

DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM COMBINATION BOILERS, RECOVERY FURNACES, AND THERMAL OXIDIZERS – ISOKINETIC METHOD

This method has been approved as a CTM on combination boilers and recovery furnaces.

The isokinetic version of the method is pending approval as a CTM for use on Thermal Oxidizers.

1.0 Introduction

Sulfuric acid emissions from combustion sources have traditionally been measured using EPA Method 8. EPA Method 8 adopts the principle of selective solvent absorption (SSA) and captures sulfur trioxide/sulfuric acid ($\text{SO}_3/\text{H}_2\text{SO}_4$) in 80% isopropyl alcohol (IPA) and SO_2 in 3% hydrogen peroxide. However, this method was originally promulgated for determining $\text{SO}_3/\text{H}_2\text{SO}_4$ emissions from stationary sources in the absence of other particulate matter. The drawback of this method is the absence of a filter to effectively remove particulates before the capture of $\text{SO}_3/\text{H}_2\text{SO}_4$ in IPA. For instance, particulate matter in flue gases from combination boilers, recovery furnaces, and thermal oxidizers would be captured in the IPA along with $\text{SO}_3/\text{H}_2\text{SO}_4$, contribute SO_4^{2-} ions, and cause positive biases in the sulfate measurements. NCASI Method 8A was developed as an alternative to EPA Method 8 and uses a heated quartz filter for capturing particulates, thereby eliminating the potential for interference from particulate sulfate. The quartz filter is maintained at temperatures $> 500^\circ\text{F}$, thereby allowing the gaseous $\text{SO}_3/\text{H}_2\text{SO}_4$ to pass through and be selectively condensed in a temperature controlled condenser. The condenser cools the flue gases below the dew point of $\text{SO}_3/\text{H}_2\text{SO}_4$ but above the dew point of water, thereby eliminating the potential for interference from SO_2 . This method was tested extensively on kraft recovery furnaces and was approved by the EPA for use on recovery furnaces in December 1996 (NCASI 1997).

The measurement method described here was developed and validated as an alternative for determining sulfuric acid emissions from combination boilers and recovery furnaces equipped with dry particulate control devices. The method combines the heated quartz probe/filter portion of NCASI Method 8A along with the impinger train used in EPA Method 8. This allows for the efficient separation of particulates while obviating the need for controlled condensation (CC) which is cumbersome and difficult to implement in the field. Sulfuric acid is not retained on the filter as the filter temperatures are well above the dew point of sulfuric acid. The isokinetic version of the method, summarized in the following sections, can be used to sample combustion sources in pulp mills equipped with wet control devices.

2.0 Method Description

2.1 Principle and Applicability

2.1.1 Principle – A gas sample is extracted isokinetically from the sampling point on the stack. The particulates are captured on the quartz filter. $\text{SO}_3/\text{H}_2\text{SO}_4$ and SO_2 pass through the filter and are captured by the isopropyl alcohol (IPA) and 3% hydrogen peroxide, respectively. The two sulfate fractions are quantified separately using either suppressed Ion Chromatography (IC) or the barium-thorin titration method.

2.1.2 Applicability – This method is suitable for use on combustion sources equipped with wet particulate control devices, for the determination of SO₃/H₂SO₄ in the presence of other particulate matter. Sulfur dioxide can also be quantified by analyzing the sulfate content in the peroxide impinger catches. Ion Chromatographic analyses for sulfate ions in the IPA and peroxide matrices provide a method detection limit (MDL) of 0.2 mg/L in the impinger solution, corresponding to an injection volume of 25 µL. Corresponding flue gas detection limits can be calculated for the applicable impinger catch volumes and sampling flow rates.

Possible interfering agents of this method are fluorides, free ammonia, and dimethyl aniline.

2.2 Apparatus

2.2.1 Sampling – A schematic of the sampling train is shown in Figure 1. A detailed schematic is provided in Figure 8-1 of EPA Method 8. The components of the train are discussed in the following sections. Greenburg-Smith impingers, similar to those used in EPA Method 8, are employed. The impingers are downstream of a heated quartz probe and quartz filter holder, housing the requisite quartz filter.

2.2.1.1 Probe Liner – Quartz probe liner with a heating system capable of reaching temperatures ranging from 450°F to 500°F. The probe is maintained at approximately 400°F during sampling.

2.2.1.2 Probe Nozzle – Same as EPA Method 5.

2.2.1.3 Quartz Filter Holder - The filter holder is placed inside a box and heated using a high temperature-heating mantle. The temperature of the filter holder is maintained above 500°F during sampling. This allows sulfur trioxide (SO₃) and sulfuric acid vapor to pass through the filter without being captured. A schematic of the filter holder is shown in Figure 2. An Omega woven glass insulated thermocouple is placed in the thermocouple well and is used for temperature control.

