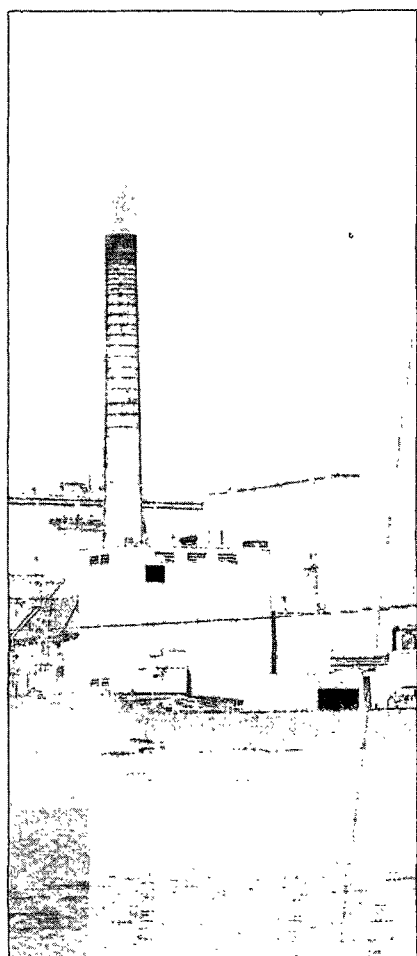


Environmental Protection Series



Reference Method for Source Testing: Measurement of Releases of Total Reduced Sulphur (TRS) Compounds from Pulp and Paper Operations

Reference Method EPS 1/RM/6
January 1992

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1-RM-6

Canada

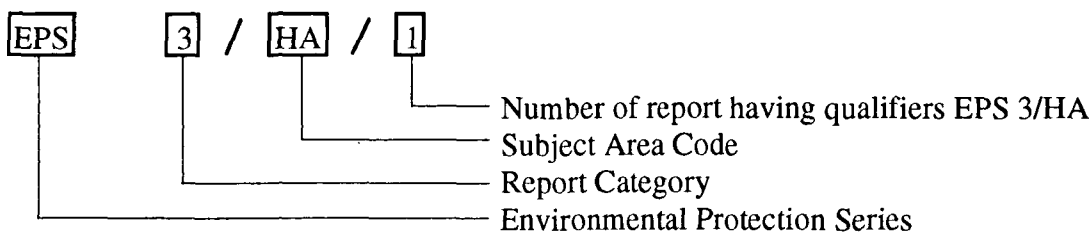


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Reference Method for Source Testing: Measurement of Releases of Total Reduced Sulphur (TRS) Compounds from Pulp and Paper Operations

Pollution Measurement Division
Technology Development Branch
Environmental Protection
Conservation and Protection
Environment Canada

Reference Method EPS 1/RM/6
January 1992

CANADIAN CATALOGUING IN PUBLICATION DATA

Main entry under title:

Reference method for source testing : measurement of releases of total reduced sulphur (TRS) compounds from pulp and paper operations

(Report ; EPS 1/RM/6)

Text in English and French with French text on inverted pages.

Title on added t.p.: Méthode de référence en vue d'essais aux sources, mesure des rejets de soufre réduit total (SRT) des usines de pâtes et papiers.

ISBN 0-662-58703-0

DSS cat. no. En49-21/1-6

1. Wood-pulp industry -- Canada -- Waste disposal.
2. Factory and trade waste -- Canada. 3. Sulphur compounds. I. River Road Environmental Technology Centre. Pollution Measurement Division. II. Canada. Environment Canada. III. Title: Méthode de référence en vue d'essais aux sources, mesure des rejets de soufre réduit total (SRT) des usines de pâtes et papiers. IV. Series: Report (Canada. Environment Canada) ; EPS 1/RM/6.

TD899.W65R43 1991

676'.042

C92-099528-4E

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Foreword

This Environment Canada Reference Method (RM) is used to measure the total reduced sulphur (TRS) compounds released into the ambient air from stationary sources of pulp and paper operations. This method is used in conjunction with those described in Environment Canada Reference Method EPS 1/RM/8, "Standard Reference Methods for Source Testing: Measurement of Releases of Particulate from Stationary Sources". The complexity of the procedures in these methods warrants that personnel performing them should be trained and experienced.

Application of this RM for compliance testing requires strict adherence to the method in all respects. Deviation from the method may invalidate the test results. Any changes in equipment, reagents, materials, procedures, or calculations from those specified in the RM must be approved in writing by Environment Canada before testing. If deviations are made without prior approval, the validity of the tests shall be determined by Environment Canada on a case-by-case basis.

Note: Mention of trade names or commercial products does not constitute endorsement for use by Environment Canada.

