

**Environment Protection Authority**

# **Emission Testing Methodology for Air Pollution**

---

**Version 2, August 2012**

---

**Emission Testing Methodology for Air Pollution, Version 2, August 2012**

**Issued by the Environment Protection Authority**

For further information please contact:

Information Officer  
Environment Protection Authority  
GPO Box 2607  
Adelaide SA 5001

Telephone: (08) 8204 2004

Facsimile: (08) 8124 4670

Free call (country): 1800 623 445

Website: <[www.epa.sa.gov.au](http://www.epa.sa.gov.au)>

Email: <[epainfo@epa.sa.gov.au](mailto:epainfo@epa.sa.gov.au)>

ISBN 978-1-921495-28-1

Issued March 1995

Updated August 2012

© Environment Protection Authority

This document may be reproduced in whole or part for the purpose of study or training, subject to the inclusion of an acknowledgment of the source and to it not being used for commercial purposes or sale. Reproduction for purposes other than those given above requires the prior written permission of the Environment Protection Authority.

# Contents

1	Introduction .....	1
2	Stack emissions.....	2
3	Assessment process for new test methods or technologies .....	26
Appendix A	Test method assessment process .....	27
Appendix B	Quality assurance/quality control requirements .....	32
Appendix C	Definitions for the purpose of this document .....	35
Appendix D	Referenced South Australian Environment Protection Authority Methods .....	36
Acknowledgments	.....	124

## List of tables

Table 2.1	Sources of test methods and their associated websites.....	8
Table 2.2	Approved manual sampling and analysis test methods for stack emissions.....	11
Table 2.3	Approved continuous stack emission monitoring test methods .....	17
Table 2.4	Compound Approved Stack Test Methods .....	19



# 1 Introduction

## 1.1 Air quality

Air quality continues to be among the top environmental concerns for South Australians. Industry can use an air monitoring program to assist in addressing its environmental responsibilities, and its responsibility as a local community member. Industry performance monitoring enables industrial plant to be managed in an environmentally sustainable manner, and to the requirements of the [Environment Protection Act 1993](#) (EP Act) and the [Environment Protection \(Air Quality\) Policy 1994](#) [Air Quality EPP]. In addition, the data can be useful in the design and implementation of clean technology systems and assist with identifying waste minimisation opportunities, leading to cost savings.

## 1.2 Scope and purpose

The primary purpose of industry performance monitoring is to provide information to the Environment Protection Authority (EPA) and licensees to compare emissions against relevant EPA standards and any requirements of an environmental authorisation.

This manual applies to testing of chimney stack gas and particulate emissions for the EPA under Schedule 1 of the Air Quality EPP. Methods in this manual must be used for testing under this schedule. Any variation to the requirements of this methodology for this testing by the licensee must have prior written approval from the EPA. **The use of this manual is mandatory under section 4 part 6 of the Air Quality EPP.**

This manual also contains methods for testing of emissions not listed in Schedule 1. These methods should be used for emission testing of additional pollutants should it be required under an environmental authorisation or environmental improvement plan.

The manual provides a basis for a standardised approach to emission testing in South Australia, incorporating relevant procedures, protocols, codes of practice, performance standards, Australian Standards and other methodology approved by the EPA.

This manual will assist licensees, test laboratories and analytical laboratories to monitor and report on air quality in a consistent manner using approved methods.

This manual establishes approved practices and procedures, for sampling and analysing stack emissions. It is also designed to assist licensees, test laboratories and analytical laboratories with background information and guidance on performance monitoring for environmental purposes.

## 2 Stack emissions

### 2.1 Introduction

The following section includes information on:

- designing and planning a monitoring program
- stack emission sampling
- health and safety precautions
- stack sampling for industrial activities.

### 2.2 Planning a monitoring program

The primary purpose of industry performance monitoring is to provide information to the EPA and licensees to compare emissions against relevant EPA standards and any requirements of an environmental authorisation. In addition, the data can be useful in the design and implementation of clean technology systems, to assist in identifying waste minimisation opportunities and for process management and reporting. This will involve sampling from chimney stacks or other designated discharge points and determining the characteristics of the emission gas stream.

Performance or compliance monitoring must provide timely, reliable and accurate information, regarding the composition and rate of emission of pollution to the environment. This will enable prompt action on any issues.

Holders of EPA licences must ensure that the provisions of sampling, including sampling plane, access ports and work platforms meet the requirements specified in the relevant methods and standards and in this manual. **Safety is of prime importance.**

Reporting must be as detailed in the requirements of section 2.6.2.

Sampling of a pollution discharge must be undertaken at the frequency and locations specified in the license issued by the EPA.

A detailed knowledge of the operation of the source(s) and any associated air pollution control devices is also important in obtaining a representative sample of the gas stream.

The choice of measurement methods must be compatible with the objectives of the monitoring program and conditions of the EPA license.

### 2.3 Stack emission testing

There is no single sampling method to cope with the variable and complex nature of source emissions. This section provides information on aspects of sampling that must be considered prior to embarking on a sampling program.

Staff of the testing laboratory and licensee are responsible to ensure the safety of all involved in testing. Should there be doubt about the safety of a given test situation then the test must be postponed until safety issues are resolved. Rescheduling will require consultation with the EPA for the required tests. When the monitoring is to be conducted on a site not under the control of the test laboratory, arrangements will need to be made with site management.

All site safety procedures must be followed. If the test laboratory assesses that there is unacceptable risk involved in testing/monitoring, then site management and other relevant parties should be informed and monitoring must not proceed until the safety issues are resolved.

The sample(s) analysed must be representative of the gas stream being tested. Therefore, the objective of the stack sampling technique is to ensure that the sampled gas stream is representative of either the total or a known portion of the source emissions.

It is essential that test and analytical laboratory personnel are familiar and competent in individual methods. This facilitates the capture of accurate, representative samples and ensures sample handling and preservation requirements are met. Sampling, monitoring or field measurements must be undertaken within the framework of a well documented quality system. This applies whether the licence holder or the test laboratory is responsible for the sampling, or another organisation is contracted to conduct the tests.

Selection of sampling points in a chimney, duct, or other emission location is critical in obtaining representative results. The licensee must ensure that sampling location, provision and access meet the requirements detailed in this manual. In some circumstances, the sampling location on a stack may not meet the requirements specified in the *Australian Standard AS4323.1* because of the existing design limitations. When this occurs, the licensee must modify sampling to allow for non-ideal conditions as detailed in AS4323.1. If this is not possible the licensee must contact the EPA to determine whether test results from non-complying sampling locations will be acceptable or an alternative is required. Once an agreed sampling plane and protocol has been decided upon it will be documented for inclusion in the licence. However should changes be made to the process then consideration must be given to setting up sample ports in an ideal sampling plane.

### **2.3.1 Requirement for accreditation**

All test and analytical laboratories performing sampling, analysis or on-site monitoring of air emissions for licence compliance purposes under Air Quality EPP must be accredited by the National Association of Testing Authorities (NATA) or maintain other equivalent accreditation for all tests concerned.

### **2.3.2 Health and safety precautions**

The risks associated with stack emission testing must be carefully assessed prior to commencement. Appropriate risk management steps must be put in place to ensure that obligations under the *Health, Safety and Welfare Act 1986* are fulfilled. Risks may arise from any number of hazards associated with the tasks to be done and the prevailing physical conditions. Some of the hazards involved include but are not limited to:

- working at height or on temporary platforms
- exposure to toxic gases
- electrical hazards
- trip hazards
- noise or heat from plant equipment
- objects falling from work platforms
- flammability
- environmental (eg sun, temperature, rain).

When the test laboratory is not the licensee, site management should be notified of impending tests and information sought on the site's safety policy and details of:

- requirements for safety work permits
- location of emergency equipment and safety signs
- location of refuge areas or muster points
- reporting procedures in the event of safety problems.

All site safety procedures should be followed. If the test laboratory assesses that the risk involved in testing/monitoring or taking samples is not acceptable, site management and any other relevant parties (including the EPA) must be advised that testing will not proceed until the safety issues are resolved.

### 2.3.3 Designing a sampling program

Planning a source emission test program requires that the objectives of the program be clearly defined to ensure that the data will meet the stated objectives. Designing an adequate sampling program requires a sound knowledge and understanding of the system to be sampled. The data user, test laboratory and analytical laboratory must be involved in the planning stage if the program is to be successful.

The following information must be acquired prior to sampling and testing:

- requirements of the EPA for testing and reporting
- detailed information on the process conditions, eg is it batch, continuous or cyclic, how long are the batches/cycles?
- details on emissions to be tested and why, as this is a significant factor in determining methods
- test method to be used
- the process conditions under which the test is required eg is the plant operating at a level required or suitable for testing?
- the location of the sampling plane
- provision of access ports and safe working platform
- selection of the number and location of sampling points
- safe access to the area
- suitable sampling equipment
- availability of sufficiently sensitive and specific methods of analysis
- availability of the test and analytical laboratory(s).

There are wide variations in process conditions in most industrial plants, which may produce different characteristics and quantities of emissions. The sample time will need to vary depending on whether the process is continuous, cyclic or batch and the end use of the data such as compliance, process development or modelling.

For compliance testing the sample time must be consistent with requirements in the environmental licence. If there are no such requirements sample times must ensure capture of the peak value and/or the mass emission rates considering limitations of test methods. The sampling times may vary depending on whether the results are required to reflect peak, average or any other designated plant operating conditions. They will also need to vary depending on the concentration of the pollutant of interest. Sample times must also ensure that sufficient amounts of sample are obtained to allow for the sensitivity and limitations of the test method being used. If these considerations result in sample times different to the recommended times listed in tables 2.2 and 2.4 then the actual sample time(s) must be reported along with test results.

For continuous monitoring the minimum data averaging period will be a reflection of the combined performance of the sampling system, the measuring equipment and the source of emissions.

During the design stage of the sampling program, the test laboratory must consider the physical and chemical variability of the discharge. This will have implications for selection of the test method as some methods, although validated and accepted, may not be applicable to some emission sources.

In all test situations consideration must be given to:

- fluctuations in velocity, temperature or pollutant concentration due to variation in the process

- moisture content (particularly wet stack gases)
- expected gas composition and likely interfering compounds
- high vacuum, high pressure or high temperature gas streams
- corrosive or very reactive compounds
- calculation requirements of the Air Quality EPP under the EP Act
- Reporting requirements of this manual.

### ***Preliminary site inspection***

Prior to testing, physical inspection of the source to be tested is used to establish the location of sampling access ports and determine accessibility and work platform requirements (including power and safety). Discussions with site personnel must include plant operating conditions and plant safety requirements for testing equipment and testing personnel.

The inspection should also determine if access ports are pre-existing, and that access port covers can be removed for sampling (not corroded or jammed shut). Preliminary determinations of temperature, velocity, pressure and moisture content can then be made to assist in later sampling. If the sampling plane fails to meet the requirements necessary for obtaining a representative sample then alternative-sampling locations should be sought, or sampling adjusted as in AS4323.1 otherwise consult the EPA in writing.

Following the inspections, and after considering the test objectives and plant operating conditions, a decision can be made on the sampling equipment and test procedures to be employed.

### ***Numbers of samples, sampling times and volumes***

A manual sampling program must consist of a minimum of two test runs per pollutant unless agreed otherwise with the EPA prior to testing. Minimum sampling times should be as specified in this manual, in the test method or in licence conditions. Test methods may specify the minimum sampling time at each sampling point in a traverse across a stack or duct. Minimum sampling times appearing in test methods must be taken to be the primary document but consideration must also be given to test methods, their analytical sensitivity and the process under test.

The minimum sampling times in this document may be altered for variable or batch processes. These cases require sampling during an entire cycle or taking sufficient samples to characterise the gas stream to meet the objective of the sample program.

Sample volume is also an important consideration as the volume required to obtain sufficient sample for analysis will depend on concentrations existing in the emissions. The test laboratory must ensure that in addition to sampling for appropriate time(s) during the process, sufficient volume is taken to ensure amounts of the emissions captured are suitable for the analysis method(s) being used. At the same time consideration must be given to issues of moisture, particle loading and pollutant concentration to ensure that issues such as filter loading, capacity of traps and absorbants and capture solution/s are accounted for. The test laboratory must be sufficiently familiar with the methods of sampling and analysis, and the source being tested to be able to determine the required sample volume and times to give a representative result.

### **2.3.4 Notes for stack sampling**

All stack tests must, as a minimum, measure and report measurements of the parameters detailed in section 2.6 to enable the calculation of mass emission rates of the pollutant(s) in the discharge.

To minimise the process variables, tests should be conducted when there is, as near as possible, a constant flow through the duct or chimney, usually when the plant is operating at greater than 50% of maximum capacity, (but in any case as stipulated in the company's environmental authorisation or at average working capacity). This rate should remain constant over the period of the test within the operating parameters of the plant.

Sample conditioning is often required to successfully transfer the analyte to the collection medium. This often incorporates filtration, heating, cooling, absorption or condensation but the integrity of the sample, in regard to the analyte of interest, must be maintained.

Conditioning of sampling equipment is also important especially for pollutants that can be absorbed or react with equipment. It is important that sufficient conditioning time is allowed for equipment to reach equilibrium and allow for reactive pollutants. In this same vein, materials coming into contact with the sample must be appropriate so as not to affect the result.

### ***Sampling emissions for particles***

To obtain a representative sample of the gas stream containing solid or liquid particles, the sample must be withdrawn from the emission source at a rate where the velocity and direction of the gas entering the sampling nozzle is the same as that of the gas in the duct at the sampling point (iso-kinetic sampling). The number of points is dependent upon the cross-sectional area of the stack and distance of the sampling plane from flow disturbance within the stack (AS4323.2).

AS4323.2 describes an iso-kinetic gravimetric method for the determination of total solid particulate matter emitted from stationary sources.

### ***Sampling emissions for gases***

Multi-point sampling is generally not required for sampling of gaseous emissions. However, in some situations, notably after the junction of several different streams, stratification of the gas stream will persist for some distance downstream and must be accounted for.

A survey of a suitable constituent of the gas stream, for example carbon dioxide or oxygen, should be performed to determine the degree of stratification. In cases where stratification does not exist, single point sampling at one quarter the diameter across the stack should be considered representative of the gaseous emission provided it is far enough from the side of the stack to eliminate effects from stack walls.

If stratification exists, the gaseous emission determination will require multi-point sampling, unless an alternative suitable sampling plane can be found.

### ***Sampling emissions for organic compounds***

The environmental issues normally associated with stack emissions of organic compounds are:

- toxicity and potential for detrimental environmental and human health effects
- odorous properties of the volatile species
- potential to participate in photochemical reaction to produce oxidants
- greenhouse gas or ozone depleting potential.

Emissions of organic compounds to the environment may be in various phases or combinations of phases (solid, liquid or gas). Sampling techniques are therefore governed by the phase(s) of the compounds. To establish the most appropriate sampling method(s) for determination of organic compounds from emission sources, information on the composition and expected concentration is required. Details of the process operation are also required to establish whether the emission is intermittent, cyclic or continuous. Selection of an appropriate test method will be based on factors including:

- the chemical composition of the organic compounds emitted
- the expected concentration range
- the chemical and physical properties (eg boiling point, reactivity, solubility)
- the characteristics of the discharge (eg temperature, moisture, solid, gas).

When the type and concentration of organic compounds in the discharge are unknown, it is recommended that preliminary sampling and analysis be undertaken to identify and determine approximate concentrations of organic compounds beforehand to facilitate the selection of an appropriate test method. Some of this information can be obtained from literature surveys, plant personnel or previous experience with similar industrial processes.

### ***Sampling organic emissions with solid sorbents***

For multi-phase sampling of organic compounds a common practice is to utilise a filter for solids, and a solid sorbent cartridge for vapour-phase compounds. For example this approach is used for sampling of semi-volatile organic compounds in US EPA Method 23 and US EPA SW 846 Method 0010.

Victorian EPA Method 4230 (and US EPA M18 alternative method) is generally applicable to hydrocarbons in the boiling point range 36–126°C and involves collection of a representative sample of stack gas on a solid sorbent. The method should not be used to sample very volatile organic compounds because low molecular weight hydrocarbons such as methane and propane breakthrough the absorption trap and are not measured.

### ***Sampling organic compounds with bags/containers***

If the discharge contains only very volatile gaseous organic compounds, gas samples may be collected in an inert sample container, then analysed by gas chromatographic techniques, US EPA M18.

## **2.4 Approved test methods—stack emissions**

This section of the methodology summarises the approved methods for the sampling and analysis of industrial stack emissions for pollutants under Schedule 1 of the Air Quality EPP. It is the responsibility of the test and analytical laboratories to obtain copies of test methods not included within this methodology. EPA methods referenced in this manual are included in [Appendix D](#).

When selecting a method for a particular test the following priorities must be used:

- Select a method for stack emission testing from approved methods in Table 2.2

or

Methods that are indicated as being a preferred method must be the first method of choice. If there is a valid technical reason for not using preferred methods the reasons for use of another listed method should be included in the report. For a method not listed in this manual, procedures in section 3 of this manual must be followed.

- If no suitable method is listed, an alternative method designed for emission testing should be tested against the Test Method Assessment protocol in Appendix A

or

If no suitable method can be determined then discussions must be held and documented between the test laboratory, analytical laboratory, the licensee and EPA to agree on a course of action.

Copies of the approved methods can be obtained through the relevant organisation's websites. Table 2.1 lists the websites for each organisation at the time of writing of this manual. The source of each approved test method is identified for each parameter in tables 2.2, 2.3 and 2.4. Where previous EPA methods are used, they are included in [Appendix D](#).

Documents listed or contained within this methodology have approval at the time of publishing of this manual. Approval is not to be assumed for any subsequent revisions of documents mentioned in this methodology. New or subsequent methods will need to undergo the process of assessment as in Appendix A, prior to acceptance and approval by the EPA. However it is expected that the most recent, approved version of test methods should be used.

**Table 2.1 Sources of test methods and their associated websites**

Organisation	Abbreviation	Website
California Environmental Protection Agency	–	<a href="http://www.arb.ca.gov/testmeth/testmeth.htm">http://www.arb.ca.gov/testmeth/testmeth.htm</a>
International Standards Organisation	ISO	<a href="http://www.standards.com.au/">http://www.standards.com.au/</a>
National Institute of Occupational Safety and Health	NIOSH	<a href="http://www.cdc.gov/niosh/homepage.html">www.cdc.gov/niosh/homepage.html</a>
NSW Office of Environment and Heritage	NSW EPA	<a href="http://www.environment.nsw.gov.au">www.environment.nsw.gov.au</a>
SafeWork Australia	NOSHC	<a href="http://www.safeworkaustralia.gov.au/">http://www.safeworkaustralia.gov.au/</a>
Occupational Safety and Health Administration	OSHA	<a href="http://www.osha.gov">www.osha.gov</a>
Office of Environment and Heritage NSW	NSW EPA	<a href="http://www.environment.nsw.gov.au">www.environment.nsw.gov.au</a>
Solid Waste Authority USA	–	<a href="http://www.epa.gov/epaoswer/hazwaste/test/index.htm">http://www.epa.gov/epaoswer/hazwaste/test/index.htm</a>
South Australian EPA	SA EPA	<a href="http://www.epa.sa.gov.au">www.epa.sa.gov.au</a>
Standards Australia	AS	<a href="http://www.standards.com.au">www.standards.com.au</a>
United States EPA	US EPA	<a href="http://www.epa.gov/ttn/emc">www.epa.gov/ttn/emc</a> <a href="http://www.epa.gov/sw-846/">http://www.epa.gov/sw-846/</a>
Victorian EPA	Vic EPA	<a href="http://www.epa.vic.gov.au">www.epa.vic.gov.au</a>
Workcover NSW	WCA	<a href="http://www.workcover.nsw.gov.au">www.workcover.nsw.gov.au</a>

Note: This list was compiled at the time of writing this document and is indicative only. Testing bodies are advised to keep their own current lists.

Table 2.2 specifies the approved sampling and analysis methods to be used for manual stack emission monitoring, along with the minimum sampling time per run (in minutes). This sample time may be varied to ensure the amount of sample obtained is appropriate for the analysis method and the plant conditions and to ensure a representative sample is obtained.

Table 2.3 specifies the approved sampling methods for the continuous stack emission monitoring. Table 2.4 specifies the approved stack sampling methods for individual industrial compounds.

Each table includes the following information:

- parameter
- approved sampling and analysis method

- abbreviation of the approved method
- source (organisation) of the approved method
- minimum sampling time per run (in minutes).

Key for the tables 2.2 to 2.4 is as follows:

AS	=	Australian Standard
Carb	=	California Air Resources Board
CA	=	Canadian Test Method
US M	=	United States (US) Environment Protection Agency (EPA) Test Method #
VIC	=	Victorian Environment Protection Authority (EPA) Test Method
SA	=	South Australian EPA Test Method
ISO	=	International Standards Organisation
SW	=	Solid Waste US EPA-46 method

**Table 2.2 Approved manual sampling and analysis test methods for stack emissions****Notes:**

Test methods marked with a 'P' are the preferred methods to be used where more than one method is available.

\* These methods can only be used if the analyser is validated to comply with US EPA standard methods ie 7e for NO and NO<sub>2</sub>.

† Can be sampled with same sampling device as Carb 429 or SW0010.

‡ Test Method has been superseded and is in the process of being phased out.

§ Note sample volume is also critical for analysis, see text in section 2.3.3.

Sampling method abbreviations are those used by the method source.

Parameter	Approved manual sampling and analysis test methods for stack emissions		Sampling method abbreviation	Source	Recommended minimum sampling time (minutes) per run <sup>§</sup>
Selection of sampling positions	Australian Standard 4323.1:1995–Stationary source emissions–Method 1: Selection of sampling positions	<b>P</b>	AS4323.1	Standards Australia	N/A
	SA EPA 3.09–Determination of sampling points in a stack or duct		SA EPA 3.09 <sup>†</sup>	SA EPA	N/A
Gas density	US EPA Method 3–Gas analysis for the determination of dry molecular weight	<b>P</b>	US M3	US EPA	N/A
	SA EPA 3.08–Gas analysis for carbon dioxide and dry molecular weight		SA 3.08 <sup>†</sup>	SA EPA	N/A
Velocity	US EPA Method 2–2D–Measurement of gas volume flow rate in small pipes and ducts	<b>P</b>	US M2–2D	US EPA	N/A
	SA EPA 3.10–Determination of stack velocity and volumetric flow rate		SA 3.10 <sup>†</sup>	SA EPA	N/A
	ISO 10780–Stationary source emissions–Measurement of velocity and volume flow rate of gas streams in ducts		ISO 10780	ISO	N/A

Emission Testing Methodology for Air Pollution

Parameter	Approved manual sampling and analysis test methods for stack emissions		Sampling method abbreviation	Source	Recommended minimum sampling time (minutes) per run <sup>§</sup>
Volumetric flow rate	US EPA Method 2–2D–Measurement of gas volume flow rate in small pipes and ducts	P	US M2–2D	US EPA	N/A
Volumetric flow rate	SA EPA 3.10–Determination of stack velocity and volumetric flow rate		SA 3.10 <sup>‡</sup>	SA EPA	N/A
	ISO 10780–Stationary source emissions–Measurement of velocity and volume flow rate of gas streams in ducts		ISO 10780	ISO	N/A
Aldehyde & ketones	Method 0011–Sampling for selected aldehyde and ketone emissions from stationary sources		SW–0011	US EPA	120
Carbon monoxide	US EPA Method 10–Determination of carbon monoxide emissions from stationary sources	P	US M10	US EPA	10–60
	SA EPA 3.12–Determination of carbon monoxide		SA 3.12	SA EPA	10–60
Chlorine	US EPA Method 26–Determination of hydrogen halide and halogen emissions from stationary sources		US M26	US EPA	60
Chromium	Determination of chromium emissions from decorative and hard chromium electroplating and chromium anodising operations–isokinetic method		METHOD 306	US EPA	120
Halides	US EPA Method 26A–Determination of hydrogen halide and halogen emissions from stationary sources isokinetic method		US M26A	US EPA	60
	SA EPA 3.04–Determination of chlorine		SA 3.04 <sup>‡</sup>	SA EPA	60
Dioxin/furans	US EPA Method 23–Determination of polychlorinated dibenzo–p–Dioxins and polychlorinated dibenzofurans from municipal waste combustors		US M23 <sup>†</sup>	US EPA	180

Parameter	Approved manual sampling and analysis test methods for stack emissions		Sampling method abbreviation	Source	Recommended minimum sampling time (minutes) per run <sup>§</sup>
Fluorine	US EPA Method 13B–Determination of total fluoride emissions from stationary sources (specific ion electrode method)	<b>P</b>	US M13B	US EPA	60
	SA EPA 3.03–Determination of fluorine		SA 3.03 <sup>†</sup>	SA EPA	60
Fluoride (total water soluble)	EPA Method 3142–Total water soluble fluoride (brick industry)		VIC 3142	Victorian EPA	60
Heavy metals	US EPA Method 29–Determination of metals emissions from stationary sources	<b>P</b>	US M29	US EPA	60–120
	SA EPA 3.07–Determination of metals (Pb, Cu, Sb, Cd, As, Hg)		SA 3.07	SA EPA	60–120
Hydrofluoric acid	US EPA Method 26–Determination of hydrogen halide and halogen emissions from stationary sources		US M26	US EPA	60
	US EPA Method 26A–Determination of hydrogen halide and halogen emissions from stationary sources isokinetic method		US M26A	US EPA	60
Hydrogen chloride	US EPA Method 26–Determination of hydrogen halide and halogen emissions from stationary sources		US M26	US EPA	60
	US EPA Method 26A–Determination of hydrogen halide and halogen emissions from stationary sources isokinetic method		US M26A	US EPA	60
Hydrogen sulfide	Canadian EPA 1/RM/6–Reference method for source testing–Measurement of releases of total reduced sulfur (TRS) compounds from pulp and paper operations	<b>P</b>	CA EPA 1/RM/6	Environment Canada–Air Resources Board	1–10
	SA EPA 3.05–Determination of hydrogen sulfide		SA 3.05	SA EPA	1–10
	US EPA Method 11–Determination of hydrogen sulfide–Content of fuel gas streams in petroleum refineries		US M11	US EPA	1–10

Parameter	Approved manual sampling and analysis test methods for stack emissions		Sampling method abbreviation	Source	Recommended minimum sampling time (minutes) per run <sup>§</sup>
Nitrogen oxides	US EPA Method 7D–Determination of nitrogen oxides from stationary sources (ion chromatographic method)		US M7D	US EPA	60
	SA EPA 3.06–Determinations of nitrogen oxides		SA 3.06 <sup>‡</sup>	SA EPA	60
	US EPA Method 7E–Determination of nitrogen oxide emissions from stationary sources (instrumental analyser procedure)	<b>P</b>	US M7E	US EPA	60
	SA EPA 3.14–Continuous measurement of gas concentrations		SA 3.14	SA EPA	60
Odour	AS 4323.3–2001:Stationary source emissions–Part 3: Determination of odour concentration by dynamic olfactometry		AS4323.3	Standards Australia	10
Oxygen and carbon dioxide	US EPA Method 3–Gas analysis for the determination of dry molecular weight		US M3	US EPA	10–60
	US EPA Method 3A–Determination of oxygen and carbon dioxide concentrations in emissions from stationary sources	<b>P</b>	US M3A	US EPA	10–60
	SA EPA 3.08–Gas analysis for carbon dioxide and dry molecular weight		SA 3.08 <sup>‡</sup>	SA EPA	10–60
	SA EPA 3.14–Continuous measurement of gas concentrations		SA 3.14	SA EPA	10–60
Particulate matter less than 10 microns	US EPA Method 201A–Determination of PM <sub>10</sub> centre test method		US EPA M201A	US EPA	60

Parameter	Approved manual sampling and analysis test methods for stack emissions		Sampling method abbreviation	Source	Recommended minimum sampling time (minutes) per run <sup>§</sup>
Polycyclic aromatic hydrocarbons (PAHs)	Method 429–Determination of polycyclic aromatic hydrocarbons (PAH) emissions from stationary sources		Carb 429	California Environment Protection Agency–Air Resources Board	120
	Method 0010–Modified Method 5 sampling train		SW–0010	US EPA	120
Poly chlorinated biphenyls (PCB)	Method 429–Determination of polycyclic aromatic hydrocarbons (PAHs) emissions from stationary sources		Carb 429	California Environment Protection Agency–Air Resources Board	120
	Method 0010–Modified Method 5 sampling train		SW–0010	US EPA	120
Sulfur dioxide	US EPA Method 8–Determination of sulfuric acid and sulfur dioxide emissions from stationary sources		US M8	US EPA	60
	US EPA Method 6C–Determination of sulfur dioxide emissions from stationary sources (instrumental analyser procedure)		US M6C	US EPA	60
	SA EPA 3.02–Determination of sulfuric acid mist and/or sulfuric trioxide		SA 3.02 <sup>†</sup>	SA EPA	60
Sulfur trioxide/sulfur acid mist	US EPA Method 8–Determination of sulfuric acid and sulfur dioxide emissions from stationary sources		US M8	US EPA	60
	SA EPA 3.02–Determination of sulfuric acid mist and/or sulfuric trioxide		SA 3.02 <sup>†</sup>	SA EPA	60
Total acidity	SA EPA 3.11–Determination of total acidity		SA 3.11	SA EPA	60

## Emission Testing Methodology for Air Pollution

Parameter	Approved manual sampling and analysis test methods for stack emissions		Sampling method abbreviation	Source	Recommended minimum sampling time (minutes) per run <sup>§</sup>
Total nitrogen oxides	US EPA Method 7D–Determination of nitrogen oxide emissions from stationary sources (alkaline-permanganate/ion chromatographic method)		US M7D	US EPA	60
	US EPA Method 7E–Determination of nitrogen oxide emissions from stationary sources (instrumental analyser procedure)	<b>P</b>	US M7E	US EPA	60
	SA EPA 3.14–Continuous measurement of gas concentrations		SA 3.14	SA EPA	60
Total solid particulates	AS 4323.2:1995–Stationary source emissions–Method 2: Determination of total particulate matter–isokinetic manual sampling–gravimetric method	<b>P</b>	AS4323.2	Standards Australia	60
	SA EPA 3.01 Determination of total solid particulate matter–isokinetic manual sampling		SA 3.01 <sup>‡</sup>	SA EPA	60
Volatile organic compounds (VOCs)	US EPA Method 18–Determination of gaseous organic compound emissions by gas chromatography		US M18	US EPA	10–60
	US EPA Method 25A–Determination of total gaseous organic concentration using a flame ionisation analyser	<b>P</b>	US M25A	US EPA	10–60
	Method 0010–Modified Method 5 sampling train		SW–0010	US EPA	10–60
Leak detection of VOCs	Method 21–Determination of volatile organic compound leaks		US M21	US EPA	N/A
Water vapour	US EPA Method 4–Determination of moisture content in stack gases		US M4	US EPA	30
	SA EPA Method 3.13–Determination of moisture content of stack gas		SA 3.13 <sup>‡</sup>	SA EPA	30

**Table 2.3 Approved continuous stack emission monitoring test methods****Note:**

Test methods marked with a 'P' are the preferred methods to be used.

