Section 3.9

METHOD 13B - DETERMINATION OF TOTAL FLUORIDE EMISSIONS FROM STATIONARY SOURCES

(Specific-Ion Electrode Method)

OUTLINE

SUMMARY

In Method 13B, total fluorides (gaseous and particulate) are extracted isokinetically from the source by using a sampling train similar to the one specified in Method 5 (Section 3.4 of this Handbook); however, the filter does not have to be heated, and it may be located either immediately after the probe or between the third and fourth impingers.

The specific-ion electrode method for quantitatively measuring the fluorides collected in the train is applicable to fluoride (F) emissions from stationary sources, but not to fluorocarbons such as Freon. The concentration range of the method is from 0.02 to 2,000 μg F/ml; <0.1 μg F/ml requires extra care. Sensitivity of the method has not been determined.

An interferent in the collection of fluorides is grease on sample-exposed surfaces. The fluoride absorption into the grease causes low results due to a lack of sample recovery. If it can be shown to the satisfaction of the administrator that samples contain only water soluble fluorides, fusion and distillation may be omitted from the analysis.

METHOD HIGHLIGHTS

Section 3.9 (Method 13B) describes specifications for the sampling and analysis of total fluoride emissions from stationary sources. A gas sample is isokinetically extracted from the source stream, and the fluorides in the stream are collected in the sampling train.

The sampling train is similar to that in EPA Method 5, with a few exceptions--the filter does not have to be heated, and it may be located either immediately after the probe or between the third and fourth impingers. If it is between the probe and the first impinger, a borosilicate glass or stainless steel filter holder with a 20-mesh stainless steel screen filter support and a silicone rubber gasket must be used. If it is between the third and fourth impingers, a glass frit filter support may be used.

Sampling is generally the same as in Method 5, but a nozzle size that will maintain an isokinetic sampling rate of <28 ℓ/min (<1.0 ft^3/min) must be used. Samples and standards must be the same temperature during analysis by the specific-ion electrode (SIE). A change of 1°C (2°F) will cause a 1.5% relative error in the sample measurements. Lack of stability in the electrometer can also cause significant error in the results, but the main cause of error has been found to be distillation during sample analyses.

The collected sample is recovered by transferring the measured condensate and impinger water to a sample container, adding the filter and the rinsings of all sample-exposed surfaces to this container, and fusing and distilling the sample. The distilled sample is then analyzed with a SIE. Fusion and distillation may be omitted if it can be shown to the satisfaction of the administrator that the samples contain only water soluble fluorides.

Collaborative tests have shown that fluoride concentrations from 0.1 to 1.4 μg F/m^3 could be determined with an intralaboratory precision of 0.037 μg F/m^3 and an interlaboratory precision

of 0.056 μg F/m^3. For these tests six contractors simultaneously took duplicate samples from a stack. The collaborative test did not find any bias in the analytical method.[1]

The Method Description (Sections 3.9.1 to 3.9.9) is based on the detailed specifications in the Reference Method (Section 3.9.10) promulgated by EPA on June 20, 1980.[2]

1. Procurement of Apparatus and Supplies

Section 3.9.1 gives specifications, criteria, and design features for the required equipment and materials. The sampling apparatus for Method 13B has the same design features as that of Method 5, except for the positioning of the filter in the sampling train. This section can be used as a guide for procurement and initial checks of equipment and supplies. The activity matrix (Table 1.1) at the end of the section is a summary of the details given in the text and can be used as a quick reference.

2. Pretest Preparations

Section 3.9.2 describes the required calibration procedures for the Method 13B sampling equipment (same as Method 5), except for the SIE. A pretest checklist (Figure 3.1 or a similar form) should be used to summarize the calibration and other pertinent pretest data.

Section 3.9.3 describes the preparation of supplies and equipment needed for the sampling. The pretest preparation form (Figure 3.2 of Section 3.4.3) can be used as an equipment checklist. Suggestions for packing the equipment and supplies for shipping are given to help minimize breakage.

Activity matrices for the calibration of equipment and the presampling operations (Tables 2.1 and 3.1) summarize the activities detailed in the text.

3. On-site Measurements

Section 3.9.4 describes procedures for sampling and sample recovery. A checklist (Figure 4.5) is an easy reference for field personnel to use in all sampling activities.

4. Posttest Operations

Section 3.9.5 describes the postsampling activities for checking the equipment and the analytical procedures. A form is given for recording data from the posttest equipment calibration checks; a copy of the form should be included in the emission test final report. A control sample of known (F) concentration should be analyzed before analyzing the sample for a quality control check on the analytical procedures. The detailed analytical procedures can be removed for use as easy references in the laboratory. An activity matrix (Table 5.1) summarizes the postsampling operations.

Section 3.9.6 describes calculations, nomenclature, and significant digits for the data reduction. A programmed calculator is recommended to reduce calculation errors.

Section 3.9.7 recommends routine and preventive maintenance programs. The programs are not required, but their use should reduce equipment downtime.

5. Auditing Procedures

Section 3.9.8 describes performance and system audits. Performance audits for both the analytical phase and the data processing are described. A checklist (Figure 8.2) outlines a system audit.

Section 3.9.9 lists the primary standards to which the working standards or calibration standards should be traceable.

6. References

Section 3.9.10 contains the promulgated Reference Method; Section 3.9.11 contains the references used throughout this text; and Section 3.9.12 contains copies of data forms recommended for Method 13B.

PRETEST SAMPLING CHECKS
(Method 13B, Figure 3.1)

Date _____ Calibrated by _____

Meter box number _____ ΔH@ _____

Dry Gas Meter*

Pretest calibration factor Y _____ (within ±2% of the average factor for each calibration run).

Impinger Thermometer

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ (within ±1°C (2°F) of reference values for calibration and within ±2°C (4°F) of reference values for calibration check)

Dry Gas Meter Thermometers

Was a pretest temperature correction made? _____ yes _____.no
If yes, temperature correction _____ (within ±3°C (5.4°F) of reference value for calibration and within 6°C (10.8°F) of reference values for calibration check)

Stack Temperature Sensor*

Was a stack temperature sensor calibrated against a reference thermometer? _____ yes _____ no
If yes, give temperature range with which the readings agreed within ±1.5% of the reference values _____ to _____K (°R)

Barometer

Was the pretest field barometer reading correct? ___ yes ___ no
(within ±2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer)

Nozzle*

Was the nozzle calibrated to the nearest 0.025 mm (0.001 in.)?
_____ yes _____ no

*Most significant items/parameters to be checked.

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ON-SITE MEASUREMENTS
(Method 13B, Figure 4.5)

Apparatus

Probe nozzle: stainless steel _____ glass _____
Button-hook _____ elbow _____ size _____
Clean? _____
Probe liner: borosilicate _____ quartz _____ other _____
Clean? _____
Heating system* _____
Checked? _____
Pitot tube: Type S _____ other _____
Properly attached to probe?* _____
Modifications _____
Pitot tube coefficient _____
Differential pressure gauge: two inclined manometers _____
other _____ sensitivity _____
Filter holder: borosilicate glass _____ glass frit _____
filter support _____ silicone gasket _____ other _____
Clean? _____
Condenser: number of impingers _____
Clean? _____
Contents: 1st _____ 2nd _____ 3rd _____ 4th _____
Cooling system _____
Proper connections? _____
Modifications _____
_____
Barometer: mercury _____ aneroid _____ other _____
Gas density determination: temperature sensor type _____
pressure gauge _____
temperature sensor properly attached to probe?* _____

Procedure

Recent calibration: pitot tubes* _____
meter box* _____ thermometers/thermocouples* _____
Filters checked visually for irregularities?* _____
Filters properly labeled?* _____
Sampling site properly selected? _____
Nozzle size properly selected?* _____
Selection of sampling time? _____
All openings to sampling train plugged to prevent pretest contamination? _____
Impingers properly assembled? _____
Filter properly centered? _____
Pitot tube lines checked for plugging or leaks?* _____

(continued)

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Figure 4.5 (continued)

Meter box leveled? _____ Periodically? _____
Manometers zeroed? _____
ΔH@ from most recent calibration _____
Nomograph setup properly? _____
Care taken to avoid scraping nipple or stack wall?* _____
Effective seal around probe when in-stack? _____
Probe moved at proper time? _____
Nozzle and pitot tube parallel to stack wall at all times?* _____
  Filter changed during run? _____
  Any particulate lost? _____
Data forms complete and data properly recorded?* _____
Nomograph setting changed when stack temp changed significantly?
_____
Velocity pressure and orifice pressure readings recorded
  accurately?* _____
Sampling performed at a rate less than 1.0 cfm _____
Posttest leak check performed?* _____ (mandatory)
Leakage rate _____ @ in. Hg _____
  Orsat analysis _____ from stack _____ integrated _____
  Fyrite combustion analysis _____ sample location _____
  Bag system leakchecked?* _____
  If data forms cannot be copied, record:
    approximate stack temp _____ volume metered _____
    % isokinetic calculated at end of each run _____

SAMPLE RECOVERY

Brushes: nylon bristle _____ other _____
  Clean? _____
Wash bottles: polyethylene or glass _____
  Clean? _____
Storage containers: polyethylene _____ other _____
  Clean? _____ Leakfree? _____
Graduated cylinder/or balance: subdivisions ≤2 ml?* _____
  other _____
  Balance: type _____
Probe allowed to cool sufficiently? _____
Cap placed over nozzle tip to prevent loss of particulate?* _____
_____
During sampling train disassembly, are all openings capped? _____
Clean-up area description: _____
  Clean? _____ Protected from wind? _____
Filters: paper _____ type _____
  Silica gel: type (6 to 16 mesh)? new? _____ used? _____
  Color? _____ Condition? _____
Filter handling: tweezers used? _____
  surgical gloves? _____ other _____
  Any fluoride spilled?* _____

(continued)

Figure 4.5 (continued)

Water distilled? _____
Stopcock grease: acetone-insoluble? _____
heat-stable silicone? _____ other _____
Probe handling: distilled water rinse _____
Fluoride recovery from: probe nozzle _____
probe fitting _____ probe liner _____
front half of filter holder _____
Blank: filter _____ distilled water _____
Any visible particles on filter holder inside probe?:* _____
_____
All jars adequately labeled? _____ Sealed tightly? _____
Liquid level marked on jars?* _____
Locked up? _____
Filter blank _____

*Most significant items/parameters to be checked.

METHOD 13B CHECKLIST FOR AUDITORS
(Method 13B, Figure 8.2)

Yes	No	Comment	OPERATION
			Presampling Preparation
___	___	_____	1. Knowledge of process conditions
___	___	_____	2. Calibration of equipment, before each field test
			On-Site Measurements
___	___	_____	3. Sample train assembly
___	___	_____	4. Pretest leak check
___	___	_____	5. Isokinetic sampling
___	___	_____	6. Posttest leak check
___	___	_____	7. Record process conditions during sample collection
___	___	_____	8. Sample recovery and data integrity
			Postsampling
___	___	_____	9. Accuracy and precision of control sample analysis
___	___	_____	10. Recovery of samples for distillation
___	___	_____	11. Calibration checks
___	___	_____	12. Calculation procedure/check

General Comments:

METHOD DESCRIPTION

1.0 PROCUREMENT OF APPARATUS AND SUPPLIES

A schematic of the sampling train used in Method 13B is shown in Figure 1.1. The train and the sampling procedures are similar to EPA Method 5; the procedures and equipment for Methods 13A and 13B are identical. Commercial models of the train are available. For those who want to build their own, construction details are in APTD-0581;[3] allowable modifications are described herein. The operating, maintenance, and calibration procedures for the sampling train are in APTD-0576.[4] Since correct usage is important in obtaining valid results, all users are advised to read this document and to adopt its procedures unless alternatives are outlined herein.

Specifications, criteria, and/or design features are given in this section to aid in the selection of equipment which assures collection of good quality data. Procedures and limits (where applicable) for acceptance checks are also given.

During procurement of equipment and supplies, a log (Figure 1.2) should be used to record the descriptive titles and identification numbers (if applicable) of the equipment and the results of the acceptance checks; a blank copy of the procurement log is in Section 3.9.12 for the convenience of the Handbook user. If calibration is required for the acceptance check, a calibration log should be used to record the data. Table 1.1 at the end of this section summarizes the quality assurance activities for the procurement and acceptance of apparatus and supplies.

1.1 Sampling Apparatus

1.1.1 Probe Liner - The sampling probe should be constructed of borosilicate glass (Pyrex) or 316 stainless steel tubing with an outside diameter (OD) of about 16 mm (0.625 in.); it should be encased in a stainless steel sheath with an OD of 25.4 mm (1.0 in.).

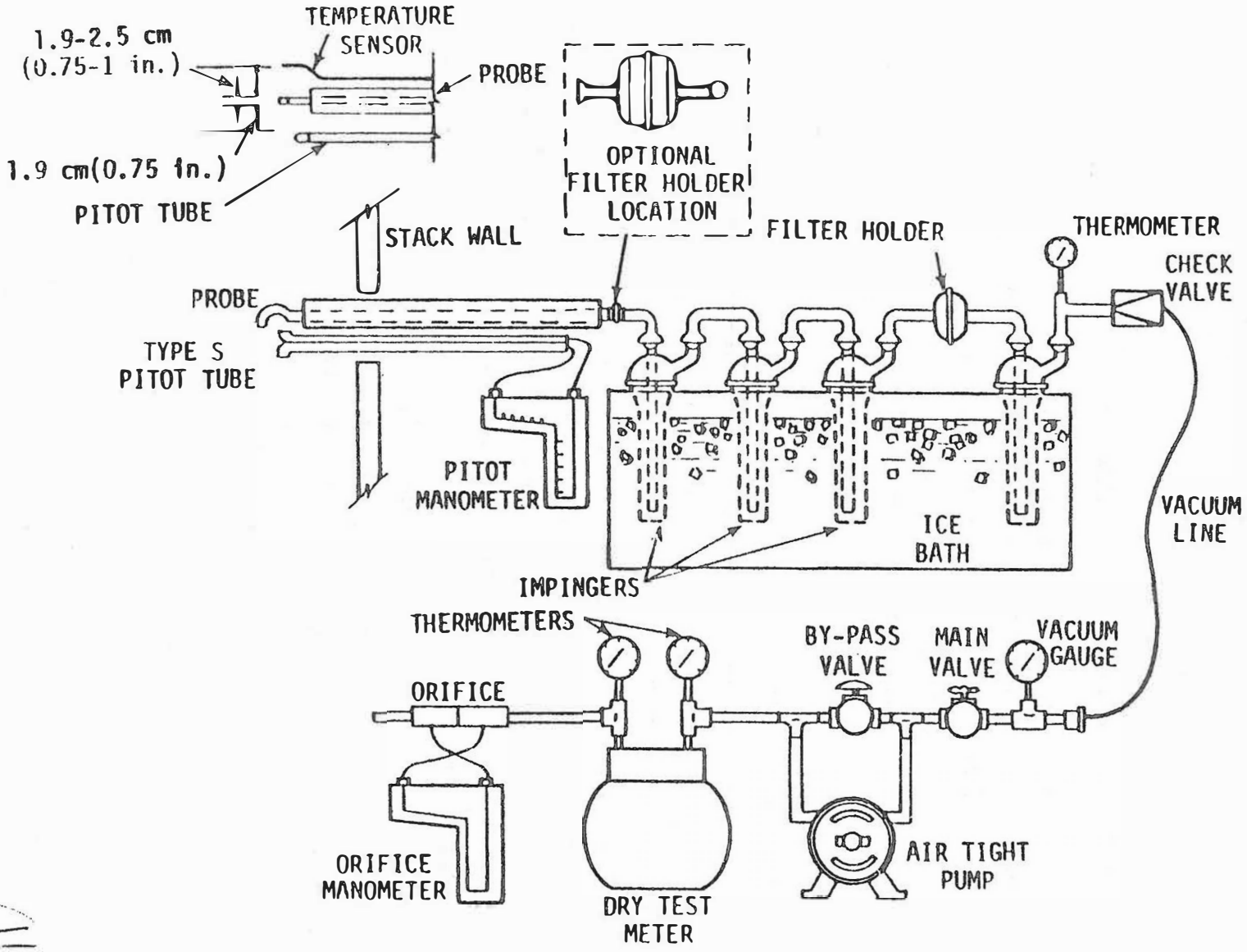

Figure 1.1. Fluoride sampling train.

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Item description	Quantity	Purchase order number	Vendor	Date		Cost	Dispo-sition	Comments
				Ordered	Received			
Meter Console	1	26549	West Co	4/3/80	5/7/80	24.50	In Service	

Figure 1.2. Example of a procurement log.

A heating system may be required to maintain the exit gas at 120° ±14°C (248° ±25°F) during sampling. Other temperatures may be specified by a subpart of the regulations or approved by the administrator. Since the probe outlet temperature is not usually monitored during sampling, probes constructed in accordance to APTD-0581[3] and calibrated with procedures in APTD-0576[4] will be acceptable.

Upon receiving a new probe, visually check for specifications (i.e., the length and composition ordered) and for breaks or cracks; leak check on a sampling train (Figure 1.1); and check the nozzle-to-probe connection with a Viton-O-ring or with Teflon ferrules for glass liners or stainless steel ferrules for stainless steel liners.

The probe heating system should be checked as follows:

1. Connect the probe by attaching the nozzle to the pump inlet.

2. Connect the probe heater to the electrical source, and turn it on for 2 or 3 min; it should become warm to the touch.

3. Start the pump, and adjust the needle valve until a flow rate of about 0.02 m^3/min (0.75 ft^3/min) is achieved.

4. Be sure that the probe remains warm to the touch and that the heater maintains the exit gas at a minimum of 100°C (212°F); if not, repair, return to the supplier, or reject the probe.

1.1.2 Probe Nozzle - The probe nozzle should be designed with a sharp, tapered leading edge and should be constructed of either seamless 316 stainless steel tubing or glass formed in a buttonhook or elbow configuration. The tapered angle should be $\leq$30°, with the taper on the outside to preserve a constant inside diameter (ID).

A range of nozzle ID's [e.g., 0.32 to 1.27 cm (0.125 to 0.5 in.) in increments of 1.6 mm (0.0625 in.)] should be available for isokinetic sampling. Larger nozzle sizes may be required

for hi-vol sampling trains or for very low stack gas velocities. Each nozzle should be engraved with an identification number for inventory and for calibration purposes.

Upon receipt of the nozzle from the manufacturer and before each test, inspect it for roundness and corrosion and for damage (nicks, dents, and burrs) to the tapered edge, and check the ID with a micrometer. (Calibration procedures are in Section 3.9.2.) Slight variations from exact ID's should be expected due to machining tolerances. Reshape, return to supplier or reject.

1.1.3 Pitot Tube - The pitot tube, preferably of Type S design, shown in Figure 1.1 should meet the requirements of Method 2 (Section 3.1.2). Proper pitot-tube-sampling-nozzle configuration for prevention of aerodynamic interference is shown in Figures 2.6 and 2.7 of Method 2 (Section 3.1.2).

Visually inspect the vertical and horizontal tip alignments. If the tube is purchased as an integral part of a probe assembly, check the dimensional clearances using Figures 2.6 and 2.7 of Section 3.1.2. Repair or return any pitot tube that does not meet specifications.

1.1.4 Differential Pressure Gauge - The differential pressure gauge should be an inclined manometer or the equivalent, as specified in Method 2, Section 3.1.2. Two gauges are required. One is used to monitor the stack velocity pressure, and the other to measure the orifice pressure differential.

Initially, check the gauges against a gauge-oil manometer at a minimum of three points--0.64, 12.7, and 25.4 mm (0.025, 0.5, and 1.0 in.) H_2O--to see if they read within 5% at each test point. Repair or return to the supplier any gauge that does not meet these requirements.

1.1.5 Filters - If the filter is between the third and fourth impingers, use a Whatman No. 1 (or equivalent) filter, sized to fit the filter holder. If it is between the probe and the first impinger, use any suitable medium (e.g., paper or organic membrane) as long as the filter can withstand prolonged exposure up

to 135°C (275°F) and has ≥95% collection efficiency (≤5% penetration) for 0.3-μ dioctyl phthalate smoke particles.

Conduct the filter efficiency test before beginning the sampling by using either the ASTM Standard Method D2986-71 or test data from the supplier's quality control program. The filter should have a low F blank value (≤0.015 mg F/cm^2 of filter area); determine the average values of at least three filters from the lot to be used for sampling. Glass fiber filters generally have high and/or variable F blank values, and thus are not acceptable.

1.1.6 Filter Holder - If the filter is located between the probe and first impinger a borosilicate glass or stainless steel filter holder with a 20 mesh stainless steel mesh frit filter support and a silicone rubber gasket is required by the Reference Method. If it is between the third and fourth impingers, the tester may use borosilicate glass with a glass frit filter support and a silicone rubber gasket. Other gasket materials (e.g., Teflon or Viton) may be used if approved by the administrator.

The holder design must provide a positive seal against leakage from the outside or around the filter. The holder should be durable, easy to load, and leak free in normal applications. Check visually before use. If immediately following the probe, the filter should be positioned toward the flow.

1.1.7 Filter Heating System - Any heating system may be used which is capable of maintaining the filter holder at 120° ±14°C (248° ±25°F) during sampling. Other temperatures may be specified by a subpart of the regulations or approved by the administrator. The heating element should be easily replaceable in case of malfunction during sampling. A gauge capable of measuring within 3°C (5.4°F) should be used to monitor the temperature around the filter during sampling.

Check the heating system and the temperature monitoring device before sampling.

1.1.8 Condenser - Four impingers with leak-free, noncontaminated ground-glass or similar fittings should be connected in series. The first, third, and fourth impingers must be a modified Greenburg-Smith design that has a glass tube (instead of inserts) with an unconstricted 13-mm (0.5-in.) ID extending to within 13 mm (0.5 in.) of the flask bottom. The second impinger must be a Greenburg-Smith with the standard tip and plate. Modifications--for example, using flexible connections between impingers, using materials other than glass, or using a flexible vacuum hose to connect the filter holder to the condenser--must be approved by the administrator. The fourth impinger outlet connection must allow insertion of a thermometer capable of measuring ±1°C (2°F) of true value in the range of 0° to 25°C (32° to 77°F).

Alternatively, any system that cools the gas stream and allows measurement of the condensed water and the water vapor leaving the condenser, each to within 1 ml or 1 g, may be used with approval from the administrator.

Upon receipt of a standard Greenburg-Smith impinger, fill the inner tube with water; if the water does not drain through the orifice in 6 to 8 s or less, replace or enlarge the impinger tip to prevent an excessive pressure drop in the sampling system. Check each impinger visually for damage--breaks, cracks, or manufacturing flaws such as poorly shaped connections.

1.1.9 Metering System - The metering system should consist of a vacuum gauge, a vacuum pump, thermometers capable of measuring ±3°C (5.4°F) of true value in the range of 0° to 90°C (32° to 194°F), a dry gas meter with ±2% accuracy at the required sampling rate, and related equipment shown in Figure 1.1. Other metering systems capable of maintaining rates within 10% of isokinetic and determining sample volumes within 2% may be used if approved by the administrator. Sampling trains with metering systems designed for rates higher than those described in APTD-0581[3] and APTD-0576[4] may be used if the above specifications can be met.

When the metering system is used with a pitot tube, the system should permit verification of an isokinetic sampling rate with a nomograph or by calculation.

Upon receipt or after construction of the equipment, perform both positive and negative pressure leak checks before beginning the calibration procedure (Section 3.9.2). Adjust, repair, or replace the malfunctioning item. Reject a dry gas meter if it behaves erratically or if it cannot be adjusted. Reject the thermometer if unable to calibrate.

1.1.10 Barometer - A mercury, aneroid, or other barometer capable of measuring atmospheric pressure to within ±2.5 mm (0.1 in.) Hg is required.

Check a new barometer against a mercury-in-glass barometer or the equivalent. In lieu of this, obtain the absolute barometric pressure from a nearby weather service station and adjust it for the elevation difference between the station and the sampling point; accordingly, either subtract 2.5 mm Hg/30 m (0.1 in. Hg/100 ft) from the station value for an elevation increase or add the same for an elevation decrease. If the barometer cannot be adjusted to agree within 2.5 mm (0.1 in.) Hg of the reference barometric pressure, either return it to the manufacturer or reject it.

1.1.11 Gas Density Determination Equipment - A temperature sensor and a pressure gauge (Method 2, Section 3.1.2) are required. A gas analyzer (Method 3, Section 3.2.2) may be required.

The temperature sensor should be permanently attached to either the probe or the pitot tube; in either case, a fixed configuration (Figure 1.1) should be maintained. Alternatively, the sensor may be attached just before field use (Section 3.9.2).

1.2 Sample Recovery Apparatus

1.2.1 Probe Liner and Nozzle Brushes - Nylon bristle brushes with stainless steel wire handles are recommended. The probe brush must be at least as long as the probe. A separate, smaller, and very flexible brush should be used for the nozzle.

