

**Compendium of Methods
for the Determination of
Inorganic Compounds
in Ambient Air**

Compendium Method IO-4.1

**DETERMINATION OF THE STRONG
ACIDITY OF ATMOSPHERIC
FINE-PARTICLES (< 2.5 μm)**

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U.S. Environmental Protection Agency
Cincinnati, OH 45268

June 1999

Method IO-4.1

Acknowledgments

This Method is a part of *Compendium of Methods for the Determination of Inorganic Compounds in Ambient Air* (EPA-625/R-96/010a), which was prepared under Contract No. 68-C3-0315, WA No. 2-10, by Midwest Research Institute (MRI), as a subcontractor to Eastern Research Group, Inc. (ERG), and under the sponsorship of the U.S. Environmental Protection Agency (EPA). Justice A. Manning, John O. Burckle, Scott R. Hedges of EPA's Center for Environmental Research Information (CERI), and Frank F. McElroy, National Exposure Research Laboratory (NERL), all in the EPA's Office of Research and Development, were responsible for overseeing the preparation of this method. Other support was provided by the following members of the Compendia Workgroup:

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This Method is the result of the efforts of many individuals. Gratitude goes to each person involved in the preparation and review of this methodology.

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Method IO-4.1
Determination of the Strong Acidity of Atmospheric
Fine-Particles (< 2.5 µm)

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Chapter IO-4

ATMOSPHERIC ACIDIC CONSTITUENTS

Method IO-4.1

DETERMINATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES (< 2.5 µm)

1. Scope

1.1 The quantitative determination of equivalent strong-acid (H₂SO₄) acidity of fine-particles (< 2.5 µm) in the atmosphere as hydrogen ion by pH analysis, is described in this method. The method is a composite of methodologies developed by U. S. Environmental Protection Agency (EPA), University of Kansas, Robert Johnson Medical School, New York State University, Harvard University and the CNR Laboratories (Italy). It is currently employed in a number of air pollution studies in Italy, United States, Canada, Mexico, Germany, Austria, and Spain, and in public health services and epidemiology and environmental research centers. The techniques, procedures, equipment, and other specifications comprising this method are derived from those used by the contributing research organizations and, therefore, are known to be serviceable and effective. At this stage, this method is a unified, consensus, tentative, draft method intended for further application and testing. Users should be advised that the method has not yet been adequately tested, optimized, or standardized. Many of the specifications have been initially established by technical judgment but have not been subjected to ruggedness testing. In some cases, alternative techniques, equipment, or specifications may be acceptable or superior. In applying the method, users are encouraged to consider alternatives, with the understanding that they should be tested to determine their adequacy and to confirm and document their possible advantages. Information and comments are solicited on improvements, alternative equipment, techniques, specifications, performance, or any other aspect of the method.

1.2 The equipment described herein can be modified to measure acidity of atmospheric reactive acidic and basic gases in both indoor and outdoor atmospheres, as documented in Method IO-4.2, entitled "*Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles in Ambient Air Using the Annular Denuder Technology.*" Modifications to this methodology were developed for monitoring regional-scale acidic and basic gases and particulate matter in support of EPA field programs involving the Integrated Air Cancer Research Program and the Acid Deposition Network. Similarly, the methodology has been used to characterize urban haze in Denver, Houston, Boston, and Los Angeles.

2. Applicable Documents

2.1 ASTM Standards

- D1356 *Definitions of Terms Related to Atmospheric Sampling and Analysis.*

2.2 Other Documents

- Ambient Air Studies (1-24).
- U.S. EPA Acid Aerosol Document (25).

3. Summary of Method

3.1 The annular denuder system (ADS) consists of an inlet with an impactor or cyclone preseparator designed to remove all particles with a diameter (aerodynamic) of 2.5 μm or greater, an annular denuder to remove ammonia, and a filter for collecting the aerosol. In operation, air is drawn through a cyclone or a elutriator-accelerator jet assembly followed by an impactor frit and coupler assembly, through the denuder to remove ammonia, and into a single-stage filter assembly. The single-stage filter assembly contains a 47-mm Teflon[®] filter supported by a stainless steel screen. The filter is a 2 μm pore-size Teflon[®] membrane filter, Zefluor (Gelman Sciences). The Teflon[®] filter collects the fine aerosol. A pump unit maintains a flow of 10 Lpm, and a timer allows programmed start and end times. The ADS with a cyclone assembly, the ADS with an impactor assembly, and the field sampling box with the pump-timer system are shown in Figure 1a, 1b, and 2, respectively.

3.2 Following each run, the ADS assembly is removed from its field housing, its ends are capped, and it is brought back to the laboratory. In the laboratory, the assembly pieces are uncoupled and capped. The denuder tube is not extracted. The Teflon[®] filter is unloaded from the filter assembly in an ammonia-free atmosphere and either immediately extracted or stored in an ammonia-free container for later extraction. A glove-box, lined with citric-acid soaked paper, is used to maintain an ammonia-free atmosphere. To remove the Teflon[®] filter, it is placed in an extraction vessel, particle-laden side down. The filter is wetted with 200 μL of methanol, then removed with 6.0 mL of extraction solution (ES). The extraction vessel is put in an ultrasonic bath for 20 min. The extraction solution is then decanted into a container.

3.3 Acidity determination is made using pH measurements of 1 mL aliquot of the extracted filter solution. Filter acidity is calculated based on standards made with sulfuric acid. The standards range from 0-160 μg , equivalent strong acid aerosol. A pH meter is used to measure the pH of the filter extract. For each batch of filter extracts, a calibration curve is calculated using the mean pH of each standard.

4. Significance

4.1 Acid aerosols are found in the atmosphere as a result of atmospheric reactions of emissions from a variety of fossil fuel combustion sources, including power plants, industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. The effects of concentrations of acid aerosols on human health and property has been documented over the past several years. The Clean Air Act Amendments of 1970 required EPA to develop uniform national ambient air quality standards (NAAQS) for criteria pollutants because of the interstate nature of certain air pollutants. NAAQS were established for pollutants that were recognized as widespread (emitted by numerous mobile and stationary sources) and that endangered public health and welfare. Further, Section 109 of the Clean Air Act as amended, requires EPA to periodically review the NAAQS as well as the scientific information and data on which they are based. New pollutants are to be identified for NAAQS development if the Administrator concludes that they reasonably may be anticipated to endanger the public health and welfare. To assist the Administrator in evaluating the need for new or revised NAAQS, the Clean Air Act created the Clean Air Scientific Advisory Committee (CASAC). This committee's mandate is to provide the Administrator with scientific advice and research recommendations on critical areas of knowledge on new or revised NAAQS. The Acid Aerosol Subcommittee of CASAC identified a need for a coordinated acid aerosol research program to assist the Agency in making recommendations on a new acid aerosol NAAQS. The Subcommittee recommended a research program involving characterization and exposure assessment, animal toxicity, human exposure research, and epidemiology. As documented in the CASAC Reporter to the Administrator, the foundation for any research program and potential air quality standard development is "...a measurement method, not only because the standard itself must specify the method, but equally important, because before establishing

a standard the contaminant must be fully characterized and exposure measurements made to correlate with health outcomes."

4.2 Unique features of the annular denuder that separate it from other established monitoring methods are the elimination of sampling artifacts due to interaction between the collected gases and particles and the preservation of the samples for subsequent analysis. These features are accomplished in Method IO-4.2 by removing ammonia (NH_3) in the gas stream with the citric acid-coated denuder to reduce the probability of the acid aerosol captured by the Teflon[®] filter in the filter pack from being neutralized to ammonium sulfate [$(\text{NH}_4)_2\text{SO}_4$].

5. Definitions

[Note: Definitions used in this document and any user-prepared Standard Operating Procedures (SOPs) should be consistent with those used in ASTM D1356. All abbreviations and symbols are defined within this document at the point of first use.]

5.1 Secondary Particles (or Secondary Aerosols). Aerosols that form in the atmosphere as a result of chemical reactions, often involving gases. A typical example is sulfate ions produced by photochemical oxidation of sulfur dioxide.

5.2 Aerosol. A dispersion of solid or liquid particle in a gas-phase medium and a solid or liquid disperse phase. Aerosols are formed by (1) the suspension of particles due to grinding or atomization or (2) the condensation of supersaturated vapors.

5.3 Coarse and Fine Particles. Coarse particles are those with diameters (aerodynamic) greater than $2.5 \mu\text{m}$ that are removed by the sampler's inlet; fine particles are those with diameters (aerodynamic) less than $2.5 \mu\text{m}$ that are collected on the Teflon[®] filter. These two fractions are usually defined in terms of the separation diameter of a sampler.

5.4 Annular. Refers to rotating to, or forming a ring. In the annular denuder sampler, the annular refers to the annulus between two concentric tubes. Chemical coating applied to the interior surfaces removes gaseous pollutants that diffuse to the surface.

5.5 Denuder. Refers to the sections in which interfering gases are removed from the sample stream prior to filtration in determining fine particle ($< 2.5 \mu\text{m}$) strong acidity.

5.6 Equivalent Weight. The equivalent weight, or combining weight of a compound or ion is its formula weight divided by the number of replaceable hydrogen atoms.

5.7 Normal Solution. Solution that contains a gram-equivalent weight of solute in a liter of solution.

6. Apparatus

[Note: This method was developed using the annular denuder system provided by University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC 27516, (919) 942-2753, as a guideline. EPA has experience in use of this equipment during various field monitoring program over the last several years. Other manufacturers' equipment should work as well. Denuder systems are also available from Rupprecht

and Patashnick Co., Inc., 25 Corporate Circle, Albany, NY 12203, (513) 452-0065 and Ogawa & Company, USA, Inc., 1230 S.E. 7th Avenue, Pompano Beach, Florida 33060, (305) 781-6223. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]

6.1 Sampling

6.1.1 Elutriator and acceleration jet (inlet) assembly. Under normal sampling conditions, the elutriator or entry tube is made of either Teflon®-coated glass or aluminum, as illustrated in Figure 3. When using glass, the accelerator jet assembly, which directs the air flow towards an impactor plate, is fixed onto the elutriator and the internal surfaces of the entire assembly are coated with Teflon® (Figure 3a). When aluminum is used, the accelerator jet assembly is removable. The jet is made of Teflon® or polyethylene, and the jet support is made of aluminum (Figure 3b). Again, all internal surfaces are coated with Teflon®.

6.1.2 Teflon® impactor support pin and impactor frit support tools (see Figure 4). These parts are made of either Teflon® or polyethylene and aid in assembling, removing, coating and cleaning the impactor frit.

6.1.3 Impactor frit and coupler assembly (see Figure 5). The impactor frit is 10 mm x 3 mm and is available with a porosity range of 10-20 µm. The frits should be made of porous ceramic material or fritted stainless steel. Before use, the impactor frit surface is coated with a Dow Corning 660 oil and toluene solution and sits in a Teflon® seat support fixed within the coupler. The coupler is made of thermoplastic and has Teflon® clad sealing "O"-rings that are located on both sides of the seat support inside the coupler.

[Note: In situations with substantial high concentrations of coarse particles (> 2.5 µm), a Teflon®-coated aluminum cyclone should be used in place of the acceleration jet and impactor assembly, as illustrated in Figure 1. The location of the cyclone with respect to the denuder, heated enclosure, and meter box is illustrated in Figure 1.]

6.1.4 Annular Denuder (see Figure 6). The denuder consists of two or more concentric glass tubes with an outer stainless steel shell. The tubes create a 1 mm annular spacing, which allows the air sample to pass through. Flow in the annular space is maintained in the laminar range and allows fine particles with diameters less than 2.5 µm to pass through with negligible removal. The inner tube is inset 25 mm from one end of the outer tube; this end is called the flow straightener end. The other end of the inner tube is flush with the end of the outer tube. Both ends of the inner tube are sealed. In this configuration, the flow straightener end is etched to provide greater surface area for the coating. The inner glass tubes are inset 25 mm from one end of the outer Teflon®-coated aluminum tube to serve as the flow straightener end. All denuder types should be equipped with thermoplastic (Bakelite) or polyethylene caps when purchased.

6.1.5 Caps for Annular Denuder. Caps are made of either polyethylene (Caplugs, Protective Enclosure, Inc.) or thermoplastic (Bakelite) and are used in the coating and drying processes and for storage and shipment. The thermoplastic caps include a removable Teflon® seal plate when purchased.