Continuous emission monitoring	Approved continuous sampling and analysis methods for stack emissions		Source
Carbon dioxide	US EPA Performance Specification 3—Specifications and test procedures for carbon monoxide continuous emission monitoring systems in stationary sources.	<b>P</b>	US EPA
	ISO 10396—Stationary source emissions—Sampling for the automated determination of gas concentrations		ISO/Standards Australia
Carbon monoxide	US EPA Performance Specification 4—Specifications and test procedures for carbon monoxide continuous emission monitoring systems in stationary sources.	<b>P</b>	US EPA
	ISO 10396—Stationary source emissions—Sampling for the automated determination of gas concentrations		ISO/Standards Australia
Mass concentration of Particles	ISO 10155—Stationary source emissions—Determination of mass concentrations of particles—Performance characteristics, test methods and specifications		ISO/Standards Australia
Oxygen	US EPA Performance Specification 3—Specifications and test procedures for O <sub>2</sub> and CO <sub>2</sub> continuous emission monitoring systems in stationary sources.	<b>P</b>	US EPA
	ISO 10396—Stationary source emissions—Sampling for the automated determination of gas concentrations		ISO/Standards Australia
Sulfur dioxide	US EPA Performance Specification 2—Specifications and test procedures for SO <sub>2</sub> and NO <sub>x</sub> continuous emission monitoring systems in stationary sources.	<b>P</b>	US EPA
	ISO 10396—Stationary source emissions—Sampling for the automated determination of gas concentrations		ISO/Standards Australia
	ISO 10849—Stationary source emissions—Determination of the mass concentration of sulfur dioxide—Performance characteristics of automated measuring systems.		ISO/Standards Australia

Continuous emission monitoring	Approved continuous sampling and analysis methods for stack emissions	Source
Total of nitrogen oxides	US EPA Performance Specification 2–Specifications and test procedures for SO <sub>2</sub> and NO <sub>x</sub> continuous emission monitoring systems in stationary sources.	US EPA
	ISO 10396–Stationary source emissions–Sampling for the automated determination of gas concentrations	ISO/Standards Australia
	ISO 10849–Stationary source emissions–Determination of the mass concentration of nitrogen oxides–Performance characteristics of automated measuring systems.	ISO/Standards Australia
Volume flow rate (automated)	US EPA Performance Specification 6–Specifications and test procedures for continuous emission rate monitoring systems in stationary sources.	US EPA
	ISO 14164–Stationary source emissions–Determination of volume flow rate of gas stream in ducts–Automated method	ISO/Standards Australia

**Table 2.4 Compound Approved Stack Test Methods****Note:**

United States Solid Waste Authority has validated a method for each of the compounds listed. However the US EPA M18 can be used for most of these compounds and is the preferred method where possible.

Parameter	Approved stack sampling and analysis method	Abbreviation	Source	Recommended minimum sampling time (min) per run
Biphenyl	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Bromoform	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
	Method 0040–Sampling of principal organic hazardous constituents from combustion sources using tedlar bags	SW–0040	US EPA	120
Carbon tetrachloride	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120,60
Chloroform	Method 0030–Volatile organic sampling train	SW–0030	US EPA	60
	Method 0031–Sampling method for volatile organic compounds (SMVOC)	SW–0031	US EPA	60
	Method 0040–Sampling of principal organic hazardous constituents from combustion sources using tedlar bags	SW–0040	US EPA	60
Chloromethane	Method 0030–Volatile organic sampling train	SW–0030	US EPA	60
	Method 0031–Sampling method for volatile organic compounds (SMVOC)	SW–0031	US EPA	60
Dichlorvos	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Dinitrotoluene	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Ethyl benzene	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Ethylene glycol	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120

## Emission Testing Methodology for Air Pollution

Parameter	Approved stack sampling and analysis method	Abbreviation	Source	Recommended minimum sampling time (min) per run
Formaldehyde	Method 0011–Sampling for selected aldehyde and ketone emissions from stationary sources	SW–0011	US EPA	60
Hexane	Method 0030–Volatile organic sampling train	SW–0030	US EPA	120
	Method 0040–Sampling of principal organic hazardous constituents from combustion sources using tedlar bags	SW–0040	US EPA	120
Methyl bromide	Method 0030–Volatile organic sampling train	SW–0030	US EPA	60
Methyl chloride	Method 0040–Sampling of principal organic hazardous constituents from combustion sources using tedlar bags	SW–0040	US EPA	60
1,1,2–trichlorethane	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Acetaldehyde	Method 0011–Sampling for selected aldehyde and ketone emissions from stationary sources	SW–0011	US EPA	120
Chlorobenzene	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Cumene	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Ethyl acrylate	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Methanol	US EPA M308–Procedure for the determination of methanol emissions from stationary sources	US M308	US EPA	60
Methyl ethyl ketone	Method 0011–Sampling for selected aldehyde and ketone emissions from stationary sources	SW–0011	US EPA	120
Methy isobutyl ketone	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
	Method 0011–Sampling for selected aldehyde and ketone emissions from stationary sources	SW–0011	US EPA	120
Nitrobenzene	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120

Parameter	Approved stack sampling and analysis method	Abbreviation	Source	Recommended minimum sampling time (min) per run
Phenol	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Phosphine	US EPA M29–Determination of metals emissions from stationary sources	US M29	US EPA	60–120
Styrene	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Toluene	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	60–120
	Method 0030–Volatile organic sampling train	SW–0030	US EPA	60–120
	Method 0040–Sampling of principal organic hazardous constituents from combustion sources using tedlar bags	SW–0040	US EPA	60–120
Xylenes	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
Acrolein	Method 0010–Modified Method 5 sampling train	SW–0010	US EPA	120
	Method 0011–Sampling for selected aldehyde and ketone emissions from stationary sources	SW–0011	US EPA	120
Benzene	Method 0030–Volatile organic sampling train	SW–0030	US EPA	60
	Method 0031–Sampling method for volatile organic compounds (SMVOC)	SW–0031	US EPA	60
Toluene di-isocyanate (TDI)	US EPA Method 207 Method for Measuring Isocyanates in Stationary Source Emissions	US M207	US EPA	60
Trichloroethylene	Method 0030–Volatile organic sampling train	SW–0030	US EPA	60
	Method 0031–Sampling method for volatile organic compounds (SMVOC)	SW–0031	US EPA	60
	Method 0040–Sampling of principal organic hazardous constituents from combustion sources using tedlar bags	SW–0040	US EPA	60

## Emission Testing Methodology for Air Pollution

<b>Parameter</b>	<b>Approved stack sampling and analysis method</b>	<b>Abbreviation</b>	<b>Source</b>	<b>Recommended minimum sampling time (min) per run</b>
Vinyl chloride	Method 0030–Volatile organic sampling train	SW–0030	US EPA	60
	Method 0040–Sampling of principal organic hazardous constituents from combustion sources using tedlar bags	SW–0040	US EPA	60
	US M106–Determination of vinyl chloride emissions from stationary sources	US M106	US EPA	60

## 2.5 Quality assurance requirements

To ensure consistency and reliability of results and processes, all sampling and analysis required by the EPA must be undertaken by NATA (National Association of Testing Authorities), or equivalent, accredited test and analytical laboratories. The test and analytical laboratories must have gained accreditation for test methods to be used wherever possible (see following paragraph). NATA is an independent assessment body that provides internationally recognised accreditation for test and analytical laboratories and other testing facilities. NATA provides accreditation against *AS/ISO IEC 17025 General requirements for the competence of testing and calibration laboratories*. This standard outlines the requirements for development of a quality system in line with NATA endorsement.

There may be occasions where NATA (or equivalent) accredited laboratories do not exist for a specific process or test. In this case the test laboratory must as a minimum be an accredited body for stack emission testing for flows, particulates and sample plane selection. The analytical laboratory must be accredited for similar analyses. Both laboratories must comply with specifications set out in [Appendix B](#) and in alignment with AS17025. The testing body must obtain accreditation for ongoing use of such a test.

## 2.6 Reporting requirements

This section of the methodology specifies EPA reporting requirements.

### 2.6.1 Stack monitoring reports

Physical or chemical measurements on discharges to air must be reported with the following information:

- statement of objectives of the monitoring plan
- monitoring plan details including: equipment to be used, methods of measurement, and quality assurance program and relevant quality control steps for the monitoring
- a scale diagram showing each discharge point with each testing access port and distances from upstream and downstream flow disturbances
- a scale diagram showing the sampling platform and access
- the dimensions of all access ports.

The results of manual testing must, also contain the following information taking into account any requirements defined in an environmental authorisation and the test methods used:

- purpose of the test
- date and time of the test
- name and location of plant (address)
- plant operating conditions during the test
- brief description of the section of the plant under test relating it to the entire plant
- test procedure(s) used and any variations from those procedure(s) and reasons for selecting non-preferred methods
- sample time if different than recommended
- internal stack/duct diameters or stack/duct dimensions (in metres) at the test plane
- internal stack/duct diameter or stack/duct dimensions (in metres) at the outlet of the stack
- stack height in meters above ground level
- stack/duct location (latitude and longitude with datum reference) and reference within the plant
- altitude above mean sea level of the base of the stack

- location of sampling plane with respect to the nearest upstream and downstream flow disturbances
- average stack/duct gas velocity in metres/second at STP
- average ambient barometric pressure during the test (kilopascals)
- average stack/duct gas pressure during the test (Pascals)
- average stack/duct gas flow rate, cubic metres/second at STP
- average stack/duct gas temperature, K or degrees Celsius
- moisture content, % v/v or w/v
- composition of stack/duct gas where applicable, % volume, dry basis
- concentration of the pollutant under test such as total particulates, heavy metals, or any specific gaseous pollutant, mg/m<sup>3</sup> at STP, dry basis, adjusted if necessary to reference conditions
- estimate of the measure of uncertainty for the test results
- comments on whether data exceed the EPA emission limits
- percent isokineticity—this must be reported along with a statement indicating requirements for isokineticity of the test method used.
- any other factors which may have affected results.

(Note: STP is 0° Celsius and 1 standard atmosphere pressure.)

- 1 Test results must be forwarded to the EPA as outlined in licence conditions, and in any case within eight weeks after the test.
- 2 Where testing for reporting to the EPA is of a continuous nature over an extended period of time (greater than that for a corresponding manual stack emission test), the results must be reported as indicated in the environmental authorisation or as agreed beforehand with the EPA.
- 3 Reports must be provided to the EPA in the format required by the EPA or as directed in the environmental authorisation, in electronic format as a Word© document file on a write-once media and in paper copy. This is to be accompanied by a letter of verification from the licensee. The letter of verification is a statement by a person authorised to sign on behalf of the licensee that the provided report is a true and correct record of the testing conducted on the premises.
- 4 Testing and analytical laboratory information: All information concerning testing, monitoring and ancillary equipment, charts, raw data, calibration records and other relevant documentation must be provided at the request of an authorised officer of the EPA. Monitoring equipment includes both ambient and stack monitoring equipment for both continuous or discrete testing. All data gathered from the monitoring equipment, along with a copy of the test report, must be stored on a computer data system available through the company premises for seven years or the operational period of the plant whichever is the lesser.
- 5 Information supplied may, at the discretion of the EPA, be published in full, in summary form, in annual or other reports with reference to the source.
- 6 The test and analytical laboratories must determine a person who is a director, or legally responsible person in the company able to sign documentation on behalf of the company, to verify the correctness of any reports or documentation supplied to EPA. All documents related to a test, supplied under a works approval/environmental authority or under other EPA requirement must be signed by the nominated person.

### **2.6.2 Adjustment to reference conditions**

Under the Air Quality EPP, it is a mandatory requirement that all stack emissions must be reported to 0°C, 1 standard atmosphere pressure and on a dry basis (STP dry).

In addition some emissions defined under the policy must also be adjusted to a reference concentration of oxygen or carbon dioxide. This requires that oxygen and/or carbon dioxide concentration must also be measured. Adjustments are to be made as follows:

- Adjustment to a reference concentration of carbon dioxide

$$C_a = C_i \times (CO_{2r}) / (CO_{2m})$$

where:

$C_a$  = adjusted emission concentration at 0 °C and 1 standard atmosphere on a dry basis having a specified reference concentration of carbon dioxide volume %  $CO_{2r}$

$C_i$  = initial unadjusted pollutant emission concentration at 0 °C and 1 standard atmosphere on a dry basis and at known carbon dioxide concentration ( $CO_{2m}$ ) before admixture with air or other gases

$CO_{2r}$  = a specified reference concentration of carbon dioxide (volume %)

$CO_{2m}$  = actual measured carbon dioxide concentration (volume %)

- Adjustment to a reference concentration of oxygen

$$C_b = C_i \times (20.9 - O_{2r}) / (20.9 - O_{2m})$$

where:

$C_b$  = adjusted emission concentration at 0 °C and 1 standard atmosphere pressure having a specified reference concentration of oxygen volume %  $O_{2r}$

$O_{2r}$  = a specified reference concentration of oxygen (volume %)

$C_i$  = initial unadjusted emission concentration at 0 °C and 1 standard atmosphere on a dry basis and at a known oxygen concentration ( $O_{2m}$ ) before admixture with air or other gases

$O_{2m}$  = actual measured oxygen concentration (volume %)

In both adjustments, the value reported to the EPA for purposes of compliance is the adjusted value ( $C_a$  or  $C_b$ ) at its reference carbon monoxide or oxygen concentration along with the measured oxygen and/or carbon monoxide concentration.

## **3 Assessment process for new test methods or technologies**

### **3.1 Assessment process**

To achieve a consistent and open approach for selection and inclusion of methods in this methodology, the assessment protocol described in [Appendix A](#) has been developed for use as a guide in the assessment of methods. This protocol acts as a guide to assess the key requirements needed when selecting a test method not listed in this manual.

Where a method is not included within this manual the assessment protocol described in [Appendix A](#) must be followed prior to testing. The results of this assessment must be reported to the EPA as part of the process for use of the method in question. Methods may have not been included in this manual through:

- development of new methods or technologies
- previous versions of a method in existence at the time of writing may not have been suitable.

### **3.2 EPA approval of new methods**

Upon completion of the process outlined above and in [Appendix A](#), the following information should be supplied to the EPA for consideration of the proposed method:

- one copy of the proposed method in either electronic or hard copy. Due to copyright restrictions this requirement may need to be varied but the EPA will need to access the method.
- the source of the method
- evidence of information supplied as part of [Appendix A Protocol–assessment notes](#)
- any other evidence or arguments supporting the suitability of the method in question.

## Appendix A Test method assessment protocol

### Protocol—test method assessment process

To determine the suitability of the proposed sampling and analysis method, the following must occur:

- 1 Determine if the test is an ambient or stack emission test.
- 2 Obtain a copy of the protocol worksheet listed in this manual under protocol.
- 3 Assess the proposed method, assessment notes and complete the stack/ambient test assessment protocol worksheet allocation scores as described in this appendix.
- 4 If all information is not available in the method it may be possible to obtain details from the source of the method or other laboratories that have used it.
- 5 Add up the points column.
- 6 If the total points scored are **less than 0** then the test method **should not be considered**.
- 7 If the total points scored are **above 250**, the test method **can be considered** unless alternative methods of 400 points or above are available.
- 8 If the total points scored are **greater than 0 but less than 250**, then the test method should only be considered if it is the only method available.
- 9 There may be occasions when limiting factor(s) occur that would normally preclude a test method. If supporting evidence to show that no other options are available the method will be considered.

### Protocol—assessment notes

The following comments relate to the completion of the assessment protocol for stack and ambient test methods. These notes will assist you when completing a review of a new technology or test method.

#### Where method is approved

Give points if it is approved for use in other Australian states, USA or Britain or other nationally recognised agency.

#### New technology

Give points equal to the method that the new technology was validated to. For example, if the new technology was validated by SA Method 3.06, and this method was approved, then 90 points would be allocated.

#### Estimated capture efficiency

Some methods have estimated capture efficiencies of the pollutant to be captured; if so allocate points to percentage given.

If no capture efficiency is stated give minus 30 points.

#### Detection limit versus EPA limit

Methods give an estimated lowest detection limit under normal sampling techniques.

Unless this lowest detection limit is higher than the relevant EPA emission or ambient limit then the method cannot determine if a pollutant is above limits set. A more sensitive method must be used. Detection limits are normally 2 or 3

times the standard deviation of the base variation of the measurement and any values less than this cannot be compared with limits.

### Uncertainty

Some methods provide an uncertainty value. This is the potential deviation from the measured value (expressed as a percentage). For example, a measured value of 5 micrograms/m<sup>3</sup> (µgm/m<sup>3</sup>) with a 20% uncertainty would have a true value between 4–6 µgm/m<sup>3</sup>.

### Bias

A bias is a known interferent to accurately capturing and analysing a pollutant or a known output of the method not related to the pollutant of concern.

### Costs

A lower cost is more acceptable provided the result is within required uncertainties. A lower cost is not acceptable if the uncertainty or lowest detectable limit of the measurement is such that it renders the data unsuitable for its purposes such as compliance or comparison with standards.

### Onsite setup and sampling

This assesses whether there are companies available to undertake the sampling and analysis of the parameter. It may include a facility with NATA accreditation for the test in question or another facility holding NATA accreditation for similar methods.

Site setup requirements for stack emission tests can limit the time available for sampling and affect costs. These should be rated using points allocation in accordance with the protocol.

### Availability of testing

Some tests are not available in Australia, due to low volume, high start-up costs or other reasons. If a method cannot be assessed in Australia then it should only be considered where no other options are available as it will be a new method and sampling and analysis techniques will be unfamiliar to the test laboratory.

### Protocol

	Notes	Points to allocate
<b>Where method is approved</b>		
Australian Standard		200
Australian Standard (used for other purposes)		100
SA EPA		90
Interstate EPA		80
More than one interstate EPA		200
USA		70
ISO		70
British Standard		50
Other agency		50
None or not promulgated		0

	<b>Notes</b>	<b>Points to allocate</b>
<b>New technology</b>	State method used for independent validation or to which it is equivalent, eg validated by SA Method 3.06 approved by SA EPA	Same as validation method 90
<b>Estimated capture efficiency</b>	Unknown 100–75% <75%	–30 10 –20
<b>Lower detection limit versus EPA limit</b>	Lower detection limit >1 factor of limit Lower detection limit same factor as limit Lower detection limit > limit Lower detection limit specified and no EPA limit Unknown lower detection limit and no EPA limit/EPA limit	50 0 –300 50 0
<b>Uncertainty</b>	<20% of value <50% of value <100% of value >100% of value Unknown	0 –20 –50 –100 0
<b>Bias</b>	Known bias <20% Known bias >20% and <50% Known bias >50% >5 known interferents that are typically in stack gas Unknown	0 –50 –200 –200 0
<b>On-site setup and sampling (stack tests)</b>	0–2hrs 2–4 hrs 4–6 hrs 6–8 hrs >8 hrs	40 30 20 10 0

	<b>Notes</b>	<b>Points to allocate</b>
<b>Lab analysis costs per sample</b>	Completed on site	50
	<\$250	40
	>\$250 and <\$500	30
	>\$500 and <\$1000	20
	>\$1,000 and <\$2,000	10
	>\$2,000	0
	Unknown	0
<b>Availability of sampling organisations</b>	NATA approved samplers	100
	Other approved samplers	80
	No samplers available	-400
<b>Availability of analytical laboratory</b>	NATA approved lab	100
	Other approved lab	80
	Overseas lab	10
	No lab available	-400
	Unknown	0
	Completed on site	50

\* EPA limit refers to the emission limit applicable to the test being performed.

**Protocol worksheet**

<b>Pollutant</b>	<b>Comments</b>	<b>Protocol points</b>
Method evaluated		
Notes (is same as method xx)		
Where is the method approved (approving agency)		
New technology	State method used for validation	
Estimated capture efficiency		
Lower detection limit		
EPA limit		
Uncertainty		
Bias		
Onsite setup and sampling time		
Lab analysis costs per sample		
Availability of sampling organisations		
Availability of analytical laboratories		

## **Appendix B Quality assurance/quality control requirements (for use when no suitably accredited test and/or analytical laboratories are available for a selected method)**

---

### **Quality assurance/control procedures for stack air monitoring**

#### **Introduction**

Sampling and analysis must be undertaken through National Association of Testing Authorities (NATA) accredited facilities (or equivalent).

NATA is an independent assessment body that provides internationally recognised accreditation for test and analytical laboratories and other testing facilities. NATA provides accreditation against *AS/ISO IEC17025 General requirements for the competence of testing and calibration laboratories*. This standard outlines the requirements for development of a quality system in line with NATA endorsement.

Where suitably accredited facilities do not exist for a specific test requirement, then testing may continue if it is conducted to AS17025 by a laboratory with accreditation for similar test methods. In these instances, the quality assurance/quality control (QA/QC) procedures described in this appendix and in alignment with AS17025 must be followed. If ongoing testing is required (for more than two years) then accreditation for the test must be obtained.

#### **Semi-continuous monitoring**

Semi-continuous (batch) monitoring involves the transport of instrumental analysers to the monitoring site. Test equipment is operated either at the sampling platform or located in a mobile laboratory nearby. Sample gas is withdrawn from the discharge, often through a gas conditioning system to remove particulate matter and moisture, from the sample before presentation to the gas analyser. The conditioning system must not change the integrity of the sample gas. As the conditioning system and instrumental analysers are normally cold started, sufficient warm-up and conditioning time must be allowed before calibration and measurements commence.

#### **Continuous monitoring**

Continuous chimney stack emission monitoring equipment can be located in harsh physical and chemical environments, and at times in not easily accessible areas. Although it may be protected from these environments, samples being measured can be wet, corrosive, contain high levels of particles which can effect measurement equipment over time. For these reasons it is important that a good quality assurance system is developed to ensure reliable, accurate data are produced and maintained.

#### **Quality system**

For stack and ambient air monitoring the following activities must be undertaken to achieve the required level of quality assurance and control.

#### **Staff**

The licensee must ensure training and supervision of staff is carried out by suitably trained and experienced personnel. Staff must be trained to a sufficient standard to ensure they are capable of undertaking the relevant tasks in a competent manner.

The licensee must ensure that the training program consists of extensive instruction. This could occur through inhouse training programs and specialist courses by external organisations. Records of all training (including on-the-job training) received by staff and the level of skill attained must be maintained and such records must be available to EPA for inspection upon request.

### ***Auditing***

Internal audits must be conducted in accordance with a predetermined schedule and procedure that includes all elements of the quality system over a 12-month period. An external auditor must be appointed to conduct an audit at least once in any two-year interval. The audits must ensure that the operating procedures and equipment used comply with relevant operating manuals, methods outlined in this methodology and sound laboratory practice. The results of these audits must be documented and all audit reports must be available for inspection by the EPA upon request.

### ***Monitoring procedures***

All measurements must be made, and equipment operated, in accordance with requirements outlined in the manufacturers manual, relevant test methods and with procedures in this methodology as applicable.

### ***Service and maintenance***

The licensee must ensure that all emission monitoring equipment and procedures produce high quality, accurate data and continuity of measurements by following a comprehensive and documented service and maintenance regime. Where relevant, this regime must incorporate short, medium and long-term service and maintenance requirements. This information should be available in relevant documents such as instrument manuals, Australian Standards and methods outlined in this methodology. All changes, such as adjustments, modifications or maintenance and service to the equipment or systems, must be recorded for each instrument, preferably in a dedicated logbook or computer system.

All records must clearly identify the person making the entry and the date on which the entry is made.

Appropriate service schedules must be recorded for continuous emission monitoring equipment.

### ***Equipment or system malfunction***

Any malfunctions, faults, data discrepancies or performance problems that are encountered must be registered, corrected and the correction documented. Any data produced by a faulty instrument, from the date of the last valid calibration until its return to service with a valid calibration, must be recorded as invalid and may not be used for any reporting or assessments.

The facility must ensure that:

- A record is kept of all instrument maintenance.
- Repaired instruments undergo performance testing and are recalibrated prior to their return to service.
- Records of installation and removal of instruments are documented along with identification of the individual instruments (eg serial numbers).
- Logbooks assigned to individual instruments have sufficient detail to establish an audit trail for identification of reasons behind invalid data and instrument malfunction.

### ***Calibration***

Calibrations must be scheduled and performed according to good laboratory practice and in accordance with manufacturers' specifications. Where appropriate, requirements within Australian Standards and methods outlined in this methodology should be adhered to. In addition performance testing and/or calibrations must also be performed after servicing, repairs or major breakdown.

Calibration procedures must be documented in the test and analytical laboratories' quality manual, and clear and comprehensive calibration records must be maintained. Calibration standards must be certified and traceable to a primary calibration source. Only calibration standards with current certification may be used. Any discrepancies between the current and historical calibration results must be investigated and documented in an appropriate log.

### **Data validation**

The test and analytical laboratories must ensure that the data are examined and validated so that they have been adjusted to account for calibration and instrument adjustments. Any data produced during equipment malfunction or fault must be clearly identified and declared invalid. Sources of error may include data logger malfunction, equipment malfunction, and errors in transmission, calculation, sampling or analysis and in reporting.

### **Records and reporting**

All records, individual instrument logbooks, validation calculations, work sheets, alterations and calibration data must be signed by suitably trained and authorised personnel with data and calculation validation cross checked by a second person. All records must be archived for a minimum of seven years or for the life of the plant, whichever is the lesser.

The test or analytical laboratory must notify EPA in writing within four weeks of information becoming available that casts doubt on the accuracy or correctness of any report, data or other information supplied to EPA.

Where records are electronic, a written, signed verification document must be kept on record and archived as above.

Data known to be invalid must not be used in reporting or for calculating averages or other statistics to be reported.

### **Reports to be verified**

The test and analytical laboratories must determine a person who is a director, or legally responsible person in the company able to sign documentation on behalf of the company, to verify the correctness of any reports or documentation supplied to EPA.

All documents supplied under a works approval/environmental authority or under other EPA requirement must be signed by the nominated person.

---

## Appendix C Definitions for the purpose of this document

---

<i>Accreditation</i>	This is the process whereby a test or analytical laboratory is audited by an independent body to relevant standards to ensure suitable processes and procedures are in place and implemented, and staff have the skills, training, resources and management support to implement them.
<i>Analytical laboratory</i>	The laboratory and its staff that carry out analysis of samples taken by the test laboratory to produce measurements on the pollutants of concern.
<i>Licence</i>	Includes an environmental authorisation, works approval or environmental improvement program under the <i>Environment Protection Act 1993</i> .
<i>Licensee</i>	Includes the holder of an environmental authorisation, works approval or environmental improvement program under the <i>Environment Protection Act 1993</i> .
<i>Must or shall</i>	Indicate mandatory requirements.
<i>STP</i>	0°C (273 K) and 1 standard atmosphere pressure (101.3 kPa).
<i>Percent Iso-kineticity</i>	For the purposes of this methodology, percent iso-kineticity is  $100 \times (\text{average measured sampling velocity} / \text{calculated iso-kinetic sampling velocity})$
<i>Test equipment</i>	Include all equipment used in obtaining and analysing samples for stack emissions and ambient air testing. This equipment must comply with requirements of approved methods and standards.
<i>Test laboratory</i>	The laboratory and its staff that carry out sampling of emissions from licensee's premises through chimney stacks or of ambient air to determine performance of the licensee.

Note: the test laboratory and analytical laboratory may or may not be the same laboratory.

## **Appendix D Referenced South Australian Environment Protection Authority Methods**

---

### **IMPORTANT NOTES FOR THE USE OF APPENDIX D:**

- **Appendix D contains copies of the original methods developed by Dr T H GOH and published in 1995. Should any conflict arise with other parts of this methodology the most recent part will take precedence**
- **These referenced methods may refer to Australian or international standards no longer in use in which case the current standard must be used where possible.**
- **For: “EPA, Department of Environment and Natural Resources” Read: “EPA”**
- **Where appropriate subscripts and superscripts have been added**
- **For sulfur and compounds the older “ph” spelling has been retained**
- **Some methods require the use of supplied work-sheets. As recording methods have changed the use of other methods such as computers is acceptable as long as the required data are recorded in a secure manner**

**Contents**

03.01	Determination of total solid particulate matter–isokinetic manual sampling
03.02	Determination of sulfuric acid mist and/or sulfur trioxide
03.03	Determination of fluorine
03.04	Determination of chlorine
03.05	Determination of hydrogen sulfide
03.06	Determination of nitrogen oxides
03.07	Determination of metals (Pb, Cu, Sb, Cd, As, Hg)
03.08	Gas analysis for carbon dioxide and dry molecular weight
03.09	Determination of sampling points in a stack or duct
03.10	Determination of stack gas velocity and volumetric flow rate
03.11	Determination of total acidity
03.12	Determination of carbon monoxide
03.13	Determination of moisture content of stack gas
03.14	Continuous measurement of gas concentrations
Appendix 1	Data sheets
Appendix 2	Specifications of ancillary apparatus recommended for stack sampling

## South Australian Environment Protection Authority Method 03.01

### Determination of total solid particulate matter– iso-kinetic manual sampling

Prepared by: TH Goh, May 1995

#### Contents

1	Scope
2	Principle
3	Apparatus
4	Reagents
5	Calibration
6	Procedure
7	Calculations
8	Modifications to methods
Figure 1.1	Particulate sampling train

---

## 1 Scope

This isokinetic manual gravimetric method is applicable for the determination of particulate matter emitted from stationary sources.

## 2 Principle

A representative sample in the gas stream of a stack or duct is withdrawn iso-kinetically through a nozzle and collected on a pre-weighed filter. The mass of the particulate matter is then determined gravimetrically after removal of uncombined water and its concentration calculated by relating to sample gas volume. Except where approval is given by the EPA, Department of Environment and Natural Resources, the collection of the particulate matter must be carried out from within the stack.

Note: Iso-kinetic sampling—sampling at a rate such that the velocity and direction of the gas entering the sampling nozzle is the same as that of the gas in the sampled gas stream at the sampling point.

## 3 Apparatus

### 3.1 Sampling train

A diagram of the particulate sampling train is given in Figure 1.1.

- 3.1.1 Nozzle—that part of the equipment which first admits a sample of the gas stream to the sampling train. Nozzles shall be manufactured from type 316 stainless steel or other suitable material capable of withstanding stack temperatures. The leading edge of the nozzle must be sharp and tapered with goose neck or plain bend configuration. Nozzle diameter should be not less than 4 mm and nozzles of less than 6 mm should be avoided whenever possible to minimise particle segregation. A set of nozzles ranging incrementally up to 22 mm diameter will be required to cover a range of stack parameters, eg gas velocity.

3.1.2 Probe head assembly—the first part consists of bent tubing joined to a cap. The other end of the tubing has a suitable fitting to attach a nozzle. The cap is detachable from the body of the filter holder and a suitable filter (the second part of the assembly). The unit shall be constructed of stainless steel or other suitable material capable of withstanding stack temperatures.

3.1.3 Probe tube and connection—that part of the equipment which enables nozzle and probe head assembly to be placed within the stack or duct in order that a sample of the gas stream may be taken.

The probe tube shall be constructed of type 316 stainless steel or other material capable of withstanding stack temperatures. It is threaded at one end to take the probe head assembly. The other end is capable of being inserted into a 25-mm hose. The hose must be capable of withstanding maximum temperatures of the flue gas after the gases have been drawn through the probe.

3.1.4 Cooled catchpot or any other water removing device (condenser, silica gel) capable of efficiently removing the water from stack or duct gases.

3.1.5 Silica gel drying tubes—to ensure a dry gas sample entering the metering system.

Tubing shall be composed of glass, perspex or metal with suitable adaptors on each end of the tubing to connect into sampling line. If metal is used, a window to observe the state of the silica gel must be provided. The tubing should be of convenient size to hold not less than 200 g of silica gel. A convenient sized tube is 5 cm in diameter and 30 cm in length.

3.1.6 Metering system—vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring temperature to within +1% of absolute temperature; dry gas meter to measure dry sample gas volume to within +2% accuracy; orifice meter, rotameter or equivalent, as required to maintain an isokinetic sampling rate accurately to within +5%; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.

3.1.7 Pitot tube—Type S, or equivalent, to monitor stack gas velocity.

3.1.8 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined liquid manometer or equivalent capable of being read to within +5 Pa.

3.1.9 Barometer—to measure atmospheric pressure to +1 kPa. An aneroid type barometer standardised against a Fortin type barometer would be acceptable.

## **3.2 Sample recovery**

3.2.1 Suitable storage containers for holding filters, thimbles or glass cloth bags.

## **3.3 Analysis**

3.3.1 Oven.

3.3.2 Desiccator.

3.3.3 Analytical balance to measure to  $\pm 0.1$  mg.

3.3.4 Laboratory balance—300g capacity to measure  $\pm 0.05$  g.

## 4. Reagents

### 4.1 Sampling

- 4.1.1 Filters—alundum thimbles (standard or fine porosity) plain or packed with glass wool  
or  
paper thimbles Whatman\* double thickness soxhlet thimbles (or equivalent)  
or  
glass fabric bags of the continuous filament type or of the staple type.

(Note: The type of filtration material is dependent on the circumstances. Approval to use any filter material must be obtained from the EPA, Department of Environment and Natural Resources).

- 4.1.2 Silica gel—indicating type 6–20 mesh dried at 175°C for 2 hours.

### 4.2 Sample recovery

There are none.

## 5 Calibration

- 5.1 The orifice meter, rotameter, pitot tube, dry gas meter and probe heater must be calibrated against standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources. All analytical apparatus and equipment other than the above items should be calibrated by accepted analytical procedures.

