United States Environmental Protection Agency Office of Research and Development Washington, DC 20460

November 1992



Determination of the Strong Acidity of Atmospheric Fine-Particles (<2.5 um) Using Annular Denuder Technology

Standard Method Enhanced Method

TECHNICAL REPORT DATA				
1. REPORT NO. EPA/600/R-93/037	2.	^{3.} ₽B93-178234		
4. TITLE AND SUBTITLE Determination of the Strong Acidity of Atmospheric Fine Particles (<2.5 μm) Using Annular Denuder Technology		5.REPORT DATE November 1992		
		6.PERFORMING ORGANIZATION CODE		
7. AUTHOR(S)		8. PERFORMING ORGANIZATION REPORT NO.		
Larry J. Purdue				
9. PERFORMING ORGANIZATION NAM	IE AND ADDRESS	10.PROGRAM ELEMENT NO.		
Atmospheric Research and	Exposure Assessment	A101/C/A/66		
Laboratory Human Exposure and Field	Research Division (MD 56)	11. CONTRACT/GRANT NO.		
Research Triangle Park, 1	NC 27711	68-D0-0123, WA I-49		
12. SPONSORING AGENCY NAME AND	ADDRESS	13.TYPE OF REPORT AND PERIOD COVERED		
Office of Research and D	evelopment	Methods Manual		
Atmospheric Research and Exposure Assessment Laboratory Research Triangle Park, NC 27711		14. SPONSORING AGENCY CODE		
15. SUPPLEMENTARY NOTES		-		
16. ABSTRACT				
This report is a standar	dized methodology description	for the determination of		

(1668 or rine than 2.5 micron annular denuder technology. This methodology description includes two parts: Part A - Standard Method and Part B - Enhanced Method. The unique features of the annular denuder method which separates it from other established monitoring methods are elimination of sampling artifacts due to interaction between the collected gases and particles, and preservation of the samples for subsequent analysis. The Standard Method utilizes a denuder for removing ammonia and a filter assembly for determination of atmospheric strong acidity fine particle aerosols in ambient air, but does not account for potential interferences from nitric acid, ammonium nitrate aerosol or other ammonium salts which might bias the acidity measurement. The Enhanced Method adds an additional denuder upstream of the filter assembly to selectively remove acid gases (nitric acid vapors, nitrous acid and sulfur dioxide) from the gas stream prior to filtration. In addition, backup nylon and citric acid impregnated filters are used to correct for biases due to the dissociation of ammonium nitrate aerosol. The techniques, procedures, equipment, and other specifications comprising this method are derived and composited from those actually used by the contributing research organizations and thereby known to be serviceable and effective. At this stage, this method is a unified, consensus, tentative method intended for further application and testing. The method is presented in document control format to facilitate appropriate changes as experience is gained with its use.

17.	KEY WOR	KEY WORDS AND DOCUMENT ANALYSIS				
1 .	DESCRIPTORS	b.IDENTIFIERS/ OPEN ENDED TERMS	c.COSATI			
18. DISTRIBUTION STATEMENT		19. SECURITY CLASS (This Report)	21.NO. OF PAGES 134			
		20. SECURITY CLASS (This Page)	22. PRICE			

EPA/600/R-93/037 November 1992

DETERMINATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES (<2.5 μ m) USING ANNULAR DENUDER TECHNOLOGY

- STANDARD METHOD
- ENHANCED METHOD



EPA Project Manager Larry J. Purdue

Atmospheric Research and Exposure Assessment Laboratory Office of Research and Development U. S. Environmental Protection Agency Research Triangle Park, NC 27711

Revision 0

November 1992

DISCLAIMER

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency under Contract 68-DO-0123 to Midwest Research Institute. It has been subjected to the Agency's peer and administrative review, and has been approved for publication as an EPA document. It is being distributed solely for evaluation of its technical content and accuracy. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGEMENT

This manual was prepared for the U.S. Environmental Protection Agency by Midwest Research Institute (MRI) Cary, North Carolina. Mr. William T. "Jerry" Winberry, Jr. was the principle author for MRI. Mr. Larry J. Purdue, USEPA, Atmospheric Research and Exposure Assessment Laboratory (AREAL) served as EPA Project Manager. Mr. Tom Ellestad and Mr. Frank McElroy, USEPA, AREAL, served as project advisors.

Acknowledgement is given to Dr. Ivo Alligrini, Director and the initial developer of this methodology at the Laboratory for Atmospheric Pollution of C.N.R., Rome, Italy. We also acknowledge the contributions of R.K. Stevens of USEPA, Dr. P. Koutrakis of Harvard School of Public Health, Dr. J. Waldman of Robert Wood Johnson Medical School and Dr. Joe Sickles of Research Triangle Institute, for their insights and contributions to the development of an improved version of the annular denuder system.

FOREWORD

The Atmospheric Research and Exposure Assessment Laboratory (AREAL) in Research Triangle Park, North Carolina, is one of three laboratories in the Office of Modeling, Monitoring Systems, and Quality Assurance (OMIMSQA). It conducts research programs in the chemical, physical, and biological sciences designed to (1) characterize, monitor, and quantify the current status of ambient air quality and air pollutant exposure to humans and ecosystems through both direct and indirect pathways, (2) develop and apply mathematical models over broad spatial and temporal domains to interpolate between measured environmental parameters and the transport and transformation of air pollutants and to predict future changes, (3) report on trends, (4) determine source-receptor relationships, (5) provide research support to program offices, (6) carry out long term multidisciplinary research programs, and (7) collect, analyze and interpret (both numerically and visually) air quality and other environmental and human exposure related data.

Recently, AREAL has been given the responsibility by the Clean Air Scientific Advisory Committee (CASAC) of obtaining information needed for scientific assessment of the possible need for a fine particle standard for acid aerosols to protect human health. To this end, AREAL conducted a workshop in 1989 to determine and exchange views on the various methods that have been and are being used to measure aerosol acidity. Based upon the recommendations from that workshop, AREAL sponsored an Intercomparison Study at EPA's RTP facility to quantify the performance of methods currently used in characterizing aerosol acidity in epidemiology studies to ensure comparability of measurements by different groups. The participating groups were:

- Harvard School of Public Health,
- Robert Wood Johnson (RWJ) Medical School, and
- Research Triangle Institute

All three research teams used variations of the annular denuder system (ADS) to determine fine-particle strong acidity.

Based upon the findings of the Intercomparison Study, AREAL has developed this standard methodology for determination of fine-particle strong acidity and to promote the accurate determination and assessment of human exposure to strong acid aerosol acidity.

Gary J. Foley Director Atmospheric Research and Exposure Assessment Laboratory Research Triangle Park, NC 27711

INTRODUCTION

Acid aerosols are found in the atmosphere as a result of atmospheric reaction of emissions from a variety of fossil fuel combustion sources including power plants, industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Awareness of the effects of concentrations of acid aerosols on human health and property has been documented over the past several years. The Clean Air Act Amendments of 1970 required the U. S. Environmental Protection Agency (U. S. EPA) to develop uniform national ambient air quality standards (NAAQS) for pollutants which were recognized as widespread (emitted by numerous mobile and stationary sources) and which endangered public health and welfare. Further, Section 109 of the Clean Air Act, as amended, requires EPA to periodically review the NAAQS as well as the scientific information and data on which they are based. New pollutants are identified for NAAQS development if the Administrator concludes that they may reasonably be anticipated to endanger the public health and welfare.

To assist the Administrator in evaluating the need for new or revised NAAQS, the Clean Air Act created the Clean Air Scientific Advisory Committee (CASAC). This committee's mandate is to provide the Administrator with scientific advice and research recommendations on critical areas of knowledge on new or revised NAAQSs. The Acid Aerosol Subcommittee of CASAC identified a need for a coordinated acid aerosol research program to assist the Agency in making recommendations on a new acid aerosol NAAQS. The Subcommittee recommended a research program involving characterization and exposure assessment, animal toxicity, human exposure research, and epidemiology. As documented in the CASAC Report to the Administrator, the foundation for any research program and potential air quality standard development is "...a measurement method, not only because the standard itself must specify the method, but equally important, because before establishing a standard the contaminant must be fully characterized and exposure measurements made to correlate with health outcomes." The Atmospheric Research and Exposure Assessment Laboratory (AREAL) was directed by CASAC of obtaining information needed for scientific assessment of a possible fine particle standard for acid aerosols to protect human health.

In 1989, AREAL conducted a workshop to determine and exchange views on the various methods that have been and are being used to measure aerosol acidity. It was held in response to recommendations by CASAC to identify issues associated with the characterization of aerosol acidity and acid aerosol measurement methods. The workshop was structured to accomplish two principal objectives. The first was to identify appropriate indicators and methodology for characterizing aerosol acidity. The second was to develop ideas and recommendations for the evaluation of acid aerosol methods currently in use. The workshop participants identified the development of an accurate, reliable, and interference-free method as an important initial research objective.

They concluded that the most appropriate indicator of aerosol acidity is the fine particle, strong acidity, i.e. the amount of strong acidity available in the fine particle component of the atmospheric aerosol. The available hydrogen ion is measured, either by titration or by pH, after extracting the aerosol in the size range below 2.5 μ m with an

aqueous solution of perchloric acid at a pH of approximately 4.00 (to prevent dissociation of weak acids). This definition includes free hydrogen ion and hydrogen ion available from either undissociated of weak ion available from either undissociated sulfuric acid or from undissociated bisulfate ion. Available hydrogen ion may be reported either as nanomoles of hydrogen ion per cubic meter of air (nmoles/m³) or as equivalent sulfuric acid in micrograms per cubic meter of air (μ g/m³). It is recognized that in salts of partially neutralized sulfuric acid or in concentrated sulfuric acid droplets some hydrogen ion may be tied up in the bisulfate ion. However, it is assumed that this hydrogen ion would be available for reaction after the particle impacted the surface of the lung.

In addition, the workshop participants considered procedures to evaluate current acid aerosol measurement methods and concluded that audit standards must be developed and distributed to establish analytical accuracy and precision, and that laboratory and field tests should be conducted to evaluate and compare acid aerosol sampling and analysis systems. The primary objective for both laboratory and field evaluations should be to quantify the performance of methods currently used in epidemiology studies to ensure comparability of measurements by different groups.

In December 1989 and February 1990, Intercomparison Studies were held at the AREAL facility in Research Triangle Park, NC to quantify the performance of methods currently used in measuring aerosol acidity in epidemiology studies to ensure comparability of measurements by different groups. The criterion for selecting the three participants for the initial Pilot Intercomparison Study was that they represented denuder systems being used in epidemiological field studies currently in progress or had developed a prototype sampler under contract to EPA that the agency wanted evaluated. The three invited research groups, Harvard School of Public Health, Robert Wood Johnson (RWJ) Medical School and Research Triangle Institute (RTI), used variations of the annular denuder system (ADS) to determine fine-particle strong acidity.

Based upon the findings of the Pilot Intercomparison Study, AREAL has developed this methodology entitled: "Determination of the Strong Acidity of Atmospheric Fine-Particles (<2.5 μ m) Using Annular Denuder Technology." This standard methodology represents a composite of the most viable features of the three research methods utilized in the Pilot Intercomparison Study. This methodology includes two parts:

- Part A--Standard Method, and
- Part B--Enhanced Method.

The unique features of the annular denuder which separates it from other established monitoring methods are elimination of sampling artifacts due to interaction between the collected gases and particles, and the preservation of the samples for subsequent analysis. The Standard Method utilizes a denuder for removing ammonia and a filter assembly for determination of atmospheric strong acidity fine particle aerosols in ambient air, but does not account for potential interferences from nitric acid, ammonium nitrate aerosol (NH_4NO_3) or other ammonium salts which might bias the acidity measurement. The Enhanced Method

adds an additional denuder upstream of the filter assembly to selectively remove acid gases (nitric acid vapor, nitrous acid and SO_2) from the gas stream prior to filtration. In addition, to correct for biases due to the dissociation of ammonium nitrate aerosol captured on the Teflon[®] filter, a backup nylon filter has been incorporated to capture the dissociated HNO₃ from NH₄NO₃, followed by a glass-fiber filter impregnated with citric acid to retain the dissociated NH₃ from NH₄NO₃. The ammonia concentration is subtracted from the nitrate value, and the result added to the acidity measurement on the Teflon[®] filter to give a corrected measurement of the atmospheric fine particle strong acidity.

The techniques, procedures, equipment, and other specifications comprising this method are derived and composited from those actually used by the contributing research organizations and thereby known to be serviceable and effective. At this stage, this method is a unified, consensus, tentative, draft method intended for further application and testing. Users should be advised that the method has not yet been adequately tested, optimized, or standardized. Many of the specifications have been initially established by technical judgment and 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 to confirm and document their possible advantages. Information and comments are solicited on improvements, alternative equipment, techniques, or specifications, performance, or any other aspect of the method. All such information should be sent to the EPA Project Manager identified on the cover page and will be considered for incorporation in future revisions of the method.

This method has been presented in document control format to facilitate appropriate changes as experience is gained with use of the method. As advancements are made, the current method will be modified from time to time.

DETERMINATION OF THE STRONG ACEDITY OF ATMOSPHERIC FINE-PARTICLES (<2.5 μm) USING ANNULAR DENUDER TECHNOLOGY

.

STANDARD METHOD

TABLE OF CONTENTS

To	<u>pic</u> Page
1.	Scope A-1
2.	Applicable Documents
3.	Summary of Method A-2
4.	Significance
5.	Definitions A-4
ნ.	Apparatus
7.	Reagents and Materials
8.	Preparation of Impactor Frit and Denuder Coating
9.	Impactor Frit Installation
10.	Filter Preparation and Assembly
11.	Annular Denuder System Preparation
	11.1 Coating Procedure

TABLE OF CONTENTS (continued)

•

<u>To</u>	pic	<u>Page</u>
12.	Sampling	A-16
	12.1 Placement of Denuder System12.2 Start-up12.3 Sample Shutdown12.4 Corrective Action for Leak Test Failure	A-16 A-17 A-19 A-19
13.	ADS Disassembly	A- 20
14.	Extraction Procedure	A-2 1
15.	pH Analysis	A-22
	 15.1 Standard and Reagent Preparation 15.2 Calibration of pH Meter 15.3 Pre-analysis Calibration 15.4 pH Test of HClO₄ Solutions 15.5 Analysis of Working Standard 15.6 Analysis of Filter Extracts 	A-22 A-26 A-26 A-27 A-27 A-27 A-28
16.	Assumption of Annual Denuder System	A-29
17.	Atmospheric Species Concentration Calculations	A- 29
	 17.1 Calculations Using Results from pH Measurement	. A-29 A-31 . A-32
18.	Variations of the Acid Aerosol Denuder System	. . A-3 2
19.	Method Safety	A-3 3
20.	Performance Criteria and Quality Assurance (QA)	. A-33
	20.1 Standard Operating Procedures (SOPs) 20.2 Quality Assurance Program	A-33 A-34
21.	References	A-35

PART A

DETERMINATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES (<2.5 µm) USING ANNULAR DENUDER TECHNOLOGY

(STANDARD METHOD)

DETERMINATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES $(<2.5 \ \mu m)$ USING ANNULAR DFNUDER TECHNOLOGY

STANDARD METHOD

1. <u>Scope</u>

- 1.1 This document describes the protocol for the quantitative determination of equivalent strong-acid (H_2SO_4) acidity of fine-particle (<2.5 μ m) atmospheric aerosol as hydrogen ion by pH.
- 1.2 The methodology detailed in this document is a composite of methodologies developed by U.S. Environmental Protection Agency (USEPA), University of Kansas, Rebert Johnson Medical School, New York State University, Harvard University and the CNR Laboratories. It is currently employed in a number of air pollution studies in Italy, U.S.A., Canada, Mexico, Germany, Austria, and Spain, and in such institutions as public health services and epidemiology and environmental research centers.

The technicues, procedures, equipment, and other specifications comprising this method are derived and composited from those actually used by the contributing research organizations and thereby known to be serviceable and effective. At this stage, this method is a unified, consensus, tentative, draft method intended for further application and testing. Users should be advised that the method has not yet been adequately tested, optimized, or standardized. Many of the specifications have been initially established by technical judgment and 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 to confirm and document their possible advantages. Information and comments are solicited on improvements, alternative equipment, techniques, or specifications, performance, or any other aspect of the method. All such information should be sent to the EPA Project Manager identified on the cover page and will be considered for incorporation in future revisions of the method.

1.3 The equipment described herein can be modified to measure acidity of atmospheric gases and particulate matter contained in both indoor and outdoor atmospheres. Modification to this methodology were developed for monitoring regional-scale acidic and basic gases and particulate matter in support of U.S. EPA field programs involving the Integrated Air Cancer Research Program and the Acid Deposition Network. Similarly, the methodology has been used to characterize urban haze in Denver, Houston, Boston and Los Angeles.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis

2.2 Other Documents

Ambient Air Studies (1-23) U.S. EPA Technical Assistance Document (24)

3. Summary of Method

3.1 The annular denuder system (ADS) consists of an inlet with an impactor or cyclone preseparator designed to remove all particles with a DP₅₀ of 2.5 μ m or greater, an annular denuder to remove ammonia, and a filter for collecting the aerosol. In operation, air is drawn through a cyclone or a elutriator-accelerator jet assembly followed by an impactor frit and coupler assembly, through the denuder to remove ammonia, then into a single-stage filter assembly. The single-stage filter assembly contains a 47-mm Teflon[®] filter supported by a stainless steel screen. The filter is a 2 μ m pore-size Teflon[®] membrane filter, Zefluor (Gelman Sciences). The Teflon[®] filter collects the fine aerosol. A pump unit maintains a flow of 10 Lpm, and a timer allows programmed start and end times.

Figure 1a illustrates the ADS with a cyclone assembly, while Figure 1b illustrates the ADS with an impactor assembly. Figure 2 shows the field sampling box with the pump-timer system.

3.2 Following each run, the ADS assembly is removed from its field housing, its ends capped, and it is brought back to the laboratory. In the laboratory, the assembly pieces are uncoupled and capped. The denuder tube is not extracted. The Teflon[®] filter is unloaded from the filter assembly in an ammonia free atmosphere and either immediately extracted or stored in a ammonia free container for later extraction. A glove-box, lined with citric-acid soaked paper, is used to maintain an ammonia-free atmosphere.

To extract the Teflon[®] filter, it is placed in an extraction vessel, particle-laden side down. The filter is wetted with 200 μ L of methanol, then extracted with 6.0 mL of extraction solution (ES). The extraction vessel is put in an ultrasonic bath for 20 minutes. The extraction solution is then decanted into a container. 3.3 Acidity determination is made using pH measurements of 1 mL aliquot of the extracted filter solution. Filter acidity is calculated based on standards made with sulfuric acid. The standards range from 0 to 160 μ g equivalent of strong acid aerosol. A pH meter is used to measure the pH of the filter extract. For each batch of filter extracts, a calibration curve is calculated using the mean pH of each standard.

4. Significance

4.1 Acid aerosols are found in the atmosphere as a result of atmospheric reactions of emissions from a variety of fossil fuel combustion sources including power plants, industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Awareness of the effects of concentrations of acid aerosols on human health and property has been documented over the past several years. The Clean Air Act Amendments of 1970 required the U.S. Environmental Protection Agency (U.S. EPA) to develop uniform national ambient air quality standards (NAAQS) for criteria pollutants because of the interstate nature of certain air pollutants. NAAQS's were established for those pollutants which were recognized as widespread (emitted by numerous mobile and stationary sources) and which endangered public health and welfare. Further, Section 109 of the Clean Air Act as amended, requires EPA to periodically review the NAAQS as well as the scientific information and data on which they are based. New pollutants are to be identified for NAAQS development if the Administrator concludes that they may reasonably be anticipated to endanger the public health and welfare.

To assist the Administrator in evaluating the need for new or revised NAAQSs, the Clean Air Act created the Clean Air Scientific Advisory Committee (CASAC). This committee's mandate is to provide the Administrator with scientific advice and research recommendations on critical areas of knowledge on new or revised NAAQSs. The Acid Aerosol Subcommittee of CASAC identified a need for a coordinated acid aerosol research program to assist the Agency in making recommendations on a new acid aerosol NAAQS. The Subcommittee recommended a research program involving characterization and exposure assessment, animal toxicity, human exposure research, and epidemiology. The foundation for any research program and potential air quality standard development is "...a measurement method, not only because the standard itself must specify the method, but equally important, because before establishing a standard the contaminant must be fully characterized and exposure measurements made to correlate with health outcomes."

