

DETERMINATION OF SULFURIC ACID AND SULFUR DIOXIDE EMISSIONS FROM COMBINATION FUEL BOILERS AND RECOVERY FURNACES

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 (bark and fossil fuel) boilers and recovery furnaces 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 to EPA Method 8 for determining sulfuric acid emissions from combination boilers and recovery furnaces equipped with dry particulate control devices. This modified 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.

2.0 Method Description

2.1 Principle and Applicability

2.1.1 Principle – A stack gas sample is extracted 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 dry particulate control devices and utilizes midjet impingers at sampling flow rates ranging from 1000 to 1100 mL/min. This method is suitable for the determination of $\text{SO}_3/\text{H}_2\text{SO}_4$ in the presence of other particulate matter. Sulfur dioxide can also be quantified by analyzing the sulfate content in the peroxide impinger catches. Analyses by Ion Chromatography indicate that the minimum detection limit for sulfate ions in IPA and peroxide matrices is 0.2 mg/L of

impinger solution, corresponding to an injection volume of 25 μL . For sulfuric acid, this translates to 80 $\mu\text{g}/\text{m}^3$ gas sampled, assuming an impinger volume of 40 ml and a sampling volume of 100 liters. For SO_2 , this corresponds to 160 $\mu\text{g}/\text{m}^3$ gas, assuming an impinger volume of 80 ml and a sampling volume of 100 liters. Upper limits have not been established as the analytical technique allows for dilution of samples before analysis.

The midjet impinger train can be replaced by the impinger train used in EPA Method 8 while sampling wet sources that require isokinetic sampling.

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. The components of the train are discussed in the following sections. Midget impingers (similar to EPA Method 6) are used in this train. The details are provided in section 2.2.1.5. The impingers are downstream of a heated quartz probe and quartz filter holder that houses the requisite quartz filter.

2.2.1.1 Probe – Quartz probe. Straight tube, approximately 10 mm inside diameter. This is protected inside an aluminum sheath and heated with a woven glass insulated heating tape. A thermocouple taped on the probe, below the woven glass tape, measures the probe temperature used for temperature control during sampling. The probe is maintained at 400°F during sampling.

2.2.1.2 Quartz Filter Holder - The filter holder is placed inside a box and heated using a high temperature-heating mantle. The filter holder is maintained at temperatures $> 260^\circ\text{C}$ (500°F) during sampling. This allows the sulfur trioxide (SO_3) 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.

2.2.1.3 Quartz filter – 37-mm diameter, QM-A grade quartz filters manufactured by Whatman®. The filter is placed on a coarse quartz frit.

2.2.1.4 Unheated Filter Holder – Teflon filter holder with membrane filter. This unheated filter is placed between the first and second impinger.

2.2.1.5 Midget Impingers – Four midget impingers (50 ml) are used as shown in Figure 1. The impingers have tapered stems and use $\frac{1}{4}$ ” tubing connectors and are connected using Teflon tubing. The tubing into the second impinger is cut off in order to isolate the first impinger and unheated filter from the peroxide impingers. This prevents back surges of peroxide from contaminating the unheated filter and the isopropyl alcohol (IPA) in the first impinger. The tubing is immersed in the impinger solutions in all the other impingers as shown in Figure 1. The first impinger holds 25 ml of 80% IPA. The second impinger is a blank impinger and the third and fourth impingers hold 25 ml each of 3% hydrogen peroxide (H_2O_2).

2.2.1.6 Metering System – As shown in Figure 1. Leak-free diaphragm pump. Rotameter capable of measuring flowrate around 1100 ml/min. Critical orifices capable of flow around 1100 ml/min.

2.2.1.7 Vacuum gauge – Same as EPA Method 6, Section 2.1.12.

2.2.2 Sample Recovery

2.2.2.1 Wash Bottles – Polyethylene, 500 ml, Two

2.2.2.2 Graduated Cylinders – 25ml, 50 ml, 100 ml

2.2.2.3 Storage Bottles – 125 ml leak-free Nalgene® bottles to store impinger samples and filter/filter holder rinses. Five bottles are needed for each sampling run when the catches from impingers 3 and 4 of the sampling train are combined. All sample bottles need to be pre-weighed so that the impinger volume can be accounted for at the end of the run.