[Note: Recent evaluation of the caps for the denuder system has indicated that the thermoplastic (Bakelite) screen caps and the polyethylene screw caps are useful to seal the ends of the denuders when they are dry. However, during coating and extracting, the Caplugs (Protective Enclosures, Inc.) provide a better seal, preventing contamination that would occur from the Teflon® liner of the thermoplastic screw caps or direct contact with the unprotected thermoplastic screw caps. Therefore the user should use Caplugs during coating and extraction operations.]

6.1.6 Annular Denuder Couplers. The couplers should be made of thermoplastic and equipped with Teflon® "O"-rings that sandwich a silicone rubber ring on three sides. This design provides elasticity for better sealing under extremely cold temperature conditions in which Teflon® does not give. The couplers are equipped with permanent seal rings, which provide more even threading and a better seal when coupled. The couplers are used to couple the annular denuders together when used in series (see Method IO-4.2) and for coupling the last denuder with the filter assembly.

Caution: When utilizing the couplers, do not overtighten when applying a glass denuder. Overtightening may "chip" the ends of the denuder, preventing a tight seal.

6.1.7 Drying Manifold Assembly (see Figure 7). The manifold is made of glass and is available to accommodate as many as four drying denuders. The denuders are attached to the manifold with back-to-back Bakelite bored caps, as illustrated in Figure 7. Air is pushed through an air dryer/cleaner bottle made of 2 ½" heavy wall glass that contains a mixture of silica gel/activated carbon/sodium carbonate (~ 50 g). The Teflon® tubing that connects the dryer/cleaner bottle to the drying manifold should be secured at each cap with either Teflon® washers or Teflon® washers coupled with Teflon® hose barbs. The air stream then passes through a fine particle filter to remove fines. Alternatively, dry compressed air from a cylinder may be used in place of the dryer/cleaner bottle assembly.

6.1.8 Filter Assembly. The denuder is followed by a single-stage filter assembly containing the Teflon® membrane filter (see Figure 8). The filter is supported by a stainless steel porous screen and housed in a polyethylene filter ring housing. The filter housing outlet component is aluminum and accommodates a polyethylene screw sleeve which seals the filter assembly.

6.1.9 Vacuum Tubing. Low density polyethylene tubing, 3/8" diameter for distances of less than 50 ft., ½" diameter for distances greater than 50 ft. [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-787-6322)].

6.1.10 Tube Fitting. Compression fittings (Swagelok®, Gyrolok® or equivalent) are used to connect vacuum tubing (above) to an NPT female connector or filter holder and connect vacuum tubing to fitting on differential flow controller. The fittings may be constructed of any material since they are downstream of the sampler [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA 15219 (412-787-6322)].

6.1.11 Annular Denuder System (ADS) Sampling Box. The housing box is made of a "high-impact" plastic and is thermally insulated. It is 2 ft long by 6" wide and 6" deep. The box contains a heater unit, a fan, and an air outlet located in the lid of the housing. The elutriator end of the ADS protrudes through one end of the box, while the denuder is supported in the box by a chrome plated spring clip. If the Teflon®-coated aluminum cyclone is used to remove coarse particles, it is also housed in the heated sampling box, with the elutriator end protruding through the sampling box.

[Note: Recent studies by the Harvard School of Public Health based on a comparison of utilizing a sampling box with and without heated enclosure indicated no difference in sampled species from winter samples. However, EPA recommends controlling the temperature in the sampling box to prevent condensation.]

6.1.12 Annular Denuder Transport Case. The transport case is made of formica backed with plywood and insulated. The corners are reinforced with metal. It is made to withstand shipping by truck, UPS, and Federal Express. Each case is stackable and lockable and has a carrying handle. Seven total annular denuder systems can be packed in the case.

6.1.13 Pump/Timer Unit. The pump/timer unit draws air through the ADS at a fixed rate of 10 L/min with a precision of ± 10% over the range of 25-250 mm Hg vacuum. A mass flow controller or a differential flow controller can be used. Typically, the flow rate is monitored with an exhaust flow rotameter. The unit includes a mechanical 7-day timer and an elapsed-time counter. A dry gas meter, when available, is placed after the pump to give a direct readout of total volume of air sampled. Otherwise, flow rate is manually measured (using a rotameter) before and after each run to calculate the air volume sampled.

6.1.14 Dry Gas Meter (DGM). The DGM should have a capacity of 10 L of gas per revolution. (Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15129, 412-787-6322).

6.1.15 Electronic Mass Flow Controller. This controller should be capable of maintaining a constant rate of 10 L/min ($\pm 10\%$) over a sampling period of up to 24 h and under conditions of changing temperature (5 - 43EC) and humidity [Tylan General, Flow Division, 19220 S. Normandie Ave., Torrance, CA 90502, (213-212-5533), Model FC-262, or equivalent].

6.2 Analysis

6.2.1 pH Meter. A pH or pH/ion meter with "integral" automatic temperature compensation, temperature probe, 2 and 4 mL analytical vials, and calibrated with standard buffers (pH 4 and 7). The Ross semi-micro glass electrode from Orion has been used by the Harvard School of Public Health and found to adequately address the requirements of this protocol [Orion Research Inc., The Schraffet Center, 529 Main Street, Boston, MA 02129, (617-242-3900)].

6.2.2 Polyethylene Bottles with Polyethylene Screw Caps. 100 mL, used for storage of coating solution; and 1L, used for storing the KCl solution.

6.2.3 Erlenmeyer Flasks. 250 mL and 2 L borosilicate glass or polyethylene flasks for calibration, best source.

6.2.4 Graduated Cylinders. 5 mL, 10 mL, 100 mL, 250 mL, and 1L borosilicate glass or polyethylene cylinders, best source.

6.2.5 Pipets. Class A 5 mL and 10 mL borosilicate glass pipettes or automatic pipettes. Calibrated "to deliver," best source.

6.2.6 Pipet Bulb. Made of natural rubber. Recommended to meet OSHA requirements, best source.

6.2.7 Micropipettes. 25 μ L, 50 FL, and 100 μ L, calibrated "to contain," borosilicate glass micropipette, best source.

6.2.8 Forceps. Recommended dressing forceps made of stainless steel or chrome-plated steel and without serrations. Used for handling filter.

6.2.9 Stopwatch. Used for measuring flow rate of gas stream through DGM, best source.

6.2.10 Ultrasonic Cleaner. Used for filter extractions and parts cleaning. The ultrasonic cleaner should have temperature control capability [Cole-Palmer Instrument Co., 7425 N. Oak Park Ave., Chicago, IL 60648 (800-323-4340)].

6.2.11 Clean Air Hood (Optional). Closed air hood with ammonia free air circulation. Used for Teflon® filter extraction for pH analysis, best source.

6.2.12 Glove-Box. Used for handling exposed filter, which is lined with citric acid impregnated paper sheets to maintain an ammonia-free atmosphere. Works best with a slight positive pressure.

6.2.13 Refrigerator. (approximately 5EC) is required for sample storage.

6.2.14 Polyethylene-Stoppered Volumetric Flasks. 25 mL, used for making sulfuric acid standards.

7. Reagents and Materials

7.1 Filter. Zefluor® (PTFE) membrane filter, 47-mm diameter, with a 2 μ m pore size. The Teflon® filter has a coarse mesh Teflon® side and a fine pore membrane side. The fine pore membrane side should face the air stream. [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI 48106, Part No. P5PJ047, (800-521-1520)].

7.2 Filter Extract Storage Vials. 100 mL polyethylene vials (Nalgene or equivalent).

- 7.3 Labels.** Adhesive for sample vials, best source.
- 7.4 Parafilm.** Used for covering flasks and pH cups during pH analysis, best source.
- 7.5 Kimwipes® and Kay-dry Towels.** Used for cleaning sampling apparatus and analysis equipment, best source.
- 7.6 Stoppers.** Polyethylene, best source.
- 7.7 Sodium Carbonate (Na₂CO₃).** ACS reagent grade, best source.
- 7.8 Citric Acid [Monohydrate - HOC [(CH₂CO) OH]₂COOH : H₂O.** ACS reagent grade, best source.
- 7.9 Ethanol (C₂H₅OH).** ACS reagent grade, best source.
- 7.10 Sulfuric Acid (H₂SO₄).** ACS reagent grade, 1.000 N solution, best source.
- 7.11 Distilled Deionized Water (DDW).** ASTM Type I water.
- 7.12 pH Buffers.** Standard buffers, 4.00 and 7.00, for internal calibration of pH meter, best source.
- 7.13 Silica Gel.** ACS reagent grade (indicating type), best source.
- 7.14 Gloves.** Polyethylene disposable. Used for impactor frit assembly and filter assembly, best source.
- 7.15 Dow Corning High Temperature Vacuum Oil.** Dow Corning 660 oil used for impactor frit coating solution, best source.
- 7.16 Zero Air.** A supply of compressed clean air, free from particles and ammonia. The supply may be either from a commercial cylinder or generated on site, best source.
- 7.17 BRIJ-35.** Composed of 0.1% of BRIJ-35 in DI water [Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA 15129, (412-787-6322)].
- 7.18 Perchloric Acid (HClO₄).** 60-62%, in water, best source.
- 7.19 Toluene (C₇H₈).** ACS reagent grade, best source.
- 7.20 Potassium Chloride (KCl).** ACS reagent grade, best source.
- 7.21 Acetone (C₃H₆O).** ACS reagent grade, best source.
- 7.22 1% Glycerol (Glycerine -CH₂OHCHOHCH₂OH).** ACS reagent grade, best source.

8. Preparation of Impactor Frit and Denuder Coating

8.1 Impactor Frit Coating Solution Preparation. Weigh 1 g of silicone oil (Dow Corning high temperature 660 oil) and place in a 100 mL polyethylene storage vial. Add 100 mL of toluene. Mix thoroughly, close container, and store at room temperature. (WARNING - FLAMMABLE LIQUID).

8.2 Annular Denuder Citric Acid Coating Solution. Clean a 100 mL polyethylene storage vial and let dry at room temperature. Measure 50 mL of ethanol (WARNING - TOXIC, FLAMMABLE LIQUID) with a graduated cylinder and pour into vial. Weigh 0.5 g of citric acid and add to vial. Add enough glycerol to the vial to make a 1% solution. Mix thoroughly; cover and store at room temperature.

9. Impactor Frit Installation

9.1 Impactor Frit Installation

The impactor-coupler assembly shown in Figure 4 is composed of two parts: the replaceable impactor frit and the coupler-impactor housing seat. The impactor surface is a porous ceramic or porous stainless steel frit, 10 mm x 3 mm. Insert this frit into the coupler-impactor housing using the tools illustrated in Figure 4. Press the impactor frit gently, but firmly, into the seat of the impactor housing with a clean, gloved finger. The impactor should fit into the housing so that it does not protrude above the seat. During sampling, particles accumulate on the impactor's plate surface. After each sampling event, clean the assembly to prevent the build-up of contaminants that may lead to loss of key acidic species being collected by the ADS. Cleaning involves immersing the elutriator, coupler-impactor, and frit in 0.1% BRIJ-35 cleaning solution and ultrasonically for about 5 min. Rinse thoroughly with DDW for additional 5 min. Rinse and dry with zero air or in dust-free environment and store with ends plugged and capped.

9.2 Impactor Frit Coating

With the impactor frit in the impactor seat of either the coupler (see Figure 5) or the Teflon® impactor seat support pin that fits into the first denuder, pipette 50 µL (about two drops) of the toluene-660 oil coating solution onto the impactor frit surface and allow to dry in a dust-free environment at room temperature. Cap both sides of the coupler impactor or denuder-impactor until use.

[Note: Only the minimum amount of oil should be on the frit because any excess will be blown off during sampling and will contaminate the surfaces of the first denuder.]

10. Filter Preparation and Assembly

[Note: A clean and dedicated indoor work space is required for the daily preparation, assembly and disassembly of the denuder and filter assembly. Approximately 2-3 m of bench space is adequate, with additional space for storing supplies.]

[Note: All loading and unloading of the filter assembly must be performed in an ammonia-free glove box. Generally, the filter assembly should be reloaded after cleaning, at the same time as unloading.]