## 6 Procedure

### 6.1 Sampling

- 6.1.1 Advance preparation for sampling train

Label a filter of suitable dimensions, dry as in paragraph 6.1.1.1, cool in desiccator and weigh. Repeat drying, cooling and weighing process to constant mass, ie less than 0.5 mg change between weighings. Store filter in a container for subsequent transportation to the sampling site.

#### 6.1.1.1 Drying of filter material

- a New alundum thimbles and glass fabric bags. Condition new alundum thimbles and glass fabric bags by heating in an oven to 105°C for 1 hour.
- b Used alundum thimbles and glass fabric bags and new paper thimbles. Dry at 105°C for 1 hour.

Note: If the temperature of the stack is greater than 105°C, it should be determined whether the mass of the filter changes under the conditions of sampling. If the filter mass does change, the filter should be preconditioned at least to the same temperature as the stack.

- 6.1.2 Transfer at least 2 portions of silica gel into two silica gel drying tubes.
- 6.1.3 Measure the internal dimensions of the stack or duct by a measuring device, eg calibrated rod, with accuracy to within  $\pm 1\%$  of the linear dimensions.
- 6.1.4 Determine the following source parameters:
- a minimum number of sampling points (Test Method 03.09)
  - b gas velocity, volumetric flow rate and iso-kinetic nozzle size (Test Method 03.10)
  - c molecular weight of stack gas (Test Method 03.08)

d moisture content of stack gas (Test Method 03.13).

6.1.5 Assemble the preweighed filter in filter holder and set up the sampling train with the probe as shown in Figure 1.1. Leak check the sampling train at the sampling site by plugging up the inlet to the filter holder and pulling a 50 kPa vacuum. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  is acceptable. Maintain sufficient flow of water through cooling coils of catchpot or sufficient ice around catchpot (or any other water removing device) to keep the temperature of the gases to the gas meter below  $20^\circ\text{C}$ .

Temperatures higher than  $20^\circ\text{C}$  may result in damage to the dry gas meter from excessive moisture or excessive heat.

### 6.1.6 Particulate train operation

The procedure shall be as follows:

- a Set up the sampling train as described in section 6.1.5 and install the correct entry nozzle and preweighed filter. Note: For each sample run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the nozzle is located at the first sampling point. Turn the probe tube so that the nozzle is at  $90^\circ$  to the gas flow.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases
- d Turn the probe tube until the nozzle is pointing directly into the gas stream.
- e Start the pump and adjust the gas flow to isokinetic conditions. Sample for at least 5 minutes.
- f After sampling has been completed at the first sampling point, quickly move the probe tube to reposition the nozzle at the next sampling point.
- g Adjust the control valve immediately to the isokinetic flow reading appropriate to the next sampling point.
- h Repeat steps (e) to (g) until sampling has been taken at all the points on the first traverse. Maintain isokinetic conditions throughout the sampling period and use the same time interval at each sampling point.  
Where the sampling train is equipped with a dry gas meter, record the meter readings at the beginning and end of sampling time at each sampling point.
- i At the completion of the first sampling traverse, turn off the pump. Remove the probe tube and nozzle from the access hole.
- j Where sampling is to be carried out at more than one sampling traverse, repeat steps (b) to (i).
- k At the conclusion of the sampling, handle carefully the probe tube and filter assembly in accordance with the sample recovery process (section 6.2)
- l If velocity measurement and gas sampling have not been carried out simultaneously at adjacent sampling points, repeat the readings of gas velocity and temperature at each sampling point as soon as sampling at all sampling points is complete. If the average of the gas velocity readings differ by more than  $\pm 10\%$  from the average of the original readings recorded in section 6.1.4(b), the test result shall be regarded as inaccurate.
- m When repeat samples are required, steps (a) to (l) shall be repeated under comparable plant conditions and as soon as is practicable.

If this second sampling follows immediately after the first, the gas velocity and temperature readings taken at step (l) may be used as the initial readings for the second test.

## 6.2 Sample recovery

6.2.1 Exercise care in moving the collection train from the sampling site to the sample recovery area to minimise the loss of collected sample or the gain of extraneous particulate matter.

6.2.3 Remove the filter from the filter holder and place it into its identified container. Seal the container.

## 6.3 Analysis

6.3.1 Dry the filter at 105°C for 1 hour, cool in a desiccator for 15 minutes and weigh in accordance with section 6.1.1. Record weighings in [Appendix 1, Data Sheet 2](#).

Note: If the temperature of the stack is greater than 105°C, it should be determined whether the mass of the filter changes under the conditions of sampling. If the filter mass does change, the filter should be pre-conditioned at least to the same temperature as the stack.

## 7 Calculations

### 7.1 Dry gas volume

Sample gas volume measured by the dry gas meter shall be corrected to standard conditions (273 K, 101.3 kPa) in accordance with the following procedures, as appropriate:

- **Orifice meter as the gas flow rate measuring device**

If an orifice meter is used to adjust and maintain isokinetic sampling, the dry gas volume shall be corrected to standard conditions by using the following equation:

$$V_{std} = \frac{273V_m(P_{bar} + P_d)}{101.3T_m}$$

Equation 1.1

where:

$V_{std}$  = Volume of dry gas sample at standard conditions, m<sup>3</sup>

$V_m$  = Volume of dry gas through dry gas meter at meter conditions, m<sup>3</sup>

$P_{bar}$  = Barometric pressure at the sampling site, kPa

$P_d$  = Average pressure drop across the orifice meter, kPa

$T_m$  = Average dry gas meter temperature, K

- **Rotameter as the gas flow metering device**

If the rotameter is used, the sample gas volume shall be corrected to standard conditions from the following equation:

$$V_{std} = \frac{273V_m P_{bar}}{101.3T_m}$$

Equation 1.2

7.2 Concentration of particulate matter in gas stream

$$C_s = \frac{M_n}{V_{std}}$$

Equation 1.3

where:

- $C_s$  = Concentration of particulate matter in stack gas,  $mg\ m^{-3}$ , dry basis, standard conditions
- $M_n$  = Total amount of particulate matter collected, mg
- $V_{std}$  = Volume of dry gas sample, standard conditions,  $m^3$  (see section 7.1)

8 Modifications to method

Alternative equipment and procedures for determining particulate matter may be used where approval is given by the EPA, Department of Environment and Natural Resources.

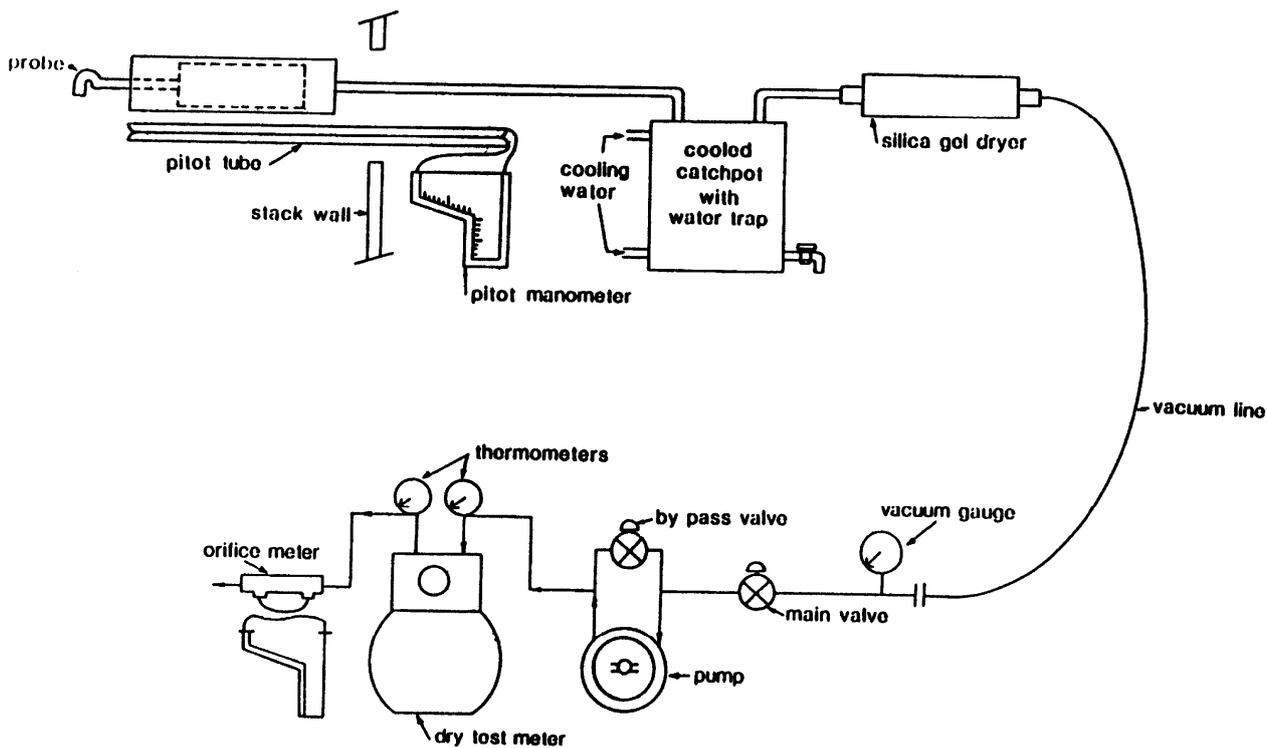


Figure 1.1 Particulate sampling train

## South Australian Environment Protection Authority Method 03.02

### Determination of sulfuric acid mist and/or sulphur trioxide

Prepared by: TH Goh, May 1995

#### Contents

1	Scope
2	Applicability
3	Principle
4	Apparatus
5	Reagents
6	Calibration
7	Procedure
8	Calculations

Figure 2.1 Sulphuric acid mist sampling train

---

## 1 Scope

This method is applicable for the determination of sulfuric acid and/or sulphur trioxide emitted from stationary sources.

## 2 Applicability

### 2.1 Sulfur trioxide from sources other than the manufacture of sulfuric acid and fuel burning processes

The regulations regarding emission limits of sulfuric acid mist or sulphur trioxide from processes other than the manufacture of sulfuric acid and other than combustion processes require that sulfuric acid mist and/or sulphur trioxide emission rates be expressed as sulphur trioxide equivalent per cubic metre of effluent gas.

This method of sulphur trioxide estimation, neglecting the estimation of sulfur dioxide, shall be used.

### 2.2 Sulphur trioxide from contact plants

The regulations require that in the case of contact plants for the manufacture of sulfuric acid, emission rates of acid gases shall be expressed as sulphur trioxide per cubic metre of effluent gas.

This method of sulphur trioxide estimation, together with the subsequent method for the determination of sulfur dioxide expressed as sulfur trioxide shall be used.

### 2.3 Sulphur trioxide from chamber plants

The regulations require that in the case of chamber plants for the manufacture of sulfuric acid, emission rates of acid gases shall be expressed as sulphur trioxide per cubic metre of effluent gas.

As 'acid gases' are interpreted as sulphur trioxide, sulphur dioxide and total oxides of nitrogen excluding nitrous oxide, all these substances must be evaluated. Method 03.11 shall be used for the estimation of total acid gas concentration expressed as sulphur trioxide.

### 3 Principle

A gas sample is extracted from a sampling point in the stack or duct and the acid mist including sulphur trioxide is separated from sulphur dioxide. Removal of sulphur dioxide from the gas sample before passing through a dry gas meter is essential otherwise damage to the meter may result. The sulphur trioxide fraction is estimated by the barium–thorin titration method.

### 4 Apparatus

#### 4.1 Sampling train

See Figure 2.1. Many of the design specifications of this sampling train are described in [Appendix 2](#).

- 4.1.1 Nozzle—any suitable material substantially resistant to attack by the components of the gas stream may be used. The leading edge of the nozzle must be sharp and tapered.
- 4.1.2 Probe—for most cases a borosilicate glass probe will be suitable, however it may be constructed of any material substantially resistant to chemical attack by components of the gas stream and having the necessary mechanical strength. The probe must be fitted with a heating system to prevent visible condensation during sampling. The internal dimensions of the probe should be chosen so that for iso-kinetic sampling the flow rate through the impingers lies in the range  $0.02\text{--}0.03\text{ m}^3\text{ min}^{-1}$ .
- 4.1.3 Pitot tube—Type S, or equivalent, attached to the probe to monitor stack gas velocity.
- 4.1.4 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined liquid manometer or equivalent capable of being read to within  $\pm 5\text{ kPa}$ .
- 4.1.5 Filter holder—borosilicate glass or other suitable material not subject to attack by the components of the gas stream.
- 4.1.6 Impingers—four impingers with glass ball-joint fittings as shown in Figure 2.1. The first and third are of the Greenburg–Smith design with standard tip. The second and fourth are of Greenburg–Smith design, modified by replacing the standard tip with a 1.2-cm internal diameter tube extending to 1 cm from the bottom of the impinger flask. Other collection systems of similar design approved by the EPA, Department of Environment and Natural Resources may be used.
- 4.1.7 Metering system—vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring temperature to within  $\pm 1\%$  of absolute temperature; dry gas meter to measure dry sample gas volume to within  $\pm 2\%$  accuracy; orifice meter, rotameter or equivalent, as required to maintain an isokinetic sampling rate accurately to within  $\pm 5\%$ ; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.
- 4.1.8 Barometer—to measure atmospheric pressure to  $\pm 1\text{ kPa}$ . An aneroid barometer calibrated against a Fortin barometer would be acceptable.

#### 4.2 Sample recovery

- 4.2.1 Wash bottles—2.
- 4.2.2 Glass storage containers.
- 4.2.3 Standard flasks—250 ml, 500 ml.
- 4.2.4 Graduated cylinder—250 ml.

### **4.3 Analysis**

- 4.3.1 Pipette—25 ml, 100 ml.
- 4.3.2 Burette—50 ml.
- 4.3.3 Erlenmeyer flask—250 ml.
- 4.3.4 Graduated cylinder—100 ml.
- 4.3.5 Laboratory balance—300-g capacity, to measure to +0.05 g.
- 4.3.6 Dropping bottle—for dispensing indicator solution.

## **5 Reagents**

### **5.1 Sampling**

- 5.1.1 Filters—glass fibre, MSA type 1106 BH#, or equivalent, of suitable size to fit the filter holder.
- 5.1.2 Silica gel—self-indicating type, 6–20 mesh, dried at 175°C for 2 hours.
- 5.1.3 Water—deionised, distilled.
- 5.1.4 Isopropanol, 80%—mix 800 ml of isopropanol with 200 ml of deionised, distilled water.
- 5.1.5 Hydrogen peroxide, 3%—dilute 100 ml of 30% hydrogen peroxide to 1 litre with deionised, distilled water.
- 5.1.6 Crushed ice.

### **5.2 Sample recovery**

- 5.2.1 Water—deionised, distilled.
- 5.2.2 Isopropanol, 80%.

### **5.3. Analysis**

- 5.3.1 Water—deionised, distilled.
- 5.3.2 Isopropanol.
- 5.3.3 Thorin indicator—1-(o-arsenophenylazo), -2-naphthol-3, 6-disulphonic acid, di-sodium salt. Dissolve 0.20 g of the di-sodium salt (or equivalent) in 100 ml of deionised, distilled water.
- 5.3.4 Barium perchlorate\* (0.02M)—freshly prepare by dissolving 7.808 g of barium perchlorate [Ba (ClO<sub>4</sub>)<sub>2</sub> 3H<sub>2</sub>O] in 200 ml of deionised, distilled water and dilute to 1 litre with isopropanol. Standardise with 25 ml of sulfuric acid (0.02M) to which is added 100 ml of isopropanol.
- 5.3.5 Sulfuric acid standard (0.02M) —standardise to +0.0005M against freshly prepared sodium hydroxide (0.05M) which has been standardised against primary standard potassium acid phthalate. If a solution of potassium acid phthalate is used this also must be freshly prepared.

## 6 Calibration

The orifice meter, rotameter, pitot tube, dry gas meter and probe heater must be calibrated against standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources.

## 7 Procedure

### 7.1 Sampling

7.1.1 Determine the following source parameters:

- a minimum number of sampling points (Test Method 03.09)
- b gas velocity, volumetric flow rate and isokinetic nozzle size (Test Method 03.10)
- c molecular weight of stack gas (Test Method 03.08)
- d moisture content of stack gas (Test Method 03.13).

7.1.2 Preparation of sample collection train. Place 80 ml of 80% isopropanol in the first impinger, 75 ml of 3% hydrogen peroxide in both the second and third impingers, and about 200 g of silica gel in the fourth impinger. Retain a portion of the reagents for use as blank solutions. Assemble the sampling train with the probe as shown in Figure 2.1 and with the filter between the first and second impingers. Leak check the system at the sampling site by disconnecting the probe and plugging the inlet to the first impinger and pulling a 50-kPa vacuum. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  at a vacuum of 50 kPa is acceptable. Following the leak check, reconnect the probe to the sampling train. Turn on the probe heating system and adjust the probe heater setting to prevent visible condensation during sampling. Place crushed ice around the impingers. As necessary add more ice during the run to keep the temperature of the gases leaving the last impinger at 20°C or less.

7.1.3 Train operation. The procedure shall be as follows:

- a Set up the sampling train as described in section 7.1.2 and install the correct entry nozzle.  
Note: For each sample run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the nozzle is located at the first sampling point. Turn the probe tube so that the nozzle is at 90° to the gas flow.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases.
- d Turn the probe tube until the nozzle is pointing directly into the gas stream.
- e Start the pump and adjust the gas flow to isokinetic conditions. Sample for at least 5 minutes.
- f After sampling has been completed at the first sampling point, quickly move the probe tube to reposition the nozzle at the next sampling point.
- g Adjust the control valve immediately to the isokinetic flow reading appropriate to the next sampling point.
- h Repeat steps (e) to (g) until sampling has been taken at all the points on the first sampling traverse. Maintain isokinetic conditions throughout the sampling period and use the same time interval at each sampling point.

Where the sampling train is equipped with a dry gas meter, record the meter readings at the beginning and end of sampling time at each sampling point.

- i At the completion of the first sampling traverse, turn off the pump. Remove the probe tube and nozzle from the access hole.
- j Where sampling is to be carried out at more than one sampling traverse, repeat steps (b) to (i).

- k At the completion of sampling, disconnect the probe and nozzle from the impinger train.
- l Disconnect the impingers and handle carefully in accordance with the sample recovery process (section 7.2).
- m If velocity measurement and gas sampling have not been carried out simultaneously at adjacent sampling points, repeat the readings of gas velocity and temperature at each sampling point as soon as sampling at all sampling points is complete. If the average of the gas velocity readings differ by more than  $\pm 10\%$  from the average of the original readings recorded in section 7.1.1(b), the test result shall be regarded as inaccurate.
- n When repeat samples are required, steps (a) to (m) shall be repeated under comparable plant conditions and as soon as is practicable.

If second sampling follows immediately after the first, the gas velocity and temperature readings taken at step (m) may be used as the initial readings for the second test.

## 7.2 Sample recovery

7.2.1 Remove the isopropanol from the first impinger. Rinse the probe, first impinger and all connecting glassware before the filter with 80% isopropanol. Combine the rinse solution and that from the first impinger and dilute to 100 ml with 80% isopropanol. Add the filter to the solution, mix and transfer to a suitable storage container. If it is not desired to analyse for sulphur dioxide discard all other solutions. To analyse for sulphur dioxide, transfer the solution from the second and third impingers to a 250-ml volumetric flask. Rinse all glassware between the filter and the silica gel impinger with deionised, distilled water and add the rinse water to the volumetric flask. Dilute the combined solution to 250 ml with deionised, distilled water. Transfer the solution to a suitable storage container.

## 7.3 Analysis

7.3.1 Sulphur trioxide, sulfuric acid mist—shake the container holding isopropanol and the filter. If the filter breaks up, allow the fragments to settle for a few minutes before removing a sample. Pipette a 10 millilitre aliquot of sample into a 250-ml Erlenmeyer flask and add 2 to 4 drops of thiorin indicator. Titrate the sample with barium perchlorate to a pink end point. Repeat the titration with a second aliquot of sample.

7.3.2 Sulphur dioxide—shake the container holding the contents from the second and third impingers. Pipette 10 ml aliquot of sample into a 250-ml Erlenmeyer flask. Add 40 ml of isopropanol and 2 to 4 drops of thiorin indicator. Titrate the sample with barium perchlorate to a pink end point. Repeat the titration with a second aliquot of sample.

7.3.3 Titrate the blanks in the same manner as the samples.

## 8 Calculations

### 8.1 Sulfuric acid content (as SO<sub>3</sub>)

$$C_{H_2SO_4}^* = \frac{k^* (V_t - V_b) M (V_{iso} / V_a)}{V_{std}}$$

Equation 2.1

where:

$C_{H_2SO_4}^*$  = Concentration of sulphuric acid, as SO<sub>3</sub>, at standard conditions, dry gas basis, mg m<sup>-3</sup>

$k^*$  = Conversion factor for molar barium perchlorate to mg. SO<sub>3</sub>, 80 mg. litre g-mol<sup>-1</sup> ml<sup>-1</sup>

$V_t$	=	Volume of barium perchlorate titrant used for the sample, ml
$V_b$	=	Volume of barium perchlorate titrant used for the blank, ml
$M$	=	Molarity of barium perchlorate titrant, g-mol, litre <sup>-1</sup>
$V_{iso}$	=	Total volume of isopropanol solution (first impinger and filter), ml
$V_a$	=	Volume of sample aliquot titrated, ml
$V_{std}$	=	Volume of dry gas sample, standard conditions, m <sup>3</sup> (see Test Method 03.01, section 7.1)

\* See note at end of method

## 8.2 Sulphur dioxide content (as SO<sub>3</sub>)

$$C_{SO_2}^* = \frac{k^{1*} (V_t - V_b) M (V_{H_2O_2} / V_a)}{V_{std}}$$

Equation 2.2

where:

$C_{SO_2}^*$	=	Concentration of sulfur dioxide at standard conditions, dry basis, mg m <sup>-3</sup>
$K^{1*}$	=	Conversion factor for molar barium perchlorate to mg. SO <sub>3</sub> , 80 mg. litre. g-mol <sup>-1</sup> ml <sup>-1</sup>
$V_t$	=	Volume of barium perchlorate titrant used for the sample, ml
$V_b$	=	Volume of barium perchlorate titrant used for the blank, ml
$M$	=	Molarity of barium perchlorate titrant, g-mol litre <sup>-1</sup>
$V_{H_2O_2}$	=	Total volume of sulfur dioxide as hydrogen peroxide solution (second and third impingers), ml
$V_a$	=	Volume of sample aliquot titrated, ml
$V_{std}$	=	Volume of dry gas sample, standard conditions, m <sup>3</sup> (see Test Method 03.01, section 6.1)

## 8.3 Total acid gases from contact plants (as SO<sub>3</sub>)

$$C_{TSO_3} = C_{H_2SO_4}^* + C_{SO_2}^*$$

Equation 2.3

where:

$C_{TSO_3}^*$	=	Total acid gas concentration expressed as SO <sub>3</sub> at standard conditions, dry gas basis, mg m <sup>-3</sup>
$C_{H_2SO_4}^*$		obtained from Equation 2.1
$C_{SO_2}^*$		obtained from Equation 2.2

\* See note at end of method

**\* Note:**

The molarity of the barium perchlorate, the volume of sample aliquot, and the conversion factor used in the calculations will depend on the concentration of the material being determined. Appropriate changes in the values given in the method should be made where the volume of barium perchlorate titrant is likely to become excessively large. The values stated in the method should be found satisfactory for a sample volume, dry gas basis (standard conditions),  $V_{std, 0\%O_2}$  of  $1 \text{ m}^3$  provided the concentrations of sulphur trioxide and sulphur dioxide do not exceed  $400 \text{ mg m}^{-3}$  and  $1.0 \text{ g m}^{-3}$  respectively.

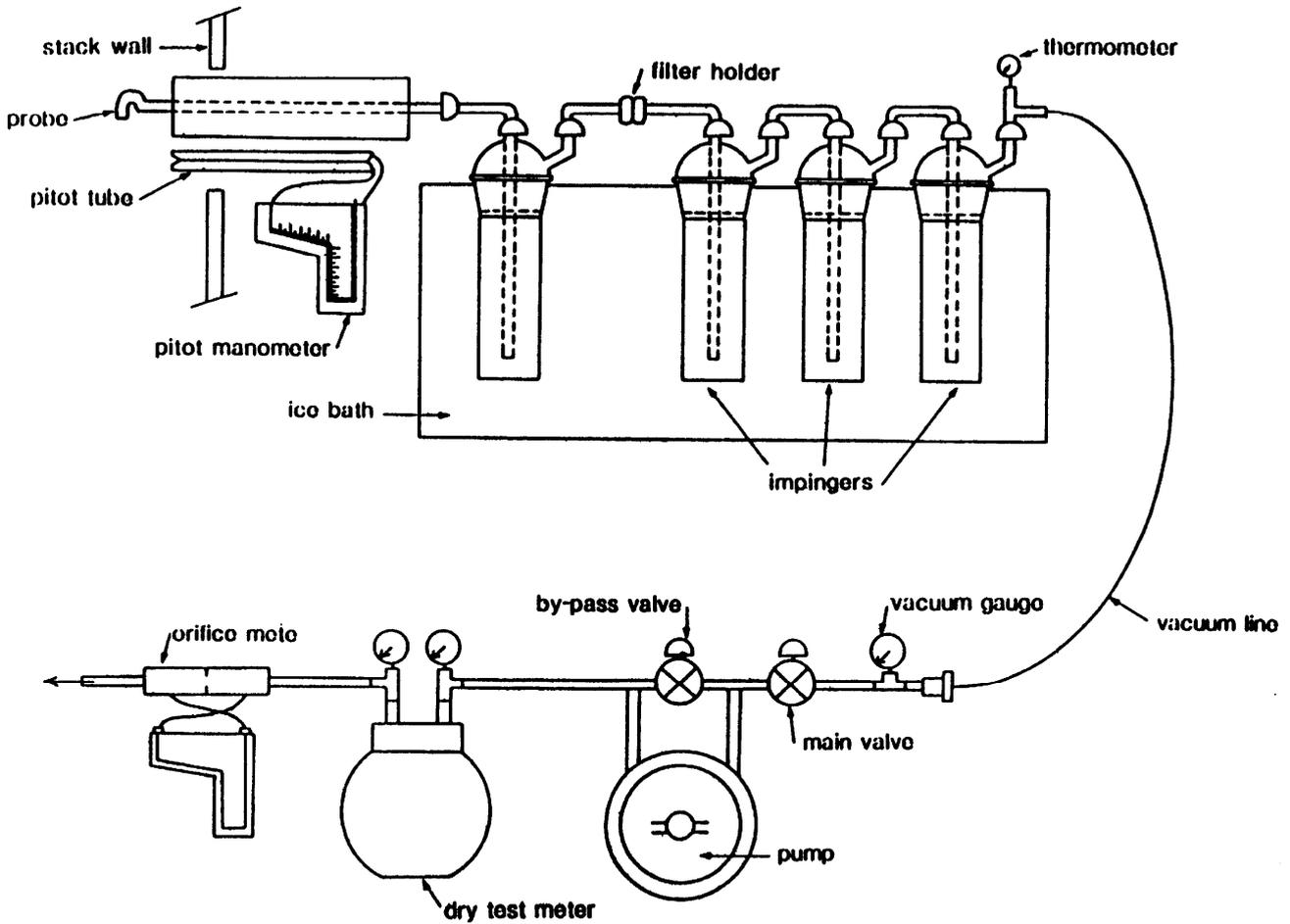


Figure 2.1 Sulfuric acid mist sampling train

---

**South Australian Environment Protection Authority Method 03.03****Determination of fluorine****Prepared by: TH Goh, May 1995****Contents**

- 1 Scope
- 2 Principle
- 3 Apparatus
- 4 Reagents
- 5 Calibration
- 6 Procedure
- 7 Calculations

Figure 3.1 Fluorine sampling train

---

**1 Scope**

This method is specific for inorganic fluorine compounds including free fluorine and hydrofluoric acid.

**2 Principle**

Sampling is carried out isokinetically in a stack or duct to collect particulate fluorides on a filter and gaseous fluorides in two impingers containing sodium hydroxide solution. The fluorides are subsequently measured with a specific ion meter.

Care must be exercised in applying this method as metals such as aluminium, if present in the gas stream, will cause interference.

Interferences where they occur can be overcome by the correct application of sequestering agents.

For accurate results it is essential that all solutions be correctly buffered before measurement with the specific ion electrode. Further, the specific ion electrode will require a period of time, which may be as long as 30 minutes, to establish an equilibrium potential if the concentration of fluoride ion in a series of solutions being measured varies widely from sample to sample.

**3 Apparatus****3.1 Sampling train**

See Figure 3.1. Many of the design specifications of this sampling train are described in Appendix 2.

- 3.1.1 Nozzle—any suitable material substantially resistant to attack by components of the gas stream may be used. The leading edge of the nozzle must be sharp and tapered.
- 3.1.2 Probe—316 stainless steel, PTFE or borosilicate glass. The probe must be fitted with a heating system to prevent condensation during sampling. Isokinetic sampling must be employed and the probe should be chosen so that the flow rate through the impingers lies in the range  $0.02\text{--}0.03\text{ m}^3\text{ m}^{-1}$ .
- 3.1.3 Pitot tube—Type S, or equivalent, attached to the probe to monitor stack gas velocity.

- 3.1.4 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined manometer or equivalent capable of being read to within +5 Pa.
- 3.1.5 Filter holder—borosilicate glass or stainless steel with a 20-mesh stainless steel screen filter support and a silicone rubber gasket. Do not use a glass frit or a sintered metal filter support. The filter is located between the probe and first impinger. Attach a heating unit to the filter to prevent filter plugging resulting from moisture condensation.
- 3.1.6 Impingers—three impingers with glass ball-joint fittings as shown in Figure 3.1. The first and third are of the Greenburg–Smith design modified by replacing the standard tip with 1.2-cm internal diameter tube extending to 1 cm from the bottom of the impinger flask. The second is of the Greenburg–Smith design with standard tip.

Other collection systems of similar design approved by the EPA, Department of Environment and Natural Resources may be used.

- 3.1.7 Metering system—vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring temperature to within +1% of absolute temperature; dry gas meter to measure dry sample gas volume to within +2% accuracy; orifice meter, rotameter or equivalent, as required to maintain an iso-kinetic sampling rate accurately to within +5%; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.
- 3.1.8 Barometer—to measure atmospheric pressure to +1 kPa. An aneroid barometer calibrated against a Fortin barometer would be acceptable.

## **3.2 Sample recovery**

- 3.2.1 Wash bottle—1.
- 3.2.2 Polyethylene storage containers.
- 3.2.3 Suitable storage containers for holding filters.

## **3.3 Analysis**

- 3.3.1 Specific ion meter—any expanded scale pH meter should be suitable together with a fluoride specific ion electrode and a saturated KCl calomel reference electrode of the fritted junction or sleeve type.
- 3.3.2 Pipette—10 ml.
- 3.3.3 Volumetric flasks—1,000 ml, 250 ml, 100 ml.
- 3.3.4 Burette—50 ml.
- 3.3.5 Beakers—150 ml.
- 3.3.6 Graduated cylinder—100 ml.

## **4 Reagents**

### **4.1 Sampling**

- 4.1.1 Filters—Whatman 541, or equivalent, of suitable size to fit the filter holder.
- 4.1.2 Silica gel—self-indicating type, 6–20 mesh, dried at 175°C for 2 hours.

- 4.1.3 Water—deionised, distilled.
- 4.1.4 Sodium hydroxide (0.5M)—Prepare a solution containing 20-g sodium hydroxide in 1 litre of distilled water. This solution should be prepared freshly each time it is required and should not be kept for more than 7 days before use.

4.1.5 Crushed ice.

## 4.2 Sample recovery

4.2.1 Water—deionised, distilled.

## 4.3. Analysis

4.3.1 Water—deionised, distilled.

4.3.2 Sulfuric acid (1M)—purchase or prepare sulfuric acid of approximately 1M.

4.3.2 Sulfuric acid (0.5M)—dilute 500 ml of 1M sulfuric acid to 1 litre with distilled water.

4.3.3 Sodium hydroxide (1M) —prepare a solution containing 40 g sodium hydroxide in 1 litre of distilled water.

4.3.4 Citrate buffer—dissolve 294 g sodium citrate dihydrate in approximately 800 ml of distilled water. Adjust to pH 7 with perchloric acid and dilute to 1 litre.

