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**UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
REGION 4**

Science and Ecosystem Support Division  
Enforcement and Investigations Branch  
980 College Station Road  
Athens, Georgia 30605-2720

November 10, 2010

**4SESD-EIB**

**MEMORANDUM**

**SUBJECT:** Yellow Bluff Air Study, QAPP  
SESD Project No. 11-0068

**FROM:** Mike Crowe, Environmental Scientist  
Air and Superfund Section *me*

**THRU:** Archie Lee, Chief *Archie*  
Enforcement and Investigations Branch

**TO:** Doug Neeley, Chief  
Air Toxics and Monitoring Branch  
Air, Pesticides, and Toxics Management Division

Attached you will find a copy of the approved QAPP for the Yellow Bluff Air Study.

If you have any questions, please contact me by phone at (706)355-8630 or at [crowe.mike@epa.gov](mailto:crowe.mike@epa.gov).

Attachment

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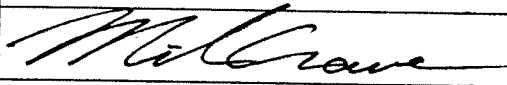
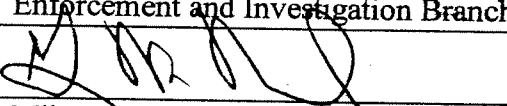
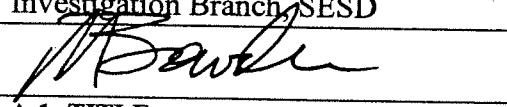


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**SECTION A: Project Planning Elements**

<b>A1. Title (Project Name):</b>		Yellow Bluff Air Study
<b>Project Location:</b>		Vicinity of 7600 Highway 10, Yellow Bluff, Alabama (Figure 1)
<b>Project Requestor and Organization:</b>		Doug Neeley, Chief, ATMB, APTMD Region 4 USEPA, 61 Forsyth St., SW, Atlanta, GA 30303-8909
<b>Project Leader's Name, Position, and Organization:</b>		Mike Crowe, Environmental Scientist, Superfund and Air Section, Enforcement and Investigation Branch, SESD
<b>Project Leader's Signature:</b>		 Date: 11/10/2010
<b>Technical Reviewer's Name and Position:</b>		Greg Noah, Environmental Scientist, Superfund and Air Section, Enforcement and Investigation Branch, SESD
<b>Technical Reviewer's Signature:</b>		 Date: 11/10/2010
<b>Section Chief/DAO's Name and Position:</b>		Mike Bowden, Chief, Superfund and Air Section, Enforcement and Investigation Branch, SESD
<b>Section Chief/DAO's Signature:</b>		 Date: 11/10/2010
<b>A2. Table of Contents</b>		<p>A-1: TITLE</p> <p>A-2: TABLE OF CONTENTS</p> <p>A-3: DISTRIBUTION LIST</p> <p>A-4: PROJECT PERSONNEL</p> <p>A-5: PROJECT BACKGROUND</p> <p>A-6: PROJECT DESCRIPTION</p> <p>A-7: QUALITY OBJECTIVES AND CRITERIA</p> <p>A-8: SPECIAL TRAINING / CERTIFICATIONS</p> <p>A-9: DOCUMENTS AND RECORDS</p> <p>B-1: SAMPLING DESIGN</p> <p>B-2: SAMPLING METHODS, GENERAL PROCEDURES</p> <p>B-3: SAMPLE HANDLING &amp; CUSTODY</p> <p>B-4: ANALYTICAL METHODS</p> <p>B-5: QUALITY CONTROL</p> <p>B-6: INSTRUMENT / EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE</p> <p>B-7: INSTRUMENT / EQUIPMENT CALIBRATION AND FREQUENCY</p> <p>B-8: INSPECTION / ACCEPTANCE FOR SUPPLIES AND CONSUMABLES</p> <p>B-9: NON-DIRECT MEASUREMENTS</p> <p>B-10: DATA MANAGEMENT</p> <p>C-1: ASSESSMENT &amp; RESPONSE ACTIONS</p> <p>C-2: REPORTS TO MANAGAMENT</p> <p>D-1: DATA REVIEW, VALIDATION AND VERIFICATION</p> <p>D-2: VERIFICIATION AND VALIDATION METHODS</p> <p>D-3: RECONCILIATION WITH USER REQUIREMENTS</p>



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	<p><b>FIGURES</b></p> <p>Figure 1 – Map of Yellow Bluff, Alabama.          Figure 2 – Map of Yellow Bluff, Alabama and surrounding area.</p> <p><b>APPENDICES</b></p> <p>Appendix A – 2008 International Paper Pine Hill Mill TRI Data</p> <p>Appendix B – Wilcox County Selected Health Status Indicators report</p> <p>Appendix C – SESD Operating Procedure for Ambient Air Sampling          SESDPROC-303-R2</p> <p>Appendix D – <i>Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles (&lt;2.5µm) Method IO-4.2</i></p> <p>Appendix E – Purafil Corrosion Classification Coupon Environmental Monitoring Procedure</p>
<p><b>A3. Distribution List</b></p>	<p>Archie Lee, Branch Chief          Enforcement and Investigation Branch          Science and Ecosystem Support Division          US EPA Region 4          980 College Station Rd.          Athens, GA 30605</p> <p>Mike Bowden, Section Chief          Air and Superfund Section          Science and Ecosystem Support Division          US EPA Region 4          980 College Station Rd.          Athens, GA 30605</p> <p>Tim Slagle, Chemist          Air and Superfund Section          Science and Ecosystem Support Division          US EPA Region 4          980 College Station Rd.          Athens, GA 30605</p> <p>Greg Noah, Environmental Scientist          Air and Superfund Section</p>





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	<p>           Science and Ecosystem Support Division            US EPA Region 4            980 College Station Rd.            Athens, GA 30605         </p> <p>           Van Xavier Shrieves, Environmental Scientist            Air Toxics and Monitoring Branch            Air Pesticides and Toxics Management Division            US EPA, Region 4            61 Forsyth Street SW            Atlanta, GA 30303         </p> <p>           Doug Neeley, Branch Chief            Air Toxics and Monitoring Branch            Air Pesticides and Toxics Management Division            US EPA, Region 4            61 Forsyth Street SW            Atlanta, GA 30303         </p>	
A4. Project Personnel	Organization	Responsibilities
Mike Crowe	SESD, EIB, SAS	Project Leader, Sampler
Greg Noah	SESD, EIB, SAS	Sampler, HSO
Van Shrieves	APTMD, ATMB	Technical Advisor
Doug Neely	APTMD, ATMB	Requestor
Comments:		
<b>A5. Project Background:</b>	<p> <b>Orientation</b>            The issue of potential environmental concerns within the town of Yellow Bluff, Alabama was brought to EPA's attention during the Summer of 2010. Public officials of Yellow Bluff indicated that there were concerns regarding air emissions from a nearby paper mill. They believed the mill to be contributing to the corrosion of metal objects within the town, and adversely affecting public health.         </p> <p> <b>Site Description</b>            The town of Yellow Bluff is located in southern Alabama at approximately 31.96 North latitude and -87.48 West longitude (decimal degrees) in Wilcox county. Immediately to the north of Yellow Bluff, across Highway 10, is the International Paper Pine Hill Mill (IP) facility (formerly owned by Weyerhaeuser Co.) located at 7600 Highway 10 W, Pine Hill, Alabama 36769 (Figure 1).         </p>	



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	<p><b>Pollutants and Potential Sources</b>          Although the origin of air pollutants in the community are likely from a wide range of sources (e.g., large facilities, small businesses, cars and trucks, and sources outside of Wilcox County), primary concern has focused on air pollutants released from the IP facility.</p> <p><b>Objective</b>          The overall goal of this monitoring effort is to collect air monitoring data of sufficient quality and quantity to determine if Yellow Bluff residents are being exposed to elevated airborne pollutants that may be contributing to a reportedly high incidence of respiratory illnesses.</p>
<p><b>A6. Project Description:</b></p>	<p><b>Task Description</b>          Science and Ecosystem Support Division (SESD) personnel will conduct ambient air monitoring activities in the Yellow Bluff area to determine if there is a measureable difference in the levels of monitored pollutants within the town of Yellow Bluff compared to those detected at a background location, and collect meteorological data to determine whether the town of Yellow Bluff is predominantly downwind from the IP facility.</p> <p>The Air, Pesticides, and Toxics Management Division (APTMD) has provided 2008 Toxics Release Inventory (TRI) air emissions data regarding the International Paper facility (Appendix A), as well as epidemiological information (Appendix B) regarding the health concerns from Yellow Bluff officials. Based on the combination of the TRI data, and the nature of the secondary citizen's complaint, regarding the alleged corrosion of metal objects, the following will be the primary pollutants of concern for this project: hydrogen sulfide, sulfur dioxide, and reactive particles and gases. In addition, because there are other pollutants associated with the paper mill that while not typically being thought of as having the potential to cause corrosion of metal, do have the potential to cause adverse health effects, volatile organic compound, and aldehyde analyses will also be performed. Thus, the specific pollutants/parameters that will be monitored are:</p> <ul style="list-style-type: none"> <li>• Sulfur Dioxide (SO<sub>2</sub>)</li> <li>• Hydrogen Sulfide (H<sub>2</sub>S)</li> <li>• Reactive Gases (SO<sub>2</sub>, HNO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>) and Particles (SO<sub>4</sub><sup>=</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup> and H<sup>+</sup>) (Method IO-4.2)</li> <li>• Volatile Organic Compounds (VOCs) (Method TO-15)</li> <li>• Aldehydes (Method TO-11A)</li> </ul>



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- Corrosion
- Meteorology (wind speed and direction)

**Monitoring activities**

The monitoring aspect of the entire project should last approximately three weeks. During that time a number of different monitoring activities will take place. These activities have been divided into three different types (continuous, manual, and corrosion) and can be seen in Table 1.

The following monitoring activities will include:

- 1) Continuous (H<sub>2</sub>S, SO<sub>2</sub>, and Meteorological)
- 2) Manual (VOCs, Aldehydes, Reactive Gases and Particles)
- 3) Corrosion (Corrosion Classification Coupons (CCC))

**Table 1. Timeline for Yellow Bluff sampling event.**

Day #	Corrosion	Continuous	Manual
1	Travel to Yellow Bluff		
2	Deploy Corrosion Coupons	Final reconnaissance for Primary and Background locations.	
3	Inspect Corrosion Coupons	Return travel to SESD	
4			
5			
6			
7			
8			
9			
10			
11			
12			
13			
14		Travel to Yellow Bluff	
15	Inspect Corrosion Coupons. Collect/ deploy coupons as necessary	Setup and calibrate instrumentation at Primary and Background locations	Setup instrumentation at Primary and Background locations
16	Inspect Corrosion Coupons	Begin Continuous monitoring	24-hour sampling
17	Inspect Corrosion Coupons	Precision Zero Span (PZS) check	24-hour sampling
18	Inspect Corrosion Coupons	Precision Zero Span (PZS) check	24-hour sampling
19	Inspect Corrosion Coupons	Precision Zero Span (PZS) check	Complete Chain of Custody (COC)



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	<b>20</b>	Collect All Corrosion Coupons	Final PZS Check. Take down instrumentation.	Take down instrumentation
	<b>21</b>	Ship samples to laboratories.	Return Travel to SESD	Ship samples to laboratories.

Shaded areas indicate when monitoring is taking place.

**Lab Completion**  
 Projected Lab Completion Date:  
 Analytical data for the Non-Continuous samples will be back from the laboratories within 35 days of the conclusion of the study.

**Final Report / Decision Criteria**  
 The data collected during the study will be validated by SESD within 30 days after receiving all of the non-continuous laboratory data. After validation, a data report will be submitted to APTMD. All decisions concerning the final use of the data will be made by APTMD.

**A7. Quality Objectives and Criteria**

**Qualitative Objectives**

A sampling design has been developed (section B1) that will accomplish the objective that is identified in section A5. Based on the background information that was received, the sampling design adequately addresses site location, number of samples, timing of sampling event, length of sampling event, and monitored parameters. If at any time during the project it becomes necessary to adjust the sampling design, or if technical issues require modification to the project, then those adjustments or modifications will be described and justified in the final report.

**Quantitative Objectives and Criteria for Measurement Data**

**Precision and accuracy**

These are quantitative measures that characterize the amount of variability and bias inherent in a data set. Duplicate Manual samples at the Primary sampling location are established to provide precision data for each of the Manual methods utilized in this study. At the end of the study, duplicate results are expected to be within +/- 15% of one another. For continuous H<sub>2</sub>S and SO<sub>2</sub> sampling, multiple Precision Zero Span (PZS) checks will provide the precision and accuracy quality control checks. Following each PZS check, accuracy for non-zero values will be calculated as a percent difference from the true value of the calibration gas concentration. Accuracy for each PZS check is expected to be within +/- 10% at the full-scale setting of the instrument. Precision will be reported as the standard deviation of 10 consecutive minute data points, at least 10 minutes after the introduction of calibration gas. A statement will be made in the final report, using the above criteria, concerning the precision and accuracy of the Continuous and Manual monitoring results.



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**Completeness**

The completeness of data recovery of this study is expected to be at least 75%. A statement will be made in the final report concerning the completeness of all monitoring activities.

**Comparability**

This refers to the ability to compare data from different sources with a degree of confidence. Two different methods within this study provide results for SO<sub>2</sub> concentrations in ambient air. The 24-hour SO<sub>2</sub> results from Manual reactive gases and particle samples (IO-4.2) will be compared to hourly continuous SO<sub>2</sub> monitoring data at the conclusion of the study, and a statement about method comparability will be made in the final report. The SO<sub>2</sub> data from two different methods is expected to agree within +/- 25% of one another, on average, over a 24-hour time period, and will be calculated as such.

**A8. Special Training /Certifications**

Field personnel participating in this study have been deemed competent to perform air sampling duties in accordance with the requirement set forth in the *SESD Operating Procedure for Training*, SESDPROC-007-R2, and are eligible to perform air sampling duties as indicated in *SESD's Table of Authorizations* as of the writing of this QAPP.

**A9. Documents and Records**

The field data will be provided to APTMD as a final report and will be prepared in accordance with the requirements of the *SESD Operating Procedure for Report Preparation and Distribution*, SESDPROC-003-R3. All field observations, measurements and sampling activities supporting the field investigation will be recorded and documented according to the *SESD Operating Procedure for Logbooks*, SESDPROC-010-R3. Project files will be maintained according to the *SESD Operating Procedure for Control of Records*, SESDPROC-002-R4.

**SECTION B: Data Generation and Acquisition**

**B1. Sampling Design**

**Locations**

A Primary sampling location within the town of Yellow Bluff will be chosen based upon discussion with local officials, as well as accessibility to shelter and electrical power resources. One primary location within the town of Yellow Bluff is adequate, as variations in meteorological and exposure conditions within the town are likely to be minimal due to 1) the geographically small area that the town occupies in relation to the IP facility, and 2) the close proximity to the IP facility itself. The sampling will take place



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as one continuous event, designated to occur during a cooler seasonal time (between November 2010 and February 2011) over a three week. One Background location will be chosen that is far enough away from Yellow Bluff as to likely be less affected by the IP facility. Currently, the Primary sampling location is likely to be at the Yellow Bluff Town Hall, located at 81 Park Avenue, within the Town of Yellow Bluff, Alabama. The Background location with likely be approximately 15 miles from Yellow Bluff, within the vicinity of the Roland Cooper State Park, located at 285 Deer Run Drive, in Camden, Alabama (Figure 2). These locations are subject to modification based upon the final reconnaissance. Siting criteria for both locations will adhere to 40 CFR Part 58, Appendix E as closely as possible. However, for this special purpose, source-oriented study, some exceptions may be unavoidable due to restrictions in shelter and electrical power resources. Approximately seven additional locations for performing Corrosion Classification Coupon (CCC) monitoring will be chosen at the discretion of SESD field investigators in cooperation with Yellow Bluff public officials from a list of locations that was visited during an initial reconnaissance (SESD Project #10-0670). The final locations for CCC deployment will be described in the final report.

#### **Continuous**

Monitoring for H<sub>2</sub>S and SO<sub>2</sub> will occur continuously for approximately five days at two locations, the Primary sampling location, and the Background sampling location. To allow for a more complete understanding of the meteorological conditions associated with pollutant concentrations, wind speed and direction will be recorded at the Primary sampling location at the same time that H<sub>2</sub>S and SO<sub>2</sub> is being monitored.

#### **Manual**

Monitoring for VOCs, aldehydes, and reactive gases / particles (IO-4.2) will also occur at two locations, the Primary sampling location, and the Background sampling location. All Manual samples will be collected over a 24-hour period and later analyzed using their independent methods. All three Manual parameters will be sampled for concurrently, at both locations, on three different days within the same continuous monitoring time period.

#### **Corrosion**

Monitoring will be performed using Corrosion Classification Coupons (CCC). The CCC method is a passive method that measures the buildup of corrosion on a strip of metal over time. This method is designed to determine if there are conditions present that contribute to accelerated rates of corrosion. It is not an EPA-approved air monitoring method and the sample results can not be definitively linked to ambient air quality data. However, it will be used as a screening, comparative method in this study, to help evaluate its efficacy. The data generated from the CCC method will be considered ancillary data. The corrosion coupons will be deployed at the Primary and Background sampling locations, as well as at approximately seven other locations within Yellow Bluff, for approximately three weeks.

Sample nomenclature for all samples will be defined during the sampling event. Air is the only matrix being analyzed during this sampling event. The number of samples, including duplicates and other QC samples, and their respective analyses are listed in Table 2.



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Table 2. Media, number of samples, and analyses.