10.1 With clean gloves, disassemble the filter assembly (see Figure 8) by unscrewing the large outer Delrin® collar (sleeve) from the aluminum filter housing outlet component.

[Note: Remove the polyethylene cap first. Lay the pieces out on clean Kimwipes® (see Figure 8).]

10.2 Lay a clean Teflon® filter ring housing, with its large opening face up, on a clean Kimwipe®. Place a clean stainless steel screen in the filter ring housing.

10.3 Using clean filter forceps, place a Teflon® filter on the screen.

[Note: If a Zefluor® Teflon® filter is used, be sure to place the membrane coated side, not the coarse side, toward the air stream. By observing the filter in the light, one can differentiate between the coarse and membrane side.]

10.4 Place the Teflon® filter housing inlet component (see Figure 8) on top of the Teflon® filter. This design forms a "sandwich" with the Teflon® filter held between the second filter ring housing and the housing inlet component. The housing inlet component connects the filter assembly to the annular denuder through a thermoplastic coupler. Be careful not to twist the filter assembly components, or damage will occur to the filter.

10.5 Lay the aluminum filter housing outlet component, with its large opening face up, on a clean Kimwipe®.

10.6 Insert the filter ring sandwich with the filter housing inlet component extending upward. Place the larger outer Delrin® sleeve over the filter sandwich and screw onto the aluminum filter base. DO NOT OVERTIGHTEN!

10.7 Install the "quick-release" plug into the filter outlet component. Tighten the housing outlet to the Detrin® screw sleeve. DO NOT OVERTIGHTEN!

10.8 Install the polyethylene cap onto the filter inlet component and the orange dust cover onto the quick release plug. The filter assembly should be sealed tight before it is removed from the glove-box.

10.9 Leak-check the filter assembly is leak-checked according to Section 12.2.4.

11. Annular Denuder System Preparation

Clean all new annular denuder parts obtained from suppliers by placing them in a dilute BRIJ-35 solution. The parts should then be thoroughly rinsed in DDW, rinsed with acetone, and allowed to dry to room temperature. Store with end caps in place.

11.1 Coating Procedure

11.1.1 Cap one end of a denuder using Caplugs (which has the inner tube flush to the outer tube) and set the denuder upright on the capped end. For the denuder with flow-straighteners at both ends, either end may be capped. Measure 10 mL of the citric acid solution and pour into the denuder.

11.1.2 Cap the open end of the denuder and, holding it horizontally, rotate the denuder to distribute the coating solution evenly, wetting all surfaces.

11.1.3 Remove cap and decant excess coating solution into a 100 mL polyethylene bottle.

11.1.4 For the impactor denuder, the coating is performed without the impactor pin in place.

11.2 Drying Procedure

[Note: As denuders dry, they change from translucent to a frosted appearance. Denuders are dry when they become uniformly frosted.]

[Note: A supply of zero air is needed to dry the annular denuder tubes after applying the coating solutions. This air should be free of ammonia, moisture, and particles. Either a tank of pure air or an air purifier assembly can be used.]

11.2.1 Assemble the drying train and manifold as illustrated in Figure 7. Drying train and manifold clean air flow should be adjusted to 2-3 L/min through each denuder. Close toggle valve controlling clean air flow through manifold before attaching denuders.

11.2.2 Attach the flow-straightener end of the denuder to the drying manifold port (see Figure 7).

11.2.3 Open the toggle valve and allow clean air to flow through the denuder tube for 5 min. *Caution:* Excess air flow will cause uneven coating to the tube walls.

11.2.4 Close toggle valve and reverse ends of the denuder attached to the manifold. Start clean air flow again.

11.2.5 When an even frosted appearance is achieved, remove denuder from manifold, cap both ends with clean caps, and store until ready for use. Turn off air to drying manifold. Affix label indicating coating date on denuder.

11.3 Denuder System Assembly

[Note: Described herein is an annular denuder system consisting of one denuder. Extreme care should be exercised in handling and assembling of the ADS if the denuder is made of glass. The coupling of components must be effective to prevent leaks but, at the same time, not stress the glassware. Only patience and practice with the ADS will enable the operators to obtain optimum performance from the system with minimum breakage.]

The annular denuder system (ADS) assembly consists of (1) an inlet nozzle/impactor or cyclone assembly, (2) 1 glass or stainless steel annular denuder tube, and (3) a 1-stage filter assembly. The following procedure involves an inlet nozzle/impactor assembly.

11.3.1 Lay the ADS pieces on a clean surface (i.e., Kimwipes®).

11.3.2 Remove the end caps from the citric acid coated denuder. Gently insert the impactor support pin and coated frit assembly into the denuder-pin support.

11.3.3 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon® clad "O"-ring inside the coupler, if needed.

11.3.4 Attach the filter assembly inlet to the denuder coupler assembly. (The filter assembly has been previously loaded with a Teflon® filter. The components are assembled with plastic couplers.)

11.3.5 Attach the elutriator-acceleration jet assembly to the other end of the denuder. Tighten very gently. DO NOT OVERTIGHTEN.

11.3.6 Tighten the remaining couplers very gently.

11.3.7 Cap elutriator with orange dust cover until used. Attach "quick-release" tube to outlet of filter assembly.

11.4 Laboratory Leak-Check of ADS

Caution: Do not subject the system to sudden pressure changes or filter may tear.

11.4.1 Remove the orange dust cap from the impactor opening. Attach the "quick-release" outlet of the filter assembly to a pump module. Turn on the pump. Be certain that flow through the ADS occurs by checking the rotameter.

11.4.2 Briefly cap the elutriator with the orange dust cap. The flow, as indicated on the rotameter, should drop to zero if no leaks exist.

11.4.3 Disconnect the pump from the ADS at the "quick-release" plug. Cap the "quick-release" plug with an orange dust cover. Turn off the pump. REMEMBER -- Never overtighten joints or breakage will result. If the joints cannot be sealed with gentle tightening, then the Teflon® "O"-rings are worn or defective and must be replaced.

11.4.4 Place the assembled sampler in its field-to-lab carrying case for transport to the field.

[Note: The ADS joints should be loosened slightly when extreme temperature changes are incurred during transportation. This procedure will prevent unnecessary breakage or distortion of the ADS components. Remember to allow the system to adjust to the outdoor air temperature before tightening the joints and checking for leaks.]

11.4.5 Before proceeding to the field, review the following checklist:

- Run IDs on the Field Test Data Sheet (See Figure 9) match labels affixed to the ADS components and filter assembly;
- Recessed ends of the denuder face the inlet;
- ADS ends are capped; and
- Transport case is secured firmly containing the ADS along with chain-of-custody and Field Test Data Sheet.

12. Sampling

12.1 Placement of Denuder System

12.1.1 The placement of the fine particle strong acidity aerosol monitor must conform to a consistent set of criteria and guidance to ensure data comparability and compatibility. A detailed set of monitor siting criteria for ambient air monitoring and meteorological programs is given in the EPA document *Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD)*, EPA-450/4-87-007, EPA Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, May 1987.

Because aerosol acidity is subject to rapid neutralization by ambient bases, the site must be away from localized sources of ammonia, such as composting and livestock operations, landfills, sewage treatment plants, fertilizer plants and storage facilities, and recently plowed fertilized fields.

12.1.2 A summary of key factors that should be considered as part of the placement of an air quality monitoring station containing an ADS are:

- Vertical placement above ground;
- Horizontal spacing from obstructions and obstacles;
- Unrestricted air flow; and
- Adequate spacing from roads.

The ADS sampler is mounted on a supported mast pole or tripod. The ADS inlet should be located 2-3 m above ground level. Placing the inlet closer to ground level should be considered *only* if the surface is flat and man-made (i.e., not unpaved dirt).

12.1.3 A summary of key criteria associated with these siting factors for air monitoring stations is included in Table 1.0. The information included in the table should be used as part of the monitoring network design to ensure that the monitoring program provides representative and unbiased data. However, site-specific constraints could make it very difficult to meet all criteria. For example, wooded areas around a site would make the siting very difficult. The use of the information in Table 1.0, coupled with a balanced evaluation by an experienced air quality and meteorology specialist, is highly recommended.

12.1.4 In general, for a site with no major obstruction and obstacles, the air sampler intake should be about 2-3 m aboveground. For a site with nearby roadways, however, intake placement should take into account the effects of road dust re-entrainment and vehicular emissions. In fact, a linear relationship should be established between the horizontal distance of the sampler intake from the roadway and the aboveground elevation of that intake. For any roadway accommodating more than 3,000 vehicles per day, the intake should be between 5 and 25 m from the edge of the nearest traffic lane. It should also be 15 m aboveground for a distance of 5 m from the nearest traffic lane and 2 m aboveground for a distance of 25 m from the nearest lane. For a roadway supporting less than 3,000 vehicles per day, the intake should be placed at a distance greater than 5 m from the edge of the nearest traffic lane and at a height of 2-15 m aboveground.

12.2 Start-Up

12.2.1 Remove the ADS from its field-to-lab carrying case and load into the field sampling box. Place the assembly in the box with the impactor extended outside the case. The ADS field sampling box is insulated and configured to hold the ADS without allowing movement. Chrome plated spring clips hold the denuder in place. Automatic and manual control switches allow the sampling box to control the temperature of the ADS. The automatic switch should be used when the ADS is not in use and when the ADS is sampling for extended periods of time without constant supervision to prevent low temperature or sudden pressure change exposure of the ADS (these types of exposure can cause leaks to occur, condensation, or the filter to tear). When sampling, the ADS should be kept 1EC above the outdoor temperature to prevent condensation.

12.2.2 Allow the pump to warm up for about 5 min prior to testing.

12.2.3 To check the Heat/Cool cycles, flip one switch from "AUTO" to "MANUAL" and the other between "COOL" and "HEAT." Check to insure that the fan and heater work, respectively.

12.2.4 With the elutriator still capped, turn on the pump with the switch on the timer. The rotameter should indicate zero flow. Run leak check for 5-10 s; then turn off pump and remove elutriator cap. Record leak rate on Field Test Data Sheet (see Figure 9). If there is a flow, refer to Section 12.4 for corrective action for leak test failure. The Field Test Data Sheet is used to keep track of the denuder tube, filter and impactors; it contains information such as run date, sampling period, pump flow rates, start and end times, and other data relevant to each run.

12.2.5 Attach a DGM output to the inlet of the annular denuder system. Turn on pump. Record start time on Field Test Data Sheet. Using a stopwatch, record the time for 20.0 L to pass through the DGM. Record the DGM temperature and the absolute pressure of the DGM.

12.2.6 Calculate the flow rate as follows:

$$Q_{std} = (V/t)(P_b/P_{std})(T_{std}/T_m)(F_c)$$

where:

Q_{std} = flow rate corrected to standard conditions, 25EC and 760 mm Hg, L/min.

V = volume of gas pulled through denuder system, L.

t = time required to pull gas through denuder system, minutes.

P_b = barometric pressure, mm Hg.

P_{std} = standard barometric pressure, 760 mm Hg.

T_{std} = standard temperature, 298EK.

T_m = temperature of dry gas meter, EK(= EC + 273).

F_c = dry gas meter correction factor, dimensionless.

12.2.7 If the calculated flow rate is not between 9.5 and 10.5 L/min, readjust the flow rate until the rate is in the above range. Stop the pump.

12.2.8 Record the flow rate on Field Test Data Sheet.

12.2.9 Remove DGM connection tubing from elutriator inlet. With all information correctly on the Field Test Data Sheet, start the pump and begin sampling. Periodically check system during sampling for constant flow rate.

12.3 Sample Shutdown

12.3.1 Attach DGM connection tubing to the elutriator inlet with pump still running. Measure flow rate. Record calculated flow rate, temperature, and pressure on Field Test Data Sheet.

12.3.2 Turn off the pump. Record time and elapsed time meter reading on Field Test Data Sheet. Remove DGM connection tubing from elutriator inlet. Remove ADS from the sampling box, cap the ends, and place the ADS in field-to-lab carrying case for transport to lab. Secure the latches on the transport case. Be careful not to stress the ADS during the transfer or breakage will result.

Caution: When the ADS is brought from a cold field sampling location to a warm laboratory, loosen the denuder couplings to prevent thermal expansion from breaking the denuder.

12.4 Corrective Action for Leak Test Failure

[Note: These steps should be followed when failure occurs during testing at the laboratory before transport to the field and in the field before sampling.]

