg measured in the  $HNO_3/H_2O_2$  and  $KMnO_4/H_2SO_4$  impingers is reported as elemental Hg. The Hg measured on the filter is defined as particulate-bound mercury. To NCASI's knowledge, this method is not currently applied at Canadian forest products manufacturing facilities. In Ontario, regulations concern total, and not speciated, Hg.

## **11.3.2** EPA Method 101A: Determination of Particulate and Gaseous Mercury Emissions from Sewage Sludge Incinerators

Method 101A measures total Hg gaseous emissions from sewage sludge incinerators and drying plants. Like Method 29, Method 101A can be used to measure total particulate matter.

In this method, the gas stream is sampled isokinetically from the source and the gaseous Hg is captured in an acidic potassium permanganate solution. The collected Hg is reduced to its elemental form, aerated into an optical cell where it is measured by an atomic absorption (AA) spectrophotometer. The sampling train consists of the following primary components:

- (a) A heated probe that may be connected to a heated out-of-stack glass fibre filter, if the gas stream is expected to contain high concentration of particulate matter.
- (b) Four chilled impingers connected in series, with the first three impingers containing a KMnO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub> (4%/10% v/v) absorbing solution, and the fourth impinger containing silica gel.
- (c) An acid trap, following the last impinger.

A vacuum pump pulls the gas through the sampling train, and Hg is captured in the impingers' permanganate solution. Samples recovered for analysis are the following:

- (a) Sample 1: Contents of first three impingers together with rinse from washing these impingers and the front half of sampling train with a fresh permanganate absorbing solution, and then with water.
- (b) Sample 2: If, after the water rinse, visible deposits still remain on the surface of the first three impingers, the impingers are washed with a solution of hydrochloric acid and the rinse is also collected.
- (c) Sample 3: If a filter was used, it is removed from the filter holder and combined with a fresh permanganate absorbing solution.

Samples 1 and 2 are separately filtered to remove the manganese dioxide precipitate (MnO<sub>2</sub>). Sample 3 is heated and digested with concentrated nitric acid. The resulting digested solution is filtered, and the filtrate is combined with that generated from Filtering Sample 1. The combined filtrates are water diluted and thoroughly mixed (Analytical Sample 1). The filter used to remove MnO<sub>2</sub> from Sample 1 is digested with a hydrochloric acid solution, and the digestate is filtered. The resulting filtrate is combined with that generated from Filtering Sample 2. The combined filtrates are water diluted (Analytical Sample 2).

Both analytical samples are quantified in identical manner. The sample is mixed in a closed container with a sodium chloride-hydroxylamine solution to remove excess  $KMnO_4$ , and then with a stannous chloride solution ( $SnCl_2$ ) to reduce the Hg to its elemental form and release it, as vapour, from the solution. The closed container is subjected to aeration with nitrogen, and then both nitrogen and the Hg vapour flow through a heated optical cell connected to an AA spectrophotometer for analysis.

Excessive oxidizable organic matter may be an interferent, as it depletes the potassium permanganate solution thereby preventing further collection of Hg. Condensation of water vapour on the optical cell windows causes a positive interference.

Depending on the degree to which the analytical sample aliquot is diluted, the range of this method can vary between 20 and 800 ng Hg/mL.

#### 11.4 Synthesis of Test Methods for Hg

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure Hg. The intent is to help the reader pin down the most important similarities and/or differences between methods using similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagram.

All the methods approved in Canada for measuring Hg are indirect; i.e., the sampling and measurement of Hg are not performed continuously as sample recovery and analysis are performed off-line. The schematic comparison between these methods is shown in Figure 16. All methods rely primarily on absorbing solutions to capture Hg emissions. Differences between methods are essentially associated with the type and number of absorbing solutions used and the way samples are recovered and prepared for analysis (see Figures 17 and 18).



Figure 16 Indirect Hg Methods



Figure 17 Analytical Summary Diagram A – EPA Method 29



Figure 18 Analytical Summary Diagram B – EPA Method 101A

## 12.0 CARBON MONOXIDE (CO)

## 12.1 Sources of CO at Forest Products Manufacturing Facilities

Carbon monoxide is generally formed during combustion processes, specifically as a result of partial oxidation of carbon-containing compounds when there is not enough oxygen to produce carbon dioxide (CO<sub>2</sub>) (Pfafflin and Ziegler 2006). Hence, CO emissions can result from the burning of wood, oil, gas, and coal in pulp mill boilers. In kraft pulp mills and pulp mills that practice either oxygen delignification or pulp bleaching with chlorine dioxide (ClO<sub>2</sub>), CO can also be formed during these delignification processes and released to the atmosphere. Kraft pulp mills that burn concentrated non-condensable gases (NCGs) and stripper off-gases (SOGs) in thermal oxidizers may also emit some CO. For combustion sources, CO emissions are related to combustion efficiency.

In wood products mills, CO is primary emitted from wood dryers, lumber kilns, panel presses, combustion units (boilers/thermal oil heaters/conical burners), and hardboard tempering ovens. Direct fired wood products dryers generate CO both at the direct fired burners and within the dryer. Exhaust gases from sanders, chippers, saws, and other wood handling and finishing sources are expected to contain negligible amounts of CO.