Media	Number of Samples	Analyses
Annular denuders and filter stack.	10	Reactive gases and particles PM2.5 speciation (IO-4.2)
DNPH cartridge	10	Aldehydes
6-liter stainless steel evacuated canister.	10	VOCs
Continuous analyzer	Reported as one-hour averages.	H <sub>2</sub> S/SO <sub>2</sub>
Corrosion Coupon	20	Corrosion

**B2. Sampling Methods, General Procedures**

Sampling methods and procedures used during this study will be consistent with the *SESD Operating Procedure for Ambient Air Sampling, SESDPROC-303-R2 (with the exception of the CCC method)*.

**Continuous Monitoring**

Monitoring for H<sub>2</sub>S and SO<sub>2</sub> will be performed using a Thermo Electron Corporation's pulsed fluorescence H<sub>2</sub>S/SO<sub>2</sub> analyzer, model 450C. Two of these instruments will be deployed during the study. One will be located at the Primary monitoring location in Yellow Bluff, and the other will be deployed at the Background location. The monitors will be deployed in sheltered, air-conditioned environments per manufacturer's instructions. A probe line will be attached such that the monitor can sample the ambient air outside the shelter. The monitor will sample the air continuously thru a Teflon probe line with a Teflon Savillex filter attached at the inlet. Quality Control checks will be performed at least daily. The instrument and data logger will continue to operate in the normal operating mode during QC checks, and the channel will be placed in maintenance mode. Continuous sampling will last for a period of approximately five days. The Thermo 450C will be attached to an ESC 8832 data logger. The continuous monitoring data will be stored within an ESC 8832 data logger as one-minute averages for QA purposes, but will ultimately be reported as one-hour averages. An RM Young Model 05305 Wind Monitor-AQ (or similar) portable meteorological monitoring instrument will be located at the Primary monitoring site. Wind speed and direction will be continuously monitored and logged for a period of approximately five days. This data will also be logged in the ESC 8832 data logger. Data will be retrieved daily from the data logger using Agilaire's E-DAS software.

**Manual Sampling**

A total of ten Manual samples for the *Determination of Reactive Acidic and Basic Gases and Strong Acidity of Atmospheric Fine Particles (<2.5µm) Method IO-4.2* will be collected using URG-3000-02BAM outdoor sampling pump and the URG-2000 insulated sampling box. The URG-2000 insulated sampling box will be deployed outside on a tripod. Three days of Manual sampling will occur. Six 24-hour samples (including daily duplicates) will be collected at the Primary sampling location. Three 24-



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hour samples will be collected concurrently at the Background location. The laboratory that will be providing the sample media and analytical support is RTI International (RTI), located in Research Triangle Park, North Carolina. SESD owns a number of the denuders and filter-stacks that are required for this analysis. The denuders and filter will be returned to RTI for reconditioning prior to the sampling event. There is a 30 day holding time for completed samples. All samples will be shipped to RTI in one shipment at the end of the study. Depending upon the configuration of denuders and filter-stacks, the method can be adjusted to obtain a number of different analyses. A copy of this method is available in Appendix D. The following is the list of IO-4.2 analytical parameters that are planned for this study:

Analyses, Gaseous  $\text{NH}_4$   
Analyses, Acid Gases ( $\text{SO}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ )  
Particulate Speciation, Ions ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{H}^+$ )  
Gravimetric  $\text{PM}_{2.5}$

Manual sampling for Aldehydes will be conducted according to *Formaldehyde Sampling with Dinitrophenylhydrazine Cartridges using Method TO-11A*. ATEC Model 100 Cartridge Samplers will be deployed outside on tripods and will be used to collect the 24-hour samples. Six samples, including duplicates, will be collected at the Primary Sampling location. Three samples will be collected at the Background location. The laboratory that will be providing sample media and analytical support is Eastern Research Group, Inc. (ERG), located in Morrisville, North Carolina. All samples will be shipped to ERG in one shipment at the end of the study. A copy of this method is available in the *SESD Operating Procedure for Ambient Air Sampling*, SESDPROC-303-R2, Section 3.1 (Appendix C).

Manual sampling for VOCs will be performed in accordance with the following method: *Volatile Organic Compound Sampling with SUMMA Electropolished Stainless Steel Canisters or Silcosteel Canisters using Method TO-15A*. The canisters will be supplied by SESD and will be deployed using SESD's mechanical flow controllers. The flow controllers will allow 24-hour time-integrated samples to be collected at a rate of approximately 3.5 cc/min. The flow controllers will have their flow-rates checked and will be cleaned using zero-air prior to the study. The canisters and flow controllers will be deployed outside on tripods. The samples will be hand-delivered to SESD at the conclusion of the study. A copy of this method is available in the *SESD Operating Procedure for Ambient Air Sampling*, SESDPROC-303-R2, Section 3.2 (Appendix C).

### Corrosion

Monitoring for corrosion will be performed using Corrosion Classification Coupons. Sample media and analytical support will be obtained from Purafil, located in Duluth, Georgia. The CCCs are composed of two strips of metal, one of copper and one of silver. The analytical method is a proprietary method that measures the amount of corrosion that develops on the metals strip (measured in angstroms) over a 30-day period. The strips are attached to a coupon holder. For this study, the coupon holders will be affixed to an outdoor structure for a maximum of approximately three weeks. The amount of time that the strips are exposed to ambient outdoor conditions will be recorded. Periodic visual inspections will be performed and photographs will be collected. If the strips begin to take on a dark, tarnished appearance, they will be removed prior to the end of the three week period, and possibly replaced with new strips. All samples





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will be shipped to Purafil at the end of the study. A copy of this method is available in Appendix E.

**B3. Sampling Handling and Custody**

All samples will be handled and custody maintained according to the following:

- SESD Analytical Support Branch Laboratory Operations and Quality Assurance Manual*, January 2009.
- SESD Operating Procedure for Sample and Evidence Management*, SESDPROC-005-R1.
- SESD Operating Procedure for Packing, Labeling and Shipping of Environmental and Waste Samples* SESDPROC-209-R1.
- SESD Ambient Air Sampling*, SESDPROC-303-R2.

**B4. Analytical Methods**

**LABORATORY**

**METHOD**

<b>SESD:</b>	Continuous monitoring of hydrogen sulfide and sulfur dioxide using Thermo Electron Corporation Model 450C Pulsed-Fluorescence analyzers.  Volatile Organic Compound Sampling with SUMMA® Electropolished Stainless Steel Canisters or Silcosteel® Canisters using Method TO-15A.
<b>ERG:</b>	Formaldehyde Sampling with Dinitrophenylhydrazine Cartridges using Method TO-11A
<b>RTI</b>	Method IO-4.2 DETERMINATION OF REACTIVE ACIDIC AND BASIC GASES AND STRONG ACIDITY OF ATMOSPHERIC FINE PARTICLES (<2.5µm)
<b>Purafil</b>	Corrosion Classification Coupon – Environmental Monitoring Procedure.

**B5. Quality Control**

<b>Field:</b>	<p><b>Continuous</b></p> <p>Consistent with the operation of similar continuous monitors, the Thermo 450Cs will be calibrated upon installation. Calibration involves supplying a certified gas of known concentration to a dilution calibrator, and then configuring the dilution calibrator to supply calibration gases at multiple concentrations to the analyzer. The analyzer is then adjusted such that its readings are consistent with the known concentration values. An Environics model 6100 calibrator will be used for this study. A Precision, Zero, Span (PZS) check will be performed at the beginning of</p>
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the study before data collection begins, in the event of malfunction or repair, a minimum of once every day, and at the end of the study. A PZS involves challenging the analyzer with certified gas concentrations while the instrument is in its normal operating mode. For SO<sub>2</sub> a precision point of 140 parts per billion (ppb) will be used. For H<sub>2</sub>S a precision point of 145 ppb will be used. A zero point is generated using exclusively zero air that is supplied thru the dilution calibration system. A span point is a gas concentration that is generated that is within +/- 80% of the full-scale of the instrument. Full-scale for both SO<sub>2</sub> and H<sub>2</sub>S will initially be set at 200 ppb. If it becomes necessary to adjust the full-scale set points due to higher than anticipated ambient concentrations, then it will be documented in site logbooks. No adjustments are made to the analyzer during a PZS check. The passing criteria for the zero point will be 0 +/- 5.0 ppb. The passing criteria for the precision and span points will be within +/- 10% of the true value. If the passing criteria are not met during a PZS check then the data that has been collected since the previous PZS will have qualifiers attached to it that will appear in the final report. Trouble shooting steps (as dictated by the instrument manual) will be initiated, and another PZS will be attempted. If the PZS fails a second time, then the instrument will be recalibrated. Additional checks may be conducted at lower concentrations for both H<sub>2</sub>S and SO<sub>2</sub> in order to assess linearity, accuracy, and precision of the instrumentation at lower ambient concentrations, but will not be subject to the same +/- 10% passing criteria. All checks will be documented in field logbooks.

**Manual**

A duplicate (simultaneous collected, and located within 3 meters) sample will be collected at the Primary sampling location on all three sampling days for all Manual methods. In addition, a field blank will be collected for both the IO-4.2 and the aldehyde samples. A field blank refers to a sample in which sample media is placed in the sampling equipment for the same time period as a typical sample, but no sample air is allowed to flow thru the sample media. A VOC trip blank will also be collected. A VOC trip blank is a SUMMA canister that is transported to the field and exposed to the same environmental and handling conditions, but it not opened to the ambient air.

**Corrosion**

At least four (20%) duplicate corrosion samples will be deployed and collected. Duplicate samples will be samples in which two or more corrosion coupons holders are deployed at the same structure, and will be located within 12-inches of one another. The duplicated samples are intended to provide a measure of method precision. One field blank will be collected during the course of the study. The field blank will not be exposed as a typical sample, but is intended to measure the effects of shipping and handling.



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<b>Laboratory:</b>	To better evaluate the Manual analytical methods, and the quality of the data that is received from the various laboratories, the identity of duplicate Manual samples will be blind to the laboratories.
<b>B6. Instrument/Equipment Testing, Inspection and Maintenance</b>	
<p>All instrumentation used for sampling and collecting data will be used in the manner that is recommended by the manufacturers and/or <i>SESD Ambient Air Sampling, SESDPROC-303-R2</i>. In addition, the equipment will be managed in accordance with <i>SESD Operating Procedure for Equipment Inventory and Management, SESDPROC-108-R2</i>.</p>	
<b>B7. Instrument/Equipment Calibration and Frequency</b>	
<p>Flow checks will be performed on the all air monitoring equipment, as well the Environics 6100 gas dilution calibrator system, at the beginning and end of the project. Flows must fall into the acceptable range that is specified by the manufacturer for each individual sampler. Flow checks will be performed on the VOC mechanical flow controllers at the beginning of the project only, and must be between 3.0 and 4.0 cc/min. Measurements from the vacuum gauges on the individual VOC flow controllers will be used to ensure adequate sample volumes are achieved for each 24-hour sample.</p>	
<b>B8. Inspection /Acceptance for Supplies and Consumables</b>	
<p>All critical supplies and consumables for this field investigation are inspected and maintained in accordance with the following procedures:</p> <p><i>SESD Operating Procedure for Purchasing of Services and Supplies, SESDPROC-015-R2.</i>  <i>SESD Operating Procedure for Equipment Inventory and Management, SESDPROC-108-R2.</i>  <i>SESD Operating Procedure for Field Sampling Quality Control, SESDPROC-011-R2.</i></p> <p>The SESD Field Quality Manager and the Branch Quality Assurance Officers are responsible for ensuring that these requirements are met.</p>	
<b>B9. Non-direct Measurements:</b>	
N/A	
<b>B10. Data Management</b>	
<p>The field project leader will be responsible for ensuring that all requirements for data management are met. All data generated for this field investigation, whether hand-recorded or obtained using an electronic data logger will be recorded, stored and managed according to the following procedures:</p> <p><i>SESD Operating Procedure for Control of Records, SESDPROC-002-R4.</i>  <i>SESD Operating Procedures for Logbooks, SESDPROC-010-R3.</i></p>	



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**SECTION C: Assessment/Oversight**

**C1. Assessments and Response Actions**

Assessments will be conducted during the field investigation according to the *SESD Operating Procedure for Project Planning*, SESDPROC-016-R1, to ensure the QAPP is being implemented as approved. The Project Leader is responsible for all corrective actions while in the field.

**C2. Reports to Management**

The Project Leader will be responsible for notifying the Project Manager (Requestor) and appropriate SESD management if any circumstances arise during the field investigation that may adversely impact the quality of the data collected.

**SECTION D: Data Validation and Usability**

**D1. Data Review, Verification, and Validation**

All analytical data will be provided by the SESD Analytical Support Branch and reviewed, verified and validated in accordance with the *SESD Analytical Support Branch Laboratory Operations and Quality Assurance Manual*, January 2009.

All data derived from SESD field measurements will be reviewed, verified, and validated in accordance with the *SESD Operating Procedure for Report Preparation and Distribution*, SESDPROC-003-R3.

**D2. Verification and Validation Methods**

All analytical data will be provided by the SESD Analytical Support Branch and reviewed, verified and validated in accordance with the *SESD Analytical Support Branch Laboratory Operations and Quality Assurance Manual*, January 2009.

All data derived from SESD field measurements will be reviewed, verified, and validated in accordance with the *SESD Operating Procedure for Report Preparation and Distribution*, SESDPROC-003-R3.

**D3. Reconciliation with User Requirements**

The usability of all data derived from SESD field sampling and measurements conducted during this field investigation will be evaluated in accordance with the *SESD Operating Procedure for Report Preparation and Distribution*, SESDPROC-003-R3.

**\*\*Footnotes:** This Quality Assurance Project Plan (QAPP) has been prepared and approved according to the EPA Requirements for Quality Assurance Project Plans (EPA QA/R5 EPA/240/B-01/003), U.S. Environmental Protection Agency, Office of Environmental Information, Washington, DC, March 2001(USEPA, 2001). This document will be used to ensure that the environmental data collected for this project are of the type and quality for the intended purposes. **This document is for SESD use only.**



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# FIGURES



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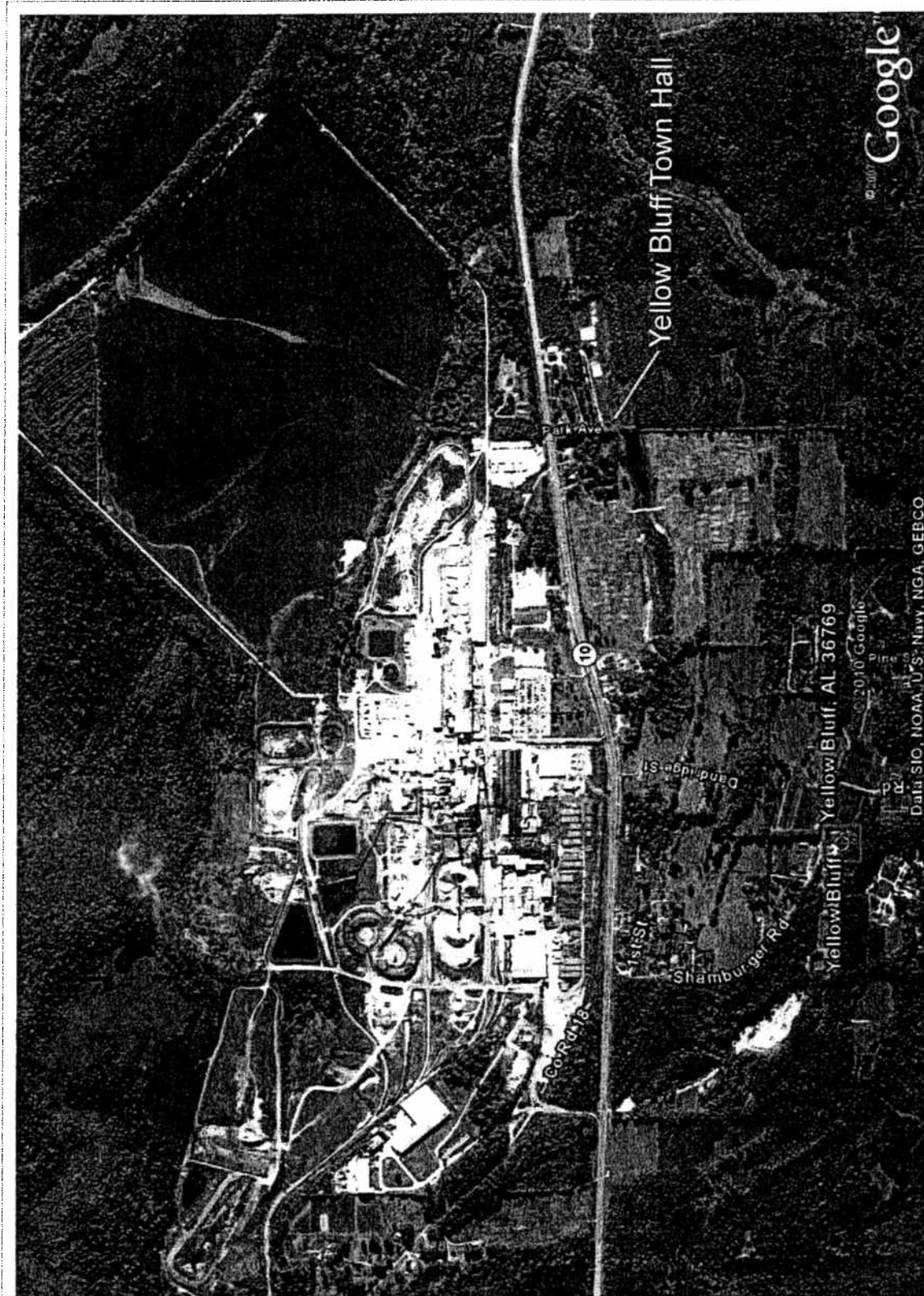