12.4.1 Sampler Leaks. Note the problem on the Field Test Data Sheet. Check assembly of ADS components. Replace gaskets. Check for proper seating of denuder surfaces. Replace any defective parts.

12.4.2 Cracked or Chipped Denuder or Elutriator Assembly. Note problem on Field Test Data Sheet. Discard defective pieces. Do not try to extract cracked pieces.

WARNING: USE CAUTION WHEN DISASSEMBLING CRACKED GLASSWARE. PIECES MAY SHATTER AND CAUSE SEVERE CUTS. WEAR PROTECTIVE CLOTHING.

12.4.3 Flow Rate Disagreement. Note problem on Field Test Data Sheet. Check vacuum gauge on flow module. If a high vacuum exists, the sampler has become blocked. This blockage may be due to dust or smoke particles clogging the filter or to obstructions in the system or tubing. Check flow module. Repair as needed.

12.4.4 Inadequate Flow Rate. Note problem on Field Test Data Sheet. Check rotameter on flow controller. If adequate flow is shown here, a leak exists between the controller and the DGM. If no flow is shown on rotameter, check vacuum gauge on controller. If no vacuum exists, pump needs repair. If a high vacuum is shown, an obstruction exists in the system. Check to see that the paper filter dividers were not accidentally installed with the filter in the filter assembly. Check tubing for kinks.

13. ADS Disassembly

13.1 In the laboratory, remove the ADS from the field-to-lab carrying case using both hands. To prevent stress, hold the ADS by its ends.

Caution: Do not stress the ADS while removing it from the case.

13.2 Decouple the elutriator-jet assembly from the first denuder-impactor-coupler assembly.

13.3 The impactor assembly and the denuders *will not* be extracted. However, begin each run with a clean impactor and charged denuder.

13.4 Handling the exposed Teflon® filter requires protection from contamination with NH₃, which rapidly neutralizes aerosol acidity on the filter and may bias the sample results. To ensure ammonia-free air occupies the glove-box, a positive pressure is maintained by blowing air through a PVC tube (4" O.D.) filled with glass-wool dosed with citric acid before entering the manifold which enables uniform distribution of air from top of the glove-box. Flow the ammonia-free air for 5 min before retrieving the filter. Place a citric acid soaked filter paper on the bottom to deplete ammonia when unused. Disassemble the filter assembly in the clean, ammonia-free glove-box. Clean all glove-box surfaces and utensils with methanol. Wearing clean gloves and using clean filter forceps, remove the filter and place in the 100 mL bottle, with the exposed filter surface facing downward. Label the bottle with appropriate information.

14. Extraction Procedure

14.1 Samples should be analyzed as soon after collection as possible. The solutions and extraction procedures must be prepared and performed on the day of pH analysis. Keep samples in a refrigerator until extracted and analyzed.

14.2 Samples should not be extracted until the day of analysis; however, if samples are extracted and it is not possible to analyze them that day, they should be refrigerated. Allow the samples to return to room temperature before analysis.

14.3 The same extract solution (ES) must be used for the samples to be analyzed, the working standards, and the EA solution. Also, the same batch of alcohol must be used to prepare the EA solution and the working standards and to extract the Teflon® filters.

14.4 Handling and extraction must take place in an ammonia-free glove box.

[Note: Teflon® is not wetted by water; therefore, the filter will float on top of an aqueous solution. The use of alcohol aids wetting. Also, all types of Teflon® curl to some extent. The analyst must ensure that the extraction solution makes complete contact with the particle deposit on the Teflon® filter during extraction. A clean plastic (Teflon® or polyethylene) rod or tubing stub may be needed to hold the filter in better contact with the fluid during extraction.]

14.5 Teflon® Filter Extraction

14.5.1 Flush the glove-box with ammonia-free air for at least 5 min before proceeding.

14.5.2 Process the filters in the same order in which they will be analyzed.

14.5.3 Open the sample vial and pipet 200 µL ethanol onto the filter.

14.5.4 As soon as the ethanol has wet the entire surface of the filter, deliver 6.00 mL of ES solution into the vial. Cap the vial.

14.5.5 Put a batch of vials into the ultrasonic bath and sonicate for a total of 20 min, rotating the position of the vials 90° every 5 min.

14.6 Aliquot Preparation

14.6.1 Using a 1 mL automatic pipet, transfer 1 mL of the sample extract into each of two labeled 2 mL vials, one labeled A and the other labeled A1. Subsequent samples will be labeled B and B1, C and C1, etc.

14.6.2 Recap each vial after its aliquots are drawn. Store the original sample vials in a refrigerator for possible repeat analysis or for analysis of other components.

14.6.3 Proceed immediately with pH analysis.

15. pH Analysis

15.1 Standard and Reagent Preparation

15.1.1 Standard H₂SO₄ Solution, 1.000 N

[Note: Each of the standard H₂SO₄ stock solutions must be prepared fresh the day of pH analysis.]

15.1.1.1 Label seven 25 mL polyethylene stoppered volumetric flasks. Also, label each flask with the volume of 1.000 N H₂SO₄ solution that will be added (See Table 2).

15.1.1.2 Use the 25 μ L automatic pipet to add the 1 N stock H₂SO₄ solution to flasks 2 and 3. Use the 100 μ L pipet to add 1.000 N stock H₂SO₄ solution to flasks 4 through 7. Dilute all flasks to the 25 mL mark with ethanol. Cap with stoppers or parafilm and mix well. Proper dilution ratios are indicated in Table 2.

15.1.2 2 M Potassium Chloride (KCl) Solution

15.1.2.1 Weigh 149.2 ± 0.1 g of KCl. Add the KCl to a 2 L flask.

15.1.2.2 Add about 700 mL of DDW water to the flask. Swirl the solution until the KCl is completely dissolved.

15.1.2.3 Pour this mixture into a 1 L graduated cylinder. Rinse the flask with a small amount of DDW water and transfer the rinse into the cylinder. Fill the cylinder to the 1 L mark.

15.1.2.4 Pour the solution from the cylinder into the 1 L polyethylene bottle. Cap and shake the bottle to mix well. Mark the bottle with date of preparation.

15.1.3 0.100 N Perchloric Acid (HClO₄) Solution

15.1.3.1 Fill a 1 L graduated cylinder about half full with DDW. Transfer 10 ± 0.1 mL of 60-62% HClO₄ into the 1 L cylinder with a 10 mL pipet.

15.1.3.2 Fill the cylinder to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.

15.1.3.3 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.

15.1.4 0.010 N HClO₄ Solution

15.1.4.1 Fill a 1 L graduated cylinder about 1/2 full with DDW.

15.1.4.2 Measure 100 mL of the 0.1 N HClO₄ solution with the 100 mL graduated cylinder. Add this to the 1 L cylinder.

15.1.4.3 Fill the 1 L cylinder with DDW to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.

15.1.4.4 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.

15.1.5 Extraction Solution (ES)

[Note: This solution must be prepared fresh on the day of pH analysis.]

15.1.5.1 Measure 20 ± 0.5 mL of 2 M KCl into 2 L erlenmeyer flask.

15.1.5.2 Using a 5 mL calibrated automatic pipet, add 10 ± 0.1 mL of 0.01 N perchloric acid (HClO_4), to the flask. Add 970 ± 10 mL of DDW to the flask.

15.1.5.3 Mix well and cover with parafilm until ready for use.

15.1.6 Extraction Solution with Ethanol (EA Solution)

15.1.6.1 Measure 150 ± 2 mL of ES (prepared in Section 15.1.5) into a 250 mL graduated cylinder. Transfer to a 250 mL erlenmeyer flask.

15.1.6.2 Using a 5 mL graduated cylinder, add 5 ± 0.1 mL of ethanol (from the same fresh bottle of ethanol that was used to prepare the standards in Section 15.1.1) to the flask.

15.1.6.3 Mix well and cover with parafilm until ready for use. (pH of the EA solution should be 4.09 ± 0.04 . If not, the solution must be reprepared.)

15.1.7 Working Standard Test Solutions

15.1.7.1 Place fourteen 4 mL polystyrene sample vials (as used with Technicon Auto-Analyzer II system) labeled 1A, 1B, 2A 2B...7A, 7B into support racks. Using the calibrated dispensing pipet bottle, add 3 mL of ES solution to each 4 mL vial.

15.1.7.2 Using the displacement pipet, add 50 μL of ethanol to each vial. Pour about 3 mL of Standard Flask #1 H_2SO_4 standard (see Section 15.1.1) into a labeled 4 mL vial.

15.1.7.3 Immediately pipet 50 μL of this standard into the 4 mL vials labeled 1A and 1B containing the ES solution and ethanol.

[Note: This transfer must be done without delay to prevent the standard concentration from increasing significantly due to evaporation of the ethanol solvent.]

15.1.7.4 Repeat the procedure for each of the other 6 standards. If there is a delay of more than 5 min between the preparation of these mixtures and the next step, put caps on the 4 mL vials.

[Note: There should be 14 vials, each containing 3 mL of ES solution, 50 μL of ethanol, and 50 μL of Standard H_2SO_4 solution (see Section 15.1.1). Two aliquots from each vial (1A, 1B, 2A, 2B, 3A, 3B,...7A, 7B) will be analyzed.]

15.1.7.5 Place vial 1A in a rack. In a second rack place two 2 mL vials labeled 1A1 and 1A2. Use the 1 mL automatic pipet to mix the contents of vial 1A by drawing 1 mL into the pipet tip and then dispensing it back into the vial three times. Then use the same pipet to transfer 1 mL of the contents of vial 1A to each of the two labeled (1A1, 1A2) 2 mL vials. Place caps on the vials. After transferring the two aliquots, rinse the automatic pipet tip in a flask of DDW. Repeat the transfer procedure for each of the other working standard pairs. (1B aliquot into vials 1B1 and 1B2, 2A aliquot into vials 2A1 and 2A2, etc.). These are the working standards.

15.2 Calibration of pH Meter

The pH meter requires temperature calibration whenever a new electrode is used. Use the manufacturer's procedure in the instrument manual. This calibration should be repeated every 3 months when not in use. The pH meter is left with the power cord plugged into the AC outlet, the mode control knob is left in the

standby position, and the combination electrode is immersed in a 4 M KCl solution (a slit rubber stopper seals the bottle with the electrode in it). Keep a record of the temperature calibrations in a lab notebook.

15.3 Pre-Analysis Calibration

[Note: The steps for proper calibration and set-up for analysis of the Teflon® filter sample for pH determination are outlined in Figure 10. Analysis should be performed at room temperature.]

[Note: The pH buffer solutions are not used for any quantitative purpose. They are used to standardize the electrodes and as a diagnostic to verify that the pH measurement system is working as expected before beginning analysis of the samples.]

15.3.1 Use a pH Analytical Laboratory Log Form (see Figure 11) to record all data.

15.3.2 Fill three 4 mL vials with pH 7 buffer. Withdraw the electrode from the 4 M KCl bottle and wipe the tip gently with a Kimwipe® to remove the bulk of the solution. Rinse the electrode with one vial of pH 7 buffer. Do not test pH of the first vial.

15.3.3 Immerse the electrode in the second vial of the pH 7 buffer. Use a small bottle or other support to hold the vial up to the electrode while waiting for the meter reading to equilibrate.

15.3.4 Test the pH by turning to the pH mode of the meter. Allow the reading to stabilize for at least 30 s. Record the result on the Analytical Laboratory Log Form for pH 7, entry 2.

15.3.5 Turn to standby mode and test the last vial of pH 7 buffer. Record the results on the log form for pH 7, entry 3. If the pH value for the 2nd cup is not 7.00 ± 0.01 , adjust the "calib." knob to obtain a reading of 7.00. Note this adjustment on the log form.

15.3.6 Fill three 4 mL vials with pH 4 buffer. With the meter in the standby mode, remove the cup containing pH 7 buffer, wipe the tip of the electrode gently with a Kimwipe®, and then rinse the electrode with the first vial of pH 4 buffer. Do not record pH.

15.3.7 Test the next two vials of pH 4 buffer as above, recording the results on the log form. If the pH value for the third vial is not 4.00 ± 0.01 , adjust the "slope" knob to get a reading of 4.00. If the value for the second vial was not 4.00 ± 0.01 , the calibrations at pH 7 and at pH 4 must both be repeated.