4.2 The unique features of the annular denuder which separates it from other established monitoring methods are elimination of sampling artifacts due to interaction between the collected gases and particles and the preservation of the samples for subsequent analysis. These features are accomplished by removing NH_3 in the gas stream with the citric acid-coated denuder to reduce the probability of the acid aerosol captured by the Teflon[®] filter in the filter pack being neutralized to ammonium sulfate [$(NH_4)_2SO_4$].

5. Definitions

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

- 5.1 Secondary particles (or secondary aerosols) Aerosols that form in the atmosphere as a result of chemical reactions, often involving gases. A typical example is sulfate ions produced by photochemical oxidation of SO₂.
- 5.2 Aerosol A dispersion of solid or liquid particle in a gas-phase medium and a solid or liquid disperse phase. Aerosols are formed by (1) the suspension of particles due to grinding or atomization, or (2) condensation of supersaturated vapors.
- 5.3 Coarse and fine particles These two fractions are usually defined in terms of the separation diameter of a sampler. Coarse particles are those with diameters (aerodynamic) greater than 2.5 μ m and are removed by the sampler's inlet; the fine particles are those with diameters (aerodynamic) less than 2.5 μ m that are collected on the Teflon[®] filter.
- 5.4 Annular Of, rotating to, or forming a ring. In the annular denuder sampler, the annular refers to the annulus between two concentric tubes. Chemical coating applied to the interior surfaces removes gaseous pollutants which diffuse to the surface.
- 5.5 Denuder The denuder refers to the sections in which interfering gases are removed from the sample stream prior to filtration in determining fine particle $(2.5 \ \mu m)$ strong acidity.
- 5.6 Equivalent weight The combining weight, or the equivalent weight, of a compound or ion is its formula weight divided by the number of replaceable hydrogen atoms.
- 5.7 Normal solution A normal (N) solution is one that contains a gram-equivalent weight of solute in a liter of solution.

6. Apparatus

<u>Note</u>: The following descriptions relate to Figure 2. Most of these parts are available commercially from University Research Glassware, 118 E. Main Street, Carrboro, North Carolina, 27510, 919-942-2753. However, these items can be made by any qualified vendor. Therefore, it is not necessary that these specific items are obtained and utilized.

6.1 Sampling

- 6.1.1 Elutriator and acceleration jet (inlet) assembly Under normal sampling conditions, the elutriator or entry tube is made of either Teflon[®] coated glass or aluminum, as illustrated in Figure 3. When using glass, the accelerator jet assembly, which directs the air flow towards an impactor plate, is fixed onto the elutriator and the internal surfaces of the entire assembly are coated with Teflon[®] [Figure 3(a)]. When aluminum is used, the accelerator jet assembly is removable. The jet is made of Teflon[®] or polyethylene and the jet support is made of aluminum [Figure 3(b)]. Again, all internal surfaces are coated with Teflon[®].
- 6.1.2 Teflon[®] impactor support pin and impactor frit support tools (see Figure 4) - Made of either Teflon[®] or polyethylene and are used to aid in assembling, removing, coating and cleaning the impactor frit.
- 6.1.3 Impactor frit and coupler assembly (see Figure 5) The impactor frit is 10 mm x 3 mm and is available with a porosity range of 10-20 μ m. 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 650 cil 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 which are located on both sides of the seat support inside the coupler.

<u>Note</u>: In situations when there are substantial high concentrations of coarse particles (>2.5 μ m), it is recommended that a Tefton⁶-coated aluminum cyclone be used in place of the acceleration jet and impactor assembly, as illustrated in Figure 2. Figure 2 illustrates the location of the cyclone with respect to the denuder, heated enclosure and meter box assembly.

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

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

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

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

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

6.1.7 Drying manifold assembly - The manifold is made of glass and is available to accommodate as many as four drying denuders. The denuders are attached to the manifold with back-to-back Bakelite bored caps, as illustrated in Figure 7. Air is pushed through an air dryer/cleaner bottle made of 2 1/2 inch heavy wall glass which contains silica gel. The Teflon[®] tubing which connects the dryer/cleaner bottle to the drying manifold should be secured at each cap with either Teflon[®] washers or Teflon[®] washers coupled with Teflon[®] hose barbs. The air stream then passes through a fine particle filter to remove fines. Alternatively, dry compressed air from a cylinder may be used in place of the dryer/cleaner bottle assembly.

6.1.8 Filter assembly - The denuder is followed by a single-stage filter assembly containing the Teflon[®] membrane filter, as illustrated in Figure 3. The filter is supported by a stainless steel porous screen sandwiched between two Viton[®] O-rings for sealing and housed in a polyethylene filter ring housing. The filter housing outlet component is aluminum and accommodates a polyethylene screw sleeve which seals the filter assembly.

Note: Over time and repeated compression, the Viton[®] O-rings may wear, causing poor leak checks due to inadequate sealing. The user is encouraged to replace these rings after fifteen (15) sampling events or when the filter pack assembly does not pass an adequate leak check. Other users have utilized high density polyethylene (HDPE) to prolong the life of the ring.

- 6.1.9 Vacuum tubing Low density polyethylene tubing, 3/8 inch diameter for distances of less than 50 ft., 1/2 inch diameter for distances greater than 50 ft. [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219 (412-787-6322)]
- 6.1.10 Tube fitting Compression fittings (Swagelok[®], Gyrolok[®] or equivalent) to connect vacuum tubing (above) to an NPT female connector or filter holder and connect vacuum tubing to fitting on differential flow controller. The fittings may be constructed of any material since they are downstream of the sampler. [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219 (412-787-6322)]
- 6.1.11 Annular denuder system (ADS) sampling box The housing box is made of a "high-impact" plastic and is thermally insulated. It is 2 feet long by 6 inches wide and 6 inches deep. The box contains a heater unit, a fan, and an air outlet located in the lid of the housing. The elutriator end of the ADS protrudes through one end of the box, while the denuder is supported in the box by a chrome plated spring clip. If the Teflon[®]coated aluminum cyclone is used to remove coarse particles, it is also housed in the heated sampling box, with the elutriator end protruding through the sampling box, as illustrated in Figure 2.

Note: Recent studies by the Harvard School of Public Health based on a comparison of utilizing a sampling box with and without heated enclosure indicated no difference in sampled species from winter samples. It is therefore the discretion of the user to determine whether a heated sampling box is required.

- 6.1.12 Annular denuder transport case The transport case is made of formica backed with plywood and insulated. The corners are reinforced with metal. It is made to withstand shipping by truck, UPS and Federal Express. Each case is stackable and lockable and has a carrying handle. Seven total annular denuder systems can be packed in the case.
- 6.1.13 Pump/timer unit The pump/timer unit draws air through the ADS at a fixed rate of 10 L/min with a precision of ± 5 percent over the range of 25 to 250 mm Hg vacuum. A mass flow controller or a differential flow controller can be used. Typically, the flow rate is monitored with an exhaust flow rotameter. The unit includes a mechanical 7-day timer and an elapsed-time counter. A dry gas meter, when available, is placed after the pump to give a direct readout of total volume of air sampled. Otherwise, flow rate is manually measured (using a rotameter) before and after each run to calculate the air volume sampled.
- 6.1.14 Dry gas meter (DGM) The DGM should have a capacity of 10 L of gas per revolution. [NuTech Corp., 4022 Stirrup Creek Road, Suite 325, Durham, NC 27703, 919-544-8535)]
- 6.1.15 Electronic mass flow controller Capable of maintaining a constant rate of 10 L/min (±5 percent) over a sampling period of up to 24 hours and under conditions of changing temperature (5° to 43°C) and humidity. [Tylan General, Flow Division, 19220 S. Normandie Ave., Torrance, CA, 90502, 213-212-5533, Model FC-262, or equivalent]

6.2 Analysis

- 6.2.1 pH meter A pH or pH/ion meter with "integral" automatic temperature compensation, temperature probe, 2 and 4 mL analytical vials, and calibrated with standard buffers (pH 4 and 7). The Ross semi-micro glass electrode from Orion has been used by the Harvard School of Public Health and found to adequately address the requirements of this protocol. [Orion Research Inc., The Schraffet Center, 529 Main Street, Boston, MA 02129, 617-242-3900]
- 6.2.2 Polyethylene bottles with polyethylene screw caps 100 mL, used for storage of coating solution; and 1L, used for storing the KCl solution.

- 6.2.3 Erlenmeyer flasks 250 mL and 2 L borosilicate glass or polyethylene flasks for calibration, best source.
- 6.2.4 Graduated cylinders 5 mL, 10 mL, 100 mL, 250 mL and 1L borosilicate glass or polyethylene cylinders, best source.
- 6.2.5 Pipets Class A 5 mL and 10 mL borosilicate glass pipettes or automatic pipettes. Calibrated "to deliver," best source.
- 6.2.6 Pipet bulb Made of natural rubber. Recommended to meet OSHA requirements, best source.
- 6.2.7 Micropipettes 25 μ L, 50 μ L, and 100 μ L, calibrated "to contain," borosilicate glass micropipette, best source.
- 6.2.8 Forceps Recommended dressing forceps made of stainless steel or chrome-plated steel and without servations. Used for handling filter.
- 6.2.9 Stopwatch Used for measuring flow rate of gas stream through DGM, best source.
- 6.2.10 Ultrasonic cleaner Used for filter extractions and parts cleaning. The ultrasonic cleaner should have temperature control capability.
 [Cole-Palmer Instrument Co., 7425 N. Oak Park Ave., Chicago, IL, 60648 (800-323-4340)]
- 6.2.11 Clean air hood (optional) Closed air hood with ammonia free air circulation. Used for Teflon[®] filter extraction for pH analysis, best source.
- 6.2.12 Glove-box Used for handling exposed filter, which is lined with citric acid impregnated paper sheets to maintain an ammonia-free atmosphere. The glove-box works best with a slight positive pressure.
- 6.2.13 Refrigerator (approximately 5°C) is required for sample storage.
- 6.2.14 Polyethylene-stoppered volumetric flasks 25 mL, used for making sulfuric acid standards.

7. <u>Reagents and Materials</u>

- 7.1 Teflon[®] filter Zefluor[®] (PTFE) membrane filter, 47 mm diameter, with a 2 μm pore size. The Teflon[®] filter has a coarse mesh Teflon[®] side and a fine pore membrane side. The fine pore membrane side should face the air stream. [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, Part No. P5PJ047, (800-521-1520)].
- 7.2 Teflo[®] membrane filter, 47 mm diameter, with a 2 μm pore size. This filter has a thin Teflon[®] membrane stretched across a plastic ring. [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, Part No. R2PJO47, (800-521-1520)].
- 7.3 Filter extract storage vials 100 mL polyethylene vials (Nalgene or equivalent).
- 7.4 Labels Adhesive, for sample vials, best source.
- 7.5 Parafilm Used for covering flasks and pH cups during pH analysis, best source.
- 7.6 Kimwipes[®] and Kay-dry towels Used for cleaning sampling apparatus and analysis equipment, best source.
- 7.7 Stoppers Polyethylene, best source.
- 7.8 Sodium carbonate (Na_2CO_3) ACS reagent grade, best source.
- 7.9 Citric acid [monohydrate HOC (CH₂CO) OH]₂COOH : H₂O) ACS reagent grade, best source.
- 7.10 Methanol (CH₃OH) ACS reagent grade, best source.
- 7.11 Sulfuric acid (H_2SO_4) ACS reagent grade, 1.000 N solution, best source.
- 7.12 Distilled deionized water (DDW) ASTM Type I water.
- 7.13 pH buffers Standard buffers, 4.00 and 7.00, for internal calibration of pH meter, best source.
- 7.14 Silica gel ACS reagent grade (indicating type), best source.
- 7.15 Gloves Polyethylene disposable. Used for impactor frit assembly and filter assembly, best source.
- 7.16 Dow Corning high temperature vacuum oil Dow Corning 660 oil used for impactor frit coating solution, best source.

- 7.17 Zero air A supply of compressed clean air, free from particles and ammonia. The supply may be either from a commercial cylinder or generated on site, best source.
- 7.18 BRU-35 Composed of 0.1 percent of BRU-35 in DI water. [Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA, 15129, 412-787-6322]
- 7.19 Perchloric Acid (HClO₄) 60 to 62 percent, in water, best source.
- 7.20 Toluene (C₇H₈) ACS reagent grade, best source.
- 7.21 Potassium Chloride (KCI) ACS reagent grade, best source.
- 7.22 Acetone (C_3H_60) ACS reagent grade, best source.

8. Preparation of Impactor Frit and Denuder Coating

- 8.1 Impactor frit coating solution preparation Weigh 1 g of silicone oil (Dow Corning high temperature 660 oil) and place in a 100 mL polyethylene storage vial. Add 100 mL of toluene. Mix thoroughly, close container, and store at room temperature. (WARNING - FLAMMABLE LIQUID).
- 8.2 Annular denuder citric acid coating solution Clean a 100 mL polyethylene storage vial and let dry at room temperature. Measure 50 mL of methanol (WARNING TOXIC, FLAMMABLE LIQUID) with a graduated cylinder and pour into vial. Weigh 0.5 g of citric acid and add to vial. Mix thoroughly; store, covered at room temperature.

9. Impactor Frit Installation

9.1 Impactor frit installation - The impactor-coupler assembly shown in Figure 4 is comprised 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 illustrated in Figure 4. The impactor frit is pressed gently, but firmly, into the seat of the impactor housing so that it does not protrude above the seat. During sampling, particles accumulate on the impactor's plate surface. After each sampling event, the assembly must be cleaned to prevent the build-up of contaminants which may lead to loss of key acidic species being collected by the ADS. Cleaning involves immersing the elutriator, coupler-impactor, and frit in 0.1 percent BRU-35 cleaning solution and ultrasonicating for about 5 minutes. Rinse thoroughly with DDW for additional 5 minutes. Rinse and dry with zero air or in dust-fee environment and store with ends plugged and capped.

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

<u>Note</u>: It is important to have only the minimum amount of oil on the frit because any excess will be blown off during sampling and will contaminate the surfaces of the first denuder.

10. Filter Preparation and Assembly

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

<u>Note</u>: All loading and unloading of the filter assembly must be performed in an ammonia free glove-box. Generally, it is most convenient to reload the filter assembly after cleaning, at the same time as unloading.

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

Note: It is necessary to remove the polyethylene cap first. Lay the pieces out on clean Kimwipes[®]. Insert black viton "O"-rings (see Figure 8).

- 10.2 Lay a clean Teflon[®] filter ring housing, with its large opening face-up, on a clean Kimwipe[®]. Place a clean stainless steel screen in the filter ring housing.
- 10.3 Using clean filter forceps, place a Teflon[®] filter on the screen.

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

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

- 10.5 Lay the aluminum filter housing outlet component, with its large opening faceup, on a clean Kimwipe[®]. Insert a black viton "O"-ring in the aluminum filter base.
- 10.6 Insert the filter ring sandwich with the filter housing inlet component extending upward, on the black viton "C"-ring in the aluminum filter base. Place the larger outer Delrin[®] sleeve over the filter sandwich and screw onto the aluminum filter base. DO NOT OVERTIGHTEN! Then install the second black viton "O"-ring on top of the filter sandwich support.
- 10.7 Install the "quick-release" plug into the filter outlet component. Tighten the housing outlet to the Detrin[®] screw sleeve. DO NOT OVERTIGHTEN!
- 10.8 Install the polyethylene cap onto the filter inlet component and the orange dust cover onto the quick release plug. The filter assembly should be sealed tight before it is removed from the glove-box.
- 10.9 As an option, the filter assembly is leak-checked according to Section 12.4.

11. Annular Denuder System Preparation

All new annular denuder parts obtained from suppliers should be cleaned by placing them in a dilute BRLJ-35 solution in an ultrasonic cleaner for about 30 minutes. The parts should then be thoroughly rinsed in DDW, then rinsed with acetone, and allowed to dry to room temperature. Store with end caps in place.

11.1 Coating Procedure

- 11.1.1 Cap one end of a denuder using Caplugs (which has the inner tube flush to the outer tube) and set the denuder upright on the capped end. For the denuder with flow-straighteners at both ends, either end may be capped. Measure 10 mL of the citric acid solution and pour into the denuder.
- 11.1.2 Cap the open end of the denuder and, holding it horizontally, rotate the denuder to distribute the coating solution evenly, wetting all surfaces.
- 11.1.3 Remove cap and decant excess coating solution into a 100 mL polyethylene bottle.
- 11.1.4 For the impactor denuder, the coating is performed without the impactor pin in place.

11.2 Drying Procedure

<u>Note</u>: As denuders dry, they change from translucent to a frosted appearance. Denuders are dry when they become uniformly frosted.

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

- 11.2.1 Assemble the drying train and manifold as illustrated in Figure 7. Drying train and manifold clean air flow should be adjusted to 2 to 3 L/min through each denuder. Close toggle valve controlling clean air flow through manifold before attaching denuders.
- **11.2.2** Attach the flow-straightener end of the denuder to the drying manifold port (see Figure 7).
- 11.2.3 Open toggle valve and allow clean air to flow through the denuder tube for 5 minutes.

<u>Caution</u>: Excess air flow will cause uneven coating to the tube walls.

- 11.2.4 Close toggle valve, and reverse ends of the denuder attached to the manifold. Start clean air flow again.
- 11.2.5 When an even frosted appearance is achieved, remove denuder from manifold, cap both ends with clean caps and store until ready for use. Turn off air to drying manifold. Affix label indicating coating date on denuder.

11.3 Denuder System Assembly

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

The annular denuder system (ADS) assembly consists of:

- an inlet nozzle/impactor or cyclone assembly;
- 1 glass annular denuder tube; and
- a 1-stage filter assembly.

è

The following procedure involves an inlet nozzle/impactor assembly.

- 11.3.1 Lay the ADS pieces on a clean surface (i.e., Kimwipes[®]).
- 11.3.2 Remove the end caps from the citric acid coated denuder. Gently insert the impactor support pin and coated frit assembly into the denuder-pin support.
- 11.3.3 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon[®] clad "O"-ring inside the coupler, if needed.
- 11.3.4 The filter assembly has been previously loaded with a Tefion[®] filter. The components are assembled with plastic couplers.
- 11.3.5 Attach the filter assembly inlet to the denuder coupler assembly.
- 11.3.6 Attach the elutriator-acceleration jet assembly to the other end of the denuder. Tighten very gently DO NOT OVERTIGHTEN or breakage will result.
- 11.3.7 Tighten the remaining couplers very gently.
- 11.3.8 Cap elutriator with orange dust cover until used. Attach "quick-release" tube to outlet of filter assembly.
- 11.4 Laboratory Leak-Check of ADS

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

- 11.4.1 Remove the orange dust cap from the impactor opening. Attach the "quick-release" outlet of the filter assembly to a pump module. Turn on the pump. Be certain that flow through the ADS occurs by checking the rotameter.
- 11.4.2 Briefly cap the elutriator with the orange dust cap. The flow, as indicated on the rotameter, should drop to zero if no leaks exist.
- 11.4.3 Disconnect the pump from the ADS at the "quick-release" plug. Cap the "quick-release" plug with an orange dust cover. Turn off the pump. REMEMBER - Never overtighten joints or breakage will result. If the

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

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

<u>Note</u>: It is recommended that the ADS joints be loosened slightly when extreme temperature changes are incurred during transportation. This will prevent unnecessary breakage or distortion of the ADS components. Remember to allow the system to adjust to the outdoor air temperature before tightening the joints and checking for leaks.

- 11.4.5 Before proceeding to the field, review the following checklist:
 - Run IDs on the Field Test Data Sheet should match labels affixed to the ADS components and filter assembly;
 - Recessed ends of the denuder should face the inlet;
 - ADS ends are capped; and
 - Transport case is secured firmly containing the ADS along with chain-of-custody and Field Test Data Sheet.

12. Sampling

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

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.

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

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

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

- 12.1.3 A summary of key criteria associated with these siting factors for air monitoring stations is included in Table 1.0. The information included in the table should be used 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, the occurrence of wooded areas around a site would make the siting very difficult. The use of the information in Table 1.0, coupled with a balanced evaluation by an experienced air quality and meteorology specialist, is highly recommended.
- 12.1.4 In general, for a site with no major obstruction and obstacles, the air sampler intake should be about 2-3 meters 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 3000 vehicles per day, the intake should be between 5 and 25 meters from the edge of the nearest traffic lane. It should also be 15 meters aboveground for a distance of 5 meters from the nearest traffic lane and 2 meters aboveground for a distance of 25 meters from the nearest lane. For a roadway supporting less than 3000 vehicles per day, the intake should be placed at a distance greater than 5 meters from the edge of the nearest traffic lane and a height of 2-15 meters aboveground.