Figure 1  
Town of Yellow Bluff, AL and  
International Paper - Pine Hill Mill Facility





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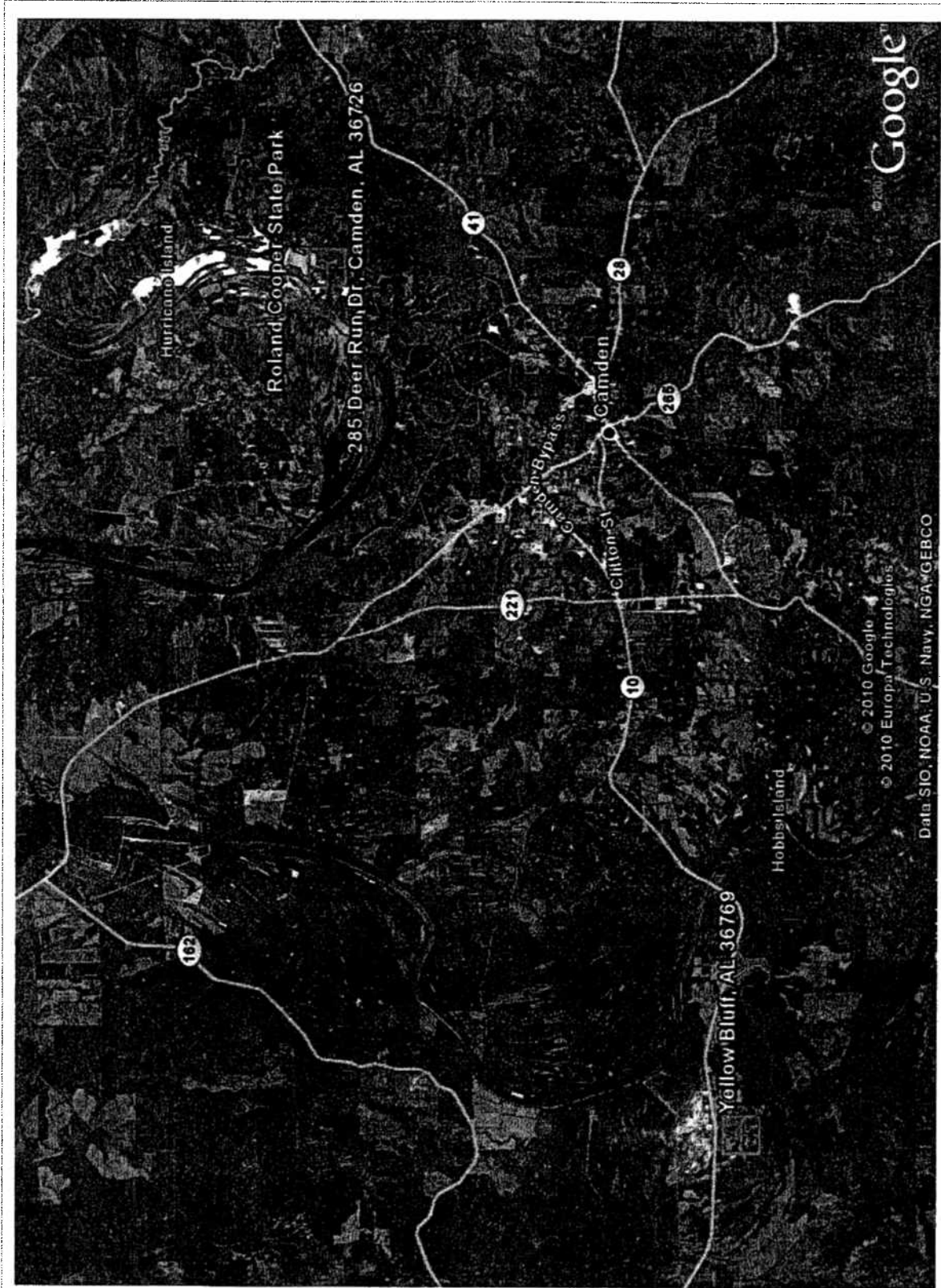


Figure 2  
Town of Yellow Bluff, AL and  
Roland Cooper State Park







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# APPENDICES





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# Appendix A



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Appendix A – TRI Data (4 pages)



Toxics Release Inventory (TRI)

Last updated on Tuesday, July 13, 2010

You are here: [EPA Home](#) [Envirofacts](#) [TRI](#) [Envirofacts Report](#)



Envirofacts Report

Query executed on JUL-13-2010  
 Results are based on data extracted on JUL-09-2010

Click on "View Facility Information" to view EPA Facility Information for the facility.

<b>Facility Name:</b>	INTERNATIONAL PAPER PINE HILL MILL	<b>Mailing Name:</b>	INTERNATIONAL PAPER PINE HILL MILL
<b>Address:</b>	7600 HWY 10 W PINE HILL AL 36769	<b>Mailing Address:</b>	PO BOX 250 PINE HILL AL 36769
<b>County:</b>	WILCOX	<b>Region:</b>	4
<b>Facility Information:</b>	<a href="#">View Facility Information</a>	<b>TRI ID:</b>	3676WNTRMT76HIG
<b>TRI Preferred Latitude:</b>		<b>FRS ID:</b>	110039204278
<b>Public Contact:</b>	HELEN HAWKINS	<b>TRI Preferred Longitude:</b>	
<b>Parent Company:</b>	INTERNATIONAL PAPER	<b>Phone:</b>	3343615004
		<b>Parent CLINS:</b>	001316581
		<b>CLINS Number:</b>	614743698

Starting with Reporting Year 2008, TRI facilities began reporting NAICS codes, instead of SIC codes, to identify their Primary Business Activities.

NAICS Codes for 2008

NAICS CODE	PRIMARY	NAICS DESCRIPTION
322121	YES	Paper (except Newsprint) Mills

The above information comes from 2008, which was the last year NAICS code data was reported for this facility. The earliest NAICS code data on file for this facility was reported in 2008.



Map this facility using one of Envirofact's mapping utilities.

Total Aggregate Releases of TRI Chemicals to the Environment:

For all releases estimated as a range, the mid-point of the range was used in these calculations. This table summarizes the releases reported by the facility. NR - signifies nothing reported by this facility for the corresponding medium.

Total Aggregate Releases of TRI Chemicals excluding Dioxin and Dioxin-like Compounds (Measured in Pounds)

Media	2008
Air Emissions	902737.23
Surface Water Discharges	871810.059
Releases to Land	NR



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Underground Injection	NR
Total On-Site Releases	1774547.289
Transfer Off-Site to Disposal	NR
Total Releases	1774547.289

Graphic Summary of 2008 Releases

Total Aggregate Releases of Dioxin and Dioxin-Like Compounds  
 (Measured in Grams)

Media	2008
Air Emissions	1.421649
Surface Water Discharges	3.02814
Releases to Land	NR
Underground Injection	NR
Total On-Site Releases	4.449789
Transfer Off-Site to Disposal	NR
Total Releases	4.449789

Graphic Summary of 2008 Releases

TRI Chemicals Reported on Form A:

Please note that there were no chemicals reported on Form A for this facility

NOTE:

All chemicals reported below have release or transfer amounts greater than zero. To see a list of all chemicals reported by this facility click [here](#).

Names and Amounts of Chemicals Released to the Environment by Year.

For all releases estimated as a range, the mid-point of the range was used in these calculations. NR - signifies nothing reported for this facility by the corresponding medium. Rows with all "0" or "NR" values were not listed.

Chemical Name	Media	Unit Of Measure	2008
ACETALDEHYDE (TRI Chemical ID: 000075070)	AIR FUG	Pounds	12260
ACETALDEHYDE (TRI Chemical ID: 000075070)	AIR STACK	Pounds	34000
ACETALDEHYDE (TRI Chemical ID: 000075070)	WATER	Pounds	3900
AMMONIA (TRI Chemical ID: 007664417)	AIR FUG	Pounds	500
AMMONIA (TRI Chemical ID: 007664417)	AIR STACK	Pounds	104577
AMMONIA (TRI Chemical ID: 007664417)	WATER	Pounds	4952
BARIUM (TRI Chemical ID: 007440393)	AIR STACK	Pounds	1100
BENZON(1,2,3,4-DIPYRILENE (TRI Chemical ID: 000191242)	AIR STACK	Pounds	1
CATECHOL (TRI Chemical ID: 000120809)	AIR FUG	Pounds	890
CATECHOL	WATER	Pounds	895

[http://easpub.epa.gov/enviro/tris\\_control/tris\\_print?tris\\_id=3676WNTRNT76HIG](http://easpub.epa.gov/enviro/tris_control/tris_print?tris_id=3676WNTRNT76HIG)



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(TRI Chemical ID: 000120009)			
DIOXIN AND DIOXIN-LIKE COMPOUNDS (TRI Chemical ID: N150)	AIR STACK	Grams	1.421649
DIOXIN AND DIOXIN-LIKE COMPOUNDS (TRI Chemical ID: N150)	WATER	Grams	3.02814
ETHYLENE GLYCOL (TRI Chemical ID: 000107211)	AIR FLG	Pounds	288
ETHYLENE GLYCOL (TRI Chemical ID: 000107211)	WATER	Pounds	576000
FORMALDEHYDE (TRI Chemical ID: 000050000)	AIR FLG	Pounds	25877
FORMALDEHYDE (TRI Chemical ID: 000050000)	AIR STACK	Pounds	26000
FORMALDEHYDE (TRI Chemical ID: 000050000)	WATER	Pounds	240
HYDROCHLORIC ACID (1995 AND AFTER "ACID AEROSOLS" ONLY) (TRI Chemical ID: 007647010)	AIR STACK	Pounds	65400
LEAD COMPOUNDS (TRI Chemical ID: N420)	AIR STACK	Pounds	94
LEAD COMPOUNDS (TRI Chemical ID: N420)	WATER	Pounds	595
MANGANESE COMPOUNDS (TRI Chemical ID: N450)	AIR STACK	Pounds	461
MANGANESE COMPOUNDS (TRI Chemical ID: N450)	WATER	Pounds	22654
MERCURY COMPOUNDS (TRI Chemical ID: N458)	AIR STACK	Pounds	17.03
MERCURY COMPOUNDS (TRI Chemical ID: N458)	WATER	Pounds	.259
METHANOL (TRI Chemical ID: 000067561)	AIR FLG	Pounds	122322
METHANOL (TRI Chemical ID: 000067561)	AIR STACK	Pounds	452002
METHANOL (TRI Chemical ID: 000067561)	WATER	Pounds	3635
NABAM (TRI Chemical ID: 000142596)	AIR FLG	Pounds	59
NABAM (TRI Chemical ID: 000142596)	WATER	Pounds	37821.8
NICKEL COMPOUNDS (TRI Chemical ID: N495)	AIR STACK	Pounds	71.7
NICKEL COMPOUNDS (TRI Chemical ID: N495)	WATER	Pounds	283
NITRATE COMPOUNDS (TRI Chemical ID: N511)	WATER	Pounds	178077
PHENOL (TRI Chemical ID: 000108952)	AIR FLG	Pounds	40
PHENOL (TRI Chemical ID: 000108952)	AIR STACK	Pounds	3121
POLYCYCLIC AROMATIC COMPOUNDS (TRI Chemical ID: N590)	AIR STACK	Pounds	113.5
SODIUM DIMETHYLDITHIOCARBAMATE (TRI Chemical ID: 000128041)	AIR FLG	Pounds	59
SODIUM DIMETHYLDITHIOCARBAMATE (TRI Chemical ID: 000128041)	WATER	Pounds	37841
SULFURIC ACID (1994 AND AFTER "ACID AEROSOLS" ONLY) (TRI Chemical ID: 007664939)	AIR STACK	Pounds	40309

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VANADIUM COMPOUNDS (TRI Chemical ID: N770)	AIR STACK	Pounds	12748
VANADIUM COMPOUNDS (TRI Chemical ID: N770)	WATER	Pounds	725
ZINC COMPOUNDS (TRI Chemical ID: N982)	AIR STACK	Pounds	427
ZINC COMPOUNDS (TRI Chemical ID: N982)	WATER	Pounds	4191

**Discharge of Chemicals into Streams or Bodies of Water:**

For all releases estimated as a range, the mid-point of the range was used in these calculations. Rows with Release Amount equal to "0" were not listed.

**WATER**

Chemical Name (TRI Chemical ID)	Year	Unit of Measure	Release Amount	Stream Or Body of Water
ACETALDEHYDE (TRI Chemical ID: 000075070)	2008	Pounds	3900	ALABAMA RIVER
AMMONIA (TRI Chemical ID: 007664417)	2008	Pounds	4952	ALABAMA RIVER
CATECHOL (TRI Chemical ID: 000120809)	2008	Pounds	895	ALABAMA RIVER
DIOXIN AND DIOXIN-LIKE COMPOUNDS (TRI Chemical ID: N150)	2008	Grams	3.02814	ALABAMA RIVER
ETHYLENE GLYCOL (TRI Chemical ID: 000107211)	2008	Pounds	576000	ALABAMA RIVER
FORMALDEHYDE (TRI Chemical ID: 000050000)	2008	Pounds	240	ALABAMA RIVER
LEAD COMPOUNDS (TRI Chemical ID: N420)	2008	Pounds	595	ALABAMA RIVER
MANGANESE COMPOUNDS (TRI Chemical ID: N450)	2008	Pounds	22654	ALABAMA RIVER
MERCURY COMPOUNDS (TRI Chemical ID: N458)	2008	Pounds	.259	ALABAMA RIVER
METHANOL (TRI Chemical ID: 000067561)	2008	Pounds	3635	ALABAMA RIVER
NAGAM (TRI Chemical ID: 000142596)	2008	Pounds	37821.8	ALABAMA RIVER
NICKEL COMPOUNDS (TRI Chemical ID: N495)	2008	Pounds	283	ALABAMA RIVER
NITRATE COMPOUNDS (TRI Chemical ID: N511)	2008	Pounds	178077	ALABAMA RIVER
SODIUM DIMETHYLDITHIOCARBAMATE (TRI Chemical ID: 000128041)	2008	Pounds	37841	ALABAMA RIVER
VANADIUM COMPOUNDS (TRI Chemical ID: N770)	2008	Pounds	725	ALABAMA RIVER
ZINC COMPOUNDS (TRI Chemical ID: N982)	2008	Pounds	4191	ALABAMA RIVER

**Transfer of Chemicals to Off-Site Locations other than POTWs:**

Please Note that there were no Transfer of Chemicals to Off-Site Locations other than POTWs. Rows with Total Transfer Amount equal to "0" were not listed.

**Summary of Waste Management Activities**

Please note that chemical amounts shown here are not included in Total Aggregate Releases shown above.

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# Appendix B



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# Selected Health Status Indicators



Jointly produced to assist those seeking to improve health care in rural Alabama

By

The Office of Primary Care and Rural Health,  
Alabama Department of Public Health  
and  
The Alabama Rural Health Association

Special thanks to the National Rural Health Association for funding assistance in the production of this publication.

July 2009



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**SELECTED HEALTH STATUS INDICATORS**  
**United States, Alabama, and Wilcox County**

Indicators	United States		Alabama		Wilcox County	
	Number	Pct. of Total	Number	Pct. of Total	Number	Pct. of Total
<b>2007 Population</b>						
Total	301,621,157	100.0	4,627,851	100.0	12,779	100.0
African American (alone)	38,756,452	12.8	1,224,496	26.5	9,223	72.2
White (alone)	241,166,890	80.0	3,287,453	71.0	3,491	27.3
American Indian (alone)	2,938,436	1.0	24,315	0.5	19	0.1
Asian (alone)	13,366,154	4.4	44,086	1.0	21	0.2
Hispanic	45,504,311	15.1	124,741	2.7	144	1.1
Age 19 Years or Less	82,361,752	27.3	1,251,776	27.0	4,056	31.7
Age 65 Years or More	37,887,958	12.6	707,781	15.3	1,813	14.2
Age 85 Years or More	5,512,298	1.8	82,025	1.8	307	2.4
<b>Population Change</b>						
1910 - 2000	91,972,266 to 281,421,906	206.0	2,138,093 to 4,447,100	108.0	33,810 to 13,183	-61.0
2000 - 2025 Projected	281,421,906 to 349,695,000	24.3	4,447,100 to 5,385,997	21.1	13,183 to 13,021	-1.2
Age 65+: 2000 - 2025 Projected	34,991,753 to 63,042,500	80.2	579,907 to 999,769	72.4	1,810 to 2,460	35.9
Hispanic: 1990 - 2007 Estimated	22,354,059 to 45,504,311	103.6	24,629 to 124,741	406.5	40 to 144	260.0
<b>Income Related Indicators</b>						
Population Below Poverty Level - 2007	38,052,247	13.0%	750,197	16.6%	4,507	35.7%
Children Under 18 Below Poverty Level - 2007	13,097,100	18.0%	261,151	23.6%	1,709	46.7%
Per Capita Personal Income - 2006	N.A.	\$36,714	N.A.	\$30,894	N.A.	\$18,895
Medicaid Eligible Population - 2007	N.A.	N.A.	932,521	19.8%	5,306	40.8%
Medicaid Eligible Children (Under 21) - 2007	N.A.	N.A.	514,486	38.1%	2,620	59.0%
Medicaid Births - 2007	N.A.	N.A.	30,624	48.5%	113	66.9%
<b>Access to Health Care Indicators</b>						
Primary Care Physicians - 2006 (Per 10,000 Pop.)	209,550	7.2	3,044	6.5	4	3.1
Dentists - 2007 (Per 10,000 Pop.)	86,110	2.9 (2006)	1,996	4.3	2	1.6
Psychiatrists - 2006 (Per 10,000 Pop.)	24,730	0.9	298	0.6	0	0.0
Hospital Beds - 2009 (Per 10,000 Pop.)	N.A.	N.A.	16,814	36.3	32	25.0
Households With No Vehicle - 2000	10,861,067	10.3%	143,594	8.3%	959	20.1%
Uninsured Population Under 65 Years of Age - 2006						