Visually check for damage upon receipt, and replace or return to supplier if defective.

1.2.2 Wash Bottles - Two 500-ml wash bottles are recommended for the probe and the glassware rinsings. Glass or polyethylene are acceptable.

1.2.3 Sample Storage Containers - Recommended are 500 ml or 1000 ml chemically resistant, high-density polyethylene bottles for storage of samples. The bottles must have leak proof screw caps with leak proof, rubber-backed Teflon cap liners, or they must be constructed to preclude leakage and to resist chemical attack; wide-mouthed bottles are easiest to use.

Prior to field use, inspect the cap seals and the bottle cap seating surfaces for chips, cuts, cracks, and manufacturing deformities which would allow leakage.

1.2.4 Graduated Cylinder and/or Triple Beam Balance - Either a 250-ml glass (Class A) graduated cylinder or a triple beam balance may be used to measure the water condensed in the impingers during sampling. The graduated cylinder may also be used to measure water initially placed in the first and second impingers. In either case, the required accuracy is 1 ml or 1 g; therefore, the cylinder must have subdivisions $\leq$2 ml, and the balance should be capable of weighing to the nearest 0.1 g.

1.2.5 Plastic Storage Containers - Several airtight plastic containers are needed for storage of silica gel.

1.2.6 Funnel and Rubber Policeman - A funnel and a rubber policeman are needed to transfer the used silica gel from the impinger to a storage container unless silica gel is weighed in the field after the test. A Teflon policeman is helpful for recovery of the filter. The funnel should be glass with a 100-mm diameter and a 100-mm stem.

Visually check on receipt, and replace or return if damaged.

1.3 Distilling Apparatus

The fluoride distillation setup is shown in Figure 1.3.

1.3.1 Flasks - A long-necked, round bottom 1-liter flask with 24/40 joint grindings is needed for boiling the sample solution.

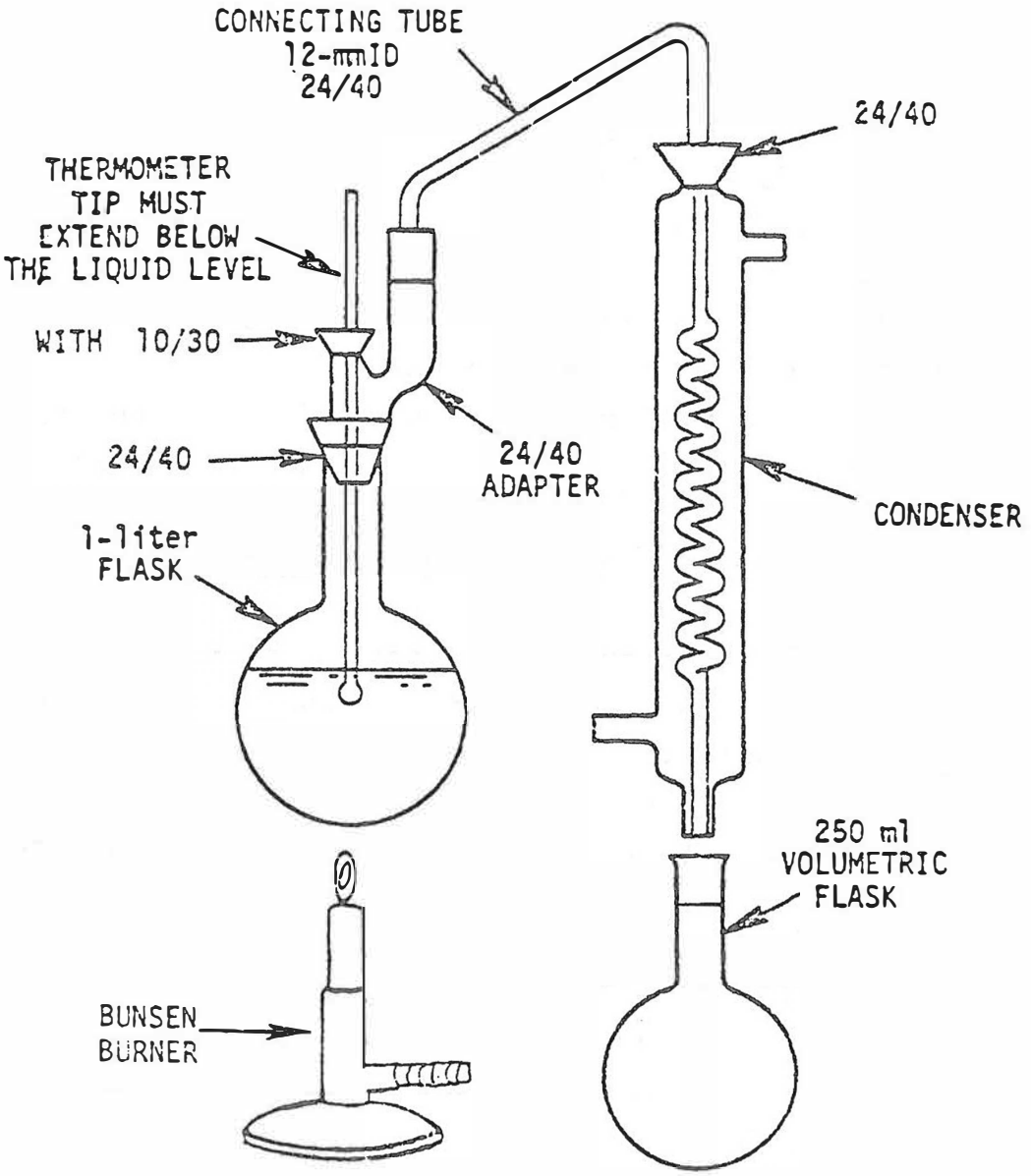

Figure 1.3. Fluoride distillation apparatus.

Also, a 250-ml volumetric (Class A) flask is needed to receive the condensate.

1.3.2 Thermometer - A thermometer for checking the temperature of the sample in the boiling flask should read within ±1°C (±2°F) of the true value in the range of 100° to 200°C (212° to 392°F). Check it against a mercury-in-glass thermometer.

1.3.3 Adapter - An adapter should have joint grindings (inner and outer parts) that are 24/40 at the bottom and 10/30 at the top that will hold a thermometer, and it should have a 24/40 joint grinding (inner part) at the end of the top sidearm that joins the connector tube.

1.3.4 Connector Tube - A tube with a standard or a medium wall and with a 13-mm (0.5 in.) ID is needed for connecting the adapter to the condenser.

1.3.5 Condenser - A coiled integral Graham condenser (joint grinding 24/40) with a jacket length of 300 mm (12 in.) is needed for condensation of the distillate.

1.4 Miscellaneous Glassware

1.4.1 Beaker - A 1500-ml glass beaker (Class A) with 5-ml subdivisions is needed to receive the filtered sample from container No. 1 or No. 2.

1.4.2 Pipettes - Several volumetric pipettes (Class A)--including 5, 10, 20, 25, 50 ml's--should be available. Record the stock numbers, and visually check for cracks, breaks, or manufacturer's flaws. If irregularities are found, either replace or return to the supplier.

1.4.3 Volumetric Flasks - The following volumetric flasks are needed for performing the analysis: a 50-ml glass volumetric flask (Class A) is needed to dilute the sample aliquot to 50 ml with TISAB (total ionic strength adjustment buffer) in determination of fluoride concentration; a 1-ℓ glass volumetric flask (Class A) to dilute the fused sample to volume with distilled water; and several 100-ml polyethylene volumetric flasks to prepare the fluoride standardizing solution.

1.5 Reagents and other Supplies (Sampling)

Unless otherwise indicated, all reagents should meet the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS); otherwise, use the best available grade.

1.5.1 Silica Gel - Use indicating type 6-16 mesh. If previously used, dry at 175°C (347°F) for at least 2 h before reusing. New silica gel may be used as received.

1.5.2 Water - Deionized distilled water should conform to ASTM specification D1193-74, Type 3. At the option of the analyst, the $KMnO_4$ (potassium permanganate) test for oxidizable organic matter may be omitted if high concentrations of organic matter are not expected.

1.5.3 Crushed Ice - Enough crushed ice is needed around the impingers to maintain <20°C (68°F) at the impinger silica gel outlet in order to avoid excessive moisture loss.

1.5.4 Stopcock Grease - Acetone insoluble, heat stable silicone grease is required unless screw-on connectors with Teflon or similar sleeves are used.

1.6 Reagents and Supplies (Sample Recovery and Analysis)

Unless otherwise indicated, all reagents should meet the specifications of the Committee on Analytical Reagents of the American Chemical Society (ACS); otherwise, use the best available grade.

1.6.1 Calcium Oxide (CaO) - A reagent grade or a certified ACS grade of CaO should contain $\leq$0.005% F.

1.6.2 Filters - Whatman No. 541 (or equivalent) filters are required for filtration of the impinger contents and preparation of the sample for analysis.

1.6.3 Phenolphthalein Indicator - A reagent grade or a certified ACS 0.1% phenolphthalein should be a 1:1 ethanol-water mixture.

1.6.4 Sodium Hydroxide - An ACS reagent grade (or the equivalent) NaOH pellets and 5M NaOH reagent grade or ACS is needed.

1.6.5 Sulfuric Acid - An ACS reagent grade (or the equivalent) concentrated H_2SO_4 and 25% (v/v) reagent grade or ACS is needed.

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1.6.6 Total Ionic Strength Adjustment Buffer (TISAB) - To approximately 500 ml of distilled water in a 1-ℓ beaker, add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilotetra acetic acid (CDTA). Stir to dissolve. Place the beaker in a water bath until it cools. Then, slowly add 5 M NaOH, while measuring the pH continuously with a calibrated pH-reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-ℓ flask, and dilute to volume with distilled water. Commercially prepared TISAB buffer may be substituted for the above.

1.6.7 Fluoride Standard Solution - To prepare a 0.1M fluoride reference solution, add 4.20 grams of reagent grade sodium fluoride (NaF) to a 1-ℓ volumetric flask, and add enough distilled water to dissolve it. Dilute to volume with distilled water. The NaF must be oven dried at 110°C for at least 2 h prior to weighing.

1.7 Analytical Equipment

1.7.1 Bunsen Burner - A Bunsen burner capable of distilling 200 ml in <15 min is required for the boiling flasks.

1.7.2 Crucible - A nickel crucible with a capacity of 75 to 100 ml is needed to evaporate the water from the sample on a hot plate.

Upon receipt, check for cracks or manufacturing flaws as well as for capacity. If it does not meet specifications replace or return it to the manufacturer.

1.7.3 Hot Plate - A hot plate capable of 500°C (932°F) is required for heating the sample in a nickel crucible.

Check upon receipt and before each use for damage. Check the heating capacity against a mercury-in-glass thermometer. If inadequate, repair or return the hot plate to the supplier.

1.7.4 Electric Muffle Furnace - An electric muffle furnace capable of heating to 600°C (1112°F) is needed to fuse the sample.

Check the heating capacity against a mercury-in-glass thermometer. Replace or return to the manufacturer any unit which does not meet specifications.

1.7.5 Balance - A balance with a capacity of 300 g ±0.5 g is needed to determine moisture.

Check for damage against a series of standard weights upon receipt and before each use. Replace or return to the manufacturer if damaged or if it does not meet specifications.

1.7.6 Analytical Balance - An analytical balance capable of weighing to within 0.1 mg is needed for preparation of the standard fluoride solution and the analytical reagents. Check the balance frequently with Class S weights.

1.7.7 Constant Temperature Bath - A water bath is needed to maintain a constant room temperature for optimum measurement of the sample concentration.

1.7.8 Fluoride Ion Activity-Sensing Electrodes - A fluoride ion (F^-) activity-sensing electrode is required in Method 13B for determining of F^- ion activity in concentrations of from 1 to 10^{-6} mol/ℓ (19,000 to 0.02 ppm). The electrode should be usable from a pH of 1 to 8.5 at 10^{-6} mol/ℓ, up to a pH of 11 at 10^{-2} mol/ℓ F^- concentration. Due to the complexing of F^- below pH of 4 and to the limited resistance of the electrode body to certain concentrated acids, it is usually advisable to adjust the pH of strongly acidic samples.

Check for damage and F^- sensing accuracy with a known concentration upon receipt and before each use. If not suitable, replace or return to manufacturer. Either a single junction, sleeve type reference electrode or a combination type fluoride ion-sensing electrode built into one unit may be used.

1.7.10 Electrometer - Either a pH meter with a millivolt scale capable of ±0.1-mV resolution or a ion meter made especially for specific-ion use is needed to read the ion activity or the F^- concentration.

1.7.11 Magnetic Stirrer - A magnetic stirrer and TFE* fluorocarbon-coated stirring bars are needed for uniform mixing of the sample solution.

1.7.12 Stopwatch or Clock - A stopwatch or a clock is needed to check minimum immersion time of electrode in sample.

*Mention of any trade name or specific product does not constitute endorcement by the Environmental Protection Agency.

TABLE 1.1 ACTIVITY MATRIX FOR PROCUREMENT OF APPARATUS AND SUPPLIES

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sampling			
Probe liner	Specified material of construction; equipped with heating system capable of maintaining 120°±14°C (248° ±25°F) at the exit	Visually check the probe and run the heating system	Repair, return to supplier, or reject
Probe nozzle	Stainless steel (316) with sharp, tapered angle ≤30°; difference in measured diameters ≤0.1 mm (0.004 in.); no nicks, dents, or corrosion	Visually check upon receipt and before each test; use a micrometer to measure ID before field use after each repair	Reshape and sharpen, return to the supplier, or reject
Pitot tube	Type S (Meth 2, Sec 3.1.2); attached to probe with impact (high pressure) opening plane even with or above nozzle entry plane	Visually check for vertical and horizontal tip alignments; check the configuration and the clearances; calibrate (Sec 3.1.2, Meth 2)	Repair or return to supplier
Differential pressure gauge (inclined manometer)	Meets criteria (Sec 3.1.2); agrees within 5% of gauge-oil manometer	Check against a gauge-oil manometer at a minimum of three points: 0.64(0.025); 12.7 (0.5); 25.4(1.0) mm (in.) H_2O	As above
Filters	Capable of withstanding temperatures to 135°C (275°F), 95% collection efficiency for 0.3 μm particles, low F blank (≤0.015 mg F/cm^2)	Check each batch for F blank values, visibly inspect for pin holes or flaws	Reject batch

(continued)

TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Filter holder	Leak free; borosilicate glass	Visually check before use	Return to supplier
Condenser	Four impingers, standard stock glass; pressure drop not excessive	Visually check upon receipt; check pressure drop	As above
Vacuum gauge	0-760 mm (0-30 in.) Hg, ±25 mm (1 in.) at 380 mm (15 in.) Hg	Check against mercury U-tube manometer upon receipt	Adjust or return to supplier
Vacuum pump	Leak free; capable of maintaining flow rate of 0.02-0.03 m^3/min (0.7 to 1.1 ft^3/min) for pump inlet vacuum of 380 mm (15 in.) Hg	Check upon receipt for leaks and capacity	Repair or return to supplier
Barometer	Capable of measuring atmospheric pressure ±2.5 mm (0.1 in.) Hg	Check against a mercury-in-glass barometer or equivalent; calibrate (Sec 3.1.2)	Determine correction factor, or reject
Orifice meter	ΔH@ of 46.74± 6.35 mm (1.84 ± 0.25 in.) H_2O at 20°C (68°F); optional	Upon receipt, visually check for damage; calibrate against wet test meter	Repair or return to supplier
Dry gas meter	Capable of measuring volume within ±2% at a flow rate of 0.02 m^3/min (0.7 ft^3/min)	Check for damage upon receipt and calibrate (Sec 3.9.2) against wet test meter	Reject if damaged, behaves erratically, or cannot be properly adjusted

(continued)

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Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Thermometers	±1°C (2°F) of true value in the range of 0° to 25°C (32° to 77°F) for impinger thermometer and ±3°C (5.4°F) of true value in the range of 0°C to 90°C (32° to 194°F) for dry gas meter thermometers	Check upon receipt for dents or bent stem, and calibrate (Sec 3.9.2) against mercury-in-glass thermometer	Reject if unable to calibrate
Sample Recovery			
Probe liner and probe nozzle brushes	Nylon bristles with stainless steel handles; properly sized and shaped	Visually check for damage upon receipt	Replace or return to supplier
Wash bottles	Polyethylene or glass, 500 ml	Visually check for damage upon receipt	As above
Storage container	High-density polyethylene, 1000 ml	Visually check for damage upon receipt; be sure caps make proper seals	As above
Graduated cylinder	Glass, Class A, 250 ml	Upon receipt, check for stock number, cracks, breaks, and manufacturer flaws	As above
Funnel	Glass, Class A, diameter 100 mm; stem length 100 mm	Visually check for damage upon receipt	As above
Rubber policeman	Properly sized	Visually check for damage upon receipt	As above

(continued)

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TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Pipettes, volumetric flask beaker, flask adapter, condenser, connection tube, Erlenmeyer flask	Glass, Class A	Upon receipt, check for stock number, cracks, breaks and manufacturer flaws	Replace or return to supplier
Distallation Apparatus			
Bunsen burner	Capable of distilling 220 ml in <15 min	Visually check upon receipt; check heating capacity, check for damage	Replace
Crucible	Nickel material; 75-100 ml	Check upon receipt for cracks or flaws	Replace or return to manufacturer
Analytical Equipment			
Hot plate	Heating capacity of 500°C (932°F)	Check upon receipt and before each use for damage; check heating capacity against mercury-in-glass thermometer	Replace or return to manufacturer
Electric muffle furnace	Heating capacity of 600°C (1112°F)	Check upon receipt and before each use for damage; check heating capacity upon receipt against mercury-in-glass thermometer	Replace or return to manufacturer

(continued)

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Table 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Balance	Capacity of 300 g ±0.5g	Check for damage and against series of standard weights upon receipt and before each use	Replace or return to manufacturer
Water bath	Capable of maintaining constant room temperature	Check with mercury-in-glass thermometer	Repair
Fluoride ion activity-sensing electrode	Capable of measuring F^- concentration from 1 to 10^{-6} mol/ℓ (19,000 to 0.02 ppm)	Check for damage and F^- sensing accuracy with a known concentration upon receipt and before each use	Replace or return to manufacturer
Reference electrode	Should provide stable output	Check visually for cracks or breaks	Replace or return to manufacturer
Electrometer	Capable of reading to ±0.1 mV resolution with temperature compensation	Upon receipt and before each use, check for performance accuracy with a known standard F^- solution	Replace or return to manufacturer
Reagents			
Filters	Whatman No. 541 or equivalent	Visually check for damage upon receipt	Replace or return to supplier
Silica gel	Indicating Type 6-16 mesh	Upon receipt check label for grade or certification	Replace or return to manufacturer

(continued)

TABLE 1.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Reagents			
Distilled water	Must conform to ASTM-D1193-74, Type 3	Check each lot	Replace or return to manufacturer
Crushed ice		Check frozen condition	
Stopcock grease	Acetone insoluble, and heat stable silicon grease	Upon receipt, check label for grade or certification	As above
Calcium oxide powder	Reagent grade or certified ACS	As above	As above
Phenolphthalein	0.1% in 1:1 ethanol-water mixture; reagent grade or certified ACS	As above	As above
Sodium hydroxide	NaOH pellet 5M NaOH reagent grade or certified ACS	As above	As above
Sulfuric acid	Concentrated, reagent grade or certified ACS; 25% (v/v) reagent grade or ACS	As above	As above
Fluoride standard solution	Reagent grade or ACS; 1 M concentration	As above	As above

2.0 CALIBRATION OF APPARATUS

Calibration of apparatus is one of the most important functions in maintaining data quality. The detailed calibration procedures in this section are designed for the equipment specified in Method 13B and described in the previous section. A laboratory log book of all calibrations must be maintained. Table 2.1 at the end of this section summarizes the quality assurance activities for calibration.

2.1 Metering System

2.1.1 Wet Test Meter - A wet test meter with a capacity of 3.4 m^3/h (120 ft^3/h) will be needed to calibrate the dry gas meter. Wet test meters are calibrated by the manufacturer to an accuracy of $\pm$0.5%; the calibration must be checked initially upon receipt and yearly thereafter. For large wet test meters (>3ℓ/rev), there is no convenient procedure for checking the calibration; for this reason, several methods are suggested, and others may be approved by the administrator.

The initial calibration may be checked by any of the following methods:

1. Certification from the manufacturer that the wet test meter is within $\pm$1% of true value at the wet test meter discharge, so that only a leak check is needed.

2. Calibration by any primary air or liquid displacement method that displaces at least one complete revolution of the wet test meter.

3. Comparison against a smaller wet test meter that has previously been calibrated by a primary air or liquid displacement method (Section 3.5.2).

4. Comparison against a dry gas meter that has previously been calibrated by a primary air or liquid displacement method.

The calibration of the test meter should be checked annually. This yearly calibration check can be made by the same method

as that of the original calibration; however, the comparison procedure need not be recalibrated if the check is within ±1% of the true value; if not within ±1%, either the comparison procedure or the wet test meter must be recalibrated against a primary air or liquid displacement method.

2.1.2 Sample Meter System - The sample meter system--consisting of the pump, vacuum gauge, valves, orifice meter, and dry gas meter--should be initially calibrated by stringent laboratory procedures before it is used in the field. After initial acceptance, the calibration should be rechecked after each field test series. The recheck procedure can be used by the tester often and with little time and effort to ensure that calibration has not changed. When the quick check indicates that the calibration factor has changed, the tester must again use the complete laboratory procedure to obtain a new calibration factor. After recalibration, the metered sample volume must be multiplied by either the initial or the recalibrated calibration factor--that is, the one that yields the lower gas volume for each test run.

Before initial calibration, a leak check is recommended, but it is not mandatory. Both positive (pressure) and negative (vacuum) leak checks should be performed. Following is a pressure leak-check procedure for checking the metering system from the quick disconnect inlet to the orifice outlet and for checking the orifice-inclined manometer:

1. Disconnect the orifice meter line from the downstream orifice pressure tap (the one closest to the exhaust of the orifice), and plug this tap (Figure 2.1).

2. Vent the negative side of the inclined manometer to the atmosphere. If the manometer is equipped with a three-way valve, merely turn the valve that is on the negative side of the orifice-inclined manometer to the vent position.

3. Place a one-hole rubber stopper with a tube through its hole into the exit of the orifice, and connect a piece of rubber or plastic tubing to the tube, as shown in Figure 2.1.

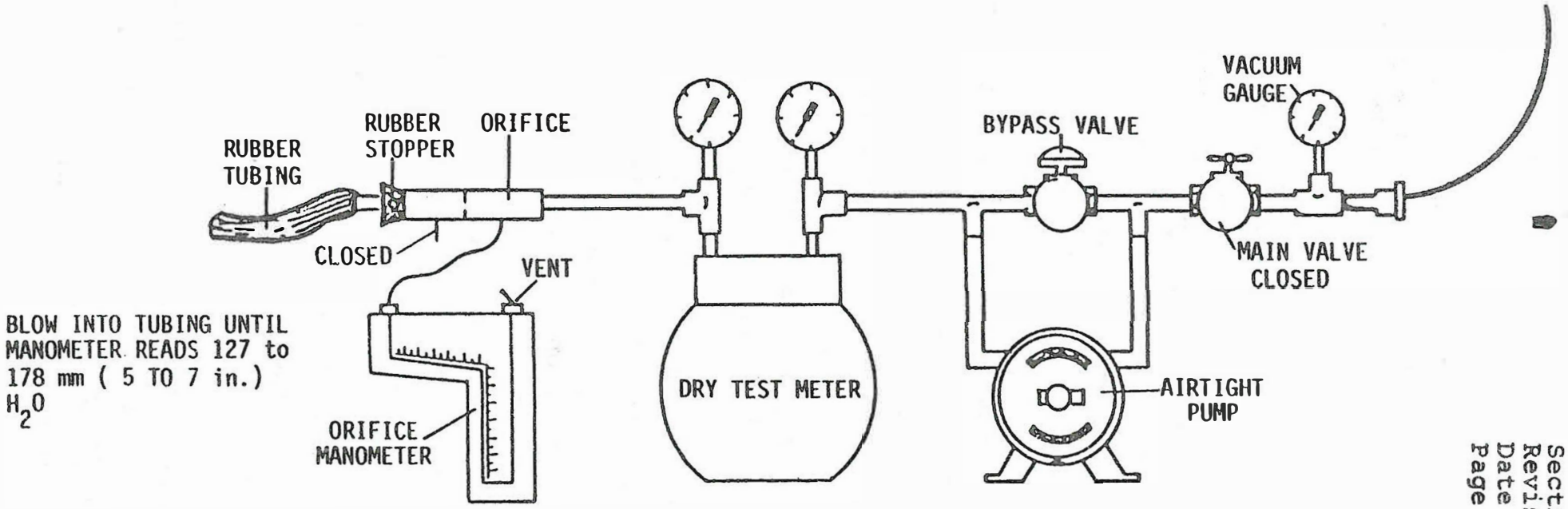

Figure 2.1. Positive leak check of metering system.