4.3.5 Standard fluoride solution (1,000 ppm HF)—dissolve 2.100 g of pure NaF, dried at 120°C for 24 hours, in distilled water and dilute to 1 litre. The resulting solution will be equivalent to 1,000 ppm HF. Working standards may then be prepared from this solution by appropriate dilution. Store in plastic bottles.

## 5 Calibration

5.1 The orifice meter, rotameter, pitot tube, dry gas meter and probe heater must be calibrated against standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources.

5.2 The specific ion meter must be calibrated against a series of working standard fluoride solutions prepared from the standard fluoride solution. Pipette 10 ml of each working standard into a 150-ml beaker and further dilute with 100 ml citrate buffer. Adjust the instrument zero using its asymmetry control and with the electrodes immersed in a solution prepared from a 1,000-ppm working standard. Prepare a calibration curve on semi-logarithmic graph paper plotting measured potentials against ppm of HF (logarithmic scale). The theoretical change in potential between solutions of decade difference in fluoride ion concentration is 59.15 mV, in practice values in the range 57–59 mV will be found.

## 6. Procedure

### 6.1 Sampling

6.1.1 Determine the following source parameters:

- a minimum number of sampling points (Test Method 03.09)
- b gas velocity, volumetric flow rate, and iso-kinetic nozzle size (Test Method 03.10)
- c molecular weight of stack gas (Test Method 03.08)
- d moisture content of stack gas (Test Method 03.13).

6.1.2 Preparation of sample collection train. Place 75 ml of 0.5M sodium hydroxide solution in each of the first and second impingers, and about 200 g of silica gel in the third impinger. Retain a portion of the sodium hydroxide

solution for use as a blank. Assemble the sampling train with the probe as shown in Figure 3.1 and with the filter located before the first impinger. Leak check the system at the sampling site by disconnecting the probe and plugging the inlet to the first impinger and pulling a 50-kPa vacuum. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  at a vacuum of 50 kPa is acceptable. Following the leak check, reconnect the probe to the sampling train. Turn on the probe heating system, and adjust the probe heater setting to prevent condensation during sampling. Place crushed ice around the impingers. As necessary add more ice during the run to keep the temperature of the gases leaving the last impinger at  $20^\circ\text{C}$  or less.

6.1.3 Train operation. The procedure shall be as follows:

- a Set up the sampling train as described in section 6.1.2 and install the correct entry nozzle. Note: For each sample run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the nozzle is located at the first sampling point. Turn the probe tube so that the nozzle is at  $90^\circ$  to the gas flow.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases.
- d Turn the probe tube until the nozzle is pointing directly into the gas stream.
- e Start the pump and adjust the gas flow to iso-kinetic conditions. Sample for at least 5 minutes.
- f After sampling has been completed at the first sampling point, quickly move the probe tube to reposition the nozzle at the next sampling point.
- g Adjust the control valve immediately to the iso-kinetic flow reading appropriate to the next sampling point.
- h Repeat steps (e) to (g) until sampling has been taken at all the points on the first sampling traverse. Maintain iso-kinetic conditions throughout the sampling period and use the same time interval at each sampling point.

Where the sampling train is equipped with a dry gas meter, record the meter readings at the beginning and end of sampling time at each sampling point.

- i At the completion of the first sampling traverse, turn off the pump. Remove the probe tube and nozzle from the access hole.
- j Where sampling is to be carried out at more than one sampling traverse, repeat steps (b) to (i).
- k At the conclusion of sampling, disconnect the probe and nozzle from the impinger train.
- l Disconnect the impingers and remove the filter. Handle carefully in accordance with the sample recovery process (section 6.2).
- m If velocity measurement and gas sampling have not been carried out simultaneously at adjacent sampling points, repeat the readings of gas velocity and temperature at each sampling point as soon as sampling at all sampling points is complete. If the average of the gas velocity readings differ by more than +10% from the average of the original readings recorded in section 6.1.1(b), the test result shall be regarded as inaccurate.
- n When repeat samples are required, steps (a) to (m) shall be repeated under comparable plant conditions and as soon as is practicable.

If this second sampling follows immediately after the first, the gas velocity and temperature readings taken at step (m) may be used as the initial readings for the second test.

## 6.2 Sample recovery

- 6.2.1 Disconnect the impingers and pour the contents of the first and second impingers into the storage container. Rinse the impingers with distilled water and add the rinsings to the polyethylene storage container.

6.2.2 Remove the filter from its holder, place it in a container and seal.

### 6.3 Analysis

Neutralise the gaseous sample in the storage container and adjust to approximately pH 7 with 1M sulphuric acid. Transfer the solution, with appropriate washings, to a 250-ml volumetric flask and dilute to volume with distilled water. Remove a 10 ml of aliquot, add to a 150-ml beaker, and dilute with 100 ml citrate buffer. With the specific ion meter measure the potential developed by the solution from the calibration curve. Repeat this procedure for the blank solution. In the case of the filter, extract it into 0.5M sulphuric acid solution, adjust to pH 7 with 1M sodium hydroxide and follow the remaining procedure as for the gaseous sample.

## 7 Calculations

### 7.1 Fluorine concentration (equivalent HF) for gaseous or particulate fluorides

$$(C_{HF})_g \text{ or } (C_{HF})_p = \frac{(C_{ppm} - C_b)(V_{soln} / 1000)}{V_{std}}$$

Equation 3.1

where:

$(C_{HF})_g$	=	Concentration of fluorine (equivalent HF) for gaseous fluorides in test sample, at standard conditions, dry basis, $\text{mg m}^{-3}$
$(C_{HF})_p$	=	Concentration of fluorine (equivalent HF) for particulate fluorides in test sample, at standard conditions, dry basis, $\text{mg m}^{-3}$
$C_{ppm}$	=	Concentration of fluoride (equivalent HF), ppm as measured with the specific ion meter for the test solution
$C_b$	=	Concentration of fluoride (equivalent HF), ppm as measured with the specific ion meter for the blank solution
$V_{soln}$	=	Total volume of fluoride ions solution (first and second impingers), ml (usually 250 ml)
1000	=	ml in 1 litre, $\text{ml litre}^{-1}$
$V_{std}$	=	Volume of dry gas sample, standard conditions, $\text{m}^3$ (see Test Method 03.01, section 7.1).

### 7.2 Total fluorine concentration

$$(C_{HF})_T = (C_{HF})_g + (C_{HF})_p$$

Equation 3.2

where:

$(C_{HF})_T$	=	Total concentration of fluorine (equivalent HF), at standard conditions, dry basis, $\text{mg m}^{-3}$
$(C_{HF})_g$		obtained from Equation 3.1
$(C_{HF})_p$		obtained from Equation 3.1

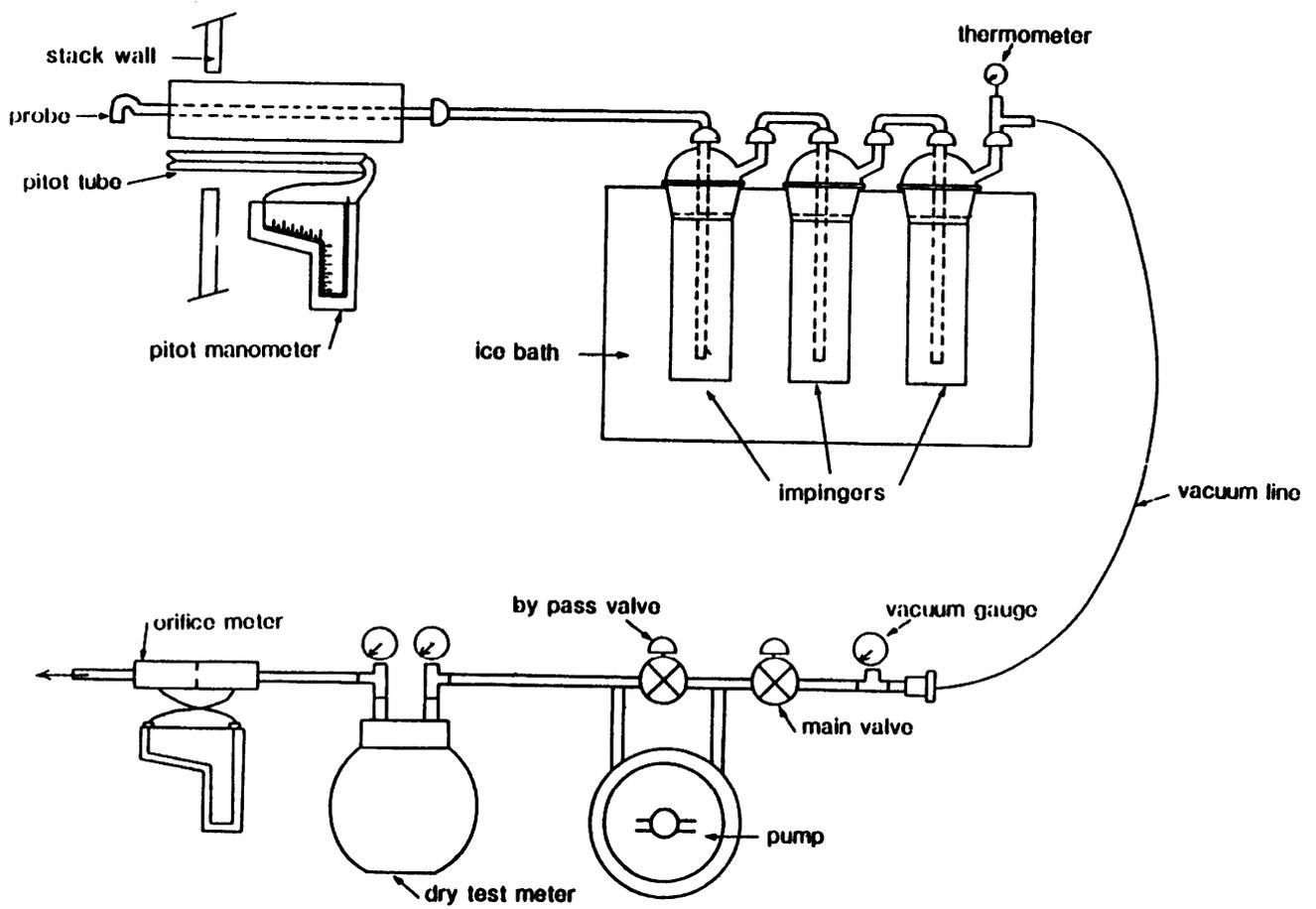


Figure 3.1 Fluorine sampling train

## South Australian Environment Protection Authority Method 03.04

### Determination of chlorine

Prepared by: TH Goh, May 1995

#### Contents

- 1 Scope
- 2 Principle
- 3 Apparatus
- 4 Reagents
- 5 Calibration
- 6 Procedure
- 7 Calculations

Figure 4.1 Chlorine sampling train

---

## 1 Scope

This method is applicable for the determination of chlorine emissions from stationary sources.

## 2 Principle

A gas sample is extracted from a sampling point in the stack or duct and reacted with a potassium iodide solution. The iodine liberated is titrated with standard thiosulphate solution using starch indicator. Oxidising substances may cause interference.

## 3 Apparatus

### 3.1 Sampling train

See Figure 4.1. Many of the design specifications of this sampling train are described in [Appendix 2](#).

- 3.1.1 Nozzle—any suitable material substantially resistant to attack by components of the gas stream may be used. The leading edge of the nozzle must be sharp and tapered.
- 3.1.2 Probe—any suitable material substantially resistant to chemical attack by components of the gas stream and having the necessary mechanical strength and heat resistance may be used. The probe must be fitted with a heating system to prevent condensation during sampling. The internal diameter of the probe should be approximately 5–6 mm.
- 3.1.3 Pitot tube—Type S, or equivalent, attached to the probe to monitor stack gas velocity.
- 3.1.4 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined manometer or equivalent capable of being read to within +5 Pa.
- 3.1.5 Impingers—3 impingers with glass ball joint fittings as shown in Figure 4.1. The first and third are of the Greenburg–Smith design modified by replacing the standard tip with a 1.2–cm internal diameter tube extending to 1 cm from the bottom of the impinger flask. The second is of the Greenburg–Smith design with standard tip.

Other collection systems of similar design approved by the EPA, Department of Environment and Natural Resources may be used.

- 3.1.6 Metering system—vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring temperature to within +1% of absolute temperature; dry gas meter to measure dry sample gas volume to within +2% accuracy; orifice meter, rotameter or equivalent, as required to maintain a proportional sampling rate ( $0.02\text{--}0.03\text{ m}^3\text{ min}^{-1}$ ) accurately to within +5%; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.
- 3.1.7 Barometer—to measure atmospheric pressure to +1 kPa. An aneroid barometer calibrated against a Fortin barometer would be acceptable.

## **3.2 Sample recovery**

- 3.2.1 Wash bottle—1.
- 3.2.2 Glass storage containers.

## **3.3 Analysis**

- 3.3.1 Volumetric flask—250 ml.
- 3.3.2 Burette—50 ml.
- 3.3.3 Wash bottle—1.
- 3.3.4 Pipette—25 ml.

# **4 Reagents**

## **4.1 Sampling**

- 4.1.1 Silica gel—self indicating type, 6–20 mesh, dried at 175°C for 2 hours.
- 4.1.2 Water—deionised, distilled.
- 4.1.3 Potassium iodide (0.1M).
- 4.1.4 Crushed ice.

## **4.2 Sample recovery**

- 4.2.1 Water—deionised, distilled.

## **4.3 Analysis**

- 4.3.1 Water—deionised, distilled.
- 4.3.2 Sodium thiosulfate (0.02M) —prepared by dissolving approximately 5 g of pure grade sodium thiosulphate pentahydrate ( $\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}$ ) in recently boiled distilled water and making to 1 litre. To prevent decomposition where the solution is to be kept for other than a few days, 3 drops of chloroform or 10 mg of mercuric iodide, and 0.1g of sodium carbonate must be added. At the first appearance of any growth or precipitate, and at least each 4 months the prepared sodium thiosulfate must be discarded. The sodium thiosulfate is to be standardised against potassium iodate or potassium bromate as primary standard.

- 4.3.3 Starch indicator solution—make a paste of 1 g of soluble starch with a little water, and pour the paste, with stirring, into 100 ml of boiling water, and boil for 1 minute. Allow the solution to cool and add approximately 2 g of potassium iodide and 5 mg of mercuric iodide. Store the solution in a stoppered bottle. The indicator may be kept for several months.

## 5 Calibration

The orifice meter, rotameter, pitot tube, dry gas meter and probe heater must be calibrated against standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources.

## 6 Procedure

### 6.1 Sampling

6.1.1 Determine the following source parameters:

- a minimum number of sampling points (Test Method 03.09)
- b gas velocity and volumetric flow rate (Test Method 03.10)
- c molecular weight of stack gas (Test Method 03.08)
- d moisture content of stack gas (Test Method 03.13).

6.1.2 Preparation of sample collection train. Place 75 ml of 0.1M potassium iodide solution in each of the first and second impingers, and about 200 g of silica gel in the third impinger. Retain a portion of the potassium iodide for use as a blank. Assemble the train with the probe as shown in Figure 4.1. Leak check the system at the sampling site by disconnecting the probe and plugging the inlet to the first impinger and pulling a 50-kPa vacuum. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  at a vacuum of 50 kPa is acceptable. Following the leak check, reconnect the probe to the sampling train. Turn on the probe heating system and adjust the probe heater setting to prevent condensation during sampling. Place crushed ice around the impingers. As necessary add more ice during the run to keep the temperature of the gases leaving the last impinger at  $20^\circ\text{C}$  or less.

6.1.3 Train operation. The procedure shall be as follows:

- a Set up the sampling train as described in section 6.1.2. Note: For each sample run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the nozzle is located at the first sampling point. Turn the probe tube so that the nozzle is at  $90^\circ$  to the gas flow.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases.
- d Turn the probe tube until the nozzle is pointing directly into the gas stream.
- e Start the pump and adjust the gas flow proportionally to a rate within the range  $0.02\text{--}0.03 \text{ m}^3 \text{ min}^{-1}$ . Sample for at least 5 minutes.
- f After sampling has been completed at the first sampling point, quickly move the probe tube to reposition the nozzle at the next sampling point. Adjust the control valve immediately to the flow rate that was appropriate for the first sampling point.
- g Repeat steps (e) to (g) until sampling has been taken at all the points on the first sampling traverse. Maintain proportional (non-isokinetic) conditions throughout the sampling period and use the same time interval at each sampling point.
- h At the completion of the first sampling traverse, turn off the pump. Remove the probe tube and nozzle from the access hole.

- i Where sampling is to be carried out at more than one sampling traverse, repeat steps (b) to (h).
- j At the conclusion of sampling, disconnect the probe and nozzle from the impinger train.
- k Disconnect the impingers and handle carefully in accordance with the sample recovery process (section 6.2).
- l Where repeat samples are required, steps (a) to (k) shall be repeated under comparable plant conditions and as soon as is practicable.

## 6.2 Sample recovery

Disconnect the impingers and pour the contents of the first and second impingers into the storage container. Rinse the impingers with distilled water and add the rinsings to the storage container.

## 6.3 Analysis

Transfer the sample from the storage container to a 250-ml volumetric flask and make to volume. Pipette a 25-ml aliquot of the sample solution into a 250-ml Erlenmeyer flask, add 50 ml of water and titrate with standard sodium thiosulphate to a pale yellow colour. Add 1 ml of starch indicator and continue the titration until the blue starch-iodine colour just disappears.

Repeat the titration twice more and on the potassium iodide blank. Record the volumes of titrant used in each case.

## 7 Calculation

### 7.1 Chlorine concentration

$$C_{Cl} = \frac{k(V_t - V_b)M(V_{soln})}{V_{std}}$$

$$C_{Cl} = \frac{35.5(V_t - V_b)M V_{soln}}{V_{std} V_a}$$

Equation 4.1

where:

$C_{Cl}$	=	Concentration of chlorine, at standard conditions, dry gas basis, $\text{mg m}^{-3}$
$V_t$	=	Volume of titrant used to titrate potassium iodide aliquot, ml
$V_b$	=	Volume of titrant used to titrate blank, ml
$V_{soln}$	=	Total of volume of potassium iodide solution (first and second impingers), ml
$V_a$	=	Volume of aliquot, ml
$k$	=	Conversion factor, $35.5 \text{ mg litre mol}^{-1} \text{ ml}^{-1}$
$V_{std}$	=	Volume of dry gas, standard conditions, $\text{m}^3$ (see Test Method 03.01, section 7.1)
$M$	=	Molarity of sodium thiosulphate solution, $\text{mol litre}^{-1}$

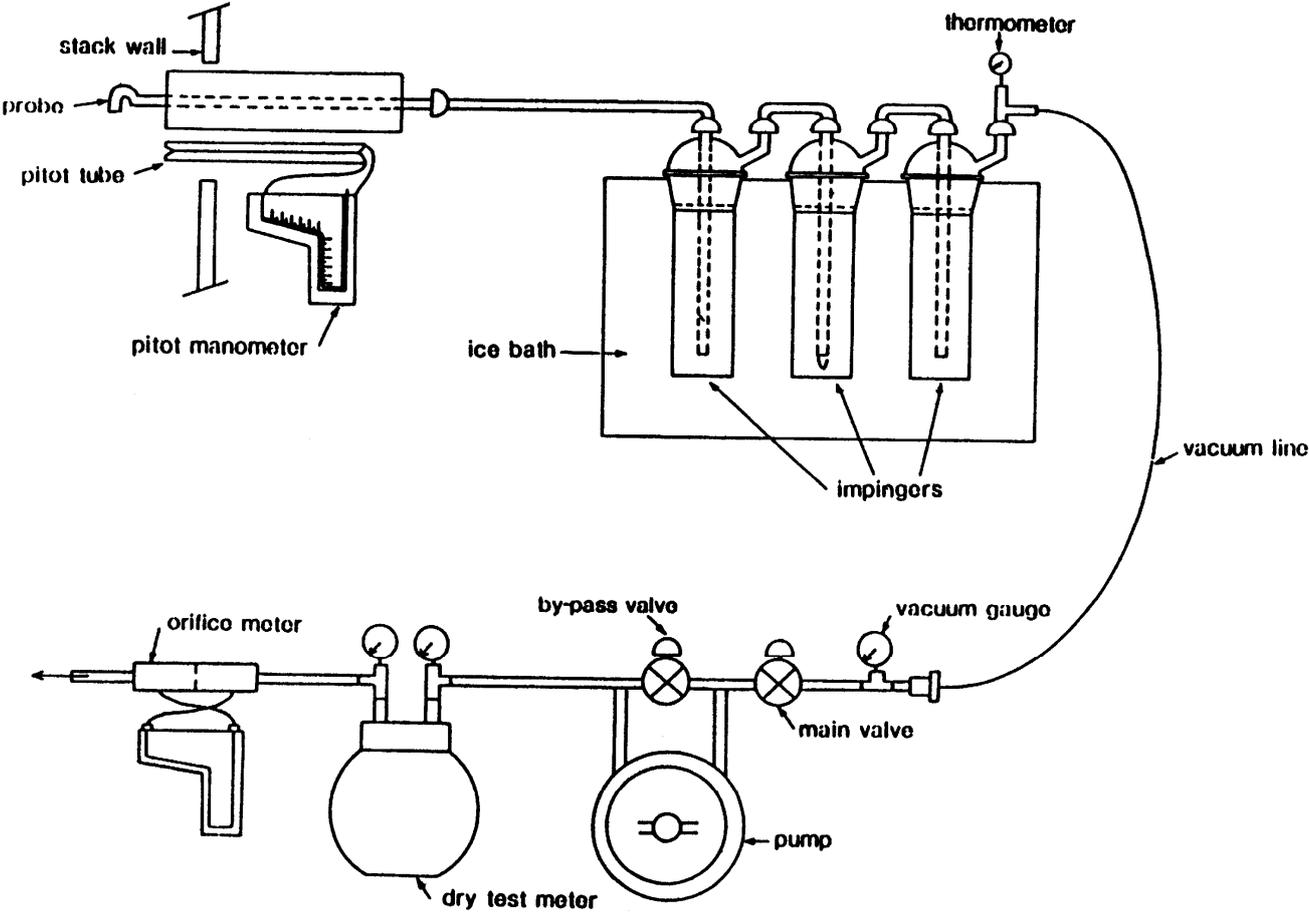


Figure 4.1 Chlorine sampling train

## South Australian Environment Protection Authority Method 03.05

### Determination of hydrogen sulphide

Prepared by: TH Goh, May 1995

#### Contents

- 1 Scope
- 2 Principle
- 3 Apparatus
- 4 Reagents
- 5 Calibration
- 6 Procedure
- 7 Calculations
- 8 Modifications to method

Figure 5.1 Hydrogen sulphide sampling train

---

## 1 Scope

This method is specific for the determination of hydrogen sulphide emissions from stationary sources.

## 2 Principle

A gas sample is extracted from a sampling point in the stack or duct and reacted with alkaline cadmium hydroxide to form cadmium sulphide. To minimise photo-decomposition of the precipitated sulphide the impingers are wrapped in aluminium foil. The collected sulphide is determined by spectro-photometric measurement of the methylene blue produced by the reaction of the sulphide ion with p-aminodimethylaniline in the presence of ferric chloride. An impinger containing hydrogen peroxide is included to remove sulphur dioxide as an interfering species.

## 3 Apparatus

### 3.1 Sampling train

Many of the design specifications for the sampling train, shown in Figure 5.1, are given in [Appendix 2](#).

- 3.1.1 Nozzle—the nozzle may be made of any material substantially resistant to chemical attack by components of the gas stream, and having the necessary mechanical strength and heat resistance. The leading edge of the nozzle must be sharp and tapered.
- 3.1.2 Probe—constructed of any suitable material substantially resistant to chemical attack by components of the gas stream, and having the necessary mechanical strength and heat resistance. The probe must be fitted with a heating system to prevent condensation during sampling.
- 3.1.3 Pitot tube—Type S, or equivalent, attached to monitor stack gas velocity.
- 3.1.4 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined manometer or equivalent capable of being read to within +5 Pa.

- 3.1.5 Filter holder—borosilicate glass or other suitable material which will not react with components of the gas stream, and fitted with a heating system to prevent condensation during sampling.
- 3.1.6 Impingers—5 impingers with glass ball-joint fittings connected in series (Figure 5.1). The first, third and fourth impingers are of the Greenburg–Smith design with standard tip. The second and fifth are of the Greenburg–Smith design, modified by replacing the standard tip with a 1.2-cm internal diameter tube extending to 1 cm from the bottom of the impinger flask.

Other collection systems of similar design approved by the EPA, Department of Environment and Natural Resources may be used.

- 3.1.7 Metering system—vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring temperature to within  $\pm 1\%$  of absolute temperature; dry gas meter to measure dry gas volume to within  $+2\%$  accuracy; orifice meter, rotameter or equivalent, as required to maintain a proportional sampling rate ( $0.02\text{--}0.03\text{ m}^3\text{ min}^{-1}$ ) to within  $+5\%$  accuracy; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.
- 3.1.8 Barometer—to measure atmospheric pressure to  $\pm 1\text{ kPa}$ . An aneroid type barometer standardised against a Fortin type barometer would be acceptable.

## 3.2 Sample recovery

- 3.2.1 Wash bottle—1.
- 3.2.2 Glass storage container.

## 3.3 Analysis

- 3.3.1 Spectrophotometer—any spectrophotometer capable of being operated in the visible region of the spectrum having an adjustable wavelength scale and with either percent transmittance or absorbance read out. The spectrophotometer must be fitted to take cells of 1 cm light path.
- 3.3.2 Wash bottle—1.
- 3.3.3 Volumetric flasks—250 ml.
- 3.3.4 Pipette—10 ml, 2 ml.

# 4 Reagents

## 4.1 Sampling

- 4.1.1 Filter—glass fibre, MSA 1106 BH™ or equivalent.
- 4.1.2 Silica gel—indicating type, 6–20 mesh, dried at  $175^\circ\text{C}$  for 2 hours.
- 4.1.3 Water—deionised, distilled.
- 4.1.4 Crushed ice.
- 4.1.5 Absorbing solution—dissolve 4.3 g of cadmium sulphate ( $3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) in deionised, distilled water. Mix with a solution containing 0.3 g of sodium hydroxide in deionised, distilled water and dilute to 1 litre. Mix well before using. Store in a dark bottle.
- 4.1.6 Hydrogen peroxide, 3%—dilute 100 ml of 30% hydrogen peroxide to 1 litre with deionised, distilled water.

## 4.2 Sample recovery

4.2.1 Water—deionised, distilled.

## 4.3 Analysis

4.3.1 Water—deionised, distilled.

4.3.2 Amine-sulphuric and stock solution—add 50 ml of concentrated sulfuric acid (S.G. 1.84) to 30 ml of deionised, distilled water and cool. Dissolve 12 g of N,N-dimethyl-p-phenylenediamine dihydrochloride in the acid. Store the stock solution in the refrigerator.

4.3.3 Amine-sulphuric acid test solution—dilute 25 ml of the amine-sulphuric acid stock solution with 1:1 sulphuric acid to a total volume of 1 litre.

4.3.5 Sodium sulphide standard solution—dissolve 0.71 g of sodium sulfide ( $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ ) in deionised, distilled water and dilute to 1 litre. The approximate concentration of the standard solution is equivalent to 100 ug of hydrogen sulfide per ml of solution. Determine the exact concentration by iodometric titrations with standard iodine and thiosulfate solutions.

## 5 Calibration

5.1 The orifice meter, rotameter, pitot tube, dry gas meter probe heater and filter heater must be calibrated against standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources.

5.2 Spectrophotometer—prepare a calibration curve of concentration of hydrogen sulphide (ug  $\text{H}_2\text{S}$ ) against absorbance at 670 nm by making the appropriate dilutions of the sodium sulphide standard solution (section 4.3.5), adding each of the diluted solutions to 75ml of the absorbing solution (section 4.1.5) and following the analysis procedure set out in section 6.3.1.

## 6 Procedure

### 6.1 Sampling

6.1.1 Determine the following source parameters:

- a minimum number of sampling points (Test Method 03.09)
- b gas velocity and volumetric flow rate (Test Method 03.10)
- c molecular weight of stack gas (Test Method 03.08)
- d moisture content of stack gas (Test Method 03.13).

6.1.2 Preparation of sample collection train. Place 75 ml of 3% hydrogen peroxide in the first impinger, leave the second impinger empty, place 75 ml of the cadmium sulphate absorbing solution in the third and fourth impingers and about 200 g of silica gel in the fifth impinger. Protect the third and fourth impingers from light with aluminium foil wrapping. Retain a 150-ml portion of the absorbing solution for use as a blank solution. Assemble the filter in the filter holder and set up the sample collection as shown in Figure 5.1 with the probe. Leak check the sampling train at the sampling site by disconnecting the probe and plugging the inlet to the first impinger and pulling a 50-kPa vacuum. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  at 50 kPa is acceptable. Following the leak check, reconnect the probe to the sampling train. Turn on the probe heating system and adjust the probe heater to prevent condensation during sampling. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at  $20^\circ\text{C}$  or less.

6.1.3 Sample train operation. The procedure shall be as follows:

- a Set up the sampling train as described in section 5.1.2. Note: For each sample run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the nozzle is located at the first sampling point. Turn the probe tube so that the nozzle is at 90° to the gas flow.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases.
- d Turn the probe tube until the nozzle is pointing directly into the gas stream.
- e Start the pump and adjust the gas flow proportionally to a rate within the range 0.02–0.03 m<sup>3</sup> min<sup>-1</sup>. Sample for at least 5 minutes.
- f After sampling has been completed at the first sampling point, quickly move the probe tube to reposition the nozzle at the next sampling point. Adjust the control valve immediately to the flow rate that was appropriate for the first sampling point.
- g Repeat steps (e) to (f) until sampling has been taken at all the points on the first sampling traverse. Maintain proportional (non-iso-kinetic) conditions throughout the sampling period and use the same time interval at each sampling point.

Where the sampling train is equipped with a dry gas meter, record the meter readings at the beginning and end of sampling time at each sampling point.

- h At the completion of the first sampling traverse, turn off the pump. Remove the probe tube and nozzle from the access hole.
- i Where sampling is to be carried out at more than one sampling traverse, repeat steps (b) to (h).
- j At the conclusion of sampling, disconnect the probe and nozzle from the impinger train.
- k Disconnect the impingers and handle carefully in accordance with sample recovery process (section 6.2).
- l When repeat samples are required, steps (a) to (k) shall be repeated under comparable plant conditions as soon as is practicable.

## 6.2 Sample recovery

- 6.2.1 Discard the contents of the hydrogen peroxide impinger. Pour the contents of the third and fourth impingers into the storage container which is protected from light with aluminium foil wrapping. Rinse the impingers and all connecting glassware with deionised, distilled water and add the rinsings to the storage container.

## 6.3 Analysis

- 6.3.1 Transfer the sample from the storage container to a 250-ml volumetric flask, add 10 ml of amine-sulphuric acid test solution and 1 drop of ferric chloride solution and dilute to volume. A reference reagent blank is prepared by adding the above amounts of test reagent and ferric chloride to 150 ml of absorbing solution in a 250-ml volumetric flask and diluting to the mark. Allow the reference blank and test solutions to stand in the dark and measure the absorbance at 670 nm at precisely 30 minutes after the solutions have been mixed. If the colour of the test solution is too intense to measure the absorbance, make the relevant dilution in addition to that for the reference blank and remeasure the absorbance at 670 nm. Determine the concentration of hydrogen sulfide in the test and blank solutions from the calibration curve.

## 7 Calculations

### 7.1 Hydrogen sulphide concentration

$$C_{H_2S} = \frac{(C_t - C_b)D}{1000V_{std}} \quad \text{Equation 5.1}$$

where:

$C_{H_2S}$  = Concentration of hydrogen sulphide in stack gas at standard conditions, dry basis,  $mg\ m^{-3}$

$C_t$  = Concentration of hydrogen sulphide in the test solution as measured with the methylene blue-spectrophotometric method,  $ug$

$C_b$  = Concentration of hydrogen sulphide in the blank solution as measured with the methylene blue-spectrophotometric method,  $ug$

$D$  = Dilution factor, applicable if the test solution is diluted for measurement with the spectrophotometer

$V_{std}$  = Dry gas volume, standard conditions,  $m^3$  (see Test Method 03.01, section 7.1)

## 8 Modifications to method

Alternative equipment and procedures for determining hydrogen sulphide may be used where approval is given by the EPA, Department of Environment and Natural Resources.