Table of Contents

Foreword	v
List of Figures	viii

Section 1

Sampling	1
1.1 Scope	1
1.2 Gas Sampling - Bag Method (Method S-1)	1
1.2.1 Principle	1
1.2.2 Apparatus	1
1.2.3 Materials	2
1.2.4 Procedures	2
1.3 Gas Sampling - Bottle Method (Method S-2)	6
1.3.1 Principle	6
1.3.2 Apparatus	6
1.3.3 Materials	6
1.3.4 Procedures	6

Section 2

Analysis	8
2.1 Analytical Method for Total Reduced Sulphur Samples (Method A-1)	8
2.1.1 Principle and Applicability	8
2.1.2 Sensitivity	8
2.1.3 Reproducibility	8
2.1.4 Interferences	8
2.1.5 Apparatus	8
2.1.6 Gases	8
2.1.7 Procedures	9
2.1.8 Calibration of the Gas Chromatograph	9
2.1.9 Calculations	11

List of Figures

1	Probe Details	2
2	Impinger Modifications	3
3	Total Reduced Sulphur Sampling Data Sheet	4
4	“Leak-Checking” Sample Bag or Bottle	5
5	Sampling Train Using Bag	5
6	Three-way Valve Positions	6
7	Sampling Train Using Teflon Bottle	7
8	Total Reduced Sulphur Analysis Data Sheet	10

Section 1

Sampling

1.1 Scope

The procedures described in this section are applicable to the sampling of stacks or ducts in pulp and paper operations. The following procedures, contained in Reference Method EPS 1/RM/8 "Standard Reference Methods for Source Testing: Measurement of Releases of Particulate from Stationary Sources", form part of this method:

- (a) Determination of Sampling Site and Traverse Points (Method A);
- (b) Determination of Stack Gas Velocity and Volumetric Flow Rate (Method B);
- (c) Determination of Molecular Weight by Gas Analysis (Method C);
- (d) Determination of Moisture Content (Method D).

1.2 Gas Sampling - Bag Method (Method S-1)

1.2.1 Principle

A gas sample is withdrawn from a point at the centre of a stack or duct. The sample is drawn through an impinger containing concentrated phosphoric acid to remove water vapour, and collected in a Teflon or Tedlar bag.

1.2.2 Apparatus

The following equipment is required.

Probe: A probe consisting of a Teflon tube with an outside diameter of 6 mm (1/4 in.) and encased in a rigid pipe. A fitting, modified as shown in Figure 1, is provided at the probe exit to prevent air from diluting

the sample gas. The sample is extracted from the centre of the stack or duct. If this sampling point cannot be used due to practical limitations on the probe length, then a sample extraction point may be selected no less than 30 cm (12 in.) from the wall of the duct or stack. Note the location on a diagram and append to the other documents in the report.

Temperature Gauge: A temperature gauge capable of measuring to within 3°C (5°F) for the range of temperatures encountered in the stack.

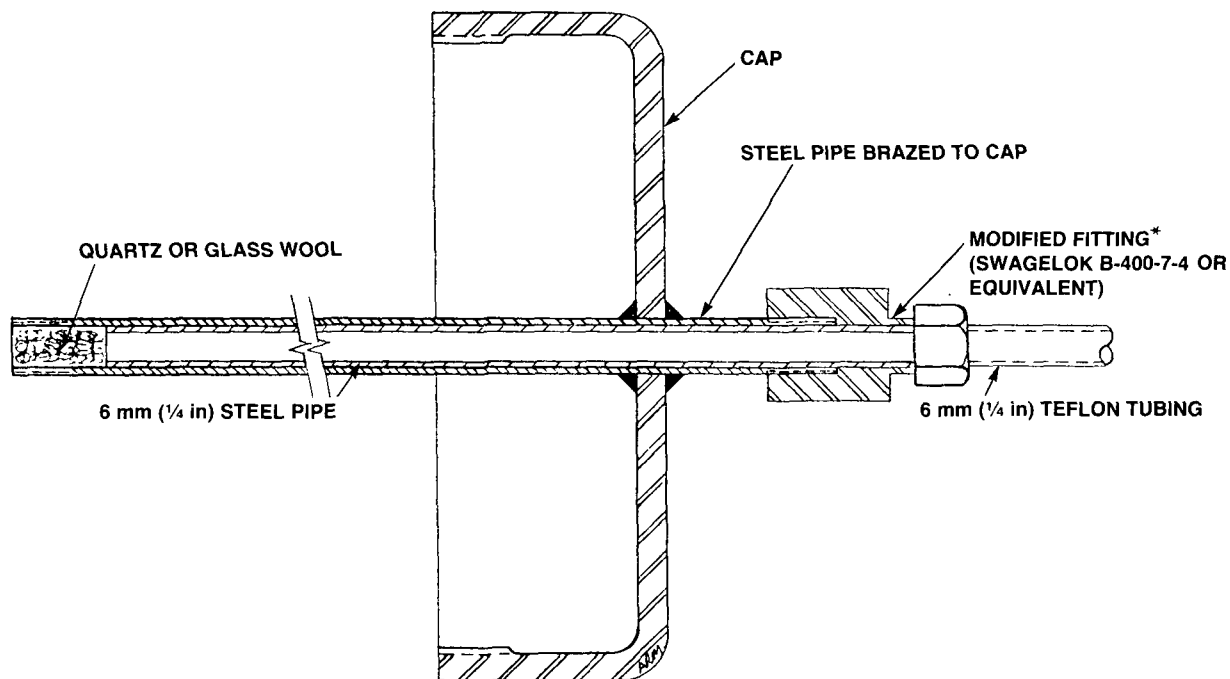
Sample Bag: A Tedlar or Teflon bag, of approximately 1 L volume, with inside dimensions of 25 × 15 cm (10 × 6 in.) fitted with a Teflon male connector with an "O" ring seal.