4. Open the positive side of the manometer to the "reading" position; if the manometer is equipped with a three-way valve, this will be the line position.

5. Plug the inlet to the vacuum pump. If a quick disconnect with a leak-free check valve is used on the control module, the inlet will not have to be plugged.

6. Open the main valve and the bypass valve.

7. Blow into the tubing connected to the end of the orifice until a pressure of 127 to 178 mm (5 to 7 in.) H_2O has built up in the system.

8. Plug or crimp the tubing to maintain this pressure.

9. Observe the pressure reading for 1 min. No noticeable movement in the manometer fluid level should occur. A bubbling-type leak-check solution may aid in locating any leak in the meter box.

After the metering system is determined to be leak free by the positive leak-check procedure, check the vacuum system to and including the pump.

1. Plug the air inlet to the meter box. If a quick disconnect with a leak-free stopper system is on the meter box, the inlet will not have to be plugged.

2. Turn the pump on and pull a vacuum within 7.5 cm (3 in.) Hg of absolute zero.

3. Observe the dry gas meter. If leakage is >0.00015 m^3/min (0.005 ft^3/min), find and minimize the leak(s) until the above specifications are satisfied.

For metering systems with diaphragm pumps, the leak-check procedures above will not detect leakages within the pump; the following procedure is suggested:

1. Make a 10-min calibration run at 0.00057 m^3/min (0.02 ft^3/min).

2. At the end of the run, find the difference between the measured wet test meter and the dry gas meter volumes, and divide the difference by 10 to get the leak rate. The leak rate should not exceed 0.00057 m^3/min (0.02 ft^3/min).

2.1.2.1 Initial calibration - The dry gas meter and the orifice meter can be calibrated simultaneously, and both should be calibrated when first purchased and any time the posttest check yields a Y outside the range of the calibration factor Y ±0.05Y.

Use a calibrated wet test meter (properly sized, with ±1% accuracy) to calibrate both the dry gas meter and the orifice meter (Figure 2.2) in the following manner:

1. Leak check the metering system (Subsection 2.1.2), and eliminate any leaks before proceeding.

2. Connect the air outlet of the wet test meter to the needle valve at the inlet side of the meter box (Figure 2.2).

3. Run the pump for 15 min with the orifice meter differential (ΔH) set at 12.7 mm (0.5 in.) H_2O to allow the pump to warm up and to permit the interior surface of the wet test meter to be wetted.

4. Adjust the needle valve so that the vacuum gauge on the meter box is between 50 and 100 mm (2 to 4 in.) Hg during calibration.

5. Record the required data on Figure 2.3A or 2.3B, using sample volumes as shown.

6. Calculate Y_i for each of the six runs, using the equation in Figure 2.3A or 2.3B, and record the results on the form in the space provided.

7. Calculate the average Y (calibration factor) for the six runs, using the following equation:

$$Y = \frac{Y_1 + Y_2 + Y_3 + Y_4 + Y_5 + Y_6}{6} .$$

Record the average in the space provided on Figure 2.3A or 2.3B.

8. Clean, adjust, and recalibrate, or reject the dry gas meter if one or more values are outside the interval Y ±0.02Y; otherwise, the average Y is acceptable and should be used for future checks and test runs.

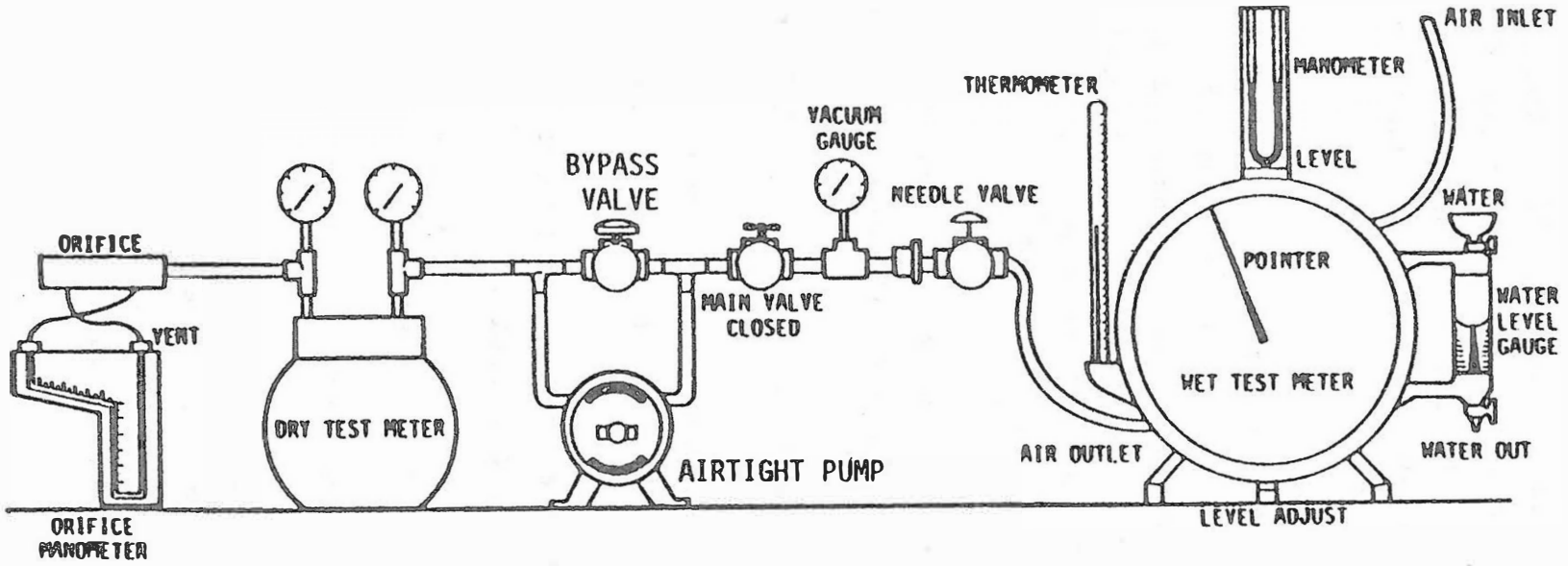

Figure 2.2. Sample meter system calibration setup.

Date 4/31/80 Meter box number FM-2

Barometric pressure, P_b = 29.64 in. Hg Calibrated by [illegible]

Orifice manometer setting (ΔH), in. H_2O	Gas volume: Wet test meter (V_w), ft^3	Gas volume: Dry gas meter (V_d), ft^3	Temperatures: Wet test meter (t_w), °F	Temperatures: Dry gas meter: Inlet (t_{d_i}), °F	Temperatures: Dry gas meter: Outlet (t_{d_o}), °F	Temperatures: Dry gas meter: Avg[a] (t_d), °F	Time (θ), min	Y_i	$\Delta H@_i$, in. H_2O
0.5	5	130.000 135.140	71.5 71.5	91 98	82 85	89	12 47/60	1.004	1.79
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
							Avg		

ΔH, in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 460)}$	$\Delta H@_i = \frac{0.0317\ \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460)\ \theta}{V_w}\right]^2$
0.5	0.0368	$\frac{5(29.64)(549)}{5.14(29.67)(531.5)}$	$\frac{(0.0317)(0.5)}{(29.64)(549)}\left[\frac{(531.5)(12.78)}{5}\right]^2$
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

Figure 2.3A. Dry gas meter calibration data (English units). (front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3.

V_d = Gas volume passing through the dry gas meter, ft^3.

t_w = Temperature of the gas in the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °F.

t_d = Average temperature of gas in dry gas meter, obtained by average t_{d_i} and t_{d_o}, °F.

ΔH = Pressure differential across orifice, in. H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance Y_i = Y±0.02 Y.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives 0.75 ft^3/min of air at standard conditions for each calibration run, in. H_2O; tolerance = ΔH@±0.15 (recommended).

ΔH@ = Average orifice pressure differential that gives 0.75 ft^3/min of air at standard conditions for all six runs, in. H_2O; tolerance = 1.84±0.25 (recommended).

θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

Figure 2.3A. Dry gas meter calibration data (English units). (backside)

Date 4/31/79 Meter box number FM-2

Barometric pressure, P_b = 736 mm Hg Calibrated by [illegible]

Orifice manometer setting (ΔH), mm H_2O	Gas volume: Wet test meter (V_w), m^3	Gas volume: Dry gas meter (V_d), m^3	Temperatures: Wet test meter (t_w), °C	Temperatures: Dry gas meter: Inlet (t_{d_i}), °C	Temperatures: Dry gas meter: Outlet (t_{d_o}), °C	Temperatures: Dry gas meter: Avg[a] (t_d), °C	Time (θ), min	Y_i	$\Delta H@_i$, mm H_2O
10	0.15	25.0320 24.8800	18 18	20 19	18 17	18	10 49/60	.986	23
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
							Avg		

ΔH, mm H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 273)}$	$\Delta H@_i = \frac{0.00117\ \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273)\ \theta}{V_w}\right]^2$
10	0.7	$\frac{(0.15)(736)(291)}{(0.152)(737)(291)}$	$\frac{(0.00117)(10)}{(736)(291)} \left[\frac{(291)(10.82)}{0.152}\right]^2$
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

Figure 2.3B. Dry gas meter calibration data (metric units). (front side)

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3.

V_d = Gas volume passing through the dry gas meter, m^3.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °C.

t_d = Average temperature of gas in dry gas meter, obtained by average of t_{d_i} and t_{d_o}, °C.

ΔH = Pressure differential across orifice, mm H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance Y_i = $Y \pm 0.02$ Y.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs.

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives 0.021 m^3 of air at standard conditions for each calibration run, mm H_2O; tolerance $\Delta H@_i$ = $\Delta H@ \pm 3.8$ mm H_2O (recommended).

$\Delta H@$ = Average orifice pressure differential that gives 0.021 m^3 of air at standard conditions for all six runs, mm H_2O; tolerance $\Delta H@$ = 46.74 ± 6.3 mm H_2O (recommended)

θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

Figure 2.3B Dry gas meter calibration data (metric units). (backside)

9. Calculate $\Delta H@_i$ for each of the six runs, using the equation in Figure 2.3A or 2.3B, and record the results on the form in the space provided.

10. Calculate the average $\Delta H@$ for the six runs, using the following equation:

$$\Delta H@ = \frac{\Delta H@_1 + \Delta H@_2 + \Delta H@_3 + \Delta H@_4 + \Delta H@_5 + \Delta H@_6}{6} .$$

Record the average in the space provided on Figure 2.3A or 2.3B.

11. Adjust the orifice meter or reject it if $\Delta H@_i$ varies by more than ±3.8 mm (0.15 in.) H_2O over the range of 10 to 100 mm (0.4 to 4.0 in.) H_2O; otherwise, the average $\Delta H@$ is acceptable and should be used for subsequent test runs.

2.1.2.2 Posttest calibration check - After each field test series, conduct a calibration check of the metering system (Subsection 2.1.2) except for the following variations:

1. Three calibration runs at a single intermediate orifice meter setting may be used with the vacuum set at the maximum value reached during the test series. The single intermediate orifice meter setting should be based on the previous field test. To adjust the vacuum, insert a valve between the wet test meter and the inlet of the metering system.

2. If a temperature-compensating dry gas meter was used, the calibration temperature for the dry gas meter must be within ±6°C (10.8°F) of the average meter temperature during the test series.

3. Use Figure 2.4A or 2.4B to record the required data.

If the recalibration factor Y deviates by <5% from the initial Y (determined in Subsection 2.1.2), the dry gas meter volumes recorded during the test series are acceptable; if Y deviates by >5%, recalibrate the metering system (Subsection 2.1.2), and use the coefficient (initial or recalibrated) that yields the lower gas volume for each test run.

Alternate procedures--for example, using the orifice meter coefficients--may be used, subject to the approval of the administrator.

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Test numbers AB 1-3 Date 5-13-80 Meter box number FM-7 Plant Acme Power Plant

Barometric pressure, P_b = 28.72 in. Hg Dry gas meter number FM-7 Pretest Y 0.986

Orifice manometer setting, (ΔH), in. H_2O	Gas volume: Wet test meter (V_w), ft^3	Gas volume: Dry gas meter (V_d), ft^3	Temperature: Wet test meter (t_w), °F	Temperature: Dry gas meter: Inlet (t_{d_i}), °F	Temperature: Dry gas meter: Outlet (t_{d_o}), °F	Temperature: Dry gas meter: Average[a] (t_d), °F	Time (θ), min	Vacuum setting, in. Hg	Y_i	$Y_i \frac{V_w P_b (t_d + 460)}{V_d \left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 460)}$
1.41	10	886.544 876.321	72	83	75	79	13.35	3.0	0.987	$\frac{10(28.72)(539)}{10.223\left(28.72+\frac{1.41}{13.6}\right)(532)}$
	10									
	10									
									Y =	

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

V_w = Gas volume passing through the wet test meter, ft^3.

V_d = Gas volume passing through the dry gas meter, ft^3.

t_w = Temperature of the gas in the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °F.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o}, °F.

ΔH = Pressure differential across orifice, in. H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs; tolerance = pretest Y $\pm$0.05Y

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

Figure 2.4A. Posttest dry gas meter calibration data form (English units).

Test numbers AB 1-3 Date 5-13-80 Meter box number FM-7 Plant Acme Power Plant

Barometric pressure, P_b = _____ mm Hg Dry gas meter number FM-7 Pretest Y 0.993

Orifice manometer setting, (ΔH), mm H_2O	Gas volume: Wet test meter (V_w), m^3	Gas volume: Dry gas meter (V_d), m^3	Temperature: Wet test meter (t_w), °C	Temperature: Dry gas meter: Inlet (t_{d_i}), °C	Temperature: Dry gas meter: Outlet (t_{d_o}), °C	Temperature: Dry gas meter: Average[a] (t_d), °C	Time (θ), min	Vacuum setting, mm Hg	Y_i	Y_i $\frac{V_w P_b (t_d + 273)}{V_d \left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 273)}$
36	0.30	26.1742 19.8730	21	23.5	21.5	22.5	13.50	75	0.996	$\frac{0.30\ (730)(295.5)}{0.3012\ (732.6)(294)}$
	0.30									
	0.30									
									Y =	

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

V_w = Gas volume passing through the wet test meter, m^3.

V_d = Gas volume passing through the dry gas meter, m^3.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °C.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o}, °C.

ΔH = Pressure differential across orifice, in. H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs; tolerance = pretest Y ±0.05Y

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

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Figure 2.4B. Posttest meter calibration data form (metric units).

2.2 Temperature Gauges

2.2.1 Impinger Thermometer - The thermometer used to measure temperature of the gas leaving the impinger train should initially be compared with a mercury-in-glass thermometer which meets ASTM E-1 No. 3C or 3F specifications. The procedure is as follows:

1. Place both the reference thermometer and the test thermometer in an ice bath, and compare readings after they stabilize.

2. Remove the thermometers from the bath, and allow both to come to room temperature, compare readings after they stabilize.

3. Accept the test thermometer if both of its readings agree within 1°C (2°F) of the reference thermometer reading. If the difference is greater than ±1°C (2°F), either adjust and recalibrate it until agreement is obtained, or reject it.

2.2.2 Dry Gas Thermometers - The thermometers used to measure the metered gas sample temperature should initially be compared with a mercury-in-glass thermometer, using a similar procedure.

1. Place a dial type or an equivalent thermometer and a mercury-in-glass thermometer in a hot water bath, 40° to 50°C (105° to 122°F); compare the readings after the bath stabilizes.

2. Allow both thermometers to come to room temperature and compare readings after they stabilize.

3. Accept the dial type or equivalent thermometer if the values agree within 3°C(5.4°F) at both points or if the temperature differentials at both points are within ±3°C(5.4°F); tape the temperature differential to the thermometer, and record them on the pretest sampling check form (Figure 3.1 of Section 3.9.3).

4. Before each field trip, compare the reading of the mercury-in-glass thermometer at room temperature with that of the meter system thermometer; the values or the corrected values should agree within ±6°C (10.8°F) of one another, or the meter thermometer should be replaced or recalibrated. Record any correction factors on Figure 3.1 or on a similar form.

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2.2.3 Stack Temperature Sensor - The stack temperature sensor should be calibrated upon receipt or checked before field use. Each sensor should be uniquely marked for identification. The calibration should be performed at three points and then extrapolated over the temperature range anticipated during actual sampling. For the three-point calibration, a reference mercury-in-glass thermometer should be used. The following procedure is recommended for calibrating stack temperature sensors (thermocouples and thermometers) for field use.

1. For the ice point calibration, form a slush from crushed ice and water (preferably deionized distilled) in an insulated vessel such as a Dewar flask; being sure that the sensor does not touch the sides of the flask, insert the stack temperature sensor into the slush to a depth of at least 2 in. Wait 1 min to achieve thermal equilibrium, and record the readout on the potentiometer. Obtain three readings taken in 1-min intervals. Note: Longer times may be required to attain thermal equilibrium with thick-sheathed thermocouples.

2. Fill a large Pyrex beaker with water to a depth $\geq$4 in. Place several boiling chips in the water, and bring the water to a full boil using a hot plate as the heat source. Insert the stack temperature sensor(s) in the boiling water to a depth of at least 2 in., taking care not to touch the sides or bottom of the beaker.

Alongside the sensor(s), an ASTM reference thermometer should be placed. After 3 min, both instruments will attain thermal equilibrium. Simultaneously record temperatures from the ASTM reference thermometer and the stack temperature sensor three times at 1-min intervals.

If the entire length of the mercury column in the thermometer cannot be immersed, a temperature correction will be required to give the correct reference temperature.

3. For a thermocouple, repeat Step 2 with a liquid (e.g., cooking oil) that has a boiling point 150° to 250°C (300° to

500°F), and record all data on Figure 2.5. For thermometers other than thermocouples, either repeat Step 2 with a liquid that boils at the maximum temperature that the thermometer is to be used or place the stack thermometer and the reference thermometer in a furnace or other device to attain the desired temperature. Note: If the thermometer is to be used at temperatures higher than the reference thermometer will record, calibrate the stack thermometer with a thermocouple previously calibrated by the above procedure.

4. If the absolute temperature of the reference thermometer and the thermocouple(s) agree within ±1.5% at each of the three calibration points, either plot the data on linear graph paper and draw the best-fit line between the points or calculate the linear equation using the method of least-squares. For the thermocouple, the data may be extrapolated above and below the calibration points to cover the manufacturer's suggested range," for the portion of the plot (or equation) that agrees within 1.5% of the absolute reference temperature, no correction is needed, but for all other portions that do not agree within ±1.5%, use the plot (or equation) to correct the data.

If the absolute temperatures of the reference thermometer and stack temperature sensor (other than the thermocouple) agree within ±1.5% at each of the three points, the thermometer may be used for testing without applying any correction factor over the range of calibration points, but the data cannot be extrapolated outside the calibration points.

2.3 Probe Heater

The probe heating system should be calibrated before field use according to the procedure in APTD-0576.[4] Probes constructed according to APTD-0581[3] need not be calibrated if the curves of APTD-0576[4] are used.

2.4 Barometer

The field barometer should be adjusted initially and before each test series to agree within ±2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer reading or with the value reported by

1146

Date 5-12-80 Thermocouple number TC-46

Ambient temperature 21 °C Barometric pressure 29.67 in. Hg

Calibrator BB Reference: mercury-in-glass ASTM 3C

other

Reference point number	Source[a] (specify)	Reference thermometer temperature, °C	Thermocouple potentiometer temperature, °C	Temperature difference,[b] %
0°	ICE WATER	1°	1°	—
100°	boiling WATER	101.5°	101°	0.1%
—	boiling cooking oil	205.5°	203°	0.5%

[a] Type of calibration system used.

[b] $\left[\frac{(\text{ref temp, °C} + 273) - (\text{test thermom temp, °C} + 273)}{\text{ref temp, °C} + 273}\right] 100 \leq 1.5\%$.

Figure 2.5 Stack temperature sensor calibration data form.

a nearby National Weather Service station and corrected for elevation. Correction for the elevation difference between the station and the sampling point should be applied at a rate of -2.5 mm Hg/30 m (0.1 in. Hg/100 ft). Record the results on the pretest sampling check form (Figure 3.1).

2.5 Probe Nozzle

Probe nozzles should be calibrated initially before use in the field.

1. Use a micrometer to measure the ID of the nozzle to the nearest 0.025 mm (0.001 in.).

2. Make three measurements using different diameters each time.

3. Average the three measurements. The difference between the high and the low numbers should not be $\leq$0.1 mm (0.004 in.).

4. Label each nozzle permanently and uniquely for identification.

5. Record the data on Figure 2.6, the nozzle calibration form. If nozzles become nicked, dented, or corroded, reshape, sharpen, and recalibrate before use.

2.6 Pitot Tube

The Type S pitot tube assembly should be calibrated using the procedure in Section 3.1.2, Method 2.

2.7 Trip Balance

The trip balance should be calibrated initially by using Class-S standard weights, and it should agree within ±0.5 g of the standard weight. Adjust or return the balance to the manufacturer if limits are not met.

2.8 Fluoride Electrode

The fluoride (F^-) electrode should be calibrated daily, and checked hourly against serial dilutions of the 0.1M fluoride standard solution. Use the following procedure to prepare and to measure the concentration of the dilutions.

1. Pipette 10 ml of 0.1M NaF into a 100-ml volumetric flask, and dilute to the mark with distilled water to get 0.01M NaF; dilute 10 ml of the 0.01M solution to make a 0.001M

Date 5/14/80 Calibrated by 4343

Nozzle identification number	Nozzle Diameter[a]			ΔD,[b] mm (in.)	D_{avg}[c]
	D_1, ~~mm~~ (in.)	D_2, ~~mm~~ (in.)	D_3, ~~mm~~ (in.)		
37	0.251	0.252	0.253	0.002	0.252

where:

[a] $D_{1,2,3}$ = three different nozzles diameters, mm (in.); each diameter must be within (0.025 mm) 0.001 in.

[b] ΔD = maximum difference between any two diameters, mm (in.), $\Delta D \leq$ (0.10 mm) 0.004 in.

[c] D_{avg} = average of D_1, D_2, and D_3.

Figure 2.6 Nozzle calibration data form.

solution; continue in the same manner to get the 0.001M and the 0.00001M dilutions.

2. Pipette 50 ml of each NaF dilution into separate beakers.

3. Add 50 ml of TISAB to each beaker.

4. Immerse the electrode into the most dilute standard solution, and measure the developed potential while stirring the solution with a magnetic stirrer. Note: Avoid stirring the solution before immersing the electrode because entrapped air around the crystal can cause erroneous readings or needle fluctuations.

5. Keep the electrodes immersed in the solution 3 min in order for it to stabilize before taking a final positive millivolt reading.

6. Record the reading on the laboratory form, Figure 2.7, and remove the electrode from the sample.

7. Soak the electrode for 30 s in distilled water, and then blot it dry.

8. Plot the millivolt value on the linear axis of semilog graph paper and plot the known concentrations of fluoride standards on the log axis as shown in Figure 2.8. Note: Plot the nominal value for concentrations of the standards on the log axis; for example, when 50 ml of the 0.01M standard is diluted with 50 ml TISAB, the concentration is plotted as 0.01M. Measure the most dilute standard first and the most concentrated standard last, as shown on Figure 2.8, to get a straight-line calibration curve with nominal concentrations of 0.00001, 0.0001, 0.001, 0.01, and 0.1M NaF. To obtain the required precision, use 4 or 5 cycle semilog paper similar to that in Figure 2.8.

To check the accuracy of the calibration curve, prepare and measure a control sample (Section 3.9.5). Prepare fresh standardizing solutions of $\leq$0.01M NaF daily, and store the solutions in polyethylene or polypropylene contains.

The fluoride electrode should be checked periodically after repeated use for responsiveness and sensitivity. Compare the

LABORATORY WORKSHEET

Date 3-5-80

Date standards prepared 3-5-80

Temperature of standards 20.5°C Electrode number 104

Standard number	Concentration (M)	Electrode potential (mV)
1	0.000001	—
2	0.00001	300
3	0.0001	267
4	0.001	209
5	0.01	149
6	0.1	90
Control Sample	0.005	166

Note: The concentration of the control sample determined from the calibration curve must be between 0.002M and 0.01M.