15.4 pH Test of HClO₄ Solutions

[Note: The 0.01 N HClO₄ solution is used to prepare the ES solution, which is used to prepare the EA solution. The pH value for the EA solution must be 4.09 ± 0.04 . If this pH value is not achieved, one or more of the HClO₄ solutions must be reprepared.]

15.4.1 Finish the calibration of the pH meter with pH 4 buffer.

15.4.2 Rinse the pH electrode with DDW. Wipe the tip of the electrode with a Kimwipe®.

15.4.3 Fill three 4 mL vials with EA solution. Measure the pH of the test EA solution in similar fashion to the buffer solutions. The values must be 4.09 ± 0.04 .

15.4.4 If the above pH values are not achieved, follow Section 15.1.6 to reprepare the solutions. Test the pH of the new solutions. Repeat as necessary to obtain an average pH of 4.09 ± 0.04 .

15.4.5 Leave the electrode immersed in the "3rd vial" with the meter in the standby mode until ready to start analysis of the working standards.

15.5 Analysis of Working Standard

[Note: Immediately following the EA analysis, start testing the working standards.]

15.5.1 With the pH meter still in the standby mode, remove the last vial from the electrode, gently wipe the tip with a Kimwipe®, and immerse the electrode into the working standard vial 1A1.

[Note: Only two vials are available for each working standard (also for filter extracts). Thus, pH measurement is made for both of the two vials for each sample. Also, the electrode tip is not wiped between the 1st and 2nd vials of each sample.]

15.5.2 After testing the pH of vial 1A1, test vial 1A2. Record the results of both on the Analytical Laboratory Log Form.

15.5.3 With the meter in the stand-by mode, remove vial 1A2, wipe the electrode with a Kimwipe® and test one 2 mL vial of EA solution.

15.5.4 Test a 2nd vial of EA solution; record the results on the log form. Discard the 1st vial of EA, but retain the 2nd vial to be used as the 1st vial for the next EA test.

15.5.5 Mean pH value for the EA solutions should be 4.09 ± 0.04 . If the above pH values are not achieved, follow Section 15.1.6 to reprepare the EA solution. Retest. If still outside range, investigate the problem with the probe and review previous recorded pH data for samples and EA solutions to determine validity of measurements.

15.5.6 Continue testing the remainder of the working standards, 1B1, 1B2, 2A1, 2A2, 2B1, 2B2, ... 7B1, 7B2. Remember to wipe the electrode tip both before and after each pair of test solutions, but not in between two vials of the same sample.

[Note: If there is trouble in obtaining constant pH values, a magnetic stirrer may be used to keep the contents to be measured uniform. If employed, ensure that the sample vials are insulated from any temperature increase of the stirring platform that may occur during extended use.]

15.5.7 Use the mode control knob in the "temp." position to measure the temperature of the test solutions every 5-10 samples and record the results on the Analytical Laboratory Log Form.

15.6 Analysis of Filter Extracts

After measuring the pH of the working standards, measure the pH of the filter extract and record on the Analytical Laboratory Log Form. After ten filter extracts have been tested, make an additional test with the EA solution and record temperature. At the end make a final test of pH 4 buffer. If not 4.00 ± 0.04 , perform a new calibration; the laboratory manager must then decide (and document) how to reduce the unknowns based on pre- and post-calibrations. Criteria and corrective action should be met according to Section 15.5.5. Follow manufacturer's directions for shut-down of pH meter. Immerse the electrode tip in the bottle of 4 M KCl.

16. Assumption of Annual Denuder System

16.1 Measuring acid aerosol requires that ammonia be eliminated from the sample stream to prevent inaccurate measurement of the acid aerosol, thus biasing the results. To address this issue, a citric acid coated denuder to remove (denude) ammonia from the gas stream is positioned in front of the filter assembly

where strong acid aerosols are collected. The efficiency of the citric acid denuder to remove NH_3 is assumed to be 100%.

16.2 The efficiency of the impactor collection system decreases with increased particulate loading. The average operational time before such loading occurs has not been determined. Likewise, the removal efficiency of the denuders have not been fully explored. Therefore, both the impactor and denuders are removed after each sampling event and replaced with new components.

16.3 Other assumptions associated with the performance of the annular denuder system for validity of the calculations presented in Section 17 are:

- All alkaline particles ($> 2.5 \mu\text{m}$) are removed at the sampler inlet;
- The cyclone or elutriator/impactor assembly cut particles with diameter (aerodynamic) of $2.5 \mu\text{m}$ or greater;
- The citric acid coated-denuder removes 100% of ammonia from the gas sample stream;
- Fine ($< 2.5 \mu\text{m}$) acid (H_2SO_4) aerosol losses in the denuder are less than 1%;
- The Teflon[®] filter is 100% efficient in collecting fine acid aerosols; and
- The molar ratio of NH_4NO_3 to H_2SO_4 is assumed to be less than 10%. However, if NH_4NO_3 is captured on the Teflon[®] filter, its dissociation during sampling may occur, thus affecting acidity measurements. The user is responsible for determining what is and is not a "significant" molar ratio of NH_4NO_3 to H_2SO_4 .

17. Atmospheric Species Concentration Calculations

17.1 Calculations Using Results from pH Analysis

Earlier pH determinations have been based on the pH buffer concentrations, the activity of the solution, and the antilog of the measured pH value. More recent studies have steered away from the issue of activity by comparing the results of the standards, thus alleviating errors introduced by biasing the activities of ions retained on filters on those retained in solution. The methodology developed from these more recent studies is described herein. The end results are reported in terms of mass of equivalent of ions. Appropriate values of accuracy and precision with respect to H^+ concentrations for this method are 10% and 5%, respectively, for sample pH values in the 4.00 to 7.00 range.

17.1.1 Adjustment for Filter vs. Non-Filter Standards. This adjustment is necessary because experiments showed that the measured acid concentration from filters doped with H_2SO_4 stock standards yielded concentrations, as measured by the difference from EA solution, that were about 3% lower than the values found for working standards (prepared without filters from the same stock standards). The results gave the following relation (by linear regression):

$$C_f = -0.11 + 0.971 (C_{nf})$$

where:

C_f = calculated net strong acid concentration as would be obtained from filter standards doped with H_2SO_4 .

C_{nf} = the apparent net strong acid concentration of H_2SO_4 base on standards prepared without filters.

For each working standard (non-filter), on a given analysis day, calculate the "apparent net strong acid concentration of H_2SO_4 " as follows:

$$C_{nf} = 10^{-pHWS} - 10^{-pHEA}$$

where:

pHWS = measured pH for a working standard (or apparent strong acid concentration for non-filter H_2SO_4 doped standards).

pHEA = measured pH for the EA solution (or apparent strong acid concentration for non-filter, non- H_2SO_4 doped standard).

After calculating the C_{nf} values for each working standard, use the above equation to calculate the adjusted values of C_f for each.

17.1.2 Determination of Nominal Strong Acid Concentration for Filter Samples. The apparent net strong acid concentration of each sample filter extract, C_s , is calculated as with the working standards:

$$C_s = 10^{-pHS} - 10^{-pHEA}$$

where:

pHS = measured pH of the sample filter extract (or apparent strong acid concentration for sample filters extracts).

pHEA = measured pH for the EA solution (or apparent strong acid concentration for non-filter, non- H_2SO_4 standards).

[Note: The C_s values for the filter extracts are directly comparable to the C_f values for the working standards, since the C_f values have been adjusted for the difference in apparent acid concentration for tests made with filters and tests made without filters.]

17.2 Calculation of Air Volume Sampled, Corrected to Standard Conditions

17.2.1 The total sampled air volume, V_t , for each sample is calculated using the data from the Field Test Data Sheet. These data include the initial and final elapsed times, the initial rotameter reading, and the rotameter I.D. No. Use the calibration curve for the given rotameter to calculate the flow for the sample, in LPM, if applicable. Calculate the value of V_t as follows:

$$V_t = [F] [t]$$

where:

F = flow from the calibration curve, L per minute.

t = net elapsed time, min.
 V_t = total sample volume, L.

17.2.2 Convert L to m^3 by:

$$V_s = V_t \times (10^{-3})$$

where:

V_s = total sampling volume, m^3 .
 10^{-3} = conversion factor, m^3/L .

17.2.3 Calculate the air volume sampled, corrected to EPA-reference conditions:

$$V_{std} = V_s Y \left(\frac{T_{std}}{T_m} \right) \left(\frac{P_{bar}}{P_{std}} \right)$$

where:

V_{std} = volume of sample at EPA-reference conditions, m^3 .
 V_s = volume of gas sample through the dry gas meter, or calculated volume sampled as indicated by rotameter (see Section 17.2.1), m^3 .
 T_{std} = absolute EPA-reference temperature, 298EK.
 T_m = average flowmeter or dry gas meter temperature, EK.
 P_{bar} = barometric pressure of flow or volume measurement condition, mm Hg.
 P_{std} = EPA-reference barometric pressure, 760 mm Hg.
 Y = dry gas meter calibration factor (if applicable), dimensionless.

17.3 Calculation of Strong Acidity Aerosol Concentration

17.3.1 Calculate the final concentration of apparent net fine particle (< 2.5 μm) strong acidity (as H_2SO_4):

$$C(H^+) = C_f / V_{std}$$

where:

C_{H^+} = apparent net fine particle strong acidity concentration, Fg/m^3 .
 C_f = apparent net strong acid, Fg , as calculated from standard curve.
 V_{std} = volume of sampled gas at EPA-reference conditions (see Section 17.2.3), m^3 .

18. Method Safety

This procedure may involve hazardous materials, operations, and equipment. This method does not purport to address all of the safety problems associated with its use. The user must establish appropriate safety and health practices to determine the applicability of regulatory limitations prior to the implementation of this procedure. These precautions should be part of the user's SOP manual.

19. Performance Criteria and QA

Required quality assurance measures and guidance concerning performance criteria that should be achieved within each laboratory are summarized and provided in the following section.

19.1 Standard Operating Procedures (SOPs)

19.1.1 SOPs should be generated by the users to describe and document the following activities in their laboratory: (1) assembly, calibration, leak check, and operation of the specific sampling system and equipment used; (2) preparation, storage, shipment, and handling of the sampler system; (3) purchase, certification, and transport of standard reference materials; and (4) all aspects of data recording and processing, including lists of computer hardware and software used.

19.1.2 Specific instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the monitoring work.

19.2 QA Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted regularly and should be part of the QA program. Additional QA measures (e.g., trouble shooting) and further guidance in maintaining the sampling system are provided by the manufacturer. For detailed guidance in setting up a quality assurance program, the user is referred to the *Code of Federal Regulations* (see Section 20, Citation 11) and the *EPA Handbook on Quality Assurance* (see Section 20, Citation 12).

19.2.1 Field QA. It is recommended that the flow rates of each denuder system be audited at least quarterly.

19.2.2 Laboratory Quality Control (QC). It is recommended that the laboratory QC program include the following as minimum requirements.

19.2.2.1 Include a reagent blank with each set of twenty (20) samples or less of each matrix (i.e., denuder extract, filter extract, etc.)

19.2.2.2 Include a laboratory duplicate with each set of twenty (20) samples or less of each matrix.

19.2.2.3 Include a laboratory control sample (LCS), also known as a laboratory blank spike (LBS) with each set of twenty (20) samples or less of each matrix.

20. References

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TABLE 1. SUMMARY OF KEY PROBE SITING CRITERIA FOR
ACID AEROSOL MONITORING STATIONS

Factor	Criteria
Vertical spacing above ground	<ul style="list-style-type: none"> • Representative of the breathing zone and avoiding effects of obstruction, obstacles, and roadway traffic. Height of probe intake above ground in general, 2-3 m above ground and 2-15 m above ground in the case of nearby roadways. • About 1 m or more above the structure where the sampler is located.
Horizontal spacing from obstruction and obstacles	<ul style="list-style-type: none"> • Minimum horizontal separation from obstructions such as trees should be > 20 m from the dripline and must be 10 m from the dripline when the trees act as an obstruction. • Distance from sampler inlet to an obstacle such as a building must be at least twice the height the obstacle protrudes above the sampler. • If a sampler is located on a roof or other structures, there must be a minimum of 2 m separation from walls, parapets, penthouses, etc. • There must be sufficient separation between the sampler and a furnace or incinerator flue. The separation distance depends on the height and the nature of the emissions involved.
Unrestricted airflow Spacing from roads	<ul style="list-style-type: none"> • Unrestricted airflow must exist in an arc of at least 270E around the sampler, and the predominant wind direction for the monitoring period must be included in the 270E arc. • A sufficient separation must exist between the sampler and nearby roadways to avoid the effect of dust re-entrainment and vehicular emissions on the measured air concentrations. • Sampler should be placed at a distance of 5-25 m from the edge of the nearest traffic lane on the roadway depending on the vertical placement of the sampler inlet which could be 2-15 m above ground.