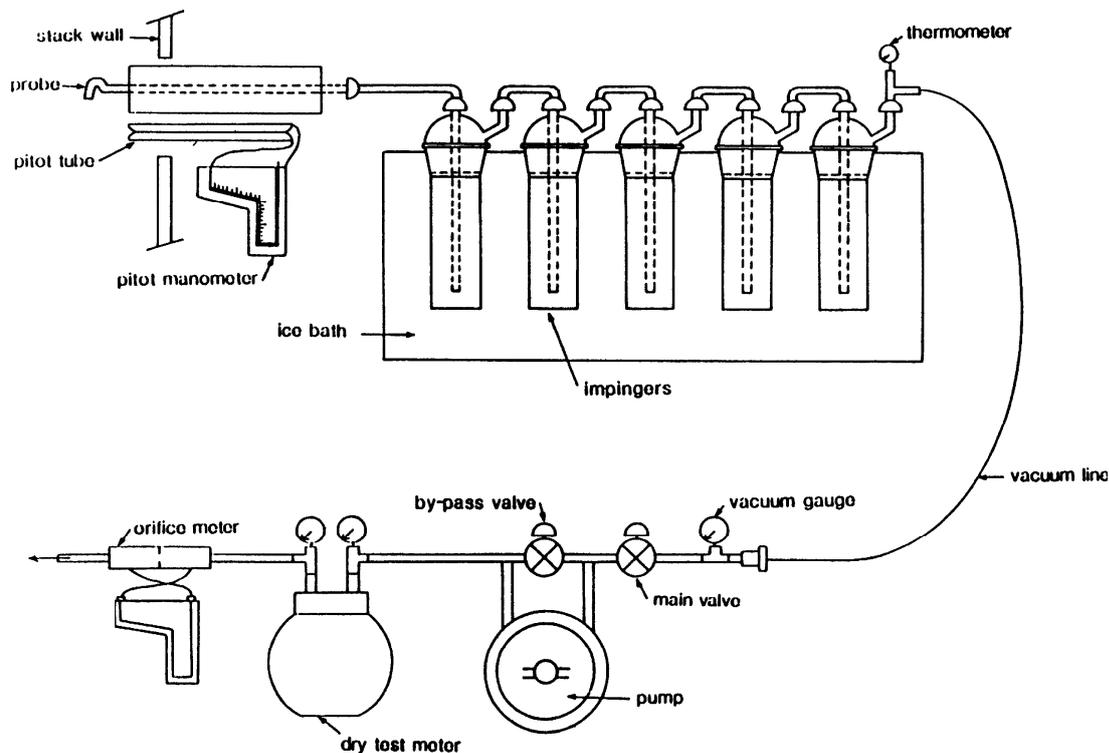


Figure 5.1 Hydrogen sulphide sampling train

**South Australian Environment Protection Authority Method 03.06****Determination of nitrogen oxides****Prepared by: TH Goh, May 1995****Contents**

1	Scope
2	Principle
3	Apparatus
4	Reagents
5	Calibration
6	Procedure
7	Calculations
8	Modifications to method

Figure 6.1 Sampling train—flask valve and flask

---

**1 Scope**

This method is applicable for the determination of nitrogen oxides in stationary sources.

**2 Principle**

A grab sample from the stack or duct is collected in an evacuated flask containing dilute sulphuric acid-hydrogen peroxide absorbing solution, and the nitrogen oxides, except nitrous oxide are determined colorimetrically using the phenol-disulphonic acid procedure.

Interference to the analysis is caused by nitrites and chlorides.

**3 Apparatus****3.1 Sampling**

See Figure 6.1.

- 3.1.1 Probe—borosilicate glass or other suitable material substantially resistant to attack by the components of the gas stream. The probe must be fitted with a heating system to prevent condensation during sampling, and a filter to remove particulate matter. Heating of the probe is unnecessary if it remains dry during the purging period.
- 3.1.2 Collection flask—2 litre, borosilicate glass, round bottom with a short neck and 24/40 standard taper opening, with implosion shield.
- 3.1.3 Flask valve—T-bore stopcock connected to a 24/40 standard taper joint and two ball and socket joints as shown in Figure 6.1.
- 3.1.4 Thermometer—capable of measuring to  $\pm 1\%$  of absolute temperature.

- 3.1.5 Barometer—capable of measuring atmospheric pressure to +1 kPa.
- 3.1.6 Vacuum line—tubing capable of withstanding a vacuum of 100 Pa absolute pressure, with 'T' connection and T-bore stopcock, or equivalent.
- 3.1.7 Pressure gauge—101.3 kPa U-tube mercury manometer, or equivalent, capable of being read to an accuracy of +1 kPa.
- 3.1.8 Pump—capable of producing a vacuum of 1 kPa, or better.
- 3.1.9 Squeeze bulb—one way.

### **3.2 Sample recovery**

- 3.2.1 Pipette or dropper.
- 3.2.2 Glass storage containers—suitable for transport.
- 3.2.3 Wash bottle.

### **3.3 Analysis**

- 3.3.1 Steam bath.
- 3.3.2 Beakers or casseroles—250 ml, one for each sample and standard (blank).
- 3.3.3 Volumetric pipettes—1, 2 and 10 ml.
- 3.3.4 Transfer pipette—10 ml with 0.1 ml divisions.
- 3.3.5 Volumetric flasks—100 ml, sufficient for calibration of spectrophotometer and 1,000 ml, one for each sample, and one for the standard (blank).
- 3.3.6 Spectrophotometer—any type capable of measuring absorbance at 410 nm. The spectrophotometer must be fitted to take cells of a 1-cm light path.
- 3.3.7 Graduated cylinder—100 ml with 1.0 ml divisions.
- 3.3.8 Analytical balance—to measure to 0.1 mg.

## **4 Reagents**

### **4.1 Sampling**

- 4.1.1 Absorbing solution—add 3 ml of sulphuric acid (S.G. 1.84) to 1 litre of distilled water. Mix well and add 25 ml of 3% hydrogen peroxide. Prepare a fresh solution weekly, store in a dark bottle and avoid exposure to heat.

### **4.2 Sample recovery**

- 4.2.1 Sodium hydroxide (1M)—dissolve 40 g of sodium hydroxide in distilled water and dilute to 1 litre.
- 4.2.2 Red litmus paper.
- 4.2.3 Water—deionised, distilled.

## 4.3 Analysis

- 4.3.1 Fuming sulphuric acid—15 to 18% by weight free sulphur trioxide.
- 4.3.2 Phenol—white solid reagent grade.
- 4.3.3 Sulphuric acid—reagent grade (S.G. 1.84).
- 4.3.4 Standard solution—dry potassium nitrate ( $\text{KNO}_3$ ) for a minimum of 2 hours at 105–110°C and cool in a desiccator. Prepare a standard solution by dissolving 0.5495 g of the dry potassium nitrate in distilled water and diluting to 1 litre. For the working standard solution, dilute 10 ml of the resulting solution to 100 ml with distilled water. One ml of the working standard is equivalent to 25 ug nitrogen dioxide.
- 4.3.5 Water—deionised, distilled.
- 4.3.6 Phenoldisulphonic acid solution—dissolve 25 g of pure white phenol in 150 ml of sulphuric acid (S.G. 1.84) on a steam bath. Cool, add 75 ml of fuming sulphuric acid, and heat at 100°C for 2 hours. Store in a dark, stoppered bottle.
- 4.3.7 Concentrated ammonium hydroxide.

## 5 Calibration

### 5.1 Flask volume

Assemble the flask and flask valve and fill with water to the stopcock. Measure the volume of water to  $\pm 1$  ml. Number and record the volume on the flask.

### 5.2 Spectrophotometer

Prepare suitable reference solutions by adding measured volumes (0–16 ml) of working standard to each of a series of beakers containing 25 ml of absorbing solution. Add sodium hydroxide (1M) dropwise to each solution until alkaline to litmus paper. Follow the analysis procedure set out in section 5.3 below, making each reference solution to 100 ml. Measure the absorbance at 410 nm and plot a calibration curve of concentration nitrogen dioxide equivalent ( $\mu\text{g NO}_2$ ) against absorbance.

## 6 Procedure

### 6.1 Sampling

- 6.1.1 Determine the following source parameters:
- gas velocity and volumetric flow rate (Test Method 03.10)
  - molecular weight of stack gas (Test Method 03.08)
  - moisture content of stack gas (Test Method 03.15).
- 6.1.2 Pipette 25 ml of absorbing solution into a sample flask. Insert the flask valve stopper into the flask with the valve in the 'Purge' position. Assemble the sampling train as shown in Figure 6.1 and place the probe at the sampling point. Turn the flask valve and the pump valve to the 'Evacuate' positions. Carefully evacuate the flask to the point where the absorbing solution begins to boil gently. Turn the pump valve to its 'Vent' position, remove squeeze bulb and turn off the pump. Replace squeeze bulb. Check the manometer for any fluctuations in the mercury level. If there is a visible change over the span of one minute, check for leaks.

- 6.1.3 Record the initial volume, temperature, and pressure, and also record the barometric pressure. Turn the flask valve to its 'Purge' position and then do the same with the pump valve. Purge the probe and the vacuum tube using the squeeze bulb. If condensation occurs in the probe and flask valve area, heat the probe and purge until the condensation disappears. Then turn the pump valve to its 'Sample' position and allow sample to enter the flask for about 15 seconds. After collecting the sample, turn the flask valve to its 'Purge' position and disconnect the flask and stopcock from the sampling train. Shake the flask for 5 minutes.

## 6.2 Sample recovery

- 6.2.1 Let the flask set for a minimum of 16 hours and then shake the contents for 2 minutes. Connect the flask to a mercury filled U-tube manometer, open the valve from the flask to the manometer and record the flask pressure and final temperature along with the barometric pressure. If the barometric pressure differs from that when the initial readings were taken adjust the valve of the flask pressure to compare with the initial conditions, otherwise record the flask pressure as the final pressure. Transfer the flask contents to a container for transport or to a 250-ml beaker for analysis. Rinse the flask twice with distilled water (approx. 10 ml) and add the rinsings to the sample. For a blank use 25 ml of absorbing solution and the same volume of distilled water as used in rinsing the flask.

Prior to shipping or analysis, add sodium hydroxide (1M) dropwise to both the sample and the blank until alkaline to litmus paper (about 25–35 drops in each).

## 6.3 Analysis

- 6.3.1 If the sample has been transported in a container, transfer the contents to a 250-ml beaker using a small amount of distilled water. Evaporate the solution to dryness on a steam bath and then cool. Add 2 ml of phenol-disulphonic acid solution to the dried residue and triturate thoroughly with a glass rod. Make sure the solution contacts all the residue. Add 1 ml distilled water and four drops of concentrated sulphuric acid (S.G.1.84). Heat the solution on a steam bath for 3 minutes with occasional stirring. Cool, add 20 ml distilled water, mix well by stirring, and add concentrated ammonium hydroxide dropwise with constant stirring until alkaline to litmus paper. Transfer the solution to a 100-ml volumetric flask and wash the beaker three times with approximately 10-ml portions of distilled water. Dilute to the mark and mix thoroughly. If the sample contains solids, transfer a portion of the solution to a clean, dry centrifuge tube, and centrifuge, or filter a portion of the solution. Measure the absorbance of each sample at 410 nm using the blank solution as a zero. Dilute the sample and the blank with a suitable amount of distilled water if the absorbance falls outside the range of calibration.

## 7 Calculations

### 7.1 Sample volume

$$V_{sc} = \frac{T_{std}(V_f - V_a)(P_f / T_f - P_i / T_i)}{P_{std}}$$

$$V_{sc} = (0.359)(V_f - 25)(P_f / T_f - P_i / T_i)$$

Equation 6.1

where:

$V_{sc}$  = Sample volume at standard conditions (dry basis), ml

$T_{std}$  = Absolute temperature at standard conditions, 273 K

$P_{std}$  = Pressure at standard conditions, 101.3 kPa

$V_f$	=	Volume of flask and valve, ml
$V_a$	=	Volume of absorbing solution, 25 ml
$P_f$	=	Final absolute pressure of flask, kPa
$P_i$	=	Initial absolute pressure of flask, kPa
$T_f$	=	Final absolute temperature of flask, K
$T_i$	=	Initial absolute temperature of flask, K

## 7.2 Sample concentration

Determine the concentration of oxides of nitrogen (as NO<sub>2</sub>) from the spectrophotometer calibration curve.

$$C = \frac{(10^3 C_s)D}{V_{sc}}$$

Equation 6.2

where:

$C$	=	Concentration of nitrogen dioxide (as NO <sub>2</sub> ) equivalent at standard conditions, dry basis, mg m <sup>-3</sup>
$C_s$	=	Concentration of nitrogen dioxide equivalent as measured with the spectrophotometer, ug
$D$	=	Dilution factor, applicable if the test solution is diluted for measurement in spectrophotometer
$V_{sc}$	=	Sample volume at standard conditions (dry basis), ml (see Equation 6.1)

## 8 Modifications to method

Alternative equipment and procedures for determining nitrogen oxides may be used where approval is given by the EPA, Department of Environment and Natural Resources.

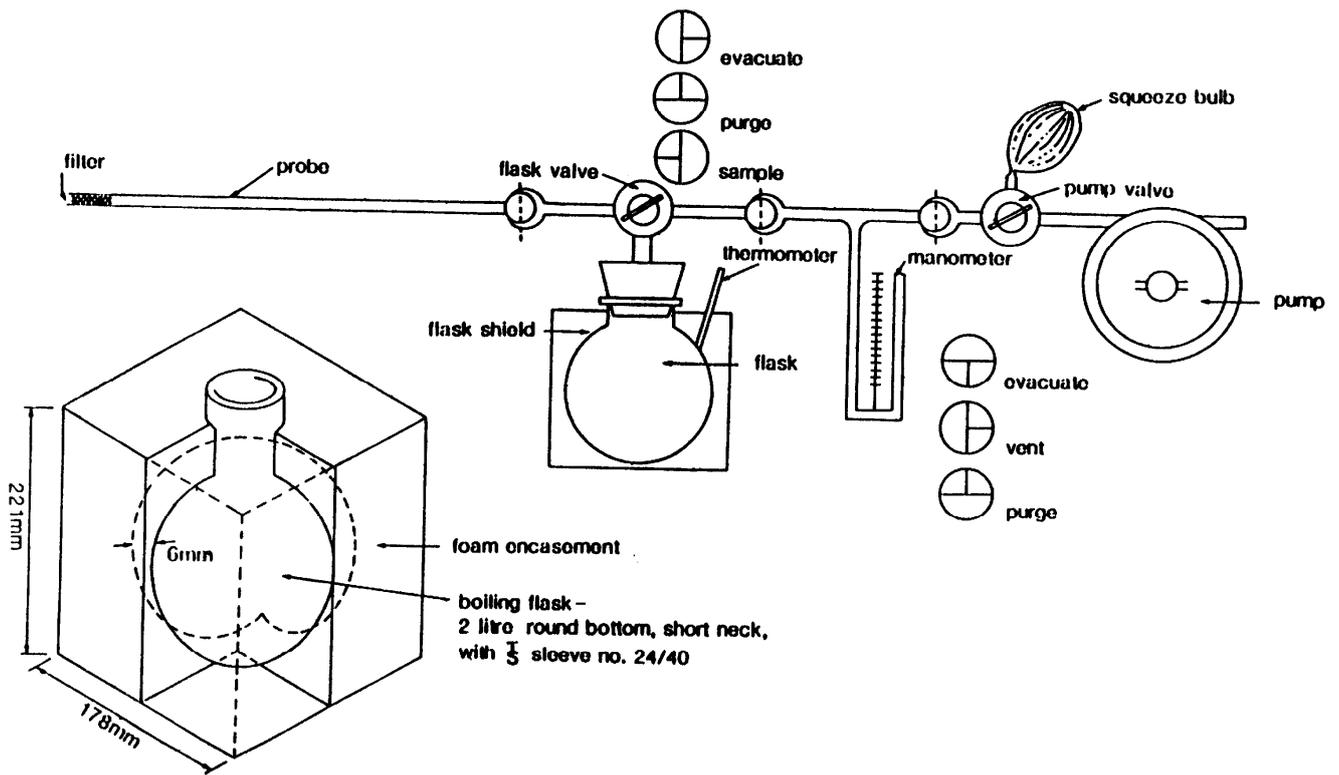


Figure 6.1 Sampling train-flask valve and flask

**South Australian Environment Protection Authority Method 03.07****Determination of metals: lead, copper, antimony, cadmium, arsenic, mercury****Prepared by: TH Goh, May 1995****Contents**

- 1 Scope
- 2 Principle
- 3 Apparatus
- 4 Reagents
- 5 Calibration
- 6 Procedure
- 7 Calculations

Figure 7.1 Metal vapour sampling train

---

**1 Scope**

This method is applicable for the determination of six heavy metals in stationary sources.

**2 Principle**

A sample from a gas stream is absorbed in a molar nitric acid solution and analysed for each of the six metals to which the method applies by conventional atomic absorption techniques. When organo-metallic compounds are present an absorbing solution of greater oxidising power may be necessary.

**3 Apparatus****3.1 Sampling train**

See Figure 7.1. Many of the design specifications of this sampling train are described in [Appendix 2](#).

- 3.1.1 Nozzle—any suitable material substantially resistant to the components of the gas stream may be used. The leading edge of the nozzle must be sharp and tapered.
- 3.1.2 Probe—any suitable material substantially resistant to chemical attack by components of the gas stream and having the necessary mechanical strength and heat resistance may be used. The probe must be fitted with a heating system to prevent condensation during sampling. The internal dimensions of the probe should be chosen so that for isokinetic sampling the flow rate through the impingers lies in the range  $0.02\text{--}0.03\text{ m}^3\text{ min}^{-1}$ .
- 3.1.3 Pitot tube—Type S, or equivalent.
- 3.1.4 Pitot manometer—a differential and static pressure instrument attached to pitot tube. It shall be an inclined manometer or equivalent capable of being read to within +5 Pa.
- 3.1.5 Impingers—3 impingers with glass ball joint fittings connected in series (Figure 7.1). The first and second impingers are of the Greenburg–Smith design. The third is modified by replacing the standard tip with a 1.2-cm internal diameter tube extending to 1 cm from the bottom of the flask.

- 3.1.6 Metering system—vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring to within +1% of absolute temperature; dry gas meter to measure dry gas volume to within +2% accuracy; orifice meter, rotameter or equivalent, as required to maintain isokinetic sampling rate to within +5% accuracy; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.
- 3.1.7 Barometer—to measure atmospheric pressure to  $\pm 1$  kPa. An aneroid barometer calibrated against a Fortin barometer would be suitable.

### **3.2. Sample recovery**

- 3.2.1 Wash bottle—1.
- 3.2.2 Glass storage containers.

### **3.3 Analysis**

- 3.3.1 Volumetric flask—1,000 ml.
- 3.3.2 Pipette—10 ml.
- 3.3.3 Atomic absorption spectrometer—any type of instrument should be found suitable.

## **4 Reagents**

### **4.1. Sampling**

- 4.1.1 Silica gel—self-indicating type, 6–20 mesh, dried at 175°C for 2 hours.
- 4.1.2 Absorbing solution—nitric acid (1M). For a solution of greater oxidising power, 3 g of potassium permanganate may be added to each litre of nitric acid used. This mixture should be used immediately and not stored.
- 4.1.3 Crushed ice.

### **4.2 Sample recovery**

- 4.2.1 Water—deionised, distilled water.

### **4.3. Analysis**

- 4.3.1 Water—deionised, distilled water.
- 4.3.2 Hydrogen peroxide—30% solution. This solution is only required for absorbing solutions containing potassium permanganate.
- 4.3.3 Hydroxylamine hydrochloride solution—dissolve 50 g of hydroxylamine in 100 ml of distilled water. This solution is only required for absorbing solutions containing potassium permanganate.
- 4.3.4 Sulphuric acid—S.G. 1.84, pure grade.
- 4.3.5 Standard solutions—the following standard solutions each containing 1 mg ml<sup>-1</sup> of the appropriate metal may be prepared by dissolving the stated reagent and making the resultant solution to 1 litre with distilled water.
- a Standard lead solution—dissolve 1.599 g of A.R. lead nitrate [Pb(NO<sub>3</sub>)<sub>2</sub>] in 500 ml of 1M nitric acid and dilute to 1 litre with distilled water.

- b Standard antimony solution—dissolve 2.669 g of A.R. antimony potassium tartrate ( $\text{KSbOC}_4\text{H}_4\text{O}_6$ ) in distilled water and dilute to 1 litre with distilled water.
- c Standard copper solution—dissolve 1 g of A.R. copper metal in 50 ml of concentrated nitric acid (S.G.1.52) and dilute to 1 litre with distilled water.
- d Standard cadmium solution—dissolve 2.282 g of A.R. cadmium sulphate ( $\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$ ) in 500 ml of 1M hydrochloric acid and dilute to 1 litre with distilled water.
- e Standard arsenic solution—dissolve 1.320 g A.R. arsenious oxide in the minimum volume of 1M sodium hydroxide, acidify with dilute hydrochloric acid and dilute to 1 litre with distilled water.
- f Standard mercury solution—dissolve 1.356 g of mercuric (II) chloride in 0.1M sulphuric acid and dilute to 1 litre with distilled water.

## 5 Calibration

5.1 The orifice meter, pitot tube, dry gas meter and probe heater must be calibrated against the standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources.

### 5.2 Atomic absorption spectrometer

Use appropriate dilutions of the standard metal solutions to prepare a series of working standards and calibrate the spectrometer against these solutions. Draw a calibration graph of concentration metal ion ( $\mu\text{g m}^{-1}$ ) against absorption.

## 6 Procedure

### 6.1 Sampling

6.1.1 Determine the following source parameters:

- a minimum number of sampling points (Test Method 03.09)
- b gas velocity, volumetric flow rate and isokinetic nozzle size ( Test Method 03.10)
- c molecular weight of stack gas (Test Method 03.08)
- d moisture content of stack gas (Test Method 03.13).

6.1.2 Preparation of the sample collection train. Place 75 ml of the absorbing solution in each of the first and second impingers, and about 200 g of silica gel in the third impinger. Retain a 150-ml portion of the absorbing solution for use as a blank solution. Assemble the sample collection train as shown in Figure 7.1 with the probe. Leak check the sampling train at the sampling site by disconnecting the probe and plugging up the inlet to the first impinger and pulling a 50-kPa vacuum. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  at 50 kPa is acceptable. Following the leak check, reconnect the probe to the sampling train. Turn on the probe heating system and adjust the probe heater to prevent condensation during sampling. Place crushed ice around the impingers. Add more ice during the run to keep the temperature of the gases leaving the last impinger at  $20^\circ\text{C}$  or less.

6.1.3 Sample train operation. The procedure shall be as follows:

- a Set up the sampling train as described in section 6.1.2 and install the correct entry nozzle. Note: for each run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the nozzle is located at the first sampling point. Turn the probe tube so that the nozzle is at  $90^\circ$  to the gas flow.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases.
- d Turn the probe tube until the nozzle is pointing directing into the gas stream.

- e Start the pump and adjust the gas flow to iso-kinetic conditions. Sample for at least 5 minutes.
- f After sampling has been completed at the first sampling point, quickly move the probe tube to reposition the nozzle at the next sampling point.
- g Adjust the control valve immediately to the iso-kinetic flow reading appropriate to the next sampling point.
- h Repeat steps (e) to (g) until sampling has been taken at all the points on the first sampling traverse. Maintain isokinetic conditions throughout the sampling period and use the same time interval at each sampling point.

Where the sampling train is equipped with a dry gas meter, record the meter readings at the beginning and end of sampling time at each sampling point.

- i At the completion of the first sampling traverse, turn off the pump. Remove the probe tube and nozzle from the access hole.
- j Where sampling is to be carried out at more than one sampling traverse, repeat steps (b) to (i).
- k At the conclusion of sampling, disconnect the probe and nozzle from the impinger train.
- l Disconnect the impingers and handle carefully in accordance with the sample recovery process (section 6.2).
- m If velocity measurement and gas sampling have not been carried out simultaneously at adjacent sampling points, repeat the readings of gas velocity and temperature at each sampling point as sampling at all sampling points is completed. If the average of the gas velocity readings differ by more than +10% from the average of the original readings recorded in section 6.1.1(b), the test result shall be regarded as inaccurate.
- n When repeat samples are required, steps (a) to (m) shall be repeated under comparable plant conditions and as soon as is practicable.

If this second sampling follows immediately after the first, the gas velocity and temperature readings taken at step (m) may be used as the initial readings for the second test.

## 6.2 Sample recovery

- 6.2.1 Remove the absorbing solution from each of the first and second impingers and place in a glass sample storage container. Rinse the impingers and all connecting glassware with distilled water and add the rinsings to the storage container.

## 6.3 Analysis

- 6.3.1 Metal ion solution—transfer the absorbing solution to a 1-litre volumetric flask and dilute to volume with distilled water. If potassium permanganate has been added to the absorbing solution, transfer the contents of the impingers to a 250-ml beaker, add 25 ml of sulphuric acid\* (S.G. 1.84) and evaporate carefully to the first appearance of white sulphuric acid fumes. Dilute the solution to approximately 150 ml and add hydrogen peroxide solution carefully, and with constant stirring, until the permanganate colour just disappears. Add 1 ml of hydroxylamine hydrochloride solution and heat just to boiling, cool\* and dilute to 1 litre.

Follow the same procedure for the blank solution.

\* Should a white precipitate of lead sulphate appear, dilute, neutralise with ammonium hydroxide, then add sufficient 50% lead free ammonium citrate solution to dissolve precipitate.

- 6.3.2 Analysis for metal—remove an aliquot of the metal ion solution and measure the absorption at the appropriate wavelength given in Table 7.1 using an atomic absorption spectrometer. Repeat the operation for the blank solution and determine the quantity of metal ion in the solution from the appropriate calibration curve. If the

solution gives an absorption greater than the upper limit of the range of the calibration curve, make appropriate dilutions to the solution and remeasure the absorption.

**Table 7.1**

<b>Metal</b>	<b><math>\lambda</math> Max. (nm)</b>
Lead	217.0
Cadmium	288.8
Antimony	217.6
Copper	324.7
Mercury	253.7
Arsenic	193.7

## 7 Calculations

### 7.1 Metal concentration

Concentration of lead, cadmium, antimony, copper, arsenic and mercury.

$$C_m = \frac{C_a}{V_{std}}$$

Equation 7.1

where:

$C_m$  = Concentration of metal ion, at standard conditions, dry basis

$C_a$  = Concentration of metal ion measured by atomic absorption spectrometer and determined from appropriate calibration curve, ppm =  $\mu\text{g ml}^{-1}$  =  $\text{mg litre}^{-1}$  = mg collected

$V_{std}$  = Dry gas volume, standard conditions,  $\text{m}^3$  (see Test Method 03.01, section 7.1)

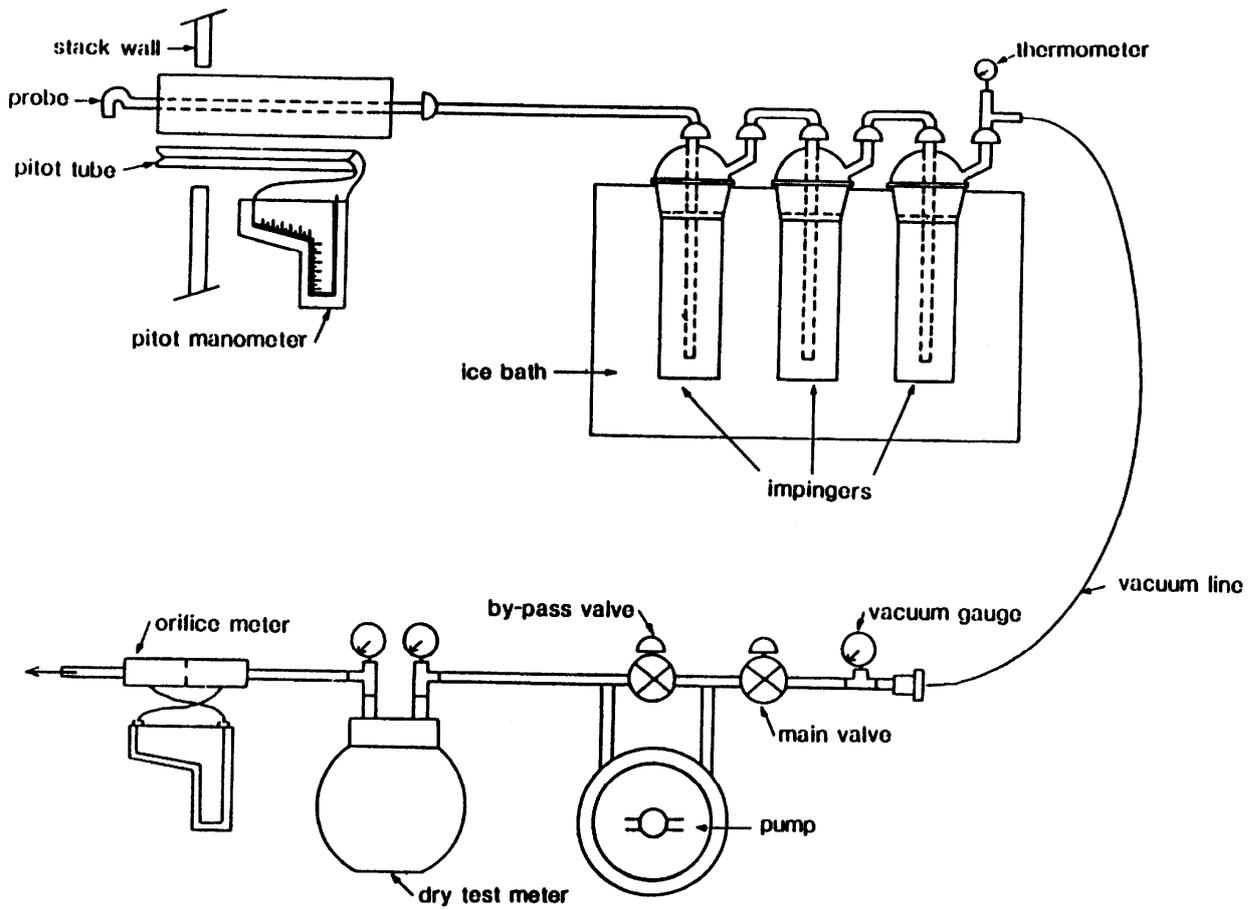


Figure 7.1 Metal vapour sampling train

**South Australian Environment Protection Authority Method 03.08****Gas analysis and dry molecular weight****Prepared by: TH Goh, May 1995****Contents**

1	Scope
2	Applicability
3	Principle
4	Apparatus
5	Procedure
6	Calculations
Figure 8.1	Grab gas sampling train
Figure 8.2	Integrated gas sampling train

---

**1 Scope**

This method is applicable for the determination of carbon dioxide and dry molecular weight in stationary sources.

**2 Applicability**

Although carbon dioxide emissions are not regulated it is necessary for carbon dioxide concentrations to be measured so that correction can be made to the emission rates of particulate material from incinerators and industrial plant. The calculation of dry molecular weight is necessary where it is desired to measure stack gas velocity and subsequently isokinetic variation.

**3 Principle**

An integrated gas sample or a series of grab gas samples is extracted for analysis for carbon dioxide or other components by means of apparatus approved by the EPA, Department of Environment and Natural Resources.

**4 Apparatus****4.1 Grab sample (Figure 8.1)**

- 4.1.1 Probe—stainless steel or borosilicate glass, equipped with a filter to remove particulate matter.
- 4.1.2 Pump—one-way squeeze bulb, or equivalent to transport gas sample to analyzer.

**4.2 Integrated sample (Figure 8.2)**

- 4.2.1 Probe—stainless steel or borosilicate glass, equipped with a filter to remove particulate matter.
- 4.2.2 Air-cooled condenser or equivalent—to remove any excess moisture.
- 4.2.3 Needle valve—to adjust flow rate.