Signature of analyst Bill Mitchell

Signature of reviewer Tom Logan

Figure 2.7. Fluoride calibration data form. (Method 13B)

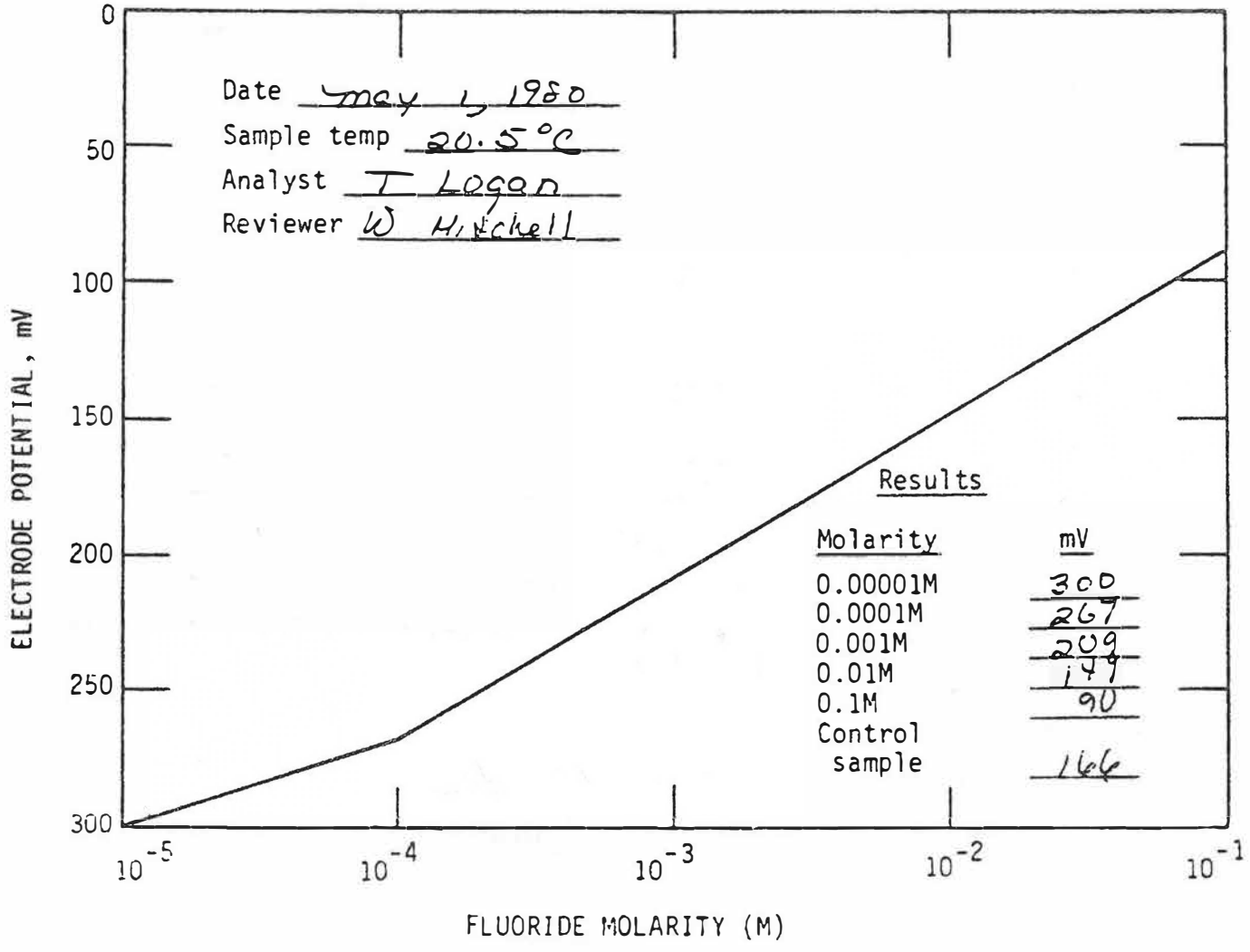

Figure 2.8. Fluoride calibration curve, Method 13B.

electrode responses or millivolt readings of samples or standards of the same fluoride concentration. For equal concentrations of fluoride, the electrode response should remain stable with each analysis, if not, repair or replace the electrode.

Certain specific-ion meters designed specifically for fluoride electrode use give direct readouts of F^- concentrations. These meters may be used over narrow concentration ranges. Calibrate the meter according to manufacturer's directions.

TABLE 2.1. ACTIVITY MATRIX FOR CALIBRATION OF EQUIPMENT

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Wet test meter	Capacity of ≥3.4 m^3/h (120 ft^3/h); accuracy within ±1.0%	Calibrate initially and yearly by liquid displacement	Adjust to meet specifications, or return to manufacturer
Dry gas meter	$Y_i = Y \pm 0.02\ Y$ at flow rate of 0.02 - 0.03 m^3/min (0.7 - 1.1 ft^3/min)	Calibrate with wet test meter initially to agree within $Y \pm 0.02\ Y$ and when post-test check is not within $Y \pm 0.05\ Y$	Repair or replace, and then recalibrate
Thermometers	Impinger thermometer ±1°C (2°F); dry gas meter thermometer ±3°C (5.4°F) over applicable range	Calibrate each initially against a mercury-in-glass thermometer; before field trip compare each with mercury-in-glass thermometer	Adjust, determine a constant correction factor, or reject
Barometer	±2.5 mm (0.1 in.) Hg of mercury-in-glass barometer	Calibrate initially vs mercury-in-glass barometer; check before and after each field test	Adjust to agree with certified barometer
Probe nozzle	Average three ID measurements of nozzle; difference between high and low ≤0.1 mm (0.004 in.)	Use a micrometer to measure to nearest 0.025 mm (0.001 in.)	Recalibrate, reshape, and sharpen when nozzle becomes nicked, dented, or corroded

(continued)

Table 2.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Stack temperature sensor	±1.5% of average stack temperature, °R	Calibrate initially; check after each field test	Adjust or reject
Trip balance	Standard Class-S weights within ±0.5 g of stated value	Verify calibration when first purchased, any time moved or subject to rough handling, and during routine operations when not within ± 0.5 g	Have the manufacturer recalibrate or adjust
Pitot tube	Type S; initially calibrated according to Section 3.1, Meth 2; tube tips undamaged	Visually check before each field test	Repair or replace
Fluoride electrode	Calibration curve plotted with F^- standard solutions of 0.1M, 0.01M, 0.001M, 0.0001M, and 0.00001M and corresponding mV reading on semilog graph paper; stable electrode response	Calibrate with each use and every hour of continuous use; check response stability of electrode after repeated use	Repair or replace

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3.0 PRESAMPLING OPERATIONS

The quality assurance activities for presampling operations are summarized in Table 3.1 at the end of this section. See Sections 3.0.1 and 3.0.2, of this Handbook for general information on preliminary site visits. See Section 3.4.3 (Method 5) for more detailed and specific information of presampling operations for sampling equipment similar to the Method 13 equipment.

3.1 Apparatus Check and Calibration

Pretest checks must be made on most of the sampling apparatus. Figure 3.1 should be used to record data on the pretest calibration checks. Figure 3.2 in Section 3.4 of this Handbook is recommended to aid the tester in preparing an equipment checklist, status form, and packing list.

3.1.1 Sampling Train - A schematic of the EPA Method 13 sampling train (Figure 1.1) should be used for assembling the components and for checking for compliance (specifications in the Reference Method, Section 3.9.10).

3.1.2 Probe and Nozzle - Clean the probe and the nozzle internally by brushing first with tap water, then with deionized distilled water, and finally with acetone; allow both to dry in the air. The probe should be sealed at the inlet or tip; should be checked for leaks at a vacuum of 380 mm (15 in.) Hg; and should be leak free under these conditions. The probe liner, in extreme cases, can be cleaned with stronger reagents; in either case, the objective is to leave the liner free from contaminants. Check the probe's heating system to see that it is operating properly and that it prevents moisture condensation.

3.1.3 Impingers, Filter Holders, and Glass Connectors - All glassware should be cleaned first with detergent and tap water and then with deionized distilled water. All glassware should be visually inspected for cracks or breakage and then repaired or discarded if defective. If a filter is to be used between the probe and the first impinger be sure that an acceptable stainless steel mesh filter support is packed; glass frit supports are not acceptable.

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Date 5-11-80 Calibrated by BEB

Meter box number FB-1 ΔH@ 1.87

Dry Gas Meter*

Pretest calibration factor Y 1.013 (within ±2% of the average factor for each calibration run).

Impinger Thermometer

Was a pretest temperature correction used? ____ yes ✓ no
If yes, temperature correction ____ (within ±1°C (2°F) of reference values for calibration and within ±2°C (4°F) of reference value for calibration check)

Dry Gas Meter Thermometers

Was a pretest temperature correction made? ____ yes ✓ no
If yes, temperature correction ____ (within ±3°C (5.4°F) of reference value for calibration and within 6°C (10.8°F) of reference values for calibration check)

Stack Temperature Sensor*

Was a stack temperature sensor calibrated against a reference thermometer? ✓ yes ____ no
If yes, give temperature range with which the readings agreed within ±1.5% of the reference values 300 to 360 K ~~(°R)~~

Barometer

Was the pretest field barometer reading correct? ✓ yes ___ no
(within ±2.5 mm (0.1 in.) Hg of the mercury-in-glass barometer)

Nozzle*

Was the nozzle calibrated to the nearest 0.025 mm (0.001 in.)?
✓ yes ____ no

*Most significant items/parameters to be checked.

Figure 3.1. Pretest sampling checks.

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3.1.4 Pump - The vacuum pump should be serviced as recommended by the manufacturer, or every 3 mo, or upon erratic behavior (nonuniform or insufficient pumping action). Check the oiler jars, if used, every 10 tests.

3.1.5 Dry Gas Meter - A dry gas meter calibration check should be made using the procedure in Section 3.4.2.

3.1.6 Silica Gel - Either dry the used silica gel at 175°C (347°F) for at least 2 h or use fresh silica gel. Weigh several 200- to 300-g portions in airtight containers to the nearest 0.5 g if the moisture content is to be determined. Record the total weight (silica gel plus container) for each container.

3.1.7 Thermometers - The thermometers should be compared to a mercury-in-glass reference thermometer at ambient temperature.

3.1.8 Barometer - The field barometer should be compared before each field trip with a mercury-in-glass barometer or with a weather station reading after making an elevation correction.

3.2 Reagents and Equipment

3.2.1 Filters - Check the filters visually against light for irregularities, flaws, and pinhole leaks. Determine the F-blank value by analyzing three filters chosen from each lot (Section 3.9.5); if the value is $\leq$0.015 mg F/cm^2 they are acceptable for field use.

3.2.2 Water - 100 ml of deionized distilled water is needed for each of the first two impingers and for sample recovery.

3.2.3 Ice - Crushed ice is needed to keep the gas that exits into the last impinger below 21°C (70°F).

3.2.4 Stopcock grease - Silicone grease that is acetone insoluble and heat stable may be used sparingly at each connection point of the sampling train to prevent gas leaks; but this is not necessary if screw-on connectors with Teflon (or similar) sleeves are used.

3.3 Equipment Packing

The accessibility, condition, and functioning of measurement devices in the field depend on careful packing and on careful

movement on site. Equipment should be packed to withstand severe treatment during shipping and field handling operations. One major consideration in shipping cases is the construction materials. The following containers are suggested, but are not mandatory.

3.3.1 Probe - Seal the inlet and outlet of the probe to protect the probe from breakage. Pack the probe inside a container that is lined with polyethylene or other suitable material that is rigid enough to prevent bending or twisting during shipping and handling; an ideal container is a wooden case (or the equivalent) with a separate compartment lined with foam material for each probe, and should have handles or eye-hooks that can withstand hoisting.

3.3.2 Impingers, Connectors, and Assorted Glassware - All impingers and glassware should be packed in rigid containers and protected by polyethylene or other suitable material. Individual compartments will help to organize and protect each piece of glassware.

3.3.3 Volumetric Glassware - A sturdy case lined with foam material is suggested for drying tubes and assorted volumetric glassware.

3.3.4 Meter Box - The meter box--which contains the manometers, orifice meter, vacuum gauge, pump, dry gas meter, and thermometers--should be packed in a shipping container unless its housing is sufficiently protective for the components during travel. Additional pump oil should be packed if oil is required. It is advisable to carry a spare meter box in case of failure.

3.3.5 Wash Bottles and Storage Containers - Storage containers and miscellaneous glassware should be packed in a rigid foam-lined container.

TABLE 3.1 ACTIVITY MATRIX FOR PRESAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sampling train probe and nozzle	1. Probe, nozzle, and liner free of contaminants; constructed of borosilicate glass, quartz, or equivalent; metal liner must be approved by administrator	1. Clean internally by brushing with tap water, deionized distilled water, and acetone; air dry before test	1. Repeat cleaning and assembly procedures
	2. Probe leak free at 380 mm (15 in.) Hg	2. Check using procedures in Subsec 2.3	2. Replace
	3. Probe heating system prevents moisture condensation	3. Check heating system initially and when moisture cannot be prevented during testing (Sec 3.4.1)	3. Repair or replace
Impingers, filter holders, and glass connectors	Clean; free of breaks, cracks, leaks, etc.	Clean with detergent, tap water, and deionized distilled water	Repair or discard
Pump	Sampling rate of 0.02-0.03 m^3/min (0.7 to 1.1 ft^3/min) up to 380 mm (15 in.) Hg at pump inlet	Service every 3 mo or upon erratic behavior; check oiler jars every 10 tests	Repair or return to manufacturer
Dry gas meter	Clean; readings ±2% of of average calibration factor	Calibrate according to Sec 3.4.2; check for excess oil	As above

(continued)

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Table 3.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Reagents and Equipment			
Filters	No irregularities, flaws, pinhole leaks; $\leq$0.015 mgF/cm^2	Visually check before testing; check each lot of filters for F content	Replace
Water	Deionized distilled conforming to ASTM-D1193-74, Type 3	Run blank evaporations before field use to eliminate high solids (only required if impinger contents to be analyzed)	Redistill or replace
Stopcock grease	Acetone insoluble; heat stable	Check label upon receipt	Replace
Packing Equipment for Shipment			
Probe	Rigid container lined with polyethylene foam	Prior to each shipment	Repack
Impingers, connectors, and assorted glassware	Rigid container lined with polyethylene foam	As above	As above
Pump	Sturdy case lined with polyethylene foam material if not part of meter box	As above	As above
Meter box	Meter box case and/or additional material to protect train components; pack spare meter box	As above	As above
Wash bottles and storage containers	Rigid foam-lined container	As above	As above

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4.0 ON-SITE MEASUREMENTS

The on-site activities include transporting equipment to the test site, unpacking and assembling the equipment, making duct measurements, performing the velocity traverse, determining molecular weights and stack gas moisture contents, sampling for fluorides, and recording the data. Table 4.1 at the end of this section summarizes the quality assurance activities for on-site activities. Blank forms to be used in recording data are in Section 3.4.12 for the convenience of the Handbook user.

4.1 Handling of Equipment

The most efficient means of transporting or moving the equipment from ground level to the sampling site should be decided during the preliminary site visit (or prior correspondence). Care should be exercised to prevent damage to the test equipment or injury to test personnel during the moving phase. A "laboratory" area should be designated for assembling the sampling train, placing the filter in the filter holder, charging the impingers, recovering the sample, and documenting the results; this area should be clean and free of excessive drafts.

4.2 Sampling

The on-site sampling includes preliminary measurements and setup, placing the filter in the filter holder, setting up the sampling train, preparing the probe, checking for leaks along the entire train, inserting the probe into the stack, sealing the port, checking the temperature of the probe, sampling at designated points, and recording the data. A final leak check must always be performed upon completion of the sampling.

4.2.1 Preliminary Site Measurements - These measurements are needed for locating the pitot tube and the probe during the sampling.

1. Be sure the site meets Method 1 specifications; if not, due to duct configuration or other reasons, have the site approved by the administrator.

2. Be sure a 115-V, 30-A electrical supply is available for operating the standard sampling train.

3. Either measure the stack and determine the minimum number of traverse points by Method 1, or check the traverse points determined during the preliminary site visit (Section 3.0).

4. Record all data on the traverse point location form shown in Method 1. These measurements will be used to locate the pitot tube and the sampling probe during preliminary measurements and actual sampling.

The site must be accepted before a valid sample can be taken.

4.2.2 Stack Parameters - By the following preliminary measurements, the user can set up the nomograph as outlined in APTD-0576.[4] An example nomograph data form is Figure 4.1. Using the stack parameters obtained, the isokinetic sampling rate can be set.

1. Check the sampling site for cylonic or nonparallel flow (Method 1, Section 3.0).

2. Determine the stack pressure, temperature, and the range of velocity heads encountered (Method 2).

3. Calculate the moisture content by using Method 4 or its alternatives. If the source has been tested before or if a good estimate of the moisture is available, this value can be used to avoid calculations. If the stack gas is saturated with moisture or has water droplets, the moisture content must be determined by using stack gas temperature sensor (Method 4).

4. Calculate the dry molecular weight (M_d) of the stack gas (Method 2). If an integrated gas sample is required, follow Method 3 procedures and take the gas sample simultaneously with and for the same total length of time as the fluoride sample.

5. Record the data on the sampling and the analytical data forms for molecular weight determinations located in Section 3.2, Method 3.

Note: The condensate collected during the sampling can be used in the final calculations of moisture content (Section 3.9.6).

Plant Pollution Free Inc.

Date 5-12-80

Sampling location Boiler outlet

Calibrated pressure differential across orifice, in. H_2O	$\Delta H_@$	1.91
Average meter temperature (ambient + 20°F), °F	$T_{m_{avg}}$	80
Percent moisture in gas stream by volume, %	B_{wo}	0.06
Barometric pressure at meter, in. Hg	P_m	29.48
Static pressure in stack, in. Hg ($P_m \pm 0.073 \times$ stack gauge pressure, in. H_2O)	P_s	-0.01
Ratio of static pressure to meter pressure	P_s/P_m	1
Average stack temperature, °F	$T_{s_{avg}}$	540
Average velocity head, in. H_2O	Δp_{avg}	0.1
Maximum velocity head, in. H_2O	Δp_{max}	0.3
C factor		1.0
Calculated nozzle diameter, in.		0.385
Actual nozzle diameter, in.		0.375
Reference Δp, in. H_2O		0.148

Figure 4.1. Nomograph data form (English units).

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4.2.3 Sampling Rate - Method 13 sampling is performed isokinetically like Method 5, but the sampling rate must be <0.03 m^3/min (1.0 ft^3/min) during the test; the maximum ΔH will limit the rate to <0.03 m^3/min (1.0 ft^3/min).

1. Select a nozzle size based on the range of velocity heads, so that the nozzle size will not have to be changed to maintain an isokinetic sampling rate.

2. Select a nozzle that will maintain the maximum sampling rate at <0.03 m^3/min (1.0 ft^3/min) during the run.

3. Check the maximum ΔH, using the following equation:

$$\text{Maximum } \Delta H \leq \frac{1.09\ P_m\ M\ \Delta H@}{T_m} \qquad \text{Equation 4-1}$$

where

Maximum ΔH = pressure differential across the orifice that produces a flow of 1.0 ft^3/min, in. H_2O;

P_m = pressure of the dry gas meter, in. Hg;

M = molecular weight of the stack gas;

ΔH@ = pressure differential across the orifice that produces a flow rate of 0.75 scfm, in. H_2O; and

T_m = temperature of the meter, °R.

4. Install the selected nozzle using a Viton A O-ring if glass or stainless steel liners are used; install the nozzle on a stainless steel liner by using a leak-free mechanical connection (APTD-0576[4]) or Teflon ferrules.

5. Mark the probe with heat resistant tape or with another acceptable means to denote the proper distance to which it should be inserted into the stack or duct at each sampling point.

6. Select a total sampling time that is greater than or equal to the minimum total sampling time specified in the test procedures for the specific industry so that--

a. The sampling time per traverse point is ≥2 min (greater time interval may be specified by the administrator);

the number of minutes sampled at each point is either an integer or an integer plus one-half minute to avoid timekeeping errors.

b. The sample volume corrected to standard conditions exceeds the required minimum total gas sample volume (can be based on an approximate average sampling rate). In some circumstances (e.g., batch cycles), it may be necessary to sample for shorter times and to obtain smaller gas sample volumes; if so, obtain the administrator's approval.

7. Record the data on the fluoride field data form (Figure 4.2).

4.2.4 Sampling Train Preparation - These steps are needed for preparing the sampling train.

1. Keep all openings where contamination can occur covered until just before assembly of the setup or before beginning the sampling.

2. Place 100 ml of distilled water (a graduated cylinder may be used) in each of the first two impingers.

3. Leave the third impinger empty.

4. Add 200-300 g of preweighed silica gel in the fourth impinger and place the empty container in a safe place for use later in the sample recovery, and record the weight of the silica gel and the container on the appropriate data form. If moisture content is to be determined by impinger analysis, weigh each of the first three impingers to the nearest 0.5 g, and record these weights.

5. Use tweezers or clean disposable surgical gloves to place the filter in the filter holder.

6. Be sure that the filter is properly centered and that the gasket is properly placed to prevent the sample gas stream from circumventing the filter.

4.2.5 Sampling Train Assemblage - The arrangement of the sampling train components is shown in Figure 1.1.

1. Apply if needed to avoid contamination a very light coat of silicone grease, but only on the outside of all ground-glass joints.

Plant ACME Power Plant
City Megawatt, Ohio
Location Unit 5, Outlet
Operator D. Redde
Date 5-15-80
Run number ATP 1
Stack diam, ~~mm~~ (in.) 102

Sample box number A
Meter box number FB-1
Meter ΔH@ 1.87

Meter calibration (Y) 1.013
Pitot tube (C_p) 0.84
Probe length 10 ft
Probe liner material S Steel
Probe heater setting 0.7
Ambient temperature 40°F
Barometric pressure (P_b) 29.23 ~~mm~~ (in.) Hg
Assumed moisture 8%
Static pressure (P_a) -0.6 ~~mm~~ (in.) H_2O
C Factor 0.96
Reference ΔP 0.295 ~~mm~~ (in.) H_2O

Sheet 1 of 1
Nozzle identification number 31
Nozzle diameter 0.3080 mm (in.)
Thermometer number CE56
Final leak rate 0.001 ~~m^3/min~~ (cfm)
Vacuum during leak check 3.0
~~mm~~ (in.) Hg
Filter position Back
Maximum ΔH 2.5
Remarks

Traverse point number	Sampling time, (θ), min	Clock time, (24 h)	Vacuum, mm ~~(in.)~~ Hg	Stack temperature (T_s), ~~°C~~(°F)	Velocity head (ΔP_s), ~~mm~~ (in.) H_2O	Pressure differential across orifice meter (ΔH), ~~mm~~ (in.) H_2O	Gas sample volume (V_m), m^3 (ft^3)	Gas sample temperature at dry gas meter		Temp of gas leaving condenser or last impinger, ~~°C~~ (°F)	Filter temp, ~~°C~~(°F)
								Inlet, ~~°C~~(°F)	Outlet, ~~°C~~(°F)		
Start	0	1332	—	—	—	—	181.733	—	—	—	—
N-1	5		1.0	309	0.37	2.3	185.792	45	46	47	280
2	10		1.0	312	0.35	2.2	189.784	53	46	48	250
3	15		2.0	314	0.36	2.25	193.773	58	47	48	270
4	20		2.0	311	0.36	2.25	197.835	60	48	49	270
5	25		2.5	315	0.40	2.5	202.058	61	49	50	
6	30	1402	2.0	313	0.39	2.4	206.189	61	50	50	
E-1	35	1420	2.5	311	0.43	2.7	211.184	62	50	51	
2	40		2.5	314	0.43	2.7	214.848	62	51	51	
3	45		2.5	313	0.40	2.5	219.085	61	51	51	
4	50		2.5	313	0.35	2.2	223.142	61	51	50	
5	55		2.5	312	0.29	1.8	226.793	62	50	51	
6	60	1445	2.0	311	0.28	1.7	230.380	62	51	52	
	Total 60		Max 2.5	Avg 312.3			Total 48.647	Avg 59	Avg 49	Max 52	

Figure 4.2. Fluoride field data form.

2. Either place the filter immediately following the probe or between the third and fourth impingers. Normally the filter will be placed after the third impinger unless the filterable particulate fluoride is to be measured. It is not necessary to have filters in both positions. If in the front filter position, use a 20-mesh stainless steel filter support with a silicone outer seal.

3. Place crushed ice and water around the impingers.

4. Check the filter to be sure there are no tears.

5. Attach a temperature sensor to the metal sheath of the sampling probe if it is not already an integral part of the assembly, so that the sensor extends beyond the probe tip and does not touch any metal; the sensor should be about 1.9 to 2.54 cm (0.75 to 1 in.) from the pitot tube and the nozzle to avoid interference with the gas flow; other arrangements are shown in Method 2.