TABLE 2. DILUTION RATIOS

Standard H ₂ SO ₄ flask	Volume of 1.000 N H ₂ SO ₄ added to each flask, (μL)	Working standard concentration, 10 ⁻³ N H ₂ SO ₄	Equivalent strong acid mass collected on filter (C _{eq}), μg ^a	Approximate pH
1	0	0	0	4.09
2	25	1	4.90	4.01
3	50	2	9.80	3.95
4	100	4	19.60	3.84
5	200	8	39.20	3.68
6	400	16	78.40	3.48
7	800	32	156.80	3.23

^aBased on 6.2 mL extraction volume.

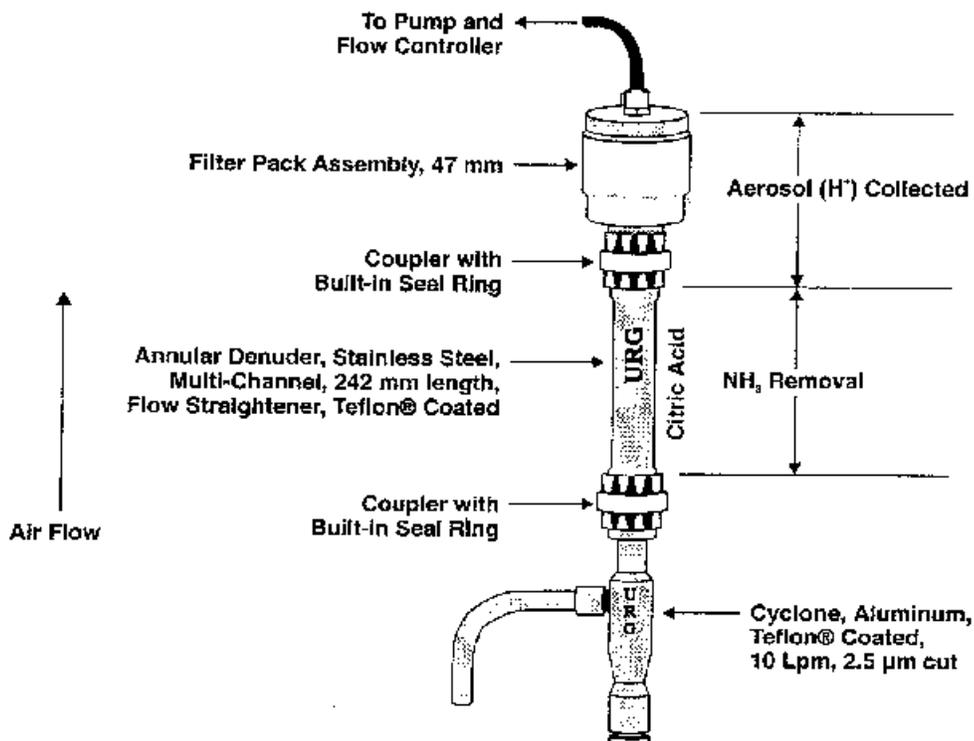


Figure 1a. Annular Denuder System (ADS) with Cyclone.

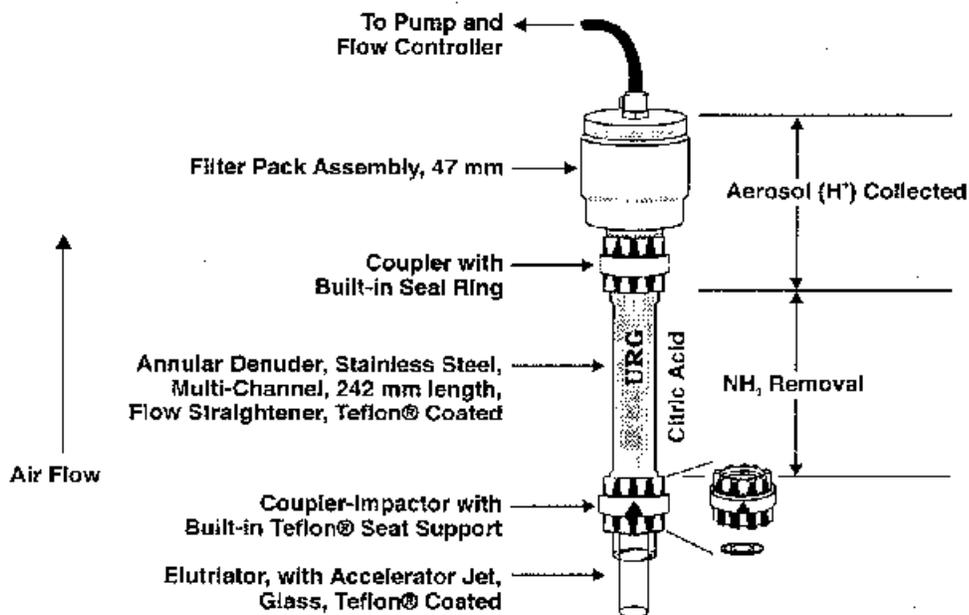


Figure 1b. Annular Denuder System With Impactor Assembly.

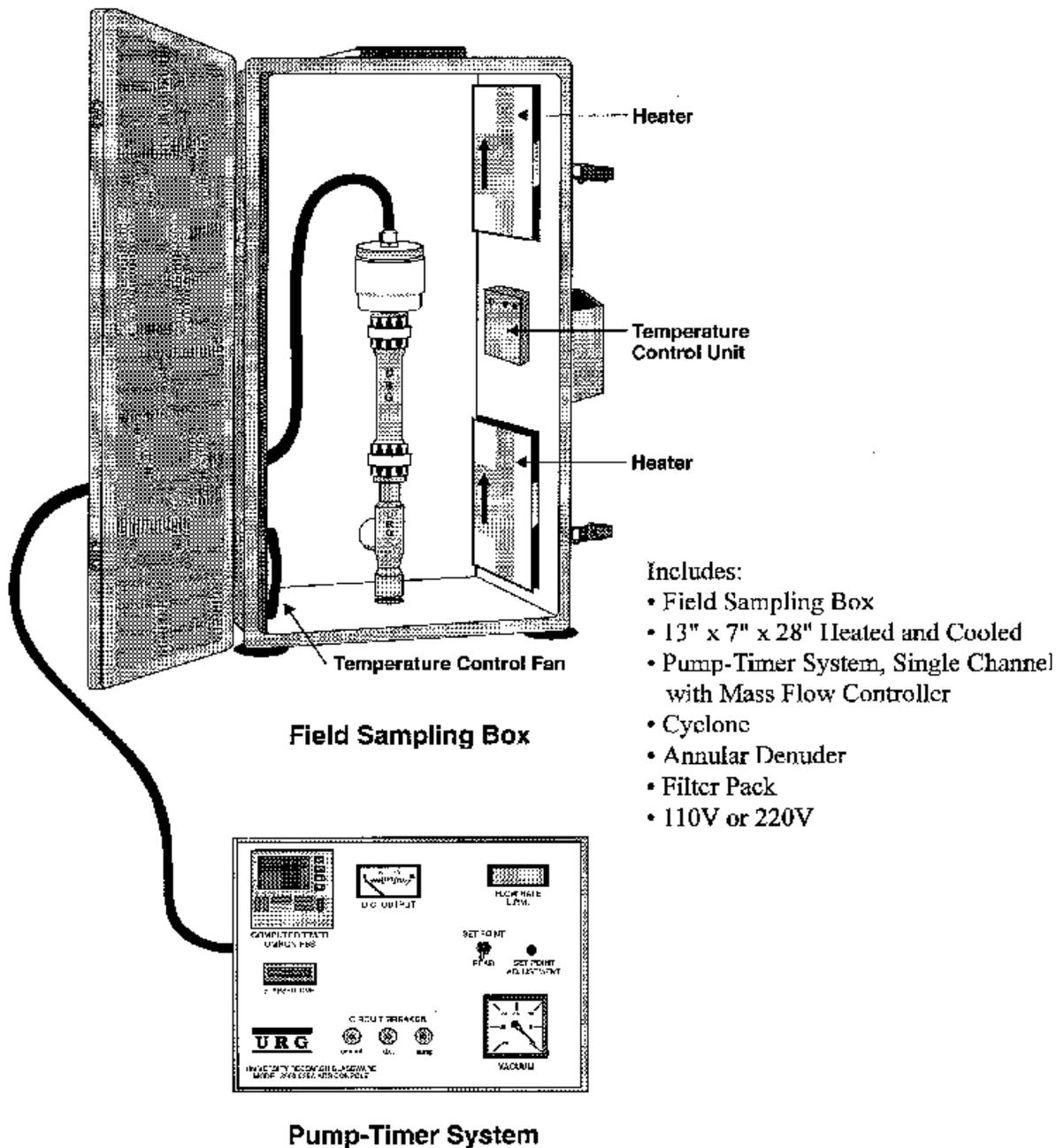


Figure 2. Annular Denuder System in Field Sampling Box With Pump-timer System.

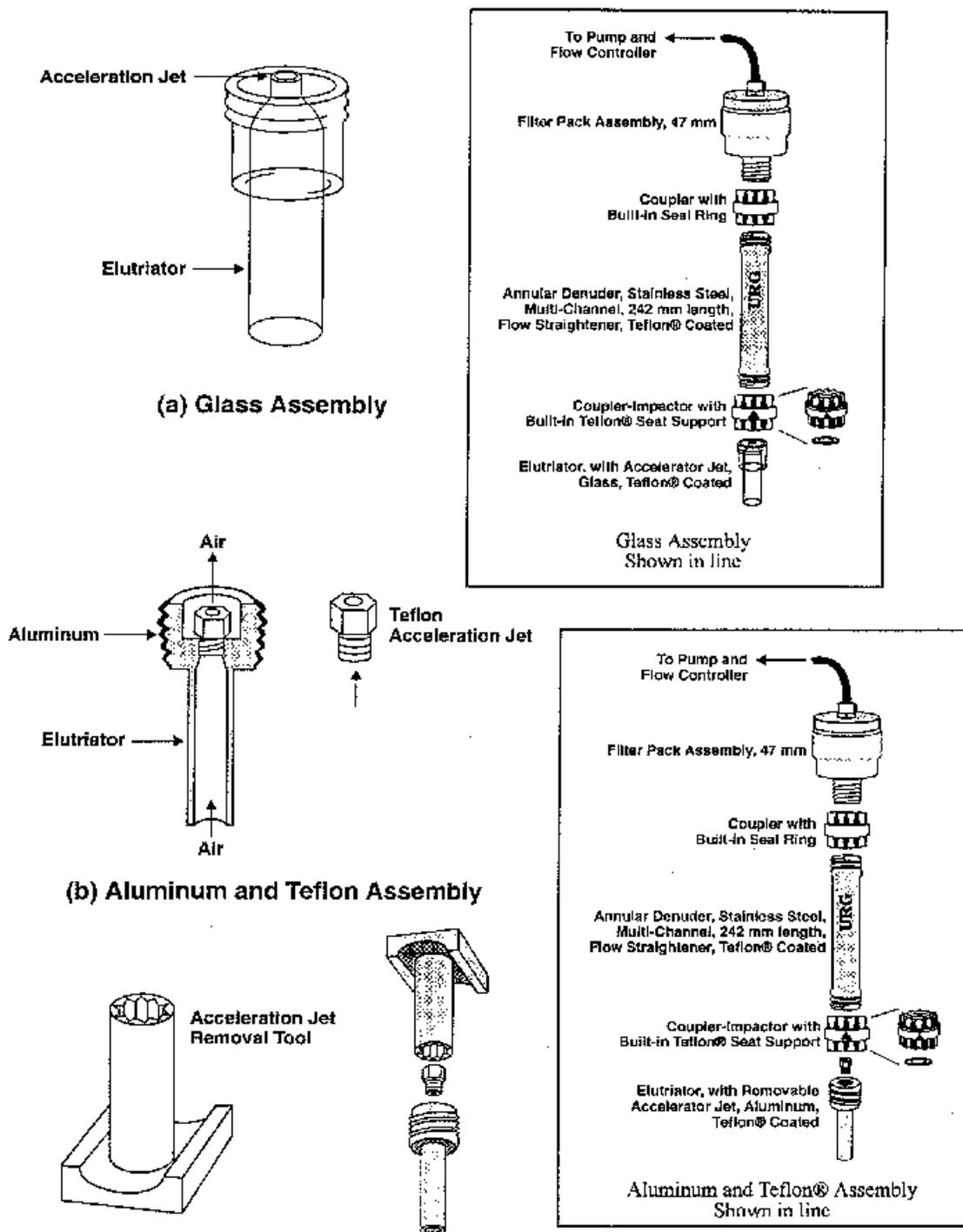


Figure 3. Available Elutriator and Acceleration Jet Assemblies.