- 4.2.4 Pump—leak-free, diaphragm type, or equivalent, to transport gas to the bag. Install a surge tank between the pump and rate meter to eliminate pulsation effect of pump on the rotameter.
- 4.2.5 Rate meter—to measure a flow range from 0 to 1.0 litre minute<sup>-1</sup>.
- 4.2.6 Flexible bag—Tedlar™, or equivalent, with a capacity of 50–80 litres. Leak test the bag in the laboratory before using.
- 4.2.7 Pitot tube—Type S, or equivalent, attached to the probe so that the sampling flow rate can be regulated proportional to the stack gas velocity when velocity is varying with time or a sample traverse is conducted.
- 4.2.8 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined manometer or equivalent capable of being read to within  $\pm 5$  Pa.

### **4.3 Analysis**

- 4.3.1 Gas analysis—apparatus approved by the EPA, Department of Environment and Natural Resources.

## **5 Procedure**

### **5.1 Grab sampling**

- 5.1.1 Set up the equipment as shown in Figure 8.1, making sure all connections are leak free. Place the probe in the stack at a sampling point and purge the sampling line.
- 5.1.2 Draw sample into the analyser.

### **5.2 Integrated sampling**

- 5.2.1 Evacuate the flexible bag. Set up the equipment as shown in Figure 8.2 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are tight and that there are no leaks.
- 5.2.2 Sample at a rate proportional to the stack gas velocity.

### **5.3. Analysis**

- 5.3.1 Determine the carbon dioxide, oxygen and carbon monoxide concentrations as soon as possible. If gas absorption apparatus is used, make as many passes as are necessary to give constant readings.
- 5.3.2 For grab sampling, repeat the sampling and analysis until three consecutive samples vary no more than 0.5 % by volume for each component being analysed.
- 5.3.3 For integrated sampling, repeat the analysis of the sample until three consecutive analyses vary no more than 0.2% by volume for each component being analysed.

## **6 Calculations**

### **6.1 Carbon dioxide**

Average the three consecutive runs and report the result to the nearest 0.1% CO<sub>2</sub>.

### **6.2 Dry molecular weight**

Use Equation 8.1 to calculate dry molecular weight and average the runs. Report the result to the nearest 0.1.

$$M_d = 0.44 (\%CO_2) + 0.32(\%O_2) + 0.28(\%N_2 + \%CO)$$

Equation 8.1.

where:

- $M_d$  = Dry molecular weight
- $\%CO_2$  = Percentage carbon dioxide by volume, dry basis
- $\%O_2$  = Percentage oxygen by volume, dry basis
- $\%N_2$  = Percent nitrogen by volume, dry basis
- 0.44 = Molecular weight of carbon dioxide divided by 100
- 0.32 = Molecular weight of oxygen divided by 100
- 0.28 = Molecular weight of nitrogen and CO divided by 100

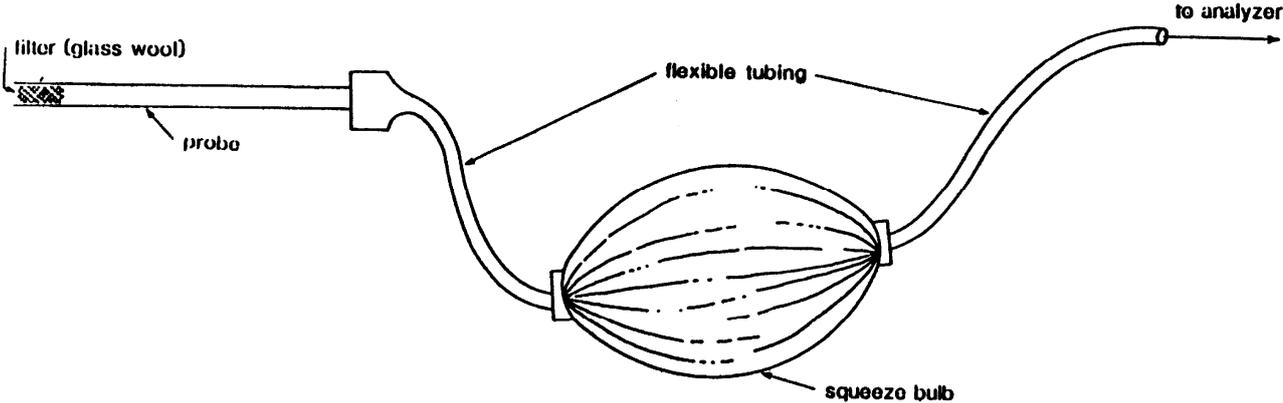


Figure 8.1 Grab gas sampling train

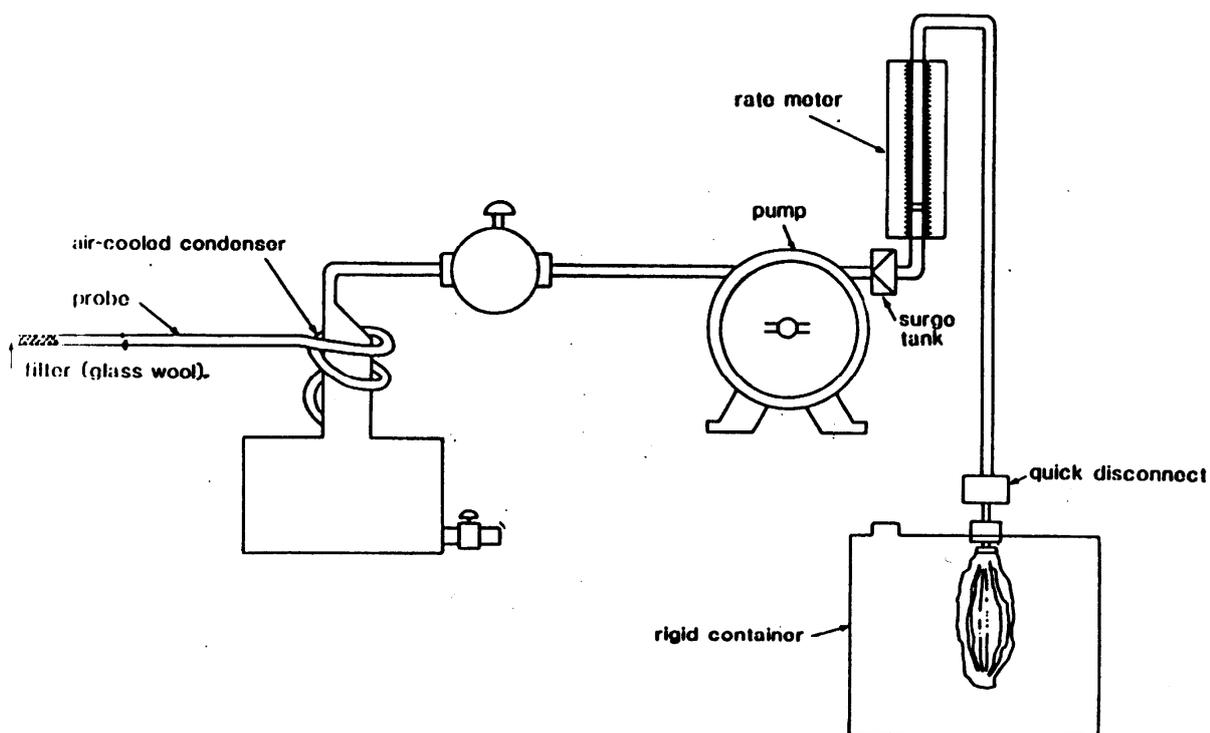


Figure 8.2 Integrated gas sampling train

## South Australian Environment Protection Authority Method 03.09

### Gas analysis and dry molecular weight

Prepared by: TH Goh, May 1995

#### Contents

1	Scope
2	Applicability
3	Principle
4	Apparatus
4.1	Selection of a sampling site and minimum number of traverse points
4.1.1	Suitable sampling sites
4.1.2	Number of sampling points
4.1.3	Location of sampling points
4.1.4	Fittings for access holes
4.1.5	Work platform requirements
4.1.6	Access to platform
4.1.7	Services
Figure 9.1	Cross-section of circular stack divided into 12 equal areas, showing location of traverse points at centroid of each area.
Figure 9.2	Cross-section of rectangular stack divided into 12 equal areas, with traverse points at centroid of each area
Figure 9.3	Flange/cover for access hole

## 1 Scope

This method sets out guidelines for the selection of sampling points in a stack or duct.

## 2 Applicability

This method is applicable to those air impurities and to the appropriate conditions as regulated. This method is not applicable to stacks containing cyclonic or swirling flow. When these cases are encountered, an alternative procedure, subject to approval of the EPA, Department of Environment and Natural Resources, is required.

## 3 Principle

Guidelines for sampling site(s) and number and location of traverse points are selected to aid in the extraction of a representative sample of the discharge to atmosphere from a stack or duct. These are governed by type of flow disturbance and dimensions of the stack or duct.

## 4 Procedure

- 4.1 Selection of a sampling site and minimum number of traverse points.
- 4.1.1 Suitable sampling sites  
Select a sampling site that is located in a straight, preferably vertical section of stack or duct as far as practicable from any flow obstructions which may cause a disturbance or other instability in the direction of the flow, eg a bend, a fan, or a partially-closed damper.

In the absence of cyclonic flow activity, an ideal sampling site will be located 7–8 diameters downstream and 2–3 diameters upstream from a flow disturbance. However, in most cases, a suitable sampling site will be a position fitting the guidelines set out in Table 9.1. In cases where a sampling site cannot be found to meet these minimum criteria, an alternative procedure, subject to approval of the EPA, Department of Environment and Natural Resources, is required.

**Table 9.1 Guidelines for selection of sampling sites**

Type of flow disturbance	Minimum distance upstream from disturbance, diameters (D)	Minimum distance downstream from disturbance, diameters (D)
Bend, connection, junction, direction change	>2D	>6D
Louvre, butterfly damper (partially closed or closed)	>3D	>6D
Axial fan	>3D	>8D
Centrifugal fan	>3D	>6D

Note: Diameter (D) is the internal diameter of a circular stack or the hydraulic diameter (4 times the stack internal area divided by the stack perimeter) of a non-circular stack.

### 3.2.2 Number of sampling points

The minimum number of sampling points for circular ducts or stacks shall be as specified in Table 9.2.

For rectangular or square ducts, Table 9.3 is used to give the minimum number of sampling points on a particular length of side. The total minimum number of sampling points shall be obtained by multiplying together the minimum number of sampling points for each of two adjacent sides. For example, in the case of a rectangular duct with sides L and l measuring 2 m and 1 m respectively, the minimum number (N) of sampling points on each sampling traverse parallel to side L is 4 (see Table 9.3). The minimum number (n) of sampling points on each sampling traverse parallel to side l is 3. Therefore the total minimum number of sampling points in the duct is equal to  $N \times n = 4 \times 3 = 12$ .

**Table 9.2 Minimum number of sampling points for circular ducts**

Sampling plane diameter (m)	Minimum number of sampling traverses	Minimum number of access holes	Minimum number of sampling points per radius	Total minimum number of sampling points
>0.20 ≤0.35	2	2	1	4
>0.35 ≤0.70	2	2	2	8
>0.70 ≤1.50	2	2	3	12
>1.50 ≤2.50	2	4	4	16
>2.50 ≤4.00	2	4	6	24
>4.00 ≤6.00	3	6	5	30
>6.00	3	6	6	36

**Table 9.3 Minimum number of sampling points for rectangular or square ducts**

Length of long side (L) or short side of duct (l) [m]	Minimum number (N) of sampling points required on each sampling traverse parallel to long side (L) and minimum number (n) required on each sampling traverse parallel to short side (l) of duct
>0.20 ≤0.35	2
>0.35 ≤0.90	2
>0.90 ≤1.70	3
>1.70 ≤2.75	4
>2.75 ≤4.00	5
>4.00 <6.00	6
>6.00	7

Note: Refer to section 4.1.2 and Figure 9.2.

#### 4.1.3 Location of sampling points

- a For circular stacks or ducts, the sampling plane is divided into equal areas and the sampling points, one at the centre of each such area, are located on two or more traverses (see Figure 9.1) and according to Table 9.4.
- b For rectangular (and square) ducts, the sampling plane is divided into equal areas by lines parallel to the sides of the duct, and a sampling point is located at the centroid of each such area (see Figure 9.2).

**Table 9.4** Location of traverse points in circular stacks or ducts (percent of stack diameter from inside wall to traverse point)

Traverse point on a diameter	Number of traverse points on a diameter												
	2	4	6	8	10	12	14	16	18	20	22	24	
1	14.6	6.7	4.4	3.3	2.5	2.1	1.8	1.6	1.4	1.3	1.1	1.1	
2	85.4	25.0	14.7	10.5	8.2	6.7	5.7	4.9	4.4	3.9	3.5	3.2	
3		75.0	29.5	19.4	14.6	11.8	9.9	8.5	7.5	6.7	6.0	5.5	
4		93.3	70.5	32.3	22.6	17.7	14.6	12.5	10.9	9.7	8.7	7.9	
5			85.3	67.7	34.2	25.0	20.1	16.9	14.6	12.9	11.6	10.5	
6			95.6	80.6	65.8	35.5	26.9	22.0	18.8	16.5	14.6	13.2	
7				89.5	77.4	64.5	36.6	28.3	23.6	20.4	18.0	16.1	
8				96.7	85.4	65.0	63.4	37.5	29.6	25.0	21.8	19.4	
9					91.8	82.3	73.1	62.5	38.2	30.6	26.1	23.0	
10					97.5	88.2	79.9	71.7	61.8	38.8	31.5	27.2	
11						93.9	85.4	78.0	70.4	61.2	39.3	32.3	
12							97.9	90.1	83.1	76.4	69.4	60.7	39.8
13								94.3	87.5	81.2	75.0	68.5	60.2
14								98.2	91.5	85.4	79.6	73.9	67.6
15									95.1	89.1	83.5	78.2	72.8
16									98.4	92.5	87.1	82.0	77.0
17										95.6	90.3	85.4	80.6
18										98.6	93.3	88.4	83.9
19											96.1	91.3	86.8
20											98.7	94.0	89.5
21												96.5	92.1
22												98.9	94.5
23													96.8
24													98.9

Note: Sampling points shall not be located within 3% of the sampling traverse length from the inner duct wall (if sampling traverse is greater than 1 m) or within 30 mm from the inner duct wall (if sampling traverse is less than 1 m).

#### 4.1.4 Sampling access holes

##### a Circular stacks or ducts

The number of access holes shall be as set out in Table 9.2. These are summarised as follows:

- Sampling plane diameter between 0.20 m and 1.50 m, 2 holes at 90° apart.
- Sampling plane diameter between 1.50 m and 4.00 m, 4 holes at 90° apart.
- Sampling plane diameter greater than 4.00 m, 6 holes at 60° apart.

##### b Rectangular or square ducts

The number of access holes shall be as set out in Table 9.3. For rectangular ducts, the access holes may be located on either the long or the short side of the duct. For example, in the case of a 2 m x 1 m rectangular duct, the total number of sampling points is equal to 12 as shown in section 4.1.2. The 12 sampling point can be reached by either 3 access holes on the 1 m side, or 4 access holes on the 2 m side.

For larger ducts, access holes at both ends of each sampling traverse would be required. Sampling traverses must be parallel with either the long or the short side of the duct.

##### c Fittings for access holes

Each access hole shall be formed by the use of a standard 100-mm pipe having a length of 100 mm. The pipe shall be fitted with a flange and a cover. The cover should be held in place by eight (8) M16 bolts on a pitch circle diameter of 178 mm (see Figure 9.3). The pipe shall not protrude into the gas stream.

#### 4.1.5 Work platform requirements

A work platform with reasonable access shall be provided for stack emission testing. The platform should be a permanent structure; however, if this is not practical, a temporary structure may be used. A permanent work platform and means of access shall comply with AS1657–Scaffolding, if used, shall conform with appropriate scaffolding regulations. In addition, both permanent and temporary platforms shall conform with the requirements:

- a Safety railings shall be placed at 0.5 m and 1 m (measured to the top of the rails) above the floor level. The axis of the vertical railing supports shall not cross the axis of the socket.
- b The platform shall provide access to all access holes on the sampling plane.
- c The platform shall provide a minimum working area of 6 m<sup>2</sup>.
- d For a stack of 1 m internal diameter, the minimum width for a permanent platform shall be 1 m. For a scaffolding platform, it shall be 1.25 m. For every 100-mm increase in stack diameter, the minimum platform width shall be increased by 25 mm.
- e The inner edge of the platform shall be as close as practicable to the stack.
- f The platform shall be 1.35 m below the access holes.
- g The platform shall be free of large openings (see AS1657) and surrounded by a 100-mm high kickboard.

#### 4.1.6 Access to platform

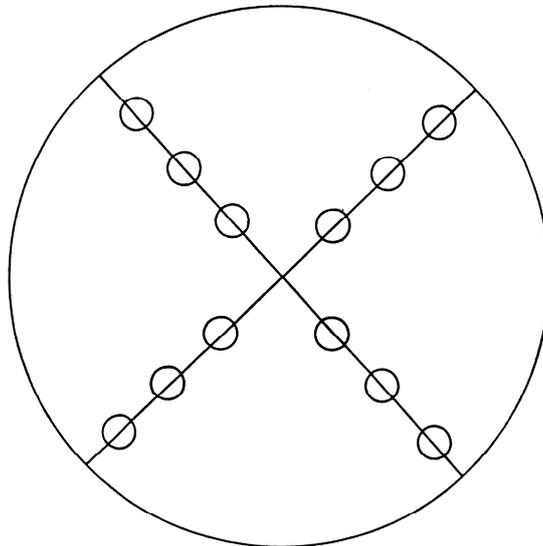
Depending on the location of the platform, access to the platform may be a walkway, stairway or fixed ladder.

Where there is no platform or where access to test holes is difficult, the use of a cherry picker may be allowed by the EPA, Department of Environment and Natural Resources. The cherry picker shall be a truck mounted elevated platform type. Suitably qualified personnel must be provided to operate the vehicle. Its operation shall

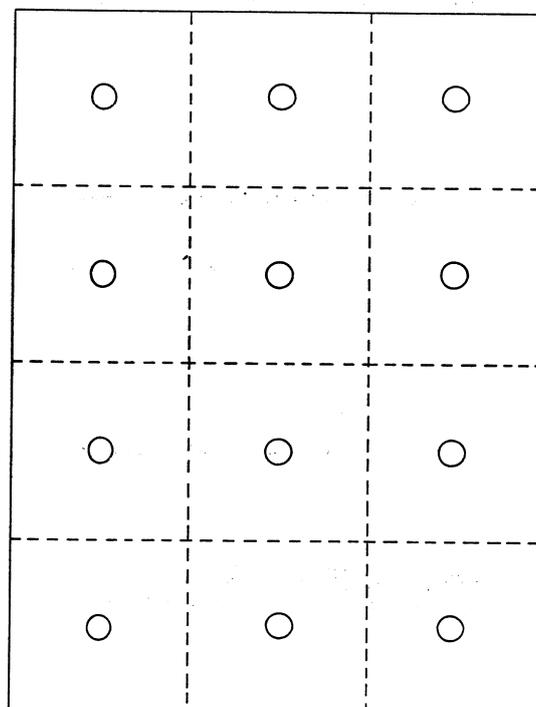
meet all safety requirements according to AS 1418.10:1987–Part 10. A safety belt must be fitted inside the bucket.

#### 4.1.7 Services

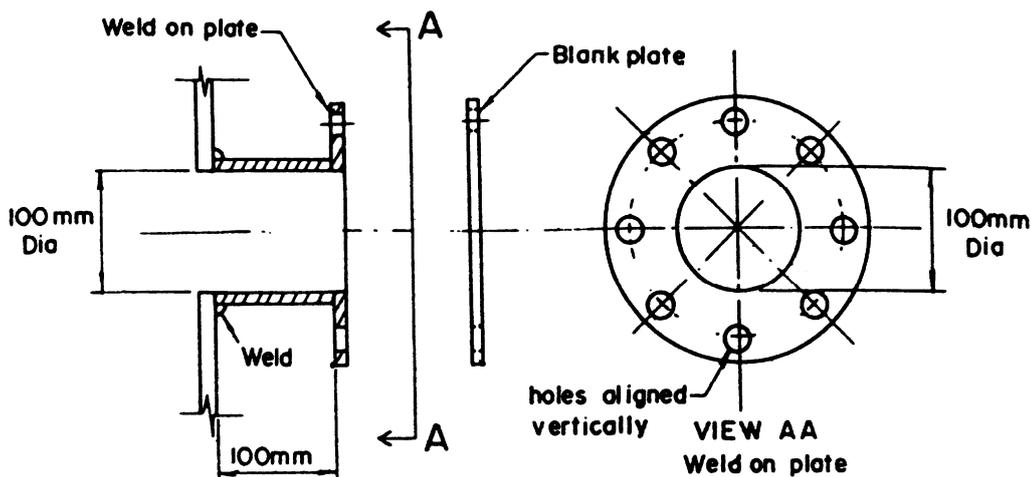
Electricity services (240 V, 10 A), suitably grounded, shall be available to within 10 m of the work platform. All electrical wiring and power outlets shall be installed in accordance with AS3000.



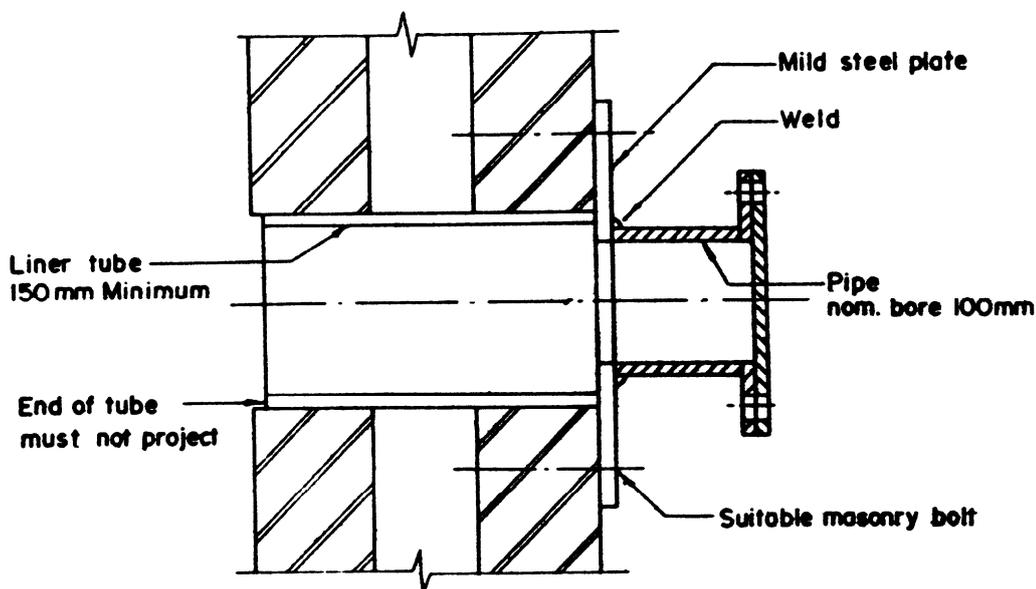
**Figure 9.1** Cross-section of circular stack divided into 12 equal areas, showing location of traverse points at centroid of each area



**Figure 9.2** Cross-section of rectangular stack divided into 12 equal areas, with traverse points at centroid of each area



a. IN METAL FLUE OR DUCT WALL



b. CAVITY WALL DUCT WITH INTERNAL LINING

WELD ON PLATE TO AS 2129:1982 NOMINAL BORE 100mm

BLANK PLATE TO MATCH

Dimensions (mm)

Flange Dia.	Bolt Circle Dia.	No. Bolts	Bolt Dia.	Hole Dia.	Flange thickness
215	178	8	16	18	13

Figure 9.3 Flange/cover for access holes

**Important to note**

Since the writing of this method Australian Standards have been written in particular *AS4323.1: Stationary source emission—Selection of sampling positions*, to which the author of this method contributed. It must be noted that the dimensions used in Figure 9.3 may not be the same as in AS4323.1. In this case the dimensions in AS4323.1 must be adhered to (R Mitchell, Manager Air Science, Air and Noise Branch, EPA, 10 February 2012)

## South Australian Environment Protection Authority Method 03.10

### Stack gas and volumetric flow rate

Prepared by: TH Goh, May 1995

#### Contents

1	Scope
2	Principle
3	Apparatus
4	Procedure
5	Calibration
6	Calculations
Figure 10.1	Pitot tube–manometer assembly
Figure 10.2	Velocity traverse data sheet

---

## 1 Scope

This method is applicable for the determination of stack gas velocity and volumetric flow rate.

## 2 Principle

Stack gas velocity and volumetric flow rate are determined from stack gas molecular weight (or gas density) and from measurement of differential pressure using a Type S (Stauscheibe type) pitot tube or equivalent and an inclined manometer or equivalent.

## 3 Apparatus

- 3.1 Pitot tube—Type S (Figure 10.1), or equivalent, with a coefficient within  $\pm 5\%$  over the working range.
- 3.2. Differential and static pressure gauge—Inclined manometer, or equivalent, to measure velocity head to within  $\pm 5$  Pa.
- 3.3 Temperature gauge—thermocouple or equivalent attached to the pitot tube to measure stack temperature to within 1% of absolute stack temperature.
- 3.4 Static pressure gauge—inclined manometer or equivalent to measure static stack pressure to within  $\pm 100$  Pa.
- 3.5 Barometer—to measure atmospheric pressure to within  $\pm 1$  kPa.
- 3.6 Gas analyser—to analyse gas composition for determining molecular weight.
- 3.7 Calibration pitot tube—standard type, to calibrate Type S pitot tube.

## 4 Procedure

- 4.1 Differential pressure ( $\Delta P$ ) readings. The procedure shall be as follows:
  - a Inspect the Type S pitot tube to be sure that the orifices are clear of obstructions.

- b Mark the traverse points (specified by Method 03.09) on the Type S pitot tube. Be sure to include the distance from the internal wall of the stack or duct to the outer edge of the socket or flange.
  - c Level and zero the inclined manometer.
  - d Connect the Type S pitot tube and manometer as shown in Figure 10.1. Be careful to connect the 'total' pressure tube of the pitot to the high pressure port of the manometer.
  - e Make sure all the connections are tight and leak free, eg blow gently into the 'total pressure tube until a substantial pressure differential registers and seal the opening. This pressure should remain stable for at least 30 seconds.
  - f Insert the Type S pitot tube into the stack or duct at the first sampling point. The pitot tube should be directed perpendicular to the sampling plane.
  - g Record the manometer reading in kPa. It may take up to a few minutes for the reading to settle. Note: Check for any cyclonic or swirling flow. This flow is not present if the Type S pitot tube measures gas velocity to within +4% when the pitot tube is aligned within +15° of the direction of the gas flow.
  - h Repeat this procedure for all the sampling points on the first traverse and subsequent traverses as required (see Test Method 03.09).
- 4.2 Measure the static pressure ( $P_{static}$ ) in the stack as follows:
- a Connect one leg of the Type S pitot tube to one side of the manometer and leave the other side open to the atmosphere.
  - b Insert the pitot tube into the stack or duct and align it with the direction of the gas flow.
  - c Rotate the pitot 90° and record the static pressure in kPa.
- 4.3 Measure and record the barometric (ambient) pressure ( $P_{bar}$ ) at the sampling site in kPa.
- 4.4 Measure the stack temperature ( $T_s$ ) at the sampling points as specified by Test Method 03.09. Note: If the temperature difference between adjacent sampling points along each traverse is less than 10% of the absolute temperature, and the temperature at any point differs by less than 10% from the mean, unacceptable flow conditions exist. A new suitable sampling site shall be selected.
- 4.5. Determine the stack gas molecular weight by gas analysis and appropriate calculations (see Test Method 03.08).
- 4.6 Determine the moisture content of stack gas in % by volume (see Test Method 03.13).

## 5. Calibration

- 5.1 To calibrate the pitot tube, measure the differential pressure at some fixed point in a flowing gas stream with both a Type S pitot tube and standard type pitot tube with known coefficient. Calibration should be done in the laboratory and the velocity of the flowing gas stream should be varied over the normal working range. It is recommended that the calibration be repeated after use at each field site.
- 5.2 Calculate the pitot tube coefficient using Equation 10.1

$$C_{P_{test}} = C_{P_{std}} \sqrt{\frac{\Delta P_{std}}{\Delta P_{test}}} \quad \text{Equation 10.1}$$

where:

$C_{P_{test}}$  = Pitot tube coefficient of Type S pitot tube.

$C_{p_{std}}$  = Pitot tube coefficient of standard type pitot tube (if unknown use 0.99).

$\lambda P_{std}$  = Differential pressure measured by standard type pitot tube.

$\lambda P_{test}$  = Differential pressure measured by Type S pitot tube.

5.3 Compare the coefficients of Type S pitot tube determined first with one leg and then the other pointed downstream. Use the pitot tube only if the two coefficients differ by not more than 0.01.

## 6 Calculations

6.1 Average stack gas velocity

Use Equation 10.2 to calculate stack gas velocity

$$V_s = C_p K_p \sqrt{\frac{T_s \Delta P}{P_s M_s}}$$

Equation 10.2

where:

$V_s$  = Average stack gas velocity, m/sec

$K_p$  = 128.53 m/sec [kg/kg-mole.K]<sup>1/2</sup>

$C_p$  = Pitot tube coefficient, dimensionless (see Equation 10.1)

$T_s$  = Average absolute stack gas temperature, K

$\lambda P$  = Average differential pressure of stack gas, kPa

$P_s$  = Absolute stack gas pressure, kPa

=  $P_{static} + P_{bar}$

$P_{static}$  = Arithmetic average for all static pressure readings at the sampling points, kPa

$P_{bar}$  = Barometric (ambient) pressure at the sampling site, kPa

$M_s$  = Molecular weight of stack gas (wet basis), kg/kg-mole

=  $M_d (1 - M_C / 100) + 18 M_C / 100$

$M_d$  = Dry molecular weight of stack gas, kg/kg-mole

$M_C$  = Moisture content of stack gas, % by volume

Figure 10.2 shows a sample recording sheet for velocity traverse data. Use the averages in the last two columns of Figure 10.2 to determine the average stack gas velocity from Equation 10.2.