2.2.1.4 Quartz filter – QM-A grade quartz filters manufactured by Whatman®. The filter is placed on a coarse quartz frit. 37-mm diameter or appropriate sizing to fit the filter holder being used.

2.2.1.5 Unheated Filter Holder – Borosilicate glass with glass frit filter support and a silicone rubber gasket – similar to unheated filter used in EPA Method 8.

2.2.1.6 Impingers – Five Greenburg-Smith impingers similar to those used in EPA Method 8 are used. The first two impingers hold 100 ml each of 100% Isopropyl Alcohol (IPA). The third and fourth impingers hold 100 ml each of 3% hydrogen peroxide (H₂O₂). The fifth impinger holds silica-gel. The unheated filter/filter holder is placed between the second and third impingers (between IPA and peroxide).

2.2.1.7 Metering System – Same as EPA Method 5, Section 2.1.8.

2.2.1.8 Barometer/Gas Density Determination Equipment – Same as EPA Method 5, Sections 2.1.9 and 2.1.10.

2.2.2 Sample Recovery

2.2.2.1 Wash Bottles – Two Polyethylene bottles 500 ml in volume.

2.2.2.2 Graduated Cylinders – 25ml, 50 ml, 100 ml, 250 ml etc.

2.2.2.3 Storage Bottles – Leak-free Nalgene® bottles, 1 liter size (for IPA and peroxide impinger contents). 125 ml size (one for heated filter and one for unheated filter)

2.2.2.4 Trip Balance – 500 gm capacity. Capable to measure 0.1 gm.

2.2.3 Analysis

2.2.3.1 Barium-thorin titration – Same as EPA Method 8, Section 2.3.

2.2.3.2 Ion Chromatography – Sulfate ions (SO_4^{2-}) in the impinger catches may also be quantified using suppressed Ion Chromatography (IC). The IC system must include the following components.

2.2.3.2.1 Column – Anion exchange or equivalent column capable of separating the sulfate peak from other components. Anion suppressor columns are used in suppressed IC. Systems that do not include suppressor columns may also be used.

2.2.3.2.2 Pump – Capable of maintaining a steady flow as required by the system.

2.2.3.2.3 Conductivity Detector

2.2.3.2.4 Recorder – Compatible with the detector and enabling quantification of peak heights and areas.

2.3 Reagents

2.3.1 Sampling – Hydrogen Peroxide, Isopropyl alcohol (IPA), DI water. Same as described in EPA Method 8, Section 3.1

2.3.2 Sample Recovery – Reagents required for sample recovery are the same as in EPA Method 8, Section 3.2.

2.3.3 Analysis

2.3.3.1 Barium-thorin titration – Same as EPA Method 8, Section 3.3.

2.3.3.2 Ion Chromatography – The following additional reagents are required when analysis is carried out by Ion Chromatography (IC).

2.3.3.2.1 Eluent Solution – An example eluent capable of separating the sulfate ion from other species is 10mM sodium carbonate (Na_2CO_3) and 2mM sodium bicarbonate (NaHCO_3). This eluent solution can be made by dissolving 4.24 g of Na_2CO_3 and 0.672 g of NaHCO_3 in 4 liters of DI water. Other eluent solutions appropriate to the column type and capable of separating sulfate may also be used.

2.4 Procedures

2.4.1 Sampling

2.4.1.1 Preparation of collection train – Measure 100 ml of 100% IPA into the first and second impingers. Measure 100 ml of 3% hydrogen peroxide into the third and fourth impingers. The unheated filter/filter holder is placed between the second and third impingers (between IPA and peroxide). Place approximately 200 gm of silica gel in the fifth impinger. Since the moisture content is to be determined, weigh all the impingers to the nearest 0.5 gm and record the weights.

2.4.1.2 Leak-check procedure – Follow the procedures laid out in EPA Method 5, Section 8.4.

2.4.1.3 Train Operation – Follow the procedures laid out in EPA Method 8, Section 4.1.5. The tubing connecting the heated quartz filter and the first impinger should be heated ($\sim 220^\circ\text{F}$) in order to minimize condensation. Condensation in this line would drop out SO_2 along with water. At the conclusion of the run, drain the ice bath, disconnect the probe, and purge the remaining part of the train by drawing clean ambient air through the system for 15 minutes at the average sampling flowrate.

2.4.2 Sample Recovery

2.4.2.1 Rinse the probe and front-half of the quartz filter holder with 100% IPA and add the rinses to the designated container along with the quartz filter. The 100% IPA extract can be analyzed for SO_4^{2-} ions using the IC. While the alkali metal particulates on the filter do not dissolve in 100% IPA, free sulfuric acid captured on the filter, if any, dissolves in 100% IPA and can be quantified as sulfates during the analysis. This procedure can be used as a tool to verify that free sulfuric acid is NOT being retained on the heated filter.