### 12.2 Source Test Methods for CO Approved Across Canada

Five source test methods have been identified as having been approved by provincial authorities for measuring CO. Provinces allow the use of at least one method. Table 11 shows the list of approved source test methods for each Canadian province. This list suggests that EPA Method 10 – *Determination Of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)* is the most commonly approved method in Canada for measuring CO from stationary sources at forest products manufacturing facilities.

				ł	Province	s			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
Alberta Stack Sampling Code: Method 10 - Determination of carbon monoxide emissions from stationary sources	Х								
<b>U.S. EPA 10:</b> Determination of carbon monoxide emissions from stationary sources (Instrumental Analyzer Procedure)		Х	Х	Х	Х		Х	Х	
<b>U.S. EPA 10B:</b> Determination of carbon monoxide emissions from stationary sources				Х					
EPS 1/RM/4: Measurement of releases of carbon monoxide from stationary sources		Х	Х						
<b>EPS 1/RM/15:</b> Reference method for the monitoring of gaseous emissions from fossil fuel-fired boilers			Х	Х		Х			Х

Table 11 Source Test Methods Approved by Provincial Authorities to Measure Carbon Monoxide

### 12.3 Principal USEPA and Environment Canada Standard Methods Used at Forest Products Manufacturing Facilities

## **12.3.1** EPA Method 10: Determination of Carbon Monoxide Emissions from Stationary Sources (Instrumental Analyzer Procedure)

In this method, stack gases are extracted and analyzed continuously for carbon monoxide. Alternatively, the gas sample is collected in a Tedlar bag (integrated sampling) and analyzed off-line. In either case, CO is measured with an instrumental analyzer. The sampling train consists of the following primary components:

- (a) A probe.
- (b) An in-stack or heated out-of-stack particulate filter.
- (c) A heated sample line from the probe to the sample conditioning equipment (condenser or dryer) to prevent condensation. Heating is not necessary on dry gases or for systems that measure CO on a dry basis.

- (d) A condenser or dryer device to remove moisture from the gas sample.
- (e) Continuous sampling:
  - i. A calibration gas manifold to allow the introduction of a calibration gas directly to the analyzer and/or into the measurement system (at the probe)
  - ii. A gas sample manifold to divert a portion of the sample to the analyzer
- (f) Integrated sampling:
  - i. Flexible Tedlar bag
- (g) A sample pump to pull the gas through the system.

CO is measured with a Luft-type nondispersive infrared analyzer (NDIR) or equivalent. The method specifies a procedure to conduct an interference test on the gas analyzer prior to its initial use. Substances having a strong absorption of infrared energy (e.g., particulate matter, water,  $CO_2$ ) may interfere to some extent in some analyzers. Filters, silica gel and ascarite traps can be used to eliminate some of these interferences. Calculated concentrations must be corrected for  $CO_2$  removal.

The minimum detectable concentration is 20 ppm for a 0 and 1,000 ppmv span.

## **12.3.2** EC Method EPS 1/RM/4: Measurement of Releases of Carbon Monoxide from Stationary Sources

This method is equivalent to the integrated sampling and analysis specified in EPA Method 10. EPS 1/RM/4 is confronted with the same interferents as EPA Method 10; however, the EC method provides more details regarding the configuration of the interference trapping system. This system consists of a pump to extract the sample from the Tedlar bag followed by two chilled impingers or tubes, one containing silica gel and the other ascarite to remove, respectively, water and CO<sub>2</sub>. The impinger set is followed by a filter to remove trapping particles larger than 3 microns in diameter.

## **12.3.3** EC Method EPS 1/RM/15: Reference Method for the Monitoring of Gaseous Emissions from Fossil Fuel-Fired Boilers

This method is applicable to the measurement of emissions of nitrogen oxides (NO species), sulphur dioxide  $(SO_2)$ , and carbon monoxide (CO) contained in the flue gases from the combustion of fossil fuels used to generate hot water or steam.

The sampling system essentially consists of a probe connected to a portable calibrated analyzer<sup>34</sup>. The gas sample is extracted from a single point in the exhaust gas from the stack under test<sup>35</sup>. The water vapour is removed from the sample, and the resulting concentrations of SO<sub>2</sub>, NO, CO and oxygen are measured using species-specific sensors. Portable packages range from single species systems designed for very short sampling to those which can operate continuously for long time periods, and measure multiple gaseous compounds. The method also has a procedure to check for interference between each of the measured compounds (SO<sub>2</sub>, NO, and CO). This method does not use a heated filter to remove particulate matter prior to the analyzer. The analytical range of the method has been determined to be 0–1,000 ppmv CO.

<sup>&</sup>lt;sup>34</sup> Ambient air (provided ambient CO concentration is less than 3 ppmv) and CO in nitrogen are used as the zero and span gas, respectively, to calibrate the analyzer for measuring CO.

<sup>&</sup>lt;sup>35</sup> A check for gas stratification must be performed.