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), and deionized (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 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 25 ml of 80% IPA into the first impinger in the train. The second impinger is empty and the Teflon tubing to this impinger is cut off to prevent any back-surge of peroxide into the first impinger. Contamination of the IPA impinger with peroxide during the run would result in the capture of SO_2 in the first impinger, thereby voiding the run. Measure 25 ml of 3% hydrogen peroxide into the third and fourth impingers. The train is assembled as shown in Figure 1. The probe heater is adjusted to maintain the probe at 400°F. The filter holders are maintained at temperatures > 500°F. This prevents the condensation of sulfuric acid vapor in the probe and on the quartz filter. The tubing connecting the quartz filter to the first impinger should be short in order to minimize the condensation of moisture. As an alternative, the tubing may be heat-traced from the back of the quartz filter to the first impinger. The impingers are connected by Teflon tubing and placed in a water bath. Crushed ice is placed around the impingers.

2.4.1.2 Leak-check and flow check procedure – Make sure that the on/off valve is in the on position, plug the probe inlet tip, and turn the pump on to draw a vacuum. When the vacuum reading is approximately 25 inches of Hg, close the on/off valve and record the time and pressure. A leak is indicated by a flow of bubbles in the impinger, liquid being drawn into the stem of the impinger, or a loss of vacuum. If a leak is present, tighten fittings, connections, and impingers and restart leak check procedure. After 2 minutes, record the pressure reading on the first pressure gauge again. The leakage rate should not be in excess of 1 inch Hg (vacuum) in 2 minutes. Slowly and carefully remove the plug from the end of the probe, turn the on/off valve back to the on position.

Check the flow rate at the probe inlet with a bubble flowmeter. The flow rate should be comparable to the flow rate of the critical orifice with the impingers off-line. Record five measurements of the flow rate and turn off the pump.

2.4.1.3 Sample Collection – To begin sampling, position the probe (at appropriate temperature) in the stack, at right angles to the direction of flow of the stack gases. Start the pump and sample at the requisite rate for 60-90 minutes. Increased levels of particulate loading may plug the filter, thereby restricting flow. The sampling flowrate is recorded periodically. During the run, add more crushed ice to keep the impingers covered. At the conclusion of the run, remove the probe from the stack, record the final readings and also perform a flow check. Conduct the post-run leak check.

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 rinse 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 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 80% IPA impinger to the designated container. Rinse the back half of the filter holder, the tubing between the filter and first impinger, and the impinger with minimal amounts of 80% 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 80% IPA. Rinse the connecting tubing from the first impinger and the front-half of the unheated filter holder with minimal amounts of 80% 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 first IPA impinger.
- 2.4.2.4** Empty the contents (if any) of the blank second impinger into a separate storage bottle. Significant quantities of liquid in this impinger at the end of the run usually indicate peroxide contamination due to back flushes during the run or during the leak-check procedure. Rinse with minimal amounts of 80% IPA and add the rinses into the storage container.
- 2.4.2.5** Empty the contents of impingers 3 and 4 into the designated storage bottle. Rinse the impingers with DI water.
- 2.4.2.6** Cap the individual storage bottles and store them in containers surrounded by ice. Mark the liquid levels in the containers, so that any sample loss during storage and shipping can be identified.
- 2.4.2.7** Field blanks are prepared by adding 25 ml of 80% IPA and 25 ml of 3% peroxide into empty storage bottles. One field blank per day or one field blank per batch of reagent is 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 – Isokinetic sampling is not required. Replace equation 8-1 in EPA Method 8, with equation 6-1 in EPA Method 6.