12.2 Start-up

12.2.1 Remove the ADS from its field-to-lab carrying case and load into the field sampling box. Place the assembly in the box with the impactor extended outside the case. The ADS field sampling box is insulated and configured to hold the ADS without allowing movement. Chrome plated spring clips holds the denuder in place. Automatic and manual

control switches allow the sampling box to control the temperature of the ADS. The automatic switch should be used when the ADS is not in use and when the ADS is sampling for extended periods of time without constant supervision to prevent low temperature or sudden pressure change exposure of the ADS (these types of exposure can cause leaks to occur, condensation, or the filter to tear). When sampling, the ADS should be kept 1°C above the outdoor temperature to prevent condensation.

- 12.2.2 Allow the pump to warm up for -5 minutes prior to testing.
- 12.2.3 To check the Heat/Cool cycles, flip one switch from "AUTO" to "MANUAL" and the other between "COOL" and "HEAT." Check to insure that the fan and heater (i.e., light bulb) work, respectively.
- 12.2.4 With the elutriator still capped, turn on the pump with the switch on the timer. The rotameter should indicate zero flow. Run leak check for 5-10 seconds, then turn off pump and remove elutriator cap. Record leak rate on Field Test Data Sheet (see Figure 9). If there is a flow, refer to Section 13.4 for corrective action for leak test failure. The Field Test Data Sheet is used to keep track of the denuder tube, filter and impactors, as to when and by whom they are prepared, assembled, extracted and data input as well as to record the installation data and time, run date, sampling period, pump flow rates, start and end times, and other data relevant to each run.
- 12.2.5 Attach a DGM output to the inlet of the annular denuder system. Turn on pump. Record start time on Field Test Data Sheet. Using a stopwatch, record the time for 20.0 L to pass through the DGM. Record the DGM temperature and the absolute pressure of the DGM.
- 12.2.6 Calculate the flow rate as follows:

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

where:

- Q_{std} = flow rate corrected to standard conditions, 25°C and 760 mm Hg, L/min
 - V = volume of gas pulled through denuder system, 20 L
 - T = time required to pull 20 L of gas through denuder system, minutes

 P_{b} = barometric pressure, run Hg

 P_{stel} = standard barometric pressure, 760 mm Hg

 T_{std} = standard temperature, 298°K

 T_m = temperature of dry gas meter, °K(= °C + 273)

 $F_c = dry gas meter correction factor, dimensionless$

- 12.2.7 If the calculated flow rate is not between 9.5 and 10.5 L/min, then readjust the flow rate until the rate is in the above range. Stop the pump.
- 12.2.8 Record the flow rate on Field Test Data Sheet.
- 12,2,9 Remove DGM connection tubing from elutriator inlet. With all information correctly on the Field Test Data Sheet, start the pump and begin sampling.
- 12.3 Sample Shutdown
 - 12.3.1 Attach DGM connection tubing to the elutriator inlet with pump still running. Measure flow rate. Record calculated flow rate, temperature, and pressure on Field Test Data Sheet.
 - 12.3.2 Turn off the pump. Record time and elapsed time meter reading on Field Test Data Sheet. Remove DGM connection tubing from elutriator inlet. Remove ADS from the sampling box, cap the ends, and place the ADS in field-to-iab carrying case for transport to lab. Secure the latches on the transport case. Be careful not to stress the ADS during the transfer or breakage will result.

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

12.4 Corrective Action for Leak Test Failure

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

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

12.4.2 Cracked or chipped denuder or elutriator assembly - Note problem on Field Test Data Sheet. Discard defective pieces. Do not try to extract cracked pieces.

<u>Warning</u>: Use caution when disassembling cracked glassware. Pieces may shatter and cause severe cuts. Wear protective clothing.

- 12.4.3 Flow rate disagreement Note problem on Field Test Data Sheet. Check vacuum gauge on flow module. If a high vacuum exists then the sampler has become blocked. This may be due to dust or smoke particles clogging the filter or to obstructions in the system or tubing. Check flow module. Repair as needed.
- 12.4.4 Inadequate flow rate Note problem on Field Test Data Sheet. Check rotameter on flow controller. If adequate flow is shown here, then a leak exists between the controller and the DGM. If no flow is shown on rotameter, then check vacuum gauge on controller. If no vacuum exists, then pump needs repair. If a high vacuum is shown, then an obstruction exists in the system. Check to see that the paper filter dividers were not accidentally installed with the filter in the filter assembly. Check tubing for kinks.

13. ADS Disassembly

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

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

- 13.2 Decouple the elutriator-jet assembly from the first denuder-impactor-coupler assembly.
- 13.3 The impactor assembly and the denuders <u>will not</u> be extracted. However, each run should begin with a clean impactor and charged denuder.
- 13.4 The handling of the exposed Teflon[®] filter requires protection from contamination with NH₃, which would rapidly neutralize aerosol acidity on the filter and bias the sample results. In order to ensure ammonia-free air occupies the glove-box, a positive pressure is maintained by blowing air through a PVC tube (4 inch O.D.) filled with glass-wool dosed with citric acid before entering the manifold which enables uniform distribution of air from top of the glovebox. Flow the ammonia-free air for five minutes before retrieving the filter. A citric acid soaked filter paper is also placed on the bottom to deplete ammonia while unused. Disassemble the filter assembly in the clean, ammonia-free

glove-box. Clean all glove-box surfaces and utensils with methanol. Wearing clean gloves and using clean filter forceps, remove the filter and place in the 100 mL bottle, with the exposed filter surface facing downward. Label the bottle with appropriate information.

14. Extraction Procedure

- 14.1 Samples should be analyzed as scon after collection as possible. It is imperative that the solutions and extraction procedures are prepared and performed on the day of pH analysis. Keep samples in a refrigerator until extracted and analyzed.
- 14.2 Samples should not be extracted until the day of analysis; however, if samples are extracted and then it is not possible to analyze them that day, they should be refrigerated. Allow the samples to return to room temperature before analysis.
- 14.3 It is imperative that the same extract solution (ES) 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, the working standards, and in extracting the Teflon[®] filters.
- 14.4 Handling and extraction must take place in an ammonia-free glove box.

<u>Note</u>: Teflon[©] is not wetted by water, therefore, the filter will float on top of an aqueous solution. The use of alcohol aids wetting. Also, all types of Teflon[©] curl to some extent. It is the analyst's responsibility to ensure the extraction solution makes complete contact with the particle deposit on the Teflon[©] filter during extraction. It may be necessary to use a clean plastic (Teflon[©] or polyethylene) rod or tubing stub to hold the filter in better contact with the fluid during extraction.

- 14.5 Teflon[®] filter extraction
 - 14.5.1 Allow the glove-box to be flushed with ammonia-free air for at least 5 minutes before proceeding.
 - 14.5.2 Process the filters in the same order in which they will be analyzed.
 - 14.5.3 Open the sample vial and pipet 0.2 mL methanol onto the filter.
 - 14.5.4 As soon as the methanol has wet the entire surface of the filter, deliver 6.00 mL of ES solution into the vial. Cap the vial.

- 14.5.5 Put a batch of vials into the ultrasonic bath and sonicate for a total of 20 minutes, rotating the position of the vials 90° every 5 minutes.
- 14.6 Aliquot preparation
 - 14.6.1 Using a 1 mL automatic pipet, transfer 1 mL of the sample extract into each of two labeled 2 mL vials, one labeled A and the other labeled A1.

Subsequent samples will be labeled B and B1, C and C1, etc.

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

15. pH Analysis

- 15.1 Standard and Reagent Preparation
 - 15.1.1 Standard H₂SO₄ Solution, 1.000 N

<u>Note</u>: Each of the standard H_2SO_4 stock solutions must be prepared fresh the day of pH analysis.

- 15.1.1.1 Label seven 25 mL polyethylene stoppered volumetric flasks. Also, label each flask with the volume of 1.000 N H₂SO₄ solution.
- **15.1.1.2** Use the 25 μ L automatic pipet to add the 1 N stock H₂SO₄ solution to flasks 2 and 3. Use the 100 μ L pipet to add 1.000 N stock H₂SO₄ solution to flasks 4 through 7. Dilute all flasks to the 25 mL mark with methanol. Cap with stoppers or parafilm and mix well. Proper dilution ratios are indicated in the following table:

Standard H ₂ SO ₄ flask	Volume of 1.000 N H ₂ SO ₄ added to each flask, (μL)	Working standard concentration, 10^{-3} N H ₂ SO ₄	Equivalent strong acid mass collected on filter (C _{B0}), μg ^a	Approximate pH
1	0	0	C	4.09
2	25	1	4.90	4.01
3	50	2	9.80	3.95
4	100	4	19.60	3.84
5	200	8	39.20	3.68
6	400	16	78.40	3.48
7	800	32	156.8	3.23

^aBased on 3.1 mL extraction volume.

15.1.2 2 M Potassium Chloride (KCl) Solution

- 15.1.2.1 Weigh 149.2 \pm 0.1 g of KCl. Add the KCl to a 2 L flask.
- 15.1.2.2 Add about 700 mL of DDW water to the flask. Swirl the solution until the KCl is completely dissolved.
- 15.1.2.3 Pour this mixture into a 1 L graduated cylinder. Rinse the flask with a small amount of DDW water and transfer the rinse into the cylinder. Fill the cylinder to the 1 L mark.
- 15.1.2.4 Pour the solution from the cylinder into the 1 L polyethylene bottle. Cap and shake the bottle to mix well. Mark the bottle with date of preparation.

15.1.3 0.100 N Perchloric Acid (HClO₄) Solution

- 15.1.3.1 Fill a 1 L graduated cylinder about half full with DDW. Transfer 10 \pm 0.1 mL of 60-62 percent HClC₄ into the 1 L cylinder with a 10 mL pipet.
- 15.1.3.2 Fill the cylinder to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.
- 15.1.3.3 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.

15.1.4 0.010 N HClO₄ Solution

- 15.1.4.1 Fill a 1 L graduated cylinder about 1/2 full with DDW.
- 15.1.4.2 Measure 100 mL of the 0.1 N HC1O₄ solution with the 100 mL graduated cylinder. Add this to the 1 L cylinder.
- 15.1.4.3 Fill the 1 L cylinder with DDW to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.
- 15.1.4.4 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.
- 15.1.5 Extraction Solution (ES)

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

- **15.1.5.1** Measure 20 ± 0.5 mL of 2 M KCl into 2 L erlenmeyer flask.
- 15.1.5.2 Using a 5 mL calibrated automatic pipet, add 10 ± 0.1 mL of 0.01 N perchloric acid (HClO₄), to the flask. Add 980 \pm 10 mL of DDW to the flask.
- 15.1.5.3 Mix well and cover with parafilm until ready for use.
- 15.1.6 Extraction Solution with methanol (EA Solution)
 - 15.1.6.1 Measure 150 ± 2 mL of ES (prepared in Section 15.1.5) into a 250 mL graduated cylinder. Transfer to a 250 mL erlenmeyer flask.
 - 15.1.6.2 Using a 5 mL graduated cylinder, add 5 ± 0.1 mL of methanol (this must be from the same fresh bottle of methanol that was used to prepare the standards in Section 15.1.1) to the flask.
 - 15.1.6.3 Mix well and cover with parafilm until ready for use.
 - 15.1.6.4 pH of the EA solution should be 4.09 ± 0.04 . If not, the solution must be reprepared.

15.1.7 Working Standard Test Solutions

- 15.1.7.1 Place fourteen-4 mL polystyrene sample vials (as used with Technicon Auto-Analyzer II system) labeled 1A, 1B, 2A 2B...7A, 7B into support racks. Using the calibrated dispensing pipet bottle, add 3 mL of ES solution to each 4 mL vial.
- 15.1.7.2 Using the displacement pipet, add 50 μ L of methanol to each vial. Pour about 3 mL of Standard Flask #1 H₂SO₄ standard (see Section 15.1.1) into a labeled 4 mL vial.
- 15.1.7.3 Immediately pipet 50 μ L of this standard into the 4 mL vials labeled 1A and 1B containing the ES solution and methanol.

<u>Note</u>: This transfer must be done without delay to prevent the standard concentration from increasing significantly due to evaporation of the methanol solvent.

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

<u>Note</u>: There should be fourteen vials, each containing 3 mL of ES solution, 50 μ L of methanol, and 50 μ L of Standard H₂SO₄ solution (see Section 16.1.1). Two aliquots from each vial (1A, 1B, 2A, 2B, 3A, 3B,...7A, 7E) will be analyzed.

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

The pH meter requires temperature calibration whenever a new electrode is used. Use the manufacturer's procedure in the instrument manual. This calibration should be repeated every three months while not in use. The pH meter is left with the power cord plugged into the AC outlet, the mode control knob is left in the standby position, and the combination electrode is immersed in a 4 M KCl solution (a slit rubber stopper seals the bottle with the electrode in it). Keep a record of the temperature calibrations in a lab notebook.

15.3 Pre-analysis Calibration

<u>Note</u>: Figure 10 outlines the steps for proper calibration and set-up for analysis of the Teflon[®] filter sample for pH determination. Analysis should be performed at room temperature.

- 15.3.1 Use a pH Analytical Laboratory Log Form (see Figure 11) to record all data.
- 15.3.2 Fill three 4 mL vials with pH 7 buffer. Withdraw the electrode from the 4 M KCl bottle and wipe the tip gently with a Kimwipe[®] to remove the bulk of the solution. Rinse the electrode with one vial of pH 7 buffer. Do not test pH of the first vial.
- 15.3.3 Immerse the electrode in the second vial of the pH 7 buffer. Use a small bottle or other support to hold the vial up to the electrode while waiting for the meter reading to equilibrate.
- 15.3.4 Test the pH by turning to the pH mode of the meter. Allow the reading to stabilize for at least 30 seconds. Record the result on the Analytical Laboratory Log Form for pH 7, entry 2.
- 15.3.5 Turn to standby mode, and then test the last vial of pH 7 buffer. Record the results on the log form for pH 7, entry 3. If the pH value for the 2nd cup is not 7.00 ± 0.01 , adjust the "calib." knob to obtain a reading of 7.00. Note this adjustment on the log form.
- 15.3.6 Fill three 4 mL vials with pH 4 buffer. With the meter in the standby mode, remove the cup containing pH 7 buffer, wipe the tip of the electrode gently with a Kimwipe[®], and then rinse the electrode with the first vial of pH 4 buffer. Do not record pH.

- 15.3.7 Test the next two vials of pH 4 buffer as above, recording the results on the log form. If the pH value for the third vial is not 4.00 ± 0.01 , adjust the "slope" knob to get a reading of 4.00. If the value for the second vial was not 4.00 ± 0.01 , the calibrations at pH 7 and at pH 4 must both be repeated.
- 15.4 pH Test of HClO₄ Solutions

<u>Note</u>: The 0.01 N HClO₄ solution is used to prepare the ES solution which, in turn, is used to prepare the EA solution. It is imperative that the pH value for the EA solution be 4.09 ± 0.04 . If this pH value is not achieved, then one or more of the HClO₄ solutions must be reprepared.

- 15.4.1 Finish the calibration of the pH meter with pH 4 buffer.
- 15.4.2 Rinse the pH electrode with DDW. Wipe the tip of the electrode with a Kinwipe[®].
- 15.4.3 Fill three 4 mL vials with EA solution. Measure the pH of the test EA solution in similar fashion to the buffer solutions. The values must be 4.09 ± 0.04 .
- 15.4.4 If the above pH values are not achieved, follow Section 15.1.6 to reprepare the solutions. Test the pH of the new solutions. Repeat as necessary to obtain an average pH of 4.09 ± 0.04 .
- 15.4.5 Leave the electrode immersed in the "3rd vial" with the meter in the standby mode until ready to start analysis of the working standards.
- 15.5 Analysis of Working Standard

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

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

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

- 15.5.2 After testing the pH of vial 1A1, test vial 1A2. Record the results of both on the Analytical Laboratory Log Form.
- 15.5.3 With the meter in the stand-by mode, remove vial 1A2, wipe the electrode with a Kimwipe[®] and test one 2 mL vial of EA solution.
- 15.5.4 Test a 2nd vial of EA solution; record the results on the log form. Discard the 1st vial of EA, but retain the 2nd vial to be used as the 1st vial for the next EA test.
- 15.5.5 Mean pH value for the EA solutions should be 4.09 ± 0.04 . If the above pH values are not achieved, follow Section 15.1.6 to reprepare the EA solution. Retest. If still outside range, investigate problem with probe, have Laboratory Manager review previous recorded pH data for samples and EA solutions to determine validity of measurements.
- 15.5.6 Continue testing the remainder of the working standards, 1B1, 1B2, 2A1, 2A2, 2B1, 2B2...7B1, 7B2. Remember that the electrode tip is wiped both before and after each pair of test solutions, but not in between two vials of the same sample.

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

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

15.6 Analysis of Filter Extracts

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

16. Assumption of Annual Denuder System

- 16.1 The measurement of acid aerosol requires that ammonia be eliminated from the sample stream to prevent inaccurate measurement of the acid aerosol, thus biasing the results. To address this issue, a citric acid coated denuder to remove (denuder) ammonia from the gas stream is positioned in front of the filter assembly where strong acid aerosols are collected. The efficiency of the citric acid denuder to remove NH₃ is assumed to be 100 percent.
- 16.2 The efficiency of the impactor collection system decreases with increased particulate loading. The average operational time before such loading occurs has not been determined. Likewise, the removal efficiency of the denuders have not been fully explored. Thus, both the impactor and denuders are removed after each sampling event and replaced with new components.
- 16.3 Other assumptions which are made associated with the performance of the annular denuder system for validity of the calculations presented in Section 17 are:
 - All alkaline particles (> 2.5 μ m) are removed at the sampler inlet;
 - The cyclone or elutriator/impactor assembly have DP_{50} cut size of 2.5 μ m;
 - The citric acid coated-denuder removes 100% of ammonia from the gas sample stream;
 - Fine (<2.5 μ m) acid (H₂SO₄) aerosol losses in the denuder are less than 1%;
 - The Teflon[®] filter is 100% efficient in collecting fine acid aerosols; and
 - The molar ratio of NH₄NO₃ to H₂SO₄ is assumed to be less than 10%. However, if NH₄NO₃ is captured on the Teflon[®] filter, its dissociation during sampling may occur, thus affecting acidity measurements. To address these concerns, the user is encouraged to consider the "Enhanced Method", as outlined in Part B of this document.

17. Atmospheric Species Concentration Calculations

- 17.1 Calculations Using Results from pH Measurement
 - 17.1.1 A convenient method of expressing concentration of the hydrogen ion was first proposed by Sorensen in 1909 and has been widely adopted by chemists.

$$pH = -\log [H^+]$$

 $[H^+] = 10^{-pH}$

17.1.2 For each working standard on a given analytical day, calculate the "apparent net strong acid concentration" as follows:

$$C_i = 10^{-pHWS}i - 10^{-pHEA}$$

where:

 C_i = apparent net strong acid concentration, molar,

 $pHWS_i = measured mean pH of a working standard, and$

pHEA = measured mean pH of the EA solution.

- 17.1.3 For each analytical day, utilizing a particular set of freshly prepared daily working standards, develop a standard curve by calculating the linear regression of C_i vs. C_{eq}, as documented in Section 15.1.1.1. Calculate slope and intercept of the standard curve.
- 17.1.4 Calculate the corresponding "apparent net strong acid concentration" from the sample pH utilizing the following equation:

$$C_{c} = 10^{-pHS} - 10^{-pHEA}$$

where:

 $C_s = apparent net strong acid concentration for unknown sample, molar,$

pHS = measured pH of the sample (S), and

pHEA = measured pH of the EA solution.

17.1.5 Utilizing the slope and intercept of the standard curve, calculate equivalent mass of strong acid:

$$C_f = [Intercept] + [C_s] [Slope]$$

where:

 C_f = apparent net strong acid mass, μg , as calculated from standard curve,

Intercept = calculated relationship from linear regression analysis of C_i vs. C_{Eq} , and

- Slope = calculated relationship from linear regression analysis of C_i vs. C_{Eq} .
- 17.2 Calculation of Air Volume Sampled, Corrected to Standard Conditions
 - 17.2.1 The actual sample air value, V, 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 as follows:

$$V = [F] [T]$$

where:

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

T = net elapsed time, min, and

V = total sample volume, L

17.2.2 Convert L to m^3 by:

$$V_{s} = V \times (10^{-3})$$

where:

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

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

$$V_{s_{std}} = V_{s}Y(\frac{T_{std}}{T_{m}})(\frac{P_{bar}}{P_{std}})$$

where:

V _{sstd} =	volume of sample at EPA-reference conditions, m ³ ,
V _s =	volume of gas sample through the dry gas meter, or calculated volume sampled as indicated by rotameter (see Section 17.2.1), m^3 ,
T _{std} =	absolute EPA-reference temperature, 298°K,
т _т =	average flowmeter or dry gas meter temperature, °K,
P _{bar} =	barometric pressure of flow or volume measurement condition, mm Hg,
P _{std} =	EPA-reference barometric pressure, 760 mm Hg, and
Y =	dry gas meter calibration factor (if applicable), dimensionless.