## 12.4 Alternative Source Test Methods

## 12.4.1 EPA Method 10B: Determination of Carbon Monoxide Emissions from Stationary Sources

In this method, a gas sample is extracted from the stack, passed through a conditioning system, and collected in a Tedlar bag. CO is separated from the sample by GC and determined by FID.

The sampling train consists of the following primary components:

- (a) A stainless steel, sheathed Pyrex glass, probe (or equivalent) equipped with an in-stack glass wool plug to remove particulate matter.
- (b) Three impingers connected in series containing a potassium permanganate solution to remove sulphur and nitrogen oxides.
- (c) A pump followed by a surge tank.
- (d) A Tedlar bag.

The gas sample is pulled through the sampling train and collected in the Tedlar bag until the bag is nearly full. The collected sample is measured with a GC/FID analyzer which primarily consists of a chromatographic column capable of separating CO from  $CO_2$  and organic compounds that may be present, and a reduction catalyst capable of reducing CO to  $CH_4$ , as quantified by FID.

Carbon dioxide and organics can potentially interfere with the analysis.  $CO_2$  is primarily removed from the sample by the impingers, while any residual  $CO_2$  and organics are separated from the CO by the chromatographic column.

# **12.4.2** Alberta Stack Sampling Code Method 10 - Determination of Carbon Monoxide Emissions from Stationary Sources

The sampling component of this method is equivalent to that specified in EPA Method 10. The details regarding the conditioning (trapping) system prior to CO analysis are similar to those specified in EPS 1/RM/4 except that the pump extracting the sample from the bag is located after the silica gel and ascarite impingers and prior to the filter.

## 12.5 Synthesis of Test Methods for CO

This subsection of the report provides a synthesis of the sampling train configuration as well as sample recovery and analysis principles behind the test methods used in Canada to measure CO. The intent is to help the reader pin down the most important similarities and/or differences between methods using similar principles. Method schematics are conceptual and grouped according to the principle used to collect and analyze the sample. Relevant characteristics associated with each method are noted on the conceptual diagram.

## 12.5.1 Direct Sampling Methods

These methods involve on-line chemical analysis of the gas sample, i.e., as soon as it is withdrawn from the stack. The schematic comparison between these methods is shown in Figure 19.

## 12.5.2 Indirect Sampling Methods

In these methods, the sampling and measurement of CO are not performed continuously; i.e., sample recovery and analysis are carried out off-line. These methods are illustrated in Figure 20.

Gas	Unheated sample Line (EPA 10: Teflon; EPS 1/RM/15: Material not specified) Gas								
Sample	Acquisition		Conditioning		Pump		Analysis		
L									
Methods									
U.S. EPA 10: Determination of carbon monoxide emissions from stationary sources (Instrumental Analyzer Procedure) - <u>Continuous Sampling/Analysis</u>			In-stack filter (or alternatively a heated out-of- stack filter in case of EPA 10). Air-				Luft-type nondispersive infrarred analyzer		
Alberta Stack Sampling Code: Method 10 - Determination of carbon monoxide emissions from stationary sources - <u>Continuous Sampling/Analysis</u>	Stainless steel, sheathed Pyrex		cooled condenser for moisture removal		Diaphragm pump		(NDIR)		
EPS 1/RM/15: Reference method for the monitoring of gaseous emissions from fossil fuel-fired boilers	glass, probe		No particulate filter is used. A mechanical trap and/or dessicants can be used to remove moisture. Chemical absorbents may be used within the system to remove interfering species or gases				Species-specific sensors capable of detecting and quantifying concentrations of NO, SO <sub>2</sub> , CO, and O <sub>2</sub> in the gas sample		

Figure 19 Direct CO Methods



Figure 20 Indirect CO Methods

## 13.0 SULPHURIC ACID (H<sub>2</sub>SO<sub>4</sub>)

## 13.1 Sources of H<sub>2</sub>SO<sub>4</sub> at Forest Products Manufacturing Facilities

In pulp and paper and wood products mills, sulphuric acid  $(H_2SO_4)$  is coincidentally manufactured in boilers that burn coal, fuel oil, or fossil fuels in combination with bark. Gaseous sulphuric acid is produced when sulphur trioxide  $(SO_3)$  reacts with water vapour, and the gases are cooled, both in the atmosphere and in the flue gas. Sulphur trioxide is formed in small amounts from further oxidation of the SO<sub>2</sub> generated from the thermal oxidation of the sulphur present in the fuel. In pulp and paper mills,  $H_2SO_4$  can also be generated from recovery furnaces, lime kilns burning fossil fuels or noncondensable gases (NCG), and during NCG and stripper off-gas (SOG) incineration in thermal oxidizers.

## 13.2 Source Test Methods for H<sub>2</sub>SO<sub>4</sub> Approved Across Canada

Only one method has been identified as having been approved by provincial authorities for measuring  $H_2SO_4$ : EPA Method 8 – *Determination of H\_2SO\_4 and Sulfur Dioxide Emissions from Stationary Sources*. Table 12 shows the provinces that approve the use of this method.

