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

Compendium Method IO-4.2

DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND STRONG ACIDITY OF ATMOSPHERIC FINE PARTICLES (< 2.5 µm)

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DISCLAIMER

Method IO-4.2
Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles (< 2.5µm) in Ambient Air

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Method IO-4.2
DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND STRONG ACIDITY OF ATMOSPHERIC FINE PARTICLES (< 2.5µm)

1. Scope

1.1 The quantitative measurement of reactive acidic and basic gases and strong acidity of atmospheric fine particles in ambient air using annual denuder technology is described in this method. The difference between Inorganic Compendium Methods IO-4.1 and IO-4.2 is that the latter accounts for possible interference from the dissociation of ammonium nitrate aerosol from particles collected on the filter by two mechanisms:

$$NH_4NO_3 = NH_3(g) + HNO_3(g)$$

$$NH_4NO_3 + NH_4HSO_4 = (NH_4)_2SO_4 + HNO_3$$

Consequently, an accurate and quantitative value for determining strong acidity of atmospheric fine particle is calculated.

1.2 The chemical species that can be determined by this method are gaseous SO_2, HNO_2, HNO_3, and NH_3 and particulate $SO_4^=$, NO_3^-, NH_4^+, and H^+. Detection and quantitation limits are given in Table 1.

1.3 This method is a composite of methodologies developed by the U. S. Environmental Protection Agency (EPA), Harvard University and the CNR Laboratories (Italy). A number of air pollution studies in Italy, United States, Canada, Mexico, Germany, Austria, and Spain, and in public health services, epidemiology, and environmental research centers have used this method.

1.4 The equipment described herein is used to measure acidic and basic gases and strong acidity of atmospheric fine particles contained in ambient air. The methodology originally was developed for monitoring regional-scale acidic and basic gases and strong acidity of atmospheric fine particle in support of EPA's field programs involving the Integrated Air Cancer Research Program and the Acid Deposition Network. Similarly, the methodology has been used to characterize the urban haze in Denver, Houston, and Los Angeles.

1.5 The techniques, procedures, equipment, and other specifications comprising this method are derived and composited from those actually used by 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 judgement 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 test any such alternatives to determine their adequacy and confirm and document their advantages. Information and comments are solicited on improvements, alternative equipment, techniques, specifications, performance, or any other aspect of the method.

2. Applicable Documents

2.1 ASTM Standards

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

2.2 Other Documents

- Ambient Air Studies (1-14).
- U. S. EPA Acid Aerosol Document (15).

3. Summary of Method

3.1 The annular denuder system (ADS) consists of (1) an inlet with an impactor or cyclone preseparator designed to remove all particles with a diameter (aerodynamic) of 2.5 µm or greater, (2) annular denuders to quantitate acidic and basic gases, and (3) a filter pack for atmospheric acidity and particles. In operation, ambient air is drawn through an elutriator-accelerator jet assembly, an impactor frit and coupler assembly, and past glass denuder walls that have been etched and coated with chemicals that absorb the gaseous species of interest. The remaining air stream is then filtered through Teflon® and Nylasorb® membrane filters. Teflon® and nylon membrane filters are used to capture ammonium and nitrate aerosol and sulfate particulate matter. Nitric acid and sulfur dioxide will also be collected by the nylon filter but these measurements are treated as interference. The ADS is illustrated in Figure 1. The field sampling box with the ADS and pump-timer system is shown in Figure 2.

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 annular denuders are extracted with 5 mL of deionized water. The extracted solutions are subsequently analyzed for ions corresponding to the collected gaseous species (see Figure 1). The filters are placed into filter bottles where 5 or 10 mL of the ion chromatographic (IC) eluent are pipetted into each filter bottle with the filters faced downward and completely covered by the eluent. The filter bottle is capped and put in an ultrasonic bath for 30 min. The bottles are stored in a clean refrigerator at 5EC until analysis.

3.3 The analysis of anion and cation concentrations collected by the denuders and filter pack is typically performed by ion chromatographic and Technicon® colorimeter autoanalytic procedures. The H^+ concentration of extracts from the Teflon® filter downstream of the denuders is performed by pH measurements using commercially available pH meters calibrated with standards.

4. Significance

4.1 Reactive acidic (SO_2 and HNO_3) and basic (NH_3) gases and particles are found in the atmosphere as a result of emissions from a variety of fossil fuel combustion sources, including industrial and commercial facilities, industrial processes, etc. Measurements of these chemical species are currently being used in a range of environmental studies, such as in (1) epidemiological programs to assess the impact of acid aerosols on respiratory impairment, (2) receptor modeling to determine the origin of particles that impact EPA's $PM_{2.5}$ or

PM_{10} air particulate standard, (3) assessment of the impact of particulate nitrate and sulfate on visibility, and (4) quantification of the impact of acidic and basic air pollutants on issues related to acid rain.

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. This preservation is accomplished by removing NH_3 in the gas stream by the citric acid coated denuder and reducing the probability of the particulate sulfate ($SO_4^{=}$) captured by the filter pack from being neutralized to ammonium sulfate [$(NH_4)_2SO_4$]. If NH_3 is not extracted from the gas stream prior to filtration, particulate sulfate and gaseous sulfur dioxide correction would be required for accurate measurements. These biases in its configuration and analytical methodology are addressed in this method.

5. Definitions

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

5.1 Particulate Mass. A generic classification in which no distinction is made on the basis of origin, physical state, and range of particle size. (The term "particulate" is an adjective, but it is commonly used incorrectly as a noun.)

5.2 Primary Particles (or Primary Aerosols). Dispersion aerosols formed from particles that are emitted directly into the air and that do not change form in the atmosphere. Examples include windblown dust and ocean salt spray.

5.3 Secondary Particles (or Secondary Aerosols). Dispersion 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 SO_2.

5.4 Particle. Any object having definite physical boundaries in all directions, without any limit with respect to size. In practice, the particle size range of interest is used to define "particle." In atmospheric sciences, "particle" usually means a solid or liquid subdivision of matter that has dimensions greater than molecular radii (~10 nm); there is also not a firm upper limit, but in practice it rarely exceeds 1 mm.

5.5 Aerosol. A disperse system with a gas-phase medium and a solid or liquid disperse phase. Often, however, individual workers modify the definition of "aerosol" by arbitrarily requiring limits on individual particle motion or surface-to-volume ratio. Aerosols are formed by (1) the suspension of particles due to grinding or atomization or (2) the condensation of supersaturated vapors.

5.6 Coarse and Fine Particles. Coarse particles are those with diameters greater than 2.5 µm but less than 10 µm; fine particles are those with diameters less than 2.5 µm. These two fractions are usually defined in terms of the separation diameter of a sampler.

[Note: Separation diameters other than 2.5 µm have been used.]

5.7 Annular. Refers to rotating to, or forming a ring. In the annular denuder sampler, the annular refers to the cylinder to which coating is applied to the interior parallel planes to remove gaseous pollutants by diffusion chemistry.

5.8 Denuder. To strip away the process gaseous pollutants from the gas stream.

5.9 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.

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

6. Factors Affecting Denuder Efficiency

6.1 Operation below 20% relative humidity (RH) may result in less than quantitative collection of SO_2. Atmospheric water vapor in concentrations above 30% RH has been shown not to be an interferant for SO_2 collection.

6.2 Studies are being conducted to identify interferents, and calculations are being developed to correct the measurements obtained by the annular denuder system for identifiable interferents. For example, the presence of ozone (O_3) is known to oxidize nitrous acid (HNO_2) to nitric acid (HNO_3); therefore, HNO_2 measurements are often underestimates. Calculations have been developed to adjust for this oxidation process and to provide more accurate estimations of HNO_2 concentrations in the atmosphere.

6.3 Other studies include the possible chemical reactions (organic and inorganic) that may occur with selected coating solutions that interfere with the accurate measurement of the chemical species of interest.

6.4 The efficiency of impactor collection decreases when the impactor surface is loaded. The average operational time before such loading occurs has not been determined.

7. Apparatus

[Note: This method was developed using the annular denuder system produced 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 programs 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, (518) 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.]

7.1 Sampling

7.1.1 Elutriator and Acceleration Jet Assembly (see Figure 3). Under normal sampling conditions, the elutriator or entry tube is made of either Teflon®-coated glass or aluminum. When using glass, the accelerator jet assembly is fixed onto the elutriator, and the internal surfaces of the entire assembly are coated with Teflon®. 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. Again, all internal surfaces are coated with Teflon®. Both assemblies are available with 2, 3 and 4 mm inside diameter jets (nozzles).

7.1.2 Teflon® Impactor Support Pin and Impactor Frit Support Tools (see Figure 4). Made of either Teflon® or polyethylene and used to aid in assembling, removing, coating and cleaning the impactor frit.

7.1.3 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 "0"-rings that are located on both sides of the seat support inside the coupler. The couplers are composed of two free moving female threads that house the support tools when assembling and removing the impactor frit, and couple the denuders when sampling. Arrows on the metal band hold the female threads together. These arrows should be pointing in the direction of air flow (see Figure 1) when the ADS is assembled.

[Note: In situations when there are 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 6.]

The cyclone is made of Teflon®-coated stainless steel. The location of the cyclone with respect to the denuder, heated enclosure, and meter box is illustrated in Figure 6.

7.1.4 Annular Denuder (see Figure 7). The original denuders (single channel denuders) consist of two concentric glass tubes (see Figure 4). The tubes create a 1 mm orifice, which allows the air sample to pass through. 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 glass surfaces facing the orifice are etched to provide greater surface area for the coating. Three types of denuders are available. One is the older version that accommodates the impactor support pin assembly and can only be the first denuder in sequence. It is available in glass with the impactor support holder made of glass and the impactor support pin assembly made of Teflon®. The denuder is 265 mm long with size #30 threads for coupling. It is available with flow straighteners at both ends; however, most denuders in use today only have one flow straightener end. The second most recent denuder version, which can be used as any denuder in sequence, is available in glass with only one flow straightener end. It is 242 mm long and has size #30 threads. Finally, the third denuder (multi-channel denuder) design involves two inner concentric glass tubes (1 mm separation) positioned around a solid center glass rod, as illustrated in Figure 7. Once again, the glass surfaces are etched to provide greater surface area for the coating. The inner glass tubes and coater rod are inset 25 mm from one end of the outer Teflon®-coated stainless steel tube to serve as the flow straightener end. Since 1992, the multi-channel denuder has been evaluated and used extensively by EPA in place of the single channel, all glass denuder. The stainless steel sheath multi-channel denuder, while more expensive, is easier to handle during coating, extraction procedures, and in field applications. Additional channels in the denuder increases capacity of the denuder, thus minimizing breakthrough.

This procedure uses two denuders in series. The first denuder, Na_2CO_3 coated, is used to trap out HNO_3 and SO_2. The Na_2CO_3 denuder can also trap out HCl, HNO_2, HF, and some organic acids. However, special care needs to be taken in the preparation of the denuder coating material and extraction procedures to quantitate HCl. This method does not quantitate HCl, HNO_2, HF, or other organic acids retained on the Na_2CO_3 denuder.

The second denuder is coated with citric acid for trapping NH_3. This procedure does cover the quantitation of NH_3.

All denuder types should be equipped with thermoplastic or polyethylene caps when purchased.

7.1.5 Caps for Annular Denuder (see Figure 2). Caps are made of either polyethylene or thermoplastic and are used in the coating and drying processes and for storage and shipment. The thermo-plastic caps include a removable Teflon® seal plate when purchased. Repeated reuse of these types of caps have caused some contamination due to improper cleaning of the cap and Teflon® seal plate (i.e., fluid tends to be trapped under the seal plate). The polyethylene caps are not equipped with seal plates. Polyethylene caps tend to dry faster and seal better than the thermoplastic caps.

7.1.6 Annular Denuder Couplers (see Figure 4). 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. Two types of couplers are available. In the older version, the couplers have removable seal rings. Problems with denuder breakage and leakage due to improper threading of the couplers with the denuders led to the development of a second type of coupler. The new couplers are equipped with permanent seal rings that provide more even threading and a better seal when coupled. Some couplers have built-in flow-straighteners. The couplers are used to couple the annular denuders and for coupling the last denuder with the filter pack.

7.1.7 Filter Pack Assembly (see Figure 8). The filters are supported by stainless steel porous screens and housed in a polyethylene filter ring housing. The Teflon® filter ring housing directly follows the Teflon® filter housing inlet component. The "nylon" filter ring housing follows the Teflon® filter ring housing and sits on a Teflon® "O"-ring, which seals the filter ring housing components to the filter housing outlet component. The filter housing outlet component is aluminum and accommodates a polyethylene screw sleeve that seals the filter pack assembly. The sleeve is available in different lengths to accommodate up to four filter ring housing units. A stainless steel "Quick-Release" plug screws into the aluminum outlet component for connecting the pump-timer to the filter pack assembly. It is equipped with an orange "dust cover" (male plug) upon purchase.

7.1.8 Drying Manifold Assembly (see Figure 9). Made of pyrex and is available to accommodate as many as four drying denuders. The denuders are attached to the manifold with back-to-back Bakalite bored caps. The bored caps are connected with a Teflon® connector ring. Air is pushed through an air dryer/ cleaner bottle made of 2 ½" heavy wall pyrex that contains silica gel, calcium sulfate, and activated charcoal (not available with assembly). The 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.

A mixture of activated carbon/drying agent/sodium carbonate flux (~ 50 g) is contained in the dryer/cleaner bottle to scrub contaminants from the supply air source.

7.1.9 Vacuum Tubing. Low density polyethylene tubing, 3/8" diameter for distances of less than 50 ft., ½" diameter for distances greater than 50 ft. Since this tubing is used downstream from the sampler, similar sized tubing or pipe of any material may be substituted. The tubing must have sufficient strength to avoid collapsing under vacuum [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA 15219, (412-787-6322)].

7.1.10 Tube Fitting. Compression fittings (Swagelok®, Gyrolok® or equivalent) 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)].

7.1.11 Annular Denuder System Sampling Case (see Figure 10). Made of a "high-impact" plastic and insulated with polyurethane. It is 4 ft long by 6" wide and 6" deep. Two heater units, a fan blower, and an air outlet are located in the lid of the housing. Also, located on the lid are the automatic and manual control switches and a 12-V power supply outlet for the heater and fan. The bottom of the box houses the ADS. The elutriator end of the ADS protrudes through one end of the box, while the denuders are supported in the box by chrome plated spring clips. 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. A vacuum plug known as a "quick-release" coupler is linked to the filter pack of the ADS. This plug connects the ADS to 1 1/4" Teflon® rubber "clad" shrink tubing that exhausts the air stream to the ambient air. The box is sledge hammer proof.

7.1.12 Annular Denuder Field-to-Lab Case (Optional). Annular Denuder Field-to-Lab Case (Optional). The field-to-lab case is made of rigid plastic and insulated with polyurethane. It is made to be hand carried, not shipped, and is used to transport four total annular denuder systems, each consisting of either three annular denuder sections or two annular denuder sections and one denuder-impactor assembly. The systems are packed already assembled and capped; they are ready for sampling or sample analysis. The case has a carrying handle, a lock, and three latches and is equipped with two keys.

7.1.13 Annular Denuder Shipping Case (Optional). Made of formica, backed with plywood and insulated with polyurethane. 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, provided each system contains four denuders each. The systems can consist of either three denuders (242-mm long) and one denuder-impactor assembly (265 mm long) or four denuders (242-mm long). Each component of the system is packed in its own storage compartment. The personal sampler assemblies can also be placed and shipped in this case.

7.1.14 Differential Flow Controller (Pump). Pumps air through the sampler at a fixed rate of between 5 and 20 standard L/min (typically 10 L/min) with a precision of ±5% over the range of 25 to 250 mm Hg vacuum.

7.1.15 Dry Gas Meter (DGM). Pulls 10 L of gas per revolution [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA 15219, (412-787-6322)].

7.2 Analysis

7.2.1 Ion Chromatograph. A chromatograph equipped with the appropriate anion and cation exchange resin filled separator and suppressor columns and conductivity detector for measuring acidic (SO_2, HNO_2 and HNO_3) and basic (NH_3) ions in solution (i.e. denuder and filter extracts) [Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086, (408-737-0700)].

7.2.2 Technicon Colorimeter Autoanalyzer. Colorimetic analyzer able to detect specific ions of interest in aqueous extracts [Technicon Industrial Systems Corp., 511 Benedict Ave., Tarrytown, NY, 10591-5097, (800-431-1970)].

7.2.3 pH Meter. A pH or pH/ion meter with an "integral" automatic temperature compensation and calibrated with standard buffers (pH 4 and 7), including 2 and 4 mL analysis cups (Orion and other vendors).

7.2.4 Polyethylene Bottles with Polyethylene Screw Caps. 50 mL and 100 mL. Used for storage of coating solutions, best source.

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

7.2.6 Graduated Cylinders. 10 mL and 100 mL borosilicate glass or polyethylene cylinders, best source.

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

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

7.2.9 Micropipettes. Recommended 50 µL. Calibrated "*to contain*," borosilicate glass micropipette, best source.

7.2.10 Forceps. Recommended dressing forceps made of stainless steel or chrome-plated steel and without serrations. Used for handling filters (Millipore).

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

7.2.12 Ultrasonic Cleaner. Used for filter extractions and parts cleaning. Most are temperature controlled. Temperature should be controlled during extraction at 65EC [Cole-Palmer Instrument Co., 7425 N. Oak Park Ave., Chicago, IL 60648, (980-323-4340)].

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

8. Reagents and Materials

8.1 Teflon® Filters. Zefluor® (PTFE) membrane filters 47-mm diameter with a 2 µm pore size. Only one side is Teflon®-coated; this side should face the air stream [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, (800-521-1520)].

8.2 Nylasorb® Filters. Membrane filters 47-mm diameter with a 1 µm pore size. These filters are specially prepared and batch analyzed for low NO_3G background levels. If other brands of nylon membrane filters are used, they should be batch analyzed to ensure low and replicable levels of NO_3G [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106 (800-521-1520)].

8.3 Denuder Extract Storage Vials. 30 mL (1 oz) screw-cap polyethylene sampling vials (Nalgene or equivalent). Allow eight per sample for each sampling period, best source.

8.4 Filter Extract Storage Vials. 25 mL polyethylene vials (Nalgene or equivalent). Allow two vials for each sampling period, best source.

8.5 IC Analysis Vials and Caps. Available in 5 mL and 0.5 mL and are made of polypropylene. The filter caps are made of plastic and contain a Teflon® filter through which the sample is extracted for analysis. Both the vials and filter caps should be disposable, best source.