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 μ L |
| Sulfate Ion Retention Time | 10.8 min |

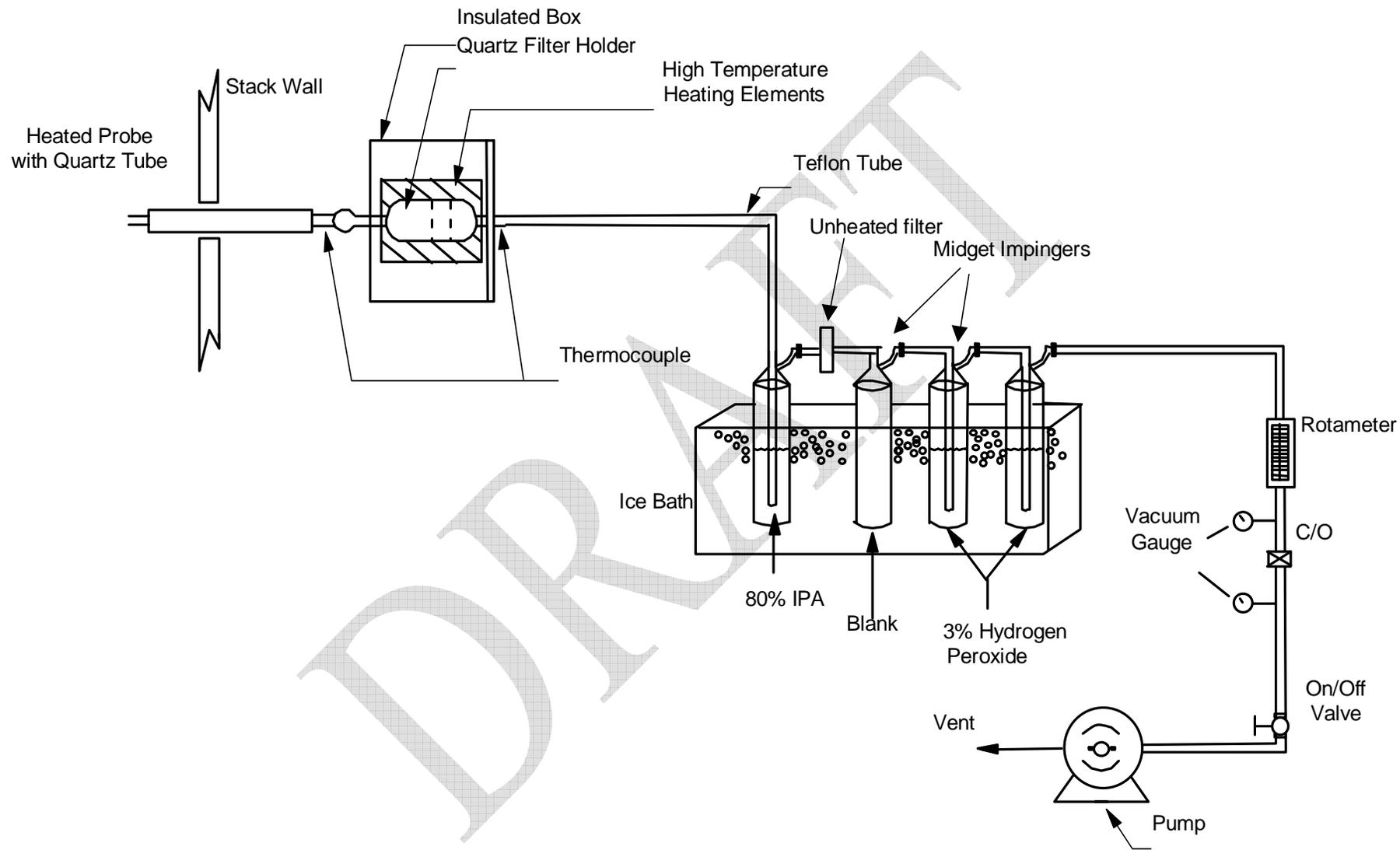