2.4.2.2 Transfer the contents of the 100% IPA impingers to the designated container. Rinse the back half of the filter holder, all connecting tubing, and the impingers with minimal amounts of 100% IPA. Add the rinses to the storage bottle. Mark the liquid level.

2.4.2.3 Transfer the unheated filter into a separate bottle containing 100% IPA. Rinse the connecting tubing from the back of the second impinger and the front-half of the unheated filter holder with minimal amounts of 100% IPA and add the rinses to the container. Breakthrough of sulfate, if any, can be

quantified separately and added to the sulfate measurements from the IPA impingers.

2.4.2.4 Empty the contents of impingers 3 and 4 into the designated storage bottle. Rinse the impingers with DI water.

2.4.2.5 Cap the individual storage bottles and store them in containers surrounded by ice. Mark the liquid levels in the containers so that sample loss during storage and shipping can be identified.

2.4.2.6 Field blanks can be prepared by adding 25 ml of 100% IPA and 25 ml of 3% peroxide into storage bottles, at the end of each run. Alternatively, one field blank per day, or one field blank per batch of reagent is also acceptable. Prepare a field blank with the DI water used for rinses.

2.4.3 Sample Analysis

2.4.3.1 Barium-thorin titration – Follow procedures laid out in the appropriate sections of EPA Method 8.

2.4.3.2 Ion Chromatography – Operating conditions will depend on analytical column type and whether suppressed or non-suppressed IC is used. An example separation procedure is provided in Table 1. Other chromatographic columns and conditions may be used if it has been established that the sulfate ion peak is adequately separated and quality control parameters are met. Once the IC system is optimized for analytical separation and sensitivity, the sample operating conditions must be used to analyze all samples, blanks, calibration standards, and quality assurance samples.

2.5 Calibration

2.5.1 Barium-thorin titration – Same as Section 5.2 of EPA Method 8.

2.5.2 Ion Chromatography – Prepare standard solutions by serial dilutions of the stock solution. Analyze each standard according to the manufacturer's recommendations. Peak areas or peak heights, if applicable, may be used to develop the calibration curve.

2.6 Calculations – Same as in EPA method 8.

2.7 Alternative Procedures – Not applicable.

2.8 References

40 CFR, Part 60, Appendix A, 1994. *EPA Method 8 – Determination of Sulfuric Acid Mist and Sulfur Dioxide Emissions from Stationary Sources.*

National Council of the Paper Industry for Air and Stream Improvement, Inc. (NCASI). 1997. *Methods Manual, Method 8A – Determination of Sulfuric Acid Vapor or Mist and Sulfur Dioxide Emissions from Kraft Recovery Furnaces,*

Research Triangle Park, NC: National Council of the Paper Industry for Air and Stream Improvement, Inc.

2.9 Tables and Figures

Table 1. Example IC Operating Conditions for Sulfate Analysis

Column	Dionex AS9-HC Anion Exchange Column
Guard Column	Dionex AG9-HC Guard Column
Suppressor	Atlas Anion Electrolytic Suppressor (AAES)
Detector	Dionex CD25A Conductivity Detector
Eluent	10mM Sodium Carbonate and 2mM Sodium Bicarbonate
Type of Elution	Isocratic
Flowrate	1.5 mL/min
Cell Temperature, °C	35
Injection Volume	25 µL
Sulfate Ion Retention Time	10.8 min

- 1, 2 - 100% isopropyl alcohol
- F - filter to capture breakthrough
- 3 and 4 - 3% peroxide
- 5 - silica gel