8.6 Labels. Adhesive, for sample vials, best source.

8.7 Parafilm. Used for covering flasks and pH cups during pH analysis, best source.

8.8 Kimwipes® and Kay-dry Towels. Used for cleaning sampling apparatus and analysis equipment, best source.

8.9 Stoppers. Cork or polyethylene, best source.

8.10 Sodium Carbonate (Na_2CO_3). ACS reagent grade, best source.

8.11 Sodium Chloride (NaCl). ACS reagent grade, best source.

8.12 Toluene. ACS reagent grade, best source.

8.13 Glycerol (Glycerine - $CH_2OHCHOHCH_2OH$). ACS reagent grade, best source.

8.14 Citric Acid [Monohydrate - $HOC(CH_2CO)OH]_2COOH : H_2O$. ACS reagent grade, best source.

8.15 Hydrogen Peroxide (H_2O_2). ACS reagent grade, best source.

8.16 Ethanol (C_2H_5OH). ACS reagent grade, best source.

8.17 Sulfuric Acid (H_2SO_4). ACS reagent grade, best source.

8.18 Potassium Chloride (KCl). ACS reagent grade, best source.

8.19 Perchloric Acid ($HClO_4$). ACS reagent grade (60-62%), best source.

8.20 Distilled Deionized Water (DDW). ASTM Type I water.

8.21 pH Buffers. Standard buffers 4.00 and 7.00 for internal calibration of pH meter, best source.

8.22 Silica Gel. ACS reagent grade (indicating type), best source.

8.23 Sodium Bromide (NaBr). ACS reagent grade, best source.

8.24 Activated Charcoal. ACS reagent grade, best source.

8.25 Balance. Electronic analytical with internal calibration weights and enclosed weighing chamber. Precision of 0.1 mg [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219, (412-787-6322)].

8.26 Gloves. Polyethylene disposable. Used for impactor frit assembly and filter pack assembly, best source.

8.27 Dow Corning High Temperature Vacuum Oil. Dow Corning 660 oil used for impactor frit coating solution, best source.

8.28 Zero Air. A supply of compressed clean air, free from particles, oil, NO, NO_2, SO_2, HNO_3, and HNO_2. The supply may be either from a commercial cylinder or generated on site, best source.

8.29 Ion Chromatographic (IC) Eluent Solution. For extracting filters. This solution should be the same eluent as used for the ion chromatographic analysis of the filters. If the filter analysis is not to be performed by ion chromatography, a slightly basic solution (e.g., 0.003 N NaOH or sodium carbonate/bicarbonate) should be used to extract the Nylasorb® filter, while the Teflon® filter should be extracted with double-distilled deionized water (DDW).

9. Preparation of Coating and Extraction Reagents

9.1 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 bottle. Add 100 mL of toluene. Mix thoroughly, close container, and store at room temperature. (WARNING - FLAMMABLE LIQUID).

9.2 Impactor Frit Extraction Solution Preparation. Add 100 mL of IC eluent to a clean polyethylene storage container. Pipette 5 mL of ethanol into container. Mix thoroughly. Store, covered at room temperature.

9.3 Annular Denuder Coating Solutions Preparation

[Note: Different coatings may be used depending on the chemical species of interest.]

9.3.1 Na_2CO_3 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. Measure 50 mL of DDW with a graduated cylinder and add to vial. Weigh 1 g of glycerol and add to DDW. Weigh 1 g of Na_2CO_3 and add to vial. Mix thoroughly, solution may fizz; wait for fizzing to stop before sealing vial. Store at room temperature.

9.3.2 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 a vial. Add enough glycerol to vial to make it a 1% solution (0.5 mL). Mix thoroughly; store, covered at room temperature.

10. Elutriator and Acceleration Jet (Inlet) Assembly

[Note: The all-glass configuration is shown in Figure 6A.]

10.1 The internal walls of the elutriator and jet assembly are coated with Teflon® to prevent losses of reactive species (SO_2, HNO_3, NH_3) during sampling. The elutriator prevents water and large particles from entering the inlet and thus extends the life of the impaction surface located immediately downstream of this assembly.

10.2 An aluminum version of this inlet is shown in Figure 3b. All inner surfaces of the aluminum unit are Teflon®-coated. The main difference between the all glass and the aluminum inlet is the jet component of the aluminum inlet is replaceable, as shown in Figure 3b. The jet component is made of either Teflon® or polyethylene and is available in various diameters as needed to accommodate selected sample flow rates. The jet may be replaced using the tool shown in Figure 3b. The jet diameter for a sample flow rate of 10 L/min is 3.33 mm. At this flow rate, the inlet has an aerodynamic cutpoint of 2.5 µm. If a different flow rate is used, the jet diameter must be changed to retain an aerodynamic cutpoint to 2.5 µm. Table 2 contains the jet diameters and Reynolds number to maintain an aerodynamic of 2.5 µm cutpoint at different flow rates between 1 and 20 L/min.

[Note: If the sampling area has substantial concentrations of coarse particles (> 2.5 µm), the user may replace the acceleration jet and impactor assembly with the Teflon®-coated aluminum cyclone.]

11. Impactor Frit Preparation and Installation

11.1 Impactor Frit Installation

11.1.1 Impactor-Coupler. The impactor-coupler assembly (shown in Figure 12) 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. This frit is inserted into the coupler-impactor housing using the tools shown in Figure 12. The in-tool must be completely screwed in behind the impactor seat before the frit is pressed into place. Press the impactor frit gently but firmly into the seat of the impactor housing with your

clean gloved finger. The impactor should fit into the housing so that it does not protrude above the seat. The impactor frit has a slight bevel. The narrow surface should be inserted into the impactor seat.

11.1.2 Impactor-Denuder. The impactor-denuder assembly (shown in Figure 4) is of three parts: the replaceable impactor frit, the impactor seat support pin, and the annular denuder impactor-pin support. The impactor frit is the same as described in Section 11.1.1 and is inserted into the impactor seat support pin. The impactor support pin can be hand-held while inserting the frit or it can be placed upright into the stainless steel frit holder #3 (see Figure 11). Press the support pin into the denuder pin support. The pin is grooved and has a viton "O"-ring to keep the pin snug in the denuder support during cold weather use (Teflon® tends to shrink at low temperatures). The support pin is removed by using the removal tool shown in Figure 4.

11.2 Impactor Frit Preparation

With the impactor frit in the impactor seat of either the coupler (see Figure 12) or the Teflon® impactor seat support pin that fits into the first denuder (see Figure 4), pipette 50 µL of the toluene-660 oil coating solution onto the impactor frit surface and allow to dry at room temperature. Cap both sides of the coupler impactor or denuder-impactor until use.

12. Filter Pack Preparation and Assembly

[Note: Any number of filters can be used depending on the target species of interest. The configuration referred to in this section does not collect NH_4^+.]

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

[Note: Remove the red Bakelite® cap first. Lay the pieces out on clean Kimwipes®.]

12.2 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.

12.3 Using clean filter forceps, place a Nylasorb® nylon filter on the screen. Insert a second filter ring housing on top of the nylon filter with its large opening face up. This design forms a "sandwich" with the nylon filter held between the two filter ring housings.

12.4 Place another clean screen on the second filter ring housing. Using clean filter forceps, place a Teflon® filter on the screen.

[Note: If a Teflasorb® Teflon® filter is used, be sure to place the Teflon®-coated side, not the webbed side, toward the air stream. If the webbed side is facing the air stream, $SO_4^=$ extraction from the filters may be inefficient.]

12.5 Place the Teflon® filter housing inlet component (see Figure 11) on top of the Teflon® filter, which forms another "sandwich" with the Teflon® filter held between the second filter ring housing and the housing inlet component. The housing inlet component connects the filter pack assembly to the last annular denuder through a thermoplastic coupler. Be careful not to twist the filterpack components, or damage will occur to the filters.

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

12.7 Insert the filter ring sandwiches (prepared in Sections 12.1 through 12.5) with the filter housing inlet component extending upward, in the aluminum filter base. Place the large outer Teflon® sleeve over the filter sandwich and screw onto the aluminum filter base. DO NOT OVERTIGHTEN! DO NOT TWIST FILTER PACK COMPONENTS!

12.8 Install the "Quick-Release" plug into the filter outlet component. DO NOT OVERTIGHTEN!

12.9 Install the red Bakalite® cap onto the filter inlet component and the orange dust cover onto the Quick-Release plug until ready to attach denuders.

13. Annular Denuder System Preparation

All new annular denuder parts obtained from suppliers should be cleaned with a dilute soap solution. The parts should then be thoroughly rinsed in DDW and allowed to dry at room temperature.

13.1 Annular Denuder Coating Procedure

[Note: If the first denuder holds the impactor, a blank Teflon® impactor support pin should be installed in the pin support holder before the coating procedure.]

13.1.1 Cap the end of the denuder that has the inner tube flush to the outer tube and set denuder upright on the capped end. For the denuders with flow-straighteners at both ends, either end can be capped. Measure 10 mL of the appropriate coating solution into a graduated cylinder. Pipette the 10 mL into the flow-straightener end of the upright capped annular denuder.

13.1.2 Cap the open end of the denuder, and holding horizontally, rotate the denuder to distribute the coating solution evenly.

13.1.3 Remove cap from flow-straightener end of denuder and decant excess coating solution into a clean denuder extract storage bottle labeled "denuder blank." Bottle label should include denuder number, coating solution and date.

13.1.4 Repeat this procedure with each denuder; label the denuders and bottles appropriately.

13.2 Annular Denuder Drying Procedure (see Figure 9)

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

13.2.1 Adjust drying train and manifold clean air flow to 2 to 3 L/min. Close toggle valve controlling clean air flow through manifold before attaching denuders.

13.2.2 Attach flow-straightener end to drying manifold port at the back-to-back bored caps (see Figure 9).

13.2.3 Open toggle valve and allow clean air to flow through the tube for several minutes.

13.2.4 Close toggle valve and reverse ends of tubes attached to manifold.

13.2.5 When an even frosted appearance is achieved, remove tubes from manifold, cap both ends with clean caps, and store until ready for use. Turn off air to drying manifold.

13.3 Annular Denuder System (ADS) Assembly

[Note: Described herein is an annular denuder system consisting of four denuders in series. Any number of denuders can be used at the operators' discretion. The denuders should be assembled in such a way that the flow-straightener end always follows the flush end of the previous denuder, except, if denuders with flow-straighteners at both ends are used. This type of assembly allows laminar flow conditions to be restored quickly.]

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

13.3.2 Remove the end caps from the first denuder. Denuder 1 is coated with Na_2CO_3 and holds the impactor frit pin support. Remove the blank impactor support pin. Gently insert the impactor support pin and coated frit assembly into the denuder-pin support. If the first denuder does not hold the impactor pin-support, attach the impactor frit seat equipped coupler assembly to the flow-straightener end of the first denuder.

[Note: DO NOT TIGHTEN! Do not tighten during the following procedure until Section 13.4.8 is reached.]

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

13.3.4 Remove the end caps from the second denuder (citric acid coated). Attach the end with the flow-straightener section to the denuder-coupler assembly.

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

13.3.6 Attach the filter pack inlet to the second denuder coupler assembly.

13.3.7 Attach the elutriator-acceleration jet assembly to the first denuder-coupler assembly. Tighten very gently--DO NOT OVERTIGHTEN!

13.3.8 Tighten the remaining couplers very gently - DO NOT OVERTIGHTEN!

13.3.9 Cap elutriator with orange dust cover until use.

[Note: When collecting and measuring gaseous HNO_3, SO_2, and particulate NO_3^- and $SO_4^=$, NH_3 must be taken out of the gas stream prior to the air stream entering the filter pack. Otherwise, reaction of the unneutralized sulfate will result. If ammonia (NH_3) and/or H^+ measurements are not to be analyzed for, then the use of a citric acid coated denuder is not important. However, with the removal of NH_3, some nitrate collected on the Teflon® filter will evaporate and be found on the nylon filter.]

13.4 Laboratory Leak-Check of ADS

[Note: CAUTION--Do not subject the system to sudden pressure changes or filters may tear.]

13.4.1 Remove the orange dust cap from the impactor opening. Attach the "Quick-Release" to a pump module. Turn on the pump. Be certain that flow through the ADS occurs by checking the rotameter.

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

13.4.3 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 can not be sealed with gentle tightening, the Teflon® "O"-rings are worn or defective and must be replaced.

13.4.4 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 precaution will prevent unnecessary breakage or distortion of the ADS components. Remember to allow the system to adjust to the indoor air temperature before tightening the joints and checking for leaks.]

14. Sampling

14.1 Placement of Denuder System

14.1.1 The placement of the annular denuder system 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, U. S. Environmental Protection Agency Office of Air Quality Planning and Standards, Research Triangle Park, NC 27711, May 1987.

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

14.1.2 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).

14.1.3 A summary of key criteria associated with these siting factors for air monitoring stations is included in Table 3.0. The information included in the table should be used to the extent possible 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 3.0, coupled with a balanced evaluation by an experienced air quality and meteorology specialist, is highly recommended.

14.1.4 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.

14.2 Start-Up

14.2.1 Remove the ADS from its field-to-lab carrying case and load into the field sampling box. The ADS field sampling box is insulated with polyurethane which is configured to hold the ADS without allowing movement. Chrome plated spring clips hold the denuders 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 filters to tear). When sampling, the ADS should be kept 1EC above the ambient temperature to prevent condensation. The sampling box has two connections with the pump timer: the plastic suction hose connected with "Quick-Release" couplers and the 12-V power cord with a "Quick-Disconnect" coupler. The power cord remains connected, and the suction hose is disconnected from the box each time the unit is opened. Inside the box, the hose is connected to the top of the filter pack with a "Quick-Release" coupler. During sampling the sample box is kept securely closed (see Figure 2).

14.2.2 Allow the pump to warm up for 20-30 min prior to testing so the pump will provide steady flow during testing.

14.2.3 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.

14.2.4 With the elutriator still capped, turn on the pump with the switch on the timer. The rotameter should indicate zero flow. If there is a flow, the assembly pieces need to be recoupled. Run leak check for 5-10 s. Turn off pump and remove elutriator cap. Record leak rate on Field Test Data Sheet (see Figure 13).

14.2.5 Attach DGM output to elutriator inlet. Turn on pump. Record start time on Field Test Data Sheet (see Figure 13). 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.

14.2.6 Calculate the flow rate as follows:

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

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_{bar} = 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.

14.2.7 If the calculated flow rate is not between 9.5 and 10.5 L/min, readjust the flow rate and repeat Sections 14.2.4 and 14.2.5 until the rate is in the above range. Preliminary studies should be conducted to obtain an estimate of the concentrations of the species of interest.

14.2.8 Record the flow rate on Field Test Data Sheet.

14.2.9 Remove DGM connection tubing from elutriator inlet. Pump should remain running so that sampling continues. Higher flow rates may be used for shorter sampling periods. Concentration of the species of interest in indoor air and the configuration of the sampling equipment, determine the appropriate flow rates. Sampling at 10 L/min, requires a sampling time of 24 h to collect pollutant concentrations between 0.02 and 0.83 µg/m^3.

14.3 Sample Shutdown

14.3.1 Attach DGM connection tubing elutriator inlet with pump still running. Measure flow rate as in Sections 14.2.5 and 14.2.6. Record flow time, temperature, and pressure on Field Test Data Sheet (see Figure 13).

14.3.2 Turn off pump. Record time and elapsed time meter reading on log 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. 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 denuders.

14.4 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 testing.]

14.4.1 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.

14.4.2 Cracked or Chipped Denuders or Elutriator Assemblies. 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.

14.4.3 Contaminated Blank Solutions. Note problem on Field Test Data Sheet. Follow parts-cleaning procedures closely. Examine the sampler preparation area for possible sources of contamination and remove source. Check DDW being used in the solution preparations and extractions. Fill a clean 25 mL polyethylene extraction bottle with the DDW used in solution preparation and extraction; send to lab for analysis. If contaminated, correct deionization system.

14.4.4 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 filters or to obstructions in the system or tubing. Check flow module. Repair as needed.

14.4.5 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 filters in the filter pack. Check tubing for kinks.

[Note: Typically the pressure drop across the filters should be approximately 1" Hg at 10 L/min flow rate at sea level. This pressure drop can vary from 1-10 L/min depending on elevation.]

15. ADS Disassembly

15.1 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.

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

15.3 When using the denuder-impactor, the frit-pin must be removed from the support in the denuder before removing the frit from the pin. The frit is then extracted from the pin using pin tool #3 and the frit extraction tool (see Figure 12). When using the impactor-coupler assembly, the frit is removed from the coupler seat using pin tool #3 and the "out" frit removal tool (see Figure 12). Put frit in covered dish and set aside for future chemical extraction (optional).

[Note: This method does not require the analysis of the particles impacted on the frit.]

15.4 Remove the denuders from the couplers and cover each end of the denuders with clean end caps until extraction.

15.5 Label a clean 100 mL polyethylene bottle with the sampler ID number and filter type (i.e., Teflon® or Nylasorb®, as appropriate) for each of the filters.

15.6 Disassemble the filter pack in a clean, ammonia-free air hood. Clean all hood surfaces and utensils with ethanol. Wearing clean gloves and using clean filter forceps, remove the filters and place each in its storage (protective) bottle, with the exposed filter surface facing downward, until extraction.

[Note: Place the filters in the properly labeled bottles.]

16. Extraction Procedures

[Special precaution: 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.

Extraction must take place in a clean, ammonia-free air hood. The extracts must be processed in the order in which they will be analyzed, so that each sample will have a similar time interval between extraction and analysis. Denuder extracts and filters should be stored in the refrigerator until just prior to analysis. Samples stored longer than 30 days tend to degrade due to bacteria growth and/or losses to the walls of the extraction vessel. Extraction volumes may vary depending upon sensitivity requirements and expected ambient concentrations.

16.1 Impactor Frit Coating Extraction (Optional)

16.1.1 Place the impactor (which was removed before denuder extraction) into a small extraction bottle.

16.1.2 Label the bottle appropriately. Pipet 10 mL of impactor extraction solution (See Section 9.2) into the bottle. The solution must cover the surface of the impactor frit.

16.1.3 Close the extraction bottle and place in an ultrasonic bath for 30 min.

16.2 Denuder Extractions

[Note: If the denuder was the first denuder and equipped with the impactor frit-pin support, insert a clean Teflon® impactor frit-pin without frit in place. Then extract as described below. This procedure is to be followed for each denuder.]

16.2.1 Cap one end of each of the denuders (i.e., Na_2CO_3 and citric acid denuders). Add 5 mL of DDW with a pipet. Cap other ends of the denuders.

16.2.2 Rotate the denuders to wet all surfaces thoroughly with the water. Remove the caps and pour the liquid from each of the two denuders into separate clean 25 mL polyethylene extraction bottles.

16.2.3 Repeat this procedure with a second 5 mL of DDW extract (total extract volume is 10 mL, which is placed into the extraction bottles).

16.2.4 Add 1 mL of hydrogen peroxide to oxidize the sulfite ($SO_3^=$) to sulfate ($SO_4^=$) in the extraction bottles containing the Na_2CO_3 coating.

16.2.5 Replace the extraction bottle caps and label the bottles with the sampler ID number and denuder number and type (as appropriate).

16.3 Filter Extraction

16.3.1 Teflon® Filter Extraction [for pH analysis followed by $SO_4^=$, NO_3^-, and/or NH_4^+ analyses)

[Note: Teflon® is not wet by water; therefore, the filter will float on top of aqueous solutions. Solutions and extraction procedures must be prepared and performed on the day of pH analysis. Extraction of the filters must take place in a clean, ammonia-free, air hood. The filters must be processed in the order in which they will be analyzed so that each sample will have a similar time interval between extraction and analysis.]