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**SELECTED HEALTH STATUS INDICATORS - continued**  
**United States, Alabama, and Wilcox County**

Indicators	United States		Alabama		Wilcox County	
	Number in 2005	Rate per 100,000 Pop.	Number in 2005 - 2007	Rate per 100,000 Pop.	Number in 2003 - 2007	Rate per 100,000 Pop. <sup>1</sup>
<b>Cause of Death Indicators</b>						
<b>All Causes</b>	<b>2,448,017</b>	<b>825.9</b>	<b>139,039</b>	<b>1,010.6</b>	<b>734</b>	<b>1,154.1</b>
Septicemia	34,136	11.5	2,407	17.5	16	25.2
Human Immunodeficiency Virus (HIV) disease	12,543	4.2	536	3.9	4	6.3
<b>Cancer</b>	<b>559,312</b>	<b>188.7</b>	<b>29,475</b>	<b>214.2</b>	<b>150</b>	<b>235.9</b>
Lip, Oral Cavity, Pharynx, and Esophagus	21,272	7.2	1,034	7.5	8	12.6
Stomach	11,514	3.9	549	4.0	7	11.0
Colon, Rectum, and Anus	53,252	18.0	2,709	19.7	18	28.3
Liver and Intrahepatic Bile Ducts	16,076	5.4	773	5.6	3	4.7
Pancreas	32,760	11.1	1,625	11.8	9	14.2
Trachea, Bronchus, and Lung	159,292	53.7	9,233	67.1	32	50.3
Melanoma of Skin	8,345	2.8	463	3.4	2	3.1
Breast (female)	41,116	27.3	2,018	28.4	13	37.7
Cervix Uteri, Corpus Uteri, and Uterus (female)	11,020	7.3	512	7.2	3	8.7
Ovary (female)	14,787	9.8	769	10.8	4	11.6
Prostate (male)	28,905	19.8	1,556	23.4	15	51.5
Kidney and Renal Pelvis	12,517	4.2	591	4.3	1	1.6
Bladder	13,253	4.5	569	4.1	3	4.7
Meninges, Brain, Other Central Nervous System	13,152	4.4	625	4.5	0	0.0
Hodgkin's Disease	55,028	18.6	56	0.4	0	0.0
Non-Hodgkin's Lymphoma	20,873	7.0	969	7.0	3	4.7
Leukemia	21,623	7.3	1,063	7.7	10	15.7
Multiple Myeloma and Immunoproliferative Neoplasms	11,200	3.8	636	4.6	2	3.1
Diabetes Mellitus	75,119	25.3	4,138	30.1	26	40.9
Nutritional Deficiencies	3,183	1.1	228	1.7	3	4.7
Parkinson's Disease	19,544	6.6	907	6.6	5	7.9
Alzheimer's Disease	71,599	24.2	4,487	32.6	27	42.5
<b>Major Cardiovascular Diseases</b>	<b>856,030</b>	<b>288.2</b>	<b>48,383</b>	<b>351.7</b>	<b>300</b>	<b>471.7</b>
<b>Heart Diseases</b>	<b>652,562</b>	<b>220.0</b>	<b>36,995</b>	<b>268.9</b>	<b>234</b>	<b>367.9</b>



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**SELECTED HEALTH STATUS INDICATORS - continued**  
**United States, Alabama, and Wilcox County**

Indicators	United States		Alabama		Wilcox County	
	Number	Measure	Number	Measure	Number	Measure
<b>Nativity Related Indicators</b>						
Infant Mortality Rate Per 1,000 Births (2005 - 2007)	28,534	6.9	1,771	9.5	4	7.6
Low Weight Births - 2007 (Percent of All Births)	331,772 (2004)	8.1 %	6,695	10.4 %	23	13.5%
Births to Teens (10-19) - 2007 (Percent of All Births)	422,043 (2004)	10.3 %	8,776	13.7 %	22	12.9%
Births With Less Than Adequate Prenatal Care - 2007 (Percent of All Births)	N.A.	N.A.	16,116	25.4%	62	36.5%
Tobacco Use During Pregnancy - 2007 (Percent of All Births)	419,429	10.2%	7,703	12.0 %	12	7.1%
Births Occurring Outside of the Mother's County of Residence - 2007 (Percent of All Births)	N.A.	N.A.	20,149	31.4 %	168	98.8%
Births to Undereducated Women - 2007	N.A.	N.A.	11,845	18.5 %	25	14.7%
<b>Other Indicators</b>	<b>Number</b>	<b>Measure</b>	<b>Number</b>	<b>Measure</b>	<b>Number</b>	<b>Measure</b>
Age 65+ With "Home Bound" Disability - 2000	6,795,517	19.4 %	139,401	24.0 %	405	22.4%
Age 25+ With Less Than High School Education - 2000	35,715,625	19.6 %	714,081	24.7 %	3,228	40.5%
Receiving Medicare Disability - 2005 (Percent of Total Population)	7,359,542	2.4 %	189,874	4.1 %	932	7.3%
Obese - 2003 (Percent of Total Population)	Not Comparable	Not Comparable	1,073,329	23.3 %	3,550	27.4%
Accidental Deaths Occurring Outside of a Health Care Facility: 2005-07 (Percent of All Accidental Deaths)	N.A.	N.A.	4,215	56.2%	41	89.1%
Life Expectancy at Birth - 2007	N.A.	77.9 years	N.A.	75.4 years	N.A.	73.0 years
Sexually Transmitted Disease Cases Reported in 2008 (Per 10,000 Pop.)	1,349,333	45.9	35,235	76.1	109	132.2
Cumulative HIV Cases as of December 31, 2008 (Per 10,000 Pop.)	Not Comparable	Not Comparable	16,222	35.1	27	21.1
Families Being Counseled for Drug Issues by the Alabama Department of Mental Health During FY 2004 (Percent of All Families)	N.A.	N.A.	20,881	1.7 %	46	7.4%

Rates, percentages, etc based upon fewer than 16 events may not be statistically reliable for specific analyses. Caution should be exercised in using these indicators.



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## SELECTED HEALTH STATUS INDICATORS - continued

### United States, Alabama, and Wilcox County

Indicators	United States		Alabama		Wilcox County	
	Number in 2005	Rate per 100,000 Pop.	Number in 2005 - 2007	Rate per 100,000 Pop.	Number in 2003 - 2007	Rate per 100,000 Pop. <sup>1</sup>
<b>Major Cardiovascular Diseases - Continued</b>						
Ischemic Heart Diseases	446,687	150.4	17,326	125.9	59	92.8
Heart Failure	58,933	19.9	6,206	45.1	23	36.2
Cerebrovascular Diseases	143,579	48.4	8,318	60.5	56	88.1
Atherosclerosis	11,841	4.0	618	4.5	0	0.0
Pneumonia	61,189	20.6	2,748	20.0	14	22.0
Chronic Lower Respiratory Diseases	130,933	44.2	7,158	52.0	19	29.9
Chronic Liver Disease and Cirrhosis	27,530	9.3	1,450	10.5	6	9.4
Nephritis, Nephrotic Syndrome, and Nephrosis	43,901	14.8	3,110	22.6	18	26.3
<b>Accidents</b>	<b>117,809</b>	<b>39.7</b>	<b>7,295</b>	<b>53.0</b>	<b>53</b>	<b>83.3</b>
Motor Vehicle Accidents	45,343	15.3	3,544	25.8	30	47.2
Falls	19,656	6.6	498	3.6	2	3.1
Drowning and Submersion	3,582	1.2	219	1.6	1	1.6
Smoke, Fire, and Flames	3,197	1.1	281	2.0	3	4.7
Poisoning and Exposure to Noxious Substances	23,618	8.0	1,008	7.3	2	3.1
Intentional Self-Harm (suicide)	32,637	11.0	1,685	12.2	3	4.7
Assault (homicide)	18,124	6.1	1,340	9.7	11	17.3
<b>Causes of Death Groupings of Special Interest</b>						
Cause of Death Indicators	Number in 2005	Rate per 100,000 Pop.	Number in 2005 - 2007	Rate per 100,000 Pop.	Number in 2005 - 2007	Rate per 100,000 Pop. <sup>1</sup>
Cataclysmic Storms	874	0.3	11	0.1	1	1.6
Firearm Deaths (intentional self-harm, assault, legal intervention, and undetermined intent)	30,364	10.4	2,306	16.8	6	9.4
Drug-Induced Deaths	33,541	11.3	1,328	9.7	2	3.1
Alcohol-Induced Deaths	21,634	7.3	732	5.3	5	7.9



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## Sources of Information and Special Notes

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**Population Change 1910-2000:** U.S. Census Bureau, County Population Census Counts 1900-90, <http://www.census.gov/population/cencounts/all190090.txt> for 1910 data, U.S. Census Bureau, American FactFinder, Census 2000 Summary File 1 (SF 1) 100-Percent Data for 2000 data.

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**Births to Teenagers (Age 10-19) - 2007:** Alabama Department of Public Health, Center for Health Statistics, Special query of the 2006 Birth Statistics File.

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**Sexually Transmitted Disease Cases - 2008:** Alabama Department of Public Health, Division of STD Prevention and Control, Statistics, County Totals - 2008. <http://www.adph.org/STD/>

**Cumulative HIV Cases as of 12/31/2008:** Alabama Department of Public Health, Division of HIV/AIDS Prevention and Control, Statistics, Public Health Area (January - December 2008). <http://www.adph.org/aids/>  
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For additional information please contact the Office of Primary Care and Rural Health Development at (334) 206-5396 or the Alabama Rural Health Association at (334) 546-3502.



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# Appendix C



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<b>Region 4</b> <b>U. S. Environmental Protection Agency</b> <b>Science and Ecosystem Support Division</b> <b>Athens, Georgia</b>	
<b>OPERATING PROCEDURE</b>	
<b>Title: Ambient Air Sampling</b>	
<b>Effective Date:</b> October 30, 2009	<b>Number:</b> SESDPROC-303-R2
<b>Authors</b>	
<b>Name:</b> Richard Guillot <b>Title:</b> Environmental Scientist <b>Signature:</b> <i>Richard Guillot</i> <b>Date:</b> 10/30/09	
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**Revision History**

This table shows changes to this controlled document over time. The most recent version is presented in the top row of the table. Previous versions of the document are maintained by the SESD Document Control Coordinator.

History	Effective Date
<p>SESDPROC-303-R2, <i>Ambient Air Sampling</i>, replaces SESDPROC-303-R1.</p> <p><b>General</b> Corrected any typographical, grammatical and/or editorial errors.</p> <p><b>Title Page</b> Under Author changed Danny France to Richard Gniliot Under Approvals changed Branch Chief from Antonio Quinones to Archie Lee</p> <p><b>History:</b> Changed Field Quality Manager to Document Control Coordinator.</p> <p><b>Section 1.3:</b> Omitted reference to the H: drive. Changed the Field Quality Manager to the Document Control Coordinator.</p> <p><b>Section 2</b> All previous sections were deleted. New sections were added.</p> <p><b>Section 3</b> Section 3.1 was rewritten.</p> <p><b>Section 3.8</b> Removed to separate guidance document.</p> <p><b>Section 3.9</b> Removed to separate guidance document.</p>	<p>October 30, 2009</p>
<p>SESDPROC-303-R1, <i>Ambient Air Sampling</i>, replaces SESDPROC-303-R0.</p> <p><b>General</b> Corrected any typographical, grammatical and/or editorial errors.</p> <p><b>Title Page</b> Changed title for Antonio Quinones from Environmental Investigations Branch to Enforcement and Investigations Branch.</p> <p><b>Section 1.3</b> Updated information to reflect that the procedure is located on the H: drive of the LAN. Clarified Field Quality Manager (FQM) responsibilities.</p>	<p>November 1, 2007</p>

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Ambient Air Sampling

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SESDPROC-303-R2  
Ambient Air Sampling(303)\_AF.R2

Effective Date: October 30, 2009



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<p><b>Section 1.5</b> Updated referenced operating procedures due to changes in title names.</p> <p><b>Section 1.6.1</b> Corrected the title of the Safety, Health, and Environmental Management Program Procedures and Policy Manual.</p> <p><b>Section 1.6.2, 4<sup>th</sup> bullet</b> Added references to the CFR and IATA's Dangerous Goods Regulations.</p> <p><b>Section 1.7</b> Updated referenced operating procedures due to changes in title names. Alphabetized and revised the referencing style for consistency. Added two references (IATA and 49 CFR).</p>	
<p>SESDPROC-303-R0, <i>Ambient Air Sampling</i>, Original Issue</p>	<p>February 05, 2007</p>



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## 1 GENERAL INFORMATION

### 1.1 Purpose

This document describes general and specific procedures, methods and considerations to be used and observed when collecting ambient air samples for field screening or laboratory analysis. Air toxics, as used in this procedure, means air pollutants for which National Ambient Air Quality Standards have not been established. Criteria pollutants mean air pollutants for which National Ambient Air Quality Standards have been established.

### 1.2 Scope/Application

The procedures contained in this document are to be used by field personnel when collecting and handling ambient air samples in the field. On the occasion that SESD field personnel determine that any of the procedures described in this section are inappropriate, inadequate or impractical and that another procedure must be used to obtain an ambient air sample, the variant procedure will be documented in the field log book, along with a description of the circumstances requiring its use.

### 1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by SESD management, based on their knowledge, skills and abilities and have been tested in practice and reviewed in print by a subject matter expert. The official copy of this procedure resides on the SESD local area network (LAN). The Document control Coordinator (DCC) is responsible for ensuring the most recent version of the procedure is placed on the LAN and for maintaining records of review conducted prior to its issuance.

### 1.4 Quality Control

Quality control for sampling associated with ambient air monitoring is method specific. The sampling methods described in the sections that follow contain the quality control procedures appropriate for each method.

### 1.5 Records

Information generated or obtained by SESD personnel will be organized and accounted for in accordance with SESD records management procedures found in SESD Operating Procedure for Control of Records, SESDPROC-002. Field notes, recorded in a bound field logbook, will be generated, as well as chain-of-custody documentation in accordance with SESD Operating Procedure for Logbooks, SESDPROC-010 and SESD Operating Procedure for Sample and Evidence Management, SESDPROC-005.



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### 1.6 General Precautions

#### 1.6.1 Safety

Proper safety precautions must be observed when collecting ambient air monitoring samples. Refer to the SESD Safety, Health and Environmental Management Program (SHEMP) Procedures and Policy Manual and any pertinent site-specific Health and Safety Plans (HASPs) for guidelines on safety precautions. These guidelines, however, should only be used to complement the judgment of an experienced professional. Address chemicals that pose specific toxicity or safety concerns and follow any other relevant requirements, as appropriate.

#### 1.6.2 Procedural Precautions

The following precautions should be considered when collecting ambient air monitoring samples.

- Special care must be taken not to contaminate samples. This includes storing samples in a secure location to preclude conditions which could alter the properties of the sample. Samples shall be custody sealed during long-term storage or shipment.
- Collected samples are in the custody of the sampler or sample custodian until the samples are relinquished to another party.
- If samples are transported by the sampler, they will remain under his/her custody or be secured until they are relinquished.
- Shipped samples shall conform to all U.S. Department of Transportation (DOT) rules of shipment found in Title 49 of the Code of Federal Regulations (49 CFR parts 171 to 179), and/or International Air Transportation Association (IATA) hazardous materials shipping requirements found in the current edition of IATA's Dangerous Goods Regulations.
- Documentation of field sampling is done in a bound logbook.
- Chain-of-custody documents shall be filled out and remain with the samples until custody is relinquished.
- All shipping documents, such as bills of lading, etc., shall be retained by the project leader and stored in a secure place.



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**1.7 References**

Ambient Monitoring Technology Information Center (AMTIC) Internet Bulletin Board:  
PM<sub>2.5</sub> QA area (<http://www.epa.gov/ttn/amtic/pmqa.html>)

Compendium of Methods for the Determination of Toxic Organic Compounds in  
Ambient Air, Method TO-4A (pesticides and PCBs) and TO-13A (polynuclear aromatic  
compounds)

Compendium of Methods for the Determination of Toxic Organic Compounds in  
Ambient Air, Method TO-9A

Compendium of Methods for the Determination of Toxic Organic Compounds in  
Ambient Air, Method TO-11A

Compendium of Methods for the Determination of Toxic Organic Compounds in  
Ambient Air, Method TO-15A

International Air Transport Authority (IATA) Dangerous Goods Regulations, Most  
Recent Version

Neutronics Model RI-2002PA Portable Automotive Refrigerant Identifier Operation  
Instruction Manual

SESD Operating Procedure for Control of Records, SESDPROC-002, Most Recent  
Version

SESD Operating Procedure for Sample and Evidence Management, SESDPROC-005,  
Most Recent Version

SESD Operating Procedure for Logbooks, SESDPROC-010, Most Recent Version

SESD Operating Procedure for Field Sampling Quality Control, SESDPROC-011, Most  
Recent Version

SESD Operating Procedure for Equipment Inventory and Management, SESDPROC-108,  
Most Recent Version

SESD Operating Procedure for Field Equipment Cleaning and Decontamination,  
SESDPROC-205, Most Recent Version

SESD Operating Procedure for Packaging, Marking, Labeling and Shipping of  
Environmental and Waste Samples, SESDPROC-209, Most Recent Version

Tekran Model 2505 Mercury Vapour Calibration Unit User Manual

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Tekran Vapour Analyzer 2537A User Manual

Title 40 Code of Federal Regulations (CFR), Part 50, Appendix A - Reference Method for the Determination of Sulfur Dioxide in the Atmosphere (Pararosaniline Method), Most Recent Version

Title 40 CFR, Part 50, Appendix B - Reference Method for The Determination Of Suspended Particulate Matter In The Atmosphere (High Volume Method), Most Recent Version

Title 40 CFR, Part 50, Appendix C - Measurement Principle and Calibration Procedure for The Measurement of Carbon Monoxide in The Atmosphere (Non-Dispersive Infrared Photometry), Most Recent Version.