				F	Province	es			
Methods	Alberta	British Columbia	Manitoba	New Brunswick	Newfoundland & Labrador	Nova Scotia	Ontario	Quebec	Saskatchewan
<b>U.S. EPA 8:</b> Determination of H <sub>2</sub> SO <sub>4</sub> and sulfur dioxide emissions from stationary sources	х	х	х	No	ot specif	ïed	Х	Х	Not specified

 Table 12
 Source Test Methods Approved by Provincial Authorities to Measure Sulphuric Acid

# **13.3** EPA Method 8 – Determination of H<sub>2</sub>SO<sub>4</sub> and Sulphur Dioxide Emissions from Stationary Sources

EPA Method 8 is the reference test method used for sulphuric acid mist and  $SO_3$ , but can also be used to measure  $SO_2$  emissions. In this method, a sample is extracted isokinetically from the source, and the  $H_2SO_4$  mist and the  $SO_2$  present in the gas sample are both captured and recovered separately for analysis using the barium-thorin titration method. The sampling train consists of the following primary components:

- (a) A probe, equipped with a heating system to prevent water condensation.
- (b) One impinger containing a solution of isopropanol (80% v/v). The isopropanol solution collects the SO<sub>3</sub> and sulphuric acid mist present in the sample.
- (c) A glass fibre filter, that need not be heated, is placed between the isopropanol impinger and the first hydrogen peroxide impinger (see below).
- (d) A set of three impingers connected in series. The first two impingers contain a solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 3% v/v), while the final impinger is packed with silica gel to dry the gas sample.

After the sampling run is complete, a post-test leak check must be conducted, and the contents of the isopropanol and  $H_2O_2$  impingers recovered for analysis. The isopropanol solution in the first impinger is combined with isopropanol rinses from the probe, the first impinger, all connecting glassware before the filter, and the front half of the filter holder. The filter is added to the combined solution, which is stored for analysis (Sample 1). The  $H_2O_2$  solutions in the second and third impingers<sup>36</sup> are combined with water rinses from the back half of the filter holder and all the connecting glassware between the filter and the silica gel impinger, and stored for analysis (Sample 2).

Although both samples are titrated with a solution of barium perchlorate<sup>37</sup>, Sample 1 is directly analyzed, whereas Sample 2 must be previously combined with pure isopropanol. The volume of titrant used on Sample 1 serves to calculate the concentration of sulphuric acid captured by the isopropanol impinger, while that used on Sample 2 serves to calculate the concentration of SO<sub>2</sub> captured by the  $H_2O_2$  impingers<sup>38</sup>.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline. The minimum detectable limit of the method is  $0.06 \text{ mg } H_2SO_4/dscm$ .

## Note on NCASI Method 8A – Determination of Sulphuric Acid Vapour or Mist and Sulfur Dioxide Emissions from Kraft Recovery Furnaces

This method was developed by NCASI to measure sulphuric acid mist from pulp mill sources. A description of the original method as applied to kraft recovery furnaces can be found in NCASI Atmospheric Quality Technical Bulletin No. 106 (NCASI 1980). The method is also available in the *NCASI Methods Manual*, and it received EPA approval in 1996 as a Conditional Test Method (CTM-013). NCASI has developed modified versions of this method, which can be used on recovery furnaces as well as on combination boilers with PM control devices. These versions have also been approved by EPA as Conditional Test Methods (CTM-013A and CTM-013B).

When testing recovery furnaces, EPA Method 8 is subject to significant interference from sulphates (present in the particulate matter) and SO<sub>2</sub>. Method 8A uses an out-of-stack quartz filter to remove particulate matter from the gas stream prior to capturing  $H_2SO_4$  with a controlled  $H_2SO_4$  condenser, which eliminates the potential for interference from SO<sub>2</sub>. The condenser is followed by a set of three impingers (two containing a solution of  $H_2O_2$  and the last one containing water) and a silica gel tube. At the conclusion of the sampling run, and following a mandatory post-test leak check, the probe, the quartz filter holder, and the  $H_2SO_4$  condenser are washed with deionized water and the rinse is collected for  $H_2SO_4$  analysis. The collected rinse is combined with an 80% (v/v) isopropanol solution and analyzed using the same barium-thorin titration method specified in EPA Method 8. If concurrent determination of SO<sub>2</sub> is desired, the contents of the two first impingers are also analyzed using the barium-thorin titration method.

<sup>&</sup>lt;sup>36</sup> First two impingers following the filter.

<sup>&</sup>lt;sup>37</sup> Provided a few drops of thorin indicator are added prior to titration.

<sup>&</sup>lt;sup>38</sup> Sulphur dioxide is trapped, in the form of sulphuric acid, by the hydrogen peroxide solution (Hocking 2005): SO<sub>2</sub> + H<sub>2</sub>O  $\rightarrow$  H<sub>2</sub>SO<sub>3</sub>; H<sub>2</sub>SO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub>  $\rightarrow$  H<sub>2</sub>SO<sub>4</sub> + H<sub>2</sub>O.