16.3.1.1 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.

16.3.1.2 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.

16.3.1.3 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.

16.3.1.4 Handling the exposed Teflon® filter requires protection from contamination with NH_3, which may rapidly neutralize aerosol acidity on the filter and 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 minutes 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 ethanol.

16.3.1.5 Allow the hood to be flushed with ammonia-free air for at least 5 min before filter extraction. All of the hood surfaces and extraction utensils must be cleaned with a Kimwipe® moistened with ethanol.

16.3.1.6 Pipet 6 mL of 0.0001 N perchloric acid ($HClO_4$) solution into the appropriately labeled extraction vials (10 mL).

[Note: Perchloric acid is used because it inhibits CO_2 from dissolving into the solution and keeps the organic compounds in solution from dissociating. Both these activities can change the ionic strength of solution.]

16.3.1.7 Wearing clean gloves and using clean filter forceps, place the Teflon® filter in the extraction vial with the exposed filter surface facing downward. Cap tightly. Store at 4EC in the dark until ready for analysis.

16.3.1.8 When ready for analysis, the filter must be prepared (within the air hood) in the following manner: Using forceps and gloved hands, lift the filter from the extraction vial. Let the excess solution drain off into the vial. Holding the filter over the extraction vial, and using an automatic pipet, apply 200 FL ± 5 FL of ethanol to the filter. Add the ethanol slowly to ensure that all portions of the membrane are wet with ethanol. Immerse the filter in the aqueous solution once again. Tap the forceps against the inside of the vial to remove liquid. Tightly replace cap. Put in ultrasonic bath for 15 min total, rotating the rack 90E every 5 min.

[Note: Perchloric acid is used in place of potassium chloride, initially, to prevent interference in the measurements of cations and anions by ion chromatography. Potassium chloride must be added to the portions of the sample extract that are used for pH analysis (the purpose of the salt, final concentration 0.04 M, is to increase the ionic strength and thus to reduce the time for equilibrium of the pH electrode used for measurement). Use the same bottle (freshly opened) of ethanol to extract the Teflon® filters that are used to prepare sulfuric acid standards.]

16.3.1.9 When ready for pH analysis, the extracts are prepared in the order of pH measurement. Inside the air hood, remove the caps from 10 mL extraction vials. Wipe off any drops which may leak onto the outside of the cup.

16.3.1.10 Using gloved hands and a 1 mL automatic pipet, transfer 1 mL of the extract to each of two correspondingly labeled 2 mL cups.

[Note: The first 2 mL cup for each extract has the same I.D.# as the 10 mL cup, and the second 2 mL cup has the same I.D.# with a hyphen (-). This system also is used with the working standards.]

16.3.1.11 After transferring the extracts to the 2 mL cups, recap the 10 mL extraction vial. Store the 10 mL vials at 4EC in a refrigerator pending analysis by IC, and for NH_4^+ analysis by Technicon auto analyzer.

16.3.2 Nylon Filter Extraction.

16.3.2.1 Pipet 10 mL of IC eluent into the appropriately labeled filter vial or bottle with caps.

[Note: Be sure that the filter lies flat on the bottom of the bottle and that all of the filter is covered by the extraction solution.]

16.3.2.2 Place the nylon filter in the extraction vial.

16.3.2.3 Replace the bottle's cap and put in an ultrasonic bath for 30 min.

16.3.2.4 Store the bottles in a clean (i.e., pollutant free) refrigerator at 4EC until analysis.

17. Ion Chromatography Analysis

[Note: The analytical procedure described here is not the only appropriate procedure available for quantifying the analytes of interest. An automated system does not have to be used. This particular analytical procedure was chosen because it is presently used by EPA. Modifications to this procedure may be required depending on the intended use of the data; however, any modifications made must be justified to obtain comparable data quality.]

17.1 Standards Preparation

Special Precaution: Storage of these solutions should be no longer than one week. All of the working standard solutions are used to calibrate the IC and are made from reagent grade stock. The crystals are dried overnight in covered petri dishes at 110EC in a vacuum oven prior to preparing the standard solutions. Any yellowish discoloration of the dried crystals indicates decomposition and crystals should be discarded.

17.1.1 Sodium Sulfate Stock Solution.

17.1.1.1 In a clean, calibrated, 1 L flask, add 500 mL of DDW.

17.1.1.2 On weighing paper, weigh out enough reagent (Na_2SO_4) to make the solution 2000 ppm concentration. The target weight is 2.958 ± 0.001 g. Record the gross weight.

17.1.1.3 Add the reagent crystals to the 500 mL of DDW. Reweigh weighing paper and subtract weight from the gross weight. The difference is the actual net weight.

17.1.1.4 Dilute to volume with DDW. Mix well and cover with parafilm.

17.1.2 Sodium Nitrate Stock Solution.

17.1.2.1 In a clean, calibrated, 1 L flask, add 500 mL of DDW.

17.1.2.2 On weighing paper, weigh out enough reagent ($NaNO_3$) to make the solution 2000 ppm concentration. The target weight is 2.742 ± 0.001 g. Record the gross weight.

17.1.2.3 Follow Sections 17.1.1.3 and 17.1.1.4.

17.1.3 Standard working solutions (100 ppm $SO_4^=$ and 100 ppm NO_3^-). The working solutions are made as follows: Add 10 mL each of the two stock solutions ($SO_4^=$ and NO_3G) to a 200 mL volumetric flask and dilute to the mark with DDW. Subsequent dilutions are carried out using a 10 mL volumetric pipet and appropriate flasks. Standards of 20, 10, 5 and 1 ppm $SO_4^=$ and NO_3G are prepared to calibrate the IC.

17.2 Reagent Preparation

[Note: Storage of these reagents should be no longer than 1 week.]

17.2.1 Anion eluent. The anion eluent is a solution of 1.8 mM Na_2CO_3 and 1.7 mM $NaHCO_3$. A concentrated solution can be prepared and diluted as needed.

[Note: See Anion Storage Solution]

17.2.1.1 Concentrated Na_2CO_3 solution (0.36 M). Weigh out 38.156 g of Na_2CO_3 (MW = 105.99). Dissolve into 1 L of DDW. Store in refrigerator until ready to dilute.

17.2.1.2 Concentrated $NaHCO_3$ solution (0.34 M). Weigh out 28.564 g of $NaHCO_3$ (MW = 84.01). Dissolve into 1 L of DDW. Store in refrigerator until ready to dilute.

17.2.1.3 Dilution of stock solutions. Bring both solutions to room temperature. Accurately pipet 10 mL of each solution into a 2000 mL volumetric flask which has been partially filled with DDW. Bring to the mark with DDW (1:200 dilution).

17.2.2 Anion regenerant. The regenerant is a 0.025 N H_2SO_4 solution. VERY CAREFULLY dispense 2.8 mL of concentrated Ultrex sulfuric acid (36 N) into a graduated cylinder. Partially fill the regenerant reservoir with DDW (3 L). Slowly add the acid to the regenerant reservoir. Bring to the mark with DDW (4 L).

[Note: Protective clothing and eye protection should be worn.]

17.2.3 Cation eluent. There are two cation eluents that are used for the analysis of monovalent and divalent cations. The strong cation eluent is: 48 mM HCl, 4 mM DAP.HCl (DAP = Diaminoproprionic acid), 4 mM Histidine.HCl. The weak eluent consists of 12 mM HCl, 0.25 mM DAP.HCl, 0.25 mM Histidine.HCl.

17.2.3.1 Strong cation eluent. Weigh 0.560 g DAP and 0.840 g histidine into a 1 L volumetric flask. Add 48 mL of 1 M HCl (Ultrex) to the flask. Bring the eluent to the final volume by bringing to the mark with DDW. Mix thoroughly to dissolve.

17.2.3.2 Weak cation eluent. Place 63 mL of the strong cation eluent in a 1 L flask. Add 9 mL of 1 M HCl to the flask. Bring the eluent to the final volume by bringing to the mark with DDW. Mix thoroughly to dissolve.

17.2.4 Cation regenerant. The cation regenerant consists of 100 mM tetrabutyl-ammonium hydroxide (TBAOH). Place the TBAOH container into a warm water bath to dissolve any crystals that may have formed. Measure 266.7 mL of the TBAOH (stock reagent is supplied as 1.5 M, 40% in water) into a graduated cylinder. Add the TBAOH to 4 L of DDW.

17.2.5 Anion storage solution. Since the anion columns contain carbonates from the eluent, protection must be taken against microorganisms that will live on this food source and clog up the columns. If the columns are not being used for long periods of time (>2 weeks), a storage solution of 0.1 M NaOH should be pumped into them.

17.3 Sample Preparation

17.3.1 Mark the auto sampler vials with the appropriate identification numbers. Place the vials in an IC autosampler tray.

17.3.2 Using clean, calibrated 0.5 mL pipets, transfer the denuder extract and the remainder of the filter extracts from the extraction vials to a clean disposable 0.5 mL IC autosampler (polyethylene) vial. Fill the autosampler vial to the line on the side.

[Note: If refrigerated, the contents of the 10 mL extraction vial must be vortex-mixed prior to transfer to the autosampler vials.]

17.3.3 Place black filter caps on top of the vials. Use the tool provided to push the caps into the vials until they are flush with the top (see the IC manual for more detailed instructions).

17.3.4 Wipe away any excess fluid from the top of the vial to avoid contamination from other samples.

17.3.5 After all of the trays are filled, place them into the left side of the autosampler. The white dot on the tray indicates the first sample. Press the button labeled RUN/HOLD to the RUN position. The trays should move until the first sample is under the sampling head. The front panel should indicate a READY message. Press local/remove switch to remove.

17.4 Basic System Operations - Start-up and Shut-down

[Note: This procedure is specific for one instrument. Other instruments can be used with these procedures.]

17.4.1 Start-up Procedure for Ion Chromatograph.

17.4.1.1 The major components of the Dionex 2020i Ion Chromatography system are illustrated in Figure 14. Turn helium and nitrogen tanks on by opening the valve on top of each tank (pressure in either tank should not be less than 500 psi.). Replace if necessary. Open valves at the outlet end of both regulators. Adjust pressure on the nitrogen regulator to 100 psi. Adjust pressure on the helium regulator to 14 psi.

17.4.1.2 Check the level of eluents and regenerating solutions. Turn the chromatography (CMA) values for the anion channel switch ON. Verify that the pressure reading on the face of the degassing unit is 7 psi. Adjust by turning dial next to pressure gauge. Turn the degas switch to HIGH.

17.4.1.3 Turn the eluent reservoir switches, corresponding to the eluents to be degassed, to the ON position. Let the eluents degas on HIGH for 3-5 min, then turn degas switch to LOW.

17.4.1.4 Select the appropriate program on the gradient pump module using the PROGRAM switch. (Programs are recalled from memory by first pressing the PROGRAM switch, then the single digit reference number corresponding to the appropriate program.)

17.4.1.5 Prime the eluent lines.

[Note: All of the eluent lines used during analysis must be primed to remove any air bubbles that may be present. The selected program identifies which lines are used.]

- Open the gradient pump drawer. Turn the pump to the START position for 10 s, or until a CLICK is heard. Turn the pump OFF. This step opens the valve to the eluent line displayed on the front panel.
- Attach a 10 mL syringe to the priming block on the face of the gradient pump module. With the priming block valve closed, pull the syringe plunger out to the end of the syringe.
- Open the priming block valve. The syringe will quickly fill with eluent. Close the valve on the priming block when the syringe is almost full. Remove syringe from block and discard collected eluant.

This priming procedure can be repeated if necessary. All of the eluent lines that are to be used during a day of analysis should be primed at this time.

17.4.1.6 Open the door of the Advanced Chromatography Module. On the back of the door, at the bottom, is the conductivity detector. Four labeled lines (anion, cation, waste, and cell) are located next to the cell. The plumbing must be configured according to the type of analysis to be performed. If anions are being analyzed, attach the ANION line to the CELL line, and the CATION line to the WASTE line. If cations are being analyzed, attach the CATION line to the CELL line, and the ANION line to the WASTE line. Attach the line coming from the pump to the correct port on the advanced chromatography module. SYSTEM 1 on the left is for anions; SYSTEM 2 on the right is for cations.

[Note: If switching from one system to the other, the pump and the lines coming from the pump must be purged of the original eluent, which is done by disconnecting the pump line from the chromatograph module, turning the pump on, and running the new eluent into a waste beaker for 2-3 min.]

17.4.1.7 Select the columns to be used (labeled pH or NO_2) by pressing the blue button located below the labels. To verify that the correct columns are being used, press the switch should at least once, and then set to the appropriate position.

17.4.1.8 Turn the power switch on the autosampler ON (switch is located on the back of the unit, on the right). The default settings will be displayed on the front panel. Attach the SAMPLE OUT line from the autosampler to the advanced chromatography module. The connection should be made to the port marked SAMPLE of the appropriate system. Turn the pump to START.

17.4.1.9 Turn the conductivity cell ON (switch is located on the gradient pump module). Turn the REGEN switch for the appropriate system ON. Verify that regenerant is flowing by inspecting the regenerant waste line which empties into the sink. Open the advanced chromatography module door and inspect for leaks at columns, fittings, etc. Shut pump off if leaks are found.

17.4.1.10 Turn stripchart recorder ON. Baseline should stabilize in less than 20 min. If baseline is not stable, see troubleshooting Section 17.5 for assistance.

17.4.2 Data acquisition start-up. The following is a description of the current data acquisition program used by the EPA. The program is available (EPA, Atmospheric Chemistry and Physics Division, Office of Research and Development, Research Triangle Park, NC) and is for IBM or IBM compatible computers. Other appropriately designed programs may be used to compile the data collected for any given sampling network. A computer programmed integrator does not need to be used to compute the data, but is recommended for large sampling networks.

17.4.2.1 Turn on the IBM XT computer. From the C:>prompt, type: cd/cchart, then type: cchart. This loads the Chromatochart software. Turn switch on relay box to ENABLE, indicator light could go on.

17.4.2.2 Press F2 to enter the methods development module. Select option number 1 - "select channel # and load method file." "Select channel # <0>" type 0 or press ENTER to select the default choice shown in the brackets (in this case 0). "Load method file named" type the name of the appropriate method, then press ENTER. A directory of all of the current methods in memory can be obtained by pressing the F2 function key.

17.4.2.3 Press F3 to enter the Data Acquisition module. At this point you will be asked to save the method file. If there has not been any changes to the methods file, it does not need to be saved. Select option #4 - "Collect Data." Press ENTER to deactivate the method queue. "Load Run Queue named," type the name of the run queue if one has been created. Type ENTER to deactivate the run queue.

17.4.2.4 "Total # runs for method <1>," type how many times the method is to be repeated (total number of samples). "Autoanalyze Data" type Y. "Autosave data to disc" type Y. "Data file name (xxxxx) change?", type data file name. "Press ENTER to begin methods." Press ENTER only after the samples have been loaded into the autosampler and the baseline has stabilized.

17.4.2.5 Figure 15 illustrates the chromatograms for each of the samples as output by the programmed Spectra-Physics integrator.

17.4.3 Calibration of IC. The instrument should be brought to normal conditions with a warm-up time of at least 30 min.

17.4.3.1 With the "Reading" light on, check to ensure the flow rate is 1.5 mL/minute, the fluid pressure is 600 psi ± 100 psi and the conductivity is constant as measured by offset difference.

17.4.3.2 Fill the IC vials with the prepared standard solutions and (20, 10, 5 and 1 ppm $SO_4^=$ and NO_3G) and pure eluent. This will allow a four-point calibration curve to be made.

[Note: For low-level applications, more standards and blanks may be necessary in order to obtain accurate reference curves.]

17.4.3.3 Load the four vials into the sample vial holder and place the holder in the automated sampler tray.

17.4.3.4 The tray is controlled by a Spectra-Physics SP4200 or SP4270 Computer Integrator. Use the integrators operation manual to begin calibrating. By using the RUN command, the analysis and data treatment phases of the calibration are set in motion. Four calibration standards are run, the chromatograms and peak areas displayed for each run, and the run results for each anion are fitted to a quadratic curve by a least squares regression calculation. The three curves are plotted and the correlation coefficients are calculated. The values of the coefficients are normally greater than 0.999, where 1.000 indicates a perfect fit. Values of less than 0.99 indicate the calibration procedure should be repeated.

[Note: Recalibration should be carried out whenever standard concentrations show consistently high or low results relative to the calibration curve is compared to the calibration curve from the old standards. Comparability of points should be within ± 0.1 ppm or ± 10%. For standard concentrations of greater than

1 ppm, comparability will normally be within 5% or better. Old standards are assumed correct since they are referenced to the entire historical series of previous standard solutions all of which are comparable.]

17.4.4 System Shut-down.

17.4.4.1 Shut off the pump. Turn the REGEN switch and the conductivity cell to the OFF position.

17.4.4.2 Switch the eluent degas switch to HIGH.

17.4.4.3 Turn the stripchart recorder OFF. Cap the pen. Press the F10 function key on the computer. Select option 3 to exit to DOS. Shut off the printer and the computer.

17.4.4.4 Shut the eluent degas system and reservoir switches and the autosampler to the OFF position. Close the valves on both gas cylinders. Close the regulator valves.

17.5 Basic Troubleshooting

Before proceeding with the troubleshooting guide, make sure the reagents used were prepared correctly and are not "old."

17.5.1 Unstable Baselines

17.5.1.1 Wavy baseline. The most common reason for a wavy baseline is an air bubble in the gradient pump. This problem is diagnosed by observing the pump head indicator lights on the gradient pump module front panel. If the baseline is pulsing in phases with pump pistons, a bubble is usually present. Other possibilities include a dirty or stuck check valve, piston seal or "O"-ring, as well as an air bubble in the conductivity cell.

17.5.1.2 Drifting baseline. Steadily increasing or decreasing baselines usually indicate that the suppressor column is not performing as it should. Parameters to change include the regenerant and eluent concentrations and flow rates. Check temperature routinely, as changes in temperature can cause drifting. Balancing these should stabilize the baseline if the suppressor is functioning correctly. The Dionex manual describes clean-up procedures if the suppressor is believed to be contaminated.

17.5.1.3 High baselines. As with drifting baselines, the parameters to change are eluent and regenerant concentrations and flow rates. A high baseline usually indicates that there is not enough baseline suppression; this condition can be controlled by increasing the regenerant flow rate.

17.5.1.4 Low baselines. Low baselines usually indicate that there is too much suppression, which can be controlled by decreasing the flow of the regenerant.

17.5.2 Backpressure. Variations in system backpressure are common and should not raise concern UNLESS the pressure change is greater than 200 psi.

17.5.2.1 High backpressure. The system is protected from pressure related damage through the high and low pressure alarm settings on the front panel of the gradient pump module. If the high pressure setting is correctly selected (200 psi above normal operating range), the pump will automatically shut-off if this value is exceeded. The reason for high backpressure is blockage in the system. Possibilities include loading against a closed valve, a plugged line, contaminated columns, etc. Diagnosis is done by removing one component of the system and observing how the pressure changes.

17.5.2.2 Low pressure. Low pressure readings usually indicate a leak somewhere in the system. Carefully check all fittings for leaks. Tighten if necessary.