Tubing: All tubing contacting the sample shall be Teflon. The tubing connecting the probe exit and impinger inlet shall be as short as possible, and heated to prevent condensation of water vapour.

Bag Container: A translucent plastic box large enough to contain the sample bag. The box is fitted with two 6-mm (1/4 in.) bulkhead connectors, one of which is enlarged to allow the 6-mm (1/4 in.) sample line to be pushed through the fitting. The lid of the box is removable but airtight when sealed.

Pump: A battery or line voltage-operated pump to create a vacuum in the bag container.

Barometer: A barometer, capable of measuring atmospheric pressure to within ± 0.35 kPa (0.1 in. Hg), shall be used.



* FITTING MODIFIED TO ALLOW 6 mm (1/4 in) TUBE TO BE DRAWN THROUGH

Figure 1 Probe Details

Valve: A three-way valve, made of Teflon or stainless steel, is used to divert gas flows (Whitey SS-42XS4 or equivalent).

Impinger: A modified 25-mL impinger, as shown in Figure 2.

Filter: A wad of quartz wool or silanized glass wool may be used at the inlet end of the probe to filter particulate matter, if required.

1.2.3 Materials

The following materials are required.

Phosphoric Acid: Reagent grade, 85% H_3PO_4 by volume.

Water and Crushed Ice.

1.2.4 Procedures

Preliminary: Select a suitable sampling site and follow the procedures in Methods A to

D of Reference Method EPS 1/RM/8 to determine the average stack gas velocity [(Us)avg] and volumetric flow (Qs). Enter these values on the Total Reduced Sulphur Sampling Data Sheet (Figure 3).

“Leak-Checking” of Bags: All bags must be “leak-checked” before use. Set up the equipment as shown in Figure 4. Open valve A and slowly pressurize the bag to 25 cm of water, then close the valve. Discard or repair any bag that demonstrates a pressure drop equivalent to more than 1 cm (0.4 in.) of water over a 20-minute period.

Sampling: Place 10 mL of fresh, concentrated phosphoric acid in a clean, modified 25-mL impinger. Before use, cool the impinger and contents by placing it in a beaker containing crushed ice and water for 15 minutes. Assemble the apparatus as