#### 14.0 LIST OF EXTRACTIVE SOURCE TEST METHODS APPROVED FOR USE AT CANADIAN FOREST PRODUCTS MANUFACTURING FACILITIES (SHADED SQUARES)

Substance	Methods	AB	BC	MB	NB	NFL	NS	ON	QC	SK
	Alberta Stack Sampling Code: Method 5 - Determination of particulate									
	emissions from stationary sources									
	U.S. EPA5: Determination of particulate matter emissions from stationary									
	sources									
	U.S. EPA5B: Determination of nonsulfuric acid particulate matter emissions									
	II S EPA 5D: Determination of particulate matter emissions from positive									
	pressure fabric filters									
	U.S. EPA17: Determination of particulate matter emissions from stationary									
	sources									
	U.S. EPACTM 003: Determination of particulate matter (modified high volume									
TPM	sampling procedure)									
	British Columbia Field Sampling Manual – Appendix 12: Method for measuring particulate emissions from stationary sources with cyclonic flow									
	pattern									
	State of Oregon Source Sampling Manual - Method 8: Sampling particulate									
	emissions from stationary sources (high volume method)									
	Environment Canada EPS 1/RM/8 (Method E): Measurement of releases of									
	particulate from stationary sources									
	emissions from stationary sources									
	Saskatchewan Environment Standard Reference Methods for Source									
	Testing, APC-31: Measurement of emissions of particulates from stationary									
	sources									
	U.S. EPA 201: Determination of PM <sub>10</sub> emissions (exhaust gas recycle									
	procedure)									
PM <sub>10</sub> /PM <sub>2.5</sub>	U.S. EPA 201A: Determination of PM <sub>10</sub> emissions (constant sampling rate									
10 2.5	procedure)									
	Ontario Source Testing Code – (Draft) Method ON-7: Determination of size									
	distribution of particulate matter from stationary sources									
	condensable particulate emissions from stationary sources									
0.014	U.S. EPA 202: Determination of condensable particulate emissions from									
СРМ	stationary sources									
	State of Oregon Source Sampling Manual - Method 7: Sampling									
	condensable emissions from stationary sources									
	Alberta Stack Sampling Code: Method 7 - Determination of NO <sub>x</sub> emissions									
from stationa	from stationary sources									
	Alberta Stack Sampling Code: Method 7A - Determination of NO <sub>x</sub> emissions									
	from stationary sources (ion chromatographic method)									
	Alberta Stack Sampling Code: Method 7C - Determination of NO <sub>x</sub> emissions									
	from stationary sources (alkaline-permanganate/colorimetric method)									
	IIS FPA7: Determination of NO emissions from stationary sources									
	U.S. EPA 7A. Determination of NO. emissions from stationary sources (ion									
	observatorraphia method)									
NO <sub>x</sub>	LIS EBA7C: Determination of NO emissions from stationary sources (alkaline									
	Dermanganate/colorimetric method)									
	US FPA7D: Determination of NO emissions from stationary sources (alkaline									
	permanganate/ion chromatographic method)									
	U.S. EPA7E: Determination of NO <sub>2</sub> emissions from stationary sources									
	(instrumental analyzer procedure)									
	Environment Canada EPS 1/RM/15: Reference method for the monitoring of									
	gaseous emissions from fossil fuel-fired boilers									
	Environment Canada EPS 1-AP-77-3: Measurement of releases of NO <sub>x</sub>									
	emissions from stationary sources									
	Alberta Stack Sampling Code: Method 8 - Determination of sulphuric acid									
	mist and SO <sub>2</sub> emissions from stationary sources									
	U.S. EPA6: Determination of SO <sub>2</sub> emissions from stationary sources									
	U.S. EPA 6A: Determination of SO <sub>2</sub> , moisture, and carbon dioxide from fossil									
	fuel combustion sources									
	U.S. EPA 6B: Determination of $SO_2$ and carbon dioxide daily average emissions									
80	from fossil fuel combustion sources									
50 <sub>2</sub>	U.S. EPA 6C: Determination of SO <sub>2</sub> emissions from stationary sources									
	(instrumental analyzer procedure)									
	U.S. EPA8: Determination of sulphuric acid and SO <sub>2</sub> emissions from stationary									
	sources									
	Environment Canada EPS 1/RM/15: Reference method for the monitoring of									
	gaseous emissions from lossi luel-filed poliers									
	stationary sources									

(Continued on next page. See note at end of table.)