17.5.3 Flow

17.5.3.1 Regenerant lines. If there is no flow at the waste outlet end of the regenerant line, check the following:

- Make sure the correct regenerant switch is turned on
- Verify that the reservoir is not empty
- Make sure the nitrogen tank is turned on
- Check that the regulator is correctly set

17.5.3.2 Eluent lines. If there is no flow at the outlet end of the eluent lines, check the following:

- Check that the pump is on
- Check that the eluent lines are connected to the correct port

17.5.4 Software. Refer to the ChromatoChart manual for detailed information on software problems.

18. Ammonia Analysis by Technicon Autoanalysis

Presented in Sections 18.1 and 18.2 are the recipes for the standards and reagents required to analyze the ammonium ion (NH_4^+ or ammonia (NH_3)) by Technicon autoanalysis. The prelude of these sections briefly describes the TRAACS 800 autoanalyzer and the sample flow through the TRAACS 800 for NH_4^+ analysis. This instrument is capable of quantifying, from a single sample, three different species simultaneously. An aliquot of the sample is taken from an automated sampler by syringe. A splitter divides the aliquot into the appropriate volumes required for the particular analyses. Each of the volumes is then transferred to the appropriate analytical cartridge. Sample flow diagrams that illustrate $SO_4^=$, NO_3^- and NH_4^+ analysis (although in Method IO-4, only ammonia is analyzed by this technique) from the citric acid denuder and Teflon® filter can be shown separately and independently of one another. The data computation (by computer) and quality assurance protocols, however, can not be readily adapted to single-channel instruments. These protocols need to be specific to the individual analytical instrument. In brief, NH_4^+ analysis is illustrated in Figure 16. The samples, along with all standards, are taken from the auto-advance sampler tray by the use of a proportioning pump and automated syringe. Air and EDTA are first added to the samples and are mixed in the first set of coils. After mixing, phenolate is added and mixed in the next set of coils. Nitroprusside is then added and mixed, followed by the addition and mixing of hypochlorite. At this stage, the sample should be a bright blue color. After the last mixing stage, the sample is sent through a heated bath, followed by another mixing stage. Finally, the sample is sent through a colorimeter where the results are recorded on a digital printer and stored in a computer file for further manipulation.

[Note: Ammonia can be analyzed by other techniques.]

18.1 Standards and Stock Solutions Preparation

[Note: Before discarding the old solution, it should be checked against the fresh solution by comparing calibration curves on the working solutions prepared from them. Slopes and intercepts are calculated for each set of standards. The old slope and intercept are used to calculate concentration values from readings for the new standards. This calculation determines if the old solution has deteriorated or if an error has been made in preparing the new solution.]

18.1.1 Ammonium Solution Standard (1,000 µg/mL). Dry ammonium chloride in an oven for 1 h at 50-60EC and desiccate over silica gel for 1 h. Weigh 2.9470 g ammonium chloride and dissolve in 800 mL DDW. Dilute to 1 L with DDW and mix thoroughly. This solution is stable for 1 y.

18.1.2 Intermediate Ammonium Standards. To make a 100 µg/mL ammonium standard, pipet 10 mL of ammonium stock standard into a 100 mL volumetric flask. Dilute to volume with DDW and mix thoroughly. Keep refrigerated. This solution remains stable for 1 month. To make a 10 µg/mL ammonium standard, pipet 1.0 mL of ammonium stock standard into a 100 mL volumetric flask. Dilute to volume with DDW and mix thoroughly. This solution remains stable for one week.

18.1.3 Working Ammonium Standards in DDW. Pipet aliquots of the 100 µg/mL ammonium intermediate standards into 100 mL volumetric flasks according to the table below. Dilute to volume with DDW. Prepare fresh daily.

Standard	Stock or intermediate standard, Fg/mL	Aliquot, mL	Concentration, Fg/mL
A	1,000	4.0	40.0
B	100	4.0	4.0
C	100	3.0	3.0
D	100	2.0	2.0
E	100	1.0	1.0
F	100	0.5	0.5
G	10	2.0	0.2
H	10	1.0	0.1

18.2 Reagent Preparation

[Note: When reagents are prepared, label the container with the contents, concentration, date prepared, and the preparer's initials.]

18.2.1 Alkaline Phenol. Add 83.0 g loose crystallized phenol to 800 mL DDW in a 1 L volumetric flask. Keeping the flask in an ice bath or under tap water, slowly add 96.0 mL 50% sodium hydroxide solution. Shake the flask while adding the sodium hydroxide. Cool to room temperature, dilute to 1 L with DDW, and mix thoroughly. Store in an amber glass container. This solution will remain stable for 3 mo, if kept out of direct light.

18.2.2 Sodium Hypochlorite Solution. The amount of sodium hypochlorite solution varies from batch to batch of sodium hypochlorite (5% commercial grade). Therefore, for each new batch, a base and gain experiment must be run to adjust the amount of sodium hypochlorite required to obtain the existing base and gain values. In a 150 mL volumetric flask, dilute 86 mL of 5% sodium hypochlorite solution to 100 mL with DDW and mix thoroughly. Check base and gain values. Reduce or increase the amount of sodium hypochlorite to obtain the same base and gain values as the previous sodium hypochlorite batch. This solution remains stable for 1 day.

18.2.3 Sodium Nitroprusside Solution. Dissolve 1.1 g of sodium nitroprusside in about 600 mL of DDW, dilute to 1 L with DDW, and mix thoroughly. Store in an amber container and keep in refrigerator. This solution remains stable for 1 month, if kept out of direct light.

18.2.4 Disodium EDTA Solution. Dissolve 1.0 mL of 50% w/w sodium hydroxide and 41.0 g of disodium EDTA mix thoroughly. Add 3.0 mL of Brij-35 and mix. Store in plastic container. This solution will remain stable for 6 months.

19. pH Analysis

19.1 Standard and Reagent Preparation

[Note: Each of the standard H_2SO_4 stock solutions must be prepared fresh the day of pH analysis.]

19.1.1 Standard H_2SO_4 Solution.

19.1.1.1 Label seven 25 mL polyethylene stoppered volumetric flasks. Also, label each flask with the volume of 1 N H_2SO_4 solution indicated in the following table:

Standard H_2SO_4, Flask No.	Volume of 1.000 N H_2SO_4 added to each flask, µL	Standard concentration, 10^{-3}N H_2SO_4
1	0	0
2	25	1
3	50	2
4	100	4
5	200	8
6	400	16
7	800	32

19.1.1.2 Use the 25 µL automatic pipet to add 1 N stock H_2SO_4 to flasks #1-3. Use the 100 µL pipet to add 1 N stock H_2SO_4 to flasks #4-7. Dilute all flasks to the 25 mL mark with absolute ethanol. Cap with stoppers or parafilm and mix well.

19.1.2 2 M Potassium Chloride (KCl) Solution.

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

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

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

19.1.2.4 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.

19.1.3 0.1 N Perchloric Acid ($HClO_4$) Solution.

19.1.3.1 Fill a 1 L graduated cylinder about ½ full with DDW. Transfer 10 ± 0.1 mL of 60-62% $HC10_4$ into the 1 L cylinder with a 10 mL pipet.

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

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

19.1.4 0.01 N $HClO_4$ Solution.

19.1.4.1 Fill a 1 L graduated cylinder about ½ full with DDW.

19.1.4.2 Measure 100 mL of the 0.1 N $HC1O_4$ solution with the 100 mL graduated cylinder. Add solution to the 1 L cylinder.

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

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

19.1.5 Extraction Solution (0.0001 N $HClO_4$).

[Note: This solution has the same composition as the solution used to fill the sample vials for Teflon® filters. It must be prepared fresh on the day of pH analysis.]

19.1.5.1 Using a 5 mL calibrated automatic pipet, add 10 ± 0.1 mL of 0.01 N perchloric acid ($HClO_4$) to a 2L Erlenmeyer flask of water. Add 990 ± 10 mL of DDW to the flask.

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

19.1.6 EA Solution.

19.1.6.1 Measure 150 ± 2 mL of 0.0001 N $HClO_4$ (prepared in Section 19.1.5) into a 250 mL graduated cylinder. Transfer to a 250 mL Erlenmeyer flask.

19.1.6.2 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 19.1.1) to the flask.

19.1.6.3 Again using a 5 mL graduated cylinder, add 3 ± 0.1 mL of 2 M potassium chloride (KCl) solution (see 19.1.2) to the flask.

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

19.1.7 Working Standard Test Solutions.

19.1.7.1 Place fourteen-4 mL polystyrene sample cups (as used with Technicon Auto-Analyzer II system) labeled 1, 1*, 2, 2*...7, 7* into racks. Using the calibrated dispensing pipet bottle, add 3 mL of EA solution to each 4 mL cup.

19.1.7.2 Using the displacement pipet, add 50 µL of absolute ethanol to each cup. Pour about 3 mL of standard (H_2SO_4 solution) #1 into a labeled 4 mL cup.

19.1.7.3 Immediately pipet 50 µL of this standard into the 4 mL cups labeled 1 and 1* containing the EA 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.]

19.1.7.4 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 cups.

19.1.7.5 To prepare for analysis, mix each mixture. Then transfer two aliquots from each cup to 2 mL sample cups. Place cup #1 in a rack. In a second rack place two-2 mL cups labeled 1 and 1-. Use the 1 mL automatic pipet to mix the contents of 4 mL cup #1 by drawing 1 mL into the pipet tip and then dispensing it back into the 4 mL cup three times. Use the same pipet to transfer 1 mL of the mixture to each of the two labeled 2 mL cups. Place caps on the two 2 mL cups. After transferring the two aliquots to 2 mL cups, rinse the automatic pipet tip in a flask of DDW. Repeat the transfer procedure for each of the other working standard pairs.

19.2 Calibration of pH Meter

The pH meter requires temperature calibration whenever a new electrode is used. Use the manufacture'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, the electrode lead is partially disconnected by pressing the plastic ring on its outer edge, 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.

19.3 Pre-Analysis Calibration

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

19.3.1 Use a pH Analytical Log Form to record all data (see Figure 17). While still in standby mode, reconnect the electrode lead at the back of the pH meter.

19.3.2 Fill three 4 mL cups 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 cup of pH 7 buffer. Do not test pH of the first cup.

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

19.3.4 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 log for "1st cup."

19.3.5 Turn to standby mode, and then test the last cup of pH 7 buffer. Record the results on the log for the "2nd cup." 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.

19.3.6 Fill three 4 mL cups 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 cup of pH 4 buffer.

19.3.7 Test the next two cups of pH 4 buffer as above, recording the results on the log. If the pH value for the 2nd cup is not 4.00 ± 0.01, adjust the "slope" knob to get a reading of 4.00. If the value for the second cup was not 4.00 ± 0.03, the calibrations at pH 7 and at pH 4 must both be repeated.

19.4 pH Test 0.01 N $HClO_4$ Solution

[Note: The 0.01 N $HClO_4$ 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, the 0.01 N $HClO_4$ solution must be reprepared.]

19.4.1 Calibrate the pH meter with pH 4 buffer.

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

19.4.3 Fill three 4 mL cups with EA solution. Measure the pH of the test EA solution as with the buffer solutions this value must be 4.09 ± 0.10.

19.4.4 If the above pH value is not achieved, follow the steps outlined in Sections 18.1.3 through 18.1.6 to reprepare the solutions. Test the pH of the new solutions. Repeat as necessary to obtain a pH of 4.09 ± 0.04.

19.4.5 Leave the electrode immersed in the "2nd cup" with the meter in the standby mode until ready to start analysis of the working standards.

19.5 Analysis of Working Standard

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

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

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

19.5.2 After testing the pH of cup #1, test cup #1-. Record the results of both on the pH Analytical Log Form.

19.5.3 With the meter in the stand-by mode, remove the #1- sample cup, wipe the electrode with a Kimwipe®, and test one 2 mL cup of EA solution. Rinse with DDW.

19.5.4 Test a 2nd cup of EA solution; record the results for both cups on the logsheet. Discard the 1st cup of EA, but retain the 2nd cup to be used as the 1st cup for the next EA test.

19.5.5 Continue testing the remainder of the working standards, #1*, 1*-, ... 7, 7-, 7*, 7*-. Remember that the electrode tip is wiped before and after each pair of test solutions, but not in between two cups of the same sample.

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

19.5.6 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 logsheet.

19.6 Analysis of Filter Extracts

After measuring the pH of the working standards, measure the pH of the filter extracts to which 20 FL of 2M KCl solution (19.1.2) has been added, and record all results on the log. After all the filter extracts have been tested make an additional test with the EA solution. At the end make a final test of pH 4 buffer. With the mode control in the standby mode, shut down the pH meter by disconnecting the electrode lead at the back of the meter, leaving the meter power cord plugged into the AC line. Immerse the electrode tip in the bottle of 4 M KCl.

20. Atmospheric Species Concentration Calculations

The system described in the previous sections collects nitric acid (HNO_3), sulfur dioxide (SO_2), ammonia (NH_3), particulate sulfate ($SO_4^=$), particulate nitrate (NO_3^-), particulate ammonium (NH_4^+), and acidic (H^+) particles. The collection of each of these species is illustrated in Figure 1. Nitric acid and sulfur dioxide gases are collected on denuder one. Ammonia gas is collected on denuder two. Particulate sulfate, nitrate, and ammonium are collected on the first (Teflon)® filter, while some of the particulate nitrate collected on the Teflon® filter evaporates and collects on the second (nylon) filter. Also collected on the Teflon® filter are fine particles that contain hydrogen ions (H^+), though probably not free H^+. Hydrogen ions are most likely present in the H_3O^+ form. The concentration of these H^+ ions indicates the atmospheres acid aerosol content and is collected on the nylon filter. Prepare the Teflon® filter extracts for pH analysis prior to IC analysis for the particulate sulfate contents. Special precautions must be taken to prevent contamination of the Teflon® filters by ammonia before either of the analyses.

20.1 Assumptions of the Annular Denuder System

20.1.1 A number of assumptions are made about the performance of the annular denuder system so that validity of the calculations presented later in this section will hold true. As discussed in Section 6, significant interferences need to be considered to make accurate estimations of species concentrations. The assumptions are as follows:

- The first denuder stage collects 100% of sampled HNO_3 as nitrate. (Since the diffusivity of HNO_3 is high, diffusion to the side walls is assumed to be very quick.)
- The first denuder collects 100% of the SO_2 as sulfite, which can oxidize to sulfate.

[Note: Before analysis, add hydrogen peroxide (H_2O_2) to oxidize the sulfite (SO_3^-) to sulfate ($SO_4^=$) to simplify the calculations.]

- The second denuder stage collects 100% of the sampled ammonia (NH_3) as ammonium ion (NH_4^+).
- The Teflon® filter is 100% efficient for particulate sulfate, nitrate, and ammonia. Particle losses are less than 1% on each denuder. This assumption may or may not stand true depending on the concentrations of the components in the air sampled. Modifications may be needed to avoid low (or underestimates of) acidic measurements. For example, another filter stage may need to be added to accurately account for the particulate ammonia content of the air sampled. If ammonium nitrate (NH_4NO_3) was collected on the Teflon® filter, its probability of evaporation is high. Therefore, a citric acid-impregnated filter downstream would correct for the loss from the Teflon® filter. Also, interaction of ammonia and sulfuric acid neutralizes the filter and causes the acidic measurement to be biased. (Again diffusion rules the particle loss assumption; particles have lower diffusivities than gases.)
- The nylon filter collects any nitrate that evaporates from the Teflon® filter.

20.1.2 Analytical results from the IC and technician autoanalysis are given in units of µg/mL from NO_3^-, $SO_4^=$, and NH_4^+, respectively.

20.1.3 The extraction volume was 11 mL for Na_2CO_3 denuder(s) and 10 mL (i.e., 0.010 L) for the citric acid denuder extractions and the nylon filter and 6.2 mL for the Teflon® filter.

20.2 Calculation of Air Volume Sampled, Corrected to Standard Conditions

20.2.1 The total sample 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.

20.2.2 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.

20.2.3 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 20.2.2), 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.

20.3 Calculations of Concentration Using Results from IC and Technicon Autoanalysis

20.3.1 Analytical Results for HNO_3 from Na_2CO_3 Denuder

$$C_g\ (HNO_3),\ \mu g/m^3 = 1.016\ [NO_3^-\ (\mu g/mL) \times 10\ mL]/V_{std}$$

This factor 1.016 represents the ratio of molecular weights of HNO_3^- and NO_3^-. Subscript "g" denotes "gas."

20.3.2 Analytical Results for SO_2 from Na_2CO_3 Denuder

$$C_g\ (SO_2),\ \mu g/m^3 = 0.667\ [SO_4^=\ (\mu g/mL) \times 10\ mL]/V_{std}$$

The factor 0.667 represents the ratio of molecular weights of SO_2 and $SO_4^=$. Subscript "g" denotes "gas."

20.3.3 Analytical Results for NH_3 from Citric Acid Denuder

$$C_g\ (NH_3),\ \mu g/m^3 = 0.944\ [NH_4^+\ (\mu g/mL) \times 10\ mL]/V_{std}$$

This factor 0.944 represents the ratio of molecular weights of ammonia to ammonium ion. Subscript "g" denotes "gas."

20.3.4 Analytical Results for Particulate $SO_4^=$ Captured on Teflon® Filter

$$C_p\ (SO_4),\ \mu g/m^3 = [SO_4^=\ (\mu g/mL) \times 6.2\ mL]/V_{std}$$

This formula expresses the assumption that essentially all of the particulate sulfate is collected on the Teflon® filter and no evaporation occurs. The subscript "p" denotes "particles."

20.3.5 Analytical Results for Particulate NH_4^+ Captured on Teflon® Filter

$$C_p\ (NH_4^+),\ \mu g/m^3 = [NH_4^+\ (\mu g/mL) \times 6.2\ mL]/V_{std}$$

This formula expresses the assumption that essentially all of the particulate ammonia is collected on this Teflon® filter and no evaporation occurs. The subscript "p" denotes "particles."

20.3.6 Analytical Results for Particulate NO_3^- Captured on Teflon® Filter

$$C_{pt}\ (NO_3^-_p),\ \mu g/m^3 = [NO_3^-\ (\mu g/mL) \times 6.2\ mL]/V_{std}$$

Nitrates evaporator from the Teflon® filter during sampling, so one must also calculate the NO_3^- on the nylon filter. The subscript "pt" denotes particles on Teflon® filters.

$$C_{pn}\ (NO_3^-),\ \mu g/m^3 = [NO_3^-\ (\mu g/mL) \times 10\ mL]/V_{std}$$

The subscript "pn" denotes particles on the nylon filter. Calculate the particulate nitrate concentration by:

$$C_p\ (NO_3^-) = C_{pt}\ (NO_3^-) + C_{pn}\ (NO_3^-)$$

20.4 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 basing 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^+ concentration for this method are 10% and 5%, respectively, for sample pH values in the 4.00 to 7.00 range.

20.4.1 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 based 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.

20.4.2 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.]

20.4.3 Calculation of Strong Acidity Aerosol Concentration. Calculate the final concentration of apparent net fine particle (<2.5 Fm) strong acidity (as H_2SO_4):

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

where:

C_H+ = apparent net fine particle str\\\\\=ong 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-referenced conditions (see Section 17.2.3), m^3.