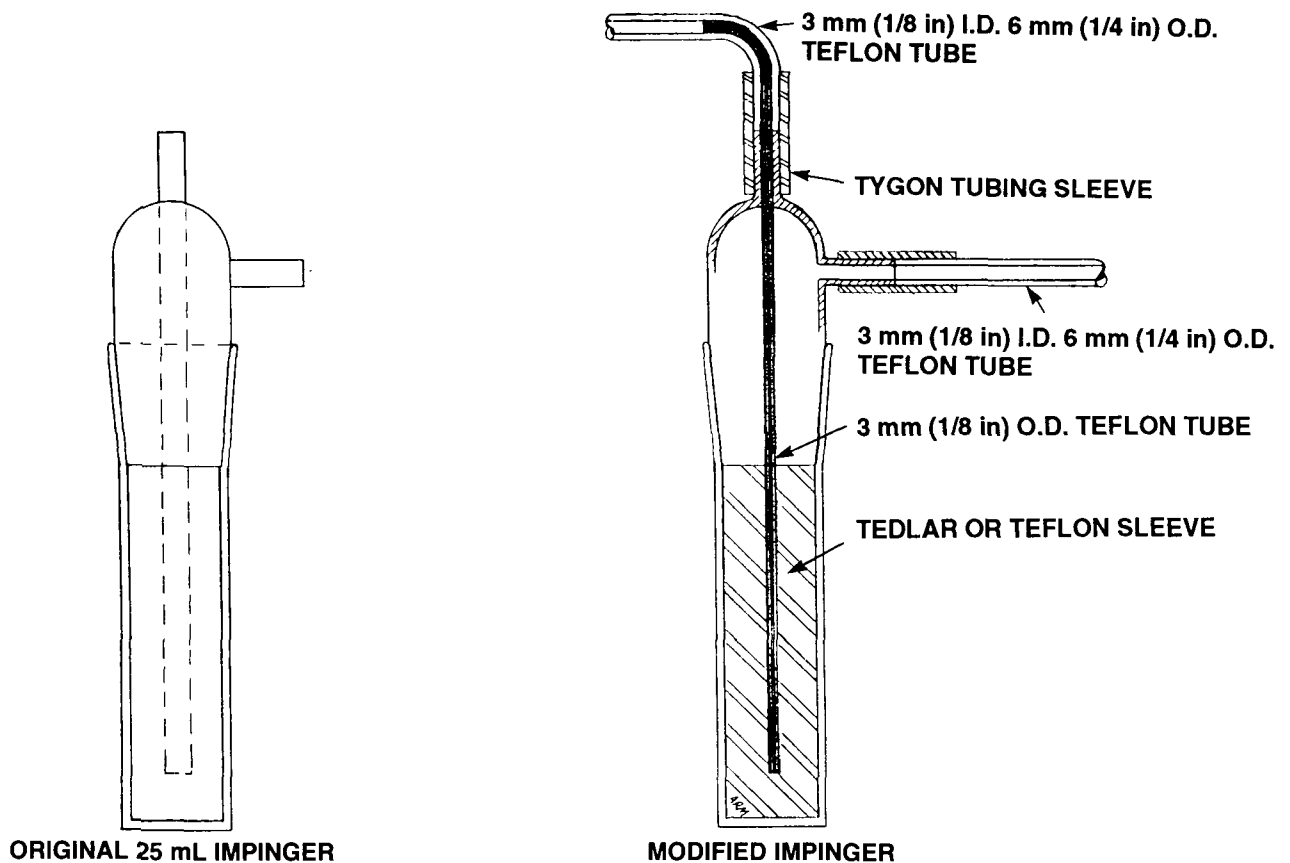


Figure 2 Impinger Modifications

shown in Figure 5, but do not connect the sample bag to the three-way valve.

The various positions of the three-way valve are illustrated in Figure 6. Connect the pump to port B on the three-way valve and turn the valve to the "sample" position. Purge the probe, sample lines and impinger with sample gas for about 30 seconds. Turn the valve to the "seal" position, disconnect the pump and connect the bag to part B on the three-way valve and connect the pump to the "evacuate" fitting on the box. Turn the valve to the "sample" position, turn on the pump and let the bag fill with stack gas. Turn off the pump and turn the valve to the "seal" position. Allow the bag to sit for 10 minutes to condition the surfaces. Connect the pump to port C of the three-way valve, then turn the valve to the "evacuate" position and turn on the pump. When the

bag is empty, turn the valve to the "seal" position, then turn off the pump.

Connect the pump to the evacuate fitting, turn the three-way valve to the "sample" position and turn on the pump to collect the sample. The bag must be filled in 30 to 60 seconds. If necessary, a flow control valve may be inserted in the tubing that connects the rigid container and the sample pump. After the bag is full, turn the three-way valve to the "seal" position and turn off the pump. Disconnect the valve and sample bag container assembly from the impinger outlet and pump. Transport the sample to the gas chromatograph for analysis.

The analysis must begin within one hour of taking the sample. Fill in one Sampling Data Sheet (Figure 3) for each sample taken.

General Information	
Company	
Plant location	
Emission source	
Date	
Sample number	
Time of sampling	

Sampling and Emission Data			
Parameter	Symbol	Value	Units
Barometric pressure	Pbar		kPa
Stack area	As		square meters
Average stack gas temperature (Note 1)	(Ts)avg		K
Average stack gas velocity (Note 1)	(Us)avg		meters per second
Stack gas volumetric flow, dry basis (Note 1)	Qs		dry standard cubic meters per hour
Molecular weight of stack gas, dry basis (note 2)	Md		dimensionless
Moisture content of stack gas (Note 3)	Bwo		dimensionless
TRS concentration (from Figure 8)	C _{TRS}		ppm
TRS mass emission rate (Note 4)	ER _{TRS}		kilograms per hour

Note 1 – from Method B, EPS 1/RM/8

Note 2 – from Method C, EPS 1/RM/8

Note 3 – from Method D, EPS 1/RM/8

Note 4 – calculated using Equation 3, Section 2.1.9 of TRS Method

Attach the following to this page
- Velocity Traverse Sheet from EPS 1/RM/8
- Moisture Data Sheet from EPS 1/RM/8
- Molecular Weight Data Sheet from EPS 1/RM/8
- Figure 8, Total Reduced Sulphur Analysis Data Sheet