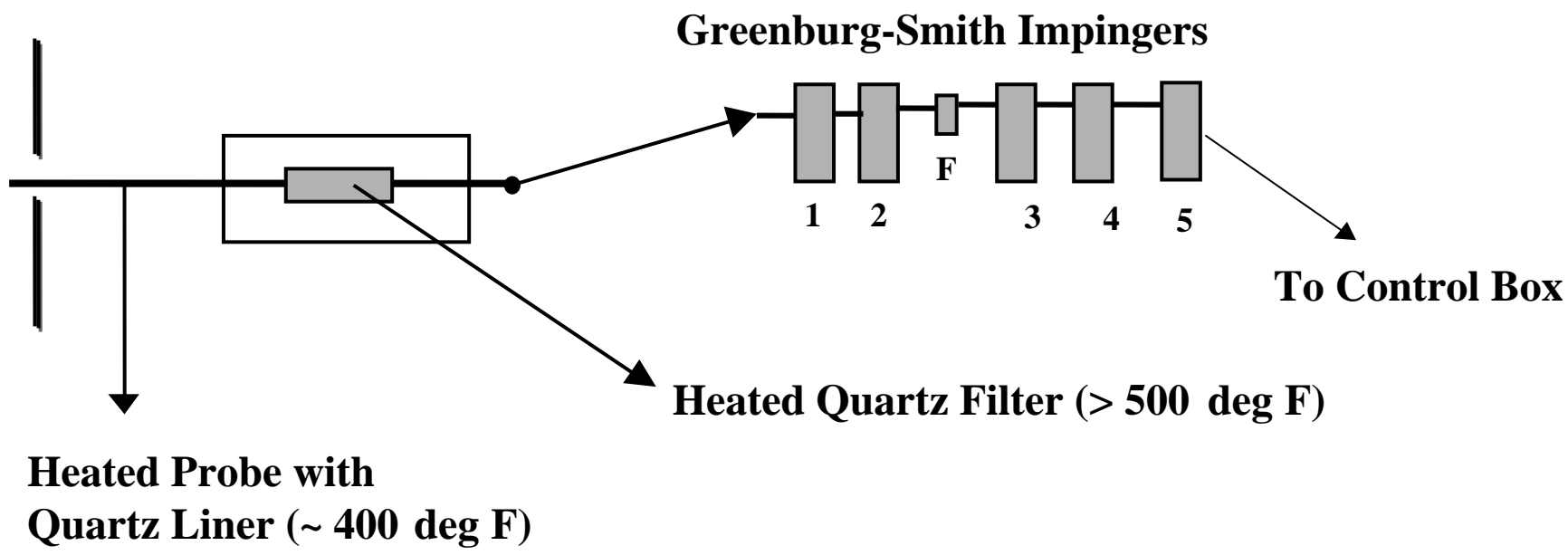


Figure 1. H₂SO₄ Sampling Train

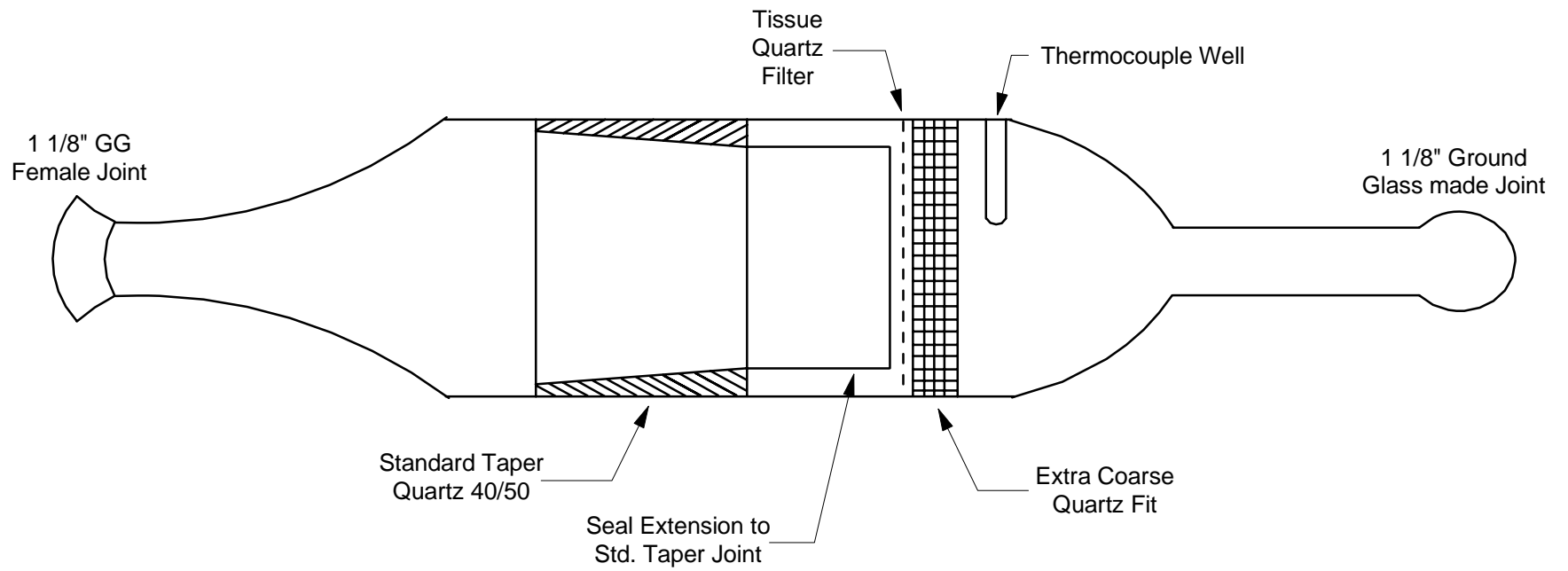


Figure 2. Quartz Filter Holder