4.2.6 Sampling Train Leak Checks - Leak checks are necessary to ensure that the sample has not been biased low by dilution air. The Reference Method (Section 3.9.10) specifies that leak checks be performed at certain times as discussed below. Leakage rates <4% of the average sampling rate or 0.00057 m^3/min (0.02 ft^3/min), whichever is less, are acceptable.

4.2.6.1 Pretest - (optional) If the tester opts to conduct the pretest leak check, the following procedure should be used after the sampling train has been assembled.

1. Set the filter heating system at the desired operating temperature.

2. Allow the temperature to stabilize.

3. If a Viton A O-ring or other leak-free gasket is used to connect the probe nozzle to the probe liner, leak check the train at the sampling site by plugging the nozzle and pulling a vacuum of 380 mm (15 in.) Hg. Note: A lower vacuum may be used if it is not exceeded during the test.

4. If an asbestos string is used for the probe gasket, do not connect the probe to the train; instead, first plug the inlet

to the filter holder and pull a vacuum of 380 mm (15 in.) Hg (see previous note), and then connect the probe to the train to leak check at a vacuum of about 25 mm (1 in.) Hg.

Alternatively, the probe may be leak checked with the rest of the sampling train in one step at a vacuum of 380 mm (15 in.) Hg (APTD-0581[3] and APTD-0576[4]).

1. Start the pump with the bypass valve fully open and the coarse adjust valve closed.

2. Open the coarse adjust valve, and slowly close the bypass valve until the desired vacuum is reached. Note: Do not reverse the direction of the bypass valve; this will cause distilled water to back up from the impingers into the filter holder. If the desired vacuum is exceeded, either leak check at the higher vacuum or end the leak check (step 3 below) and start over.

3. When the leak check is complete, slowly remove the plug from the inlet to the probe or the filter holder; close the coarse adjust valve; and immediately turn off the vacuum pump to prevent the impinger water from being forced back into the filter holder and to prevent the silica gel from being forced back into the third impinger.

4. Visually check to be sure that water did not contact the filter and that the filter has no tears before beginning the test.

4.2.6.2 During the Sampling - If a component (e.g., filter assembly or impinger) change is necessary during the test, conduct a leak check before the change, according to the step-by-step procedure outlined above.

1. Record the initial dry gas meter reading on Figure 4.2.

2. Be sure the vacuum is equal to or greater than the maximum value recorded up to that point in the test.

3. If the leakage rate is ≤ 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is less), the results are acceptable, so no correction need be applied to the total volume of dry gas metered.

4. If a higher leakage rate is obtained, either record the leakage and correct the sample volume (Section 6.3(b) of the Reference Method, Section 3.9.10), or void the sample run.

5. Record the final dry gas meter reading on Figure 4.2.

4.2.6.3 Posttest - (mandatory) At the conclusion of each sampling run, conduct a leak check in accordance with the procedures above.

1. Record the initial dry gas meter reading on Figure 4.2.

2. Be sure the vacuum is equal to or greater than the maximum recorded during the sampling run.

3. If the leakage rate is ≤ 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling rate (whichever is less), the results are acceptable, so no correction need be applied to the total volume of dry gas metered.

4. If a higher leakage rate is obtained, either record the leakage rate and correct the sample volume (Section 6.3(a) or 6.3(b) of the Reference Method, Section 3.9.10), or void the sample run.

5. Record the dry gas meter reading on Figure 4.2.

4.2.7 Sampling Train Operation - Just before beginning the sampling, clean the portholes to minimize the chance of sampling any deposited materials. Verify that the probe and the filter heating systems (if required) are up to the desired temperatures and verify that the pitot tube and the nozzle are positioned properly. Follow the procedure below for sampling:

1. Record the initial dry gas meter readings, barometric pressure, and other data on Figure 4.2.

2. Position the tip of the probe at the first sampling point with the nozzle tip pointing directly into the gas stream. When in position, block off the open area around the probe and the porthole to prevent flow disturbances and unrepresentative dilution of the gas stream.

3. Turn on the pump, and immediately adjust the sample flow to attain isokinetic conditions; maintain a sampling rate of ±10% of the isokinetic rate (unless otherwise specified by the

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administrator), and adjust the rate at any sampling point if a 20% variation in velocity pressure occurs. Note: Do not exceed the maximum ΔH. Use nomographs or programmed calculators to rapidly determine the orifice pressure drop corresponding to the isokinetic sampling rate. If the nomograph is designed as shown in APTD-0576,[4] use it only with a Type S pitot tube which has a C_p coefficient of 0.85 ± 0.02 and only when the stack gas dry molecular weight (M_d) is 29 ± 4, if C_p and M_s are outside these limits, do not use the nomograph without compensating for the differences. Recalibrate the isokinetic rate or reset the nomograph if the absolute stack temperature (T_s) changes by >10%.

4. Take other required readings (Figure 4.2) at least once at each sampling point during each time increment.

5. Record the final dry gas meter readings (Figure 4.2) at the end of each time increment.

6. Repeat steps 3 through 5 for each sampling point.

7. Turn off the pump; remove the probe from the stack; record the final readings after each traverse.

8. Conduct the mandatory posttest leak check (Subsection 4.2.6.3) at the conclusion of the last traverse. Record any leakage rate. Also, leak check the pitot lines (Method 2, Section 3.1.2); the lines must pass this leak check to validate the velocity pressure data.

9 Disconnect the probe, and then cap the nozzle and the end of the probe with polyethylene or equivalent caps.

Periodically during the test, observe the connecting glassware--from the probe, through the filter, to the first impinger--for water condensation. If any is evident, adjust the probe and/or filter heater setting upward until the condensation is eliminated; add ice around the impingers to maintain the silica gel exit temperature at 20°C (68°F).

The manometer level and zero should also be checked periodically during each traverse. Vibrations and temperature fluctuations can cause the manometer zero to shift.

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4.3 Sample Recovery

After the sampling is complete and the data are recorded for all points, begin the cleanup procedure immediately.

1. Allow the probe to cool until it can be safely handled.

2. Wipe off all external particulate matter near the tip of the probe nozzle.

3. Cap the tip loosely to keep from losing part of the sample; capping it tightly while the sampling train is cooling can cause a vacuum to form in the filter holder, and can cause impinger water to be drawn backward.

4. Remove the probe from the sample train before moving the sample train to the cleanup site.

5. Wipe off the silicone grease, and cap the open outlet of the probe; be careful not to lose any condensate that is present.

6. Wipe off the silicone grease from the filter holder inlet, and cap this inlet.

7. Remove the umbilical cord from the last impinger and cap the impinger.

8. Wipe off the silicone grease and then cap off the filter holder outlet and any open impinger inlets or outlets with ground-glass stoppers, plastic caps, or serum caps.

9. Transfer the probe and the filter-impinger assembly to an area that is clean and protected from the wind to minimize the chances of contaminating or losing any of the sample. Inspect the train before and during disassembly, and note any abnormal conditions.

4.3.1 Probe, Filter, and Impinger Catches - This step-by-step procedure should be followed carefully to recover virtually all of the sample collected in the probe, filter, and impinger.

1. Use a graduated cylinder to measure (to the nearest 1 ml) the volume of water in the first three impingers and any condensate in the probe.

2. Record the values on the sample recovery and integrity form Figure 4.3.

Plant Aluminum Smelter Sample date May 7, 1980
Sample location Potts Run number AS-1
Sample recovery person Bill Mitchell Recovery date May 6, 1980

MOISTURE

Impingers		Silica gel		
Final volume (wt)	275 ml (g)	Final wt	210.5 g	g
Initial volume (wt)	200 ml (g)	Initial wt	200.5 g	g
Net volume (wt)	75 ml (g)	Net wt	10 g	g
Total moisture	85 g			

Color of silica gel 1/4 spent
Description of impinger water slightly cloudy

RECOVERED SAMPLE

Water rinse and impinger contents container number 22007 Liquid level marked? yes
Water blank container number 22000 Liquid level marked? yes
Samples stored and locked? yes
Remarks

Date of laboratory custody May 7, 1980
Laboratory personnel taking custody Tom Logan
Remarks

Figure 4.3. Sample recovery and integrity data form.

3. Transfer the impinger water from the graduated cylinder into a polyethylene container.

4. Add the filter to this container using procedures subject to the Administrator's approval.

5. Be sure that dust on the outside of the probe or other component (e.g., the probe nozzle, probe fitting, probe liner, first three impingers, impinger connectors, and filter holder) does not get into the sample while cleaning other sample-exposed surfaces with deionized distilled water; use <500 ml for the entire wash, and add these washings to the washings and the filter in the polyethylene container. To this container add the rinsings from the probe and nozzle, as described in the following procedure.

Probe and Probe Nozzle - Having two people clean the probe should minimize sample losses. Keep brushes clean and protected from contamination at all times.

1. Carefully remove the probe nozzle, use a Nylon bristle brush to loosen particles from the inside surfaces; use a wash bottle to rinse with deionized distilled water until no particles are visible.

2. Brush and rinse the inside parts of the Swagelok fitting with deionized distilled water in a similar way.

3. Rinse the probe liner by squirting deionized distilled water into the upper end of the probe and by tilting and rotating the probe so that all inside surfaces are wetted, and let the water drain from the lower end through a funnel (glass or polyethylene) and into the container.

4. Follow the rinse with a cleaning with a probe brush. Hold the probe in an inclined position, and squirt deionized distilled water into the upper end while pushing the brush with a twisting action through the probe and catching any water and particulate matter that is brushed from the probe into the sample container. Note: Brush three times, or at least six times for stainless steel or other probes which have small crevices that entrap particulate matter.

5. Rinse the brush with deionized distilled water, and quantitatively collect these washings in the sample container.

6. After cleaning the brush, make a final rinse of the probe by repeating steps 1-3.

Impinger and Filter Assembly - To recover fine particulates from these components, brush, wash, and add the rinsings to the container.

1. Rinse the inside surface of each of the first three impingers and their connecting glassware three times using small portions of deionized distilled water for each rinse, and brush each sample-exposed surface with a Nylon bristle brush, to ensure recovery of fine particulate matter. Make a final rinse of each surface and the brush.

2. Be sure that all joints have been wiped clean of silicone grease before brushing and rinsing with deionized distilled water the inside of the filter holder (front-half only if after the third impinger) three or more times as needed; make a final rinse of the brush and filter holder.

Container - The following steps should be followed after all water washings and particulate matter have been collected in the sample container.

1. Tighten the lid so that water will not leak out when it is shipped to the laboratory.

2. Mark the height of the fluid level so that the receivers can determine whether leakage has occurred during transport.

3. Label the container clearly to identify its contents; example sample label is shown in Figure 4.4.

4.3.2 Sample Blank - Prepare a blank by placing an unused filter in a polyethylene container and by adding a volume of water equal to the total volume in the average sample. Process the blank in the same manner as the field samples.

4.3.3 Silica Gel - Note the color of the indicating silica gel to determine whether it has been completely spent, and make a notation of its condition on Figure 4.3.

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Plant *Aluminum Smelter* City *Copper City, Tenn.*

Site *Smelter Outlet* Sample type *Fluoride sample*

Date *4-28-80* Run number *AS-2*

Front rinse ☑ Front filter ☑ Front solution ☐

Back rinse ☑ Back filter ☑ Back solution ☑

Solution _____ Level marked _____

Volume: Initial _____ Final _____

Clean up by _____

Remarks:

Figure 4.4. Example of a sample label.

1. Transfer the silica gel from the fourth impinger to its original container using a funnel and a rubber policeman, and seal the container. It is not necessary to remove the small amount of dust particles that may adhere to the impinger wall; since the weight gain is used for moisture calculations, do not use water or other liquids to transfer the silica gel.

2. Determine the final weight gain to the nearest 0.5 g, if a balance is available.

4.4 Sample Logistics (Data) and Packing of Equipment

Follow the sample recovery procedures for the required number of test runs, and record all data on Figure 4.3. If the probe and the glassware (impinger, filter holder, and connectors) are to be used in the next test, rinse all with distilled deionized water and then acetone. To document the data and to prepare the sample for shipping the following steps are recommended after the test.

1. Check all sample containers for proper labeling (time, date, and location of tests, number of tests, and any other pertinent data). Be sure a blank has been taken and labeled.

2. Duplicate all data recorded during the field test, to avoid costly mistakes, by using either carbon paper or data forms and a field laboratory notebook. Avoid using water soluble pens.

3. Mail one set of data to the base laboratory or give it to another team member or to personnel in the agency; handcarry the other set.

4. Examine all sample and blank containers and sampling equipment for damage and for proper packing for shipment to the base laboratory, and label all shipping containers to prevent loss of samples or equipment.

5. Make quick checks of sampling and sample recovery procedures by using the on-site checklist, Figure 4.5.

Apparatus

Probe nozzle: stainless steel ✓ glass _____
Button-hook ✓ elbow _____ size _____
Clean? _____
Probe liner: borosilicate _____ quartz _____ other _____
Clean? _____
Heating system* _____
Checked? _____
Pitot tube: Type S ✓ other _____
Properly attached to probe?* _____
Modifications _____
Pitot tube coefficient _____
Differential pressure gauge: two inclined manometers _____
other _____ sensitivity 0.01 - 0 to 1
Filter holder: borosilicate glass ✓ glass frit _____
filter support _____ silicone gasket _____ other _____
Clean? ✓
Condenser: number of impingers 4 std.
Clean? ✓
Contents: 1st 100ml H_2O 2nd 100ml H_2O 3rd — 4th Silica Gel
Cooling system ice water
Proper connections? ✓
Modifications N/A

Barometer: mercury _____ aneroid ✓ other _____
Gas density determination: temperature sensor type thermocouple
pressure gauge 20 in. - U-tube manometer
temperature sensor properly attached to probe?* ✓

Procedure

Recent calibration: pitot tubes* ✓ dimensional check
meter box* ✓ thermometers/thermocouples* ✓
Filters checked visually for irregularities?* yes
Filters properly labeled?* yes
Sampling site properly selected? yes
Nozzle size properly selected?* yes
Selection of sampling time? yes
All openings to sampling train plugged to prevent pretest contamination? yes
Impingers properly assembled? yes
Filter properly centered? yes
Pitot tube lines checked for plugging or leaks?* yes

Figure 4.5. On-site measurements.

(continued)

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Figure 4.5 (continued)

Meter box leveled? yes Periodically? yes
Manometers zeroed? yes
ΔH@ from most recent calibration 1.90
Nomograph setup properly? yes
Care taken to avoid scraping nipple or stack wall?* yes
Effective seal around probe when in-stack? yes
Probe moved at proper time? yes
Nozzle and pitot tube parallel to stack wall at all times?* yes
Filter changed during run? no
Any particulate lost? no
Data forms complete and data properly recorded?* yes
Nomograph setting changed when stack temp changed significantly? yes
Velocity pressure and orifice pressure readings recorded accurately?* yes
Sampling performed at a rate <1.0 cfm? yes
Posttest leak check performed?* yes (mandatory)
Leakage rate 0.01 @ in. Hg 15 in.
Orsat analysis yes from stack integrated ✓
Fyrite combustion analysis sample location
Bag system leakchecked?* yes
If data forms cannot be copied, record:
approximate stack temp 317°F volume metered 81 ft³
% isokinetic calculated at end of each run 99%

SAMPLE RECOVERY

Brushes: nylon bristle yes other
Clean? yes
Wash bottles: polyethylene or glass yes
Clean? yes
Storage containers: polyethylene yes other
Clean? yes Leakfree?
Graduated cylinder/or balance: subdivisions ≤2 ml?* yes
other
Balance: type triple beam
Probe allowed to cool sufficiently? yes (25 min.)
Cap placed over nozzle tip to prevent loss of particulate?* yes
During sampling train disassembly, are all openings capped? yes
Clean-up area description: Aluminum Smelter lab
Clean? yes Protected from wind? yes
Filters: paper yes type
Silica gel: type (6 to 16 mesh)? new? yes used?
Color? blue Condition? good
Filter handling: tweezers used? yes
surgical gloves? other
Any fluoride spilled?* no

(continued)

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Figure 4.5 (continued)

Water distilled? yes
Stopcock grease: acetone-insoluble? yes
heat-stable silicone? _____ other _____
Probe handling: distilled water rinse _____
Fluoride recovery from: probe nozzle yes
probe fitting yes probe liner yes
front half of ~~filter holder~~ _____
Blank: filter _____ distilled water _____
Any visible particles on filter holder inside probe?:* no
_____
All jars adequately labeled? yes Sealed tightly? yes
Liquid level marked on jars?* yes
Locked up? _____
Filter blank yes

*Most significant items/parameters to be checked.

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TABLE 4.1. ACTIVITY MATRIX FOR ON-SITE MEASUREMENT CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sampling			
Filter	Centered in holder; no breaks, damage, or contamination during loading	Use tweezers or surgical gloves to load	Discard filter, and reload
Condenser (addition of reagents)	100 ml of distilled water in first two impingers; 200-300 g of silica gel in fourth impinger	Use graduated cylinder to add water, or weigh each impinger and its contents to the nearest 0.5 g	Reassemble system
Assembling sampling train	1. Specifications in Fig 1.1	1. Check specifications before each sampling run	1. Reassemble
	2. Leak rate <4% of sampling volume or 0.00057 m^3/min (0.02 ft^3/min), whichever is less	2. Leak check before sampling by plugging nozzle or inlet to first impinger and pulling a vacuum of 380 mm (15 in.) Hg	2. Correct the leak
Sampling (isokinetically)	1. Within ±10% of isokinetic condition and at a rate of less than 1.0 ft^3/min	1. Calculate for each sample run	1. Repeat the test run
	2. Standard checked for minimum sampling time and volume; sampling time ≥2 min/pt	2. Make a quick calculation before test, and exact calculation after	2. As above

(continued)

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TABLE 4.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
	3. Minimum number of points specified by Method 1	3. Check before the first test run by measuring duct and using Method 1	3. Repeat the procedure to comply with specifications of Method 1
	4. Leakage rate ≤ 0.00057 m^3/min (0.02 ft^3/min) or 4% of the average sampling volume, whichever is less	4. Leak check after each test run or before equipment replacement during test at the maximum vacuum during the test (mandatory)	4. Correct the sample volume or repeat the sampling
Sample recovery	Noncontaminated sample	Transfer sample to labeled polyethylene container after each test run; mark level of solution in the container	Repeat the sampling
Sample logistics, data collection, and packing of equipment	1. All data recorded correctly	1. After each test and before packing	1. Complete the data
	2. All equipment examined for damage and labeled for shipment	2. As above	2. Repeat the sampling if damage occurred during the test
	3. All sample containers and blanks properly labeled and packaged	3. Visually check after each sampling	3. Correct when possible

5.0 POSTSAMPLING OPERATIONS

The postsampling operations include checks on the apparatus used in the field during sampling to measure volumes, temperatures, and pressures, and analyses of the samples collected in the field and forwarded to the base laboratory. Table 5.1 at the end of this section summarizes the quality assurance activities for the postsampling operations.

5.1 Apparatus Checks

Posttest checks will have to be made on most of the sampling apparatus. These checks will include three calibration runs at a single orifice meter setting; cleaning; and/or routine maintenance. Cleaning and maintenance are discussed in Section 3.4.7 and in APTD-0576.[4] Figure 5.1 should be used to record data from the posttest checks.

5.1.1 Metering System - The metering system has two components that must be checked--the dry gas meter and the dry gas meter thermometer(s).

The dry gas meter thermometer(s) should be compared with an ASTM mercury-in-glass thermometer at room temperature. If the two readings agree within ±6°C (10.8°F), the meter reading is acceptable; if not, the meter thermometer must be recalibrated (Subsection 2.2, Section 3.4.2) after the posttest check of the dry gas meter. Use the higher meter thermometer reading (field or recalibration value) in the calculations. If the field readings are higher than the recalibration reading, no temperature correction is necessary; if the recalibration value is higher, add the difference in the two readings to the average dry gas meter temperature reading.

The posttest check of the dry gas meter is described in Section 3.4.2. Any leaks in the metering system should have been corrected before the posttest check. If the dry gas meter calibration factor (Y) deviates by $\leq 5\%$ from the initial calibration factor, the meter volumes obtained during the test series are

Plant Aluminum Smelter Calibrated by T. Logan

Meter box number FB-1 Date 4-31-80

Dry Gas Meter

Pretest calibration factor, Y 0.986 (within ±2%)
Posttest check, Y* 0.987 (within ±5% of pretest)
Recalibration required? _____ yes ✓ no
If yes, recalibration factor, Y _____ (within ±2%)
Lower calibration factor, Y 0.986 for calculations (pretest or posttest)

Dry Gas Meter Thermometers

Was a pretest temperature correction used? _____ yes ✓ no
If yes, temperature correction _____ (within ±3°C (5.4°F) over range)
Posttest comparison with mercury-in-glass thermometer?* (within ±6°C (10.8°F) at ambient temperature)
Recalibration required? _____ yes ✓ no
Recalibration temperature correction? _____ (within ±3°C (5.4°F) over range)*
If yes, no correction necessary for calculations if meter thermometer temperature is higher; if calibration temperature is higher, add correction to average meter temperature for calculations

Stack Temperature Sensor

Was a pretest temperature correction used? _____ yes ✓ no
If yes, temperature correction _____°C (°F) (within ±1.5% of readings in K (°R) over range)
Average stack temperature of compliance test, T_s 780 K (°R)
Temperature of reference thermometer or solution for recalibration 528 K (°R)* (within ±10% of T_s)
Temperature of stack thermometer for recalibration 528 K (°R)
Difference between reference and stack thermometer temperatures, ΔT_s 0 K (°R)
Do values agree within ±1.5%?* ✓ yes _____ no
If yes, no correction necessary for calculations
If no, calculations must be done twice--once with the recorded values and once with the average stack temperature corrected to correspond to the reference temperature differential (ΔT_s), both final result values must be reported since there is no way to determine which is correct

Figure 5.1 Posttest calibration checks.

(continued)

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Figure 5.1 (continued)

Barometer

Was the pretest field barometer reading correct? ✓ yes ____ no
Posttest comparison?* 29.55 mm (in.) Hg (±2.5 mm (0.1 in.) Hg)
Was calibration required? _____ yes ✓ no
If yes, no correction necessary for calculations when the field barometer has a lower reading; if the mercury-in-glass reading is lower, subtract the difference from the field data readings for the calculation

*Most significant items/parameters to be checked.

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acceptable; if Y deviates by >5%, recalibrate the metering system (Section 3.9.2). In the calculations, use the calibration factor (initial or recalibration) that yields the lower gas volume for each test run.

5.1.2 Stack Temperature Sensors - The stack temperature sensors (thermocouples and thermometers) should be compared with a reference thermometer or with a thermocouple if the temperature is >405°C (761°F).

For thermocouple(s), compare the thermocouple and the reference thermometer readings at ambient temperature. If the values agree within ±1.5% of the absolute temperature, the calibration is valid; if not, recalibrate the thermocouple (Section 3.9.2) to determine the difference (ΔT_s) in the absolute average stack temperature (T_s). Note: This comparison may be done in the field immediately following each test.

For thermometers, compare the stack thermometer with the reference thermometer at ambient temperatures if T_s is <100°C (212°F); compare them in boiling water if T_s is between 100°C and 200°C (212°F to 360°F); compare them in a liquid with a boiling point >200°C (360°F) if T_s is between 200°C and 405°C (360° and 751°F). Compare the stack thermometer with a thermocouple at a temperature that is within ±10% of T_s if T_s is >405°C (761°F). If the absolute temperatures agree within ±1.5% the calibration is valid; if not, determine the error ΔT_s to correct the average stack temperature.

5.1.3 Barometer - The field barometer should be compared to the mercury-in-glass barometer. If the readings agree within ±5 mm (0.2 in.) Hg, the field readings are acceptable; if not, use the lower value for the calculations. If the field readings are lower than the mercury-in-glass readings, the field data are acceptable; if not, use the difference in the two readings (the adjusted barometric value) in the calculations.

5.2 Base Laboratory Analysis

All fluoride samples should be checked by the analyst upon receipt in the base laboratory for identification and sample

integrity. Any losses should be noted on the analytical data form (Figure 5.2). Either void the sample or correct the data using a technique approved by the administrator. If a noticeable amount of sample has been lost by leakage, the following procedure may be used to correct the volume.

1. Mark the new liquid level on the sample container.
2. Treat the sample as described in Subsection 5.2.3 and note the final dilution volume (V_{soln}).
3. Add water up to the initial mark on the container, transfer the water to a graduated cylinder and record the initial sample volume (V_{solni}) in milliliters.
4. Add water to the new mark on the container. Transfer the water to a graduated cylinder, and record the final volume (V_{solnf}) in millileters.
5. Correct the volume by using the following equation:

$$V_{soln'} = V_{soln} \frac{V_{solni}}{V_{solnf}}$$

where

$V_{soln'}$ = sample volume to be used in the calculations, ml;
V_{soln} = total volume of solution in which fluoride is contained, ml;
V_{solni} = initial volume added to the container in the field, ml;
V_{solnf} = final volume removed from the container in the base laboratory, ml.