Figure 3 Total Reduced Sulphur Sampling Data Sheet

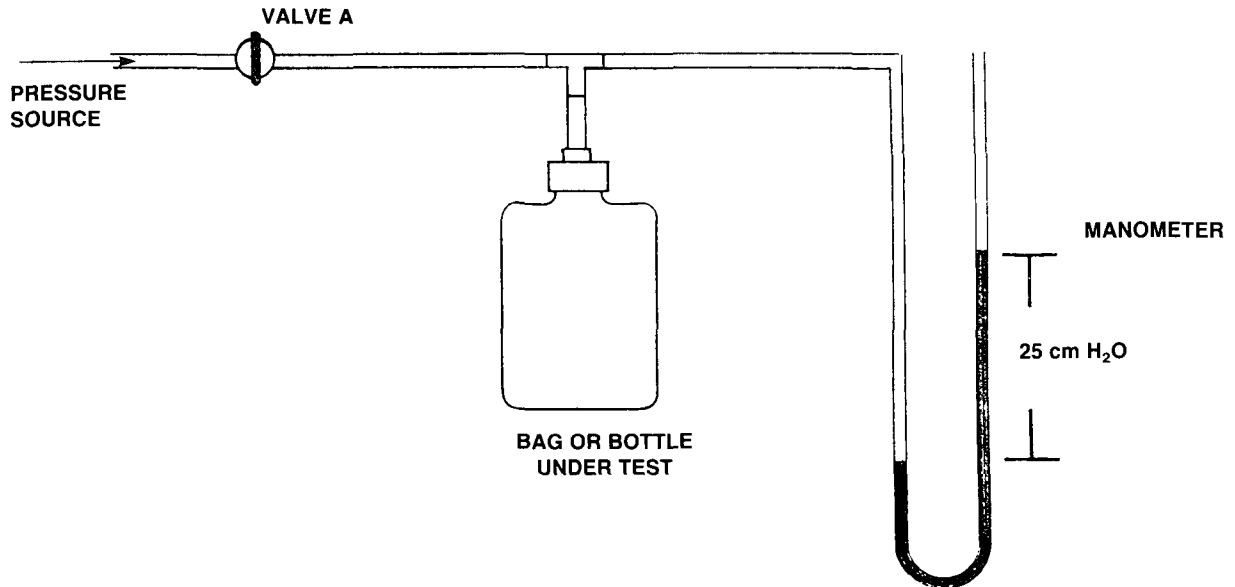


Figure 4 "Leak-Checking" Sample Bag or Bottle

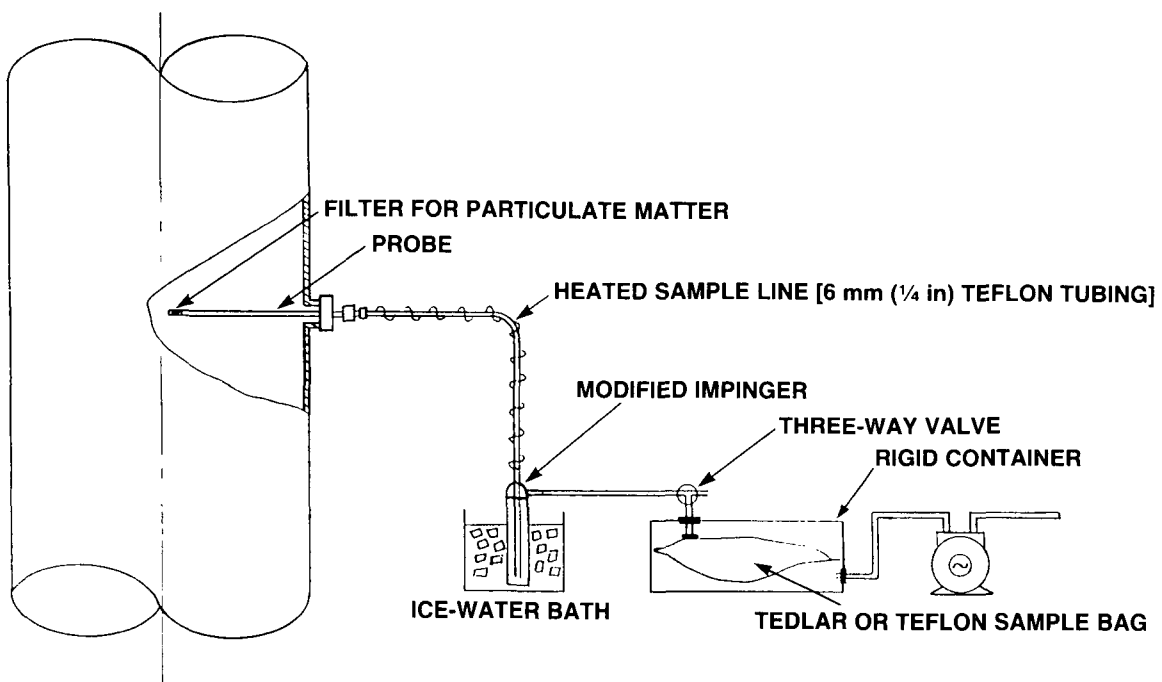
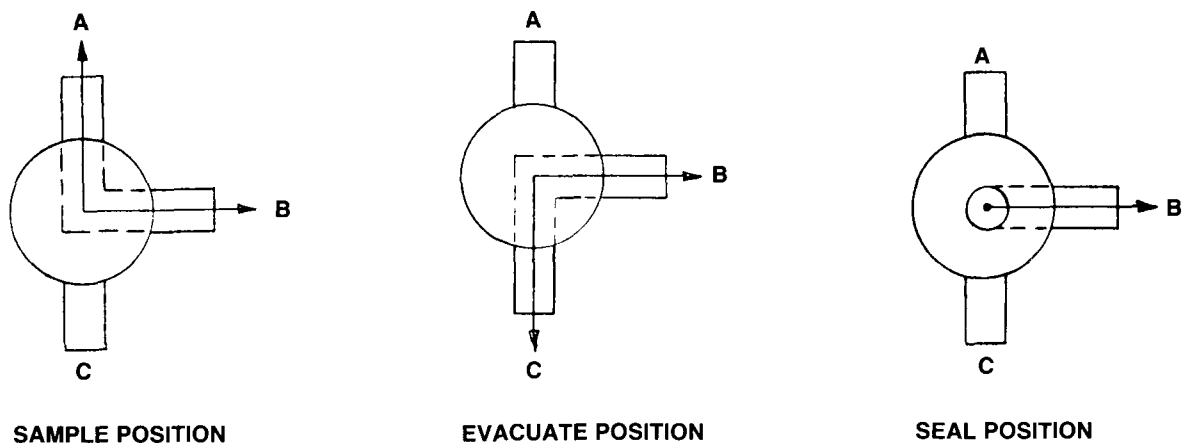