21. Variations of Annular Denuder System Usage

As described in Sections 3 and 4, the ADS is used to measure reactive acidic (SO_2 and HNO_3) and basic (NH_3) gases, particulate sulfates and nitrates, and strong acidity of atmospheric particles (<2.5 µm) found in ambient air. The unique features of the ADS that separate it from established air monitoring methods are the ability of sampling artifacts to be eliminated from the collected gases and particles and preservation of the samples for subsequent analysis, which is accomplished by removing NH_3 in the gas stream with a citric acid coated denuder, thus reducing the probability of the particulate acid sulfates ($SO_4^=$) captured on the Teflon® filter from being neutralized. The ADS configuration described in this methodology clearly illustrates these unique features. The elutriator is designed to allow only particles with <2.5 µM diameter into the system. The impactor is designed to reduce the possibility of coarse particle infiltration even further. And finally, the sequence of the

denuders reduces interference of possible chemical reactions that could cause under-or over-estimations of concentrations to be made. Although this configuration is recommended for measuring these gases and particulates, the user may wish to measure only one or two of the chemical species. The following discussion will present possible variations of the ADS to accommodate such usages.

21.1 Today, the ADS is being used in intercomparison studies to assess NH_3 concentration differences indoors and outdoors. The assembly used here consists of an elutriator-impactor assembly, an annular denuder, and a filter pack assembly. The elutriator-impactor assembly and the annular denuder are both smaller than those described earlier. The filter pack is available in the smaller size, but an adaptor is also available to assemble the smaller annular denuder to the larger filter pack assembly. This system is referred to as the personal sampler (see Figure 18). It is designed for sampling while attached to the shirt of a worker. The personal sampler can be used to measure other chemical species in indoor air by simply changing the reactive surface (coating) of the annular denuder or the types of filters used.

21.2 Another variation of ADS application is simultaneous use in parallel with a fine particle sampler. The fine particle sampler assembly is very similar to the annular denuder assembly. The main difference is that a flow-straightener tube replaces the annular denuder. The flow-straightener is a shorter version, 1-1/4 to 4" long, of the annular denuder and creates even air flow across the filters to collect particulate matter. Again the elutriator-impactor assembly and flow-straightener are available in smaller sizes with accommodating filter pack assemblies. In addition, the ADS carrying and shipping cases as well as the sampling box can be adjusted to accommodate the ADS and fine particle sampler. The assemblies as they would appear in the sampling box ready for sampling are illustrated in Figure 19.

21.3 If one has interest in quantitations HNO_2 utilizing the ADS, special sampling and analytical concerns must be addressed. As identified in Section 24, Citation 14, guidance is given for accurate quantitation of HNO_2 in ambient air.

21.4 The annular denuder methodology has been extended to other constituents, as indicated in Table 5.

22. 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 and determine the applicability of regulatory limitations prior to the implementation of this procedure. These practices should be part of the user's SOP manual.

23. Performance Criteria and Quality Assurance (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.

23.1 Standard Operating Procedures (SOPs)

23.1.1 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.

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

23.2 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. Calibration procedures provided in Sections 17 and 19, operation procedures in Sections 14 and 17, and maintenance procedures in Section 17 of this method and the manufacturer's instruction manual should be followed and included in 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* (Section 24, Citation 12) and the *U. S. EPA Handbook on Quality Assurance* (Section 24, Citation 13).

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

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

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

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

23.2.2.3 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.

24. References

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12. 40 CFR Part 58, Appendix A, B.

13. *Quality Assurance Handbook for Air Pollution Measurement Systems*, *Volume II - Ambient Air Specific Methods (Interim Edition)*, U.S. Environmental Protection Agency, EPA Office of Research and Development, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, NC, 27511, EPA-600/R-94/038b, May, 1972.

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TABLE 1. ESTIMATED DETECTION AND QUANTIFICATION LIMITS FOR THE ANNULAR DENUDER SYSTEM[1]

	Sampling period		
Detection limits, µg/m^3	1 hour	1 day	1 week
Gaseous species			
SO_2	3.1	0.13	0.02
HNO_3	2.0	0.08	0.01
NH_3	5.6	0.25	0.04
Particulate matter			
$SO_4^=$	1.6	0.07	0.01
NO_3^-	1.8	0.08	0.01
H^+	1.0	0.05	0.001
Quantification limits, Fg/m^3			
Gaseous species			
SO_2	10.4	0.43	0.06
HNO_3	6.8	0.28	0.04
NH_3	20.0	0.83	0.12
Particulate matter			
SO_4 =	5.3	0.22	0.03
NO_3^-	6.1	0.25	0.04
H^+	2.1	0.15	0.01

[1]Samples analyzed by ion chromatography. Detection limits are taken as three standards deviations above field blanks. Quantification limits are taken as ten standard deviations above field blanks. Both the detection and quantification limits were estimated assuming that the variance is independent of concentration.

TABLE 2. ACCELERATOR JET DIAMETERS AND CORRESPONDING REYNOLDS NUMBER (RE) FOR SELECTED FLOW RATES TO OBTAIN 2.5 µm DIAMETER (AERODYNAMIC) PARTICLES SEPARATION

Flow rate, L/min	Jet diameter, mm	Reynolds number (RE)
1.0	1.55	900
2.0	1.97	1,400
5.0	2.65	2,700
10.0	3.33	4,200
12.0	3.55	4,700
15.0	3.85	5,500
16.7	4.00	6,000
20.0	4.25	6,600

TABLE 3. SUMMARY OF KEY PROBE SITING CRITERIA FOR ACID AEROSOL MONITORING STATIONS

Factor	Criteria
Vertical spacing above ground	• 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	• 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	• Unrestricted airflow must exist in an arc of at least 270 degrees around the sampler, and the predominant wind direction for the monitoring period must be included in the 270 degree arc.
Spacing from roads	• 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 4. DILUTION RATES

Standard H_2SO_4 Flask No.	Volume of 1.0 N H_2SO_4 Added to Each Flask, mL	Equivalent Strong Acid Mass Collected on Filter, Fg[a]	Approximate pH
1	0.000	0	4.09
2	0.025	4.90	4.01
3	0.050	9.80	3.95
4	0.100	19.60	3.84
5	0.200	39.20	3.68
6	0.400	78.40	3.48
7	0.800	156.80	3.23

[a]Based on 6.2 mL extraction volume.

TABLE 5. OTHER CHEMICAL SPECIES
AMENDABLE TO ANNULAR DENUDER TECHNOLOGY

Symbol	Chemical Species Collected on Annular Denuder	Coating	Comments
O_3	Ozone	1% (wt/wt) $NaHCO_3$/glycerin	Analysis by IC or colorimetry
HCl HF	Hydrogen Chloride Hydrogen Fluoride	Na_2CO_3-alkali coating	Extracted with water/ analyzed by IC
PAHs SVOCs	Semi-volatile polycyclic aromatic hydrocarbons	Ground XAD-4/glycerin	Soxhlet extraction/GC/MS analysis

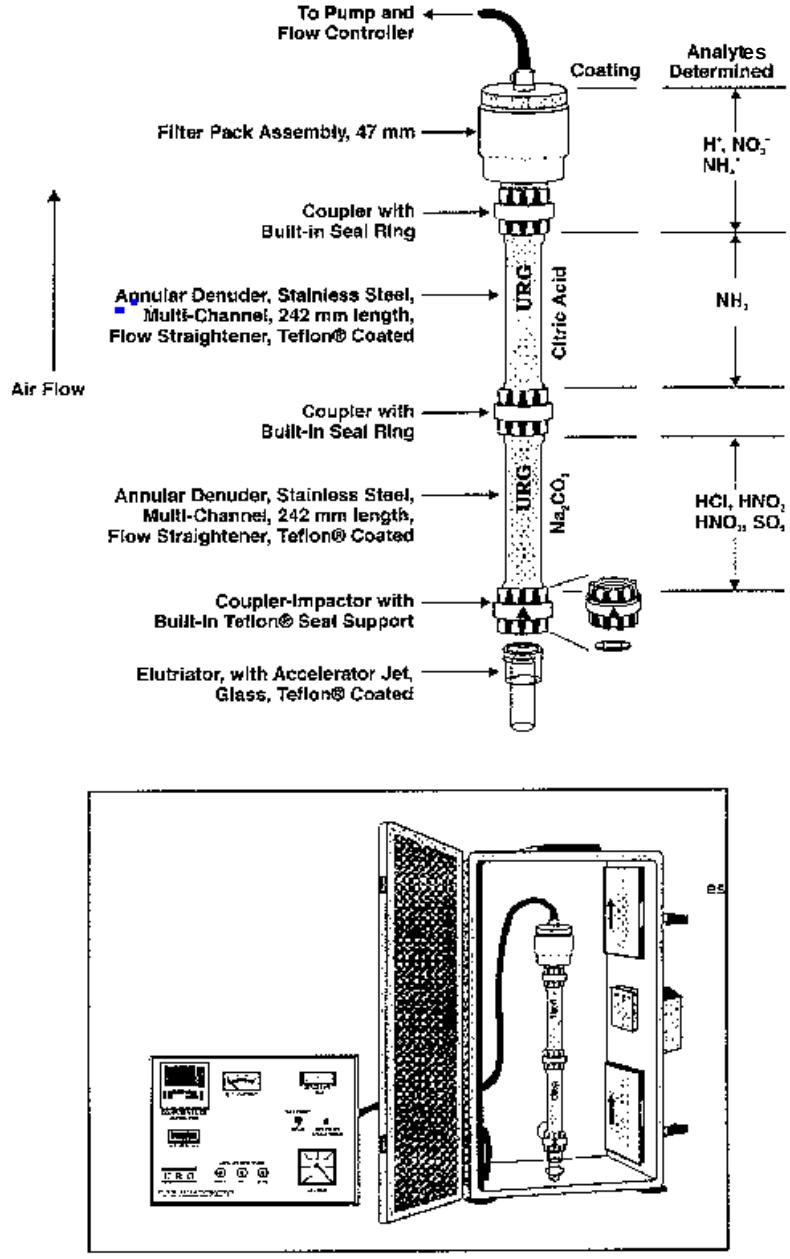

Figure 1. Schematic view of Annular Denuder showing species collected.

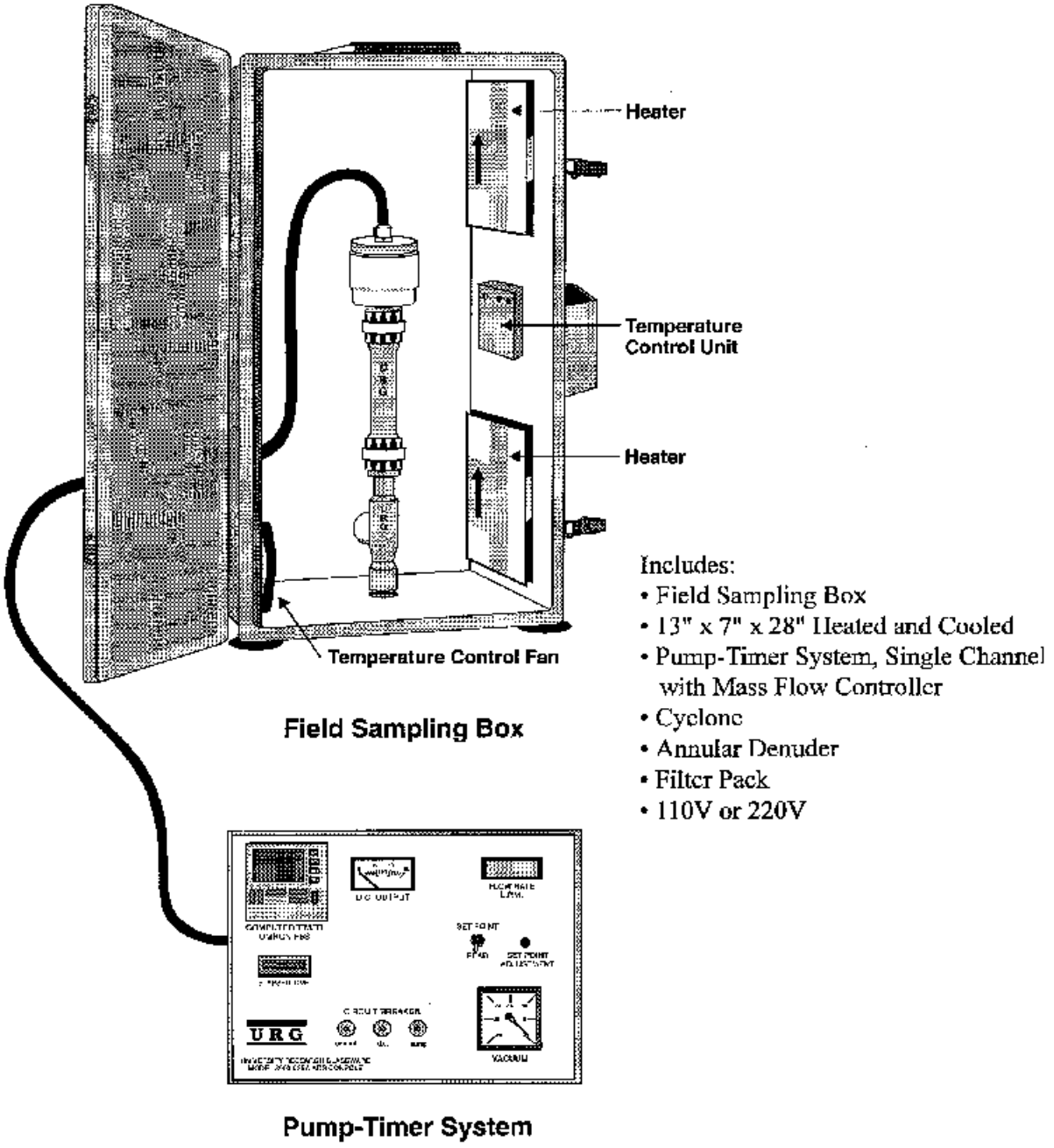

Figure 2. Annular Denuder system in field sampling box.

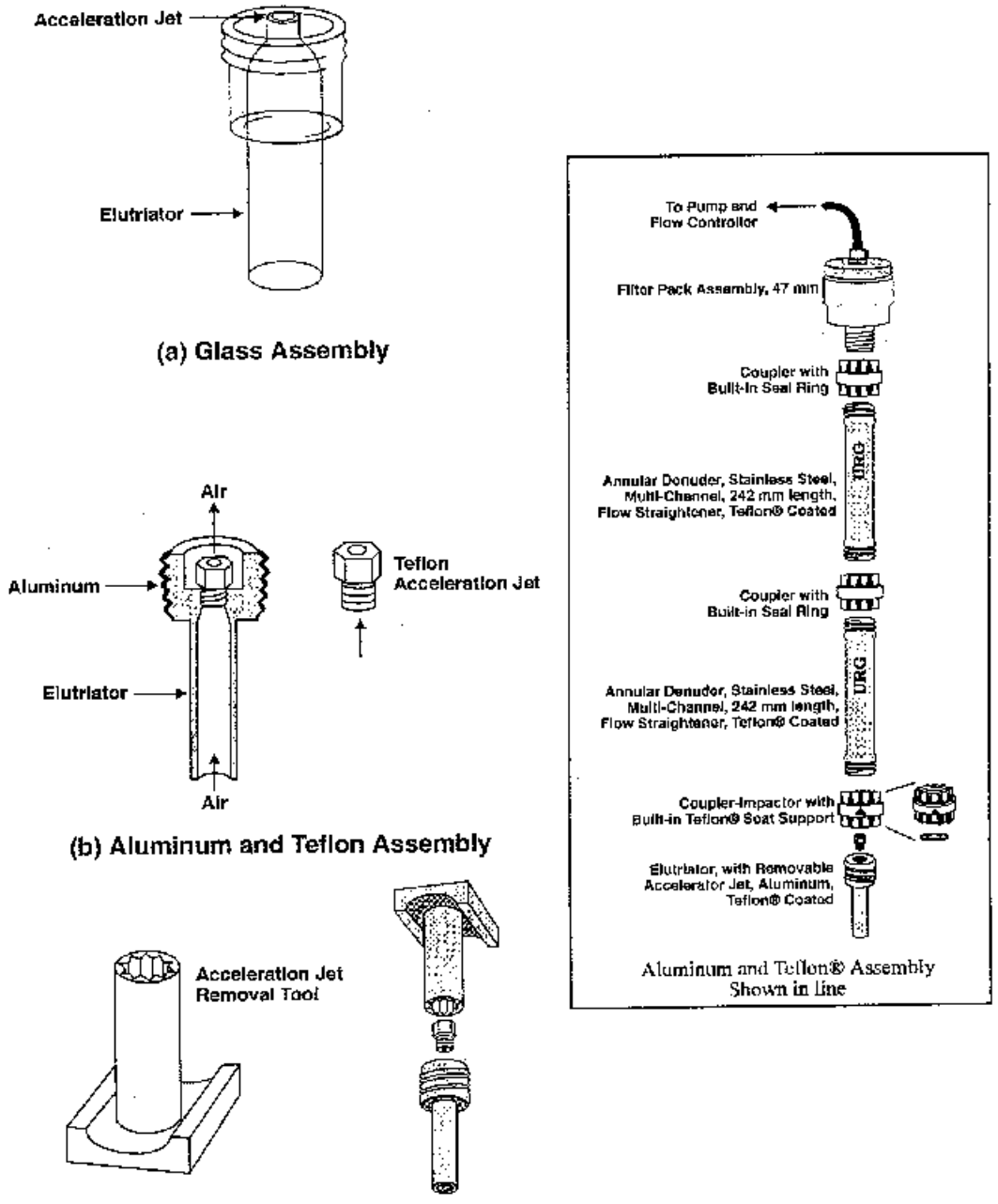

Figure 3. Available elutriator and acceleration jet assemblies.