Substance	Methods	AB	BC	MB	NB	NFL	NS	ON	QC	SK
	Alberta Stack Sampling Code: Method 25 - Determination of total gaseous									
	non-methane organic emissions as carbon									
Total V/OC	U.S. EPA 25: Determination of total gaseous non-methane organic emissions as									
Total VOO	carbon									
	U.S. EPA 25A: Determination of total gaseous organic concentration using a									
	flame ionization analyzer									
	Alberta Stack Sampling Code: Method 18 - Measurement of gaseous organic									
	compound emissions by gas chromatography									
	U.S. EPA 18: Measurement of gaseous organic compound emissions by gas									
	chromatography									
	U.S. EPA 308: Procedure for determination of methanol emission from									
	stationary sources									
	U.S. EPA SW-846 - Method 0010: Modified method 5 sampling train (semi-									
	Volatiles)									
	onissions from stationary acurace									
	IIS EPA SW-846 - Method 0030: Volatile organic sampling train									
	U.S. EPA SW-846 - Method 0305: Volatile organic sampling train									
Individual VOCs	stationary source emissions									
	NCASI Method CI/WP-98 01 Chilled impinger method for use at wood products									
	mills to measure formaldehyde, methanol, and phenol									
	NCASI Method CI/SG/PULP-94.02: Chilled impinger/silica gel test method at									
	pulp mill sources for methanol, acetone, acetaldehyde, methyl ethyl ketone and									
	formaldehyde									
	NCASI Method IM/CAN/WP-99.02: Impinger/canister source sampling method									
	for selected HAPs at wood products facilities									
	NCASI Method ISS/FP A105.01: Impinger source sampling method for									
	aldehydes, ketones, and polar compounds									
	Environment Canada EPS 1/RM/2: Measurement of releases of selected semi-									
	volatile organic compounds from stationary sources									
	Alberta Stack Sampling Code - Total reduced sulphur compounds from pulp						1			
	and paper operations									
	0.3. EFA 10. Semicontinuous determination of sulful emissions nom stationary									
	ILS EPA 16A: Determination of total reduced sulfur emissions from stationary									
TRS	sources (impinger technique)									
	U.S. EPA 16B: Determination of total reduced sulfur emissions from stationary									
	sources (GC/FPD)									
	Environment Canada EPS 1/RM/6: Total reduced sulphur compounds from									
	pulp and paper operations									
	U.S. EPA23: Determination of polychlorinated dibenzo-p-dioxins and									
	polychlorinated dibenzofurans from municipal waste combustors									
	U.S. EPA SW-846 - Method 0023A: Sampling method for polychlorinated						1			
D/F	dibenzo-p-dioxins and polychlorinated dibenzofuran emissions from stationary						1			
	sources									
	Environment Canada EPS 1/RM/2: Measurement of releases of selected semi-									
	Volatile organic compounds from stationary sources									
							1			
	EPA 40CFR63.457 – Subpart S – National emission standards for									
CIO <sub>2</sub>	hazardous air pollutants from the pulp and paper industry: Test Methods						1			
-	And Procedures (paragraphs (b)(5)(ii)(A) through (b)(5)(ii)(K))						1			
	NCASI method for the determination of chlorine and chlorine dioxide in pulp mill									
	bleach plant vents									
	U.S. EPA 29: Determination of metals emissions from stationary sources									
Hg	U.S. EPA 101A: Determination of particulate and gaseous mercury emissions									
	from sewage sludge incinerators							L		
	Alberta Stack Sampling Code: Method 10 - Determination of carbon						1			
	monoxide emissions from stationary sources						L			
	U.S. EPA10: Determination of carbon monoxide emissions from stationary						1			
	Sources (Instrumental Analyzer Procedure)						<sup> </sup>			
со	Sources						1 '			
1	EPS 1/RM/4: Measurement of releases of carbon monoxide from stationary							1		
1	sources						1 '			
1	EPS 1/RM/15: Reference method for the monitoring of gaseous emissions from									
	fossil fuel-fired boilers									
4 80	U.S. EPA 8: Determination of H <sub>2</sub> SO <sub>4</sub> and sulfur dioxide emissions from									
H25U4	stationary sources									

\* Black cells = "Not Specified"

## 15.0 HYPERLINKS TO FULL TEST METHOD WRITE-UPS

The hyperlinks provided below are accessible through the NCASI website. USEPA methods can be also found at <u>http://www.epa.gov/ttn/emc/tmethods.html</u>.