Figure 5 Sampling Train Using Bag



A - FROM IMPINGER
B - TO BAG OR BOTTLE
C - OPEN TO ATMOSPHERE

Figure 6 Three-way Valve Positions

1.3 Gas Sampling - Bottle Method (Method S-2)

1.3.1 Principle

A gas is withdrawn from a point at the centre of a stack or duct. The sample is drawn through an impinger containing phosphoric acid to remove water vapour and collected in a 500-mL Teflon bottle.

1.3.2 Apparatus

The following equipment is required.

Bottle: A 500-mL Teflon bottle, modified to accept a Teflon fitting (Swagelok T-400-1-OR or equivalent), shall be used.

Probe
 Temperature Gauge
 Tubing
 Barometer
 Valve
 Impinger

See
 Subsection 1.2.2

1.3.3 Materials

The following materials are required.

Phosphoric Acid

Water and Crushed Ice

1.3.4 Procedures

Preliminary: See procedures in Subsection 1.2.4.

“Leak-Checking” Bottles: Follow procedures in Subsection 1.2.4, substituting the sample bottles for the bags.

Sampling: Place 10 mL of concentrated phosphoric acid in a clean modified 25-mL impinger. Before use, cool the impinger and contents by placing it in a beaker containing crushed ice and water for 15 minutes.

Set up the apparatus as shown in Figure 7. With the three-way valve set for the “evacuate” position (see Figure 5), squeeze the Teflon bottle to expel as much air as possible. Turn the three-way valve to the “sample” position and release the pressure

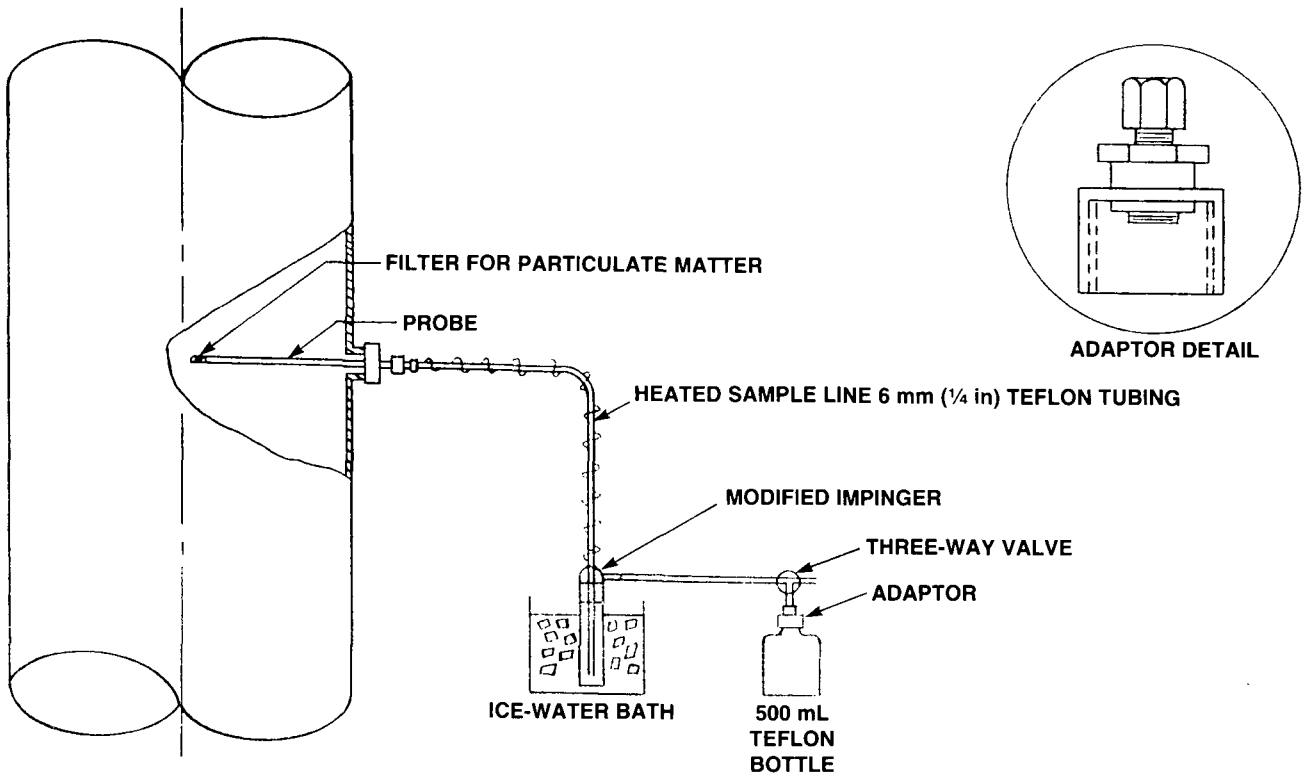


Figure 7 Sampling Train Using Teflon Bottle

on the bottle. Allow the Teflon bottle to fill completely. Repeat the evacuate/sample procedure at least 10 times to ensure that the sample contains little residual dilution air. Turn the valve to the "seal" position. Allow the bottle to stand for 10 minutes to condition the surfaces.