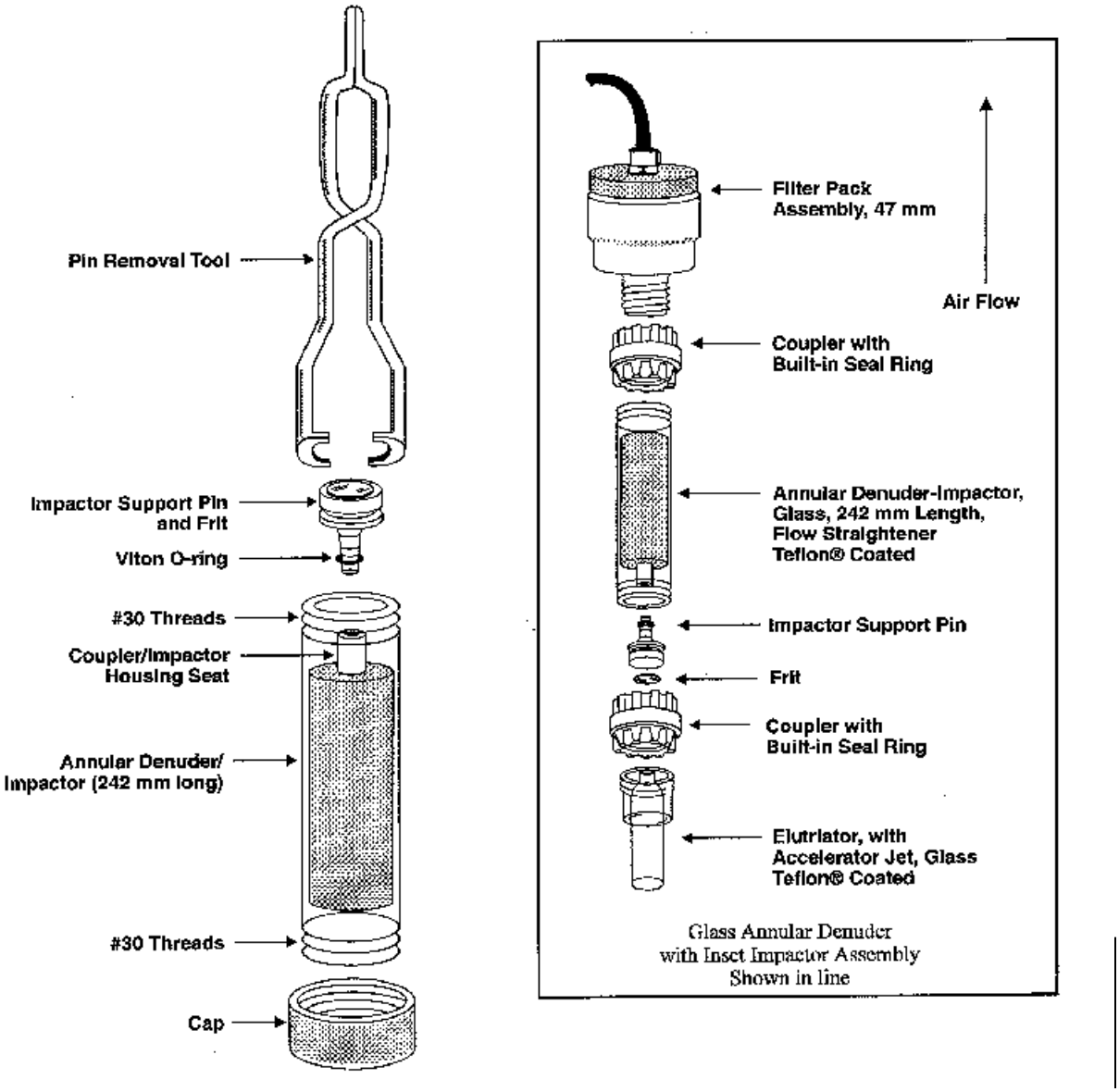

Figure 4. Glass Annular Denuder with inset impactor assembly.

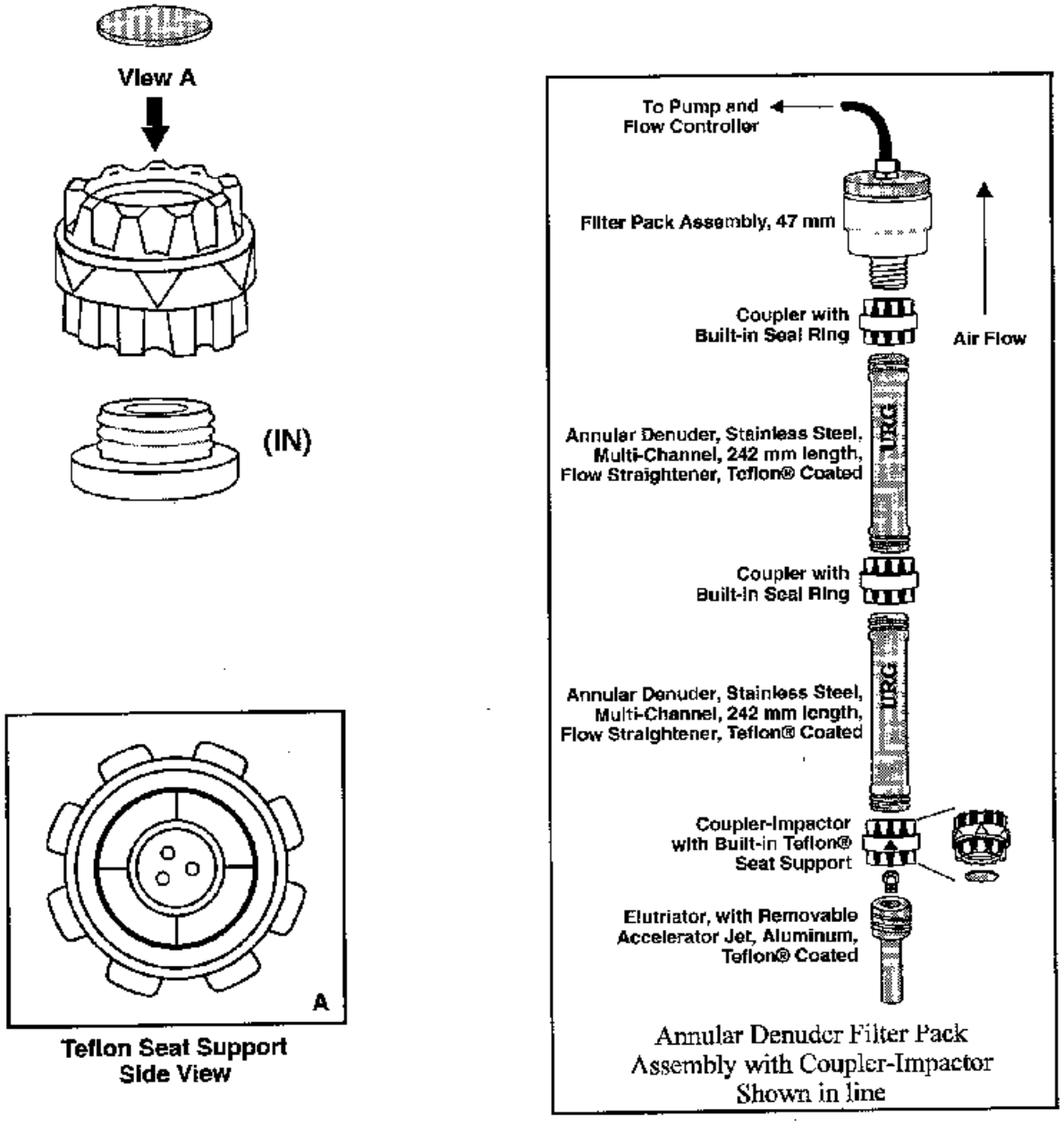

Figure 5. Side view impactor/coupler assembly.

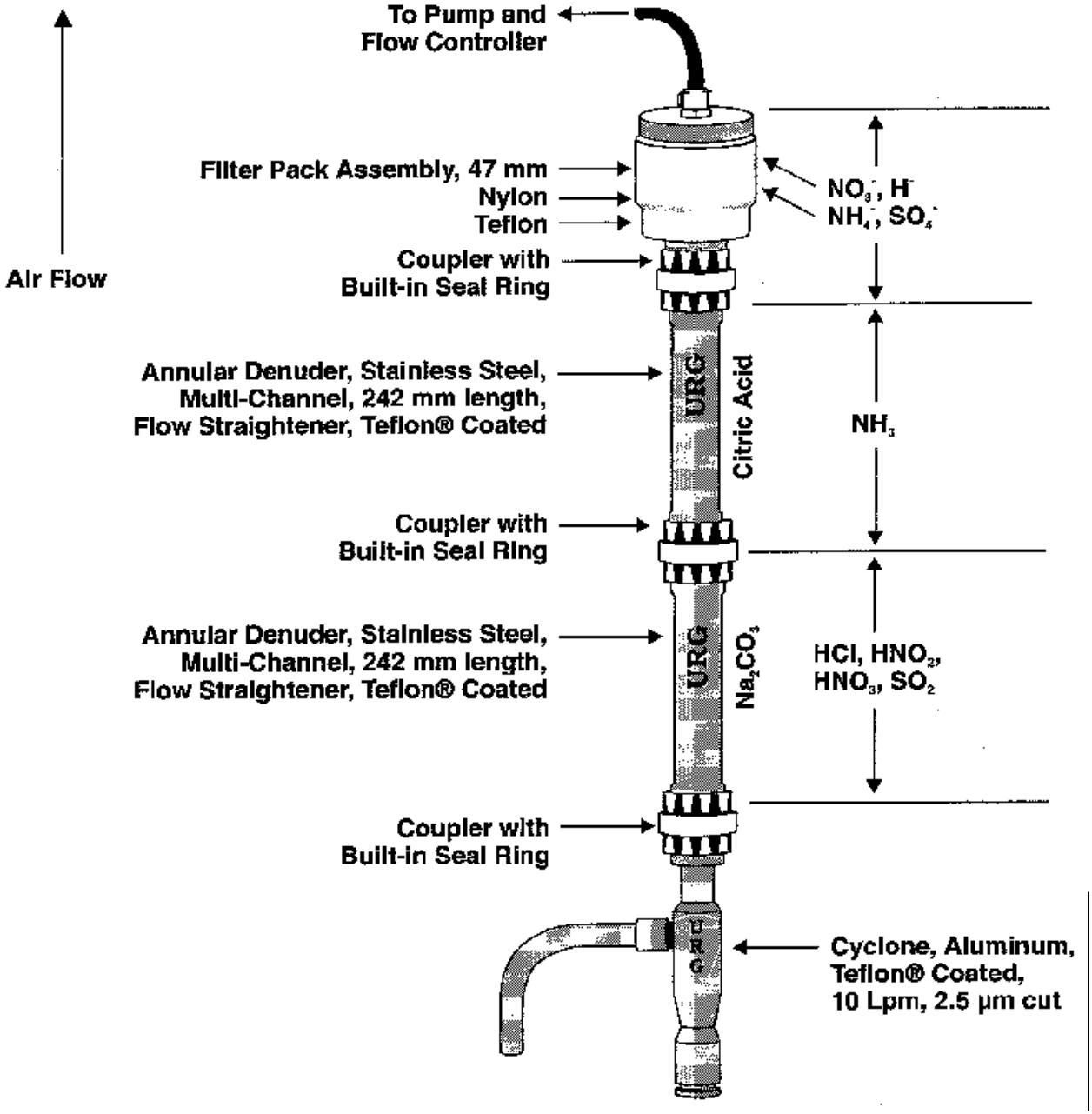

Figure 6. Schematic view of Annular Denuder with cyclone adaptor for removal of coarse particles.

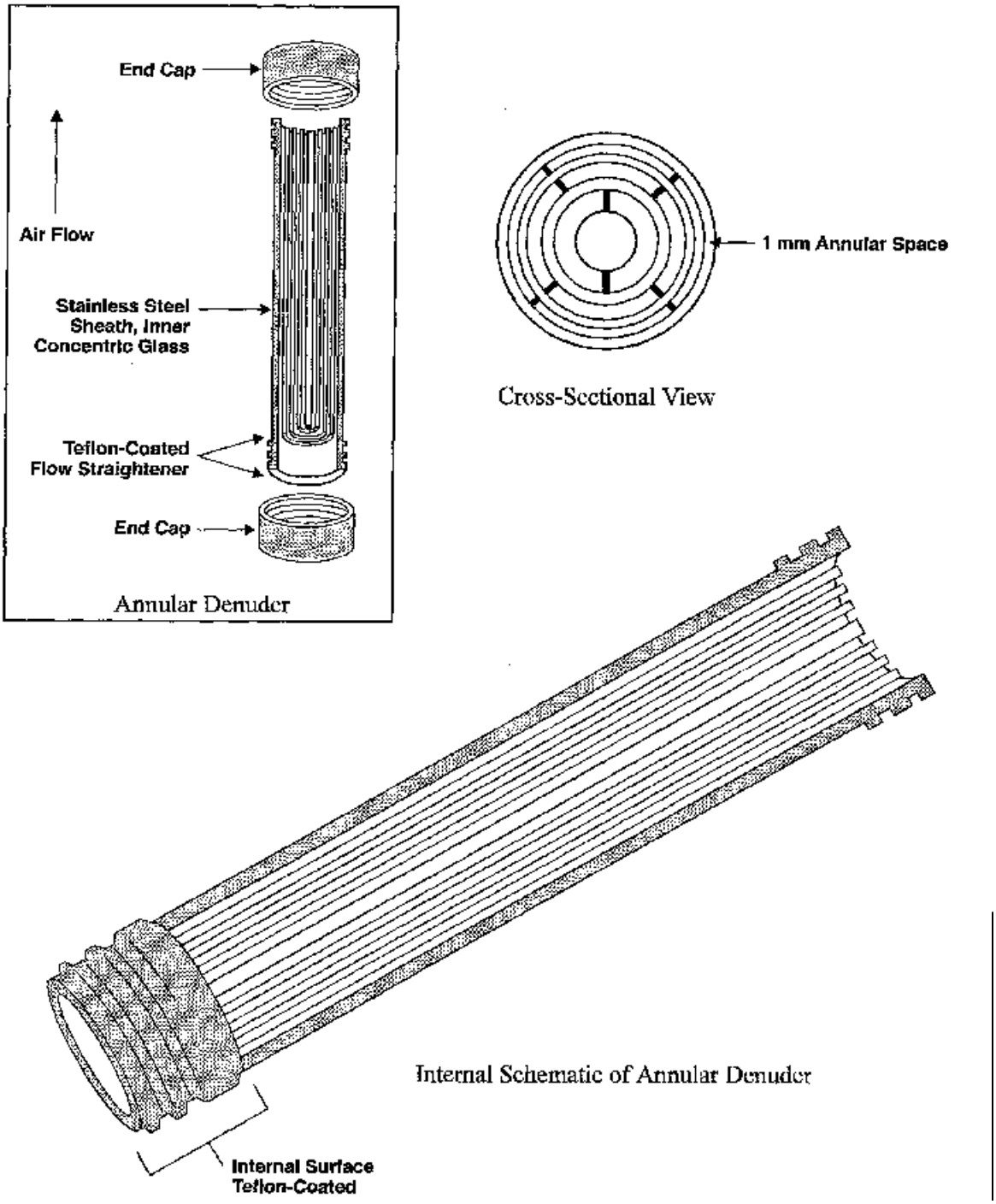

Figure 7. Internal schematic of Annular Denuder.

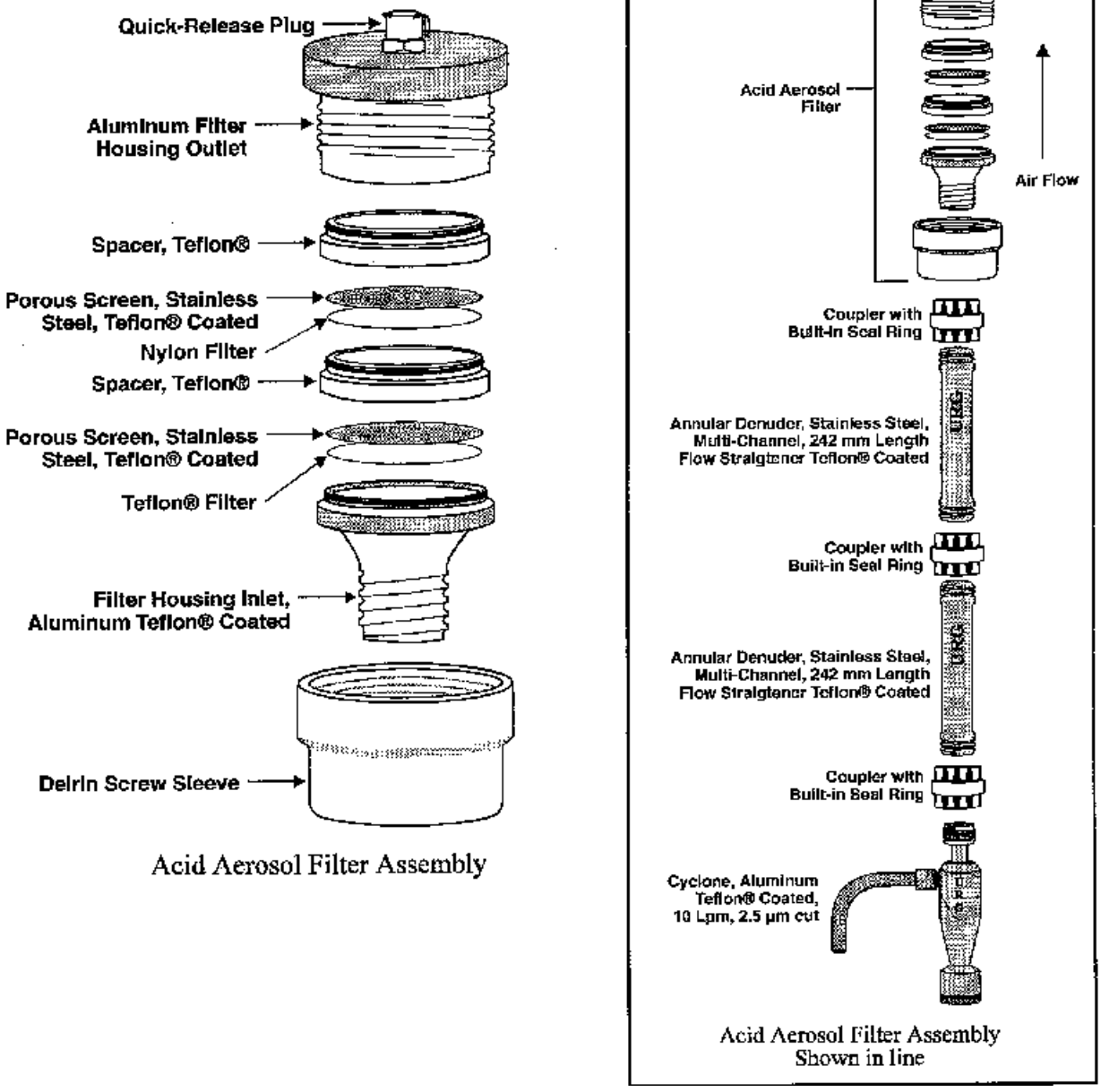

Figure 8. Filter pack assembly.