### 6.2 Stack gas volumetric flow rate

The volumetric flow rate at stack conditions may be calculated by using Equation 10.3.

$$Q_s = (V_s) (A)$$

Equation 10.3

where:

$$Q_s = \text{Volumetric flow rate, stack conditions, m}^3/\text{sec}$$

$$V_s = \text{Average stack gas velocity, m/sec (see Equation 10.2)}$$

$$A = \text{Cross-sectional area of stack, m}^2$$

Equation 10.3 can be corrected to standard conditions of 273 K and 101.3 kPa on a dry basis by equation 10.4.

$$(Q_{std})_d = (1 - MC / 100) V_s A \left( \frac{273}{T_s} \right) \left( \frac{P_s}{101.3} \right)$$

Equation 10.4

where:

$$(Q_{std})_d = \text{Volumetric flow rate, dry basis, standard conditions, m}^3/\text{sec}$$

$$T_s = \text{Absolute average stack gas temperature, K}$$

$$P_s = \text{Absolute stack gas pressure, kPa}$$

$$MC = \text{Moisture content of stack gas, \% by volume (see Test Method 03.13)}$$

### 5.3 Iso-kinetic sampling nozzle size

Typical calculations for determination of the iso-kinetic sampling nozzle size are derived from the equation:

$$V_n = V_s$$

Equation 10.5

where:

$$V_n = \text{Average gas velocity at the nozzle, m}^3/\text{sec}$$

$$V_s = \text{Average stack gas velocity, m}^3/\text{sec (see Equation 10.2)}$$

Equation 10.5 is reduced to:

$$D_n = 1000 \sqrt{\frac{4V_s}{\Pi(Q_s)_w}}$$

Equation 10.6

where:

$$D_n = \text{Diameter of sampling nozzle, mm}$$

$$(Q_s)_w = \text{Volumetric flow rate, stack conditions, m}^3/\text{sec (see Equation 10.3)}$$

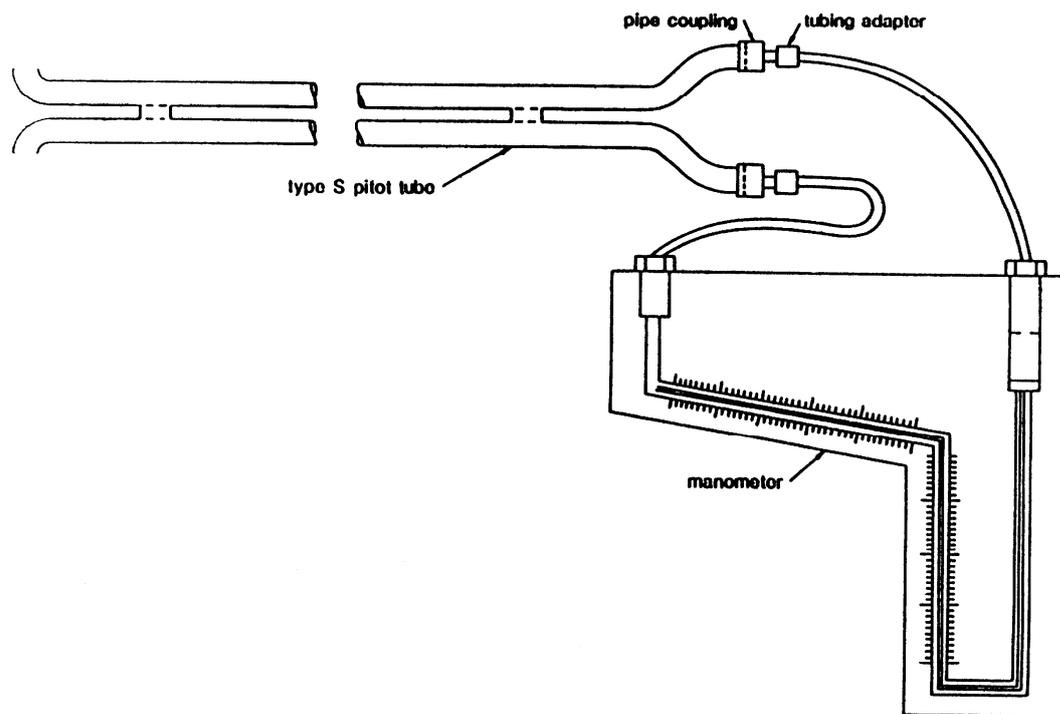


Figure 10.1 Pitot tube-manometer assembly

### Velocity traverse data sheet

Date \_\_\_\_\_

Run no \_\_\_\_\_

Stack Diameter, metres \_\_\_\_\_

Barometric Pressure, kPa \_\_\_\_\_

Static Pressure, kPa \_\_\_\_\_

Operator(s) \_\_\_\_\_



Schematic of stack cross-section

Traverse point number	Differential pressure ( $\Delta P$ ) kPa	$\sqrt{\Delta P}$	Stack temp ( $T_s$ ) K

Figure 10.2 Velocity traverse data sheet

## South Australian Environment Protection Authority Method 03.11

### Determination of total acidity

Prepared by: TH Goh, May 1995

#### Contents

1	Scope
2	Principle
3	Apparatus
4	Reagent
5	Calibration
6	Procedure
7	Calculations

Figure 11.1 Total acidity sampling train

---

## 1 Scope

This method is only applicable for the determination of total acidity expressed as sulphur trioxide from sulphuric acid manufacturing plants operating on the chamber process.

## 2 Principle

The gas sample is extracted from a sampling point in the stack, and oxides of sulphur are removed by passing through a dilute hydrogen peroxide solution. The residual gas is then passed through a permanganate solution where nitric oxide is oxidised quantitatively to the dioxide, and then through an absorbing solution of sodium hydroxide of known concentration. Total acidity is the sum of the acidity of the hydrogen peroxide solution determined by titration with standard alkali, and the acidity due to oxides of nitrogen absorbed in the sodium hydroxide solution determined by back titration.

## 3 Apparatus

### 3.1 Sampling train

See Figure 11.1. Many of the design specifications of this sampling train are described in [Appendix 2](#).

- 3.1.1 Nozzle—the nozzle may be made of any material substantially resistant to attack by components of the gas stream. The leading edge of the nozzle must be sharp and tapered.
- 3.1.2 Probe—for most cases a borosilicate glass probe will be suitable, however it may be constructed of any material substantially resistant to chemical attack by components of the gas stream and having the necessary mechanical strength. The probe must be fitted with a heating system to prevent visible condensation during sampling.

The internal dimensions of the probe should be chosen so that for iso-kinetic sampling the flow rate through the impingers lies in the range  $0.02\text{--}0.03\text{ m}^3\text{ min}^{-1}$ .

- 3.1.3 Pitot tube—Type S, or equivalent, attached to probe to monitor stack gas velocity.
- 3.1.4 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined manometer or equivalent capable of being read to within +5 Pa.
- 3.1.5 Impingers—5 impingers with glass ball-joint fittings as shown in Figure 11.1. The first, third and fourth are of the Greenburg–Smith design with standard tip.

The second and fifth are of the Greenburg–Smith design, modified by replacing the standard tip with a 1.2-cm internal diameter tube extending to 1 cm from the bottom of the impinger flask. Other collection systems of similar design approved by the EPA, Department of Environment and Natural Resources may be used.

- 3.1.6 Metering system— vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring temperature to within +1% of absolute temperature; dry gas meter to measure dry gas volume to within +2% accuracy; orifice meter, rotameter or equivalent, as required to maintain iso-kinetic sampling rate to within +5% accuracy; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.
- 3.1.7 Barometer—To measure atmospheric pressure to +1 kPa.. An aneroid barometer calibrated against a Fortin barometer would be acceptable.

## **3.2 Sample recovery**

- 3.2.1 Wash bottle—1.
- 3.2.2 Glass storage containers.
- 3.2.3 Volumetric flasks—500 ml, 250 ml.

## **3.3 Analysis**

- 3.3.1 Pipette—25 ml, 50 ml, 100 ml.
- 3.3.2 Burette—50 ml, 2.
- 3.3.3 Dropping bottles for dispensing indicator solution.

## **4 Reagents**

### **4.1 Sampling**

- 4.1.1 Silica gel—self indicating type, 6–20 mesh dried at 175°C for 2 hours.
- 4.1.2 Water—deionised, distilled.
- 4.1.3 Mixed indicator with a colour change at pH 4.5.
- 4.1.4 Sodium hydroxide solution 0.2M accurately standardised.
- 4.1.5 Sodium hydroxide solution 0.1M accurately standardised.
- 4.1.6 Hydrochloric acid 0.1M accurately standardised.

- 4.1.7 Hydrogen peroxide 3%—dilute 100 ml of 30% hydrogen peroxide to 1 litre with deionised, distilled water. Titrate 50 ml of the dilute peroxide solution with standard alkali or acid to pH 4.5 end point. Add the proportionate amount of acid or alkali as found by titration to the remainder of the diluted hydrogen peroxide solution.
- 4.1.8 Sulphuric acid (S.G. 1.02)—dilute 25 ml of sulphuric acid (S.G. 1.84) to 1 litre with deionised, distilled water.
- 4.1.9 Permanganate solution (2.5%)—dissolve 12.5 g of potassium permanganate in 500 ml of sulphuric acid (S.G. 1.02).
- 4.1.10 Crushed ice.

## 4.2 Sample recovery

- 4.2.1 Water—deionised, distilled.

## 4.3 Analysis

- 4.3.1 Water—deionised, distilled.
- 4.3.2 Sodium hydroxide solution 0.1M accurately standardised.
- 4.3.3 Hydrochloric acid solution 0.1M accurately standardised.

## 5 Calibration

The orifice meter, rotameter, pitot tube, dry gas meter and probe heater must be calibrated against standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources.

## 6 Procedure

### 6.1 Sampling

- 6.1.1 Determine the following source parameters:

- a minimum number of sampling points (Method 03.09)
- b gas velocity, volumetric flow rate and iso-kinetic nozzle size (Method 03.10)
- c molecular weight of stack gas (Method 03.08)
- d moisture content of stack gas (Method 03.13).

- 6.1.2 Preparation of sample collection train.

Place 100 ml of 3% hydrogen peroxide in both the first and second impingers, 100 ml of permanganate solution in the third impinger, 100 ml of 0.2M sodium hydroxide solution in the fourth impinger and about 200 g of silica gel in the fifth impinger.

Retain a portion of the reagents for use as blank solutions. Assemble the sampling train with the probe as shown in Figure 11.1 and with the filter between the first and second impingers. Leak check the system at the sampling site by disconnecting the probe and plugging the inlet to the first impinger and pulling a 50-kPa vacuum. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  at a vacuum of 50 kPa is acceptable. Following the leak check, reconnect the probe to the sampling train. Turn on the probe heating system and adjust the probe heater setting to prevent visible condensation during sampling. Place crushed ice around the impingers. As necessary add more ice during the run to keep the temperature of the gases leaving the last impinger at 20°C or less.

- 6.1.3 Train operation. The sampling train shall be as follows:

- a Set up the sampling train as described in section 6.1.2 and install the correct nozzle size. Note: For each sample run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the nozzle is located at the first sampling point. Turn the probe tube so that the nozzle is at 90° to the gas flow.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the the stack or duct to attain the temperature of the stack or duct gases.
- d Turn the probe tube until the nozzle is pointing directly into the gas stream.
- e Start the pump and adjust the gas flow to iso-kinetic conditions. Sample for at least 5 minutes.
- f After sampling has been completed at the first sampling point, quickly move the probe tube to reposition the nozzle at the next sampling point.
- g Adjust the control valve immediately to the iso-kinetic flow reading appropriate to the next sampling point.
- h Repeat steps (e) to (g) until sampling has been taken at all the points on the first sampling traverse. Maintain isokinetic conditions throughout the sampling period and use the same time interval at each sampling point.

Where the sampling train is equipped with a dry gas meter, record the meter readings at the beginning and end of sampling time at each sampling point.

- i At the completion of the first sampling traverse, turn off the pump. Remove the probe tube and nozzle from the access hole.
- j Where sampling is to be carried out at more than one sampling traverse, repeat steps (b) to (i).
- k At the conclusion of sampling, disconnect the probe and nozzle from the impinger train.
- l Disconnect the impingers and handle carefully in accordance with the sample recovery process (section 6.2).
- m If velocity measurement and gas sampling have not been carried out simultaneously at adjacent points, repeat the readings of gas velocity and temperature at each sampling point as soon as sampling at all sampling points is complete. If the average of the gas velocity readings differ by more than +10% from the average of the original readings recorded in section 6.1.1(b), the test result shall be regarded as inaccurate.
- n When repeat samples are required, steps (a) to (m) shall be repeated under comparable plant conditions and as soon as is practicable.

If this second sampling follows immediately after the first, the gas velocity and temperature readings taken at step (m) may be used as the initial readings for the second test.

## 6.2 Sample recovery

- 6.2.1 Pour the hydrogen peroxide absorbing solution from the first two impingers into a 500-ml graduated flask. Rinse the probe, connecting glassware and impingers with distilled water, combine the rinsings with those from the first two impingers and make to volume.

Pour the contents of the fourth impinger into a 250-ml graduated flask, and rinse with distilled water and make to volume.

Discard permanganate solution from third impinger.

## 6.3 Analysis

- 6.3.1 Acid gases principally composed of sulphur dioxide and sulphur trioxide, as sulphur trioxide. Pipette a 100-ml aliquot of the sample (hydrogen peroxide absorbing solution made to volume) into a 250-ml Erlenmeyer flask, add 2–4 drops of mixed indicator solution and titrate to pH 4.5 end point with 0.1M sodium hydroxide solution.
- 6.3.2 Acid gases principally composed of nitric oxide and nitrogen dioxide expressed as sulphur trioxide. Pipette a 50-ml aliquot of the sample (from impinger 4 made to volume) into a 250-ml Erlenmeyer flask, add 2–4 drops of mixed indicator solution and titrate with 0.1M hydrochloric acid solution to pH 4.5 end point.

## 7 Calculations

### 7.1 Total acid gases concentration (as SO<sub>3</sub>)

$$C_{AG} = \frac{k}{V_{std}} \left[ \frac{V_{N_1} M V_{s_1}}{V_{a_1}} + V_{N_2} M_{NaOH} - (V_{HCl} M_{HCl}) \frac{V_{s_2}}{V_{a_2}} \right]$$

Equation 11.1

where:

- $C_{AG}$  = Concentration of acid gases expressed as SO<sub>3</sub> at standard conditions, dry gas basis, mg m<sup>-3</sup>
- $k$  = Conversion factor for molar sodium hydroxide to mg SO<sub>3</sub>, 80 mg litre g-mol<sup>-1</sup> ml<sup>-1</sup>
- $V_{N_1}$  = Volume of sodium hydroxide solution used to titrate acidity from first two impingers, ml
- $M$  = Molarity of sodium hydroxide solution used to titrate acidity from first two impingers, g-mol litre<sup>-1</sup>
- $V_{s_1}$  = Total volume of absorbent and washings from first two impingers, ml
- $V_{a_1}$  = Volume of sample aliquot (first two impingers) titrated, ml
- $V_{N_2}$  = Initial volume of sodium hydroxide added to fourth impinger, ml
- $M_{NaOH}$  = Molarity of sodium hydroxide used in fourth impinger, g-mol litre<sup>-1</sup>
- $V_{HCl}$  = Volume of hydrochloric acid used to titrate aliquot of sodium hydroxide from fourth impinger, ml.
- $M_{HCl}$  = Molarity of hydrochloric acid used to titrate sodium hydroxide aliquot from fourth impinger, g-mol. litre<sup>-1</sup>
- $V_{s_2}$  = Volume of sodium hydroxide from fourth impinger and washings, ml
- $V_{a_2}$  = Volume of sodium hydroxide sample aliquot titrated with standard hydrochloric acid, ml
- $V_{std}$  = Volume of dry gas sample, standard conditions, m<sup>3</sup> (see Test Method 03.01, section 7.1)

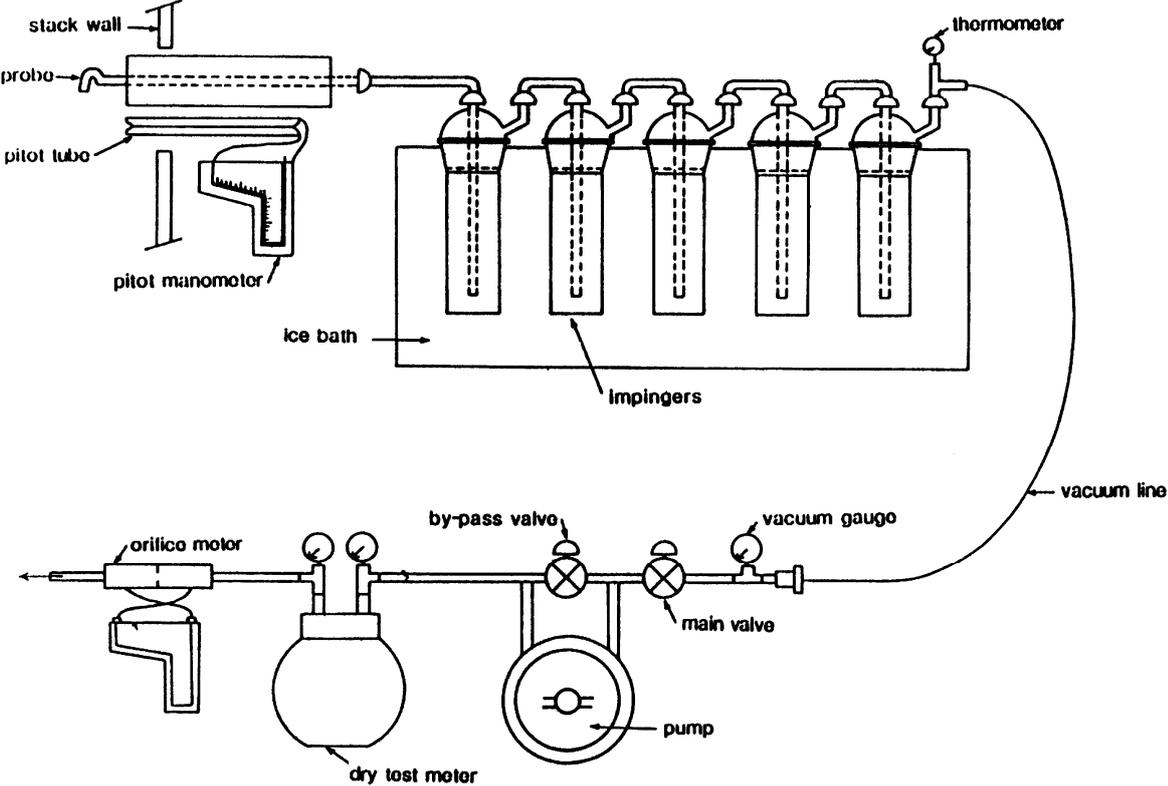


Figure 11.1 Total acidity sampling train

## South Australian Environment Protection Authority Method 03.12

### Determination of carbon monoxide

Prepared by: TH Goh, May 1995

#### Contents

1	Scope
2	Principle
3	Apparatus
4	Reagent
5	Calibration
6	Procedure
7	Calculations

Figure 12.1 Integrated gas sampling train

Figure 12.2 Analytical equipment

---

## 1 Scope

This method is applicable for the determination of carbon monoxide emissions in stationary sources.

## 2 Principle

An integrated gas sample is extracted from a sampling point in a stack or duct and analysed for carbon monoxide content using a direct-reading instrumental method.

## 3 Apparatus

### 3.1 Sampling train

See Figure 12.1.

- 3.1.1 Probe—stainless steel or borosilicate glass, equipped with a filter to remove particulate matter.
- 3.1.2 Air cooled condenser or equivalent—to remove any excess moisture.
- 3.1.3 Valve—needle valve, or equivalent, to adjust flow rate.
- 3.1.4 Pump—leak free, diaphragm type, or equivalent, to transport gas to the bag. Install a surge tank between the pump and rate meter to eliminate pulsation effect of pump on the rotameter.
- 3.1.5 Rate meter—rotameter or equivalent to measure a flow range from 0–1.0 litre minute<sup>-1</sup>.
- 3.1.6 Flexible bag—Tedlar or equivalent, with a capacity of 10 litres. Leak test the bag in the laboratory before using by evacuating the bag with a pump followed by a dry gas meter. When evacuation is complete, there should be no flow through the meter.

- 3.1.7 Pitot tube—Type S, or equivalent, attached to the probe so that the sampling rate can be regulated proportional to the stack gas velocity when velocity is varying with time or a sample traverse is conducted.

### 3.2 Sample recovery

- 3.2.1 Suitable for forwarding flexible bags to laboratory.

### 3.3 Analysis (Figure 12.2)

- 3.3.1 Carbon monoxide analyser

Any of the following types can be used:

- a non-dispersive infrared spectrometer
- b gas filter correlation spectrometer
- c gas chromatography with methanisation and flame ionisation system
- d electrochemical analyser.

- 3.3.2 Performance specifications:

The performance specifications for nondispersive infrared carbon monoxide analyser are:

<b>Range</b>	<b>0-5%</b>
Output	Multiple millivolt ranges including 0 to 5,000 millivolts
Minimum detectable sensitivity	2% of full scale or better on the most sensitive scale
Lag time	2 minute maximum
Rise time	5 minute maximum
Fall time	5 minute maximum
Zero drift 12 h and 24 h	±1% of full scale
Span drift 24 h	
At 20% of upper range limit	±5% maximum of full scale
At 80% of upper range limit	±5% maximum of full scale
Precision (minimum)	±2% of full scale
Noise (maximum)	±1% of full scale
Linearity (maximum deviation)	±2% of full scale
Interference rejection ratio	CO <sub>2</sub> –1,000 to 1, H <sub>2</sub> O–500 to 1

The definitions of performance specifications are given in *Australian Standard 2521:1982–Ambient air–Determination of Gaseous pollutants–Definitions for instruments and general requirements*.

Where appropriate the specifications also apply to instruments operating on the specified alternative principles to non-dispersive infrared.

- 3.3.3 Silica gel drying tube—a modified Greenburg–Smith impinger (Method 03.03, section 2.1.4) or tubing composed of glass, perspex or metal with suitable adaptors on each end of the tubing to connect into sampling line. If tubing is used it should be of convenient size to hold not less than 200 g of silica gel. A convenient size tube is 5 cm in diameter and 30 cm in length.
- 3.3.4 Filter—as recommended by the manufacturer of the carbon monoxide analyser. If none specified, use suitable filter with almost negligible pressure drop.
- 3.3.5 Carbon dioxide removal tube—to contain approximately 500 g of material for removal of carbon dioxide.
- 3.3.6 Ice water bath—suitable both for partial immersion of silica gel and carbon dioxide removal tubes.
- 3.3.7 Valve—needle or equivalent to adjust flow rate.
- 3.3.8 Rate meter—rotameter or equivalent to measure gas flow rate at 0–1.0 litres minute<sup>-1</sup> through analyser.
- 3.3.9 Recorder (optional)—to provide record of output of analyser.
- 3.3.10 Valve—multiport valve or appropriate single valves to admit either sample or zero gas or span gases to the analyser.

## 4 Reagents

- 4.1 Calibration gases—a known concentration of carbon monoxide in nitrogen is required for instrument span, prepurified grade of nitrogen for zero, and two additional concentrations corresponding approximately to 60% and 30% span. The span concentration shall not exceed 1,200 ppm carbon monoxide. The calibration gases shall be certified by the manufacturer to be within  $\pm 2\%$  of the specified concentration.
- 4.2 Silica gel—indicating type, 6–20 mesh, dried at 175°C for 2 hours.
- 4.3 Carbon dioxide absorbent—ascarite or equivalent.

## 5 Calibration

- 5.1 Assemble the apparatus according to Figure 12.2. Allow the analyser to warm up for the period of at least 1 hour or for the period specified by the manufacturer, and carry out the manufacturer's instructions for specific procedure. During the warm-up period check the sample conditioning apparatus ie filter, condenser, drying tube and carbon dioxide removal tube to ensure that each component is in good operating condition. Zero and calibrate the instrument according to the manufacturer's procedures using nitrogen (zero gas) and the calibration gases respectively.

## 6 Procedure

### 6.1 Sampling

- 6.1.1 Evacuate the flexible bag. Set up the equipment as shown in Figure 12.1 with the bag disconnected. Place the probe in the stack and purge the sampling line. Connect the bag, making sure that all connections are leak free.
- 6.1.2 Sample at a rate proportional to the stack velocity for a period of 5 minutes.

- 6.1.3 Determine the carbon dioxide content of the gas by using Method 03.08 integrated sampling procedure or by weighing the carbon dioxide removal tube and computing the carbon dioxide concentration from the gas volume and weight gain of the tube.

## 6.2 Analysis

- 6.2.1 Assemble the apparatus as shown in Figure 12.2. Calibrate the carbon monoxide analyser and perform other required operations as described in section 5.1. Purge the analyser with nitrogen prior to introduction of the sample. Direct the sample stream through the instrument for the test period, recording the reading. Check the zero and span gas of nearest value to the sample again after the test to assure that any drift or malfunction is detected. Record sample data.
- 6.2.2 Record temperature of the sample gas introduced to analyser to within +1% of absolute temperature.

## 7 Calculations

### 7.1 Carbon monoxide concentration

$$C_{CO} = C_{ppm} (1 - F_{CO_2}) \left( \frac{273}{T_{SG} + 273} \right)$$

Equation 12.1

where:

- $C_{CO}$  = Concentration of carbon monoxide in stack gas at standard conditions, dry basis,  $\text{mg m}^{-3}$
- $C_{ppm}$  = Concentration of carbon monoxide measured by instrument, ppm
- $F_{CO_2}$  = Volume fraction of carbon dioxide in sample, dry basis ie percentage carbon dioxide divided by 100
- $T_{SG}$  = Temperature of sample gas introduced to analyser, K
- 800 = Factor combining the molecular weight of carbon monoxide and gram molecular volume

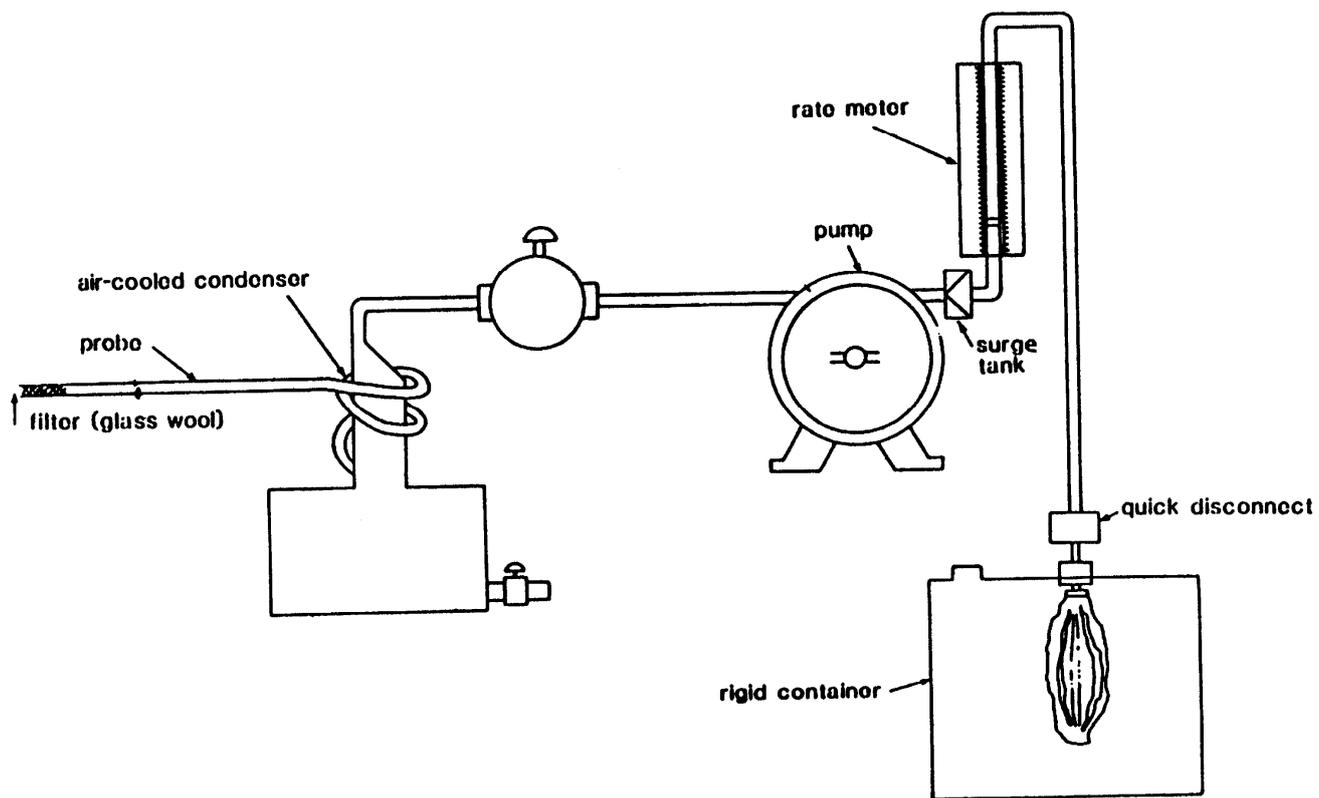


Figure 12.1 Integrated gas sampling train

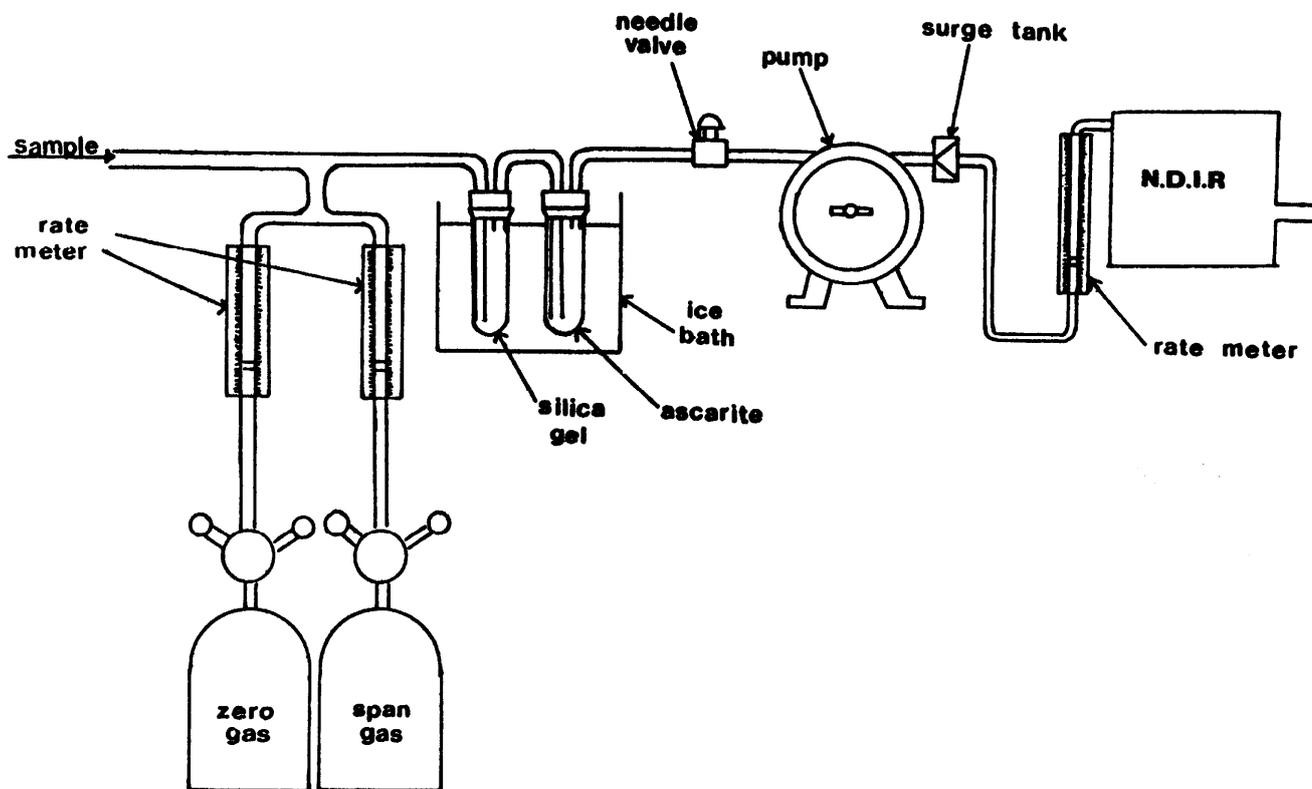


Figure 12.2 Analytical equipment

**South Australian Environment Protection Authority Method 03.13****Determination of moisture content—condensation method****Prepared by: TH Goh, May 1995****Contents**

1	Scope
2	Principle
3	Apparatus
4	Reagent
5	Calibration
6	Procedure
7	Calculations

Figure 13.1 Moisture sampling train

**1 Scope**

This method is applicable for determining the moisture content of stack or duct gas.

**2. Principle**

A gas sample is extracted from the stack or duct at a constant rate and its condensate measured either volumetrically/or gravimetrically.

**3 Apparatus****3.1 Sampling train**

See Figure 13.1. Many of the design specifications of this sampling train are described in [Appendix 2](#).

- 3.1.1 Probe—stainless steel, glass tubing or any suitable material substantially resistant to chemical attack by components of the gas stream and having the necessary mechanical strength and heat resistance. The probe must be fitted with a heating system to prevent condensation during sampling. A plug of glass wool inserted into the end of the probe is a satisfactory filter to remove any particulate matter.
- 3.1.2 Condenser—the condenser consists of four impingers with glass ball-joint fittings as shown in Figure 13.1. The first, third and fourth impingers are of the Greenburg–Smith design, modified by replacing the standard tip with a 1.2 cm internal diameter tube extending to 1 cm from the bottom of the impinger flask. The second impinger is of the Greenburg–Smith design with standard tip. Other collection systems of similar design approved by the EPA, Department of Environment and Natural Resources, may be used.
- 3.1.3 Pitot tube—Type S, or equivalent, attached to the probe to monitor stack gas velocity.

- 3.1.4 Pitot manometer—a differential and static pressure instrument connected to pitot tube. It shall be an inclined manometer or equivalent capable of being read to within +5 Pa.
- 3.1.5 Metering system—vacuum gauge; leak-free pump; thermometers or equivalent capable of measuring to within +1% of absolute temperature; dry gas meter to measure dry gas volume to within +2% accuracy; orifice meter, rotameter or equivalent, as required to maintain a sampling rate between 0.02 and 0.03 m<sup>3</sup> min<sup>-1</sup> to within +5% accuracy; and a control device having one or more adjustment controls to vary the rate of flow of gas sample through the sampling train.
- 3.1.6 Barometer—to measure atmospheric pressure to +1 kPa. An aneroid barometer calibrated against a Fortin barometer would be acceptable.