Source Test Method	Website
Alberta Stack Sampling Code - Total reduced sulphur compounds from pulp and paper operations	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_TRS.pdf
Alberta Stack Sampling Code: Method 10 - Determination of carbon monoxide emissions from stationary sources	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_10.pdf
Alberta Stack Sampling Code: Method 18 - Measurement of gaseous	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_
organic compound emissions by gas chromatography	Stack Sampling Code Method 18.pdf
Alberta Stack Sampling Code: Method 25 - Determination of total gaseous non-methane organic emissions as carbon	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_25.pdf
Alberta Stack Sampling Code: Method 5 - Determination of particulate emissions from stationary sources	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_5.pdf
Alberta Stack Sampling Code: Method 5A (AEP) - Determination of condensable particulate emissions from stationary sources	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_5A.pdf
Alberta Stack Sampling Code: Method 7 - Determination of NO <sub>x</sub> emissions from stationary sources	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_7.pdf
Alberta Stack Sampling Code: Method 7A - Determination of NO <sub>x</sub>	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_
emissions from stationary sources (ion chromatographic method)	Stack_Sampling_Code_Method_7A.pdf
Alberta Stack Sampling Code: Method 7C - Determination of NO <sub>x</sub> emissions from stationary sources (alkaline-permanganate/colorimetric method)	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_7C.pdf
Alberta Stack Sampling Code: Method 8 - Determination of sulphuric acid mist and SO <sub>2</sub> emissions from stationary sources	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_8.pdf
Alberta Stack Sampling Code: Method for measuring chlorine and chlorine dioxide gaseous emissions	http://www.ncasi.org/programs/areas/air/test_methods/Alberta_ Stack_Sampling_Code_Method_for_Chlorine_and_Chlorine_Di oxide.pdf
British Columbia Field Sampling Manual – Appendix 12: Method for measuring particulate emissions from stationary sources with cyclonic flow pattern	http://www.env.gov.bc.ca/epd/wamr/labsys/field_man_pdfs/fld_ man_03.pdf
Environment Canada EPS 1/RM/15: Reference method for the	http://www.ncasi.org/programs/areas/air/test_methods/EC_EPS
monitoring of gaseous emissions from fossil fuel-fired boilers	1RM15.pdf
Environment Canada EPS 1/RM/2: Measurement of releases of selected semi-volatile organic compounds from stationary sources	<u>http://www.ec.gc.ca/lcpe-</u> <u>cepa/default.asp?lang=En&amp;n=942FC0FB-1</u>
Environment Canada EPS 1/RM/3: Method for the Analysis of	
Polychiorinated Didenzo-p-Dioxins (PCDD), Polychiorinated	nttp://www.ncasi.org/programs/areas/air/test_methods/EU_EPS
from the incineration of PCB waste	TRIVIS (Teviseu).put
Environment Canada EPS 1/RM/6: Total reduced sulphur compounds from pulp and paper operations	http://www.ncasi.org/programs/areas/air/test_methods/EC_EPS 1RM6.pdf
Environment Canada EPS 1/RM/8: Measurement of releases of	http://www.ec.gc.ca/lcpe-
particulate from stationary sources	cepa/default.asp?lang=En&n=CBA5BD1D-1
Environment Canada EPS 1-AP-74-3: Measurement of releases of SO2	http://www.ncasi.org/programs/areas/air/test methods/EC EPS
from stationary sources	_1AP743.pdf
Environment Canada EPS 1-AP-77-3: Measurement of releases of NO <sub>x</sub>	http://www.ncasi.org/programs/areas/air/test_methods/EC_EPS
emissions from stationary sources	1AP773.pdf
monovide from stationary sources	1RM4 pdf
monoxide norm stationary sources	
EPA 40CFR63.457 – Subpart S – National emission standards for	http://www.papai.org/programs/araas/air/tast_mathada/EDA_40
hazardous air pollutants from the pulp and paper industry: Test	CER63 457 Subpart S pdf
Methods And Procedures (paragraphs (b)(5)(ii)(A) through (b)(5)(ii)(K))	
NCASI Method CI/SG/PULP-94.02: Chilled impinger/silica gel test method at pulp mill sources for methanol, acetone, acetaldehyde, methyl ethyl ketone and formaldehyde	http://www.ncasi.org/Publications/Detail.aspx?id=1709
NCASI Method CI/WP-98.01: Chilled impinger method for use at wood	http://www.ncasi.org/Publications/Detail.aspx?id=1710
NCASI method for the determination of chlorine and chlorine dioxide in	http://www.ncasi.org/Publications/Detail.aspx?id=1727
pulp mill bleach plant vents NCASI Method IM/CAN/WP-99.02: Impinger/canister source sampling	http://www.pagei.org/Dublications/Detail.com/24
method for selected HAPs at wood products facilities NCASI Method ISS/FP A105.01: Impinger source sampling method for	IIII
aldehydes, ketones, and polar compounds	http://www.ncasi.org/Publications/Detail.aspx?id=2763
ontano Source resting Code – (Draft) Method UN-7: Determination of size distribution of particulate matter from stationary sources	nup.//www.ncasi.org/programs/areas/air/test_methods/Untario
Ontario Source Testing Code - Method 5: Determination of particulate	http://www.downloads.ene.gov.on.ca/envision/env_reg/er/docum
emissions from stationary sources	ents/2001/ra00e0016d.pdf
Saskatchewan Environment Standard Reference Methods for	http://www.ncasi.org/programs/areas/air/test_methods/Measure
Source Testing, APC-31: Measurement of emissions of particulates	ment of Emissions of Particulates from Stationary Sources.p
TOT STATIONARY SOURCES	OT COT