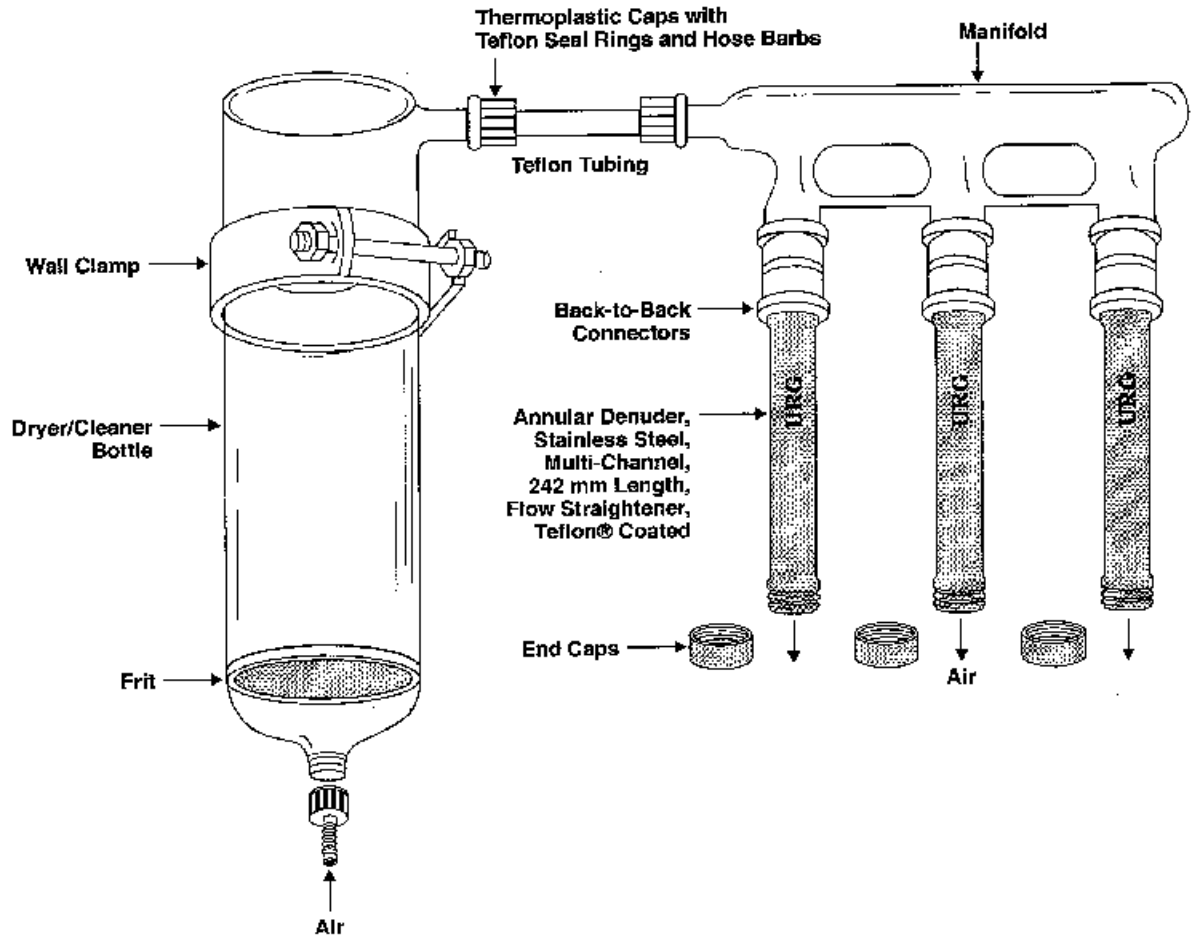

Figure 9. Drying train and manifold.

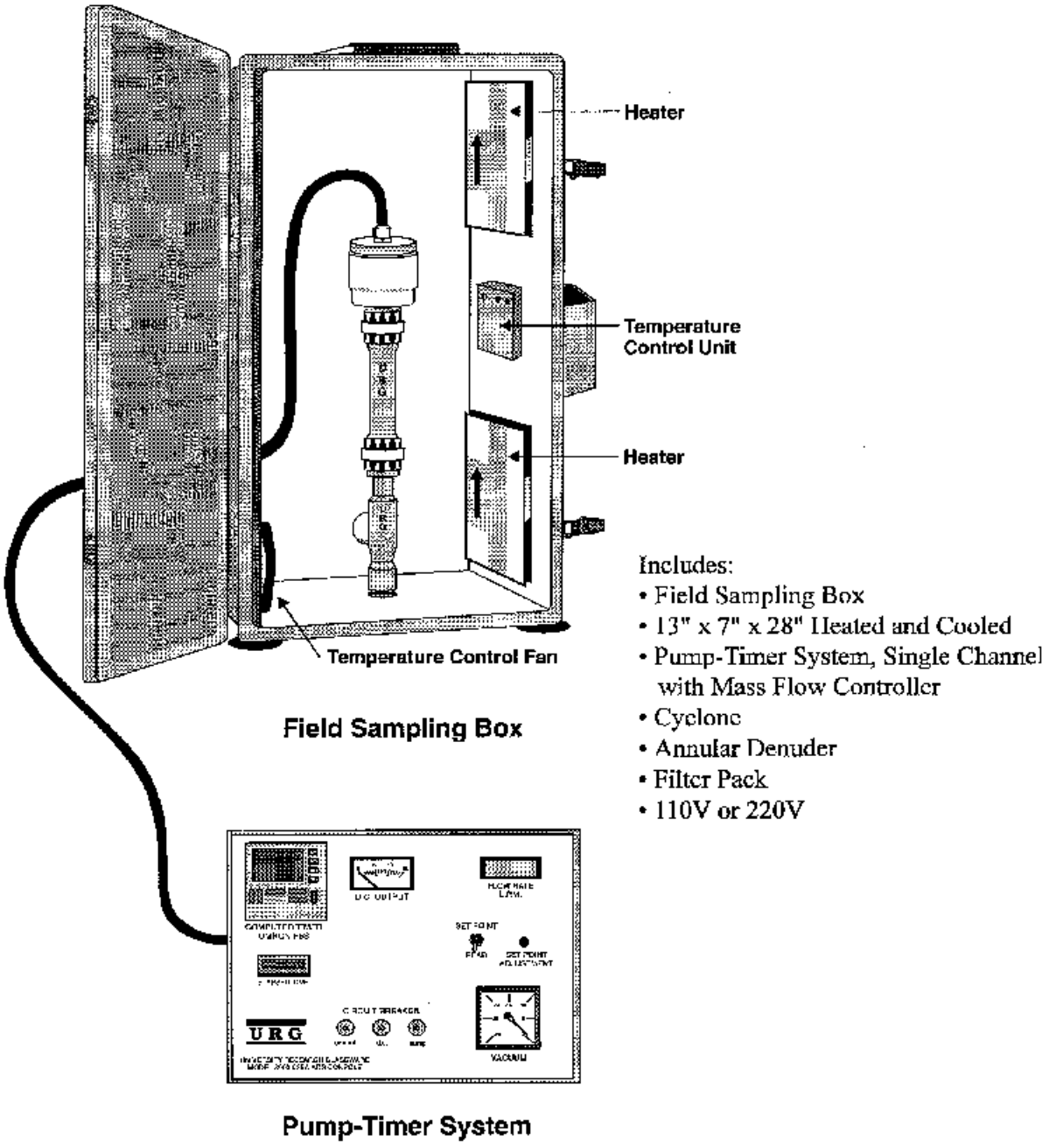

Figure 10. Annular Denuder system with cyclone in heated sampling case.

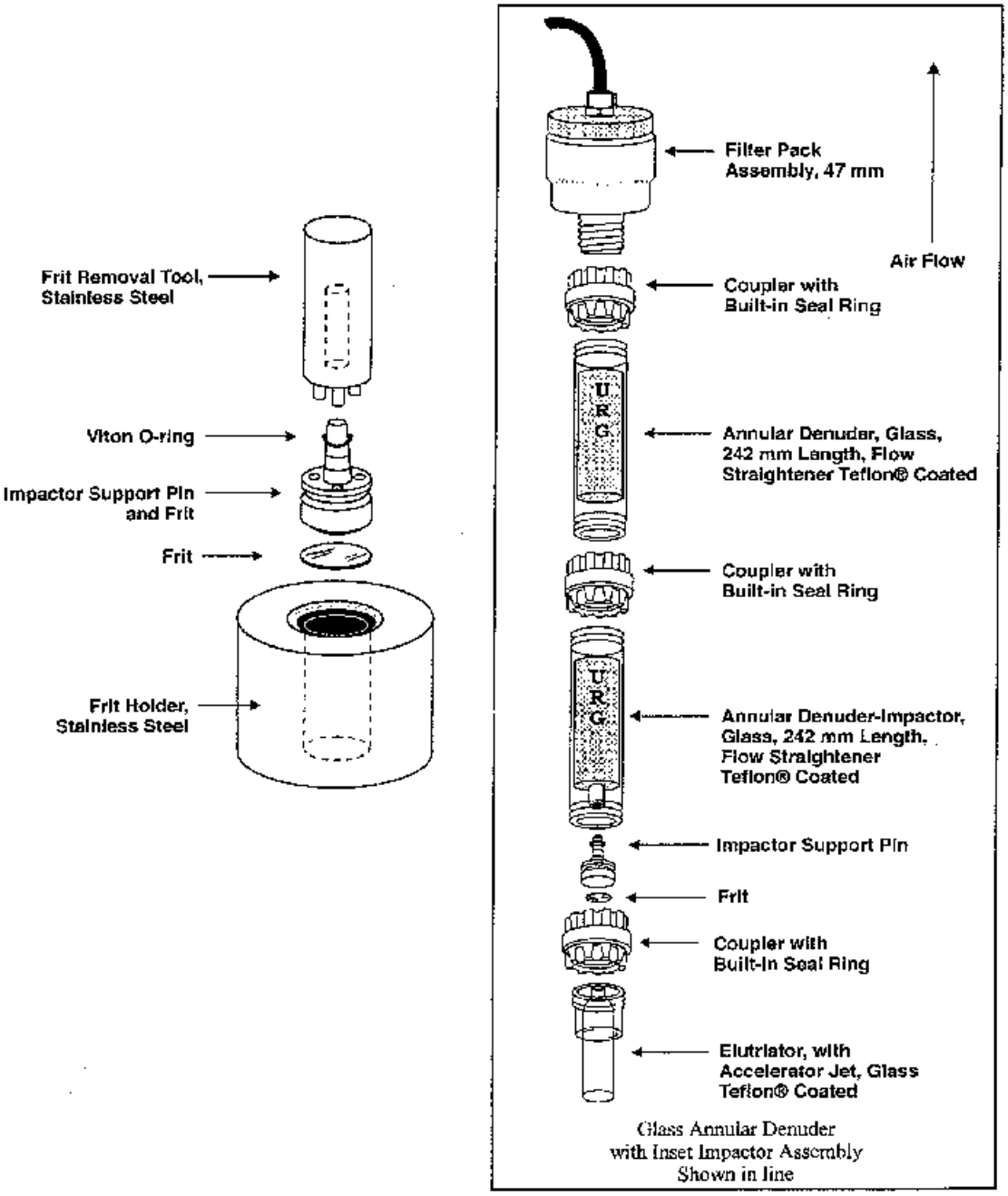

Figure 11. Frit removal from pin.

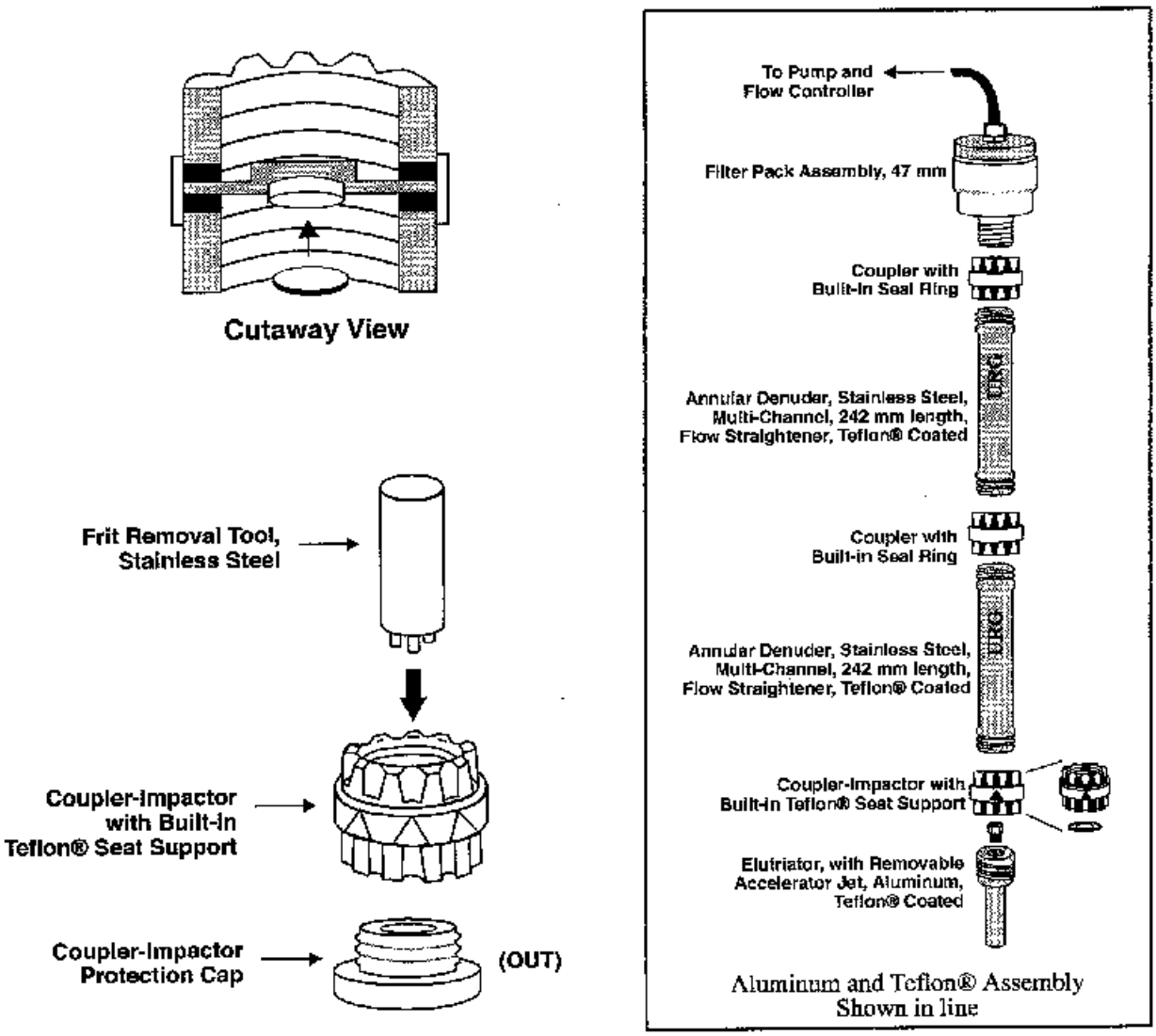

Figure 12. Side view impactor/coupler assembly with disc removal tools.

GENERAL

Project: _____ Date: _____
Site: _____ Location of Sampler: _____
Location: _____
_____
_____

Operator: _____
Sample Code: _____

EQUIPMENT

Sampler

Mass Flow
Controller No.: _____ Sodium Carbonate Denuder No. _____
Lab Calibration Date: _____ Citric Acid Denuder No.: _____
Flow Rate Set Point: _____ Filter Assembly No.: _____
Calibrated By: _____
Rotameter No.: _____
DGM No.: _____

SAMPLING DATA

Time Stop

Time: _____
Flow Rate: _____
Temperature: _____
Pressure: _____
Avg. Flow Rate: _____
Leak Check (Before): _____
(After): _____

Total Sample Vol.: _____
Flow Maintained Rate: _____ (± 5%)

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

Figure 13. Annular Denuder Field Test Data Sheet.

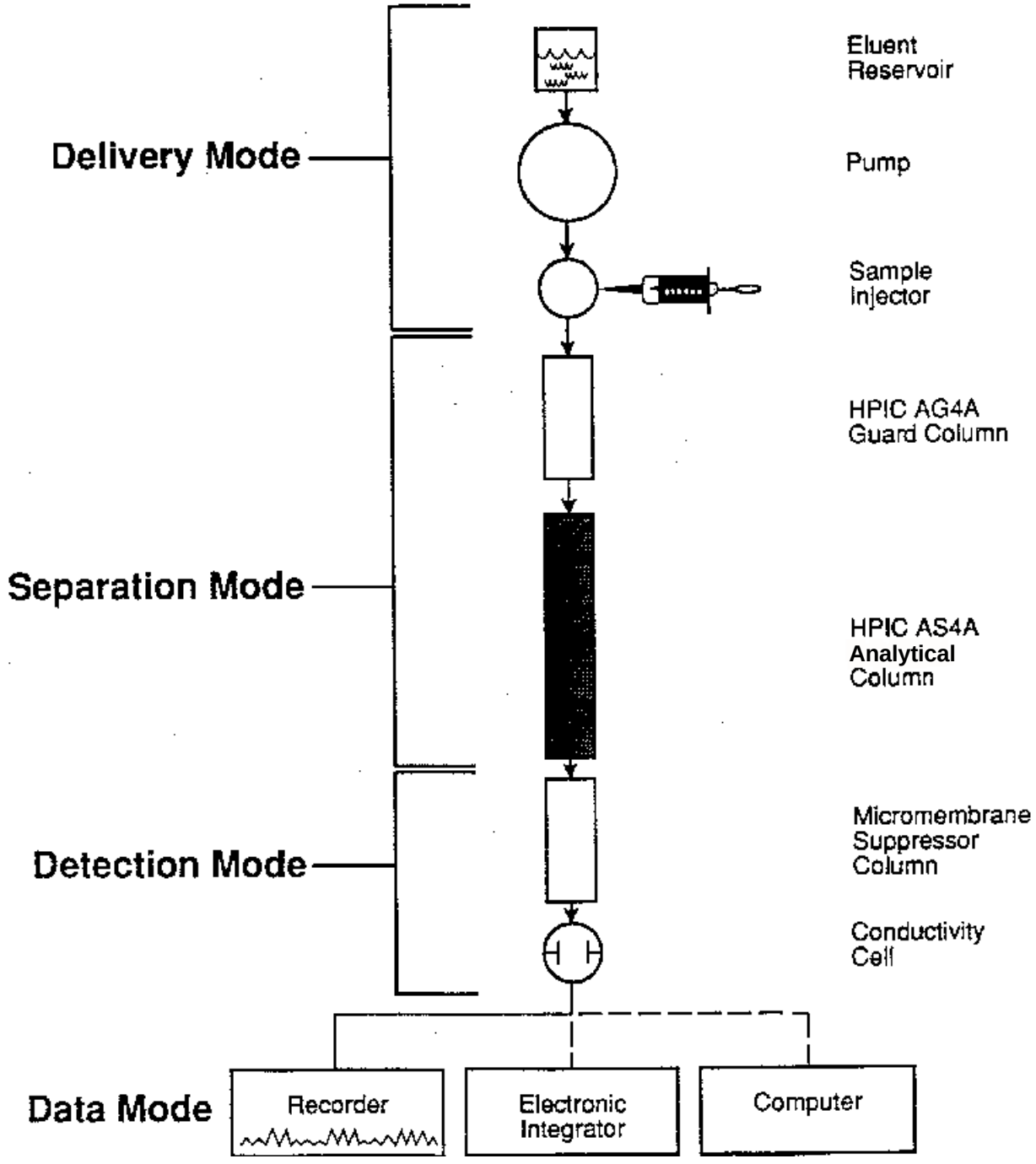

Figure 14. Major components of a commercially available ion chromatographer.