Figure 1. Sulfuric Acid / SO₂ Sampling Train

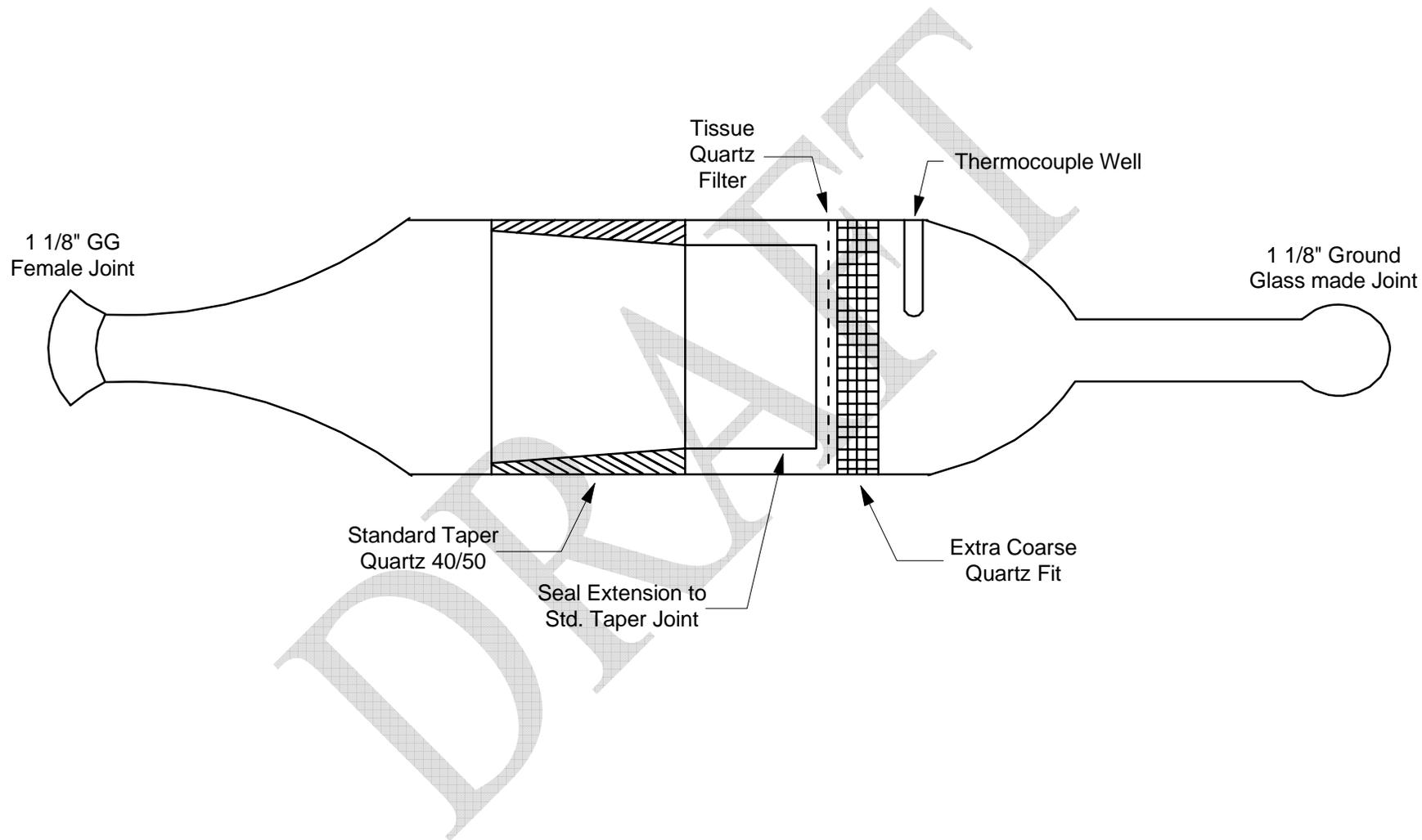


Figure 2. Quartz Filter Holder