- 17.3 Calculation of Strong Acidity Aerosol Concentration
 - 17.3.1 Calculate the final concentration of apparent net fine particle (<2.5 μ m) strong acidity (as H₂SO₄):

$$C_{H} + = C_{f} / V_{s_{std}}$$

where:

- $C_{\rm H}^{+}$ = apparent net fine particle strong acidity concentration, $\mu g/m^3$,
 - C_f = apparent net strong acid, μg , as calculated from standard curve, and
- V_{sstd} = volume of sampled gas at EPA-reference conditions (see Section 17.2.3), m³.

18. Variations of the Acid Aerosol Denuder System

One modification of the fine particle strong acidic aerosol denuder system involves adding additional denuders to selectively quantitate other gaseous and particulate species in the atmosphere, and is illustrated in Figures 12 and 13. This system was developed to measure reactive acidic and basic gases and particulate matter which are contained in ambient air. The chemical species which can be measured utilizing this system are gaseous SO₂, HNO₂, HNO₃, NH₃, and particulate SO₄⁼, NO₃, and H⁺. Other similar chemical species can be successfully collected by the system with modifications (i.e., changing the denuder coating solutions, the denuder sequence, and the filter types and sequence). Once collected, the pollutant concentrations are quantified by ion chromatography (IC) analysis and/or Technicon colorimeter auto-analysis. A full description of this methodology can be found in "Compendium of Methods for the Determination of Air Pollutants in Indoor Air," U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, N.C. 27711, EPA-600/4-90-010.

19. 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. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

20. Performance Criteria and Quality Assurance (OA)

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

- 20.1 Standard Operating Procedures (SOPs)
 - 20.1.1 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.
 - 20.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the monitoring work.

20.2 Quality Assurance 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 on a regularly scheduled basis and should be part of the quality assurance program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system are provided by the manufacturer. For detailed guidance in setting up a quality assurance program, the user is referred to the Code of Federal Regulations (see Section 21, Citation 11) and the EPA Handbook on Quality Assurance (see Section 21, Citation 12).

21. <u>References</u>

- 1. Waldman, J. M., Operations Manual for the Annular Denuder System Used in the USEPA/RIVM Atmospheric Acidity Study, UMPNJ Robert Wood Johnson Medical School, Piscataway, NJ, August 28, 1987.
- 2. American Chemical Society Subcommittee on Environmental Chemistry, "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," *Analyt. Chem.*, 52:2242-2249, 1980.
- Sickles, II, J. E., "Sampling and Analytical Methods Development for Dry Deposition Monitoring," Research Triangle Institute Report No. RTI/2823/00-15F, Research Triangle Institute, Research Triangle Park, NC, July 1987.
- 4. Forrest, J., and L. Newman, "Sampling and Analysis of Atmospheric Sulfur Compounds for Isotopic Ratio Studies," *Atmos. Environ.*, 7:562-573, 1973.
- 5. Stevens, R. K., et al., Abstract for ACGIH Symposium: on Adran COS in Air Sampling, "Inlets, Deruders and Filter Packs to Measure Acidic Inorganic Pollutants in the Atmosphere," Asilomar Conference Center, Pacific Grove, CA, February 16, 1986.
- 6. Appel B. R., Povard V., and Kothney E. L., "Loss of nitric acid within inlet devices for Atmospheric Sampling," Paper presented at 1987 EPA/APCA Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, 3-6 May 1987.
- Braman R. S., Shelley T. J., and McClenny W. A., "Tungstic Acid for Preconcentration and Determination of Gaseous and Particulate Ammonia and Nitric Acid in Ambient Air," Analyt. Chem., 54:358-364, 1983.
- 8. Ferm, M., "Concentration Measurements and Equilibrium Studies of Ammonium, Nitrate and Sulphur Species in Air and Precipitation," Doctoral Thesis, Department of Inorganic Chemistry, Goteborg University, Goteborg, Sweden, 1986.
- 9. Ferm, M., and Sjodin A., "A Sodium Carbonate Coated Denuder for Determination of Nitrous Acid in the Atmosphere," *Atmos. Environ.*, 19:979-985, 1985.
- 10. Stevens, R. K., and Rickman, E., Jr., "Research Protocol/Method for Ambient Air Sampling with Annular Denuder Systems," prepared for U.S. Environmental Protection Agency, Atmospheric Chemistry and Physics Division, Office of Research and Development, Research Triangle Park, NC, ASRL-ACPD-RPM 003, January 1988.
- 11. 40 CFR Part 58, Appendix A, B.

Acid Aerosol

- 12. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II -Ambient Air Specific Methods, EPA 600/4-77-0272, May, 1972.
- 13. Bolleter, C.J., Bushwan, and Tidwell, P.W. (1961), "Spectrophotometric Determination of Ammonia as Indophenol," Anal. Chem. <u>33</u>, 592-594.
- 14. Harwood, J.E. and Kuhn, A.L. (1970), "A Colorimetric Method for Ammonia in Natural Water," Water Res. 4, 8055-811.
- 15. Koutrakis, P., Wolfson, J.M., Slater, J.L., Brauer, M., Spengler, J.D., Stevens, R.K., and Stone, C.L., "Evaluation of an Annular Denuder/Filter Pack System to Collect Acidic Aerosols and Gases," *Environ. Sci. & Tech.* 22, 1463-1468, 1988.
- 16. Mann, L.T., Jr., "Spectrophotometric Determination of Nitrogen in Total Microkjedahl Digests," Anal. Chem. 35, 2179-2182, 1963.
- Possanzini, M., Febo, A., and Liberti, A., "New Design of a High-performance Denuder for the Sampling of Atmospheric Pollutants," Atmos. Environ. <u>17</u>, 2605-2610, 1983.
- 18. Stevens, R.K., and Rickman, E.E., Research Protocol/Method for Ambient Air Sampling with Annular Denuder Systems. Report ASRL-ACPD-RPM 003, U.S. EPA, Research Triangle Park, N.C., January 1988.
- 19. Koutrakis, P., Wolfson, J.M., and Spengler, J.D., "An Improved Method for Measuring Aerosol Strong Acidity: Results from a Nine-Month Study in St. Louis, Missouri and Kingston, Tennessee," Atmospheric Environment, 22:157-162, 1988.
- 20. Brauer, M., Koutrakis, P., Wolfson, J.M., and Spengler, J.D., "Evaluation of the Gas Collection of an Annular Denuder System Under Simulated Atmospheric Conditions," *Atmosperhic Environment*, 23:1981-1986, 1989.
- 21. Koutrakis, P., Wolfson, J.M., Brauer, M., and Spengler, J.D., "Design of a Glass Impactor For an Annual Denuder/Filter Pack System," Aeros. Sci., and Techn., 12:607-612, 1990.
- 22. Sjödin A. and Ferm, M., "Measurements of Nitrous Acid In An Urban Area," Atmospheric Environment 19, 985-992, 1985.
- 23. Vossler, T.L., Stevens, R.K., Paur, R.J., Baumgardner, R.E., and Bell, J.P., "Evaluation of Improved Inlets and Annular Denuder Systems to Measure Inorganic Air Pollutants," Atmos. Environ. 22, 1729-1736, 1988.
- 24. Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, EPA-600/8-90-005, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1990.

Table	1.0.	Summary	of	Key	Probe	Siting	Criteria	for
		Acid Aeros	iol	Mon	itoring	Statio	ns	

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 is >20 m from the dripline and 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.

~



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



Figure 1b. Annular Denuder System with Impactor Assembly



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

Revision No. 0 Date 11/92 Page 40 of 51



Figure 3. Available Elutriator and Acceleration Jet Assemblies



Figure 4. Glass Annular Denuder with Inset Impactor Assembly

Revision No. 0 Date 11/92 Page 42 of 51



Figure 5. Side View Impactor/Coupler Assembly

Revision No. 0 Date 11/92 Page 43 of 51



Figure 6. Internal Schematic of Annular Denuder

Revision No. 0 Date 11/92 Page 44 of 51





Revision No. 0 Date 11/92 Page 45 of 51

ر س



Figure 8. Acid Aerosol Filter Assembly

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

Droject:	GENERAL		Date:		
F10ject			Location of S	ampler'	
			Location of 5		
Location:					
	_		_		
Sample Code:		······································	Operator:	<u></u>	
	EQUIPMENT			Sampler	
Mass Flow	-		Citric Acid D	enuder No.:	
Controller No.	•		Filter Assemb	ly No	
Lab Calibration	n Date [.]				
Flow Rate Set	Point:				
Calibrated By:	· • • • • • • • • • • • • • • • • • • •				
Rotameter No.	,	,			
DGM No ·	, 				
	AMPI DIC DAT	·····			
3	Time	A		Stop	
Times	<u>1 IIII</u> E			<u>310</u>	
1 ime:			•		
Flow Rate:					
Temperature:	······				
Pressure:					
Avg. Flow Rat	e:				······
Leak Check (B	efore):				
(A	(fter):				
Total Sample V	/ol.:				
Flow Maintain	ed Rate:	(±5%)			
Time	Flow Rate (Q),	Ambient Temperature,	Barometric Pressure,	Relative Humidity,	Comments
			Indu Hig	<i>//</i>	Conditional
J		·		ļ	
L					

Figure 9. Annular Denuder Field Test Data Sheet



Figure 10. Calibration and Analysis Step for pH Determination

Acid Aerosol

Revision No. 0 Date 11/92 Page 48 of 51

Determination of the Strong Acidity of Atmospheric Fine-Particles ($< 2.5 \mu m$)

Name:	 	
Date:	 	
LAB:	 	

Sample I.D.:_____

Location:_____

	RUN NUMBER							
Constituent	1	2	3	4	5	6	7	
pH 7 Buffer								
1								
2								
3						L		
pH 4 Buffer								
1							8-29883. See 2883.	
2								
3							en en la constante en la	
EA Solution								
1					<u>estas</u> (†			
2					L			
3	REF ARE REPAY							
Working Standards		199 686 222	enseeddal			<u>2008</u> 2-083-1	<u>1983 - 1983 - 1989</u> 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 - 1997 -	
		-						
IAZ				<u> </u>			{	
1 <u>E</u> A								
101								
2A1								
241								
Тетр								
EA								
2 B 1						<u> </u>		
2B2								
EA							· · · · · · · · ·	
3A1								
3A2								
EA								
Temp.								
3 B 1								
3B2								
EA								

Figure 11.	DΗ	Analytical	Laboratory	Log Form
TPOID TT.	P	· mary trout		205 - 0.111

Revision No. 0 Date 11/92 Page 49 of 51

	RUN NUMBER						
Constituent	1	2	3	4	5	6	7
4A1							
4A2							
EA							
481							
4B2							
Temp.							
EA							
5A1							
5A2							
EA							
5B1						[
5B2							
EA							
6A1							
6A2							
Temp.						1	
EA						!	
6B1						<u> </u>	
6B2							
EA						l 	
EA							
7A1	[]						
7A2							
EA	[]						
7B1	[]				Į		
7B2	[]						
Тетр.	[]						
Sample Extracts							
A							
Al							
В							
B1							
C							
Cl		[[
. D			<u> </u>				
D1							
E							
El	I			ļ	ļ		
EA							
Temp.					landi es contore		aarigiri madaa 700
EA Solution	nusuronnuur	ເລຍູນເອົາຫຼາດງາງ	enterritienut meder		ini	irt primeted	
1							
2				ļ			
3							
pH4 Buffer				[<u> </u>
1							
2							
3			<u> </u>	<u> </u>	l		

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

.

Revision No. 0 Date 11/92 Page 50 of 51



 Figure 12. Schematic View of Annular Denuder with Cyclone Adaptor for Measurement of Reactive Acidic and
 Basic Gases and Particulate Matter (< 2.5 μm) in Ambient Air

Part A



Figure 13. Annular Denuder System with Cyclone in Heated Sampling Case for Measurement of Reactive Acidic and Basic Gases and Particulate Matter (< 2.5 μm) in Ambient Air</p>

Acid Aerosol

PART B

·

Ĩ

DETERMINATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES (<2.5 µm) USING ANNULAR DENUDER TECHNOLOGY

ENHANCED METHOD

.*

DETERMUNATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES (<2.5 μm) USING ANNULAR DENUDER TECHNOLOGY

ENHANCED METHOD

TABLE OF CONTENTS

Top	<u>pic</u> Page
1.	Scope B-1
2.	Applicable Documents
3.	Summary of Method B-2
4.	Significance
5.	Definitions B-5
6.	Apparatus
	6.1SamplingB-66.2AnalysisB-9
7.	Reagents and Materials
8.	Preparation of Impactor Frit and Denuder Coating
9.	Impactor Frit Installation
10.	Filter Preparation and Assembly
	10.1 Citric Acid Coated Filter B-14 10.2 Filter Pack Assembly B-14
11.	Annular Denuder System Preparation
	11.1 Coating ProcedureB-1611.2 Drying ProcedureB-1611.3 Denuder System AssemblyB-1711.4 Laboratory Leak-Check of ADSB-18

TABLE OF CONTENTS (continued)

Το	pic Page
12.	SamplingB-19
	12.1 Placement of Denuder SystemB-1912.2 Start-upB-2112.3 Sample ShutdownB-2212.4 Corrective Action for Leak Test FailureB-22
13.	ADS Disassembly
14.	Extraction Procedure
15.	pH Analysis
	15.1Standard and Reagent PreparationB-2715.2Calibration of pH MeterB-3015.3Pre-analysis CalibrationB-3015.4pH Test of HClO ₄ SolutionsB-3115.5Analysis of Working StandardB-3215.6Analysis of Filter ExtractsB-32
16.	Ion Chromatography Analysis
	16.1Standard PreparationB-3316.2Reagent PreparationB-3416.3Sample PreparationB-3316.4Basic System OperationsB-3616.5Basic TroubleshootingB-46
17.	Ammonia Analysis by Technicon Auto-analysis
	17.1 Standards and Stock Solutions Preparation B-42 17.2 Reagent Preparation B-42 17.3 Procedure for Auto-analyzer Set-up B-42 17.4 Procedure for Sample Run B-42
18.	Assumption of Annual Denuder System
19.	Atmospheric Species Concentration Calculations
	19.1 Calculations Using Results from pH MeasurementB-419.2 Calculation Using Results from IC AnalysisB-519.3 Calculation Using Results from Auto-analyzerB-5

TABLE OF CONTENTS (continued)

Top	<u>Page</u>
20.	Variations of the Acid Aerosol Denuder System
21.	Method Safety
22.	Performance Criteria and Quality Assurance (QA)
	22.1 Standard Operating Procedures (SOPs) B-52 22.2 Quality Assurance Program B-52
23.	References

_-

DETERMINATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES (<2.5 μm) USING ANNULAR DENUDER TECHNOLOGY

ENHANCED METHOD

1. <u>Scope</u>

- 1.1 This document describes the protocol for the quantitative determination of equivalent strong acidity of atmospheric fine-particle ($<2.5 \ \mu m$) in ambient air as hydrogen ion by pH.
- 1.2 The methodology detailed in the "enhanced method" is a composite of methodologies developed by U.S. Environmental Protection Agency (USEPA), University of Kansas, Robert Johnson Medical School, New York State University, Harvard University and the CNR Laboratories. It is currently employed in a number of air pollution studies in Italy, U.S.A., Canada, Mexico, Germany, Austria, and Spain, and in such institutions as public health services and epidemiology and environmental research centers.

While the "standard method" utilizes a denuder and filter assembly for determination of the strong acidity atmospheric fine-particles, it does not account for potential interferences from nitric acid (HNO₃) and nitrate aerosol (NH₄NO₃) which might bias the acidity measurement. The "enhanced method" adds an additional denuder upstream of the filter assembly to selectively remove nitric acid from the gas stream prior to filtration. In addition, to correct for biases due to the dissociation of nitrate aerosol captured on the Teflon[®] filter, thus affecting acidity measurements, a backup nylon filter has been incorporated to capture volatile HNO₃ followed by a glass-fiber filter impregnated with citric acid to retain the dissociated NH₃ from NH₄NO₃. The ammonia concentration is subtracted from the nitrate value, then combined with the acidity measurement of the Teflon[®] filter to give an unbiased measurement of the atmospheric fine particle strong acidity aerosol found on the Teflon[®] filter.

The techniques, procedures, equipment, and other specifications comprising this method are derived and composited from those actually used by the contributing research organizations and thereby known to be serviceable and effective. At this stage, this method is a unified, consensus, tentative, draft method intended for further application and testing. Users should be advised that the method has not yet been adequately tested, optimized, or standardized. Many of the specifications have been initially established by technical judgment and 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 to confirm and document their possible advantages. Information and comments are solicited on improvements, alternative equipment, techniques, or specifications, performance, or any other aspect of the method. All such information should be sent to the EPA Project Manager identified on the cover page and will be considered for incorporation in future revisions of the method.

1.3 The equipment described herein can be modified to measure acidity of atmospheric gases and particulate matter contained in both indoor and outdoor atmospheres. Modification to this methodology were developed for monitoring regional-scale acidic and basic gases and particulate matter in support of U.S. EPA field programs involving the Integrated Air Cancer Research Program and the Acid Deposition Network. Similarly, the methodology has been used to characterize urban haze in Denver, Houston, Boston and Los Angeles.

2. Applicable Documents

2.1 ASTM Standards

D1356 Definitions of Terms Related to Atmospheric Sampling and Analysis

2.2 Other Documents

Ambient Air Studies (1-23) U.S. EPA Technical Assistance Document (24)

3. Summary of Method

3.1 The annular denuder system (ADS) consists of an inlet with an impactor or cyclone preseparator designed to eliminate all particles with a DP₅₀ of 2.5 μ m or greater, annular denuders, and a three-stage filter assembly. In operation, air is drawn through the elutriator-accelerator jet assembly, an impactor frit and coupler assembly, past two denuders to remove nitric acid and ammonia, then into a three-stage filter pack assembly. The three-stage filter pack contains 47-mm filters supported by stainless steel screens and separated by polyethylene spacer rings. The-first filter is a 2 μ m pore-size Teflon[®] membrane filter, Zefluor (Gelman Sciences), followed by a 1 μ m pore-size nylon membrane filter, nylasorb[®] (Gelman Sciences), and then a citric acid-impregnated, glass-fiber filter, and a prefilter-pad, type AP filter (Millipore). The glass fiber is impregnated with 1.0 mL of 2 percent (w/v) citric acid solution in ethanol. The Teflon[®] filter collects fine acidic particles. The nylon second filter traps nitric acid arising from the dissociation of ammonium nitrate or nitric acid collected on the Teflon[®] filter.

The citric acid-impregnated glass fiber filter retains ammoria also arising from the disassociation of ammorium nitrate collected on the Teflon[®] filter. The three filters together give an unbiased measure of atmospheric acidity. A pump unit maintains a flow of 10 Lpm, and a 7-day timer allows programmed start and end times. ADS samples may be run for 8, 12, or 24-hour durations or in cycled operation (e.g., 10 minutes on/50 minutes off for 7-day periods). Figure 1 illustrates a two-stage annular denuder system assembled, ready for testing. Figure 2 shows the field sampling box with the two-stage annular denuder and pump-timer system.

3.2 Following each run, the ADS assembly is removed from its field housing, its ends capped, and brought back to the laboratory. In the laboratory, the assembly pieces are uncoupled and capped. The denuder tubes are not extracted. Filters are unloaded from the filter pack in an ammonia free atmosphere and either directly extracted or stored in a petri-dish for later extraction. A glove-box, lined with citric-acid soaked paper, is used to maintain an ammonia-free atmosphere.

As illustrated in Figure 3, the Teflon[®] filter is extracted and analyzed for hydrogen ion, or strong acidity, by pH determination. Nitrates, captured by the Nylon[®] filter are analyzed by ion chromatography. Animonium ion collected on the citric acid-impregnated glass fiber filter is analyzed by the indophenol method using an auto-analyzer.

To extract the Teflon[®] filter, it is placed in an extraction vessel, membrane side down. The filter is wetted with 100 μ L of methanol, then extracted with 3.0 mL of extraction solution (ES). The extraction vessel is put in an ultrasonic bath for 20 minutes. The extraction solution is then decanted into a container.

3.3 Acidity determinations are made using pH measurements of 1 mL of the extracted filter solution in polystyrene vials. Filter acidities are calculated from standards made with sulfuric acid. The standards range from 0 to 150 μ g equivalent of strong acid aerosol concentration. A pH meter is used to measure the pH of the filter extract. For each batch of filter extracts, a calibration curve is calculated using the mean pH of each standard reading taken before and after the batch.