Title 40 CFR, Part 50, Appendix D-Measurement Principle and Calibration Procedure for The Measurement of Ozone in The Atmosphere, Most Recent Version

Title 40 CFR, Part 50, Appendix F - Measurement Principle and Calibration Procedure for The Measurement of Nitrogen Dioxide in The Atmosphere (Gas Phase Chemiluminescence), Most Recent Version

Title 40 CFR, Part 50, Appendix G - Reference Method For The Determination Of Lead In Suspended Particulate Matter Collected From Ambient Air, Most Recent Version

Title 40 CFR Part 50, Appendix J - Reference Method for the Determination of Particulate Matter as  $PM_{10}$  in the Atmosphere, Most Recent Version

Title 40 CFR Part 50, Appendix L - Reference Method for the Determination of Fine Particulate Matter as  $PM_{2.5}$  in the Atmosphere, Most Recent Version

Title 40CFR Part 53 – Ambient Air Monitoring Reference and Equivalent Methods, Most Recent Version

Title 40 CFR, Part 58 – Ambient Air Quality Surveillance, Most Recent Version

Title 40 CFR, Part 58, Appendix A -Quality Assurance Requirements for State and Local Air Monitoring Stations (SLAMS), Most Recent Version

Title 40 CFR, Part 58, Appendix C - Ambient Air Quality Monitoring Methodology, Most Recent Version

Title 40 CFR, Part 58, Appendix D - Network Design for State and Local Air Monitoring Stations (SLAMS), National Air Monitoring Stations (NAMS), and Photochemical Assessment Monitoring Stations (PAMS), Most Recent Version





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Title 40 CFR, Part 58, Appendix E - Probe and Monitoring Path Siting Criteria for Ambient Air Quality Monitoring, Most Recent Version

Title 49 CFR, Parts 171 to 179, Most Recent Version

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US EPA. 2002. EPA Quality Assurance Guidance Document: Method Compendium, Field Standard Operating Procedures for the PM<sub>2.5</sub> Performance Evaluation Program, United States Environmental Protection Agency Office of Air Quality Planning and Standards, Revision No. 2, March 2002.

US EPA. 2005. Standard Operating Procedures for Through-The-Probe (TTP) Performance Evaluations of Ambient Air Quality Monitoring of Criteria Air Pollutants, Office of Air Quality Planning and Standards, May 2005.

US EPA Quality Assurance Document: Quality Assurance Project Plan for the Performance Evaluation Program

US EPA Implementation Plan: PM<sub>2.5</sub> Federal Reference Method Performance Evaluation Program, EPA Quality Assurance Guidance Document 2.12



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Manual. Region 4 SEDS, Athens, GA, Most Recent Version



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## 2 AUDITING OF OZONE AND CARBON MONOXIDE MONITORING SITES IN THE NATIONAL PERFORMANCE AUDIT PROGRAM (NPAP)

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### 2.1 Auditing Ozone Analyzers

The following is a synopsis of procedures which should be strictly adhered to for the auditing of ozone at ambient monitoring sites.

- The photometer (audit instrument) will meet 40 CFR Part 50, Appendix D specifications for a Primary Standard Calibration Photometer. This instrument will be re-plumbed to act as an analyzer to measure test gas concentrations.
- The photometer will be verified quarterly against a National Institute of Standards and Technology (NIST) Standard Reference Photometer before use.
- The mobile laboratory will meet the specifications of monitor reference/ equivalent designation for temperature control which is between 20-30 degrees Celsius when the analyzer is in operation.
- The probe line must meet the requirements stated in 40 CFR Part 58 for materials and sample residence time.
- Flows will be calibrated annually, and all flow calibrations will be traceable to a primary standard. Flows will be corrected to EPA standard temperature and pressure (25°C and 760 mm Hg).
- The ozone generator/calibrators flow and ozone generation output will be calibrated annually.
- The ozone generator and photometer will operate using zero air supplied by a zero air generator. The zero air scrubber components will be replaced annually or if anomalies in the zero measurement are observed. The desiccant will be regenerated when two thirds ( $2/3^{\text{rds}}$ ) of the blue indicating silica gel has turned pink.
- During the audit, stability of each audit point will be demonstrated for at least five minutes.
- All auditing will be performed at approximately ambient pressure (utilizing a vent for excess during the audit procedure). There should be excess air flow at the probe at all times.
- All audits will be conducted "through the probe" where the probe is safely accessible.



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- Chain-of-custody must be maintained at all times (monitor will be locked in the mobile laboratory when the operator is not present to prevent tampering).

### **2.1.1 Audit Procedure**

Auditing will be conducted using the procedures as summarized below, and in accordance with the EPA Standard Operating Procedure for Through-the-Probe Performance Evaluations of Ambient Air Quality Monitoring of Criteria Air Pollutants, and 40 CFR Part 50, APPENDIX A:

- Procedures detailed in the approved instrument manual will be used for installation, calibration, QA checks, maintenance, and repairs.
- The photometer will be verified quarterly against a National Institute of Standards and Technology (NIST) Standard Reference Photometer after major maintenance or when a quality assurance (QA) check shows an out-of-control condition exists.
- A data telemetry system, with electronic strip charting capability will be operated to record the audit progress and each audit activity will be annotated on the chart. This will serve as a permanent record and diagnostic tool.
- Prior to the audit, the audit equipment, including the photometer and calibrator, will be allowed a warm up period of at least 3 hours. During this time, the system should be conditioned with at least 200 ppb of ozone. The concentration of ozone used to condition the system must always be higher than the highest audit point that will be audited.
- The audit will consist of at least three consecutive levels where at least 80% of ozone measurements are expected to be at the monitoring site and a zero measurement. The prescribed audit levels are recorded in 40 CFR Part 58, Appendix A, 3.2.2.1.
- Audit data from the mobile laboratory and monitoring site will be recorded electronically on the NPAP Audit Worksheet. This worksheet, along with the electronic strip chart trace will be printed at the conclusion of each audit event. In addition, the NPAP Audit Worksheet will be copied and placed on the network drive for archival. A hard copy of the preliminary audit report and electronic strip chart will be provided to the site operator at the conclusion of the audit.
- After completion of the study, the mobile laboratory will be returned for inspection, maintenance, and repair. All field documentation will be retained by the Air Monitoring Staff.



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## 2.2 Auditing Carbon Monoxide Analyzers

The following is a synopsis of procedures which should be strictly adhered to for the auditing of carbon monoxide in air.

- Calibration systems will meet 40 CFR Part 50, Appendix C specifications.
- The mobile laboratory will meet the specifications of monitor reference/ equivalent designation for temperature control which is between 20-30 degrees Celsius when the analyzer is in operation.
- The audit analyzer will be calibrated using certified concentrations of standard gases before and after use.
- The probe line must meet the requirements stated in 40 CFR Part 58 for materials and sample residence time.
- Calibrator flows will be calibrated annually, and all flow calibrations will be traceable to a primary standard. Flows will be corrected to EPA standard temperature and pressure (25°C and 760 mm Hg).
- The gas calibrator will operate using zero air supplied by a zero air generator. The zero air scrubber components will be replaced annually or if anomalies in the zero measurement are observed. The desiccant will be regenerated when two thirds (2/3<sup>rd</sup>s) of the blue indicating silica gel has turned pink.
- During the audit, stability of each audit point must be demonstrated for at least five minutes.
- All auditing will be performed at approximately ambient pressure (utilizing a vent for excess during the audit procedure). There should be excess air flow at the probe at all times.
- All audits will be conducted "through the probe" where the probe is safely accessible.
- Chain-of-custody must be maintained at all times (monitor will be located in a locked enclosure when the operator is not present to prevent tampering).

### 2.2.1 Audit Procedure

Auditing will be conducted using the procedures summarized below, and in accordance with the EPA Standard Operating Procedure for Through-the-Probe Performance Evaluations of Ambient Air Quality Monitoring of Criteria Air Pollutants, and 40 CFR Part 50, APPENDIX C:



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- Procedures detailed in the approved instrument manual will be used for installation, calibration, QA checks, maintenance, and repairs.
- The carbon monoxide analyzer will be verified using G1 or G2 certified tank gases before and after each audit or when a quality assurance (QA) check shows an out-of-control condition exists.
- A data telemetry system, with electronic strip charting capability will be operated to record the audit progress and each audit activity will be annotated on the chart. This will serve as a permanent record and diagnostic tool.
- Prior to the audit, the audit equipment, including the carbon monoxide analyzer and calibrator, will be allowed a warm up period of at least 6 hours. During this time, the system should be conditioned with approximately 200 ppb of ozone.
- The audit will consist of at least three consecutive levels where at least 80% of carbon monoxide measurements are expected to be at the monitoring site and a zero measurement. The prescribed audit levels are recorded in 40 CFR Part 58, Appendix A, 3.2.2.1.
- Audit data from the mobile laboratory and monitoring site will be recorded electronically on the NPAP Audit Worksheet. This worksheet, along with the electronic strip chart trace will be printed at the conclusion of each audit event. In addition, the NPAP Audit Worksheet will be copied and placed on the network drive for archival. A hard copy of the preliminary audit report and electronic strip chart will be provided to the site operator at the conclusion of the audit.
- After completion of the study, the mobile laboratory and equipment will be returned for inspection, maintenance, and repair. All field documentation will be retained by the Air Monitoring Staff.

### 2.3 Sampling of Particulate Matter in Ambient Air as $PM_{2.5}$ in the $PM_{2.5}$ Performance Evaluation Program

The following is a synopsis of procedures which should be strictly adhered to for filter based sampling of  $PM_{2.5}$  in air. The procedures below are a summarized version of the procedure described in the September 2006 Revised Quality Assurance Guidance Document, Method Compendium "Field Standard Operating Procedures for the  $PM_{2.5}$  Performance Evaluation Program" which should be referenced for all low volume  $PM_{2.5}$  sampling.

- Field personnel will take the filters, field data sheets, and COC to the monitoring site and setup the portable samplers.
- Air flow rate, barometric pressure, and two temperature measuring devices

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will be verified prior to each sampling event. All flow, barometric pressure and temperature standard devices are annually calibrated and traceable to a primary standard.

- An external leak check will be performed.
- The sampler will be programmed to operate and the sampling unit will be locked to prevent tampering.
- Within 8 to 16 hours following the sampling event the exposed filters will be collected, and transported refrigerated ( $< 4^{\circ}\text{C}$ ) to the SESD Filter Weighing Laboratory.
- Field personnel will return the exposed filter, data downloads, field data sheets, and COC to SESD keeping a set of the data records in two separate locations.
- After sample collection, all filters will be stored in petri-slides, boxed, and archived for one (1) year at  $\leq 4^{\circ}\text{C}$  and at least two (2) years at ambient room temperature  $\leq 25^{\circ}\text{C}$ .

### 2.4 Sampling of Particulate Matter in Ambient Air as $\text{PM}_{10}$

The following is a synopsis of procedures which should be strictly adhered to for the sampling of particulate matter as  $\text{PM}_{10}$  in air.

- All filters used will be supplied by the EPA National Filter Distribution Program, and of the same quality as supplied to the State and Local Agency Air Monitoring Stations.
- Prior to use, all filters will be checked for pinholes, and desiccated at  $15^{\circ}\text{C} - 30^{\circ}\text{C} \pm 3^{\circ}\text{C}$ , and less than  $50 \pm 5$  percent relative humidity, for at least 24 hours.
- Initial and final (exposed) filter weights will be determined by air monitoring personnel. One of ten filters will be re-weighed as a quality assurance check. For batches less than ten, one filter will be re-weighed. Weights of clean filters should be within 2.8mg of original values, and exposed filters should be within 5mg.
- After sampling, filters will be desiccated as previously described.
- Chain-of-custody must be maintained for all samples (monitor will be locked when the operator is not present to prevent tampering).

#### 2.4.1 Sample Collection Procedure



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Particulate samples will be collected using the High Volume sampler as described, and operated in accordance with 40 CFR Part 50, Appendix J, and Red Book Sections 2.10, and 2.11.

- All flow calibration orifices will be traceable to a primary standard Rootsmeter. Flows will be corrected to EPA standard temperature and pressure (25°C and 760 mm Hg).
- Volumetric flow controllers will be used on all PM<sub>10</sub> samplers. Flows will be determined using a calibrated orifice and a digital manometer.

**2.5 Laboratory Filter Analysis of Particulate Matter in Ambient Air as PM<sub>2.5</sub> in the PM<sub>2.5</sub> Performance Evaluation Program**

The following is a synopsis of procedures which should be strictly adhered to for filter based sampling of PM<sub>2.5</sub> in air. The procedures below are a summarized version of the procedure described in the Quality Assurance Guidance Document, Method Compendium "PM<sub>2.5</sub> Mass Weighing Laboratory Standard Operating Procedures for the Performance Evaluation Program" which should be referenced for all low volume PM<sub>2.5</sub> filter analysis.

- EPA OAQPS National Filter Distribution Program will send filters to the SESD PM<sub>2.5</sub> Filter Weighing Laboratory
- Upon introduction into the weighing laboratory process, each individual batch of filters will go through lot stability testing to determine a minimum equilibration time period.
- Prior to use the filters will be checked for deformities, equilibrated at 20 - 23°C ± 2°C and 30 - 40 % ± 5 % relative humidity for a minimum of 24 hours, labeled, pre-weighed ( auto-entry into database), loaded into cassettes, and prepared for packaging and shipping.
- During the pre-weighing session, the filter batch should pass 100µg and 200µg balance checks (+/- 3µg), two consecutive weightings demonstrating stability (+/- 5µg), and provide an initial laboratory blank weighing.
- The SESD Filter Weighing Laboratory will ship the pre-weighed filters and chain-of- custody (COC) forms to the field personnel.
- Filters and COC forms for Region 4 are passed directly to the field scientists.
- After sampling, filters will be transported to the SESD Filter Weighing





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Laboratory, logged into the database, refrigerated until a batch is completed, moved to the laboratory, unloaded from the cassettes, equilibrated for at least 24 hours, and post-weighed.

- During the post-weighing session, the filter batch should pass 100mg and 200ug balance checks (+/- 3ug), post batch stability check (+/- 15ug), and laboratory blank check (+/- 15ug).
- SESD will calculate the tare weight from the laboratory analyses and will calculate a concentration from the field data. All field data and laboratory data will be archived and backup data will be kept on the network.

Chain-of-custody and all accompanying field data must be maintained for all samples.



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**3 NON-CRITERIA POLLUTANT MONITORING FOR AIR POLLUTANTS FOR WHICH NATIONAL AMBIENT AIR QUALITY STANDARDS HAVE NOT BEEN ESTABLISHED.**

**3.1 Formaldehyde Sampling With Dinitrophenylhydrazine Cartridges Using Method TO-11A**

The following is a synopsis of procedures which should be strictly adhered to for the handling and field use of dinitrophenylhydrazine (DNPH) cartridges for formaldehyde sampling. The following generic procedures should be adhered to at all times.

**Summary of Sampling Method:**

A glass cartridge using Dinitrophenylhydrazine (DNPH) is placed in a special sampler and is equipped with pumps that withdraw a calibrated air volume for a specified time to capture Formaldehyde and other carbonyl compounds. The cartridges are collected and shipped to the laboratory under controlled temperature.

- Quality Control requirements will be based on the method's DQO.
- A minimum of one trip blank shall be transported per one to ten samples collected. Instrument blanks, duplicated samples or co-located samples will be based on laboratory request.
- Chain of Custody shall be maintained for all samples.
- Polyethylene or latex gloves must be worn whenever handling any of the DNPH cartridges (in the extraction laboratory, during preparation for shipment, during field set-up, in the field during preparation for return shipment, and in the laboratory during preparation for analysis and during analysis).
- All padding material shall be either clean tissue paper or polyethylene-air bubble padding. Never use polyurethane foam, cardboard, or newspaper as padding material. DNPH cartridges which have been properly prepared for shipment should be shipped in coolers with eutectic salt packs (Blue Ice).

Due to shelf life limitations, only the number of DNPH cartridges needed for a maximum of 180 days (including trip blanks and extra DNPH cartridges for breakage) should be ordered at any one time.

- On the date of shipment or when loading out for a study, the Air Monitoring Staff will remove the capped DNPH cartridges from the refrigerator in the Air Laboratory.
- An appropriate amount of packing material shall be placed in the shipping container to prevent breakage of the glass DNPH tubes. The DNPH tubes should be shipped in coolers containing eutectic salt packs (e.g., Blue Ice) to maintain a temperature of approximately 4°C. The DNPH cartridges shall be shipped the same day they are packed.



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- At each sampling location the cooler will be opened and one plugged DNPH cartridge will be removed (wearing clean polyethylene or latex gloves) and the two end plugs will be removed from each end of the DNPH cartridge which will be immediately placed on the sampling train. (If it is the SKC brand, the glass ends of the tubes must be broken off. A trip blank will be placed in a sampler enclosure at one of the sites for the duration of the sampling event.
- The sampler will be manually turned on and allowed to run for five minutes. An initial flowrate should be recorded on the sample data sheet. The timer should be set to turn the sampler on and off at the desired times.
- The operator should retrieve and secure the sample as soon as possible after the sampling period ends. The sampler should manually be turned on and allowed to run for five minutes and a final flowrate and the elapsed time from the time meter should be recorded on the sample data sheet. The exposed DNPH cartridge will then be removed from the sampling train (wearing clean polyethylene, latex or nylon gloves). The two end caps will be placed on the ends of the DNPH cartridge. The DNPH cartridge will be placed back into the cooler. The same procedure is to be followed at each sampling site.
- At the end of each day on which the samples are collected, the exposed DNPH cartridges shall be either placed in a refrigerator for storage overnight or stored in the cooler. The cooler will be used to transport the samples to the laboratory. The duration of the non-refrigerated period shall be kept to a minimum but absolutely not more than two days (including the sampling event).
- Upon arrival of the DNPH cartridges at the laboratory, the samples shall be stored in a refrigerator until extraction.
- Chain-of-custody and all accompanying field data must be maintained for all samples.