State of Oregon Source Sampling Manual - Method 7: Sampling	http://www.deq.state.or.us/aq/forms/sourcetest/ssmVOL1.pdf (p.
condensable emissions from stationary sources	
State of Oregon Source Sampling Manual - Method 8: Sampling particulate emissions from stationary sources (high volume method)	nttp://www.deq.state.or.us/ad/forms/sourcetest/ssmVOL1.pdf (p. 21)
U.S. EPA 1: Sample and Velocity Traverses for Stationary Sources	http://www.epa.gov/ttp/emc/promgate/m-01.pdf
U.S. EPA 2: Determination of Stack Gas Velocity and Volumetric Flow Rate (Type S Pitot tube)	http://www.epa.gov/ttn/emc/promgate/m-02.pdf
U.S. EPA 3: Gas Analysis for Determining Dry Molecular Weight	http://www.epa.gov/ttn/emc/promgate/m-03.pdf
U.S. EPA 4: Determination of Moisture Content in Stack Gases	http://www.epa.gov/ttn/emc/promgate/m-04.pdf
U.S. EPA 10: Determination of carbon monoxide emissions from	http://www.epg.gov/ttp/emg/promotel/mathed10r06.pdf
stationary sources (Instrumental Analyzer Procedure)	nttp://www.epa.gov/ttn/emc/promgate/method10r06.pdf
U.S. EPA 101A: Determination of particulate and gaseous mercury emissions from sewage sludge incinerators	http://www.epa.gov/ttn/emc/promgate/m-101a.pdf
U.S. EPA 10B: Determination of carbon monoxide emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-10b.pdf
U.S. EPA 16: Semicontinuous determination of sulfur emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-16.pdf
U.S. EPA 16A: Determination of total reduced sulfur emissions from stationary sources (impinger technique)	http://www.epa.gov/ttn/emc/promgate/m-16a.pdf
U.S. EPA 16B: Determination of total reduced sulfur emissions from stationary sources (GC/EPD)	http://www.epa.gov/ttn/emc/promgate/m-16b.pdf
U.S. EPA 17: Determination of particulate matter emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-17.pdf
U.S. EPA 18: Measurement of gaseous organic compound emissions by gas chromatography	http://www.epa.gov/ttn/emc/promgate/m-18.pdf
U.S. EPA 201: Determination of PM <sub>10</sub> emissions (exhaust gas recycle procedure)	http://www.epa.gov/ttn/emc/promgate/m-201.pdf
U.S. EPA 201A: Determination of PM <sub>10</sub> emissions (constant sampling rate procedure)	http://www.epa.gov/ttn/emc/promgate/m-201a.pdf
U.S. EPA 202: Determination of condensable particulate emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-202.pdf
U.S. EPA 23: Determination of polychlorinated dibenzo-p-dioxins and	http://www.epa.gov/ttn/emc/promgate/m-23.pdf
U.S. EPA 25: Determination of total gaseous non-methane organic	http://www.epa.gov/ttn/emc/promgate/m-25.pdf
U.S. EPA 25A: Determination of total gaseous organic concentration	http://www.epa.gov/ttn/emc/promgate/m-25a.pdf
using a flame ionization analyzer	http://www.opg.gov/ttp/omg/promgate/m-20.pdf
U.S. EPA 29: Determination of metals emissions from stationary sources	nup.//www.epa.gov/un/emc/promgate/m-29.pdi
stationary sources	http://www.epa.gov/ttn/emc/promgate/m-308.pdf
U.S. EPA 5: Determination of particulate matter emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-05.pdf
U.S. EPA 5B: Determination of nonsulfuric acid particulate matter emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-05b.pdf
U.S. EPA 5D: Determination of particulate matter emissions from positive pressure fabric filters	http://www.epa.gov/ttn/emc/promgate/m-05d.pdf
U.S. EPA 6: Determination of SO <sub>2</sub> emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-06.pdf
U.S. EPA 6A: Determination of SO <sub>2</sub> , moisture, and carbon dioxide from	http://www.epa.gov/ttp/emc/promgate/m-06a.pdf
fossil fuel combustion sources	
emissions from fossil fuel combustion sources	http://www.epa.gov/ttn/emc/promgate/m-06b.pdf
(instrumental analyzer procedure)	http://www.epa.gov/ttn/emc/promgate/method6C.pdf
U.S. EPA 7: Determination of NO <sub>x</sub> emissions from stationary sources	nttp://www.epa.gov/ttn/emc/promgate/m-07.pdf
(ion chromatographic method)	http://www.epa.gov/ttn/emc/promgate/m-07a.pdf
U.S. EPA 7C: Determination of NO <sub>x</sub> emissions from stationary sources (alkaline permanganate/colorimetric method)	http://www.epa.gov/ttn/emc/promgate/m-07c.pdf
U.S. EPA 7D: Determination of NO <sub>x</sub> emissions from stationary sources (alkaline permanganate/ion chromatographic method)	http://www.epa.gov/ttn/emc/promgate/m-07d.pdf
U.S. EPA 7E: Determination of NO <sub>x</sub> emissions from stationary sources (instrumental analyzer procedure)	http://www.epa.gov/ttn/emc/promgate/method7E.pdf
U.S. EPA 8: Determination of H <sub>2</sub> SO <sub>4</sub> and sulfur dioxide emissions from stationary sources	http://www.epa.gov/ttn/emc/promgate/m-08.pdf
U.S. EPA CTM 003: Determination of particulate matter (modified high volume sampling procedure)	http://www.epa.gov/ttn/emc/ctm/ctm-003.pdf
U.S. EPA SW-846 - Method 0010: Modified method 5 sampling train (semi-volatiles)	http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/0010.p df
U.S. EPA SW-846 - Method 0011: Sampling for selected aldehyde and ketone emissions from stationary sources	http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/0011.p
U.S. EPA SW-846 - Method 0023A: Sampling method for	
polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofuran emissions from stationary sources	nttp://www.epa.gov/osw/nazard/testmethods/sw846/pdfs/0023a. pdf
U.S. EPA SW-846 - Method 0030: Volatile organic sampling train	http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/0030.p df
U.S. EPA SW-846 - Method 0207: A method for measuring isocyanates	http://www.epa.gov/ttnemc01/proposed/m-207.pdf
IN STATIONARY SOURCE EMISSIONS	

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