Loss of volatile nitrate species from the Teflon[®] filter may occur. These volatilized components (NH₃, NH₄NO₃, and HNO₃) are collected on the following nyloa and citric acid-impregnated backup glass fiber filters. The blank corrected nitrate concentration on the nylon filter is due to nitric acid from the dissociation of ammonium nitrate from the Teflon[®] filter. The blank corrected ammonium concentration on the citric acid impregnated glass fiber filter is due to ammonia liberated from the Teflon[®] filter. The final acidity correction is calculated as the difference of nylon filter nitrate less glass fiber filter ammonium.

4. Significance

4.1 Acid aerosols are found in the atmosphere as a result of atmospheric reactions of emissions from a variety of fossil fuel combustion sources including power plants, industrial and commercial facilities, hazardous waste storage and treatment facilities, etc. Awareness of the effects of concentrations of acid aerosols on human health and property has been documented over the past several years. The Clean Air Act Amendments of 1970 required the U.S. Environmental Protection Agency (U.S. EPA) to develop uniform national ambient air quality standards (NAAQS) for pollutants which were recognized as widespread (emitted by numerous mobile and stationary sources) and which endangered public health and welfare. Further, Section 109 of the Clean Air Act as amended, requires EPA to periodically review the NAAQS as well as the scientific information and data on which they are based. New pollutants are identified for NAAQS development if the Administrator concludes that they may reasonably be anticipated to endanger the public health and welfare.

To assist the Administrator in evaluating the need for new or revised NAAQSs, the Clean Air Act created the Clean Air Scientific Advisory Committee (CASAC). This committee's mandate is to provide the Administrator with scientific advice and research recommendations on critical areas of knowledge on new or revised NAAQSs. The Acid Aerosol Subcommittee of CASAC identified a need for a coordinated acid aerosol research program to assist the Agency in making recommendations on a new acid aerosol NAAQS. The Subcommittee recommended a research program involving characterization and exposure assessment, animal toxicity, human exposure research, and epidemiology. The foundation for any research program and potential air quality standard development is "...a measurement method, not only because the standard itself must specify the method, but equally important, because before establishing a standard the contaminant must be fully characterized and exposure measurements made to correlate with health outcomes."

4.2 The unique features of the annular denuder which separates it from other established monitoring methods are elimination of sampling artifacts due to interaction between the collected gases and particles and the preservation of the samples for subsequent analysis. These features are accomplished by removing NH₃ in the gas stream with the citric acid-coated denuder to reduce the probability of the acid aerosol captured by the Teflon[®] filter in the filter pack being neutralized to ammonium sulfate [(NH₄)₂SO₄].

5. <u>Definitions</u>

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

- 5.1 Secondary particles (or secondary aerosols) Aerosols that form in the atmosphere as a result of chemical reactions, often involving gases. A typical example is sulfate ions produced by photochemical oxidation of SO₂.
- 5.2 Aerosol A dispersion of solid or liquid particle in a gas-phase medium and a solid or liquid disperse phase. Aerosols are formed by (1) the suspension of particles due to grinding or atomization, or (2) condensation of supersaturated vapors.
- 5.3 Coarse and fine particles These two fractions are usually defined in terms of the separation diameter of a sampler. Coarse particles are those with diameters (aerodynamic) greater than 2.5 μ m and are removed by the sampler's inlet; the fine particles are those with diameters (aerodynamic) less than 2.5 μ m that are collected on the Teflon[®] filter.
- 5.4 Annular Of, rotating to, or forming a ring. In the annular denuder sampler, the annular refers to the annulus between two concentric tubes. Chemical coating applied to the interior surfaces removes gaseous pollutants which diffuse to the surface.
- 5.5 Denuder The denuder refers to the sections in which interfering gases are removed from the sample stream prior to filtration in determining fine particle $(2.5 \ \mu m)$ strong acidity.
- 5.6 Equivalent weight The combining weight, or the equivalent weight, of a compound or ion is its formula weight divided by the number of replaceable hydrogen atoms.
- 5.7 Normal solution A normal (N) solution is one that contains a gram-equivalent weight of solute in a liter of solution.

6. Apparatus

Note: The following descriptions relate to Figure 2. Most of these parts are available commercially from University Research Glassware, 118 E. Main Street, Carrboro, North Carolina, 27510, 919-942-2753. However, these items can be made by any qualified vendor. Therefore, it is not necessary that these specific items are obtained and utilized.

6.1 Sampling

- 6.1.1 Elutriator and acceleration jet (inlet) assembly Under normal sampling conditions, the elutriator or entry tube is made of either Teflon[®] coated glass or aluminum, as illustrated in Figure 4. When using glass, the accelerator jet assembly, which directs the air flow towards an impactor plate, is fixed onto the elutriator and the internal surfaces of the entire assembly are coated with Teflon[®] [Figure 4(a)]. When aluminum is used, the accelerator jet assembly is removable. The jet is made of Teflon[®] or polyethylene and the jet support is made of aluminum [Figure 4(b)]. Again, all internal surfaces are coated with Teflon[®].
- 6.1.2 Teflon[®] impactor support pin and impactor frit support tools (see Figure 5) - Made of either Teflon[®] or polyethylene and are used to aid in assembling, removing, coating and cleaning the impactor frit.
- 6.1.3 Impactor frit and coupler assembly (see Figure 6) The impactor frit is 10 mm x 3 mm and is available with a porosity range of 10-20 μ m. 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 which are located on both sides of the seat support inside the coupler.

<u>Note</u>: In situations when there are substantial high concentrations of coarse particles (>2.5 μ m), it is recommended that a Teflon[®]-coated aluminum cyclone be used in place of the acceleration jet and impactor assembly, as illustrated in Figure 2. Figure 2 illustrates the location of the cyclone with respect to the denuder, heated enclosure and meter box assembly.

6.1.4 Annular denuder - The denuder consists of two or more concentric glass tubes (see Figure 7) with an outer aluminum shell. The tubes create a 1 mm annular spacing which allows the air sample to pass through. Flow in the annular space is maintained in the laminar range and allows fine particles with diameters less than 2.5 μ m to pass through with negligible removal. The inner tube is inset 25 mm from one end of the outer tube; this end is called the flow straightener end. The other end of the inner tube is flush with the end of the outer tube. Both ends of the inner tube are sealed. In this configuration, the flow straightener end is etched to provide greater surface area for the coating. The inner glass tubes are inset 25 mm from one end of the outer Teflon[®]-coated aluminum tube to
serve as the flow straightener end. All denuder types should be equipped with thermoplastic (Bakelite) or polyethylene caps when purchased.

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

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

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

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

6.1.7 Drying manifold assembly - The manifold is made of glass and is available to accommodate as many as four drying denuders. The denuders are attached to the manifold with back-to-back Bakelite bored caps, as illustrated in Figure 8. Air is pushed through an air dryer/cleaner bottle made of 2 1/2 inch heavy wall glass which contains silica gel. The Teflon[®] tubing which connects the dryer/cleaner bottle to the drying manifold should be secured at each cap with either Teflon[®] washers or Teflon[®] washers coupled with Teflon[®] hose barbs. The air stream then passes through a fine particle filter to remove fines. Alternatively, dry compressed air from a cylinder may be used in place of the dryer/cleaner bottle assembly.

6.1.8 Filter pack assembly - The denuders are followed by a three-stage filter pack assembly containing a Teflon[®] membrane filter, a nylon membrane filter and a citric acid-impregnated glass fiber filter, as illustrated in Figure 9. The filters are supported by stainless steel porous screens and are 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[®] ring housing and sits on a Teflon[®] "O"-ring which seals the filter ring housing components to the filter housing outlet component. The Teflon[®] filter retains all the strong acidic particulate aerosols. Under certain conditions, nitric acid (HNO₂) and/or nitrate aerosol (NH₄NO₃) on the Teflon[®] filter can dissociate. The nylon back-up filter captures the volatile HNO₃, while the glass-fiber filter impregnated with citric acid, retains the NH₃. The three filters together give unbiased measures of strong acidic of atmospheric fineparticles ($< 2.5 \mu m$). The filter housing outlet component is aluminum and accommodates a polyethylene screw sleeve which seals the filter pack assembly.

<u>Note</u>: Over time and repeated compression, the Viton^{\oplus} O-rings may wear, causing poor leak checks due to inadequate sealing. The user is encouraged to replace these rings after fifteen (15) sampling events or when the filter pack assembly does not pass an adequate leak check. Other users have utilized high density polyethylene (HDPE) to prolong the life of the ring.

- 6.1.9 Teflon[®] tubing 3/8 inch diameter for distances of less than 50 ft., 1/2 inch diameter for distances greater than 50 ft. [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219 (412-787-6322)]
- 6.1.10 Tube fitting Compression fittings (Swagelok[®], Gyrolok[®] or equivalent) to connect vacuum tubing (above) to an NPT female connector or filter holder and connect vacuum tubing to fitting on differential flow controller. The fittings may be constructed of any material since they are downstream of the sampler. [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219 (412-787-6322)]
- 6.1.11 Annular denuder system (ADS) sampling box The housing box is made of a "high-impact" plastic and is thermally insulated. It is 4 feet long by 6 inches wide and 6 inches deep. The box contains a heater unit, a fan, and an air outlet located in the lid of the housing. The elutriator end of the ADS protrudes through one end of the box, while the 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, as illustrated in Figure 2.

Note: Recent studies by the Harvard School of Public Health based on a comparison of utilizing a sampling box with and without heated enclosure indicated no difference in sampled species from winter samples. It is therefore the discretion of the user to determine whether a heated sampling box is required.

- 6.1.12 Annular denuder transport case The transport case is made of formica backed with plywood and insulated. The corners are reinforced with metal. It is made to withstand shipping by truck, UPS and Federal Express. Each case is stackable and lockable and has a carrying handle. Seven total annular denuder systems can be packed in the case.
- 6.1.13 Pump/timer unit The pump/timer unit draws air through the ADS at a fixed rate of 10 L/min with a precision of ± 5 percent over the range of 25 to 250 mm Hg vacuum. A mass flow controller or a differential flow controller can be used. Typically, the flow rate is monitored with an exhaust flow rotameter. The unit includes a mechanical 7-day timer and an elapsed-time counter. A dry gas meter, when available, is placed after the pump to give a direct readout of total volume of air sampled. Otherwise, flow rate is manually measured (using a rotameter) before and after each run to calculate the air volume sampled.
- 6.1.14 Dry gas meter (DGM) The DGM should have a capacity of 10 L of gas per revolution. [NuTech Corp., 4022 Stirrup Creek Road, Suite 325, Durham, NC 27703, 919-544-8535)]
- 6.1.15 Electronic mass flow controller Capable of maintaining a constant rate of 10 L/min (±5 percent) over a sampling period of up to 24 hours and under conditions of changing temperature (5° to 43°C) and humidity. [Tylan General, Flow Division, 19220 S. Normandie Ave., Torrance, CA, 90502, 213-212-5533, Model FC-262, or equivalent]

6.2 Analysis

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

- 6.2.2 Ion chromatograph A chromatograph equipped with the appropriate anion exchange resin filled separator and suppressor columns and conductivity detector for measuring NO₃⁻ ion in solution (i.e., nylon filter extract). [Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086, (408-737-0700)]
- 6.2.3 Technicon colorimeter auto-analyzer Colorimetric 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)]
- 6.2.4 Polyethylene bottles with polyethylene screw caps 100 mL, used for storage of coating solution; and 1L, used for storing the KCl solution.
- 6.2.5 Erlenmeyer flasks 250 mL and 2 L borosilicate glass or polyethylene flasks for calibration, best source.
- 6.2.6 Graduated cylinders 5 mL, 10 mL, 100 mL, 250 mL and 1L borosilicate glass or polyethylene cylinders, best source.
- 6.2.7 Pipets Class A 5 mL and 10 mL borosilicate glass pipettes or automatic pipettes. Calibrated "to deliver," best source.
- 6.2.8 Pipet bulb Made of natural rubber. Recommended to meet OSHA requirements, best source.
- 6.2.9 Micropipettes 25 μ L, 50 μ L, and 100 μ L, calibrated "to contain," borosilicate glass micropipette, best source.
- 6.2.10 Forceps Recommended dressing forceps made of stainless steel or chrome-plated steel and without serrations. Used for handling filter.
- 6.2.11 Stopwatch Used for measuring flow rate of gas stream through DGM, best source.
- 6.2.12 Ultrasonic cleaner Used for filter extractions and parts cleaning. The ultrasonic cleaner should have temperature control capability.
 [Cole-Palmer Instrument Co., 7425 N. Oak Park Ave., Chicago, IL, 60648 (800-323-4340)]

- 6.2.13 Clean air hood (optional) Closed air hood with ammonia free air circulation. Used for Teflor[®] filter extraction for pH analysis, best source.
- 6.2.14 Glove-box Used for handling exposed filter, which is lined with citric acid impregnated paper sheets to maintain an ammonia-free atmosphere. The glove-box works best with a slight positive pressure.
- 6.2.15 Refrigerator (approximately 5°C) is required for sample storage.
- 6.2.16 Polyethylene-stoppered volumetric flasks 25 raL, used for making sulfuric acid standards.

7. Reagents and Materials

- 7.1 Teflon[®] filter Zefluor[®] (PTFE) membrane filter, 47 mm diameter, with a 2 μm pore size. The Teflon[®] filter has a coarse mesh Teflon[®] side and a fine pore membrane side. The fine pore membrane side should face the air stream. [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, Part No. PSPJ047, (800-521-1520)].
- 7.2 Teflo[®] membrane filter, 47 mm diameter, with a 2 μm pore size. This filter has a thin Tefloo[®] membrane stretched across a plastic ring. [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, Part No. R2PJO47, (800-521-1520)].
- 7.3 Nylasorb[®] filters Membrane filter, 47 mm diameter, with a 1 μ m pore size. These filters are specially prepared and batch analyzed for low NO₃⁻ background levels. If other brands of nylon membrane filters are used, they should be batch analyzed to ensure low and replicable levels of NO₃⁻. [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106, Part No. P5PJ047, (800-521-1520)]
- 7.4 Glass fiber filter Glass fiber filter, 47 mm diameter, with a 2 μ m pore size. ["AP" filters by Millipore, Part No. AP4004705] or Whatman 41, 47 mm ashless filter paper [Whatman Part No. 1441047EA]
- 7.5 Filter extract storage vials 100 mL polyethylene vials (Nalgene or equivalent).
- 7.6 Labels Adhesive, for sample vials, best source.
- 7.7 Parafilm Used for covering flasks and pH cups during pH analysis, best source.
- 7.8 Kinwipes[®] and Kay-dry towels Used for cleaning sampling apparatus and analysis equipment, best source.

- 7.9 Stoppers Polyethylene, best source.
- 7.10 Sodium carbonate (Na₂CO₃) ACS reagent grade, best source.
- 7.11 Citric acid [monohydrate HOC (CH₂CO) OH]₂COOH : H₂O) ACS reagent grade, best source.
- 7.12 Methanol (CH₃OH) ACS reagent grade, best source.
- 7.13 Sulfuric acid (H_2SO_4) ACS reagent grade, 1.000 N solution, best source.
- 7.14 Distilled deionized water (DDW) ASTM Type I water.
- 7.15 pH buffers Standard buffers, 4.00 and 7.00, for internal calibration of pH meter, best source.
- 7.16 Silica gel ACS reagent grade (indicating type), best source.
- 7.17 Gloves Polyethylene disposable. Used for impactor frit assembly and filter assembly, best source.
- 7.18 Dow Corning high temperature vacuum oil Dow Corning 660 oil used for impactor frit coating solution, best source.
- 7.19 Zero air A supply of compressed clean air, free from particles and ammonia. The supply may be either from a commercial cylinder or generated on site, best source.
- 7.20 BRIJ-35 Composed of 0.1 percent of BRIJ-35 in DI water. [Fisher Scientific, 711 Forbes Ave., Pittsburgh, PA, 15129, 412-787-6322]
- 7.21 IC eluent solution For extracting filters. This 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, then 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 DDW.
- 7.22 Perchloric Acid (HClO₄) 60 to 62 percent, in water, best source.
- 7.23 Toluene (C_7H_8) ACS reagent grade, best source.
- 7.24 Potassium Chloride (KCl) ACS reagent grade, best source.
- 7.25 Acetone (C_3H_60) ACS reagent grade, best source.

8. Preparation of Impactor Frit and Denuder Coating

- 8.1 Impactor frit coating solution preparation Weigh 1 g of silicone oil (Dow Corning high temperature 560 oil) and place in a 100 mL polyethylene storage vial. Add 100 mL of toluene. Mix thoroughly, close container, and store at room temperature. (WARNING - FLAMMABLE LIQUID).
- 8.2 Annular denuder citric acid coating solution Clean a 100 mL polyethylene storage vial and let dry at room temperature. Measure 50 mL of methanol (WARNING TOXIC, FLAMMABLE LIQUID) with a graduated cylinder and pour into vial. Weigh 0.5 g of citric acid and add to vial. Mix thoroughly; store, covered at room temperature.
- 8.3 Annular denuder Na₂CO₃ coating solution Clean a 100 mL polyethylene storage vial and let dry at room temperature. Measure 50 mL of methanol (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 glyceroi and add to the DDW. Weigh 1 g of Na₂CO₃ and add to the vial. Mix thoroughly, solution may fizz; wait for fizzing to stop before sealing vial. Store at room temperature.
- 8.4 Impactor frit extraction solution preparation Add 100 mL of IC eluent to a clean polyethylene storage container. Pipette 5 mL of methanol into container. Mix thoroughly. Store, covered at room temperature.

9. Impactor Frit Installation

- 9.1 Impactor frit installation The impactor-coupler assembly shown in Figure 4 is comprised 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 illustrated in Figure 5. The impactor frit is pressed gently, but firmly, into the seat of the impactor housing with a clean gloved finger. The impactor should fit into the housing so that it does not protrude above the seat. During sampling, particles accumulate on the impactor's plate surface. After each sampling event, the assembly must be cleaned to prevent the build-up of contaminants which may lead to loss of key acidic species being collected by the ADS. Cleaning involves immersing the elutriator, coupler-impactor, and frit in 0.1 percent BRU-35 cleaning solution and ultrasonicating for about 5 minutes. Rinse thoroughly with DDW for additional 5 minutes. Rinse and dry with zero air or in dust-fee environment and store with ends plugged and capped.
- 9.2 Impactor frit coating With the Teflon[®] impactor seat support pin which fits into the first denuder (see Figure 5) or the impactor frit in the impactor seat coupler

(see Figure 6), pipette 50 μ L (about two drops) of the toluene-660 oil coating solution onto the impactor frit surface and allow to dry in dust free environment at room temperature. Cap both sides of the coupler impactor or denuder-impactor until use.

<u>Note</u>: It is important to have only the minimum amount of oil on the frit because any excess will be blown off during sampling and will contaminate the surfaces of the first denuder.

10. Filter Preparation and Assembly

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

- 10.1 Citric Acid Coated Filter
 - 10.1.1 Mix 2 percent (w/v) citric acid in ethanol.
 - 10.1.2 Load the glass-fiber filter into half a petri-dish. Pipet 1.0 mL of the citric acid solution onto the filter. Dry under vacuum in a desiccator.
 - 10.1.3 Cap the petri-dish and seal with parafilm. Store in NH_3 -free glove-box or chamber.
 - 10.1.4 For Whatman 41, 47 mm, ashless filter paper, wash filters with 1 L of 10 percent HCl followed by 1 L of distilled deionized water. Dry under vacuum in a desiccator. Coat filters with 0.5 mL of 0.02 M citric acid in a glycerol/methanol (1/100) solution and dry in a vacuum desiccator. After coating the filter, store in an acid-wash petri-dish. Keep in NH₃-free glove-box until use.
- 10.2 Filter Pack Assembly

<u>Note</u>: All loading and unloading of the filter pack must be performed in the NH_3 -free glove-box. Generally, it is most convenient to reload the filter pack at the same time as unloading.

10.2.1 With clean gloves, disassemble the filter pack (see Figure 9) by unscrewing the large outer Teflon[®] collar (sleeve) from the aluminum filter housing outlet component.

<u>Note</u>: It is necessary to remove the polyethylene cap first. Lay the pieces out on clean Kimwipes[®]. Insert black viton "O"-rings (see Figure 9).

- 10.2.2 Lay a clean Teflon[®] filter ring housing, with its large opening face-up, on a clean Kinwipe[®]. Place a clean stainless steel screer in the filter ring housing.
- 10.2.3 Using a clean (wipe with clean Kimwipe[®] filters) forceps, load the citric acić-impregnateć glass-fiber or Whatman 41 filter onto the screen of the lowest stage.
- 10.2.4 Place a second stainless steel screen in the filter housing.
- 10.2.5 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 forms a "sandwich" with the nylon filter held between the two filter ring housing.
- 10.2.6 Place another clean screen on the second filter ring housing. Using clean filter forceps, place a Teflon[®] filter on the screen.