### 3.2 Volatile Organic Compounds (VOC) Sampling with SUMMA® Electropolished Stainless Steel Canisters or Silcosteel® Canisters Using Method TO-15A

The following is a synopsis of procedures which should be strictly adhered to for the cleanup and use of Summa® canisters for sampling air for Volatile Organic Compounds (VOC) analysis.

The following procedures must be followed in the preparation and use of Summa® canisters for collecting samples for VOC analysis.

- All new Summa®/Silcosteel® canisters must be individually checked for contamination by the laboratory before use. One of each batch of 10 Summa®



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canisters that are subsequently cleaned must be analyzed to check for contamination.

- All sampler tubing, fittings, and wetted parts of valves must be solvent washed in hexane and heated to  $>100^{\circ}$  C. These parts should then be assembled and flushed with nitrogen<sup>1</sup> for at least 8 hours prior to use in the sample train or in the canister cleanup apparatus.
- Each canister's valve and fitting will be inspected for damage before cleaning. Any damaged valve will be replaced with a previously cleaned (see procedure above) valve. After replacing any valve, the canister will be cleaned and analyzed to verify that it is free of contamination.
- If any canister is used to sample a high concentration source, it must be cleaned and analyzed to verify it is free of contamination before it can be used again.
- Chain-of-custody must be maintained for all samples.

1. The nitrogen should be certified 99.999% pure by the manufacturer. A scrubber should be attached to the nitrogen line after the regulator to remove any trace impurities.

### 3.2.1 Sample Collection Procedure

Two types of VOC samples can be collected with Summa®/Silcosteel® canisters. The canister can be opened and allowed to fill rapidly to obtain a grab sample or filled slowly by using a flow controller to collect a time integrated sample. With either type of sample, the following general procedures should be followed:

- A Chain-Of-Custody Record should be completed detailing time of sampling, sampling interval, and signed by the person collecting the sample.
- After the sample has been collected, the Summa®/Silcosteel® canister should be capped, an EPA pre-numbered tag should be completed and attached to the canister, and the canister should be placed in a shipping container with a copy of the Chain-Of-Custody Record and sealed with EPA sample custody tape.

### 3.2.2 Grab Sample Collection Procedure

Before a grab sample is collected for VOC analysis in a Summa®/Silcosteel® canister, the canister inlet valve should be fitted with a pre-cleaned stainless steel particulate filter. At the sample collection location, the main valve should be opened and the canister allowed to fill. After about one minute (when no audible



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sound of rushing gas can be heard), the main valve of the Summa® canister should be closed and capped.

### 3.2.3 Time Integrated Sample Collection Procedure

This sample collection method involves the use of a flow controller or a sampler containing a flow controller to slowly meter the flow of air entering a Summa®/Silcosteel® canister. With this method, a sample is collected over a longer period of time than with a grab sample. If a constant flowrate was maintained, the resulting sample will have a VOC content that is the average of the VOC concentrations during the sampling interval. The following procedures should be followed to collect time integrated samples:

- Cleaning and Adjustment  
All sampler systems should be checked for contamination prior to use or after any major repair. This is accomplished by metering humidified zero air to the inlet of the sampler. Excess zero air should be vented with a Swagelok® tee from the sampler inlet to atmosphere. The evacuated canister should then be filled at the normal sampling rate with the zero gas and verified by the laboratory to be free from contamination.
- Sample Collection  
Prior to sampling the flow controller will be calibrated a mass flow meter. The flowrate should be adjusted so that at the end of the sampling interval the ending pressure of the canister is approximately 0.9 atm. The final canister vacuum should be between 5 inches and 1 inch of Hg. The final flowrate should be at least 1 scc/min.

After sample collection, all canisters should be tagged with an EPA pre-numbered tag with all of the information filled out. Place the canister in a shipping container and seal the container with EPA sample custody tape.

### 3.3 Sampling for Semi-Volatile Organic Compounds (SVOC) Analysis with High Volume PUF Samplers Using Methods TO-4A & TO-13A

The following is a synopsis of procedures which should be strictly adhered to for use of the High Volume Polyurethane Foam (PUF) sampling method for collecting samples for semi-volatile organic compound (SVOC) analysis including pesticides and polychlorinated biphenyls.

The following procedures must be followed during preparation of PUF sampling media when using the High Volume PUF method for collecting samples for SVOC analysis:

- All PUF sampling media should be pre-cleaned, loaded into High Volume PUF sample cartridges, and sealed in solvent washed cans by the extraction laboratory prior to use.







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- Chain-of-custody shall be maintained for all samples.

### 3.3.1 PUF Cleaning Procedure

- The Air Monitoring Staff has responsibility for buying the PUF media and cutting the PUF plugs. PUF media should be specified as not containing any fire retardants. It should be stored in the dark to prevent photo-oxidation. It should be less than two years old, and should be stored in a pesticide free environment.
- Care should be exercised in cutting the PUF. It should be thoroughly wet with tap water prior to cutting. A drill press and stainless steel PUF cutting die should be used. The drill press area should be free of oil and a polyethylene cutting block should be used to stop the die at the bottom of the drill press stroke (do not use wood). Water should be sprayed on the die to help prevent snagging as the PUF is cut. After the plugs are cut, they should be rinsed with tap water and followed by a rinse with analytical-free water. Finally, the excess water should be squeezed out.
- The PUF/XAD cartridges are assembled using a modified glass sleeve containing an extra-extra coarse frit to retain the XAD resin in the following manner. A 3/4-inch layer of XAD resin is poured on top of the frit followed by a 1 1/2-inch PUF plug to retain the XAD resin.
- The assembled PUF/XAD cartridges are delivered to the extraction laboratory for cleaning and checking. The extraction laboratory will be given a minimum of three weeks notice for cleaning and checking the PUF/XAD cartridges. The cleaned PUF/XAD cartridges should be wrapped in aluminum foil and packed in pre cleaned metal cans or glass jars cushioned by new polyethylene bubble wrap to prevent breakage during shipment. Prepared PUF/XAD sample cartridges that are pre-packed in solvent washed metal cans will be obtained from the extraction laboratory prior to sampling. The cans should be packed inside coolers frozen eutectic salt packs (Blue Ice) to maintain a temperature of less than 15°C.

### 3.3.2 Sample Collection Procedure

The following procedure will be followed for all High Volume PUF/XAD sampling.

- Powder-free latex gloves will be used when handling all PUF/XAD cartridges and quartz particulate pre-filters. Assure that the red silicon upper and lower gaskets, located in the cartridge housing, are in place. Then remove the PUF/XAD cartridge from the shipping container, remove





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from the foil and insert the cartridge into the High Volume sampler's chamber. The pre-filter should be installed in the filter holder using caution not to over tighten the fittings. The foil should be placed back in the shipping container. The container should be labeled with site ID, operator's name, and sample date, and placed in the High Volume sampler enclosure until the sample is collected.

- The High Volume sampler should be turned on and allowed to run for two minutes. An initial flowrate should be recorded on the sample data sheet. The timer should be set to turn the sampler on and off at the desired times.
- The operator should retrieve and secure the sample as soon as possible after the sampling period ends. The sampler should then be manually turned on and allowed to run for two minutes. A final flowrate should be recorded on the sample data sheet. The final flowrate should be at least 150 liters per minute. The PUF/XAD cartridge should be removed, and the quartz pre-filter folded and placed in the top of the PUF/XAD cartridge. The PUF/XAD cartridge and pre-filter should be re-wrapped in the original aluminum foil and placed back in the shipping container. The container should then be tightly sealed. Complete the sample data sheet and Chain-Of-Custody Record and seal the shipping container with a sample custody seal. Finally, the shipping container containing the sample should be placed in a cooler containing frozen eutectic salt packs (at a nominal temperature of ~ 15° C). When all samples are collected from all sites, the cooler should be sealed with sample custody tape for transport back to the laboratory.
- Upon arrival of the metal container at the laboratory, the samples shall be stored in the metal container in a refrigerator until submitted for extraction.

### 3.4 Collecting Samples for Metals Analysis Using the High Volume Sampler

The following is a synopsis of procedures which should be strictly adhered to for the collection of samples for metals analysis in air using the High Volume sampler.

- All quartz filters used will be supplied by the EPA National Filter Distribution Program, and of the same quality as supplied to the State and Local Agency Air Monitoring Stations.
- Prior to use, all filters will be checked for pinholes, and desiccated at 15°C - 30°C, ± 3°C, and less than 50 percent relative humidity, ± 5 percent, for at least 24 hours.
- A filter field blank will be taken to the field, but not exposed. Filter field blanks will be analyzed by the laboratory to determine the concentration of metals



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contained in the filter matrix. The number of filter blanks will be determined based on a minimum of one blank for each ten samples collected.

- Chain-of-custody must be maintained for all samples.

### *3.4.1 Sample Collection Procedure*

Samples will be collected using the High Volume sampler as described, and operated in accordance with 40 CFR, PART 50, APPENDIX B:

- All flow calibration orifices will be traceable to a Primary Standard Rootsmeter. Flows will be corrected to EPA standard temperature and pressure (25°C and 760 mm Hg).
- Digital manometers used to determine flow rates will be calibrated by the factory annually.
- Air Monitoring Staff personnel will remove a 2-inch strip of the exposed filter from one end and discard it. Two 1-inch strips will be cut from the same end and transported to the laboratory for analysis.

### *3.4.2 Integrated Sample Collection Procedure*

The following procedure should be followed to collect time integrated samples:

- Initial and final flow rates will be determined with a calibrated orifice and a digital manometer.
- After the sample has been collected, the filter will be folded lengthwise and placed in a filter holder. The filter holder is then placed in an envelope and the envelope sealed.
- A Chain-Of-Custody Record should be completed which contains the time of sampling, the sampling interval, and the signature of the person taking the sample.

After sample collection, all sample envelopes will be placed in an appropriate container. An EPA custody seal will be placed on the container. Filters will be cut by the Air Monitoring Staff and transported to the laboratory for analysis.

### **3.5 Standard Operating Procedure for Mercury Analysis of Air Using the Tekran Mercury Vapour Analyzer model 2537A.**

The following is a synopsis of procedures which should be strictly adhered to for continuous monitoring of gaseous mercury in ambient air.



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### *3.5.1 Instrument Operation*

The Tekran Vapour Analyzer 2537A is designed to "continuously" analyze air for total gaseous mercury. The Tekran 2537A uses Cold Vapour Atomic Fluorescence Spectrophotometry (CVAFS) for the detection of mercury. The instrument has been shown to be linear from 0.1 ng/M<sup>3</sup> to ~1500 ng/M<sup>3</sup>.

Although the instrument can handle samples with high concentrations, the user must avoid exposing the instrument case and parts to high levels of mercury. Mercury contamination residing on the instrument's components could skew both analyses and calibrations.

### *3.5.2 Sample Collection Procedure*

The Tekran Vapour Analyzer 2537A continuously samples ambient air for gaseous mercury. It performs the analysis periodically as determined by the method entered by the operator into the on-board computer. The frequency of analysis (and thus the duration of the sample collection) can be varied from about every 4 minutes to 15 minutes.

The analysis begins when air is drawn into the instrument through the Sample Air Inlet. The instrument's on board computer switches a set of valves that introduces sample into one of two gold matrix cartridges at a time. As the sample passes through the cartridge, the mercury in the air amalgamates onto the encased gold mesh screen. While one cartridge samples the air, the onboard computer analyzes the other cartridge. At the start of the analysis cycle, the instrument sweeps the cartridge with argon gas, and then heats the cartridge. Mercury that was adsorbed onto the gold matrix is released during heating in argon. The mercury is then swept into the detector by the flow of the argon carrier gas.

U.V. light at 253.7 nm excites any mercury atoms present, which fluoresce and re-radiate at the same wavelength. A UV detector views the cell at right angles to the incident light. Direct light from the source is not seen, however, the fluorescence produced by the mercury in the cell is observed by the UV detector. The intensity of the fluorescence is directly proportional to the amount of mercury in the cell. Once the mass of mercury present is known, the on-board computer calculates the concentration of mercury as the mass of mercury divided by the volume of air sampled. The on-board computer sends the analysis results to a display screen and to a data-collecting computer. Although the instrument switches between chambers instantaneously, the analysis of the mercury within the chamber and calculations involved require an unavoidable lag time before the results are available. When the instrument is used for onsite sampling/analysis, the analyst must take care to link the readout to the appropriate sample.



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### 3.5.3 Interferences

Due to the unique design of the Tekran, there are no known chemical interferences. The only materials that enter the instrument are gases and vapors, and the only material that is retained by the gold screen is mercury. All other materials pass through the cartridge. The mercury is desorbed and analyzed with no other materials present to interfere with the fluorescence detection.

### 3.5.4 Required Equipment

- The Tekran 2537A
- The Tekran Model 2505 Mercury Vapor Calibration Unit. This item is used only at the SESD base laboratory. Although this item is transportable, movement can disrupt the internal mercury bead. If any of the internal mercury adheres to the syringe during calibration, the actual amount of mercury present in the sample will be drastically underreported, leading to an inflated response factor.
- Teflon<sup>®</sup> pre-filter. A 5 $\mu$  47mm Teflon<sup>®</sup> prefilter should be used on the inlet end of the sample line to prevent contamination of the sample line from the inlet to the instrument. The instrument has two additional 47mm Teflon<sup>®</sup> filters on its ambient air inlet and the zero air inlet.
- ¼" O.D. Teflon<sup>®</sup> tubing. The tubing is used to collect the sample and should be long enough to reach the most distant sample location, but not longer than 100 feet.
- A computer to record the data. (Must be capable of running the TEKTRAN data capture program)
- A scrubber tube filled with activated carbon, to attach to the vents.
- 10, 25 or 50 $\mu$ L syringes. The syringes should be gas tight, with Teflon<sup>®</sup> tipped barrels. Tekran recommends using syringes with side venting needles because they are less likely to plug on extracted septum material. Read the User's Manual to learn how to condition the syringes for use with the primary standard.

### 3.5.5 Reagents and Standards Required

- High Purity Argon to act as the carrier gas.
- Compressed zero air or high purity Nitrogen to act as the Zero Air.



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- Elemental Mercury (<5ml) for use in the Tekran 2505 Cold Vapor Calibrator as a primary standard.

### 3.5.6 Calibration

A mercury permeation tube is housed in a temperature control chamber within the Tekran 2357A for routine calibration of the instrument. This tube is maintained at 50° C. The permeation tube constantly emits mercury at a low rate that does not vary as long as the temperature remains stable and as long as there is carrier flow over the permeation tube. This mercury can be directed to the cartridges and sets the response factor of the instrument automatically. The analyst can initiate an internal calibration in three different ways. First, the method for the on-board computer can be programmed to start the calibration at a specific time. Next, the analyst may use the keyboard to start the calibration from two different operating modes. Finally, the instrument will start a calibration when an electric circuit switch on the back panel is closed from a remote device.

The permeation rate of the mercury permeation tube is only constant once the permeation tube has reached a constant temperature and has reached equilibrium. Upon instrument startup, the calibration source should be allowed to stabilize for 12-hours with power applied and carrier gas connected before a calibration is attempted. Typically, the method stored in the on-board computer will be set to perform one calibration per 24-hour period following this warm up period. Different study requirements may require different calibration intervals.

The User's Manual provides much more detail than this document. The analyst should read and understand the manual for a complete description of the calibration process. The automated calibration is initiated using the front panel control. The steps are outlined as follows:

- From the **MAIN MENU** screen, use the arrow keys to highlight **CALIBRATE** and press <Enter> to start the calibration.
- From the **CALIBRATE MENU** screen, highlight **TYPE** and press <Enter>
- Select the **SOURCE** option
- From the **CALIBRATE MENU** screen, highlight **CALIB** and press <Enter>
- From the **CALIBRATE CYCLE** screen, highlight **FULL** and press <Enter>
- From the **CALIBRATE:CALIB** screen, highlight **BOTH** and press <Enter>

It is important to routinely verify the permeation rate of the Tekran 2357A's internal permeation tube. A manual calibration procedure must be performed to certify the internal permeation rate. The manual calibration procedure utilizes the



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well documented vapor pressure of mercury to produce a "primary standard". When elemental mercury is enclosed in a sealed chamber at a fixed temperature, it reaches equilibrium and a gaseous concentration of mercury of fixed concentration is present. The amount of mercury contained per unit volume at a given temperature is a well known function that is available in tables. To simplify this calibration, the Tekran model 2505 mercury vapor calibration unit is used. It is typically operated at 15° C (it should be maintained at least two degrees below ambient to prevent condensation of mercury on the syringes).