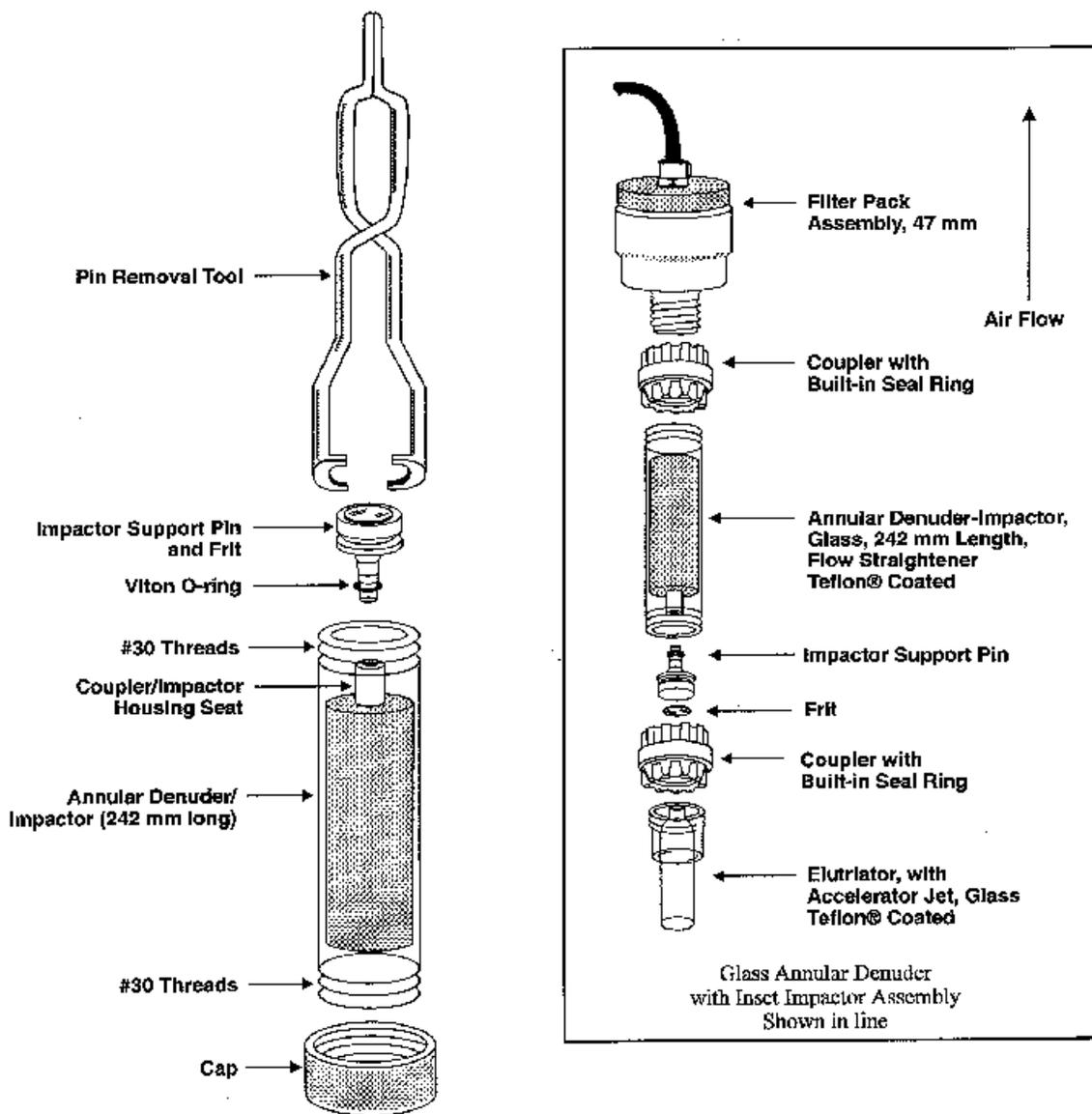


Figure 4. Glass Annular Denuder With Inset Impactor Assembly.

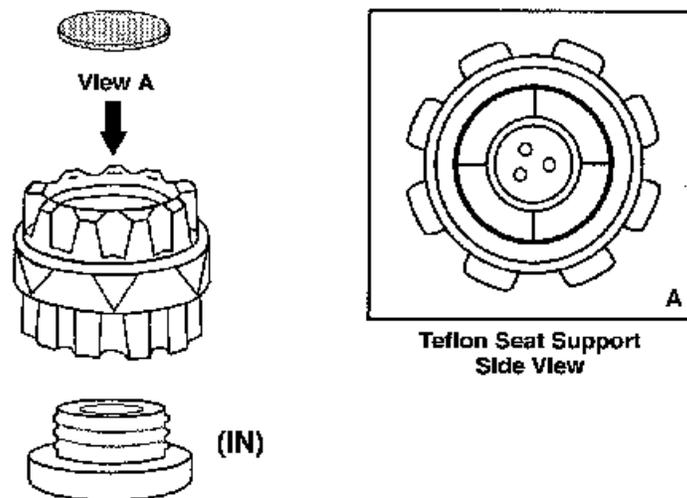
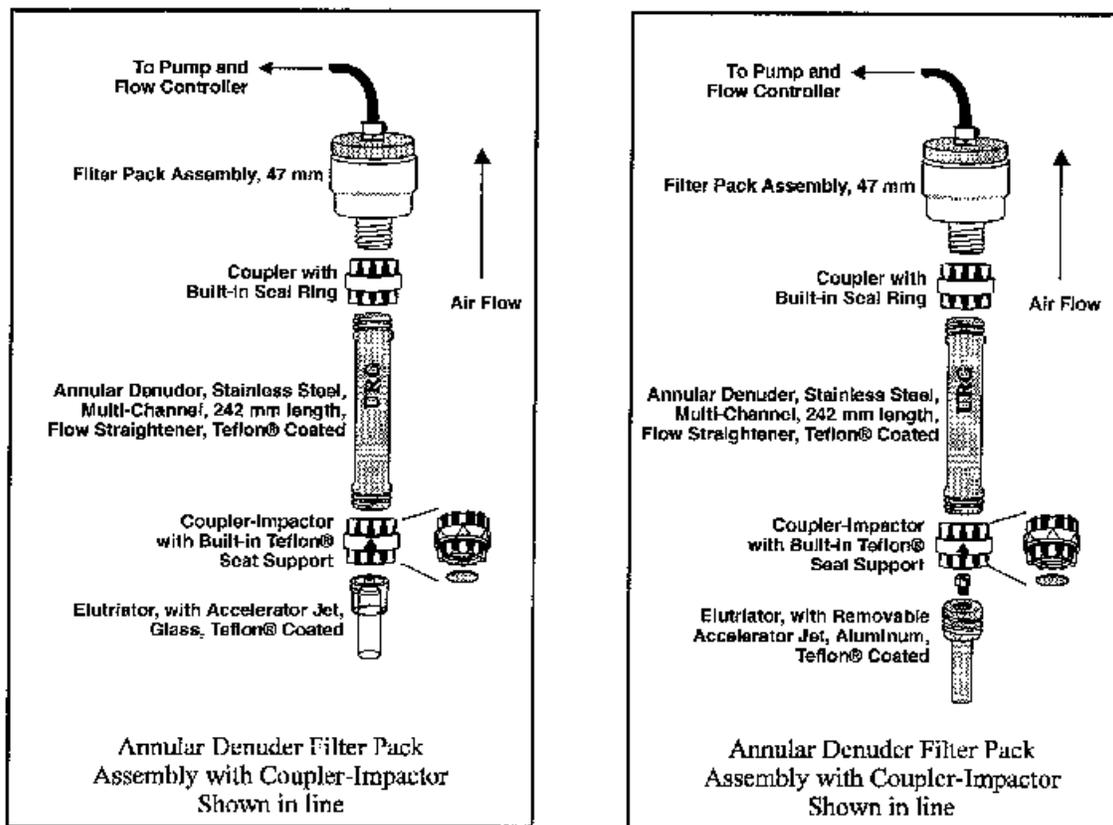


Figure 5. Side View Impactor/Coupler Assembly.

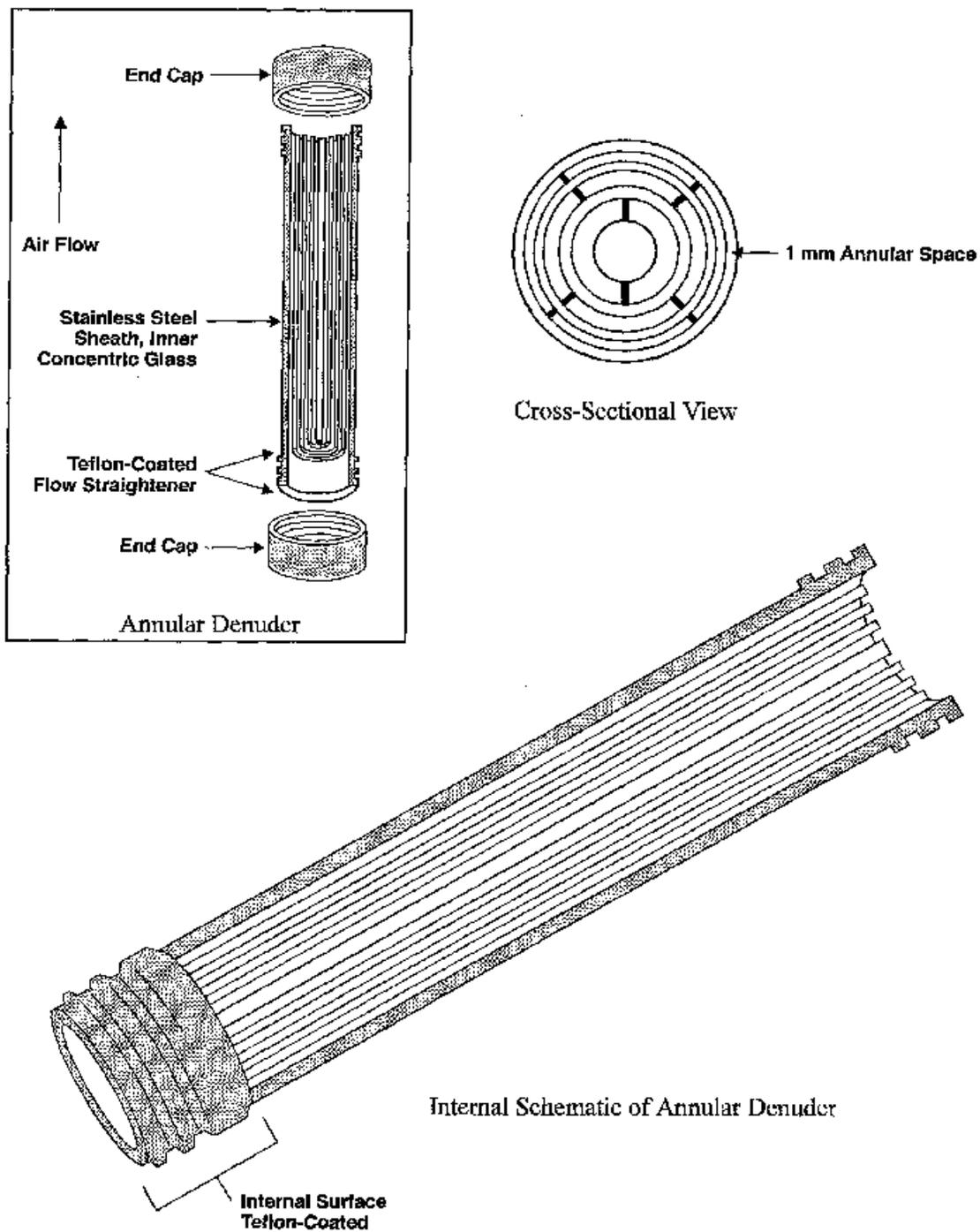


Figure 6. Internal Schematic of Annular Denuder.