<u>Note</u>: If a Zefluor^{\oplus} Teflon^{\oplus} filter is used, be sure to place the membrane side, not the coarse side, toward the air stream. By observing the filter in the light, one can differentiate between the coarse and membrane side.

- 10.2.7 Place the Teflon[®] filter housing inlet component (see Figure 9) on top of the Teflon[®] filter. This 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 annular denuder through a thermoplastic coupler. Be careful not to twist the filter pack components, or damage will occur to the filters.
- 10.2.8 Lay the aluminum filter housing outlet component, with its large opening face-up, on a clean Kimwipe[®]. Insert a black viton "O"-ring in the aluminum filter base.
- 10.2.9 Insert the filter ring sandwiches with the filter housing inlet component extending upward, on the viton "O"-ring in the aluminum filter base. Place the larger outer Teflon[®] sleeve over the filter sandwich and screw onto the aluminum filter base. DO NOT OVERTIGHTEN!

- 10.2.10 Install the "quick-release" plug into the filter outlet component. DO NOT OVERTIGHTEN!
- 10.2.11 Install the polyethylene cap onto the filter inlet component and the orange dust cover onto the quick release plug ready to attach denuder. The filter pack should be sealed tight before it is removed from the glove-box.

11. Annular Denuder System Preparation

All new annular denuder parts obtained from suppliers should be cleaned by placing them in a dilute BRIJ-35 solution in an ultrasonic cleaner for about 30 minutes. The parts should then be thoroughly rinsed in DDW, then rinsed with acetone, and allowed to dry to room temperature. Store with end caps in place.

11.1 Coating Procedure

- 11.1.1 Cap one end of a denuder using Caplugs (which has the inner tube flush to the outer tube) and set the denuder upright on the capped end. For the denuder with flow-straighteners at both ends, either end may be capped. Measure 10 mL of the citric acid solution and pour into one of the denuders. Then add sodium carbonate coating solution to the other capped denuder.
- 11.1.2 Cap the open end of the denuders and, holding them horizontally, rotate the denuders to distribute the coating solution evenly, wetting all surfaces.
- 11.1.3 Remove cap and decant excess coating solution into separate 100 mL polyethylene bottle.
- 11.1.4 For the impactor denuder, the coating is performed without the impactor pin in place.
- 11.2 Drying Procedure

<u>Note</u>: As denuders dry, they change from translucent to a frosted appearance. Denuders are dry when they become uniformly frosted.

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

- 11.2.1 Assemble the drying train and manifold as illustrated in Figure 8.
 Drying train and manifold clean air flow should be adjusted to 2 to 3
 L/min through each denuder. Close toggle valve controlling clean air flow through manifold before attaching denuders.
- 11.2.2 Attach the flow-straightener end of the denuders to the drying manifold ports (see Figure 8).
- 11.2.3 Open toggle valve and allow clean air to flow through the denuder tubes for 5 minutes.

<u>Caution</u>: Excess air flow will cause uneven coating to the tube walls.

- 11.2.4 Close toggle valve, and reverse ends of the denuders attached to the manifold. Start clean air flow again.
- 11.2.5 When an even frosted appearance is achieved, remove denuders from manifold, cap both ends with clean caps and store until ready for use. Turn off air to drying manifold. Affix label indicating coating date on denuders.
- 11.3 Denuder System Assembly

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

The annular denuder system (ADS) assembly consists of:

- an inlet nozzle/impactor or cyclone assembly;
- two glass annular denuder tubes; and
- a 3-stage filter assembly.

The following procedure involves an inlet nozzle/impactor assembly.

- 11.3.1 Lay the ADS pieces on a clean surface (i.e., Kimwipes[®]).
- 11.3.2 Remove the end caps from the denuders. Denuder 1 is coated with Na₂CO₃ and may or may not hold the impactor frit pin support. If the first denuder is equipped with the impacted frit pin support, gently

insert the impactor support pin and coated frit assembly into the denuder-pin support.

Note: DO NOT TIGHTEN!

- 11.3.3 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon[®] clad "O"-ring inside the coupler, if needed.
- 11.3.4 Remove the end caps of the second denuder (citric acid coated). Attach the end with the flow-straightener section to the first denuder-coupler assembly.
- 11.3.5 Attach a thermoplastic coupler to the opposite denuder end. Place a Teflon[®] clad "O"-ring inside the coupler, if needed.
- 11.3.6 The filter pack has been previously loaded with (a) a Teflon[®] filter,
 (b) a nylon filter, and (c) a glass-fiber filter (previously impregnated with citric acid) or Whatman 41 filter coated with citric acid in glycerol/methanol solution. The components are assembled with plastic couplers.
- 11.3.7 Attach the filter pack inlet to the denuder coupler assembly.
- 11.3.8 When using the first denuder equipped with the impactor frit-pin support, a thermoplastic coupler with a Teflon[®] clad "O"-ring is used to attack the inlet assembly. ATTACH, BUT DO NOT TIGHTEN!
- 11.3.9 Attach the elutriator-acceleration jet assembly to the first denudercoupler assembly. Tighten very gently - DO NOT OVERTIGHTEN or breakage will result.
- 11.3.10 Tighten the remaining couplers very gently do not overtighten or breakage will result.
- 11.3.11 Cap elutriator with orange dust cover until used. Attach "quick-release" tube to outlet of filter pack assembly.
- 11.4 Laboratory Leak-Check of ADS

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

11.4.1 Remove the orange dust cap from the impactor opening. Attach the "quick-release" outlet of the filter assembly to a pump module. Turn

on the pump. Be certain that flow through the ADS occurs by checking the rotameter.

- 11.4.2 Briefly cap the elutriator with the orange dust cap. The flow, as indicated on the rotameter, should drop to zero if no leaks exist.
- 11.4.3 Disconnect the pump from the ADS at the "quick-release" plug. Cap the "quick-release" plug with an orange dust cover. Turn off the pump. REMEMBER - Never overtighten joints or breakage will result. If the joints can not be sealed with gentle tightening, then the Teflon[®] "O"-rings are worn or defective and must be replaced.
- 11.4.4 Place the assembled sampler in its field-to-lab carrying case for transport to the field.

<u>Note</u>: It is recommended that the ADS joints be loosened slightly when extreme temperature changes are incurred during transportation. This will prevent unnecessary breakage or distortion of the ADS components. Remember to allow the system to adjust to the outdoor air temperature before tightening the joints and checking for leaks.

- 11.4.5 Before proceeding to the field, review the following checklist:
 - Run IDs on the Field Test Data Sheet (see Figure 10) should match labels affixed to the ADS components and filter assembly;
 - Recessed ends of the denuder should face the inlet;
 - ADS ends are capped; and
 - Transport case is secured firmly containing the ADS along with chain-of-custody and Field Test Data Sheet.

12. Sampling

- 12.1 Placement of Denuder System
 - 12.1.1 The placement of the 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 following EPA document:
 - U.S. EPA, May 1987. Ambient Monitoring Guidelines for Prevention of Significant Deterioration (PSD), EPA-450/4-87-007, Office of Air Quality Planning and Standards, Research Triangle Park, N.C. 27711.

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.

- 12.1.2 A summary of key factors that should be considered as part of the placement of an air quality monitoring station containing an ADS are:
 - Vertical placement above ground;
 - Horizontal spacing from obstructions and obstacles;
 - Unrestricted air flow; and
 - Spacing from roads.

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

- 12.1.3 A summary of key criteria associated with these siting factors for air monitoring stations is included in Table 1.0. The information included in the table should be used 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, the occurrence of wooded areas around a site would make the siting very difficult. The use of the information in Table 1.0, coupled with a balanced evaluation by an experienced air quality and meteorology specialist, is highly recommended.
- 12.1.4 In general, for a site with no major obstruction and obstacles, the air sampler intake should be about 2-3 meters 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 3000 vehicles per day, the intake should be between 5 and 25 meters from the edge of the nearest traffic lane. It should also be 15 meters aboveground for a distance of 5 meters from the nearest traffic lane and 2 meters aboveground for a distance of 25 meters from the nearest traffic lane. For a roadway supporting less than 3000 vehicles per day, the intake should be placed at a distance greater than 5 meters

from the edge of the nearest traffic lane and at a height of 2-15 meters aboveground.

12.2 Start-up

- 12.2.1 Remove the ADS from its field-to-lab carrying case and load into the field sampling box. Place the assembly in the box with the impactor extended outside the case. The ADS field sampling box is insulated and configured to hold the ADS without allowing movement. Chrome plated spring clips holds 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 filter to tear). When sampling, the ADS should be kept 1°C above the outdoor temperature to prevent condensation.
- 12.2.2 Allow the pump to warm up for ~ 5 minutes prior to testing.
- 12.2.3 To check the Heat/Cool cycles, flip one switch from "AUTO" to "MANUAL" and the other between "COOL" and "HEAT." Check to insure that the fan and heater (i.e., light bulb) work, respectively.
- 12.2.4 With the elutriator still capped, turn on the pump with the switch on the timer. The rotameter should indicate zero flow. Run leak check for 5-10 seconds, then turn off pump and remove elutriator cap. Record leak rate on Field Test Data Sheet (see Figure 10). If there is a flow, refer to Section 12.4 for corrective action for leak test failure. The Field Test Data Sheet is used to keep track of the denuder tube, filter and impactors, as to when and by whom they are prepared, assembled, extracted and data input as well as to record the installation data and time, run date, sampling period, pump flow rates, start and end times, and other data relevant to each run.
- 12.2.5 Attach a DGM output to the inlet of the annular denuder system. Turn on pump. Record start time on Field Test Data Sheet. Using a stopwatch, record the time for 20.0 L to pass through the DGM. Record the DGM temperature and the absolute pressure of the DGM.

12.2.6 Calculate the flow rate as follows:

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

where:

- Q_{std} = flow rate corrected to standard conditions, 25°C and 760 mm Hg, L/min
 - V = volume of gas pulled through denuder system, 20 L
 - T = time required to pull 20 L of gas through denuder system, minutes
 - $P_b = barometric pressure, mm Hg$
- P_{std} = standard barometric pressure, 760 mm Hg
- T_{std} = standard temperature, 298°K
- T_m = temperature of dry gas meter, °K(= °C + 273)
- $F_c = dry gas meter correction factor, dimensionless$
- 12.2.7 If the calculated flow rate is not between 9.5 and 10.5 L/min, then readjust the flow rate until the rate is in the above range. Stop the pump.
- 12.2.8 Record the flow rate on Field Test Data Sheet.
- 12.2.9 Remove DGM connection tubing from elutriator inlet. With all information correctly on the Field Test Data Sheet, start the pump and begin sampling.
- 12.2.10 Sample for pre-set period.
- 12.3 Sample Shutdown
 - 12.3.1 Attach DGM connection tubing to the elutriator inlet with pump still running. Measure flow rate. Record calculated flow rate, temperature, and pressure on Field Test Data Sheet.
 - 12.3.2 Turn off the pump. Record time and elapsed time meter reading on Field Test Data Sheet. Remove DGM connection tubing from elutriator inlet. Remove ADS from the sampling box, cap the ends, and place the

ADS in field-to-lab carrying case for transport to lab. Secure the latches on the transport case. Be careful not to stress the ADS during the transfer or breakage will result.

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

- 12.3.3 Each test run generates three samples for determination. These are analyzed by methods appropriate for the chemical species under quantifications: (a) ion chromatograph for NO₃⁻, (b) indophenol method using an auto-analyzer for NH₄⁺, and (c) pH determination for strong acidity or "H⁺".
- 12.4 Corrective Action for Leak Test Failure

<u>Note</u>: These steps should be followed when failure occurs during testing at the laboratory before transport to the field and in the field before sampling.

- 12.4.1 Sampler leaks Note the problem on the Field Test Data Sheet. Check assembly of ADS components. Replace gaskets. Check for proper seating of decuder surfaces. Replace any defective parts.
- 12.4.2 Cracked or chipped denuder or elutriator assembly Note problem on Field Test Data Sheet. Discard defective pieces. Do not try to extract cracked pieces.

<u>Warning</u>: Use caution when disassembling cracked glassware. Pieces may shatter and cause severe cuts. Wear protective clothing.

- 12.4.3 Flow rate disagreement Note problem on Field Test Data Sheet. Check vacuum gauge on flow module. If a high vacuum exists then the sampler has become blocked. This may be due to dust or smoke particles clogging the filter or to obstructions in the system or tubing. Check flow module. Repair as needed.
- 12.4.4 Inadequate flow rate Note problem on Field Test Data Sheet. Check rotameter on flow controller. If adequate flow is shown here, then a leak exists between the controller and the DGM. If no flow is shown on rotameter, then check vacuum gauge on controller. If no vacuum exists, then pump needs repair. If a high vacuum is shown, then an obstruction exists in the system. Check to see that the paper filter dividers were not accidentally installed with the filter in the filter assembly. Check tubing for kinks.

13. ADS Disassembly

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

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

- 13.2 Decouple the elutriator-jet assembly from the first denuder-impactor-coupler assembly.
- 13.3 The impactor assembly and the denuders <u>will not</u> be extracted. However, each run should begin with a clean impactor and charged denuder.
- 13.4 Label three (3) separate clean 100 mL polyethylene bottle (extraction vials) with the sampler ID number and filter type (i.e., Teflon[®] or Nylasorb[®], as appropriate) for each of the filters.
- 13.5 The handling of the exposed Teflon[®] filter requires protection from contamination with NH₃, which would rapidly neutralize aerosol acidity on the filter and bias the sample results. In order to ensure ammonia-free air occupies the glove-box, a positive pressure is maintained by blowing air through a PVC tube (4 inch O.D.) filled with glass-wool dosed with citric acid before entering the manifold which enables uniform distribution of air from top of the glovebox. Flow the ammonia-free air for five minutes before retrieving the filter. A citric acid soaked filter paper is also placed on the bottom to deplete ammonia while unused. Disassemble the filter assembly in the clean, ammonia-free glove-box. Clean all glove-box surfaces and utensils with methanol. Wearing clean gloves and using clean filter forceps, remove the filters and place each in 100 mL bottles (extraction vials) separately, with the exposed filter surface facing downward. Label the bottles with appropriate information.

Note: Be careful to place the filters in the properly labeled bottles.

14. Extraction Procedure

- 14.1 Samples should be analyzed as soon after collection as possible. It is imperative that the solutions and extraction procedures are prepared and performed on the day of pH analysis. Keep samples in a refrigerator until extracted and analyzed.
- 14.2 Samples should not be extracted until the day of analysis; however, if samples are extracted and then it is not possible to analyze them that day, they should be refrigerated. Allow the samples to return to room temperature before analysis.

- 14.3 It is imperative that the same extract solution (ES) 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, the working standards, and in extracting the Teflon[®] filters.
- 14.4 Handling and extraction must take place in an ammonia-free glove box. 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. 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.

14.5 Teflon[®] filter extraction

<u>Note</u>: Teflon[®] is not wetted by water, therefore, the filter will float on top of an aqueous solution. The use of alcohol aids wetting. Also, all types of Teflon[®] curl to some extent. It is the analyst's responsibility to ensure the extraction solution makes complete contact with the particles deposited on the Teflon[®] filter during extraction. It may be necessary to use a clean plastic (Teflon[®] or polyethylene) rod or tubing stub to hold the filter in better contact with the fluid during extraction.

- 14.5.1 Allow the glove-box to be flushed with ammonia-free air for at least 5 minutes before proceeding. All of the hood surfaces and extraction utensils must be cleaned with a Kimwipe[®] moistened with ethanol.
- 14.5.2 Process the filters in the same order in which they will be analyzed.
- 14.5.3 Remove the extraction vial from the refrigerator. Allow the contents to reach room temperature before proceeding. Using forceps and gloved hands, lift the filter from the extraction vial. Holding the filter over the extraction vial, and using an automatic pipet, apply $200 \pm 5 \,\mu$ L of methanol to the filter. Add the methanol slowly to ensure that all portions of the membrane are wet with methanol. Immerse the filter in the methanol solution. Tap the forceps against the inside of the vial to remove liquid. Tightly replace cap.
- 14.5.4 As soon as the methanol has wet the entire surface of the filter, deliver 6.00 mL of ES solution into the vial. Cap the vial.
- 14.5.5 Put a batch of vials into the ultrasonic bath and sonicate for a total of 20 minutes, rotating the position of the vials 90° every 5 minutes.

- 14.6 Nylon filter extraction
 - 14.6.1 Transfer the nylon filter (sampled surface facing up) into a sample vial. Pipet 10 mL of IC eluent into the appropriately labeled filter vial or bottle with caps.

<u>Note</u>: 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.

- 14.6.2 Replace the bottle's cap and put in an ultrasonic bath for 30 minutes.
- 14.6.3 Store the bottle in a clean (i.e., pollutant free) refrigerator at 5°C in the dark until analysis.
- 14.7 Glass-fiber Filter Extraction
 - 14.7.1 Transfer glass-fiber filter (sampled surface facing up) into a sample vial.
 - 14.7.2 Pipet 10 mL of DDW 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.

- 14.7.3 Replace the bottle's cap and put in an ultrasonic bath for 30 minutes.
- 14.7.4 Store the bottle in a clean (i.e., pollution free) refrigerator at 5°C in the dark until analysis.
- 14.8 Aliquot preparation
 - 14.8.1 When ready for pH analysis, the extracts are prepared in the order of pH measurement. Inside the glove-box, remove the caps from extraction vials. Wipe off any drops which may leak onto the outside of the vial.
 - 14.8.2 Using gloved hands and a 1 mL automatic pipet, transfer 1 mL of the sample extract to each of two correspondingly labeled 2 mL vials, one vial labeled A and the other vial labeled A1.

<u>Note</u>: The first 2 mL vial for each extract has the same letter (i.e., A, B, C etc.) as the second mL vial, except a one is added (A1, B1, C1 etc.). This is the same system used with the working standards.

- 14.8.3 After transferring the extracts to the 2 mL vials, recap the 4 mL extract vial. Store at 5°C in a refrigerator for future analysis, if applicable.
- 14.8.4 Proceed immediately with pH analysis.

15. pH Analysis

15.1 Standard and Reagent Preparation

15.1.1 Standard H₂SO₄ Solution, 1.000 N

<u>Note</u>: Each of the standard H_2SO_4 stock solutions must be prepared fresh the day of pH analysis.

15.1.1.1 Label seven 25 mL polyethylene stoppered volumetric flasks. Also, label each flask with the volume of $1.000 \text{ N H}_2\text{SO}_4$ solution indicated in the following table:

Standard H ₂ SO ₄ flask	Volume of 1.000 N H_2SO_4 added to each flask, (μ L)	Working standard concentration, 10^{-3} N H ₂ SO ₄	Equivalent strong acid mass collected on filter (C_{Eq}), μg^{a}	Approximate pH
1	0	0	0	4.09
2	25	1	4.90	4.01
3	50	2	9.80	3.95
4	100	4	19.60	3.84
5	200	8	39.20	3.68
6	400	16	78.40	3.48
7	800	32	156.8	3.23

^aBased on 3.1 mL extraction volume.

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

15.1.2 2 M Potassium Chloride (KCl) Solution

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

- 15.1.2.2 Add about 700 mL of DDW water to the flask. Swirl the solution until the KCl is completely dissolved.
- 15.1.2.3 Pour this mixture into a 1 L graduated cylinder. Rinse the flask with a small amount of DDW water and transfer the rinse into the cylinder. Fill the cylinder to the 1 L mark.
- 15.1.2.4 Pour the solution from the cylinder into the 1 L polyethylene bottle. Cap and shake the bottle to mix well. Mark the bottle with date of preparation.
- 15.1.3 0.100 N Perchloric Acid (HClO₄) Solution
 - 15.1.3.1 Fill a 1 L graduated cylinder about half full with DDW. Transfer 10 \pm 0.1 mL of 60-62 percent HCl0₄ into the 1 L cylinder with a 10 mL pipet.
 - 15.1.3.2 Fill the cylinder to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.
 - 15.1.3.3 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.

15.1.4 0.010 N HClO₄ Solution

- 15.1.4.1 Fill a 1 L graduated cylinder about 1/2 full with DDW.
- 15.1.4.2 Measure 100 mL of the 0.1 N HC1O₄ solution with the 100 mL graduated cylinder. Add this to the 1 L cylinder.
- 15.1.4.3 Fill the 1 L cylinder with DDW to the 1 L mark. Pour the solution into the 1 L polyethylene bottle.
- 15.1.4.4 Cap and shake the bottle to mix well. Mark the date of preparation on the bottle.
- 15.1.5 Extraction Solution (ES)
 - Note: This solution must be prepared fresh on the day of pH analysis.
 - 15.1.5.1 Measure 20 ± 0.5 mL of 2 M KCl into 2 L erlenmeyer flask.