## 3.2 Sample recovery

- 3.2.1 Graduated cylinder—100 ml.
- 3.2.2 Suitable storage containers for holding silica gel.

## 3.3 Analysis

- 3.3.1 Laboratory balance—300 capacity to measure +0.05 g.

# 4 Reagents

## 4.1 Sampling

- 4.1.1 Silica gel—indicating type 6–20 mesh dried at 175°C for 2 hours.
- 4.1.2 Water—deionised, distilled.
- 4.1.3 Crushed ice.

## 4.2 Sampling recovery

There are none.

# 5 Calibration

5.1 The orifice meter, pitot tube, dry gas meter and probe heater must be calibrated against standard equipment to the satisfaction of the EPA, Department of Environment and Natural Resources. All analytical apparatus and equipment other than the above items should be calibrated by accepted analytical procedures.

# 6 Procedure

## 6.1 Sampling

- 6.1.1 Transfer at least 200 g of silica gel to the fourth impinger. Weigh and record the silica gel plus the fourth impinger to the nearest 0.5 g ([Appendix 1, Data sheet 2](#)).
- 6.1.2 Preparation of sample collection train. Place 75 ml of distilled water in each of the first and second impingers, leave the third impinger empty and place a known mass of silica gel in the fourth impinger (see section 6.1.1). Assemble the train with the probe as shown in Figure 13.1. Leak check the system at the sampling site by disconnecting the probe and plugging the inlet to the first impinger and pulling a 50-kPa vacuum. A leakage not in excess of 0.0005 m<sup>3</sup> min<sup>-1</sup> at a vacuum of 50 kPa is acceptable. Following the leak check, reconnect the probe to the sampling train. Turn on the probe heating system and adjust the probe heater setting to prevent

condensation during sampling. Place crushed ice around the impingers. As necessary, add more ice during the run to keep the temperature of the gases leaving the last impinger at 20°C or less.

6.1.3 Train operation. The procedure shall be as follows:

- a Set up the sampling train as described in section 6.1.2 with a plug of steel wool inserted into the end of the probe to remove any particulate matter. Note: For each sample run, record the data as shown in [Appendix 1, Data sheet 1](#).
- b Insert the probe tube through the access hole until the probe is located at the centre of a sampling traverse.
- c Switch on any heaters for the equipment and check that they are functioning correctly. Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases.
- d Start the pump and adjust the gas flow to a rate within the range 0.02–0.03 m<sup>3</sup> min<sup>-3</sup>. Sample for 30 minutes. Where the sampling train is equipped with a dry gas meter, record the meter readings at the beginning and end of sampling time.
- e At the completion of sampling, turn off the pump. Remove the probe from the access hole and disconnect it from the impinger train.
- f Disconnect the impingers and handle carefully in accordance with the sample recovery process (section 6.2).
- g Where repeat samples are required, steps (a) to (f) shall be repeated under comparable plant conditions and as soon as is practicable.

## 6.2 Sample recovery

- 6.2.1 Pour the contents of the first and second impingers into a measuring cylinder and measure the volume of water condensed. Record the measurement as shown in [Appendix 1, Data sheet 3](#).
- 6.2.2 Seal the open ends of the fourth impinger containing the silica gel. Place the impinger in a container and seal.

## 6.3 Analysis

Weigh the spent silica gel plus the impinger and report to the nearest 0.5 g ([Appendix 1, Data sheet 3](#)).

# 7 Calculations

## 7.1 Volume of water vapour condensed in impingers

$$(V_w)_{s_1} = \frac{(V_f - V_i)\rho_w RT_s}{P_s M_w 10^6}$$

Equation 13.1

where:

$(V_w)_{s_1}$  = Volume of water vapour condensed in impingers, standard conditions, m<sup>3</sup>

$V_f$  = Final volume of impinger contents, ml

$V_i$  = Initial volume of impinger contents, ml

$\rho_w$  = Density of water, 1,000 kg/m<sup>3</sup>

- R = Ideal gas constant, 8.31 kPa m<sup>3</sup>/K kg-mole
- T<sub>s</sub> = Standard absolute temperature, 273 K
- P<sub>s</sub> = Standard absolute pressure, 101.3 kPa
- M<sub>w</sub> = Molecular weight of water, 18 kg/kg-mole

Equation 13.1 is reduced to:

$$(V_w)_{s_1} = 0.001244 (V_f - V_i)$$

Equation 13.2

## 7.2 Volume of water vapour collected in silica gel

$$(V_w)_{s_2} = \frac{(W_f - W_i)RT_s}{P_s M_w} (V_w)_{s_2} = \frac{(W_f - W_i)RT_s}{P_s M_w}$$

$$= 0.001244 (W_f - W_i)$$

Equation 13.3

(V<sub>w</sub>)<sub>s<sub>2</sub></sub> = Volume of water vapour collected in silica gel, standard conditions, m<sup>3</sup>

W<sub>f</sub> = Final weight of silica gel plus impinger, g

W<sub>i</sub> = Initial weight of silica gel plus impinger, g

## 7.3 Total volume of water vapour in the gas stream

$$(V_w)_{std} = (V_w)_{s_1} + (V_w)_{s_2}$$

Equation 13.4

where:

(V<sub>w</sub>)<sub>std</sub> = Total volume of water vapour in gas stream, standard conditions, m<sup>3</sup>

(V<sub>w</sub>)<sub>s<sub>1</sub></sub> = Obtained from Equation 13.2

(V<sub>w</sub>)<sub>s<sub>2</sub></sub> = Obtained from Equation 13.3

## 7.4 Moisture content in the gas stream

$$MC = \left[ \frac{(V_w)_{std}}{(V_w)_{std} + V_{std}} \right] [100]$$

Equation 13.5

where:

MC = Moisture content in gas stream, % by volume

$(V_w)_{std}$  = Total volume of water vapour in gas stream, standard conditions (see Equation 13,4)

$V_{std}$  = Volume of dry gas through dry gas meter, standard conditions (see Test Method 03.01, section 7.1)

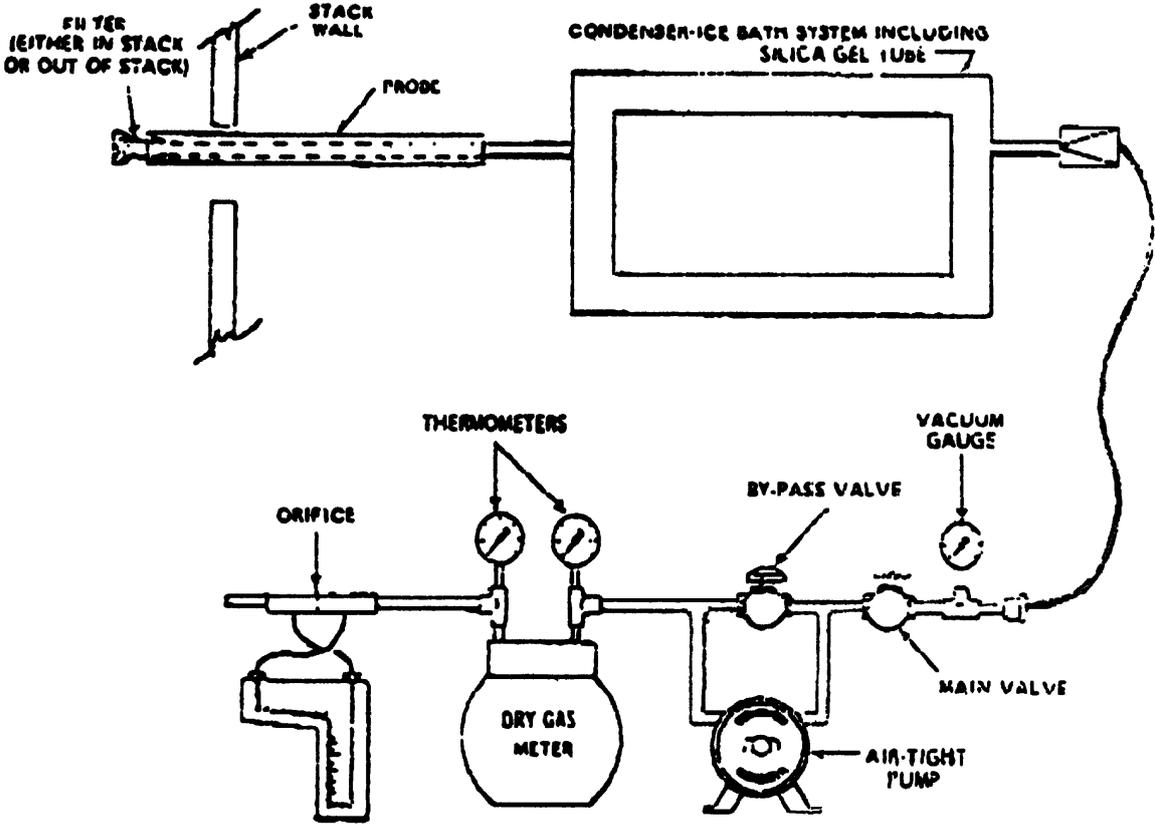


Figure 13.1 Moisture sampling train

## South Australian Environment Protection Authority Method 03.14

### Determination of moisture content—condensation method

Prepared by: TH Goh, May 1995

#### Contents

1	Scope
2	Applicability
3	Principle
4	Apparatus
5	Reagent
6	Calibration
7	Procedure
8	Calculations
Figure 14.1	Continuous gas sampling train
Figure 14.2	Dilution probe

---

## 1 Scope

This method is suitable for continuous sampling of stack or duct gases.

## 2 Applicability

This method is applicable to conventional fuel-fired equipment both before and after gas cleaning equipment, prior to emission of the gas effluent stream into the atmosphere, and for routine combustion process control purposes. It may apply to direct fuel-fired equipment where chemical reactions that can affect the measurements are considered negligible or are amenable to calculation.

## 3 Principle

This method utilises an extractive sampling procedure that will permit continuous determination of the concentrations of oxygen, carbon dioxide, carbon monoxide, sulphur dioxide, and nitrogen oxides in combustion gases contained within a stack or duct. In extractive sampling, these gases must be conditioned to remove aerosol, particulate matter and other interfering substances prior to subsequent analysis by recommended instrumentation. Velocity measurements are mentioned briefly in this method as they will be required to determine the mass flow rates of gases.

## 4 Apparatus

### 4.1 Sampling train

See Figure 14.1.

- 4.1.1 In-stack filter—stainless steel, borosilicate glass, or ceramic. The filter shall be located at the tip of the sample probe. Baffling may be added to prevent particle build-up on the leading edge of the filter.

- 4.1.2 Probe—stainless steel. Normally, probe diameter shall be at least 10 mm OD. Where short probes are used, 6.5 mm OD tubing may be used.
- 4.1.3 Heated sample line to moisture removal assembly—stainless steel or PTFE. The recommended size is 5 mm ID and 6.5 mm OD. Larger diameters should be used on runs longer than 15 m to minimise pressure drop.

The line shall be heated to a temperature at least 15 K greater than the water and acid dew point temperature of the sampled gas. A temperature control is required to keep the line temperature constant.

- 4.1.4 Secondary filter—PTFE or borosilicate glass. A secondary filter may be needed to remove the remaining particulate material in order to protect the pump and analyser. It must immediately follow the sample line from the probe. A filter porosity that retains particles greater than 1  $\mu\text{m}$  is recommended. The filter size shall be determined from the required sample flow and the manufacturer's data on flow rate per unit area. This filter shall be heated to a temperature not less than 15 K above the water and acid dew point of the sampled gas.
- 4.1.5 Sample pump—leak-free, diaphragm type, or equivalent, to withdraw a continuous gas sample from the stack or duct and through the system. The pump shall be either stainless steel or PTFE lined. The capacity of the pump shall be such that it can supply all the analysers with their required flows, plus a 10% excess flow margin. A bypass valve can be placed across the pump to control the flow rate. This valve will lengthen the life of the pump if used frequently at lower flow rates.
- 4.1.6 Water vapour removal system—a condensation/refrigeration unit or equivalent to remove water vapour from the stack or duct gas samples prior to these gases being conveyed to the instruments for analysis. The removal shall be done outside the heater box with provision for drawing condensate whilst maintaining system integrity if required.
- 4.1.7 Analyser sample line—stainless steel or PTFE. The minimum recommended size for any length of line is 6.5 mm OD and 5 mm ID. The line may be heated to avoid condensation outside of the condenser where the system extracts hot gases. If back flushing is used to clean the in-stack filter, a pressure regulated valve must be installed upstream of the conditioner to protect the equipment from damage by high pressure air.
- 4.1.8 Gas manifold—stainless steel or PTFE with a separate take-off for each analyser. The approximate size of the manifold shall be 2.5 cm in diameter and 20 cm in length. The excess gas discharge shall be located at the opposite end of the manifold from the gas inlet.
- 4.1.9 Vacuum gauge—0 to 100 kPa. The gauge shall be installed directly before the sample pump to provide an indication of proper operation of the pump and to indicate clogging or leakage when a filter change or cleaning is required.
- 4.1.10 Dilution—the dilution technique is used where there is a need to reduce the content of the stack or duct gas to a level compatible with the range of the analytical unit (see Figure 14.2). The dilution ratio shall remain constant through the test period. Suitable devices include calibrated apertures (capillaries, sonic nozzles, needle valves), flow meters by volume or mass, pressure and/or flow regulators. The dilution shall not contain more than 0.1% of full scale value of the instrument of the gas or gases being measured.

## 4.2 Analysis

- 4.2.1 Instrumental methods of analysis for oxygen, carbon dioxide, carbon monoxide, sulfur dioxide and oxides of nitrogen are as follows:

Gas measured	Instrumental method	Range
Oxygen	Paramagnetic	0–21%
Carbon dioxide	Non-dispersive Infrared	0–20%
Carbon monoxide	<ul style="list-style-type: none"> <li>• Non-dispersive Infrared</li> <li>• Gas filter correlation</li> <li>• Gas chromatography with methanisation and flameionisation</li> <li>• Electro-chemical</li> </ul>	0–5%
Sulfur dioxide	<ul style="list-style-type: none"> <li>• Non-dispersive infrared</li> <li>• Non-dispersive ultraviolet</li> <li>• Differential absorption</li> </ul>	0–3%
Oxides of nitrogen	Chemi-luminescence	0–1%

4.2.2 Performance specifications for the instruments are as follows:

Output	Multiple millivolt ranges including 0 to 5,000 millivolts
Lower detectable limit	2% of full scale or better on the most sensitive scale
Linearity	$\pm 2\%$ of full scale
Lag time	2 minute maximum
Rise time	2 minute maximum
Fall time	2 minute maximum
Zero drift 12 h and 24 h	$\pm 1\%$ of full scale
Span drift 24 h at 20% of upper range limit at 80% of upper range limit	$\pm 5\%$ maximum of full scale $\pm 5\%$ maximum of full scale
Precision at 20% of upper range limit at 80% of upper range limit	$\pm 2\%$ of full scale $\pm 2\%$ of full scale

The definitions of performance specifications are given in Australian Standard 2521–1982.

## 5 Reagents

### 5.1 Calibration gases

Standard gases (Australian Standards 3580.2.1–1990 and 3580.2.2–1990) shall be used to calibrate the instruments through the entire system where applicable.

## 6 Calibration

6.1 Instruments shall be calibrated according to the following Australian Standards:

- AS3580.7.1–1992 Determination of carbon monoxide—direct-reading instrumental method
- AS3580.4.1–1990 Determination of sulfur dioxide—direct-reading instrumental method.
- AS3580.5.1–1993 Determination of oxides of nitrogen—chemi-luminescent method.

For oxygen and carbon dioxide analysers, zero and span gas calibration shall be carried out in accordance with AS3580.7.1–1992.

## 7 Procedure

7.1 Source parameters—determine the following source parameters prior to sampling:

- a gas velocity and volumetric flow rate (Test Method 03.10)
- b molecular weight of stack gas (Test Method 03.08)
- c moisture content of stack gas (Test Method 03.13).

7.2 Instrument warm-up. The instruments are turned on overnight prior to sampling.

7.3 Leak checking—assemble the sampling train with the probe as shown in Figure 14.1. Leak check the system at the sampling site by disconnecting the sample line at the probe exit, plugging the line and adjusting the vacuum to 50 kpa with the bypass valve. The flow from the pump shall be measured with a rotameter or equivalent, located immediately after the pump. A leakage rate not in excess of  $0.0005 \text{ m}^3 \text{ min}^{-1}$  is acceptable. The manifold shall be disconnected to achieve this. If no leaks are apparent, the manifold shall be reconnected.

7.4 Train operation. The procedure shall be as follows:

- a Set up the sampling train as described in section 7.3, with overnight instrument warm-up.
- b Switch on any heaters for the instrument and check that they are functioning correctly.
- c Insert the probe tube through the access hole until the in-stack filter is located at the centre of a sampling traverse.
- d Allow the equipment within the stack or duct to attain the temperature of the stack or duct gases.
- e Start the pump and adjust the gas flow to a minimum rate of  $0.03 \text{ m}^3 \text{ min}^{-1}$ , ensuring the sampling flow is 10% above the analyser requirement.
- f Allow the stack or duct gases to be pumped through the sampling train for a conditioning period of at least 1 hour.
- g Carry out zero and span gas calibration via the probe prior to commencement of test
- h The test may now commence. Note the test number, name of operator, date and start time of test on the chart recorder paper of each instrument. Also note zero and span concentrations. Record sample range used and any changes throughout the run. Calibrations shall be performed in accordance with section 6.1 prior to and at various time intervals during the test.

- i Calibration and zero checks should be recorded in the 'Instrumentation Calibration Log'.
- j At the conclusion of sampling, turn off the pump. Remove the probe tube and in-stack filter from the access hole.
- k Perform a final calibration at the end of the test.
- l Allow a warm-down period for the analysers. A zero concentration on the chart recorder indicates that any residual sample or span gas has been flushed from the line.
- m Turn off all the instrumentation.
- n Remove the sampling train from the sampling site.

## 8 Calculations

### 8.1 Concentration of each gas

Concentration of oxygen, carbon dioxide, carbon monoxide, sulfur dioxide and oxides of nitrogen.

$$C_g = C_{\text{ppm}} \times \frac{M}{22.414}$$

Equation 14.1

where:

$C_g$  = Concentration of gas, standard conditions, dry basis, mg/m<sup>3</sup>.

$C_{\text{ppm}}$  = Concentration of gas measured by analyser, ppm.

22.414 = the volume occupied by 1 g-mole of ideal gas at 273 K and 101.3 kPa, litres.

$M$  = molecular mass of gas

$M_{O_2}$  = 32 for O<sub>2</sub>

$M_{CO_2}$  = 44 for CO<sub>2</sub>

$M_{CO}$  = 28 for CO

$M_{SO_2}$  = 64 for SO<sub>2</sub>

$M_{NO}$  = 30 for NO

$M_{NO_2}$  = 46 for NO<sub>2</sub>

### 8.2 Mass flow rate of each gas

$$(R_m)_{\text{std}} = C_p(Q_{\text{std}})_d \times 10^{-3}$$

Equation 14.2

where:

$(R_m)_{\text{std}}$  = Mass flow rate of gas, standard conditions, dry basis, g/s

$C_p$  = Concentration of gas, standard conditions, dry basis,  $\text{mg}/\text{m}^3$  (see Equation 16.1)

$Q_{\text{std}}$  = Volumetric flow rate, standard conditions, dry basis,  $\text{m}^3/\text{s}$  (see Test Method 03.10, section 6.2)

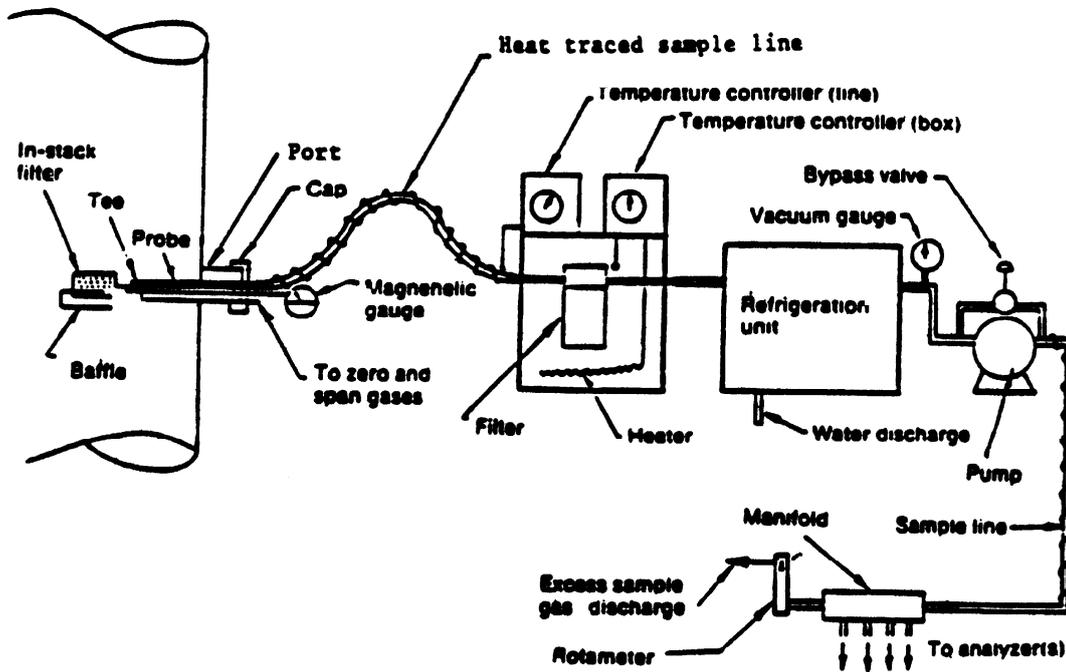
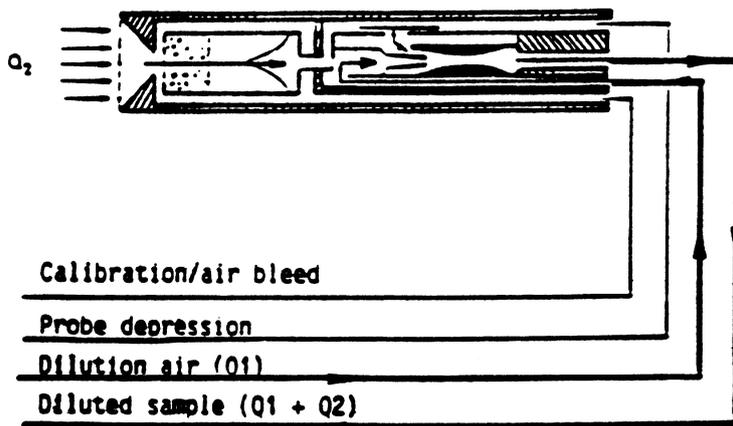


Figure 14.1 Continuous gas sampling train



$$\text{Dilution Ratio} = \frac{Q_2}{Q_1 + Q_2}$$

Figure 14.2 Dilution probe

## **Appendix 1 Data sheets**

**The following data sheets are for the source sampling of particulate and gaseous air pollutants.**

**Data sheet 1**

Plant \_\_\_\_\_

Probe heat setting \_\_\_\_\_

Location \_\_\_\_\_

Nozzle diameter, mm \_\_\_\_\_

Operator(s) \_\_\_\_\_

C factor \_\_\_\_\_

Date \_\_\_\_\_

Ambient temperature, K \_\_\_\_\_

Run no \_\_\_\_\_

Barometric pressure, kPa \_\_\_\_\_

Sample box no \_\_\_\_\_

Moisture content, % v/v \_\_\_\_\_

Meter box no \_\_\_\_\_

Heat box setting \_\_\_\_\_

Probe length, metres \_\_\_\_\_



Schematic of stack cross-section



**Data sheet 2****Particulate collection**

Plant \_\_\_\_\_

Date \_\_\_\_\_

Run no \_\_\_\_\_

Container	Weight of particulate collected, mg		
	Final weight	Tare weight	Weight gain
1			
2			
<b>Total</b>			

**Data sheet 3****Water content**

	Volume of liquid water collected	
	Impinger volume (ml)	Silica gel weight (g)
<b>Final</b>		
<b>Initial</b>		
<b>Liquid collected</b>		
<b>Total volume collected</b>		<b>g* ml</b>

\* Convert weight of water to volume by dividing total weight increase by density of water ( $\rho = 1 \text{ g} \cdot \text{ml}^{-1}$ ).

$$\frac{\text{Increase, g}}{1 \text{ g ml}^{-1}} = \text{Volume of water (ml)}$$

## Appendix 2 Specifications of ancillary apparatus recommended for stack sampling

### 1 Glassware

#### 1.1 Source sampling cyclone

Although this piece of equipment has not been specified for the collection of particulate matter in Method 03.01, its use is recommended in situations where there is danger of overloading the filter.

The probe is connected directly to the cyclone, which in turn is attached to a modified filter holder that has also been fitted with ball joints. The dimensions of the cyclone are given in Figure A.2.1.

#### 1.2 Filter holder

The filter holder is held together with a suitable clamp that is fabricated from 4-mm aluminium. This holder contains a glass frit and also has a silicone gasket.

From the filter a ball-joint fitted connector leads into the first impinger. The dimensions of the filter holder are given in Figure A.2.2.

#### 1.3 Greenburg–Smith Impinger

The details of the construction of a Greenburg–Smith Impinger for stack sampling work are given in Figure A.2.3.

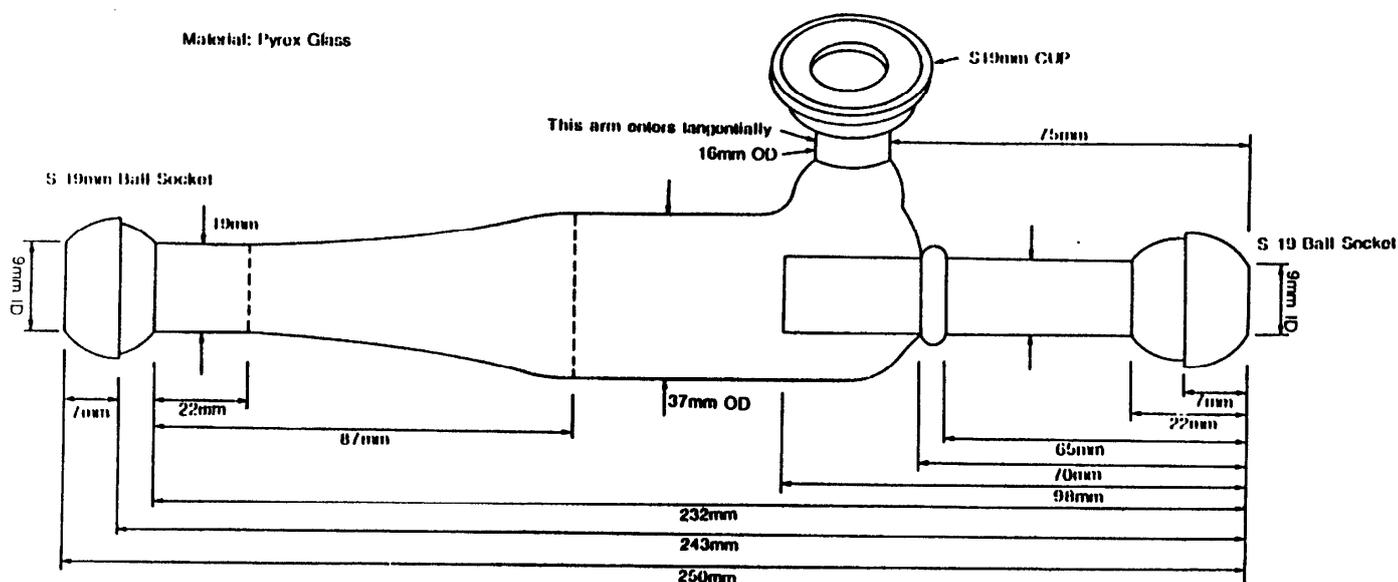


Figure A.2.1 Cyclone

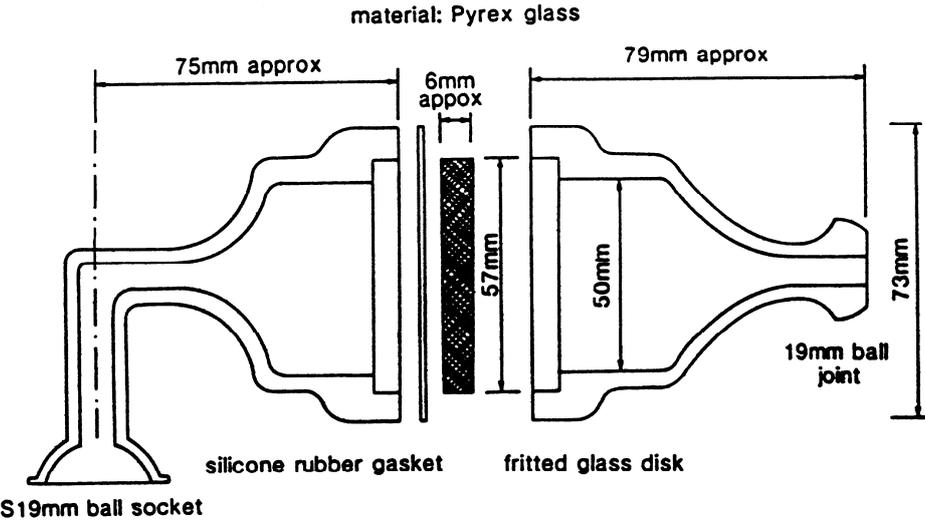


Figure A.2.2 Filter holder

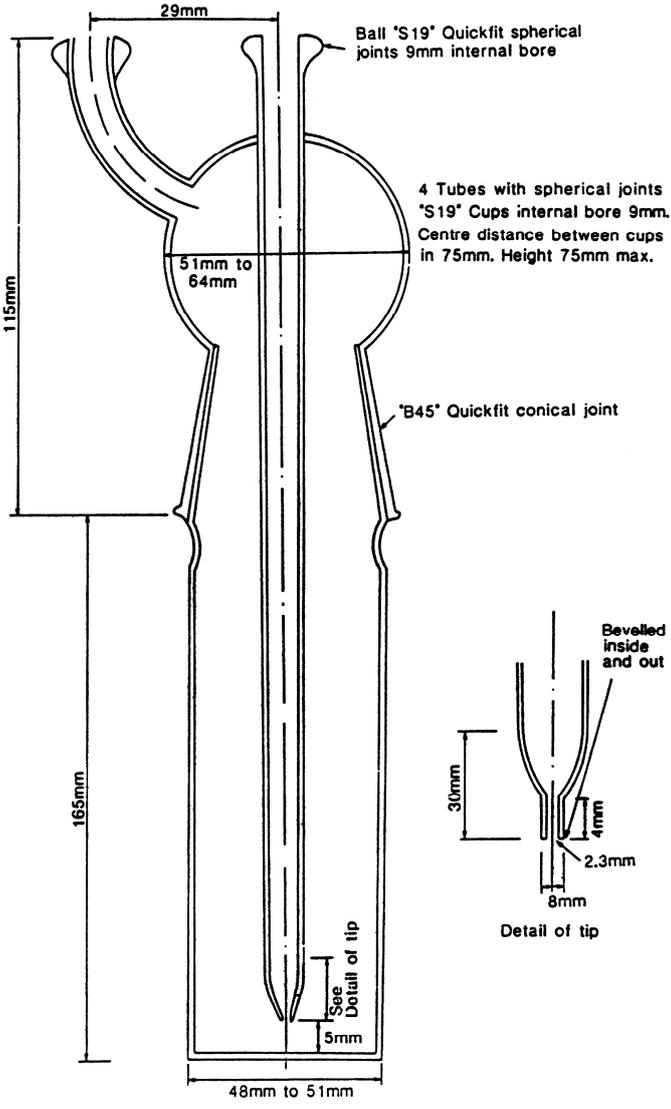


Figure A.2.3 Greenburg-Smith Impinger

## **Acknowledgments**

The EPA wishes to acknowledge the generous support of the Victorian Environment Protection Authority and its staff in the preparation and review of this document.