6. Both the corrected and uncorrected values should be submitted in the test report to the agency.

This analytical method is based on measurement of the activity or concentrations of fluoride ions (F^-) in aqueous samples by use of an appropriate calibration curve. Fluoride activity depends, however, upon the total ionic strength of the sample and the electrode does not respond to fluorides which are bound or complexed. This difficulty is largely overcome by adding a buffer of high total ionic strength and by requiring preliminary distillation to eliminate interferent ions. The sample response

Plant Acme Ferterlizer Date May 15, 1980

Sample location Super Phos outlet Analyst Bill Mitchell

Samples identifiable ✓ yes ____ no All liquid levels at marks ✓ yes ____ no

Ambient temperature 20.5°C Constant temperature bath used ____ yes ✓ no

Temperature of calibration standards 20.5°C Date calibration standards prepared May 15, 1980

Temperature of samples 20.5°C

Sample number	Sample identification number	Total volume of sample, (V_t), ml	Aliquot total sample added to still (A_t), ml	Diluted volume of distillate collected (V_d), ml	Electrode potential, mV	Concentration of fluoride from calibration curve, (M), molarity	Total weight of fluoride in sample (F_t), mg
AF-1	AF-110	1000	100	250	273	0.000074	3.515
AF-2	AF-120	1000	100	250	263	0.00012	5.699
AF-3	AF-130	1000	100	250	280	0.000046	2.185
AF-4	AF-140	1000	100	250	297	0.000012	0.570

Total weight of fluoride in sample (F_t)

$$F_t = 19\frac{V_t}{A_t}(V_d)\,(M)$$

Signature of analyst Bill Mitchell Remarks: ____

Signature of reviewer or supervisor R Midgett

Figure 5.2 Fluoride analytical data sheet.

to the ion-specific electrode is also monitored by a standard reference electrode and a modern pH meter that has an expanded millivolt scale.

Procedures are detailed herein for preparing reagents, blanks, control samples, distillation aliquots, reference and working standards (including serial dilutions), and an expanded calibration curve and procedure for treating, separating, and measuring the fluoride in samples.

5.2.1 Reagents - The following reagents are needed for the analyses of fluoride samples.

1. Calcium oxide (CaO) - ACS reagent grade powder or ACS certified grade containing $\leq$0.005% fluoride.

2. Phenolphthalein indicator - 0.1% in 1:1 ethanol-water mixture (v/v).

3. Sodium hydroxide (NaOH) - Pellets, ACS reagent grade or the equivalent.

4. Sulfuric acid (H_2SO_4) - Concentrated, ACS reagent grade or the equivalent.

5. Filters - Whatman No. 541 or the equivalent.

6. Water - Deionized distilled to conform to ASTM specification D1193-74, Type 3. The analyst may omit the MnO_4 test for oxidizable organic matter if high concentrations of organic matter are not expected.

7. Total ionic strength adjustment buffer (TISAB) - Add approximately 500 ml of distilled water to a 1-ℓ beaker; to this add 57 ml of concentrated glacial acetic acid, 58 g of sodium chloride and 4 g of CDTA (cyclohexylenedinitrilotetraacetic acid); and stir to dissolve. Place the beaker in a water bath until it has cooled, and then slowly add about 150 ml of 5M NaOH, while measuring the pH continuously with a calibrated pH electrode and a reference electrode pair, until the pH is 5.3. Cool to room temperature, pour into a 1-ℓ volumetric flask and dilute to the 1-ℓ mark with distilled water.

8. Hydrochloric acid (HCl) - Concentrated ACS reagent grade or the equivalent.

9. Sodium fluoride (NaF) standard (0.1 M) - Dissolve 4.2 g ± 0.002 g ACS reagent grade NaF, which has been dried for a minimum of 2 h at 110°C (230°F) and stored in a desiccator, in deionized distilled water, and dilute to 1-ℓ with deionized distilled water; this solution contains 0.1 M of Fluoride.

5.2.2 Blanks - The three blanks needed for the analysis are a filter blank to ensure that the quality of the filter is acceptable, a distillation blank to avoid cross contamination, and a sample blank to analyze with the samples to verify the purity of the reagents used in sampling and analyses.

1. Filter blanks - Determine the fluoride content of the sampling filters upon receipt of each new lot and at least once for each test series. Randomly select three filters from each lot.

1. Add each filter to 500 ml of distilled water.
2. Treat the filters exactly like a sample (Subsection 5.2.3).
3. Use a 200 ml aliquot for distillation. Initially, the filter blank must be <0.015 mg F/cm^2; if not, reject this batch and obtain a new supply of filters.

2. Distillation blank - Check the condition of the acid in the distillation flask (Subsection 5.2.5) for cross-contamination after every 10th sample by adding 220 ml of distilled water to the still pot and then proceed with the analysis. If detectable amounts of fluoride (>0.00001 M) are found in the blank, replace the acid in the distillation flask.

3. Sample blank - Prepare the sample blanks in the field at the same time and with the same reagents used for sample recovery.

1. Add an unused filter from the same batch used in sampling to a volume of distilled water equal to the average amount used to recover the samples.

2. Treat the sample blank in the same manner as the samples are treated (Subsection 5.2.3). Analyze the sample blanks with the samples.

5.2.3 Sample Preparation - Use the following procedure to prepare samples for distillation. Distillation is not required if it can be shown to the satisfaction of the Administrator that fluoride results are unaffected by the alternate analytical procedure (e.g., ash and fusion of particulate matter with subsequent ion selective electrode analysis, or direct electrode analysis of gases trapped in impingers).

1. Filter the contents of the sample container (including the sample filter) through a Whatman No. 541 filter or the equivalent into a 1500-ml beaker; if the filtrate volume is $\geq$900 ml, add NaOH to make the filtrate basic to phenolphthalein, and then evaporate to <900 ml.

2. Place the Whatman No. 541 filter containing the insolubles (including the sample filter) in a nickle crucible, add a few milliliters of water; and macerate the filter with a glass rod.

3. Add 100 mg or sufficient quantity of CaO to the nickel crucible to make the slurry basic; mix thoroughly; and add a couple drops of phenolphthalein indicator, which turns pink in a basic medium. Note: If the slurry does not remain basic (pink) during the evaporation of the water, fluoride will be lost; if the slurry becomes colorless, it is acidic so add CaO until the pink returns.

4. Place the crucible either in a hood area under infrared lamps or on a hot plate at low heat (approximately 50-60°C) (122-140°F), and evaporate the water completely; then place the crucible on a hot plate under a hood and slowly increase the temperature for several hours or until the filter is charred.

5. Place the crucible in a cold muffle furnace and gradually (to prevent smoking) increase the temperature to 600°C (1112°F); maintain the temperature until the crucible contents are reduced to an ash containing no organic material; and remove the crucible from the furnace to cool.

6. Add approximately 4 g of crushed NaOH pellets to the crucible, and mix; return the crucible to the furnace, and fuse the sample for 10 min at 600°C (1112°F); and then remove the sample from the furnace, and cool it to ambient temperature.

7. Use several rinsings of warm distilled water to transfer the contents of the crucible to the beaker containing the filtrate (step 1) and finally, rinse the crucible with two 20-ml portions of 25% (v/v) H_2SO_4, and carefully add the rinses to the beaker.

8. Mix well, and transfer the beaker contents to a 1-ℓ volumetric flask. Record this volume as V_t on the data form (Figure 5.2). Dilute to volume with distilled water, and mix thoroughly; and allow any undissolved solids to settle.

9. Weigh the spent silica gel and report the weight to the nearest 0.5 g on the sample integrity and recovery form.

5.2.4 Acid-water Ratio - The acid-water ratio in the distillation flask should be adjusted by following this procedure. Use a protective shield when carrying out the procedure.

1. Place 400 ml of distilled water in the 1-ℓ distillation flask, and add 200 ml of concentrated H_2SO_4. Slowly add the H_2SO_4, while constantly swirling the flask.

2. Add soft glass beads and several small pieces of broken glass tubing, and assemble the apparatus as shown in Figure 1.3.

3. Heat the flask until it reaches a temperature of 175°C (347°F), and discard the distillate, and hold the flask for fluoride separation by distillation.

5.2.5 Fluoride Separation (Distillation) - Fluoride in the acid-water adjusted flask can be separated from other constituents in the aqueous sample by distilling fluosilicic (or hydrofluoric) acid from a solution of the sample in an acid with a higher boiling point. Samples with low concentrations of fluoride (e.g., samples from an inlet and outlet of a scrubber) should be distilled first to eliminate contamination by carryover of fluoride from the previous sample. If fluoride distillation in the milligram range is to be followed by distillation in the fractional milligram range, add 200 ml of deionized distilled

water and redistill similar to the acid adjustment procedure, Subsection 5.2.4, to remove residual fluoride from the distillation system.

1. Cool the contents of the distillation flask (acid-water adjusted) to <80°C (176°F).

2. Pipette an aliquot of sample containing <10.0 mg F into the distilling flask, and add distilled water to make 220 ml. The aliquot size (A_t) should be entered on the data form (Figure 5.2). Note: For an estimate of the aliquot size that contains ≤10 mg F, see Subsection 5.2.6.

3. Place a 250-ml volumetric flask at the condenser exit; heat the distillation flask as rapidly as possible with a burner, while moving the flame up and down the sides of the flask to prevent bumping; conduct the distillation as rapidly as possible (≤15 min). Slow distillations have been found to give low fluoride recovery. Collect all distillate up to 175°C (347°F). Caution: Heating >175°C (347°F) will cause H_2SO_4 to distill over. Note: The H_2SO_4 in the distilling flask can be reused until carryover of interferent or until poor fluoride recovery is shown in the distillation blanks and the control samples.

4. Before distilling samples and after every 10th sample, distill a control sample to check the analytical procedures and interferences (Subsection 5.2.6).

5.2.6 Control Sample - A control sample should be used to verify the calibration curve and the analytical procedures before and during the analysis of the field samples. Use the following procedures.

1. The 0.05M NaF control sample stock solution - Add 2.10 g of reagent grade anhydrous NaF to a 1-ℓ volumetric flask; add enough distilled water to dissolve; and dilute to 1-ℓ with distilled water.

2. The 0.005M NaF working solution - Pipette 100 ml of the 0.05M NaF stock solution into a 1-ℓ volumetric flask, and dilute to the mark with distilled water to get the 0.005 M NaF working solution. Note: The control should be within 0.004M and 0.006M NaF; if not, take corrective action until these limits are met.

3. Analyze the working solution in the same manner as the samples are analyzed (Subsections 5.2.5, 5.2.9, and 5.2.10).

5.2.7 Distillation Aliquot - The sample volume for distillation should contain <10 mg F. Use the following procedure to estimate the aliquot size.

1. Pipette a 25-ml aliquot of sample into a polyethylene beaker.

2. Add an equal volume of TISAB buffer, and mix well.

3. Adjust the pH meter, and read the millivolts for the nondistilled sample and the calibration standard solutions (Subsection 5.2.8).

4. Determine the molarity of the nondistilled sample from the calibration curve, and determine the size of the aliquot for distillation by substituting the molarity (M) of the nondistilled sample in the following equation:

$$\text{aliquot for distillation (ml)} = \frac{200 \text{ ml} \times 0.002\text{M}}{\text{estimated F molarity (M)}}$$

The aliquot size is only an approximation since the interferring ions have not been removed by distillation. If the estimate is >220 ml, use 220 ml; if it is <220 ml, add distilled water to make the total volume 220 ml; if required, dilute the sample to get a minimum 1-ml aliquot.

5.2.8 Calibration Standards - Use the 0.1M NaF reference standard (Subsection 5.2.1) in the following procedure for preparing serial dilutions.

1. Pipette 10 ml of 0.1M NaF into a 100-ml volumetric flask, and dilute to volume with distilled water to get a 0.01M standard.

2. Pipette 10 ml of the 0.01M standard solution to make a 0.001M solution in the same manner, and so on to make 0.0001M and 0.00001M solutions.

3. Pipette 50 ml of each of the standard solutions into separate polyethylene beakers, add 50 ml of TISAB buffer to each, and mix well (50 ml of 0.01M diluted with 50 ml of TISAB is still referred to as 0.01M). Prepare fresh 0.01M NaF standards daily.

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A detailed explanation is in Section 3.9.2, Subsection 2.8 of this method along with calibration curves (Figures 2.8 and 2.9 of Section 3.9.2).

5.2.9 Sample Treatment - To treat the distilled fluoride in the volumetric flask (from Subsection 5.2.5, step 3), follow this procedure.

1. Dilute with distilled water to the 250-ml mark on the volumetric flask at the condenser exit, and mix thoroughly.

2. Pipette 25-ml of the sample into a 50-ml volumetric flask, dilute to the mark with TISAB buffer solution, and mix well.

3. Bring the calibration standards and the samples to the same temperature; if the ambient laboratory temperature fluctuates more than ±2°C (4°F), condition the samples and standards in a constant temperature bath.

5.2.10 Concentration Measurement - Some electrodes yield positive (direct F^- concentrations) and some yield negative (indirect) values; if positive, recalibrate the electrode by using a manufacturer-recommended standard, by adjusting the calibration control (if needed) to the correct value, and by verifying the calibration after measuring each standard and sample to prepare the calibration curve.

Several precautions are needed before beginning the procedure.

1. Keep the pH meter on standby, and rinse between measurements.

2. Keep the electrodes in the storage solution to prevent overdrying if long periods of time are expected between uses.

3. Do not allow the electrode to touch the side of the beaker during or between measurements.

4. Use of a stirrer will minimize electrode response time, but stirring a solution before immersing the electrode may entrap air around the crystal and cause needle fluctuations and erroneous readings.

Use an ion-specific electrode in the following procedure for measuring the F^- concentration.

1. Transfer each standard and each sample to a series of 150-ml polyethylene beakers, and arrange each series so that the lowest concentration will be read first to avoid carryovers.

2. Rotate the switch of the pH meter to standby, and allow a 30-min warm-up period.

3. Raise the electrode from the storage solution in the beaker, and rinse either the electrode thoroughly with distilled water or soak the fluoride-sensing electrodes in distilled water for 30 s before removing and blotting dry. Note: This step should be done between each measurement.

4. Turn the adjustment knob to calibrate; immerse the electrode in the NaF standard of lowest concentration.

5. Rotate the switch to millivolts (mV), and turn the adjustment knob to calibrate, read the millivolts of the known buffer solution from the meter, and record the value on Figure 5.2. Rotate the selector knob to standby.

6. Raise the electrodes carefully from the buffer solution, and rinse thoroughly (step 3).

7. Immerse the electrodes carefully into a beaker of standard solution, and set the beaker on a magnetic stirrer. Note: If stirrer generates enough heat to change solution temperature, place insulating material (e.g., cork) between the stirrer and the beaker.

8. Rotate the selector knob to mV, read the mV from the meter, and record the value on Figure 5.2; allow the electrodes to remain in the solution at least 3 min, and rotate the knob to standby; take a final reading.

9. Repeat the above steps until all samples have been read. Switch to standby, and then rinse and store the electrodes in distilled water.

5.2.11 Expanded Calibration Curve - Use the following procedure to construct an expanded calibration curve for analyzing samples in the lower concentration range of <2 mg F/250 ml distillate and

for more accurate determinations of concentrations since samples in the range are <0.001M NaF. Use this procedure to prepare calibration standards, using the 0.1M NaF standard for serial dilutions (Subsection 5.2.1).

1. Pipette 10 ml of the 0.1M NaF into a 1-ℓ volumetric flask, and dilute to volume using distilled water to get a 0.001M standard.

2. Pipette 10 ml of the 0.001M standard, and dilute it to 100 ml to make a 0.0001M standard.

3. Pipette 10 ml of the 0.0001M standard, and dilute to 100 ml to make a 0.00001M standard solution.

4. Pipette 50 ml of the 0.001M standard into a 100-ml volumetric flask, and dilute to volume with distilled water to get a 0.0005M standard.

5. Pipette 10 ml of the 0.0005M standard into a 100-ml volumetric flask, and dilute to volume to make a 0.00005M standard.

6. Calibrate the electrode, and construct a calibration curve (Subsection 5.2.8). Note: As shown in Figure 5.3, the nominal concentrations of 0.00001M, 0.00005M, 0.0001M, 0.0005M, and 0.001M NaF should be plotted on the log axis and the electrode potentials (mV) are plotted on a linear scale.

Control samples are needed to verify the expanded calibration curve and the analytical procedure before and during the analysis of the field samples. Use the 0.005M control sample (Subsection 5.2.1) for the serial dilutions.

1. Pipette 5 ml of the 0.005M control sample into a 100-ml volumetric flask, and dilute to volume to get a 0.00025M control.

2. Pipette 50 ml of the 0.00025M control into a polyethylene beaker, add 50 ml of TISAB buffer, mix well, and use to validate the calibration curve and to provide hourly checks on the daily calibration.

3. Analyze the control sample (Subsection 5.2.5), and record the data on the laboratory worksheet (Figure 5.4).

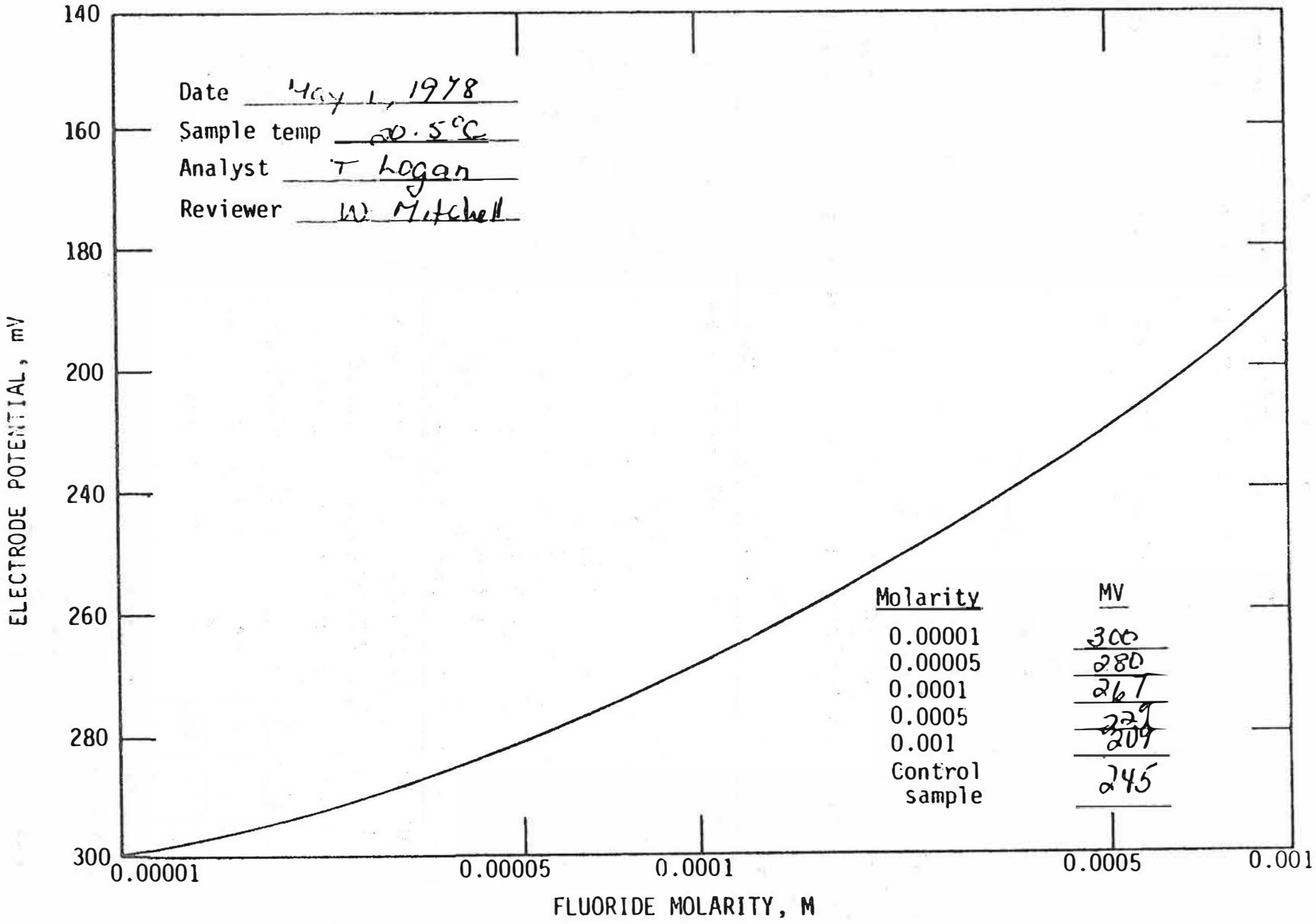

Figure 5.3. .Expanded fluoride calibration curve.

LABORATORY WORKSHEET

Date May 1, 1978

Date standards prepared May 1, 1978

Temperature of standards 20.5°C Electrode number 001

Standard number	Concentration, M	Electrode potential, mV
1	0.001	209
2	0.0005	229
3	0.0001	267
4	0.00005	280
5	0.00001	300
Control sample	0.00029	245

Note: The control sample, from the calibration curve, must be between 0.0002M and 0.0003M.

Signature of analyst Tom Logan

Signature of reviewer William Mitchell

Figure 5.4. Expanded calibration curve data form.

Table 5.1 ACTIVITY MATRIX FOR POSTSAMPLING OPERATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Sampling Apparatus			
Dry gas meter	±5% of calibration factor	Make three runs at a single intermediate orifice setting at highest volume of test (Sec 3.9.2)	Recalibrate; use factor that gives lower gas volume
Meter thermometers	±6°C (10.8°F) ambient temperature	Compare with ASTM mercury-in-glass thermometer after each test	Recalibrate; use higher temperature for calculations
Barometer	±5 mm (0.2 in.) at ambient pressure	Compare with mercury-in-glass barometer after each test	Recalibrate; use lower barometric value for calculations
Stack temperature sensors	±1.5% of the reference thermometer or thermocouple	Compare with reference temperature after each run	Recalibrate; calculate with and without temperature corrections
Base Laboratory Analysis			
Reagents	Prepare according to Subsec 5.2	Prepare a calibration curve when preparing new reagent	Prepare new solutions and calibration curves

(continued)

Table 5.1 (continued)

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Control sample	±2% when run with fluoride standards and ±10% when distilled and run with field samples	Prepare new controls before and during analysis of field samples	Prepare new solution and calibration curve, and/or change distillate solution

6.0 CALCULATIONS

Calculation errors due to procedural or mathematical mistakes can be a large part of total system error. Thus, each set of calculations should be repeated or spotchecked, preferably by a team member other than the one that performed the original calculations. If a difference greater than a typical roundoff error is detected, the calculations should be checked step-by-step until the source of error is found and corrected.

A computer program is advantageous in reducing calculation errors. If a standardized computer program is used, the original data entry should be checked and if differences are observed, a new computer run should be made.

Table 6.1 at the end of this section summarizes the quality assurance activities for calculations. Retain at least one significant digit beyond that of the acquired data. Roundoff after the final calculations for each run or sample to two significant digits, in accordance with ASTM 380-76. Record the results on Figure 6.1A or 6.1B.

6.1 Nomenclature

Terms used in Equations 6-1 through 6-7 are defined here for use in the Subsections that follow.

A_n = Area of nozzle, cross-sectional, m^2 (ft^2)

A_t = Aliquot of total sample added to still, ml

B_{ws} = Water vapor in the gas stream, proportion by volume

C_s = Concentration of fluoride in stack gas corrected to standard conditions of 20°C, 760 mm Hg (68°F, 29.92 in. Hg) on dry basis, mg/m^3 (lb/ft^3)

F_t = Total weight of fluoride in sample, mg (lb)

F_{tb} = Total weight of fluoride in sample blank, mg (lb)

I = Percent of isokinetic sampling, %

SAMPLE VOLUME (ENGLISH UNITS)

$V_m = 48.647$ ft^3, $T_m = 532.6$ °R, $P_{bar} = 29.23$ in. Hg

$Y = 0.996$, $\Delta H = 1.41$ in. H_2O

$$V_{m(std)} = 17.64\ V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m} = 47.074 \text{ ft}^3$$

Equation 6-1

FLUORIDE CONTENT IN SAMPLE

$V_t = 1000.0$ ml, $A_t = 100.0$ ml, $V_d = 250.0$ ml

$M = 0.00005$ M

$$F_t = 4.19 \times 10^{-5} \frac{V_t V_d M}{A_t} = 4.190 \times 10^{-6} \text{ lb}$$

Equation 6-4

CONCENTRATION OF FLUORIDE (ENGLIGH UNITS)

$V_{m(std)} = 47.074$ ft^3, $F_t = 4.190 \times 10^{-6}$ lb

$F_{tb} = 0.000 \times 10^{-6}$ lb

$$C_s = 35.31 \frac{F_t - F_{tb}}{V_{m(std)}} = 3.14 \times 10^{-6} \text{ lb/dscf}$$

Equation 6-5

All other equations same as Methods 2 and 5.