- 15.1.5.2 Using a 5 mL calibrated automatic pipet, add 10 ± 0.1 mL of 0.01 N perchloric acid (HClO₄), to the flask. Add 980 \pm 10 mL of DDW to the flask.
- 15.1.5.3 Mix well and cover with parafilm until ready for use.
- 15.1.6 Extraction Solution with methanol (EA Solution)
 - 15.1.6.1 Measure 150 ± 2 mL of ES (prepared in Section 15.1.5) into a 250 mL graduated cylinder. Transfer to a 250 mL erlenmeyer flask.
 - 15.1.6.2 Using a 5 mL graduated cylinder, add 5 ± 0.1 mL of methanol (this must be from the same fresh bottle of methanol that was used to prepare the standards in Section 15.1.1) to the flask.
 - 15.1.6.3 Mix well and cover with parafilm until ready for use.
 - 15.1.6.4 pH of the EA solution should be 4.09 ± 0.04 . If not, the solution must be reprepared.
- 15.1.7 Working Standard Test Solutions
 - 15.1.7.1 Place fourteen-4 mL polystyrene sample vials (as used with Technicon Auto-analyzer II system) labeled 1A, 1B, 2A 2B...7A, 7B into support racks. Using the calibrated dispensing pipet bottle, add 3 mL of ES solution to each 4 mL vial.
 - 15.1.7.2 Using the displacement pipet, add 50 μ L of methanol to each vial. Pour about 3 mL of Standard Flask #1 H₂SO_d standard (see Section 16.1.1) into a labeled 4 mL vial.
 - 15.1.7.3 Immediately pipet 50 μ L of this standard into the 4 mL vials labeled 1A and 1B containing the ES solution and methanol.
 - <u>Note</u>: This transfer must be done without delay to prevent the standard concentration from increasing significantly due to evaporation of the methanol solvent.
 - 15.1.7.4 Repeat the procedure for each of the other 6 standards. If there is a delay of more than 5 minutes between the

preparation of these mixtures and the next step, put caps on the 4 mL vials.

Note: There should be fourteen vials, each containing 3 mL of ES solution, 50 μ L of methanol, and 50 μ L of Standard H₂SO₄ solution (see Section 16.1.1). Two aliquots from each vial (1A, 1B, 2A, 2B, 3A, 3B,...7A, 7B) will be analyzed.

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

15.2 Calibration of pH Meter

The pH meter requires temperature calibration whenever a new electrode is used. Use the manufacturer's procedure in the instrument manual. This calibration should be repeated every three months while not in use. The pH meter is left with the power cord plugged into the AC outlet, the mode control knob is left in the standby position, and the combination electrode is immersed in a 4 M KCl solution (a slit rubber stopper seals the bottle with the electrode in it). Keep a record of the temperature calibrations in a lab notebook.

15.3 Pre-analysis Calibration

<u>Note</u>: Figure 11 outlines the steps for proper calibration and set-up for analysis of the Teflon[®] filter sample for pH determination. Analysis should be performed at room temperature.

- 15.3.1 Use a pH Analytical Laboratory Log Form (see Figure 12) to record all data.
- 15.3.2 Fill three 4 mL vials with pH 7 buffer. Withdraw the electrode from the 4 M KCl bottle and wipe the tip gently with a Kimwipe[®] to remove the bulk of the solution. Rinse the electrode with one vial of pH 7 buffer. Do not test pH of the first vial.

- 15.3.3 Immerse the electrode in the second vial of the pH 7 buffer. Use a small bottle or other support to hold the vial up to the electrode while waiting for the meter reading to equilibrate.
- 15.3.4 Test the pH by turning to the pH mode of the meter. Allow the reading to stabilize for at least 30 seconds. Record the result on the Analytical Laboratory Log Form for pH 7, entry 2.
- 15.3.5 Turn to standby mode, and then test the last vial of pH 7 buffer. Record the results on the log form for pH 7, entry 3. If the pH value for the 2nd cup is not 7.00 ± 0.01 , adjust the "calib." knob to obtain a reading of 7.00. Note this adjustment on the log form.
- 15.3.6 Fill three 4 mL vials with pH 4 buffer. With the meter in the standby mode, remove the cup containing pH 7 buffer, wipe the tip of the electrode gently with a Kimwipe[®], and then rinse the electrode with the first vial of pH 4 buffer. Do not record pH.
- 15.3.7 Test the next two vials of pH 4 buffer as above, recording the results on the log form. If the pH value for the third vial is not 4.00 ± 0.01 , adjust the "slope" knob to get a reading of 4.00. If the value for the second vial was not 4.00 ± 0.01 , the calibrations at pH 7 and at pH 4 must both be repeated.
- 15.4 pH Test of HClO₄ Solutions

<u>Note</u>: The 0.01 N HClO₄ solution is used to prepare the ES solution which, in turn, is used to prepare the EA solution. It is imperative that the pH value for the EA solution be 4.09 ± 0.04 . If this pH value is not achieved, then one or more of the HClO₄ solutions must be reprepared.

- 15.4.1 Finish the calibration of the pH meter with pH 4 buffer.
- 15.4.2 Rinse the pH electrode with DDW. Wipe the tip of the electrode with a Kimwipe[®].
- 15.4.3 Fill three 4 mL vials with EA solution. Measure the pH of the test EA solution in similar fashion to the buffer solutions. The values must be 4.09 ± 0.04 .
- 15.4.4 If the above pH values are not achieved, follow Section 15.1.6 to reprepare the solutions. Test the pH of the new solutions. Repeat as necessary to obtain an average pH of 4.09 ± 0.04 .

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

<u>Note:</u> Immediately following the EA analysis, start testing the working standards.

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

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

- 15.5.2 After testing the pH of vial 1A1, test vial 1A2. Record the results of . both on the Analytical Laboratory Log Form.
- 15.5.3 With the meter in the stand-by mode, remove vial 1A2, wipe the electrode with a Kimwipe[®] and test one 2 mL vial of EA solution.
- 15.5.4 Test a 2nd vial of EA solution; record the results on the log form. Discard the 1st vial of EA, but retain the 2nd vial to be used as the 1st vial for the next EA test.
- 15.5.5 Mean pH value for the EA solutions should be 4.09 ± 0.04 . If the above pH values are not achieved, follow Section 15.1.6 to reprepare the EA solution. Retest. If still outside range, investigate problem with probe, have Laboratory Manager review previous recorded pH data for samples and EA solutions to determine validity of measurements.
- 15.5.6 Continue testing the remainder of the working standards, 1B1, 1B2, 2A1, 2A2, 2B1, 2B2...7B1, 7B2. Remember that the electrode tip is wiped both before and after each pair of test solutions, but not in between two vials of the same sample.

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

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

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

16. Ion Chromatography Analysis

Ion Chromatography is a method used to determine anion concentrations (NO₃⁻) employing liquid chromatography with conductivity or UV absorbance detection.

16.1 Standard Preparation

<u>Special Precaution</u>: Storage of these solutions should be no longer than 1 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 105°C in a vacuum oven prior to preparing the standard solutions. Any yellowish discoloration of the dried crystals indicated decomposition and crystals should be discarded.

- 16.1.1 Petassium Nitrate Stock Solution
 - 16.1.1.1 Dry KNO₂ crystals at 105°C for 2 hours.
 - 16.1.1.2 In a clean, calibrated, 1 L flask, add 500 mL of DDW.
 - 16.1.1.3 On a weighing paper, weight out 0.8158 g of the dried KNO₃.
 - 16.1.1.4 Add the dried crystals to the 500 mL of DDW. Dilute to mark with DDW.
 - 16.1.1.5 This stock solution contains 1 mg/mL of NO_3^- .

16.1.2 Nitrate Working Standards

- 16.1.2.1 Make the standard series in 100 mL volumetric flask.
- 16.1.2.2 Add the following amount of stock solution and fill to the mark with DDW, as illustrated in the following table.

Flask ID	Stock Solution Added, mL	NO ₃ ⁻ Concentration, μ g/mL,
F1	0.25	2.5
F2	0.50	5.0
F3	1.00	10.0
F4	2.00	20.0
F5	5.00	50.0
F6	10.00	100.0

16.1.3 Storage Life

- 16.1.3.1 The stock solution $(5 \times 10^{-3} \text{ equiv./L of NO}_3^-)$ should be kept in an amber bottle in the refrigerator and may be stored up to 6 months.
- 16.1.3.2 The nitrate working standards must be made fresh within 2 weeks of its use.
- 16.2 Reagent Preparation

Note: Storage of these reagents should be no longer than one week.

16.2.1 Anion eluent - The anion eluent is a solution of $1.8 \ \mu M \ Na_2 CO_3$ and $1.7 \ \mu M \ NaHCO_3$. A concentration solution can be prepared and diluted as needed.

Note: See Anion storage solution.

16.2.1.1 Concentrated Na₂CO₃ solution (0.36 M) - Weigh out 38.156 g of Na₂CO₃ (MW = 105.99). Dissolve into 1 L of DDW. Store in refrigerator until ready to dilute.

- 16.2.1.2 Concentrated NaHCO₃ solution (0.34 M) Weight cut
 28.564 g cf NaHCO₃ (MW = 84.01). Dissolve into 1 of DDW. Store in refrigerator until ready to dilute.
- 16.2.1.3 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).
- 16.2.2 Anion regenerant The regenerant is a C.C25 N H₂SO₄ 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 (3L). Slowly add the acid to the regenerant reservoir. Bring to the mark with DDW (4 L).

Note: Protective clothing and eye protection should be utilized.

- 16.2.3 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.
- 16.3 Sample Preparation
 - 16.3.1 Mark the auto sampler vials with the appropriate identification numbers. Place the vials in an (IC) autosampler tray.
 - 16.3.2 Using clean, calibrated 0.5 mL pipets transfer the remainder of the nylon filter extract from the extraction vial to a clean disposable 0.5 mL (IC) autosampler (polyethylene) vial. Fill the autosampler vial up to the line on the side.

Note: If refrigerated, the contents of the 4 mL extraction vial must be vortex-mixed prior to transfer to the autosampler vials.

- 16.3.3 Place black filter cap on top of the vial. Use the tool provided to push the cap into the vial until it is flush with the top. (See the IC manual for more detailed instructions).
- 16.3.4 Wipe away any excess fluid from the top of the vial to avoid contamination from other samples.

- 16.3.5 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.
- 16.4 Basic System Operations Start-up and Shut-down
 - 16.4.1 Start-up Procedure for Ion Chromatograph
 - 16.4.1.1 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. Pressure on the nitrogen regulator is adjusted to 100 psi. Pressure on the helium regulator is adjusted to 14 psi.
 - 16.4.1.2 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.
 - 16.4.1.3 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 minutes, then turn degas switch to LOW.
 - 16.4.1.4 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).
 - 16.4.1.5 Priming the eluent lines.

<u>Note</u>: 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 seconds, or until a CLICK is heard,

.---

then 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.
- 16.4.1.6 Open the door of the Advanced Chromatography Module. On the back of the door, at the bottom, is the conductivity detector. There are four labeled lines (anion, cation, waste, and cell) located next to the cell. The plumbing must be configured according to the type of analysis to be performed. The ANION line must be attached to the CELL line, and the CATION line must be attached to the WASTE line. The line coming from the pump must be attached 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.

<u>Note</u>: If switching from one system to the other, the pump and the lines coming from the pump must be purged of the original eluent. This 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 minutes.

- 16.4.1.7 Select the columns to be used by pressing the blue button located below the labels. To verify that the correct columns are being used, the switch should be pressed at least once, and then set to the appropriate position. This is done in case the indicator light is reflecting a "default" setting, regardless of the actual position of the switch.
- 16.4.1.8 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.

- 16.4.1.9 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.
- 16.4.1.10 Turn stripchart recorder ON. Baseline should stabilize in less than 20 minutes. If baseline is not stable, see troubleshooting Section 16.5 for assistance.
- 16.4.2 Data acquisition start-up The following is a description of the current data acquisition program used by the U.S. EPA. The program is available (U.S. EPA, Atmospheric Research and Exposure Assessment Laboratory (AREAL), 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. It is not necessary to use a computer programmed integrator for the computation of data, however, for large sampling networks, it is recommended.
 - 16.4.2.1 Turn on the IBM XT computer. From the C:>prompt, type: cd/chart, then type: cchart. This loads the Chromatochart software. Turn switch on relay box to ENABLE, indicator light could go on.
 - 16.4.2.2 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.
 - 16.4.2.3 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.

- 16.4.2.4 "Total # runs for method <1>," type how many times the method is to be repeated (total number of samples). "Auto-analyze 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.
- 16.4.3 Calibration of IC The instrument should be brought to normal conditions with a warm-up time of at least thirty minutes.
 - 16.4.3.1 With the "Reading" light on, check to ensure the flow rate is 1.5 mLs/minute, the fluid pressure is 600 psi \pm 100 psi and the conductivity is constant as measured by offset difference.
 - 16.4.3.2 Fill the IC vials with the prepared standard solutions.
 - 16.4.3.3 Load the four vials into the sample vial holder, and place the holder in the automated sampler tray.
 - 16.4.3.4 The tray is controlled by a Spectra-Physics SP4200 or SP4270 Computer Integrator. Use the integrators operation manual to begin calibrating. (A typical program in Basic for integrators which illustrates integrator capability is shown in the Appendix of this procedure). 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 the nitrate anion are fitted to a quadratic curve by a least squares regression calculation. The curve is plotted and the correlation coefficient is calculated. The value of the coefficient is 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.

<u>Note</u>: 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 percent. For standard concentrations of greater than 1 ppm, comparability will normally be within 5 percent 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.

- 16.4.4 System Shut-down
 - 16.4.4.1 Shut off the pump. Turn the REGEN switch and the conductivity cell to the OFF position.
 - 16.4.4.2 Switch the eluent degas switch to HIGH.
 - 16.4.4.3 Turn the strip chart recorder FOF, 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.
 - 16.4.4.4 Shut the eluent degas system and reservoir switches and the autosampler to the OFF position. Close the valves on both gas cylinders. Then close the regulator valves.
- 16.4.5 NO₃⁻ Concentration Calculations
 - 16.4.5.1 Develop a calibration curve of conductivity versus concentration $(\mu g/mL)$.
 - 16.4.5.2 Perform a linear regression of the tabulated values.
 - 16.4.5.3 Utilize the slope and intercept of the curve, calculate the concentration of unknown filters by the following equation:

 $CNO_3 = [Intercept] + [Conductivity] [Slope]$

16.5 Basic Troubleshooting

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

16.5.1 Unstable Baselines

16.5.1.1 Wavy baseline - The most common reason for a wavy baseline is an air bubble in the gradient pump. This 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, it usually indicates a bubble. Other possibilities include a dirty or stuck check valve, piston seal or "C"-ring, as well as an air bubble in the conductivity cell.

- 16.5.1.2 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.
- 16.5.1.3 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 can be controlled by increasing the regenerant flow rate.
- 16.5.1.4 Low baselines Low baselines usually indicate that there is too much suppression. Oversuppression can be controlled by decreasing the flow of the regenerant.
- 16.5.2 Backpressure Variations in system backpressure are common and should not raise concern UNLESS the pressure change is greater than 200 psi.
 - 16.5.2.1 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 that there is some kind of blockage in the system. Possibilities include: loading against a closed valve; a plugged line; contaminated columns; etc. Diagnosis of the problem is done by removing one component of the system and observing how the pressure changes.
 - 16.5.2.2 Low pressure Low pressure readings usually indicate a leak somewhere in the system. Carefully check all fittings for leaks, tighten if necessary.

16.5.3 Flow

- 16.5.3.1 Regenerant lines If there is no flow at the waste outlet end of the regenerant line, check the following:
 - Make sure that 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

16.5.3.2 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. <u>Ammonia Analysis by Technicon Auto-analysis</u>

Presented in Sections 17.1 and 17.2 are the recipes for the standards and reagents required for the analysis of the ammonium ion $[NH_4^+ - or ammonia (NH_3)]$ by Technicon Auto-analysis. Figure 13 illustrates how the sample is carried through the Technicon Auto-analyzer. The samples, along with all standards, are taken from the auto-advance sampler tray by the use of a proportioning pump. 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. The color formation depends on having a system that allows for adequate reaction time and provides a sufficiently basic pH (pH > 11) for the reaction to occur. Color formation is enhanced by the presence of a metal catalyst. 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.

17.1 Standards and Stock Solutions Preparation

<u>Note</u>: 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 determines if the old solution has deteriorated or if an error has been made in preparing the new solution.

17.1.1 Ammonium solution standard (1000 μ g/mL) - Dry ammonium chloride in an oven for one hour at 50 to 60°C and desiccate over silica gel for one hour. Weigh 2.9470 g ammonium chloride and dissolve in 800 mL
DDW. Dilute to one liter with DDW and mix thoroughly. This solution is stable for one year.

- 17.1.2 Intermediate ammonium standards (100 μ g/mL)- To make a 100 μ g/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 one month. To make a 10 μ g/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.
- 17.1.3 Working ammonium standards in DDW Pipet aliquets of the 100 μ g/mL and 10 μ g/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, µg/mL	Aliquot, mL	· Final Concentration, μg/mL
A	100	40.0	40.0
В	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

- 17.1.4 Sodium citrate stock solution Dissolve 294.1 g of sodium citrate in 800 mL DDW. Dilute to 1 liter and mix thoroughly. Store at room temperature.
- 17.1.5 20 percent citric acid/5 percent glycerol stock solution Dissolve 25 g citric acid in 80 mL DDW. Add 5 mL glycerol and dilute to 100 mL with DDW. Mix thoroughly and store at room temperature.

17.1.6 Sodium citrate/citric acid/glycerol working solution - Put 100 mL sodium citrate stock solution into a 1000 mL volumetric flask. Add 20 mL of the 10 percent citric acid/5 percent glycerol stock solution and dilute to volume with DDW. Mix thoroughly and store at room temperature.

Note: This solution will be used to make up ammonium working standards for citric acid/glycerol-impregnated filter extract analyses.

- 17.1.7 Working ammonium standards in sodium citrate/ citric acid/glycerol working solution Pipet aliquots of the 100 μ g/mL into appropriate volumetric flasks according to the table outlined in Section 17.1.3.
- 17.1.8 Potassium chloride stock solution Dissolve 74.6 g potassium chloride in 800 mL DDW. Dilute to one liter with DDW and mix thoroughly. Store at room temperature.
- 17.1.9 Potassium chloride working solution Put 100 mL of the potassium chloride stock solution into a 1000 mL volumetric flask. Dilute to volume with DDW.
- 17.1.10 Working ammonium standards in potassium chloride working solution-Pipet aliquots of the 100 μ g/mL ammonium stock standard or intermediate standards into 100 mL volumetric flasks according to the table below. Dilute to volume with potassium chloride working solution and mix thoroughly. Prepare fresh daily.

Ammonium Standard	Stock or Intermediate Standard, µg/mL	Aliquot, mL	Ammonium Concentration, μg/mL
A	1000	40.0	40.0
B	100	4.0	4.0
C	100	3.0	3.0
D	100	2.0	2.0
Е	100	1.0	1.0
F	100	0.5	0.5
G	10	1.0	0.1
Н	10	0.5	0.005

17.2 Reagent Preparation

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

- 17.2.1 Alkaline phenol To 800 mL DDW in a one liter volumetric flask, add 83.0 g loose crystallized phenol. Keeping the flask in an ice bath or under tap water, slowly add 96.0 mL 50 percent sodium hydroxide solution. Shake the flask while adding the sodium hydroxide. Cool to room temperature, dilute to one liter with DDW and mix thoroughly. Store in an amber glass container. This solution remains stable for three months, if kept out of direct light.
- 17.2.2 Sodium hypochlorite solution The amount of sodium hypochlorite solution varies from batch to batch of sodium hypochlorite (5 percent 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 percent 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 one day.
- 17.2.3 Sodium nitroprusside solution Dissolve 1.1 g of sodium nitroprusside in about 600 mL of DDW, dilute to 1 liter with DDW and mix thoroughly. Store in an amber container, and keep in refrigerator. This solution remains stable for one month, if kept out of direct light.
- 17.2.4 Disodium EDTA solution Dissolve 1.0 mL of 50 percent 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 remains stable for six months.
- 17.3 Procedure for Auto-analyzer Set-up
 - 17.3.1 Proportioning pump Marked tubing lines should be positioned across rollers. When proportioning pump is not in use, plane press should be unlocked.
 - 17.3.2 Manifold The air tube feeds bubbles into the sample tube, breaking the sample flow into separate sample aliquots. The EDTA solution is added and this mixture goes through a double mixing coil (20 turns). Phenolate and nitroprusside are added and the solution goes through

another double mixing coil (10 turns). Bleach is added, and the mixture goes through a single mixing coil (5 turns). Then, the mixture passes through a heat bath (37°C), and a delay coil (for about 10 minutes). A debubbler diverts a fraction of the flow to waste to ensure a smooth, bubble-free flow to the colorimeter. The solution passes through single channel colorimeter (set at 630 nm) and finally to a waste stream.