The User's Manual provides much more detail than this document. The analyst should read and understand the manual for a complete description of the manual calibration process. The manual calibration is initiated using the front panel control. The steps are outlined as follows:

- From the **MAIN MENU** screen, use the arrow keys to highlight **CALIBRATE** and press <Enter> to start the calibration.
- From the **CALIBRATE MENU** screen, highlight **TYPE** and press <Enter>
- Select the **INJECT** option and press <Enter>
  
- From the **CALIBRATE MENU** screen, highlight **CALIB** and press <Enter>
- From the **CALIBRATE CYCLE** screen, highlight **FULL** and press <Enter>
- From the **CALIBRATE: CALIB** screen, highlight **BOTH** and press <Enter>

The calibration begins with the Clean Cartridge A cycle, and proceeds to the Clean Cartridge B cycle, followed by the Zero Cartridge A, Zero Cartridge B, Span Cartridge A, and finally Span Cartridge B cycle. During the Span cycles, the instrument will prompt the analyst when it is time to inject the primary standard. The amount of standard required is calculated and preset during method development. After a successful calibration, the instrument will calculate the results for both cartridges, including their Blank Correction (Blcorr) and Response Factor (Respctr). The operator should ensure that the response factor does not change more than  $\pm 10\%$  between calibrations or corrective maintenance may be necessary. Now the instrument is ready to measure samples.

### 3.5.7 Analysis and Operation

Once the instrument is calibrated, the operation is straightforward. From the main menu screen, highlight **RUN** and press <Enter>. The instrument will start sampling and analyzing the air following the method stored in memory. The results are displayed on screen, but can also be sent to an attached computer.



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**3.5.8 Calculations**

The instrument's on-board processor calculates the concentrations automatically. The user need not perform any calculations during routine sampling and analysis.

**3.5.9 Flowrate Checks**

The sample flowrate of the Tekran is controlled by an electronic mass flow controller which in turn is controlled by the on-board computer. Since the mercury permeation tube used to calibrate the instrument emits a constant mass of mercury per unit time, changes in sample flowrate won't always be apparent during calibrations. However, changes in flowrate would result in direct errors in the quantitation of the ambient air samples. So, it is important to periodically check the flowrate to verify that the electronic flow controller is working properly. Sample flowrate is best checked against a primary flow calibrator such as a soap-film bubble meter or a positive displacement calibrator such as a Dry Cal<sup>®</sup>. The calibration is conducted by attaching the calibrator to the inlet and measuring the flowrate. If the flowrate doesn't match the flowrate stated on the instrument display, the mass flow controller should be recalibrated as per the Tekran manual.

**3.5.10 Records Management and Documentation**

The data sent to the attached computer will stored for on the computer but backup copies of the data should be placed onto removable discs and stored for record keeping.

**3.5.11 Safety**

The instrument itself presents few Health & Safety concerns. However, the instrument is typically used in areas where mercury contamination is suspected. The individual responsible for sampling the air should use personal protective equipment (PPE) stipulated by the site safety officer. The manufacturer includes a tube filled with activated charcoal that can be placed on the vents to absorb the mercury vented from the instrument. The mercury lamp emits UV radiation; never look directly into the lamp, and avoid exposing skin and eyes to the UV rays.

**3.6 Sampling for Dioxin and Dibenzofuran Analyses with High Volume PUF Samplers Using Method TO-9A**

**3.6.1 General Information**

The following is a synopsis of procedures which should be strictly adhered to for use of the High Volume Polyurethane Foam (PUF) sampling method for



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collecting samples for polychlorinated dibenzo-p-dioxins and dibenzofurans analyses.

Since this method requires High-Resolution Mass Spectrometry which the Region 4 laboratory does not have, all sample media preparation and analysis will have to be contracted. At least one month's notice prior to sampling should be given to obtain a contract laboratory for any dioxin and dibenzofuran analysis. It is important that the contract specify a number of details to assure accurate results:

- All of the PUF media and a representative number of each batch of quartz pre-filters should be checked by the contract laboratory to assure that there is no contamination. Each PUF plug should be pre-spiked by the contract laboratory with dioxin and dibenzofuran surrogates as a check of the accuracy of the method.
- Each set of PUF plugs and quartz filters should be securely packed in sealed containers and in coolers to prevent damage during shipment. The sampling media should be shipped air freight to minimize the time between cleanup and sampling.
- Chain-of-custody shall be maintained for all samples.

### 3.6.2 Sample Collection Procedure

The following procedure will be followed for the collection of all High Volume PUF samples for dioxins and dibenzofurans analyses.

Latex gloves will be used when handling all PUF cartridges and quartz particulate pre-filters. Assure that the red silicon upper and lower gaskets are in place in the PUF cartridge housing. Remove the PUF cartridge from the shipping can. Unwrap and insert the PUF cartridge into the High Volume (Hi-Vol) PUF sampler's chamber. Install the pre-filter in the filter holder using caution not to over tighten the fittings. The removed aluminum foil should be placed in the shipping container which then should be resealed. The container should be labeled with the site ID, the operator's name, and the sample date, and placed in the Hi-Vol PUF sampler enclosure until the sample is collected. The Hi-Vol PUF sampler should be turned on and allowed to run for two minutes. An initial flowrate should be recorded on the sample data sheet. The timer should be set to turn the sampler on and off at the desired times.

The operator should retrieve and secure the sample as soon as possible after the sampling period ends. The sampler should then be manually turned on and allowed to run for two minutes and a final flowrate recorded on the sample data sheet. The final flowrate should be at least 150 liters/minute. The PUF cartridge should be removed, and the quartz pre-filter folded and placed in the top of the PUF cartridge. The PUF cartridge and pre-filter should be re-wrapped in the original aluminum foil and placed back in the shipping container and the container should be tightly sealed. Complete the sample data and sample custody





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sheets. Each shipping container should have a sample custody seal. Finally, the shipping container containing the sample should be placed in a cooler containing frozen eutectic salt packs (at a nominal temperature of  $\sim 4^{\circ}\text{C}$ ). When all samples are collected from all sites, the cooler should be sealed with sample custody tape for shipment to the contract laboratory.

Upon arrival of the metal container at the contract laboratory, the samples shall be stored in the metal container in a refrigerator until submitted for extraction.



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# Appendix D



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EPA/625/R-96/010a

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

Compendium Method IO-4.2

DETERMINATION OF REACTIVE  
ACIDIC AND BASIC GASES  
AND STRONG ACIDITY OF  
ATMOSPHERIC FINE PARTICLES  
( $< 2.5 \mu\text{m}$ )

Center for Environmental Research Information  
Office of Research and Development  
U.S. Environmental Protection Agency  
Cincinnati, OH 45268

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Method IO-4.2

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

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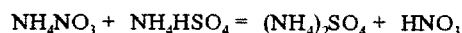
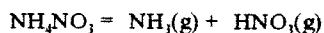
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Chapter IO-4  
Atmospheric Basic & Acidic Constituents

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

1. Scope

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



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

1.2 The chemical species that can be determined by this method are gaseous  $\text{SO}_2$ ,  $\text{HNO}_2$ ,  $\text{HNO}_3$ , and  $\text{NH}_3$  and particulate  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{H}^+$ . Detection and quantitation limits are given in Table 1.

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

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

1.5 The techniques, procedures, equipment, and other specifications comprising this method are derived and composited from those actually used by contributing research organizations and, therefore, are known to be serviceable and effective. At this stage, this method is a unified, consensus, tentative, draft method intended for further application and testing. Users should be advised that the method has not yet been adequately tested, optimized, or standardized. Many of the specifications have been initially established by technical judgement but have not been subjected to ruggedness testing. In some cases, alternative techniques, equipment, or specifications may be acceptable or superior. In applying the method, users are encouraged to consider alternatives, with the understanding that they should test any such alternatives to determine their adequacy and confirm and document their advantages. Information and comments are solicited on improvements, alternative equipment, techniques, specifications, performance, or any other aspect of the method.



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## 2. Applicable Documents

### 2.1 ASTM Standards

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

### 2.2 Other Documents

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

## 3. Summary of Method

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

3.2 Following each run, the ADS assembly is removed from its field housing, its ends are capped, and it is brought back to the laboratory. In the laboratory, the assembly pieces are uncoupled and capped. The annular denuders are extracted with 5 mL of deionized water. The extracted solutions are subsequently analyzed for ions corresponding to the collected gaseous species (see Figure 1). The filters are placed into filter bottles where 5 or 10 mL of the ion chromatographic (IC) eluent are pipetted into each filter bottle with the filters faced downward and completely covered by the eluent. The filter bottle is capped and put in an ultrasonic bath for 30 min. The bottles are stored in a clean refrigerator at 5°C until analysis.

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

## 4. Significance

4.1 Reactive acidic ( $\text{SO}_2$  and  $\text{HNO}_3$ ) and basic ( $\text{NH}_3$ ) gases and particles are found in the atmosphere as a result of emissions from a variety of fossil fuel combustion sources, including industrial and commercial facilities, industrial processes, etc. Measurements of these chemical species are currently being used in a range of environmental studies, such as in (1) epidemiological programs to assess the impact of acid aerosols on respiratory impairment, (2) receptor modeling to determine the origin of particles that impact EPA's  $\text{PM}_{2.5}$  or





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PM<sub>10</sub> air particulate standard, (3) assessment of the impact of particulate nitrate and sulfate on visibility, and (4) quantification of the impact of acidic and basic air pollutants on issues related to acid rain.

4.2 Unique features of the annular denuder that separate it from other established monitoring methods are the elimination of sampling artifacts due to interaction between the collected gases and particles and the preservation of the samples for subsequent analysis. This preservation is accomplished by removing NH<sub>3</sub> in the gas stream by the citric acid coated denuder and reducing the probability of the particulate sulfate (SO<sub>4</sub><sup>2-</sup>) captured by the filter pack from being neutralized to ammonium sulfate [(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>]. If NH<sub>3</sub> is not extracted from the gas stream prior to filtration, particulate sulfate and gaseous sulfur dioxide correction would be required for accurate measurements. These biases in its configuration and analytical methodology are addressed in this method.

#### 5. Definitions

Definitions used in this document and any user prepared Standard Operating Procedures (SOPs) should be consistent with ASTM D 1356. All abbreviations and symbols are defined within this document at the point of use.

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

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

**5.3 Secondary Particles (or Secondary Aerosols).** Dispersion aerosols that form in the atmosphere as a result of chemical reactions, often involving gases. A typical example is sulfate ions produced by photochemical oxidation of SO<sub>2</sub>.

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

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

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

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



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

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

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

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

## 6. Factors Affecting Denuder Efficiency

**6.1** Operation below 20% relative humidity (RH) may result in less than quantitative collection of SO<sub>2</sub>. Atmospheric water vapor in concentrations above 30% RH has been shown not to be an interferant for SO<sub>2</sub> collection.

**6.2** Studies are being conducted to identify interferents, and calculations are being developed to correct the measurements obtained by the annular denuder system for identifiable interferents. For example, the presence of ozone (O<sub>3</sub>) is known to oxidize nitrous acid (HNO<sub>2</sub>) to nitric acid (HNO<sub>3</sub>); therefore, HNO<sub>2</sub> measurements are often underestimates. Calculations have been developed to adjust for this oxidation process and to provide more accurate estimations of HNO<sub>2</sub> concentrations in the atmosphere.

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

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

## 7. Apparatus

*[Note: This method was developed using the annular denuder system produced by University Research Glassware, 116 S. Merritt Mill Road, Chapel Hill, NC 27516, (919) 942-2753, as a guideline. EPA has experience in use of this equipment during various field monitoring programs over the last several years. Other manufacturers' equipment should work as well. Denuder systems are also available from Rupprecht and Patashnick Co., Inc., 25 Corporate Circle, Albany, NY 12203, (518) 452-0065 and Ogawa & Company, USA, Inc., 1230 S.E. 7th Avenue, Pompano Beach, Florida 33060, (305) 781-6223. However, modifications to these procedures may be necessary if another commercially available sampler is selected.]*

### 7.1 Sampling

**7.1.1 Elutriator and Acceleration Jet Assembly (see Figure 3).** Under normal sampling conditions, the elutriator or entry tube is made of either Teflon®-coated glass or aluminum. When using glass, the accelerator jet assembly is fixed onto the elutriator, and the internal surfaces of the entire assembly are coated with Teflon®. When aluminum is used, the accelerator jet assembly is removable. The jet is made of Teflon® or



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polyethylene, and the jet support is made of aluminum. Again, all internal surfaces are coated with Teflon®. Both assemblies are available with 2, 3 and 4 mm inside diameter jets (nozzles).

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

**7.1.3 Impactor Frit and Coupler Assembly (see Figure 5).** The impactor frit is 10 mm x 3 mm and is available with a porosity range of 10-20  $\mu\text{m}$ . 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 "O"-rings that are located on both sides of the seat support inside the coupler. The couplers are composed of two free moving female threads that house the support tools when assembling and removing the impactor frit, and couple the denuders when sampling. Arrows on the metal band hold the female threads together. These arrows should be pointing in the direction of air flow (see Figure 1) when the ADS is assembled.

*[Note: In situations when there are substantial high concentrations of coarse particles ( $> 2.5 \mu\text{m}$ ), a Teflon® coated aluminum cyclone should be used in place of the acceleration jet and impactor assembly, as illustrated in Figure 6.]*

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

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

This procedure uses two denuders in series. The first denuder,  $\text{Na}_2\text{CO}_3$  coated, is used to trap out  $\text{HNO}_3$  and  $\text{SO}_2$ . The  $\text{Na}_2\text{CO}_3$  denuder can also trap out  $\text{HCl}$ ,  $\text{HNO}_2$ ,  $\text{HF}$ , and some organic acids. However, special care needs to be taken in the preparation of the denuder coating material and extraction procedures to quantitate  $\text{HCl}$ . This method does not quantitate  $\text{HCl}$ ,  $\text{HNO}_2$ ,  $\text{HF}$ , or other organic acids retained on the  $\text{Na}_2\text{CO}_3$  denuder.

The second denuder is coated with citric acid for trapping  $\text{NH}_3$ . This procedure does cover the quantitation of  $\text{NH}_3$ .

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



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

**7.1.6 Annular Denuder Couplers (see Figure 4).** The couplers should be made of thermoplastic and equipped with Teflon® "O"-rings that sandwich a silicone rubber ring on three sides. This design provides elasticity for better sealing under extremely cold temperature conditions in which Teflon® does not give. Two types of couplers are available. In the older version, the couplers have removable seal rings. Problems with denuder breakage and leakage due to improper threading of the couplers with the denuders led to the development of a second type of coupler. The new couplers are equipped with permanent seal rings that provide more even threading and a better seal when coupled. Some couplers have built-in flow-straighteners. The couplers are used to couple the annular denuders and for coupling the last denuder with the filter pack.

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

**7.1.8 Drying Manifold Assembly (see Figure 9).** Made of pyrex and is available to accommodate as many as four drying denuders. The denuders are attached to the manifold with back-to-back Bakelite bored caps. The bored caps are connected with a Teflon® connector ring. Air is pushed through an air dryer/ cleaner bottle made of 2 1/2" heavy wall pyrex that contains silica gel, calcium sulfate, and activated charcoal (not available with assembly). The tubing that connects the dryer/cleaner bottle to the drying manifold should be secured at each cap with either Teflon® washers or Teflon® washers coupled with Teflon® hose barsbs.

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

**7.1.9 Vacuum Tubing.** Low density polyethylene tubing, 3/8" diameter for distances of less than 50 ft., 1/2" diameter for distances greater than 50 ft. Since this tubing is used downstream from the sampler, similar sized tubing or pipe of any material may be substituted. The tubing must have sufficient strength to avoid collapsing under vacuum [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA 15219, (412-787-6322)].

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

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



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

**7.1.13 Annular Denuder Shipping Case (Optional).** Made of formica, backed with plywood and insulated with polyurethane. The corners are reinforced with metal. It is made to withstand shipping by truck, UPS, and Federal Express. Each case is stackable and lockable and has a carrying handle. Seven total annular denuder systems can be packed in the case, provided each system contains four denuders each. The systems can consist of either three denuders (242-mm long) and one denuder-impactor assembly (265 mm long) or four denuders (242-mm long). Each component of the system is packed in its own storage compartment. The personal sampler assemblies can also be placed and shipped in this case.

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

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

## 7.2 Analysis

**7.2.1 Ion Chromatograph.** A chromatograph equipped with the appropriate anion and cation exchange resin filled separator and suppressor columns and conductivity detector for measuring acidic ( $\text{SO}_2$ ,  $\text{HNO}_2$  and  $\text{HNO}_3$ ) and basic ( $\text{NH}_3$ ) ions in solution (i.e. denuder and filter extracts) [Dionex Corp., 1228 Titan Way, Sunnyvale, CA 94086, (408-737-0700)].

**7.2.2 Technicon Colorimeter Autoanalyzer.** 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)].

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

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

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

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

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

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

**7.2.9 Micropipettes.** Recommended 50  $\mu\text{L}$ . Calibrated "to contain," borosilicate glass micropipette, best source.

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

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

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

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



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### 8. Reagents and Materials

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

**8.2 Nylasorb® Filters.** Membrane filters 47-mm diameter with a 1 µm pore size. These filters are specially prepared and batch analyzed for low NO<sub>3</sub>G background levels. If other brands of nylon membrane filters are used, they should be batch analyzed to ensure low and replicable levels of NO<sub>3</sub>G [Gelman Sciences, 600 S. Wagner Rd., Ann Arbor, MI, 48106 (800-521-1520)].

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

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

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

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

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

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

**8.9 Stoppers.** Cork or polyethylene, best source.

**8.10 Sodium Carbonate (Na<sub>2</sub>CO<sub>3</sub>).** ACS reagent grade, best source.

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

**8.12 Toluene.** ACS reagent grade, best source.

**8.13 Glycerol (Glycerine - CH<sub>2</sub>OHCHOHCH<sub>2</sub>OH).** ACS reagent grade, best source.

**8.14 Citric Acid [Monohydrate - HOC(CH<sub>2</sub>CO)OH]<sub>2</sub>COOH : H<sub>2</sub>O.** ACS reagent grade, best source.