Turn the valve to the "evacuate" position and squeeze the bottle to expel as much gas as possible. Turn the valve to the "sample" position and release the pressure on the

Teflon bottle and allow it to fill completely. Repeat the evacuate/sample cycle at least 10 times. At the conclusion of sampling, turn the valve to the "seal" position and disconnect it from the impinger. Transport the bottle and valve to the gas chromatograph for analysis.

The analysis must begin within one hour of taking the sample. Complete a Sampling Data Sheet (Figure 3) for each sample taken.

Section 2

Analysis

2.1 Analytical Method for Total Reduced Sulphur Samples (Method A-1)

2.1.1 Principle and Applicability

An aliquot of a gaseous sample contained in a Tedlar or Teflon bag or bottle is analyzed for hydrogen sulphide (H₂S), methyl mercaptan (CH₃SH), dimethyl sulphide [(CH₃)₂S], and dimethyl disulphide [(CH₃)₂S₂] by gas chromatographic separation and flame photometric detection.

2.1.2 Sensitivity

The detection limit may vary according to the gas chromatograph specifications, separation column and the operating parameters. Under the analytical conditions described in this method, and using a 1-mL sample loop, concentrations of TRS measured as H₂S of 1.41 mg/m³ (1 ppm) can be detected.

2.1.3 Reproducibility

Successive injections of TRS mixtures and samples show a coefficient of variation of 3 to 5%. This value includes sampling and analytical variance.

2.1.4 Interferences

For most sources, there should be no interference in the chromatographic separation of TRS compounds using the chromatographic separation column and temperature parameters specified. If it is desirable to resolve SO₂ and COS, the samples may be analyzed for these compounds by using a separate Teflon column 2 m × 3 mm (79 × 0.125 in.) packed with Chromosil 310.

2.1.5 Apparatus

Gas chromatograph: A gas chromatograph with the following features is used to analyze the gaseous samples:

- a linearly programmable oven temperature;
- a flame photometric detector equipped with a narrow band pass filter of 393 nm;
- a potentiometric strip chart recorder;
- an automatic integrator.

Chromatographic column: The separation column is Teflon tubing with an outside diameter of 3 mm (0.125 in.) and 1.4 m (4.6 ft.) long, packed with Carbopack B-HT.100. Before initial use, the column should be conditioned for at least 18 hours at 120°C (248°F) with a 10 mL/min flow of helium gas. This column will resolve SO₂ and the four major reduced sulphur compounds: H₂S; CH₃SH; (CH₃)₂S; and (CH₃)₂S₂, when used with the operating parameters described in Subsection 2.1.7.

Gas controls: Carrier and fuel gases used with the gas chromatograph shall be reproducibly flow-adjustable by either pressure or flow regulation and monitored by rotameters or other flow-measuring devices.

A gas sampling valve equipped with a 1-mL sampling loop is used to inject sample gases into the chromatograph.

2.1.6 Gases

Helium: The carrier gas shall be helium, high purity.

Hydrogen: The detector hydrogen gas shall be zero grade.

Air: The detector air supply shall be zero grade.

Oxygen: The detector oxygen gas shall be of ultra high purity.

Nitrogen: High purity nitrogen shall be used to dilute TRS mixtures.

Standard total reduced sulphur (TRS) blends in cylinders: Standard commercial gas mixtures of TRS blends in nitrogen in cylinders shall be used. All mixtures shall be provided with certified analysis traceable to a certificate of analysis. Dilutions of the blends using standard dynamic dilution techniques and high purity nitrogen will provide a series of gases with appropriate concentrations for the generation of the gas chromatograph response curves.

2.1.7 Procedures

Gas chromatograph (GC) parameters:

Adjust the temperature of the gas chromatograph zones as follows:

Detector Temperature	150°C (302°F)
Injector Temperature	200°C (392°F)
Oven Temp. - Initial	50°C (122°F)
	- isothermal three min
Program rate	30°C/min (86°F/min)
Final	115°C (239°F) - hold for 10 min

Optimization of Flame Photometric Detector (FPD) response: Using the temperature settings and appropriate attenuation and gain settings on the gas chromatograph, adjust the carrier gas flow to 35 mL/min. Ignite the FPD burner, following the manufacturer's instructions. To optimize FPD response, use a series of 1-mL injections of H₂S standards and adjust the oxygen flow to the burner to produce a

maximum integrator response. Note and record the flow rates of hydrogen, air and oxygen supplying the FPD. These flows must be checked daily and maintained during all calibration and analysis runs.