Item	Flow Rate
Air	0.32 mL/min
Sample Aliquot	1.00 mL/min
Complex Solution	0.23 mL/min
Alkaline Phenol	0.60 mL/min
Bleach	0.42 mL/min
Total liquid	2.25 mL/min
Volume to waste	1.05 mL/min
Colorimetric return	1.20 mL/min
Needle washing	1.60 mL/min

17.3.3 Reagent and Sample Volumes - Typically flow rates for the autoanalyzer are listed in the following table:

- 17.4 Procedure for Sample Run
 - 17.4.1 Allow colorimeter and recorder to warm up for 30 minutes.
 - 17.4.2 Start the proportioning pump, with all reagent lines in a beaker of DDW.
 - 17.4.3 One at a time, place the reagent lines into the respective reagent bottles. Make sure that the air bubbles are being fed into the sample line at a constant interval. Obtain a baseline reading on the recorder.
 - 17.4.4 Take samples from the refrigerator and set-up the sample tray. Put the cover on sample tray to avoid evaporation.
 - 17.4.5 Run system. Standard should be run first to calibrate recorder output. Run standard levels low-to-high. Standard should be run every 10 samples for verification.

- 17.4.6 Once a week or prior to extended period of non-use, run a solution of 0.01 percent BRIJ-35 through all reagent lines.
- 17.4.7 Record peak height for all standards and samples as determined.
- 17.4.8 A calibration curve is derived from the values of ammonia standards $(\mu g/mL)$ versus peak height.
- 17.4.9 Perform a linear regression of the tabulated value.
- 17.4.10 Utilizing the slope and intercept of the curve, calculate the concentration of NH_4^+ on the unknown filter by the following equation:
 - $CNH_4^+ = [Intercept] + [Peak Height] [Slope]$

18. Assumption of Annual Denuder System

- 18.1 The measurement of acid aerosol requires that ammonia be eliminated from the sample stream to prevent inaccurate measurement of the acid aerosol, thus biasing the results. To address this issue, a citric acid coated denuder to remove (denuder) ammonia from the gas stream is positioned in front of the filter assembly where strong acid aerosols are collected. The efficiency of the citric acid denuder to remove NH₃ is assumed to be 100 percent.
- 18.2 The efficiency of the impactor collection system decreases with increased particulate loading. The average operational time before such loading occurs has not been determined. Likewise, the removal efficiency of the denuders have not been fully explored. Thus, both the impactor and denuders are removed after each sampling event and replaced with new components.
- 18.3 Other assumptions which are made associated with the performance of the annular denuder system for validity of the calculations presented in Section 19 are:
 - All alkaline particles (> 2.5 μ m) are removed at the sampler inlet;
 - The cyclone or elutriator/impactor assembly have DP_{50} cut size of 2.5 μ m;
 - The citric acid coated-denuder removes 100% of ammonia from the gas sample stream;
 - Fine (<2.5 μ m) acid (H₂SO₄) aerosol losses in the denuder are less than 1%;
 - The Na₂CO₃ coated denuder collects 100 percent of the nitric acid, while the following citric acid coated denuder collects 100 percent of the ammonia.
 Particle losses are less than 1 percent in each denuder.

- The Teflon[®] filter is 100 percent efficient for collection of fine acid aerosols. If ammonium nitrate (NH₄NO₃) was collected on the Teflon[®] filter, its probability of evaporation is high. Therefore, a citric acid-impregnated filter downstream would collect some of the dissociation products from the Teflon[®] filter. Also, interaction of ammonia and sulfuric acid neutralizes the sample and causes the acidic measurement to be biased.
- The nylon filter collects any nitrate that dissociates from the Teflon[®] filter.
- The citric acid impregnated retains all the ammonia arising from the dissociation of NH_4NO_3 collected on the Teflon[®] filter.

19. Atmospheric Species Concentration Calculations

- 19.1 Calculations Using Results from pH Measurement
 - 19.1.1 A convenient method of expressing concentration of the hydrogen ion was first proposed by Sorensen in 1909 and has been widely adopted by chemists.

$$pH = - \log [H^+]$$

 $[H^+] = 10^{-pH}$

19.1.2 For each working standard on a given analytical day, calculate the "apparent net strong acid concentration" as follows:

$$C_i = 10^{-pHWS}i - 10^{-pHEA}$$

where:

 C_i = apparent net strong acid concentration, molar,

 $pHWS_i = measured mean pH of a working standard, and$

pHEA = measured mean pH of the EA solution.

- 19.1.3 For each analytical day, utilizing a particular set of freshly prepared daily working standards, develop a standard curve by calculating the linear regression of C_i vs. C_{eq}, as documented in Section 15.1.1.1. Calculate slope and intercept of the standard curve.
- 19.1.4 Calculate the corresponding "apparent net strong acid concentration" from the sample pH utilizing the following equation:

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

where:

 $C_s = apparent net strong acid concentration for unknown sample, molar,$

pHS = measured pH of the sample (S), and

pHEA = measured pH of the EA solution.

19.1.5 Utilizing the slope and intercept of the standard curve, calculate equivalent mass of strong acid:

$$C_c = [Intercept] + [C_s] [Slope]$$

where:

- C_f = apparent net strong acid mass, μg , as calculated from standard curve,
- Intercept = calculated relationship from linear regression analysis of C_i vs. C_{Eq} , and
 - Slope = calculated relationship from linear regression analysis of C_i vs. C_{Eq} .
- 19.1.6 The actual sample air value, V, 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 as follows:

$$V = [F] [T]$$

where:

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

T = net elapsed time, min, and

V = total sample volume, L

Convert L to m^3 by: $V_s = V \times (10^{-3})$

where:

$$V_s$$
 =total sampling volume, m³, and 10^{-3} =conversion factor, m³/L.

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

$$V_{s_{std}} = V_{s}Y(\frac{T_{std}}{T_{m}})(\frac{P_{bar}}{P_{std}})$$

where:

- $V_{s_{std}}$ = volume of sample at EPA-reference conditions, m³,
 - V_s = volume of gas sample through the dry gas meter, or calculated volume sampled as indicated by rotameter (see Section 12.2.6), m³,
- T_{std} = absolute EPA-reference temperature, 298°K,
- $T_m =$ average flowmeter or dry gas meter temperature, °K,
- P_{bar} = barometric pressure of flow or volume measurement condition, mm Hg,
- $P_{std} = EPA$ -reference barometric pressure, 760 mm Hg, and
 - Y = dry gas meter calibration factor (if applicable), dimensionless.
- 19.1.8 Calculate the final concentration of apparent net fine particle (<2.5 μ m) strong acidity (as H₂SO₄):

$$C_{H} + = C_{f} / V_{s_{std}}$$

where:

$$C_{H}$$
 = apparent net fine particle strong acidity concentration,
 $\mu g/m^3$,

$$C_f$$
 = apparent net strong acid, μg , as calculated from standard curve, and

$$V_{sstd}$$
 = volume of sampled gas at EPA-reference conditions
(see Section 19.1.7), m³.

19.2 Calculations Using Results from IC Analysis

These assumptions lead directly to equations for computing atmospheric concentrations from denuder measurements.

19.2.1 Analytical results are given at NO₃ - in μ g/mL.

- 19.2.2 The extraction volume was 10 mL (i.e., 0.010L).
- 19.2.3 Nitrate concentration converted to equivalent sulfuric acid:

$$CNO_3^- = [NO_3^- \text{sample} - NO_3^- \text{blank}][10 \text{ mL}][98/62]$$

19.3 Calculations Using Results from Auto-analyzer

19.3.1 Analytical results are given in NH_4^+ in $\mu g/mL$.

19.3.2 The extraction volume was 10 mL.

19.3.3 Ammonium concentration converted to equivalent sulfuric acid:

$$CNH_4^+ = [NH_4^+ sample - NH_4^+ black][10][98/18]$$

20. Variations of the Acid Aerosol Denuder System

One modification of the fine particle strong acidic aerosol denuder system involves adding additional denuders to selectively quantitate other gaseous and particulate species in the atmosphere, and is illustrated in Figures 14 and 15. This system was developed to measure reactive acidic and basic gases and particulate matter which are contained in ambient air. The chemical species which can be measured utilizing this system are gaseous SO₂, HNO₂, HNO₃, NH₃, and particulate SO₄⁻⁻, NO₃, and H⁺. Other similar chemical species can be successfully collected by the system with

modifications (i.e., changing the denuder coating solutions, the denuder sequence, and the filter types and sequence). Once collected, the pollutant concentrations are quantified by ion chromatography (IC) analysis and/or Technicon colorimeter autoanalysis. A full description of this methodology can be found in "Compendium of Methods for the Determination of Air Pollutants in Indoor Air," U.S. Environmental Protection Agency, Atmospheric Research and Exposure Assessment Laboratory, Research Triangle Park, N.C. 27711, EPA-600/4-90-010.

21. 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. It is the user's responsibility to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to the implementation of this procedure. This should be part of the user's SOP manual.

22. 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.

22.1 Standard Operating Procedures (SOPs)

- 22.1.1 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.
- 22.1.2 Specific stepwise instructions should be provided in the SOPs and should be readily available to and understood by the personnel conducting the monitoring work.

22.2 Quality Assurance 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 on a regularly scheduled basis and should be part of the quality assurance program. Additional QA measures (e.g., trouble shooting) as well as further guidance in maintaining the sampling system are provided by the manufacturer. For detailed guidance in setting up a quality assurance program, the user is referred to the Code of Federal Regulations (see Section 23, Citation 11) and the EPA Handbook on Quality Assurance (see Section 23, Citation 12).

23. <u>References</u>

- 1. Waldman, J. M., Operations Manual for the Annular Denuder System Used in the USEPA/RIVM Atmospheric Acidity Study, UMPNJ Robert Wood Johnson Medical School, Piscataway, NJ, August 28, 1987.
- 2. American Chemical Society Subcommittee on Environmental Chemistry, "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," *Analyt. Chem.*, 52:2242-2249, 1980.
- Sickles, II, J. E., "Sampling and Analytical Methods Development for Dry Deposition Monitoring," Research Triangle Institute Report No. RTI/2823/00-15F, Research Triangle Institute, Research Triangle Park, NC, July 1987.
- 4. Forrest, J., and L. Newman, "Sampling and Analysis of Atmospheric Sulfur Compounds for Isotopic Ratio Studies," *Atmos. Environ.*, 7:562-573, 1973.
- 5. Stevens, R. K., et al., Abstract for ACGIH Symposium: on Adran COS in Air Sampling, "Inlets, Denuders and Filter Packs to Measure Acidic Inorganic Pollutants in the Atmosphere," Asilomar Conference Center, Pacific Grove, CA, February 16, 1986.
- Appel B. R., Povard V., and Kothney E. L., "Loss of nitric acid within inlet devices for Atmospheric Sampling," Paper presented at 1987 EPA/APCA Symposium: Measurement of Toxic and Related Air Pollutants, Research Triangle Park, NC, 3-6 May 1987.
- 7. Braman R. S., Shelley T. J., and McClenny W. A., "Tungstic Acid for Preconcentration and Determination of Gaseous and Particulate Ammonia and Nitric Acid in Ambient Air," *Analyt. Chem.*, 54:358-364, 1983.
- 8. Ferm, M., "Concentration Measurements and Equilibrium Studies of Ammonium, Nitrate and Sulphur Species in Air and Precipitation," Doctoral Thesis, Department of Inorganic Chemistry, Goteborg University, Goteborg, Sweden, 1986.
- 9. Ferm, M., and Sjodin A., "A Sodium Carbonate Coated Denuder for Determination of Nitrous Acid in the Atmosphere," *Atmos. Environ.*, 19:979-985, 1985.
- 10. Stevens, R. K., and Rickman, E., Jr., "Research Protocol/Method for Ambient Air Sampling with Annular Denuder Systems," prepared for U.S. Environmental Protection Agency, Atmospheric Chemistry and Physics Division, Office of Research and Development, Research Triangle Park, NC, ASRL-ACPD-RPM 003, January 1988.
- 11. 40 CFR Part 58, Appendix A, B.

- 12. Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II -Ambient Air Specific Methods, EPA 600/4-77-0272, May, 1972.
- 13. Bolleter, C.J., Bushwan, and Tidwell, P.W. (1961), "Spectrophotometric Determination of Ammonia as Indephenol," Anal. Chem. <u>33</u>, 592-594.
- 14. Harwood, J.E. and Kuhn, A.L. (1970), "A Colorimetric Method for Ammonia in Natural Water," Water Res. 4, 8055-811.
- 15. Koutrakis, P., Wolfson, J.M., Slater, J.L., Brauer, M., Spengler, J.D., Stevens, R.K., and Stone, C.L., "Evaluation of an Annular Denuder/Filter Pack System to Collect Acidic Aerosols and Gases," *Environ. Sci. & Tech.* <u>22</u>, 1463-1468, 1988.
- 16. Mann, L.T., Jr., "Spectrophotometric Determination of Nitrogen in Total Microkjedahl Digests," Anal. Chem. <u>35</u>, 2179-2182, 1963.
- Possanzini, M., Febo, A., and Liberti, A., "New Design of a High-performance Denuder for the Sampling of Atmospheric Pollutants," *Atmos. Environ.* <u>17</u>, 2605-2610, 1983.
- 18. Stevens, R.K., and Rickman, E.E., Research Protocol/Method for Ambient Air Sampling with Annular Denuder Systems. Report ASRL-ACPD-RPM 303, U.S. EPA, Research Triangle Park, N.C., January 1988.
- 19. Koutrakis, P., Wolfson, J.M., and Spengler, J.D., "An Improved Method for Measuring Aerosol Strong Acidity: Results from a Nine-Month Study in St. Louis, Missouri and Kingston, Tennessee," Atmospheric Environment, 22:157-162, 1988.
- 20. Brauer, M., Koutrakis, P., Wolfson, J.M., and Spengler, J.D., "Evaluation of the Gas Collection of an Annular Denuder System Under Simulated Atmospheric Conditions," *Atmospheric Environment*, 23:1981-1986, 1989.
- Koutrakis, P., Wolfson, J.M., Brauer, M., and Spengler, J.D., "Design of a Glass Impactor For an Annual Denuder/Filter Pack System," Aeros. Sci., and Techn., 12:607-612, 1990.
- 22. Sjödin A. and Ferm, M., "Measurements of Nitrous Acid In An Urban Area," Atmospheric Environment 19, 985-992, 1985.
- 23. Vossler, T.L., Stevens, R.K., Paur, R.J., Baumgardner, R.E., and Bell, J.P., "Evaluation of Improved Inlets and Annular Denuder Systems to Measure Inorganic Air Pollutants," Annos. Environ. 22, 1729-1736, 1988.
- 24. Technical Assistance Document for Sampling and Analysis of Toxic Organic Compounds in Ambient Air, EPA-600/8-90-005, U.S. Environmental Protection Agency, Research Triangle Park, NC, 1990.

Table 1.0.	Summary of	Key P	Probe	Siting	Criteria	for
1	Acid Aerosol	Monit	oring	Station	ns	

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 is >20 m from the dripline and 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.				

Revision No. 0 Date 11/92 Page 57 of 72





Acid Aerosol

Part B



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

Revision No. 0 Date 11/92 Page 59 of 72



Figure 3. Acidity Determination of the Teflon[®] Filter with Correction For Volatilized Nitrate Species

Revision No. 0 Date 11/92 Page 60 of 72



(a) GLASS ASSEMBLY



Figure 4. Available Elutriator and Acceleration Jet Assemblies



Figure 5. Glass Annular Denuder with Inset Impactor Assembly

Revision No. 0 Date 11/92 Page 62 of 72



Figure 6. Side View Impactor/Coupler Assembly

Revision No. 0 Date 11/92 Page 63 of 72



Figure 7. Internal Schematic of Annular Denuder

Revision No. 0 Date 11/92 Page 64 of 72







Figure 9. Acid Aerosol Filter Pack Assembly

Revision No. 0 Date 11/92 Page 66 of 72

DETERMINATION OF THE STRONG ACIDITY OF ATMOSPHERIC FINE-PARTICLES ($<2.5\mu$ m)

. . . -

Project:		GENERAL					
Site:	Project:			Date:			
Location:	Site:			Location of Sa	ampler:		
Sample Code: Operator: Sample Code:	Location:				- 		
Sample Code: Operator: EQUIPMENT Sampler Mass Flow Citric Acid Denuder No.: Controller No.:	<u> </u>		<u></u>			··	
EQUIPMENT Sampler Mass Flow Citric Acid Denuder No.:	Sample Code:			Operator:		·	
Mass Flow Citric Acid Denuder No.: Controller No.:		EQUIPMENT			Sampler		
Controller No.:	Mass Flow			Citric Acid D	enuder No.:		
Lab Calibration Date:	Controller No .:			Filter Assemb	ly No.:		
Flow Rate Set Point:	Lab Calibration	1 Date:					
Calibrated By:	Flow Rate Set I	Point:					
Rotameter No.:	Calibrated By:						
DGM No.:	Rotameter No .:						
SAMPLING DATA Time Stop Time:	DGM No.:						
Time Stop Time:	SA	AMPLING DAT	Ά				
Time:		Time	•	•	Stop		
Flow Rate:	Time:		<u> </u>				
Temperature:	Flow Rate:						
Pressure:	Temperature: _						
Avg. Flow Rate:	Pressure:				_		
Leak Check (Before):	Ave Flow Rate	<u>.</u>					
Interview Interview Interview	Leak Check (Re	efore).					
Total Sample Vol.: (±5%) Flow Maintained Rate: (±5%) Flow Ambient Barometric Relative Humidity, Rate (Q), Temperature, Pressure, Humidity, Comments		for)					
Total Sample Vol.:	(A)						
Flow Ambient Barometric Relative Time L/min °C Pressure, mm Hg Humidity, %	Total Sample V Flow Maintaine	ol.:	(+5%)				
Flow Rate (Q), L/minAmbient Temperature, °CBarometric Pressure, mm HgRelative Humidity, %TimeL/min°CPressure, mm HgComments					<u> </u>		
	Time	Flow Rate (Q), L/min	Ambient Temperature, °C	Barometric Pressure, mm Hg	Relative Humidity, %	Comments	
		······································					

Figure 10. Annular Denuder Field Test Data Sheet



Figure 11. Calibration and Analysis Step for pH Determination

Determination of the Strong Acidity of Atmospheric Fine-Particles ($< 2.5 \mu m$)

Name:_____

Sample I.D.:_____

Location:_____

Date:_____

	RUN NUMBER								
Constituent	1	2	3	4	5	6	7		
pH 7 Buffer									
1	949696								
2									
3									
pH 4 Buffer									
1									
2									
3									
EA Solution							etoet ji		
1									
2						Ļ			
3			A	al en la competition de					
Working Standards			8488-111 1		<u>geerer</u> ee		14, 1497년년		
1A1									
1A2									
EA									
181									
182						ļ			
EA		<u> </u>							
2A1									
2A2 T									
Temp.									
281									
EA									
2A1									
3A7		·							
FA				<u> </u>					
Temn									
тешр. 3R1									
387									
FA									
LU									

Figure	12.	DΗ	Analytical	Laboratory	Log	Form
		r	·······································		-~~p	

•

Revision No. 0 Date 11/92 Page 69 of 72

	1		RU	N NUMB	ER	•	
Constituent	1	2	3	4	5	6	7
4A1							
4A2							
EA							
4B1							
4B2							
Temp.							
EA							
5A1							
5A2							
EA							<u> </u>
5B1							
5B2							
EA						ļ	
6A1				ļ			
6A2				·			{
Temp.							
EA							
6B1			·				·
632							
⊐A St							
EA							
	ļ					<u> </u>	{
						}	
						{	
					<u>*</u>	<u> </u>	
<u> </u>							
A 1							
R							
Ř1	}						
Č							
ČI							
D						1	
DI							
E						[
El						[
EA							
Temp.							
EA Solution] <u></u>						
1							
2							
3							
pH4 Buffer							
1							
2							
3							

Figure 12. pH Analytical Laboratory Log Form (cont.)

Revision No. 0 Date 11/92 Page 70 of 72





Revision No. 0 Date 11/92 Page 71 of 72



Figure 14. Schematic View of Annular Denuder with Cyclone Adaptor for Measurement of Reactive Acidic and Basic Gases and Particulate Matter (< 2.5 μ m) in Ambient Air