Figure 6.1A. Fluoride calculation form (English units).

SAMPLE VOLUME (METRIC UNITS)

V_m = 1.378 m^3, T_m = 310.6 °K, P_{bar} = 742.0 mm Hg

Y = 0.996, ΔH = 36.0 mm H_2O

$$V_{m(std)} = 0.3858\ V_m\ Y\ \frac{P_{bar} + (\Delta H/13.6)}{T_m} = 1.269\ m^3$$ Equation 6-1

FLUORIDE CONTENT IN SAMPLE

V_t = 1000.0 ml, A_t = 100.0 ml, V_d = 250.0 ml

M = 0.00005 M

$$F_t = 19\ \frac{V_t\ V_d}{A_t}\ M = 2.375\ mg$$ Equation 6-4

CONCENTRATION OF FLUORIDE (METRIC UNITS)

$V_{m(std)}$ = 1.269 dscm, F_t = 2.375, F_{tb} = 0.000 mg

$$C_s = \frac{F_t - F_{tb}}{V_{m(std)}} = 1.872\ mg/dscm$$ Equation 6-5

All other equations same as Methods 2 and 5.

Figure 6.1B. Fluoride calculation form (metric units).

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M = Concentration of fluoride from calibration curve, M

M_w = Molecular weight of water, 18.0 g/g-mole (18.0 lb/lb-mole)

P_{bar} = Barometric pressure at sampling site, mm (in.) Hg

P_s = Absolute stack gas pressure at sampling site, mm (in.) Hg

P_{std} = Standard absolute pressure, 760 mm (29.92 in.) Hg

R = Ideal gas constant, 0.066236 mm Hg-m^3/K-g-mole (21.83 in. Hg-ft^3/°R-lb-mole)

T_m = Absolute average dry gas meter temperature, K (°R)

T_s = Absolute average stack gas temperature, K (°R)

T_{std} = Standard absolute temperature, 293K (528°R)

V_a = Volume of distillate collected, ml

V_{ic} = Total volume of liquid collected in impingers and silica gel, ml. (Volume of water in silica gel = grams of silica gel weight increase × 1 ml/g; volume of liquid collected in impinger = final volume - initial volume)

V_m = Volume of gas sample measured by dry gas meter, dcm (dcf)

$V_{m(std)}$ = Volume of gas sample measured by dry gas meter corrected to standard conditions, dscm (dscf)

V_s = Stack gas velocity calculated by Method 2 (Equation 2-7) using data from Method 13, m/s (ft/s)

V_t = Total volume of sample, ml

$V_{w(std)}$ = Volume of water vapor in gas sample corrected to standard conditions, scm (scf)

Y = Dry gas meter calibration factor

ΔH = Average pressure differential across the orifice meter, mm (in.) H_2O

ρ_w = Density of water, 1 g/ml (0.00220 lb/ml)

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θ = Total sampling time, min

13.6 = Specific gravity of mercury

60 = s/min

100 = Factor for converting to percent, %

6.2 Dry Gas Volume, Corrected to Standard Conditions

Correct the sample volume measured by the dry gas meter (V_m) to standard conditions (20°C and 760 mm Hg or 68°F and 29.92 in. Hg) by using Equation 6-1. The absolute dry gas meter temperature (T_m) and orifice pressure drop (ΔH) are obtained by averaging the field data.

$$V_{m(std)} = V_m Y \frac{T_{std}}{T_m} \frac{P_{bar} + (\Delta H/13.6)}{P_{std}}$$

$$= K_1 V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m} \qquad \text{Equation 6-1.}$$

where

K_1 = 0.3858 K/mm Hg for metric units, and
= 17.64 °R/in. Hg for English units.

Note: If the leak rate observed during any mandatory leak check exceeds the acceptable rate, the tester shall either correct the value of V_m in Equation 6-1 (Subsection 3.2.6, Method 3), or invalidate the test runs.

6.3 Volume of Water Vapor

$$V_{w(std)} = V_{ic} \frac{\rho_w}{M_w} \frac{R\, T_{std}}{P_{std}} = K\, V_{ic} \qquad \text{Equation 6-2}$$

where

K = 0.00133 m^3/ml for metric units, and
= 0.04707 ft^3/ml for English units.

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6.4 Moisture Content of Stack Gas

$$B_{ws} = \frac{V_{w(std)}}{V_{m(std)} + V_{w(std)}}. \qquad \text{Equation 6-3}$$

Note: If liquid droplets are in the gas stream, assume the stream to be saturated; use a psychrometric chart to obtain estimate of the moisture percentage.

6.5 Fluoride Content in Sample (Concentration)

$$F_t = K \frac{V_t}{A_t} (V_d \times M) \qquad \text{Equation 6-4}$$

where

K = 19 mg/mmole for metric units,

K = 4.19×10^5 lbs for English units.

6.6 Concentration of Fluoride in Stack Gas

$$C_s = K \frac{F_t - F_{tb}}{V_{m(std)}} \qquad \text{Equation 6-5}$$

K = 1.00 m^3/m^3 for metric units

K = 35.31 ft^3/m^3 for English units.

6.7 Isokinetic Variation (I)

The isokinetic variation (I) can be calculated from either raw data or intermediate values using the following equations.

6.7.1 Calculation of I from Raw Data

$$I = \frac{100 \times T_s \left[K V_{ic} + (Y V_m/T_m) \left(P_{bar} + \Delta H/13.6\right)\right]}{60\theta v_s P_s A_n} \qquad \text{Equation 6-6}$$

where

K = 0.003454 mm Hg-m^3ml-K for metric units, and

= 0.002669 in. Hg-ft^3/ml-°R for English units.

6.7.2 Calculations of I from Intermediate Values

$$I = \frac{100 \times T_s V_{m(std)} P_{std}}{T_{std} v_s \theta P_s A_n 60 (1-B_{ws})} \qquad \text{Equation 6-7}$$

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$$= K \frac{T_s \, V_{m(std)}}{v_s P_s A_n \, \theta \, (1-B_{ws})}$$

where

K = 4.320 for metric units, and

= 0.09450 for English units.

6.7 Acceptable Results

If 90% $\leq$ I $\leq$ 110%, the results are acceptable. If the results are low in comparison to the standards and if I is beyond the acceptable range, the administrator may opt to accept the results; if not, reject the results and repeat the test.

Table 6.1 ACTIVITY MATRIX FOR CALCULATIONS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are mot met
Analysis data form	All data and calculations given	Visual check	Complete the missing data values
Calculations	Difference between check and original calculations within roundoff error; one decimal figure retained beyond that of acquired data	Repeat all calculations starting with raw data for hand calculations; check all raw data input for computer calculations and hand calculate one sample per test	Indicate errors on analysis data form
Isokinetic variation	90% $\leq$ I $\leq$ 110%; see Eqs 6-6 and 6-7 for calculation of I	Calculate I for each traverse point	Repeat test; adjust flow rates to maintain I within ±10% variation

7.0 MAINTENANCE

Normal use of emission testing equipment subjects it to corrosive gases, temperature extremes, vibrations, and shocks. Keeping the equipment in good operating order over an extended time requires routine maintenance and knowledge of the equipment. Maintenance of the entire sampling train should be performed either quarterly or after 1000 ft^3 of operation, whichever occurs sooner. Maintenance activities are summarized in Table 7.1 at the end of this section; the following routine checks are recommended, but not required, to increase reliabilty.

7.1 Pump

Several types of pumps are used in commercial sampling trains; two of the most common are the fiber vane pump with in-line oiler and the diaphragm pump. The fiber vane pump needs a periodic check of the oil and the oiler jar. Used oil (usually nondetergent or machine weight) should be about the same translucent color as unused or spare oil. When the pump starts to run erratically or when the head is removed each year, the fiber vanes should be changed.

The diaphragm pump requires little maintenance. If the diaphragm pump leaks or runs erratically, it is normally due to a bad diaphragm or to malfunctions in the valves; these parts are easily replaced, and should be cleaned annually by complete disassembly of the train.

7.2 Dry Gas Meter

The dry gas meter should be checked for excess oil and component corrosion by removing the top plate every 3 mo. The meter should be disassembled, and all components cleaned and checked more often if the dials show erratic rotation or if the meter will not calibrate properly.

7.3 Inclined Manometer

The fluid should be changed when it is discolored, or when it contains visible matter, and when it is disassembled yearly. No other routine maintenance is required since the inclined manometer is checked during the leak checks of both the pitot tube and the entire meter box.

7.4 Sampling Train

All other sample train components should be visually checked every 3 mo, and they should be completely disassembled and cleaned or replaced yearly. Many of the parts, such as quick disconnects, should be replaced when damaged rather than after they are periodically checked. Normally, the best maintenance procedure is to replace the entire unit--for example, a meter box, sample box, or umbilical cord.

Table 7.1 ACTIVITY MATRIX FOR EQUIPMENT MAINTENANCE CHECKS

Apparatus	Acceptance limits	Frequency and method of measurements	Action if requirements are not met
Fiber vane pump	Leak free; required flow; no erratic behavior	Periodic check of oil and oiler jar; remove head yearly and change fiber vanes	Replace as needed
Diaphragm pump	Leak-free valves functioning properly; required flow	Clean valves during yearly disassembly	Replace when leaking or when running erratically
Dry gas meter	No excess oil, corrosion, or erratic dial rotation	Check every 3 mo for excess oil or corrosion; check valves and diaphragm if dial runs erratically or if meter will not calibrate	Replace parts as needed, or replace meter
Inclined manometer	No discoloration of or visible matter in the fluid	Check periodically; change fluid during yearly disassembly	Replace parts as needed
Other sampling train components	No damage or leaks; no erratic behavior	Visually check every 3 mo; disassemble and clean or replace yearly	If failure noted, replace meter box, sample box, or umbilical cord
Nozzle	No dents, corrosion, or other damage	Visually check before and after each test run	Replace nozzle or clean, sharpen, and recalibrate

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8.0 AUDITING PROCEDURES

An audit is an independent assessment of the quality of data collected during all source tests, especially those required for enforcement. "Independent" means that the individual(s) performing the audit and the standards and equipment used in the audit are different from the regular field team and the standards and equipment used in the source test. A source test for enforcement comprises a series of runs at one source. Although quality assurance checks by a field team are necessary for routinely generating good quality data, they are not part of the auditing procedure. Table 8.1 at the end of this section summarizes the quality assurance activities for the auditors.

Based on a collaborative test[1] of Method 13B, performance audits are recommended for--

1. The sampling train volumetric flow measuring device,
2. The analytical phase, and
3. The data processing.

In addition to the three performance audits, a system audit should be conducted as specified by the quality assurance coordinator. The performance and the system audits are detailed in Subsections 8.1 and 8.2.

8.1 Performance Audits

Performance audits--independent checks by an auditor to assess data produced by the total measurement system (sample collection and analysis, and data processing)--are quantitative appraisals of data quality.

8.1.1 Audit of Sampling Train Volumetric Flow Metering Device -

The audit procedure described in this subsection can be used to determine the accuracy of the flow metering device (dry gas meter) in a sampling train. The dry gas meter is audited using a calibrated critical flow orifice housed in a quick-connect coupling and the following procedure:

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1. Remove the critical orifice from its case and insert it into the gas inlet quick-connect coupling on the source sampling meter box.

2. Turn the power to the meter box on and start the pump.

3. Completely open the coarse flow rate control valve and close the fine flow rate control valve to give a maximum vacuum reading. Caution: A vacuum reading of <425 mm (17 in.) Hg will result in flow rate errors.

4. Allow the orifice and source sampling meter box to warmup for 45 min with flow controls adjusted as described in step 3 before starting quality assurance runs. If the audit is made at the conclusion of the sample run, the warmup period is not necessary.

5. Make triplicate quality assurance runs. For each run, record the initial and the final dry gas meter volumes, the dry gas meter inlet and outlet temperatures, the internal orifice pressure drop (ΔH), the ambient temperature, and the barometric pressure. The duration of the run should be slightly >15 min. The following procedure is recommended and should be performed three times to provide the required triplicate quality assurance runs: 15 min after a run is started, watch the dry gas meter needle closely. As the needle reaches the zero (12 o'clock) position, stop the pump and stopwatch simultaneously. Record the dry gas meter volume and the time.

6. Calculate the corrected dry gas volume for each run using Equation 8-1. For each replicate, record the corrected dry gas volume in dry standard cubic meters, the sampling time in decimal minutes, the barometric pressure in millimeters of Hg; and the ambient temperature in degrees celcius.

$$V_{m(std)} = V_m Y \left(\frac{T_{std}}{T_m}\right) \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{P_{std}}\right) \qquad \text{Equation 8-1}$$

$$= K_1 V_m Y \left(\frac{P_{bar} + \frac{\Delta H}{13.6}}{T_m}\right)$$

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Responsible control agencies can obtain a calibrated critical orifice (when available) prior to each enforcement source test, conduct the audit, and return the orifice and data form to EPA for evaluation. Orifices may be obtained from the Source Test Audit coordinator, Quality Assurance Division, Environmental Monitoring Systems Laboratory, USEPA, Research Triangle Park, North Carolina 27711. It is also suggested that organizations that conduct compliance tests participate in the EPA semiannual audit of volume meters.

8.1.2 Audits of the Analytical Phase - The two recommended performance audits should be performed once during every enforcement source test as two steps: (1) an optional pretest audit, and (2) a mandatory audit during the analysis of the field samples.

8.1.2.1 Pretest Audit of Analytical Phase (Optional) - The pretest audit for determining the proficiency of the analyst, the accuracy of the analytical procedure, and the accuracy of the standards should be performed at the discretion of the agency auditor, by using aqueous sodium fluoride (NaF) samples provided to the laboratory before the enforcement source test. The NaF samples may be prepared by the same procedures used for preparing control samples (Section 3.9.5).

The pretest audit is especially recommended for a laboratory with little or no experience with the Method 13B analytical procedure (Section 3.9.5). The laboratory should notify the agency/organization requesting the performance test of the intent to test 30 days before the enforcement source test, and should request that the following audit samples be provided: a 1-ℓ sample for a low concentration (0.2 to 1.0 mg F/dscm of gas sampled or approximately 1 to 5 mg NaF/ℓ of sample) and a 1-ℓ sample for a high concentration (2.0 to 10.0 mg F/dscm of gas sampled or approximately 10 to 50 mg NaF/ℓ of sample). At least 10 days before the enforcement source test, the agency/organization should provide the audit samples. The laboratory could analyze the low and high concentrations, and submit the results to the agency/organization before the enforcement source test.

Note: The analyst performing this optional audit must perform the field sample analysis also (Subsection 8.1.3).

The agency/organization determines the percent accuracy, %A, between the measured and the known concentrations of the audit sample using Equation 8-2.

$$\% A = \frac{C_F(M) - C_F(A)}{C_F(A)} \; 100 \qquad \text{Equation 8-2}$$

where

$C_F(M)$ = concentration of the audit sample measured by lab analyst, mg/ml, and

$C_F(A)$ = known concentration of the audit sample, mg/ml.

The %A is actually a measure of the inaccuracy of the analytical phase.

The control limits for %A is expected to be within ±12% of true value.

8.1.2.2 Audit of the Analysis (Mandatory) - The purpose of this mandatory audit is to assess the data quality at the time of the analysis; this audit is useful in checking computer programs and manual methods of data processing. The agency should provide two audit samples to be analyzed along with the field samples. The percent accuracy (%A) of the audit samples (determined using Equation 8-2) should be included in the enforcement source test report as a measure of the inaccuracy (bias and imprecision) of the analytical phase of Method 13B during the actual enforcement source test.

8.1.3 Audit of Data Processing - Data processing errors may be determined by independent (audit) calculations, starting with data on the field and laboratory data forms. If a difference, other than roundoff error is detected between the original and the audit calculations, check all data calculations. Alternatively, the data processing may be audited by providing the testing laboratory with specific data sets (exactly as would occur in the field) and by requesting that the results of the data calculations be returned to the agency/organization.

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8.2 System Audit

A system audit--an on-site inspection and review of quality assurance checks on the total measurement system (sample collection and analysis, data processing, etc.)--normally is a qualitative appraisal of data quality.

Initially, a system audit is recommended for each enforcement source test. After the field team has acquired sufficient experience with the method, the frequency of system audits may be reduced--for example, to one of every four enforcement source tests.

The auditor, i.e., the person performing the system audit, should have extensive experience in source sampling, specifically with the measurement system being audited. The auditor's responsibilities are as follows:

1. Inform the field team of the results of pretest performance audits, and specify any needed attention or improvement.
2. Observe the procedures and techniques used by the field team during sample collection.
3. Check/verify the records of apparatus calibration checks and the quality control charts used in the laboratory analysis of control samples from previous source tests, if applicable.
4. Forward the results of the system audit to field team management so that appropriate corrective action may be initiated.

While on-site, the auditor should observe the field test team's overall performance, including the following:

1. Setting up and leakchecking the sampling train.
2. Preparing the absorbing solution, and adding it to the impingers.
3. Checking the isokinetic sampling.
4. Conducting the posttest leak check.
5. Conducting the sample recovery, and checking the data integrity.

Figure 8.2 is a checklist suggested for use by the auditor.

Yes	No	Comment	OPERATION
			Presampling Preparation
✓	—		1. Knowledge of process conditions
✓	—		2. Calibration of equipment, before each field test
			On-Site Measurements
✓	—		3. Sample train assembly
✓	—	10" Hg	4. Pretest leak check
✓	—		5. Isokinetic sampling
✓	—	10" Hg	6. Posttest leak check
✓	—		7. Record process conditions during sample collection
✓	—		8. Sample recovery and data integrity
			Postsampling
✓	—		9. Accuracy and precision of control sample analysis
✓	—		10. Recovery of samples for distillation
✓	—		11. Calibration checks
✓	—		12. Calculation procedure/check

General Comments:

Figure 8.1. Method 13B checklist for auditors.

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TABLE 8.1. ACTIVITY MATRIX FOR AUDITING PROCEDURES

Audit	Acceptance limits	Frequency and method of measurement	Action if requirements are not met
Performance Audit			
Analytical phase of Method 13B using aqueous sodium fluoride	Measured concentrations of audit sample within ±12% of true value	Once during every enforcement source test; measure audit samples and compare their values with known concentrations	Review operating technique
Data processing errors	Difference between original and audit calculations within roundoff error	Once during every enforcement source test, perform independent calculations starting with data recorded on field and laboratory forms	Check and correct all data; recalculate if necessary
System audit	Operation technique as described in Section 3.9	Once during every enforcement test, until experience gained and then every fourth test, observe techniques; use audit checklist (Fig 8.2)	Explain to team deviations from recommended techniques; note on Fig 8.2

9.0 RECOMMENDED STANDARDS FOR ESTABLISHING TRACEABILITY

To acquire data of good quality, two considerations are essential:

1. The measurement process must be in a state of statistical control at the time of the measurement, and

2. The systematic errors, when combined with the random variations (errors of measurement), must result in acceptable uncertainty.

Other quality assurance activities include quality control checks and independent audits of the total measurement system (Section 3.9.8); documentation of data by using quality control charts (as appropriate); use of materials, instruments, and procedures that can be traced to appropriate standards of reference; and use of control standards and working standards for routine data collection and equipment calibration. Working standards should be traceable to primary standards:

1. Dry gas meter calibrated against a wet test meter that has been verified by liquid displacement (Section 3.9.2) or by a spirometer.

2. Field samples analyzed by comparisons with standard solutions (aqueous NaF) that have been validated with independent control samples.

10.0 REFERENCE METHOD[a]

Method 13B. Determination of Total Fluoride Emissions From Stationary Sources; Specific Ion Electrode Method

1. Applicability and Principle

1.1 Applicability. This method applies to the determination of fluoride (F) emissions from stationary sources as specified in the regulations. It does not measure fluorocarbons, such as freons.

1.2 Principle. Gaseous and particulate F are withdrawn isokinetically from the source and collected in water and on a filter. The total F is then determined by the specific ion electrode method.

2. Range and Sensitivity

The range of this method is 0.02 to 2.000 μg F/ml; however, measurements of less than 0.1 μg F/ml require extra care. Sensitivity has not been determined.

3. Interferences

Grease on sample-exposed surfaces may cause low F results because of adsorption.

4. Precision and Accuracy

4.1 Precision. The following estimates are based on a collaborative test done at a primary aluminum smelter. In the test, six laboratories each sampled the stack simultaneously using two sampling trains for a total of 12 samples per sampling run. Fluoride concentrations encountered during the test ranged from 0.1 to 1.4 mg F/m³. The within-laboratory and between-laboratory standard deviations, which include sampling and analysis errors, are 0.037 mg F/m³ with 60 degrees of freedom and 0.056 mg F/m³ with five degrees of freedom, respectively.

4.2 Accuracy. The collaborative test did not find any bias in the analytical method.

5. Apparatus

5.1 Sampling Train and Sample Recovery. Same as Method 13A, Sections 5.1 and 5.2, respectively.

5.2 Analysis. The following items are needed:

5.2.1 Distillation Apparatus, Bunsen Burner, Electric Muffle Furnace, Crucibles, Beakers, Volumetric Flasks, Erlenmeyer Flasks or Plastic Bottles, Constant Temperature Bath, and Balance. Same as Method 13A, Sections 5.3.1 to 5.3.9, respectively, except include also 100-ml polyethylene beakers.

5.2.2 Fluoride Ion Activity Sensing Electrode.

5.2.3 Reference Electrode. Single junction, sleeve type.

5.2.4 Electrometer. A pH meter with millivolt-scale capable of ±0.1-mv resolution, or a specific ion meter made specifically for specific ion use.

5.2.5 Magnetic Stirrer and TFE[b] Fluorocarbon-Coated Stirring Bars.

6. Reagents

6.1 Sampling and Sample Recovery. Same as Method 13A, Sections 6.1 and 6.2, respectively.

6.2 Analysis. Use ACS reagent grade chemicals (or equivalent), unless otherwise specified. The reagents needed for analysis are as follows:

6.2.1 Calcium Oxide (CaO). Certified grade containing 0.005 percent F or less.

6.2.2 Phenolphthalein Indicator. Dissolve 0.1 g of phenolphthalein in a mixture of 50 ml of 90 percent ethanol and 50 ml deionized distilled water.

6.2.3 Sodium Hydroxide (NaOH). Pellets.

6.2.4 Sulfuric Acid (H_2SO_4), Concentrated.

6.2.5 Filters. Whatman No. 541, or equivalent.

6.2.6 Water. From same container as 6.1.2 of Method 13A.

6.2.7 Sodium Hydroxide, 5 M. Dissolve 20 g of NaOH in 100 ml of deionized distilled water.

6.2.8 Sulfuric Acid, 25 percent (V/V). Mix 1 part of concentrated H_2SO_4 with 3 parts of deionized distilled water.

[b] Mention of any trade name or specific product does not constitute endorsement by the Environmental Protection Agency.

[a] Taken from Federal Register, Vol. 45, No. 121, pp. 41857-41858, Friday, June 20, 1980.

6.2.9 Total Ionic Strength Adjustment Buffer (TISAB). Place approximately 500 ml of deionized distilled water in a 1-liter beaker. Add 57 ml of glacial acetic acid, 58 g of sodium chloride, and 4 g of cyclohexylene dinitrilo tetraacetic acid. Stir to dissolve. Place the beaker in a water bath to cool it. Slowly add 5 M NaOH to the solution, measuring the pH continuously with a calibrated pH/reference electrode pair, until the pH is 5.3. Cool to room temperature. Pour into a 1-liter volumetric flask, and dilute to volume with deionized distilled water. Commercially prepared TISAB may be substituted for the above.

6.2.10 Fluoride Standard Solution, 0.1 M. Oven dry some sodium fluoride (NaF) for a minimum of 2 hours at 110°C, and store in a desiccator. Then add 4.2 g of NaF to a 1-liter volumetric flask, and add enough deionized distilled water to dissolve. Dilute to volume with deionized distilled water.

7. Procedure

7.1 Sampling, Sample Recovery, and Sample Preparation and Distillation. Same as Method 13A, Sections 7.1, 7.2, and 7.3, respectively, except the notes concerning chloride and sulfate interferences are not applicable.