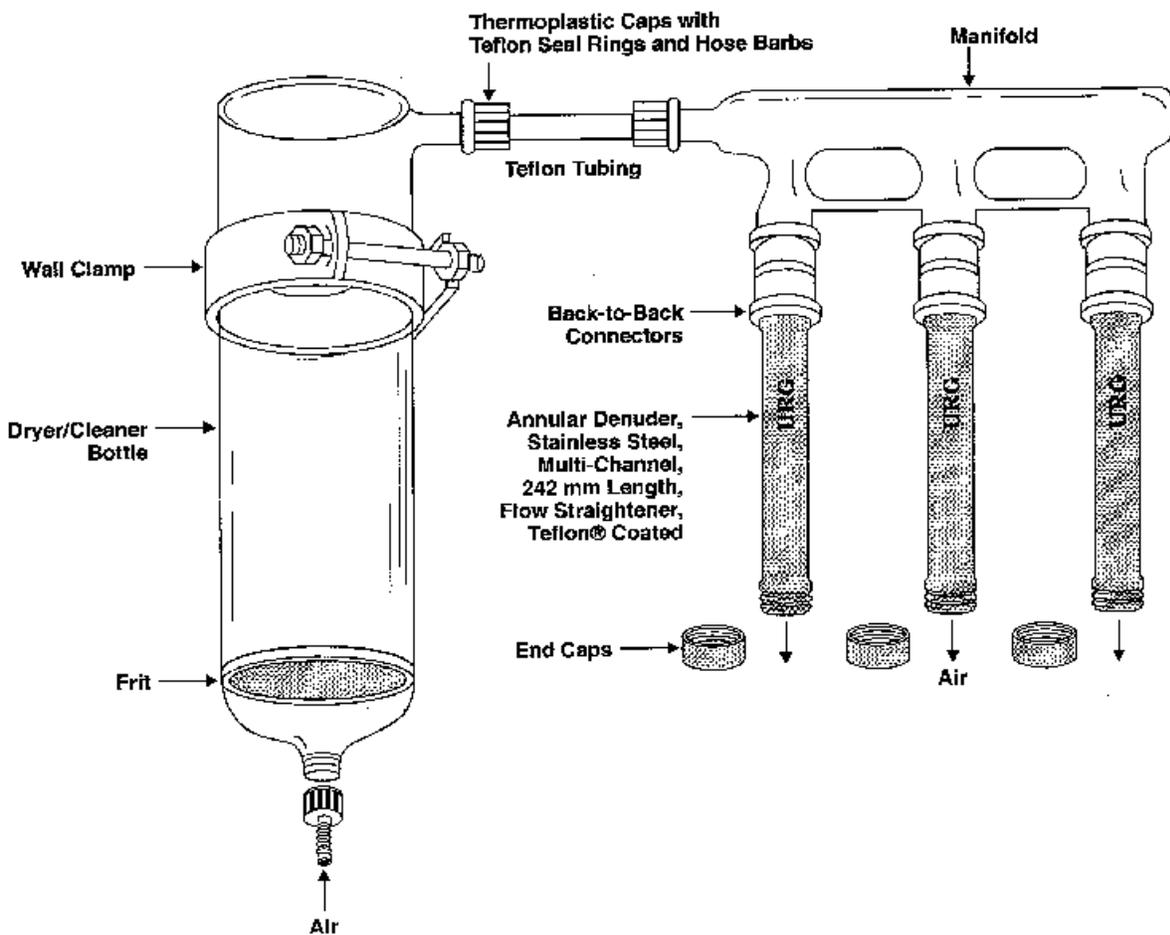


Figure 7. Drying Train and Manifold.

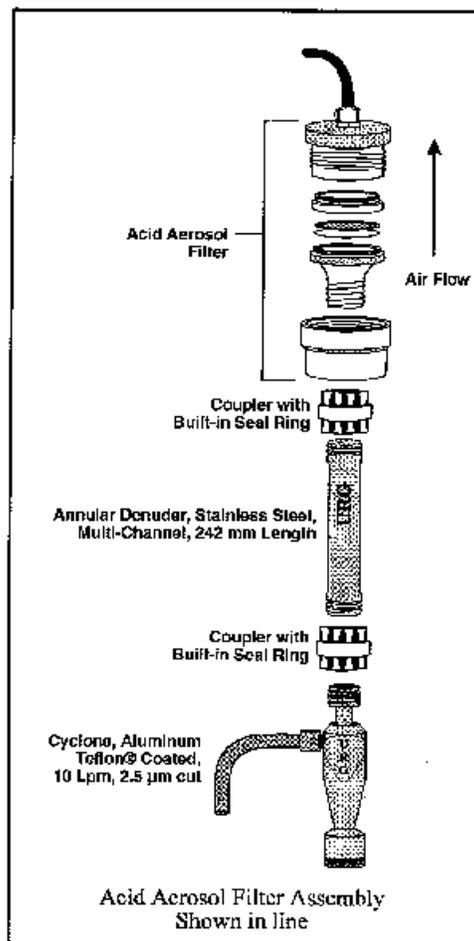
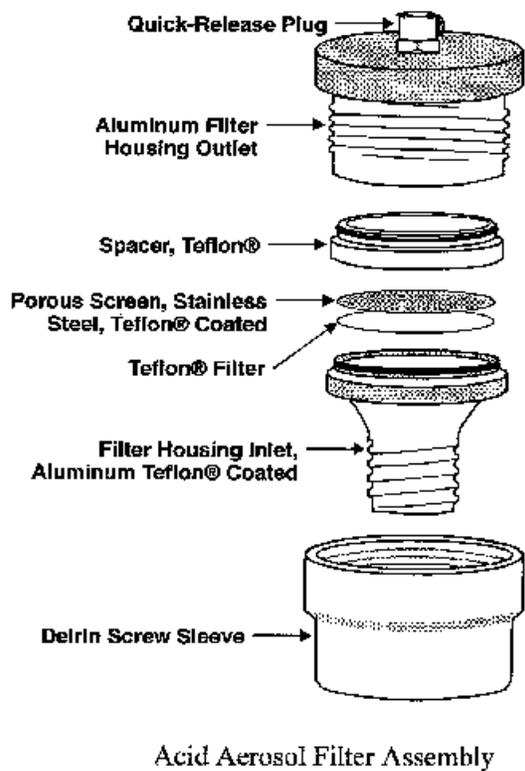


Figure 8. Acid Aerosol Filter Assembly.

DETERMINATION OF THE STRONG ACIDITY OF
ATMOSPHERIC FINE-PARTICLES (< 2.5Fm)

GENERAL

Project: _____
 Site: _____
 Location: _____

 Sample Code: _____

Date: _____
 Location of Sampler: _____

 Operator: _____

EQUIPMENT

Mass Flow
 Controller No.: _____
 Lab Calibration Date: _____
 Flow Rate Set Point: _____
 Calibrated By: _____
 Rotameter No.: _____
 DGM No.: _____

Sampler
 Citric Acid Denuder No.: _____
 Filter Assembly No.: _____

SAMPLING DATA

Time
 Time: _____
 Flow Rate: _____
 Temperature: _____
 Pressure: _____
 Avg. Flow Rate: _____
 Leak Check (Before): _____
 (After): _____
 Total Sample Vol.: _____
 Flow Maintained Rate: _____ (± 5%)

Stop

Time	Flow Rate (Q), L/min	Ambient Temperature, EC	Barometric Pressure, mm Hg	Relative Humidity, %	Comments

Figure 9. Annular Denuder Field Test Data Sheet.

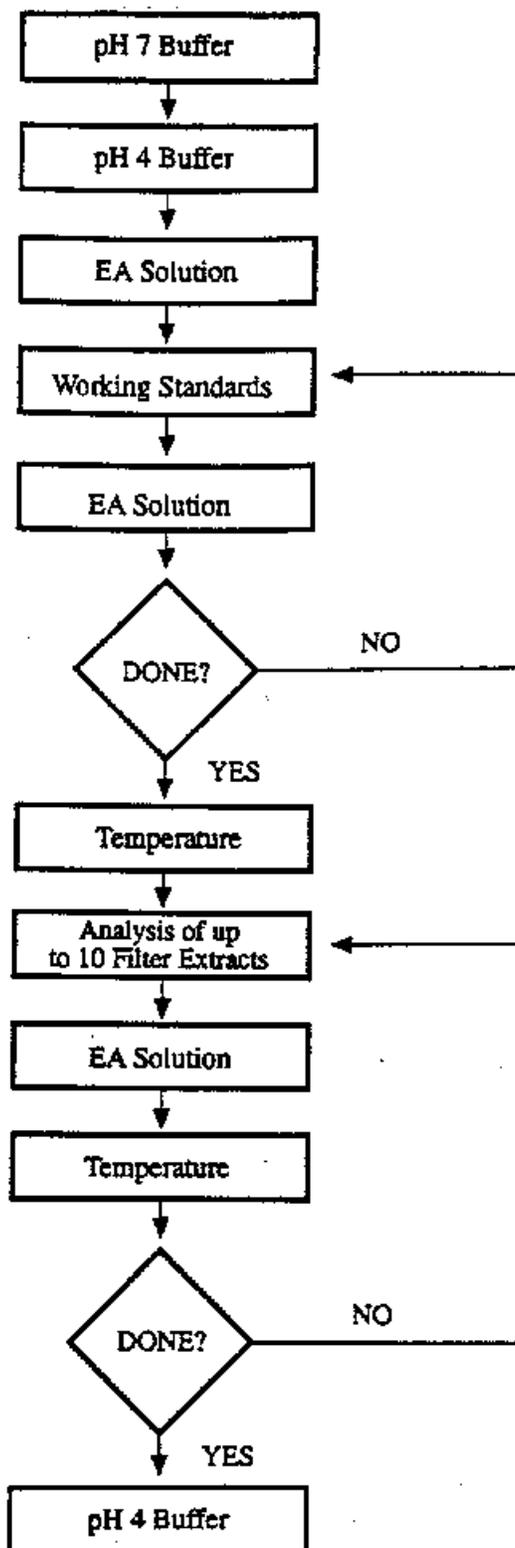


Figure 10. Calibration and Analysis Step for pH Determination.

Determination of the Strong Acidity of
Atmospheric Fine-Particles (< 2.5 Fm)

Name: _____
Date: _____
LAB: _____

Sample I.D.: _____
Location: _____

Constituent	RUN NUMBER						
	1	2	3	4	5	6	7
pH 7 Buffer							
1							
2							
3							
pH 4 Buffer							
1							
2							
3							
EA Solution							
1							
2							
3							
Working Standards							
1A1							
1A2							
EA							
1B1							
1B2							
EA							
2A1							
2A2							
Temp.							
EA							
2B1							
2B2							
EA							
3A1							
3A2							
EA							
Temp.							
3B1							
3B2							
EA							

Figure 11. pH Analytical Laboratory Log Form.

Constituent	RUN NUMBER						
	1	2	3	4	5	6	7
4A1							
4A2							
EA							
4B1							
4B2							
Temp.							
EA							
5A1							
5A2							
EA							
5B1							
5B2							
EA							
6A1							
6A2							
Temp.							
EA							
6B1							
6B2							
EA							
EA							
7A1							
7A2							
EA							
7B1							
7B2							
Temp.							
Sample Extracts							
A							
A1							
B							
B1							
C							
C1							
D							
D1							
E							
E1							
EA							
Temp.							
EA Solution							
1							
2							
3							
pH4 Buffer							
1							
2							
3							

Figure 11 (cont). pH Analytical Laboratory Log Form.