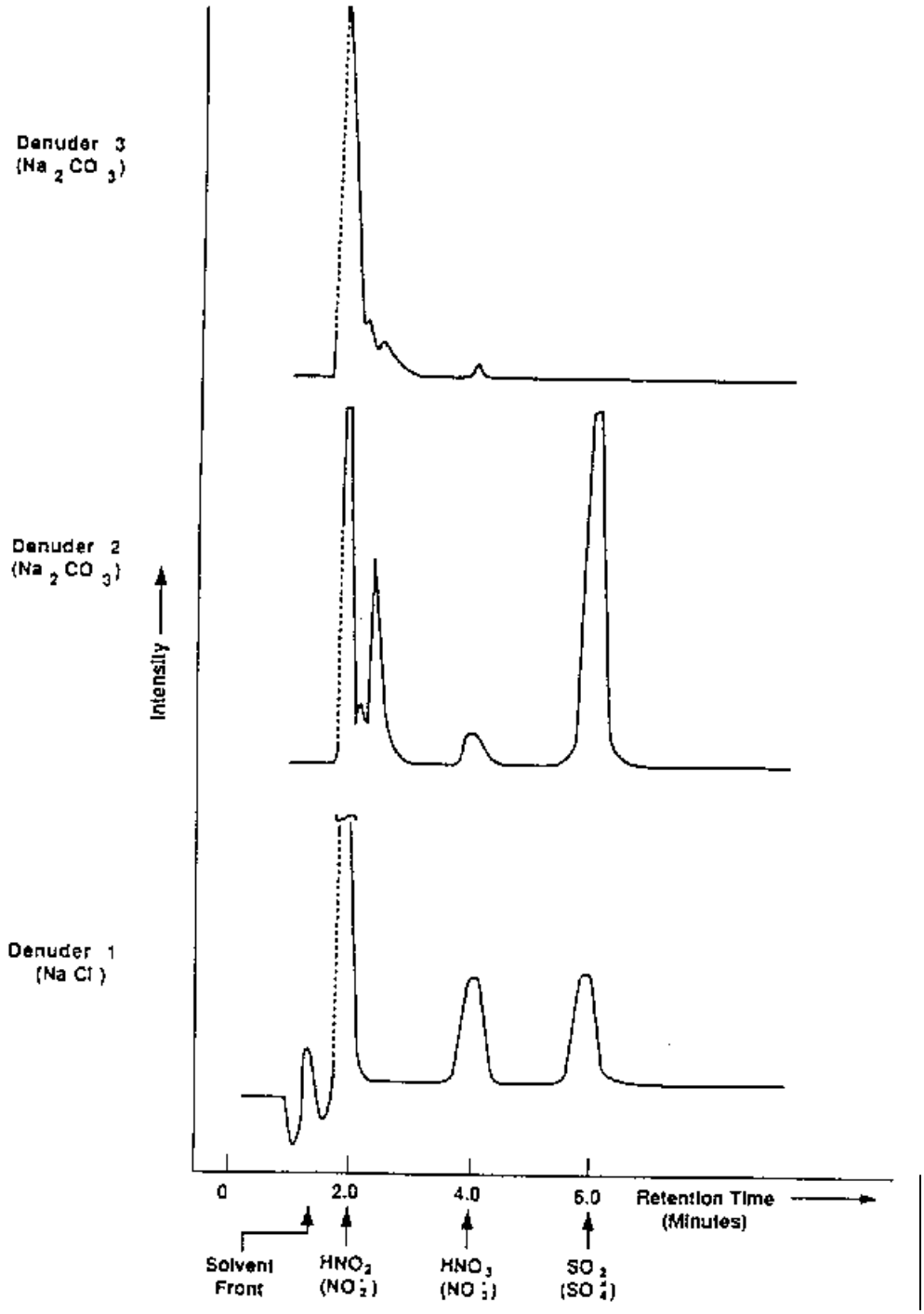

Figure 15. Chromatograms of denuder/filter extract performed by the ion chromatography.

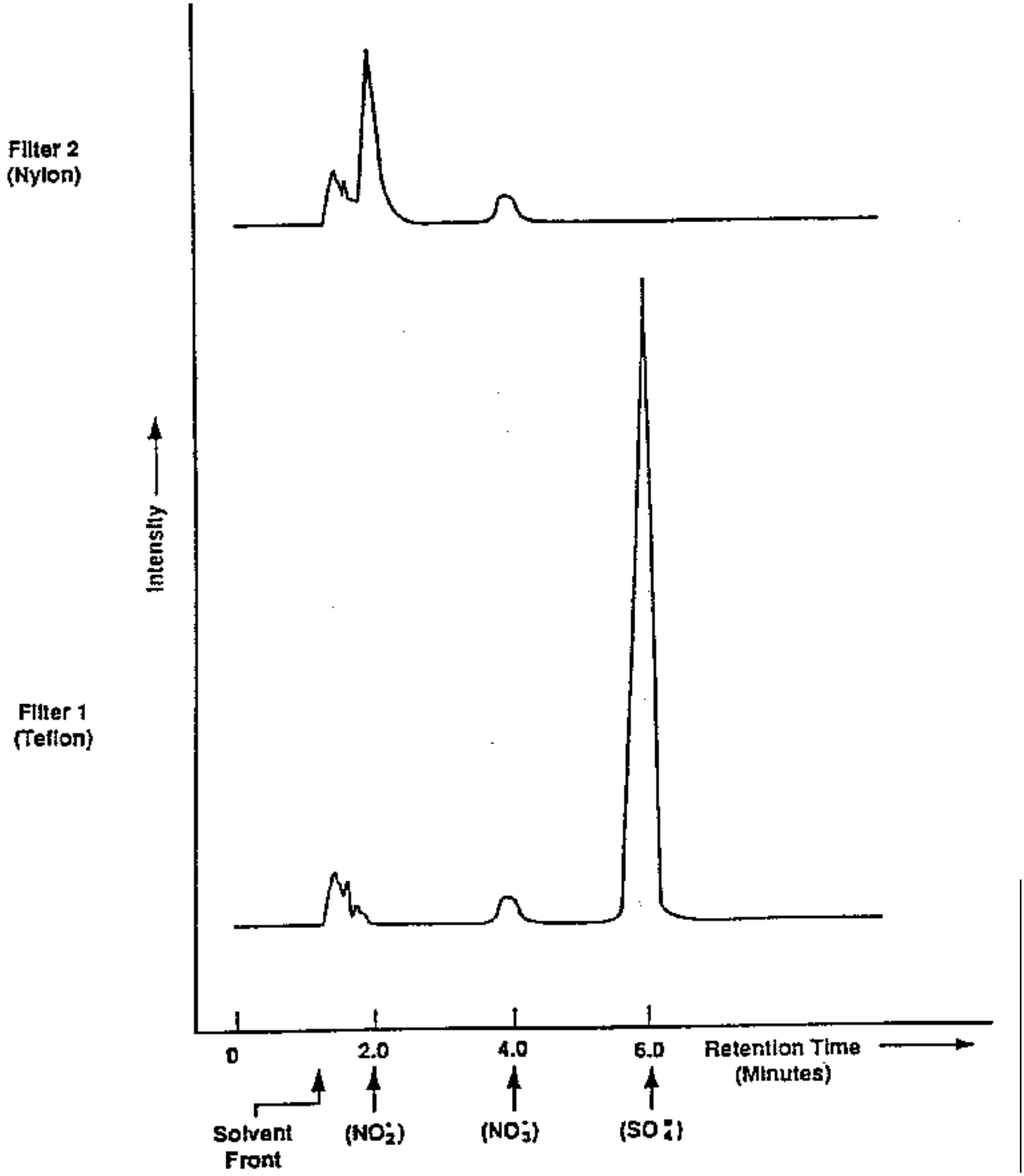

Figure 15 (Cont'd). Chromatograms of denuder/filter extract performed by the ion chromatography.

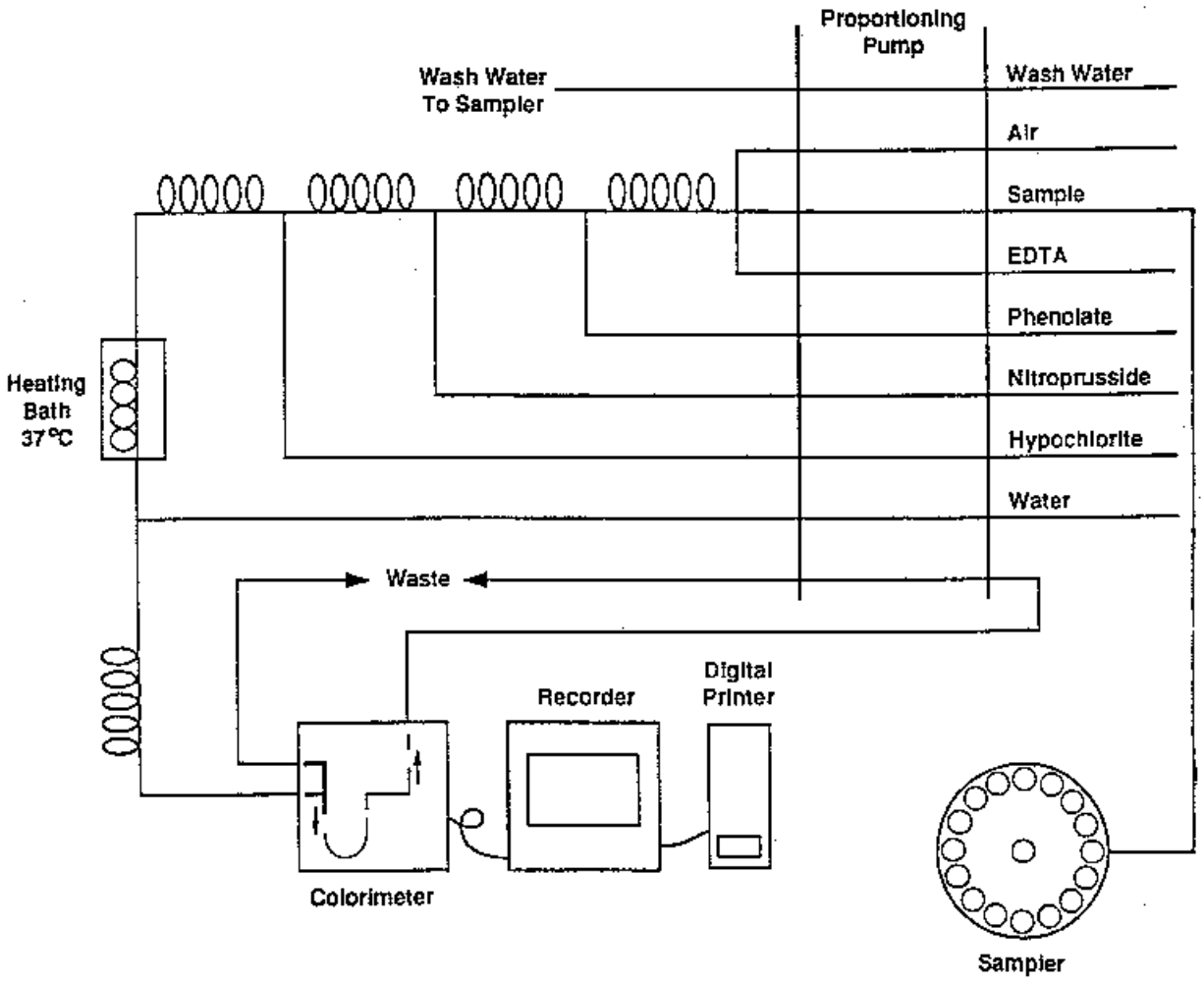

Figure 16. Technicon autoanalyzer flow diagram for ammonia analysis.

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

Name: _____ Sample I.D.: _____
Date: _____ Location: _____
LAB: _____

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 17. 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 17 (cont). pH Analytical Laboratory Log Form

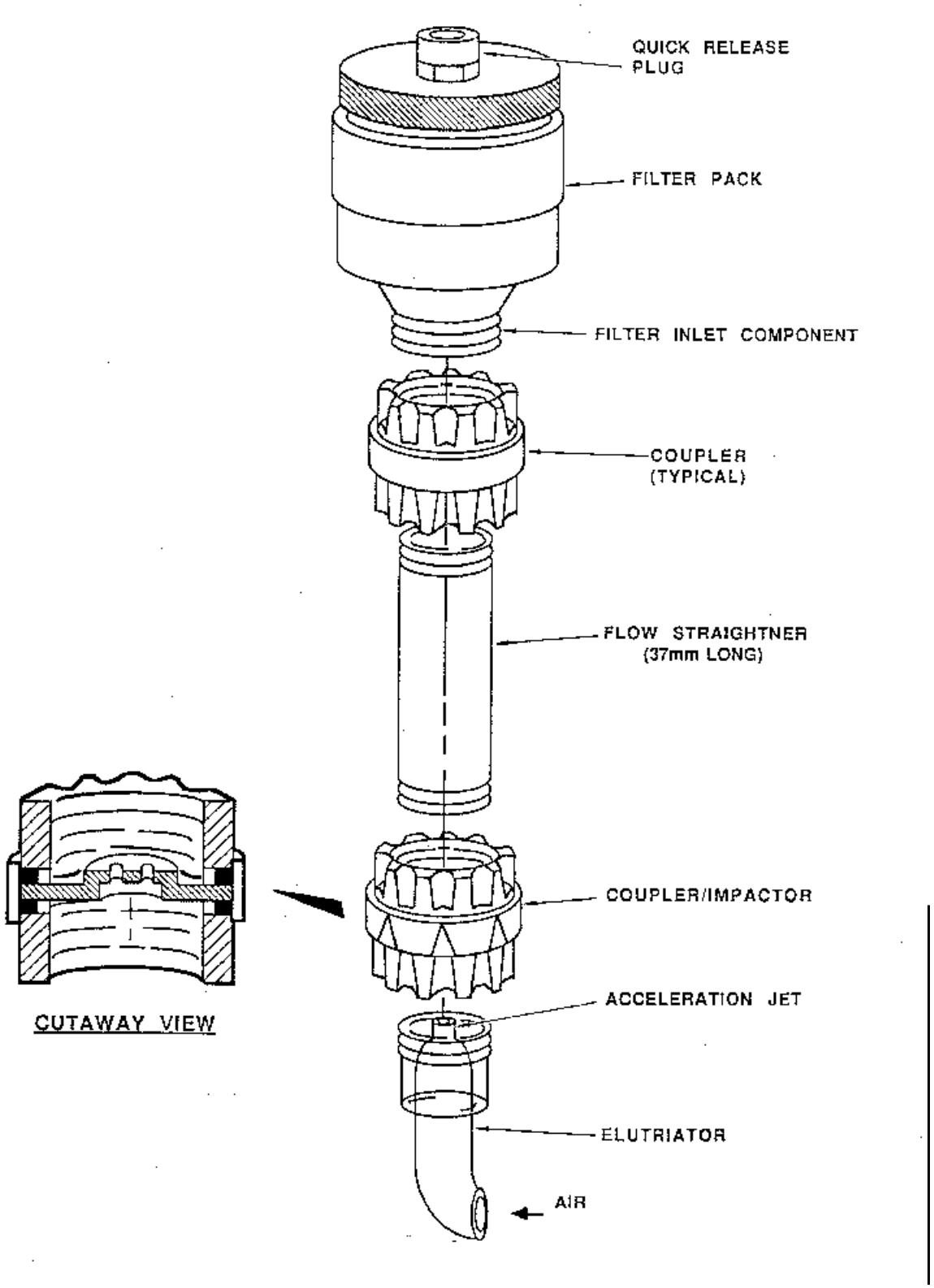

Figure 18. Field Particle personal sampler.

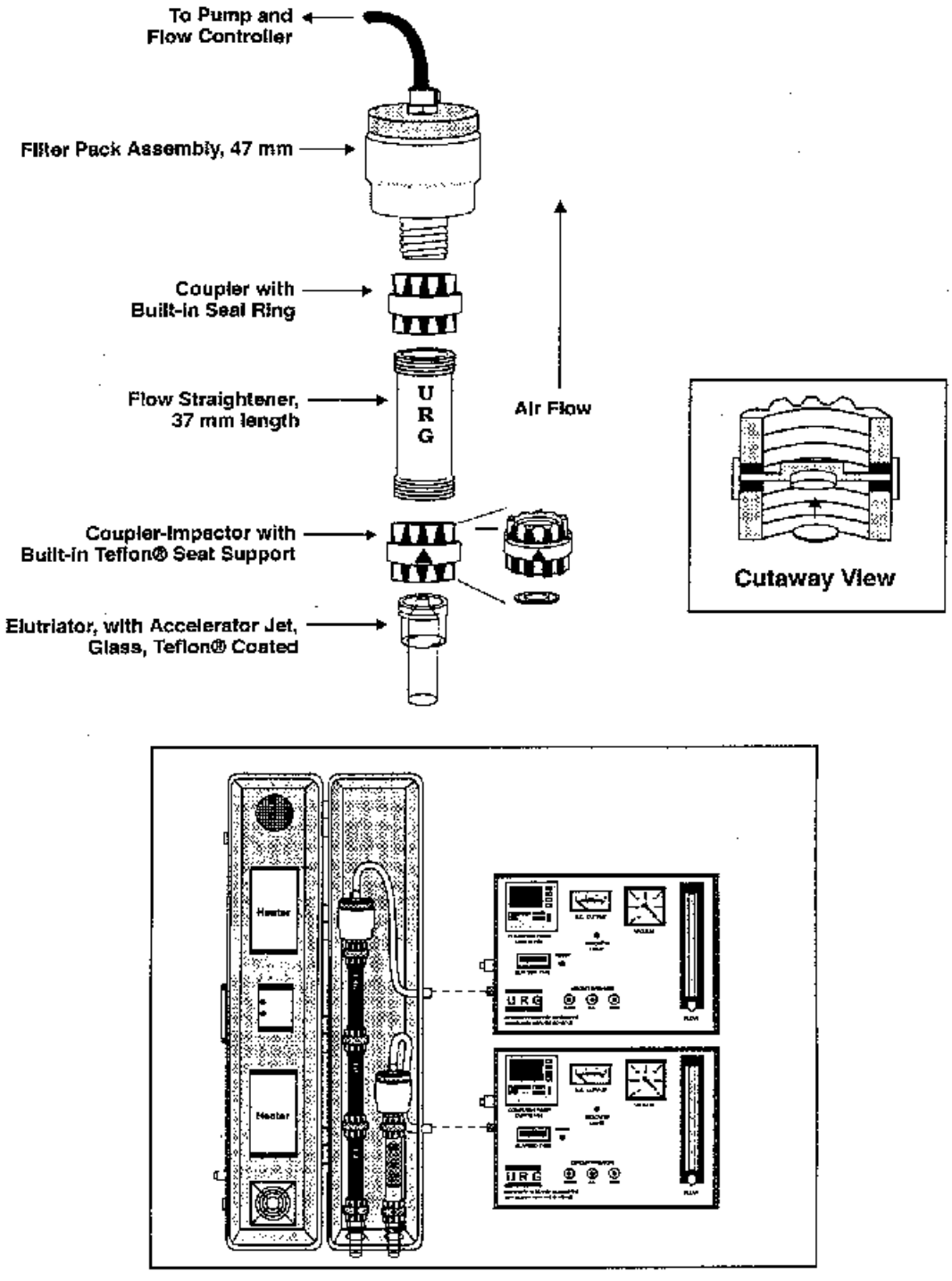

Figure 19. Annular Denuder system with parallel fine particle sampler.

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