7.2 Analysis.

7.2.1 Containers No. 1 and No. 2. Distill suitable aliquots from Containers No. 1 and No. 2. Dilute the distillate in the volumetric flasks to exactly 250 ml with deionized distilled water and mix thoroughly. Pipet a 25-ml aliquot from each of the distillate and separate beakers. Add an equal volume of TISAB, and mix. The sample should be at the same temperature as the calibration standards when measurements are made. If ambient laboratory temperature fluctuates more than ±2°C from the temperature at which the calibration standards were measured, condition samples and standards in a constant-temperature bath before measurement. Stir the sample with a magnetic stirrer during measurement to minimize electrode response time. If the stirrer generates enough heat to change solution termperature, place a piece of temperature insulating material such as cork, between the stirrer and the beaker. Hold dilute samples (below 10^{-4} M fluoride ion content) in polyethylene beakers during measurement.

Insert the fluoride and reference electrodes into the solution. When a steady millivolt reading is obtained, record it. This may take several minutes. Determine concentration from the calibration curve. Between electrode measurements, rinse the electrode with distilled water.

7.2.2 Container No. 3 (Silica Gel). Same as Method 13A, Section 7.4.2.

8. Calibration

Maintain a laboratory log of all calibrations.

8.1 Sampling Train. Same as Method 13A.

8.2 Fluoride Electrode. Prepare fluoride standardizing solutions by serial dilution of the 0.1 M fluoride standard solution. Pipet 10 ml of 0.1 M fluoride standard solution into a 100-ml volumetric flask, and make up to the mark with deionized distilled water for a 10^{-1} M standard solution. Use 10 ml of 10^{-1} M solution to make a 10^{-2} M solution in the same manner. Repeat the dilution procedure and make 10^{-4} and 10^{-5} solutions.

Pipet 50 ml of each standard into a separate beaker. Add 50 ml of TISAB to each beaker. Place the electrode in the most dilute standard solution. When a steady millivolt reading is obtained, plot the value on the linear axis of semilog graph paper versus concentration on the log axis. Plot the nominal value for concentration of the standard on the log axis, e.g., when 50 ml of 10^{-2} M standard is diluted with 50 ml of TISAB, the concentration is still designated "10^{-2} M."

Between measurements soak the fluoride sensing electrode in deionized distilled water for 30 seconds, and then remove and blot dry. Analyze the standards going from dilute to concentrated standerds. A straight-line calibration curve will be obtained, with nominal concentrations of 10^{-4}, 10^{-3}, 10^{-2}, and 10^{-1} fluoride molarity on the log axis plotted versus electrode potential (in mv) on the linear scale. Some electrodes may be slightly nonlinear between 10^{-6} and 10^{-4} M. If this occurs, use additional standards between these two concentrations.

Calibrate the fluoride electrode daily, and check it hourly. Prepare fresh fluoride standardizing solutions daily (10^{-2} M or less). Store fluoride standardizing solutions in polyethylene or polypropylene containers. (Note: Certain specific ion meters have been designed specifically for fluoride electrode use and give a direct readout of fluoride ion concentration. These meters may be used in lieu of calibration curves for fluoride measurements over narrow concentration ranges. Calibrate the meter according to the manufacturer's instructions.)

9. Calculations

Carry out calculations, retaining at least one extra decimal figure beyond that of the acquired data. Round off figures after final calculation.

9.1 Nomenclature. Same as Method 13A, Section 9.1. In addition:

M = F concentration from calibration curv molarity.

9.2 Average Dry Gas Meter Temperature and Average Orifice Pressure Drop, Dry Gas Volume, Volume of Water Vapor and Moisture Content, Fluroide Concentration in Stack Gas, and Isokinetic Variation and Acceptable Results. Same as Method 13A, Section 9.2 to 9.4, 9.5.2, and 9.6, respectively.

9.3 Fluoride in Sample. Calculate the amount of F in the sample using the following:

$$F_t = K \frac{T_t}{A_t} (V_d) (M) \qquad \text{Equation 13B-1}$$

Where:

K = 19 mg/ml.

10. References

1. Same as Method 13A, Citations 1 and 2 of Section 10.

2. MacLeod, Kathryn E. and Howard L. Crist. Comparison of the SPADNS—Zirconium Lake and Specific Ion Electrode Methods of Fluoride Determination in Stack Emission Samples. Analytical Chemistry. 45:1272–1273. 1973.

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11.0 REFERENCES

1. Standards of Performance Promulgated for Five Categories of Sources in the Phosphate Fertilizer Industry. Federal Register, Vol. 42. August 6, 1975.

2. Determination of Total Fluoride Emissions from Stationary Sources; Specific Ion Electrode Method. Federal Register, Vol. 45. June 20, 1980.

3. Martin, R. M. Construction Details of Isokinetic Source Sampling Equipment. APTD-0581, USEPA, Air Pollution Control Office, Research Triangle Park, North Carolina. 1971.

4. Rom, J. J. Maintenance, Calibration, and Operation of Isokinetic Source Sampling Equipment. APTD-0576. USEPA Office of Air Programs, Research Triangle Park, North Carolina. 1972.

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12.0 DATA FORMS

Blank data forms are provided on the following pages for the convenience of the Handbook user. Each blank form has the customary descriptive title centered at the top of the page. However, the section-page documentation in the top right-hand corner of each page of other sections has been replaced with a number in the lower right-hand corner that will enable the user to identify and refer to a similar filled-in form in the text section. For example, Form M13B-1.2 indicates that the form is Figure 1.2 in Section 3.9.1 of the Method 13B Handbook. Future revisions of this form, if any, can be documented by 1.2A, 1.2B, etc. Fifteen of the blank forms listed below are included in this section. Three are in the Method Highlights Section as shown by the MH following the form number and one is left blank in the text.

Form	Title
1.2	Procurement Log
2.3A & B	Dry Gas Meter Calibration Data Form (English and Metric units)
2.4A & B	Posttest Meter Calibration Data Form (English and Metric units)
2.5	Stack Temperature Sensor Calibration Data Form
2.6	Nozzle Calibration Data Form
2.7	Fluoride Calibration Curve Data Form
3.1 (MH)	Pretest Sampling Checks
4.1	Nomograph Data Form
4.2	Fluoride Field Data Form
4.3	Sample Recovery and Integrity Data Form
4.4	Sample Label
4.5 (MH)	On-Site Measurement Checklist
5.1	Posttest Calibration Checks

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Form	Title
5.2	Fluoride Analytical Data Form
5.3	Sample Analytical Data Form
5.4	Expanded Calibration Curve Data Form
6.1A & 6.1B	Fluoride Calculation Data Form (English and Metric units)
8.2 (MH)	Method 13B Checklist To Be Used by Auditors

PROCUREMENT LOG

Item description	Quantity	Purchase order number	Vendor	Date		Cost	Disposition	Comments
				Ordered	Received			

DRY GAS METER CALIBRATION DATA (English units)

Date _____ Meter box number _____

Barometric pressure, P_b = _____ in. Hg Calibrated by _____

Orifice manometer setting (ΔH), in. H_2O	Gas volume: Wet test meter (V_w), ft^3	Gas volume: Dry gas meter (V_d), ft^3	Temperatures: Wet test meter (t_w), °F	Temperatures: Dry gas meter: Inlet (t_{d_i}), °F	Temperatures: Dry gas meter: Outlet (t_{d_o}), °F	Temperatures: Dry gas meter: Avg[a] (t_d), °F	Time (θ), min	Y_i	$\Delta H@_i$, in. H_2O
0.5	5								
1.0	5								
1.5	10								
2.0	10								
3.0	10								
4.0	10								
							Avg		

ΔH, in. H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 460)}{V_d (P_b + \frac{\Delta H}{13.6}) (t_w + 460)}$	$\Delta H@_i = \frac{0.0317\ \Delta H}{P_b (t_d + 460)} \left[\frac{(t_w + 460)\ \theta}{V_w}\right]^2$
0.5	0.0368		
1.0	0.0737		
1.5	0.110		
2.0	0.147		
3.0	0.221		
4.0	0.294		

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

METER BOX CALIBRATION DATA AND CALCULATION FORM (English units)

Nomenclature:

V_w = Gas volume passing through the wet test meter, ft^3.

V_d = Gas volume passing through the dry gas meter, ft^3.

t_w = Temperature of the gas in the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °F.

t_d = Average temperature of gas in dry gas meter, obtained by average t_{d_i} and t_{d_o}, °F.

ΔH = Pressure differential across orifice, in. H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance Y_i = Y±0.02 Y.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs;

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives 0.75 ft^3/min of air at standard conditions for each calibration run, in. H_2O; tolerance = $\Delta H@$±0.15 (recommended).

$\Delta H@$ = Average orifice pressure differential that gives 0.75 ft^3/min of air at standard conditions for all six runs, in. H_2O; tolerance = 1.84±0.25 (recommended).

θ = Time for each calibration run, min.

P_b = Barometric pressure, in. Hg.

DRY GAS METER CALIBRATION DATA (metric units)

Date _____ Meter box number _____

Barometric pressure, P_b = _____ mm Hg Calibrated by _____

Orifice manometer setting (ΔH), mm H_2O	Gas volume: Wet test meter (V_w), m^3	Gas volume: Dry gas meter (V_d), m^3	Temperatures: Wet test meter (t_w), °C	Temperatures: Dry gas meter: Inlet (t_{d_i}), °C	Temperatures: Dry gas meter: Outlet (t_{d_o}), °C	Temperatures: Dry gas meter: Avg[a] (t_d), °C	Time (θ), min	Y_i	$\Delta H@_i$, mm H_2O
10	0.15								
25	0.15								
40	0.30								
50	0.30								
75	0.30								
100	0.30								
							Avg		

ΔH, mm H_2O	$\frac{\Delta H}{13.6}$	$Y_i = \frac{V_w P_b (t_d + 273)}{V_d (P_b + \frac{\Delta H}{13.6})(t_w + 273)}$	$\Delta H@_i = \frac{0.00117\ \Delta H}{P_b (t_d + 273)} \left[\frac{(t_w + 273)\ \theta}{V_w}\right]^2$
10	0.7		
25	1.8		
40	2.94		
50	3.68		
75	5.51		
100	7.35		

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

METER BOX CALIBRATION DATA AND CALCULATION FORM (metric units)

Nomenclature:

V_w = Gas volume passing through the wet test meter, m^3.

V_d = Gas volume passing through the dry gas meter, m^3.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °C.

t_d = Average temperature of gas in dry gas meter, obtained by average of t_{d_i} and t_{d_o}, °C.

ΔH = Pressure differential across orifice, mm H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run; tolerance Y_i = $Y \pm 0.02\ Y$.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all six runs;

$\Delta H@_i$ = Orifice pressure differential at each flow rate that gives 0.021 m^3 of air at standard conditions for each calibration run, mm H_2O; tolerance $\Delta H@_i$ = $\Delta H@ \pm 3.8$ mm H_2O (recommended).

$\Delta H@$ = Average orifice pressure differential that gives 0.021 m^3 of air at standard conditions for all six runs, mm H_2O; tolerance $\Delta H@$ = 46.74 ± 6.3 mm H_2O (recommended).

θ = Time of each calibration run, min.

P_b = Barometric pressure, mm Hg.

POSTTEST DRY GAS METER CALIBRATION DATA FORM (English units)

Test numbers _____ Date _____ Meter box number _____ Plant _____

Barometric pressure, P_b = _____ in. Hg Dry gas meter number _____ Pretest Y _____

Orifice manometer setting, (ΔH), in. H_2O	Gas volume		Temperature				Time (θ), min	Vacuum setting, in. Hg	Y_i	$Y_i \frac{V_w P_b (t_d + 460)}{V_d \left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 460)}$
	Wet test meter (V_w), ft^3	Dry gas meter (V_d), ft^3	Wet test meter (t_w), °F	Dry gas meter						
				Inlet (t_{d_i}), °F	Outlet (t_{d_o}), °F	Average[a] (t_d), °F				
	10									
	10									
	10									
									Y =	

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

V_w = Gas volume passing through the wet test meter, ft^3.

V_d = Gas volume passing through the dry gas meter, ft^3.

t_w = Temperature of the gas in the wet test meter, °F.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °F.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °F.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o}, °F.

ΔH = Pressure differential across orifice, in. H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs; tolerance = pretest Y $\pm 0.05Y$

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

POSTTEST METER CALIBRATION DATA FORM (Metric units)

Test numbers _____ Date _____ Meter box number _____ Plant _____

Barometric pressure, P_b = _____ mm Hg Dry gas meter number _____ Pretest Y _____

Orifice manometer setting, (ΔH), mm H_2O	Gas volume		Temperature				Time (θ), min	Vacuum setting, mm Hg	Y_i	$\frac{V_w P_b (t_d + 273)}{V_d \left(P_b + \frac{\Delta H}{13.6}\right)(t_w + 273)}$
	Wet test meter (V_w), m^3	Dry gas meter (V_d), m^3	Wet test meter (t_w), °C	Dry gas meter						
				Inlet (t_{d_i}), °C	Outlet (t_{d_o}), °C	Average[a] (t_d), °C				
	0.30									
	0.30									
	0.30									
									Y =	

[a] If there is only one thermometer on the dry gas meter, record the temperature under t_d.

V_w = Gas volume passing through the wet test meter, m^3.

V_d = Gas volume passing through the dry gas meter, m^3.

t_w = Temperature of the gas in the wet test meter, °C.

t_{d_i} = Temperature of the inlet gas of the dry gas meter, °C.

t_{d_o} = Temperature of the outlet gas of the dry gas meter, °C.

t_d = Average temperature of the gas in the dry gas meter, obtained by the average of t_{d_i} and t_{d_o}, °C.

ΔH = Pressure differential across orifice, in H_2O.

Y_i = Ratio of accuracy of wet test meter to dry gas meter for each run.

Y = Average ratio of accuracy of wet test meter to dry gas meter for all three runs; tolerance = pretest Y $\pm$0.05Y

P_b = Barometric pressure, in. Hg.

θ = Time of calibration run, min.

STACK TEMPERATURE SENSOR CALIBRATION DATA FORM

Date _____ Thermocouple number _____

Ambient temperature _____ °C Barometric pressure _____ in. Hg

Calibrator _____ Reference: mercury-in-glass _____

other _____

Reference point number	Source[a] (specify)	Reference thermometer temperature, °C	Thermocouple potentiometer temperature, °C	Temperature difference,[b] %

[a] Type of calibration system used.

[b] $\left[\frac{(\text{ref temp, °C} + 273) - (\text{test thermom temp, °C} + 273)}{\text{ref temp, °C} + 273}\right] 100 \leq 1.5\%$.

NOZZLE CALIBRATION DATA FORM

Date _____ Calibrated by _____

Nozzle identification number	Nozzle Diameter[a]			ΔD,[b] mm (in.)	D_{avg}[c]
	D_1, mm (in.)	D_2, mm (in.)	D_3, mm (in.)		

where:

[a] $D_{1,2,3}$ = three different nozzles diameters, mm (in.); each diameter must be within (0.025 mm) 0.001 in.

[b] ΔD = maximum difference between any two diameters, mm (in.), $\Delta D \leq$ (0.10 mm) 0.004 in.

[c] D_{avg} = average of D_1, D_2, and D_3.

FLUORIDE CALIBRATION DATA FORM

LABORATORY WORKSHEET

Date _____

Date standards prepared _____

Temperature of standards _____ Electrode number _____

Standard number	Concentration (M)	Electrode potential (mV)
	0.000001	
	0.00001	
	0.0001	
	0.001	
	0.01	
	0.1	
Control Sample		

Note: The concentration of the control sample determined from the calibration curve must be between 0.002M and 0.01M.

Signature of analyst _____

Signature of reviewer _____

NOMOGRAPH DATA FORM (English units)

Plant _____

Date _____

Sampling location _____

Calibrated pressure differential across orifice, in. H_2O	$\Delta H_@$	
Average meter temperature (ambient + 20°F), °F	$T_{m_{avg}}$	
Percent moisture in gas stream by volume, %	B_{wo}	
Barometric pressure at meter, in. Hg	P_m	
Static pressure in stack, in. Hg ($P_m \pm 0.073 \times$ stack gauge pressure, in. H_2O)	P_s	
Ratio of static pressure to meter pressure	P_s/P_m	
Average stack temperature, °F	$T_{s_{avg}}$	
Average velocity head, in. H_2O	Δp_{avg}	
Maximum velocity head, in. H_2O	Δp_{max}	
C factor		
Calculated nozzle diameter, in.		
Actual nozzle diameter, in.		
Reference Δp, in. H_2O		

PARTICULATE FIELD DATA FORM

Plant _____
City _____
Location _____
Operator _____
Date _____
Run number _____
Stack diam, mm (in.) _____
_____
Sample box number _____
Meter box number _____
Meter ΔH@ _____

Meter calibration (Y) _____
Pitot tube (C_p) _____
Probe length _____
Probe liner material _____
Probe heater setting _____
Ambient temperature _____
Barometric pressure (P_b) _____ mm (in.) Hg
Assumed moisture _____
Static pressure (P_a) _____ mm (in.) H_2O
C Factor _____
Reference ΔP _____ mm (in.) H_2O

Sheet _____ of _____
Nozzle identification number _____
Nozzle diameter _____ mm (in.)
Thermometer number _____
Final leak rate _____ m^3/min (cfm)
Vacuum during leak check _____
_____ mm (in.) Hg
Filter position _____
Maximum ΔH _____
Remarks _____
_____

Traverse point number	Sampling time, (θ), min	Clock time, (24 h)	Vacuum, mm (in.) Hg	Stack temperature (T_s), °C(°F)	Velocity head (ΔP_s), mm (in.) H_2O	Pressure differential across orifice meter (ΔH), mm (in.) H_2O	Gas sample volume (V_m), m^3 (ft^3)	Gas sample temperature at dry gas meter		Temp of gas leaving condenser or last impinger, °C (°F)	Filter temp, °C(°F)
								Inlet, °C(°F)	Outlet, °C(°F)		
	Total		Max	Avg			Total	Avg	Avg	Max	

SAMPLE RECOVERY AND INTEGRITY DATA FORM

Plant _____ Sample date _____

Sample location _____ Run number _____

Sample recovery person _____ Recovery date _____

MOISTURE

Impingers		Silica gel		
Final volume (wt)	_____ml (g)	Final wt	_____g	_____g
Initial volume (wt)	_____ml (g)	Initial wt	_____g	_____g
Net volume (wt)	_____ml (g)	Net wt	_____g	_____g

Total moisture _____g

Color of silica gel _____

Description of impinger water _____

RECOVERED SAMPLE

Water rinse and impinger contents container number _____ Liquid level marked? _____

Water blank container number _____ Liquid level marked? _____

Samples stored and locked? _____

Remarks _____

_____

Date of laboratory custody _____

Laboratory personnel taking custody _____

Remarks _____

_____

EXAMPLE OF A SAMPLE LABEL

Plant _____ City _____

Site _____ Sample type _____

Date _____ Run number _____

Front rinse ☐ Front filter ☐ Front solution ☐

Back rinse ☐ Back filter ☐ Back solution ☐

Solution _____ Level marked _____

Volume: Initial _____ Final _____

Clean up by _____

Remarks: _____

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POSTTEST CALIBRATION CHECKS

Plant _____ Calibrated by _____

Meter box number _____ Date _____

Dry Gas Meter

Pretest calibration factor, Y _____ (within ±2%)
Posttest check, Y* _____ (within ±5% of pretest)
Recalibration required? _____ yes _____ no
If yes, recalibration factor, Y _____ (within ±2%)
Lower calibration factor, Y _____ for calculations (pretest or posttest)

Dry Gas Meter Thermometers

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____ (within ±3°C (5.4°F) over range)
Posttest comparison with mercury-in-glass thermometer?* (within ±6°C (10.8°F) at ambient temperature)
Recalibration required? _____ yes _____ no
Recalibration temperature correction? _____ (within ±3°C (5.4°F) over range)*
If yes, no correction necessary for calculations if meter thermometer temperature is higher; if calibration temperature is higher, add correction to average meter temperature for calculations

Stack Temperature Sensor

Was a pretest temperature correction used? _____ yes _____ no
If yes, temperature correction _____°C (°F) (within ±1.5% of readings in K (°R) over range)
Average stack temperature of compliance test, T_s _____K (°R)
Temperature of reference thermometer or solution for recalibration _____K (°R)* (within ±10% of T_s)
Temperature of stack thermometer for recalibration _____K (°R)
Difference between reference and stack thermometer temperatures, ΔT_s _____K (°R)
Do values agree within ±1.5%?* _____ yes _____ no
If yes, no correction necessary for calculations
If no, calculations must be done twice--once with the recorded values and once with the average stack temperature corrected to correspond to the reference temperature differential (ΔT_s), both final result values must be reported since there is no way to determine which is correct

(continued)

(continued)

Barometer

Was the pretest field barometer reading correct? ____ yes ____ no
Posttest comparison?* _____ mm (in.) Hg (±2.5 mm (0.1 in.) Hg)
Was calibration required? _____ yes _____ no
If yes, no correction necessary for calculations when the field barometer has a lower reading; if the mercury-in-glass reading is lower, subtract the difference from the field data readings for the calculation

*Most significant items/parameters to be checked.

FLUORIDE ANALYTICAL DATA SHEET

Plant _____ Date _____

Sample location _____ Analyst _____

Samples identifiable _____ yes _____ no All liquid levels at marks _____ yes _____ no

Ambient temperature _____ Constant temperature bath used _____ yes _____ no

Temperature of calibration standards _____ Date calibration standards prepared _____

Temperature of samples _____

Sample number	Sample identification number	Total volume of sample, (V_t), ml	Aliquot total sample added to still (A_t), ml	Diluted volume of distillate collected (V_d), ml	Electrode potential, mV	Concentration of fluoride from calibration curve, (M), molarity	Total weight of fluoride in sample (F_t), mg

Total weight of fluoride in sample (F_t)

$$F_t = 19\frac{V_t}{A_t}(V_d)\ (M)$$

Signature of analyst _____ Remarks: _____

Signature of reviewer or supervisor _____ _____

EXPANDED CALIBRATION CURVE DATA FORM

LABORATORY WORKSHEET

Date _____

Date standards prepared _____

Temperature of standards _____ Electrode number _____

Standard number	Concentration, M	Electrode potential, mV
1	0.001	
2	0.0005	
3	0.0001	
4	0.00005	
5	0.00001	
Control sample		

Note: The control sample, from the calibration curve, must be between 0.0002M and 0.0003M.

Signature of analyst _____

Signature of reviewer _____

SAMPLE VOLUME (ENGLISH UNITS)

V_m = _ _ . _ _ _ ft^3, T_m = _ _ _ . _ °R, P_{bar} = _ _ . _ _ in. Hg

Y = _ . _ _ _, ΔH = _ . _ _ in. H_2O

$$V_{m(std)} = 17.64\ V_m Y \frac{P_{bar} + (\Delta H/13.6)}{T_m} = \_\_ . \_\_\_ ft^3$$

Equation 6-1

FLUORIDE CONTENT IN SAMPLE

V_t = _ _ _ _ . _ ml, A_t = _ _ _ . _ ml, V_d = _ _ _ . _ ml

M = _._ _ _ _ _ M

$$F_t = 4.19 \times 10^{-5} \frac{V_t V_d M}{A_t} = \_ . \_\_\_ \times 10^{-6}\ lb$$

Equation 6-4

CONCENTRATION OF FLUORIDE (ENGLIGH UNITS)

$V_{m(std)}$ = _ _ . _ _ _ ft^3, F_t = _ . _ _ _ $\times 10^{-6}$ lb

F_{tb} = _ . _ _ _ $\times 10^{-6}$ lb

$$C_s = 35.31 \frac{F_t - F_{tb}}{V_{m(std)}} = \_ . \_\_\_\_\_ \text{ lb/dscf}$$

Equation 6-5

All other equations same as Methods 2 and 5.

SAMPLE VOLUME (METRIC UNITS)

V_m = _ . _ _ _ m^3, T_m = _ _ _ . _ °K, P_{bar} = _ _ _ . _ mm Hg

Y = _ . _ _ _, ΔH = _ _ . _ mm H_2O

$$V_{m(std)} = 0.3858\ V_m\ Y\ \frac{P_{bar} + (\Delta H/13.6)}{T_m} = \_\ .\ \_\ \_\ \_\ m^3$$ Equation 6-1

FLUORIDE CONTENT IN SAMPLE

V_t = _ _ _ _ . _ ml, A_t = _ _ _ . _ ml, V_d = _ _ _ . _ml

M = _ . _ _ _ _ _ M

$$F_t = 19\ \frac{V_t\ V_d}{A_t}\ M = \_\ .\ \_\ \_\ \_\ mg$$ Equation 6-4

CONCENTRATION OF FLUORIDE (METRIC UNITS)

$V_{m(std)}$ = _ . _ _ _ dscm, F_t = _ . _ _ _, F_{tb} = _ . _ _ _ mg

$$C_s = \frac{F_t - F_{tb}}{V_{m(std)}} = \_\ .\ \_\ \_\ \_\ mg/dscm$$ Equation 6-5

All other equations same as Methods 2 and 5.