Analysis: Observe the baseline periodically to determine if the noise level has stabilized and any baseline drift has ceased.

Connect the three-way valve on the bag or bottle to the gas inlet of the GC sampling valve. Squeeze the bag or bottle to force a sample through the sample loop. Allow 30 seconds for the pressure in the loop to stabilize. Turn the injection valve to the "inject" position and simultaneously start the integrator. Turn the three-way valve to the "seal" position.

Record the required information for each sample analyzed on the Total Reduced Sulphur Analysis Data Sheet (Figure 8). From the recorder chart, select the peaks corresponding to H₂S, CH₃SH, (CH₃)₂S, and (CH₃)₂S₂. Measure the peak areas, A_m for each compound, using the automatic integrator. Record A_m and retention time for each TRS compound. Repeat the analysis at least twice or until two consecutive sets of results agree within 5%. The average value for these two area data sets will be used to calculate the TRS concentration in the sample.

2.1.8 Calibration of the Gas Chromatograph

The gas chromatograph should be calibrated using chromatographic conditions identical to those specified in Subsection 2.1.7. Ensure that the bags or bottles have been flushed with the calibration blends and allowed to stand for 10 minutes before use. Fill the sample bags or Teflon bottles with calibration gas mixtures and analyze the calibration mixtures as described under Analysis in Subsection 2.1.7. Dilutions of stock blends of TRS in nitrogen may be

General Information	
Company	
Plant location	
Emission source	
Date	
Sample number	
Time of analysis	
Analyst	

Analytical Data		
Parameter	Value	Units
Temperatures		
Injection port		°C
Detector		°C
GC oven programme		°C and minutes
Volume of injected sample		mL
Gas pressures and flows		
oxygen (FPD)	pressure	kPa
	flow	mL/min
hydrogen (FPD)	pressure	kPa
	flow	mL/min
air (FPD)	pressure	kPa
	flow	mL/min
helium (carrier)	pressure	kPa
	flow	mL/min
Analytical results		
H ₂ S		ppm
CH ₃ SH		ppm
(CH ₃) ₂ S		ppm
(CH ₃) ₂ S ₂		ppm
TRS as H ₂ S (Note 1)		ppm

Note 1 – Calculate using Equation 2 of TRS Method

Figure 8 Total Reduced Sulphur Analysis Data Sheet

made by dynamic mixing with high purity nitrogen at known flow rates. These dilutions can be measured by using rotameters or mass flow meters. At least two dilutions should be made. Inject a 1-mL sample of the high purity nitrogen. Record the column temperature, the carrier gas flow rate, chart speed, and the amplifier gain and attenuation settings. Record any peaks or detector responses that occur in the absence of TRS compounds. Maintaining the same conditions, analyze each of the calibration gas mixtures. Select the peaks that correspond to H₂S, CH₃SH, (CH₃)₂S and (CH₃)₂S₂ and record the following: retention times; concentrations of the TRS components; attenuator and amplifier gain settings; chart speed; peak area; carrier gas flow rate; barometric pressure; and volume of sample injected.

Calculate A_c, which is the sample peak area as given in the calculations (Subsection 2.1.9). Repeat the analysis until two sets of component area data agree within 5%. Plot the peak areas against concentration for each of the TRS components in the calibration blends on log-log graph paper. Draw the best fit line through the points for each of the components. Calibrate the chromatograph daily.

2.1.9 Calculations

Sample peak area determination:

Determine the sample area for each TRS component as follows:

$$A_c = A_m G_f \quad (1)$$

where:

A_c - the sample peak area

A_m - the measured peak area

G_f - the amplifier gain factor

Total reduced sulphur (TRS)

concentrations: From the calibration curves described in Subsection 2.1.8, select the concentration of each of the individual TRS components, H₂S, CH₃SH, (CH₃)₂S and (CH₃)₂S₂, that corresponds to the sample peak area. Calculate the concentration of the TRS components measured as H₂S, using Equation 2.

$$C_{\text{TRS}} = C_{\text{H}_2\text{S}} + C_{\text{CH}_3\text{SH}} + C_{\text{(CH}_3)_2\text{S}} + 2 C_{\text{(CH}_3)_2\text{S}_2} \quad (2)$$

Analysis report: Fill in the required information for each sample analyzed on the TRS Analysis Data Sheet (Figure 8).

Calculation of Mass Emission Rate: Using Equation 3, calculate the TRS emission rate in kg/h.

$$ER_{\text{TRS}} = K Q_s C_{\text{TRS}} \quad (3)$$

where:

C_{TRS} - Concentration of TRS in the sample, ppm, dry basis as H₂S

ER_{TRS} - Mass emission rate of TRS compounds in the stack gas on a dry basis at reference conditions, kg/h as H₂S

K - Constant:
1.41 × 10⁻⁶ kg/ppm·m⁻³

Q_s - Volumetric flow of stack gas on a dry basis at reference conditions, m³/h

Record this rate on the TRS Sampling Data Sheet (Figure 3).