**8.15 Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>).** ACS reagent grade, best source.

**8.16 Ethanol (C<sub>2</sub>H<sub>5</sub>OH).** ACS reagent grade, best source.

**8.17 Sulfuric Acid (H<sub>2</sub>SO<sub>4</sub>).** ACS reagent grade, best source.



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- 8.18 Potassium Chloride (KCl).** ACS reagent grade, best source.
- 8.19 Perchloric Acid (HClO<sub>4</sub>).** ACS reagent grade (60-62%), best source.
- 8.20 Distilled Deionized Water (DDW).** ASTM Type I water.
- 8.21 pH Buffers.** Standard buffers 4.00 and 7.00 for internal calibration of pH meter, best source.
- 8.22 Silica Gel.** ACS reagent grade (indicating type), best source.
- 8.23 Sodium Bromide (NaBr).** ACS reagent grade, best source.
- 8.24 Activated Charcoal.** ACS reagent grade, best source.
- 8.25 Balance.** Electronic analytical with internal calibration weights and enclosed weighing chamber. Precision of 0.1 mg [Fisher-Scientific, 711 Forbes Ave., Pittsburgh, PA, 15219, (412-787-6322)].
- 8.26 Gloves.** Polyethylene disposable. Used for impactor frit assembly and filter pack assembly, best source.
- 8.27 Dow Corning High Temperature Vacuum Oil.** Dow Corning 660 oil used for impactor frit coating solution, best source.
- 8.28 Zero Air.** A supply of compressed clean air, free from particles, oil, NO, NO<sub>2</sub>, SO<sub>2</sub>, HNO<sub>3</sub>, and HNO<sub>2</sub>. The supply may be either from a commercial cylinder or generated on site, best source.
- 8.29 Ion Chromatographic (IC) Eluent Solution.** For extracting filters. This solution should be the same eluent as used for the ion chromatographic analysis of the filters. If the filter analysis is not to be performed by ion chromatography, a slightly basic solution (e.g., 0.003 N NaOH or sodium carbonate/bicarbonate) should be used to extract the Nylasorb® filter, while the Teflon® filter should be extracted with double-distilled deionized water (DDW).

9. Preparation of Coating and Extraction Reagents

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

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



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### 9.3 Annular Denuder Coating Solutions Preparation

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

**9.3.1 Na<sub>2</sub>CO<sub>3</sub> Coating Solution.** Clean a 100 mL polyethylene storage vial and let dry at room temperature. Measure 50 mL of ethanol (WARNING - TOXIC, FLAMMABLE LIQUID) with a graduated cylinder and pour into vial. Measure 50 mL of DDW with a graduated cylinder and add to vial. Weigh 1 g of glycerol and add to DDW. Weigh 1 g of Na<sub>2</sub>CO<sub>3</sub> and add to vial. Mix thoroughly, solution may fizz; wait for fizzing to stop before sealing vial. Store at room temperature.

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

## 10. Elutriator and Acceleration Jet (Inlet) Assembly

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

**10.1** The internal walls of the elutriator and jet assembly are coated with Teflon® to prevent losses of reactive species (SO<sub>2</sub>, HNO<sub>3</sub>, NH<sub>3</sub>) during sampling. The elutriator prevents water and large particles from entering the inlet and thus extends the life of the impaction surface located immediately downstream of this assembly.

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

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

## 11. Impactor Frit Preparation and Installation

### 11.1 Impactor Frit Installation

**11.1.1 Impactor-Coupler.** The impactor-coupler assembly (shown in Figure 12) is composed of two parts: the replaceable impactor frit and the coupler-impactor housing seat. The impactor surface is a porous ceramic or porous stainless steel frit, 10 mm x 3 mm. This frit is inserted into the coupler-impactor housing using the tools shown in Figure 12. The in-tool must be completely screwed in behind the impactor seat before the frit is pressed into place. Press the impactor frit gently but firmly into the seat of the impactor housing with your





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

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

### 11.2 Impactor Frit Preparation

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

## 12. Filter Pack Preparation and Assembly

*[Note: Any number of filters can be used depending on the target species of interest. The configuration referred to in this section does not collect NH<sub>4</sub>.]*

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

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

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

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

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

*[Note: If a Teflasorb® Teflon® filter is used, be sure to place the Teflon® coated side, not the webbed side, toward the air stream. If the webbed side is facing the air stream, SO<sub>2</sub> extraction from the filters may be inefficient.]*

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



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

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

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

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

### 13. Annular Denuder System Preparation

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

#### 13.1 Annular Denuder Coating Procedure

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

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

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

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

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

#### 13.2 Annular Denuder Drying Procedure (see Figure 9)

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

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

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

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

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

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



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### 13.3 Annular Denuder System (ADS) Assembly

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

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

13.3.2 Remove the end caps from the first denuder. Denuder 1 is coated with  $\text{Na}_2\text{CO}_3$  and holds the impactor frit pin support. Remove the blank impactor support pin. Gently insert the impactor support pin and coated frit assembly into the denuder-pin support. If the first denuder does not hold the impactor pin-support, attach the impactor frit seat equipped coupler assembly to the flow-straightener end of the first denuder.

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

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

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

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

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

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

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

13.3.9 Cap elutriator with orange dust cover until use.

*[Note: When collecting and measuring gaseous  $\text{HNO}_3$ ,  $\text{SO}_2$ , and particulate  $\text{NO}_3$  and  $\text{SO}_4^{2-}$ ,  $\text{NH}_3$  must be taken out of the gas stream prior to the air stream entering the filter pack. Otherwise, reaction of the unneutralized sulfate will result. If ammonia ( $\text{NH}_3$ ) and/or  $\text{H}^+$  measurements are not to be analyzed for, then the use of a citric acid coated denuder is not important. However, with the removal of  $\text{NH}_3$ , some nitrate collected on the Teflon® filter will evaporate and be found on the nylon filter.]*

### 13.4 Laboratory Leak-Check of ADS

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

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

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

13.4.3 Disconnect the pump from the ADS at the "Quick-Release" plug. Cap the "Quick-Release" plug with an orange dust cover. Turn off the pump. REMEMBER--never overtighten joints or breakage will result. If the joints can not be sealed with gentle tightening, the Teflon® "O"-rings are worn or defective and must be replaced.

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



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

#### 14. Sampling

##### 14.1 Placement of Denuder System

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

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

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

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

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

14.1.3 A summary of key criteria associated with these siting factors for air monitoring stations is included in Table 3.0. The information included in the table should be used to the extent possible as part of the monitoring network design to ensure that the monitoring program provides representative and unbiased data. However, site-specific constraints could make it very difficult to meet all criteria. For example, wooded areas around a site would make the siting very difficult. The use of the information in Table 3.0, coupled with a balanced evaluation by an experienced air quality and meteorology specialist, is highly recommended.

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

##### 14.2 Start-Up

14.2.1 Remove the ADS from its field-to-lab carrying case and load into the field sampling box. The ADS field sampling box is insulated with polyurethane which is configured to hold the ADS without allowing movement. Chrome plated spring clips hold the denuders in place. Automatic and manual control switches



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allow the sampling box to control the temperature of the ADS. The automatic switch should be used when the ADS is not in use and when the ADS is sampling for extended periods of time without constant supervision to prevent low temperature or sudden pressure change exposure of the ADS (these types of exposure can cause leaks to occur, condensation, or the filters to tear). When sampling, the ADS should be kept 1EC above the ambient temperature to prevent condensation. The sampling box has two connections with the pump timer: the plastic suction hose connected with "Quick-Release" couplers and the 12-V power cord with a "Quick-Disconnect" coupler. The power cord remains connected, and the suction hose is disconnected from the box each time the unit is opened. Inside the box, the hose is connected to the top of the filter pack with a "Quick-Release" coupler. During sampling the sample box is kept securely closed (see Figure 2).

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

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

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

14.2.5 Attach DGM output to elutriator inlet. Turn on pump. Record start time on Field Test Data Sheet (see Figure 13). Using a stopwatch, record the time for 20.0 L to pass through the DGM. Record the DGM temperature and the absolute pressure of the DGM.

14.2.6 Calculate the flow rate as follows:

$$Q_{sd} = (V/t)(P_{br}/P_{sd})(T_{sd}/T_m)(F_c)$$

where:

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

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

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

$P_{br}$  = barometric pressure, mm Hg.

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

$T_{sd}$  = standard temperature, 298EK.

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

$F_c$  = dry gas meter correction factor, dimensionless.

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

14.2.8 Record the flow rate on Field Test Data Sheet.

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



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### 14.3 Sample Shutdown

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

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

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

### 14.4 Corrective Action for Leak Test Failure

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

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

**14.4.2 Cracked or Chipped Denuders or Elutriator Assemblies.** Note problem on Field Test Data Sheet. Discard defective pieces. Do not try to extract cracked pieces. **WARNING--USE CAUTION WHEN DISASSEMBLING CRACKED GLASSWARE.** Pieces may shatter and cause severe cuts. Wear protective clothing.

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

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

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

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

### 15. ADS Disassembly

**15.1** Remove the ADS from the field-to-lab carrying case using both hands. To prevent stress, hold the ADS by its ends.

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

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



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

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

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

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

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

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

#### 16. Extraction Procedures

*[Special precaution: Samples should be analyzed as soon after collection as possible. The solutions and extraction procedures must be prepared and performed on the day of pH analysis.]*

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

##### 16.1 Impactor Frit Coating Extraction (Optional)

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

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

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

##### 16.2 Denuder Extractions

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



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16.2.1 Cap one end of each of the denuders (i.e.,  $\text{Na}_2\text{CO}_3$  and citric acid denuders). Add 5 mL of DDW with a pipet. Cap other ends of the denuders.

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

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

16.2.4 Add 1 mL of hydrogen peroxide to oxidize the sulfite ( $\text{SO}_3^-$ ) to sulfate ( $\text{SO}_4^-$ ) in the extraction bottles containing the  $\text{Na}_2\text{CO}_3$  coating.

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

### 16.3 Filter Extraction

#### 16.3.1 Teflon® Filter Extraction [for pH analysis followed by $\text{SO}_4^-$ , $\text{NO}_3^-$ and/or $\text{NH}_4^+$ analyses]

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

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

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

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

16.3.1.4 Handling the exposed Teflon® filter requires protection from contamination with  $\text{NH}_3$ , which may rapidly neutralize aerosol acidity on the filter and bias the sample results. To ensure ammonia-free air occupies the glove-box, a positive pressure is maintained by blowing air through a PVC tube (4" O.D.) filled with glass-wool dosed with citric acid before entering the manifold which enables uniform distribution of air from top of the glove-box. Flow the ammonia-free air for 5 minutes before retrieving the filter. Place a citric acid soaked filter paper on the bottom to deplete ammonia when unused. Disassemble the filter assembly in the clean, ammonia-free glove-box. Clean all glove-box surfaces and utensils with ethanol.

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

16.3.1.6 Pipet 6 mL of 0.0001 N perchloric acid ( $\text{HClO}_4$ ) solution into the appropriately labeled extraction vials (10 mL).

*[Note: Perchloric acid is used because it inhibits  $\text{CO}_2$  from dissolving into the solution and keeps the organic compounds in solution from dissociating. Both these activities can change the ionic strength of solution.]*

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





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

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

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

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

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

**16.3.1.11** After transferring the extracts to the 2 mL cups, recap the 10 mL extraction vial. Store the 10 mL vials at 4EC in a refrigerator pending analysis by IC, and for  $\text{NH}_4^+$  analysis by Technicon auto analyzer.

**16.3.2 Nylon Filter Extraction.**

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

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

**16.3.2.2** Place the nylon filter in the extraction vial.

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

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

**17. Ion Chromatography Analysis**

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



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### 17.1 Standards Preparation

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

#### 17.1.1 Sodium Sulfate Stock Solution.

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

17.1.1.2 On weighing paper, weigh out enough reagent ( $\text{Na}_2\text{SO}_4$ ) to make the solution 2000 ppm concentration. The target weight is  $2.958 \pm 0.001$  g. Record the gross weight.

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

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

#### 17.1.2 Sodium Nitrate Stock Solution.

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

17.1.2.2 On weighing paper, weigh out enough reagent ( $\text{NaNO}_3$ ) to make the solution 2000 ppm concentration. The target weight is  $2.742 \pm 0.001$  g. Record the gross weight.

17.1.2.3 Follow Sections 17.1.1.3 and 17.1.1.4.

17.1.3 Standard working solutions (100 ppm  $\text{SO}_4^{2-}$  and 100 ppm  $\text{NO}_3^-$ ). The working solutions are made as follows: Add 10 mL each of the two stock solutions ( $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ ) to a 200 mL volumetric flask and dilute to the mark with DDW. Subsequent dilutions are carried out using a 10 mL volumetric pipet and appropriate flasks. Standards of 20, 10, 5 and 1 ppm  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  are prepared to calibrate the IC.

### 17.2 Reagent Preparation

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

17.2.1 Anion eluent. The anion eluent is a solution of 1.8 mM  $\text{Na}_2\text{CO}_3$  and 1.7 mM  $\text{NaHCO}_3$ . A concentrated solution can be prepared and diluted as needed.

[Note: See Anion Storage Solution]

17.2.1.1 Concentrated  $\text{Na}_2\text{CO}_3$  solution (0.36 M). Weigh out 38.156 g of  $\text{Na}_2\text{CO}_3$  (MW = 105.99). Dissolve into 1 L of DDW. Store in refrigerator until ready to dilute.

17.2.1.2 Concentrated  $\text{NaHCO}_3$  solution (0.34 M). Weigh out 28.564 g of  $\text{NaHCO}_3$  (MW = 84.01). Dissolve into 1 L of DDW. Store in refrigerator until ready to dilute.

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

17.2.2 Anion regenerant. The regenerant is a 0.025 N  $\text{H}_2\text{SO}_4$  solution. VERY CAREFULLY dispense 2.8 mL of concentrated Ultrex sulfuric acid (36 N) into a graduated cylinder. Partially fill the regenerant reservoir with DDW (3 L). Slowly add the acid to the regenerant reservoir. Bring to the mark with DDW (4 L).

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



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

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

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

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

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

### 17.3 Sample Preparation

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

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

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

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

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

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

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

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

#### 17.4.1 Start-up Procedure for Ion Chromatograph.

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



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

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

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

17.4.1.5 Prime the eluent lines.

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

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

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

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

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

17.4.1.7 Select the columns to be used (labeled pH or NO<sub>2</sub>) by pressing the blue button located below the labels. To verify that the correct columns are being used, press the switch should at least once, and then set to the appropriate position.

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

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



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

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

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

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

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

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

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

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

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

17.4.3.2 Fill the IC vials with the prepared standard solutions and (20, 10, 5 and 1 ppm SO<sub>4</sub><sup>-</sup> and NO<sub>3</sub><sup>-</sup>) and pure eluent. This will allow a four-point calibration curve to be made.

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

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

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

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



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

**17.4.4 System Shut-down.**

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

17.4.4.2 Switch the eluent degas switch to HIGH.

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

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

**17.5 Basic Troubleshooting**

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

**17.5.1 Unstable Baselines**

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

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

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

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

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

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

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

**17.5.3 Flow**

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

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



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

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

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

#### 18. Ammonia Analysis by Technicon Autoanalysis

Presented in Sections 18.1 and 18.2 are the recipes for the standards and reagents required to analyze the ammonium ion ( $\text{NH}_4^+$  or ammonia ( $\text{NH}_3$ )) by Technicon autoanalysis. The prelude of these sections briefly describes the TRAACS 800 autoanalyzer and the sample flow through the TRAACS 800 for  $\text{NH}_4^+$  analysis. This instrument is capable of quantifying, from a single sample, three different species simultaneously. An aliquot of the sample is taken from an automated sampler by syringe. A splitter divides the aliquot into the appropriate volumes required for the particular analyses. Each of the volumes is then transferred to the appropriate analytical cartridge. Sample flow diagrams that illustrate  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  analysis (although in Method IO-4, only ammonia is analyzed by this technique) from the citric acid denuder and Teflon® filter can be shown separately and independently of one another. The data computation (by computer) and quality assurance protocols, however, can not be readily adapted to single-channel instruments. These protocols need to be specific to the individual analytical instrument. In brief,  $\text{NH}_4^+$  analysis is illustrated in Figure 16. The samples, along with all standards, are taken from the auto-advance sampler tray by the use of a proportioning pump and automated syringe. Air and EDTA are first added to the samples and are mixed in the first set of coils. After mixing, phenolate is added and mixed in the next set of coils. Nitroprusside is then added and mixed, followed by the addition and mixing of hypochlorite. At this stage, the sample should be a bright blue color. After the last mixing stage, the sample is sent through a heated bath, followed by another mixing stage. Finally, the sample is sent through a colorimeter where the results are recorded on a digital printer and stored in a computer file for further manipulation.

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

#### 18.1 Standards and Stock Solutions Preparation

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

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

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

**18.1.3 Working Ammonium Standards in DDW.** Pipet aliquots of the 100  $\mu\text{g}/\text{mL}$  ammonium intermediate standards into 100 mL volumetric flasks according to the table below. Dilute to volume with DDW. Prepare fresh daily.



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

### 18.2 Reagent Preparation

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

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

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

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

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

## 19. pH Analysis

### 19.1 Standard and Reagent Preparation

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





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**19.1.1 Standard H<sub>2</sub>SO<sub>4</sub> Solution.**



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19.1.1.1 Label seven 25 mL polyethylene stoppered volumetric flasks. Also, label each flask with the volume of 1 N H<sub>2</sub>SO<sub>4</sub> solution indicated in the following table:

Standard H <sub>2</sub> SO <sub>4</sub> , Flask No.	Volume of 1.000 N H <sub>2</sub> SO <sub>4</sub> added to each flask, μL	Standard concentration, 10 <sup>-3</sup> N H <sub>2</sub> SO <sub>4</sub>
1	0	0
2	25	1
3	50	2
4	100	4
5	200	8
6	400	16
7	800	32

19.1.1.2 Use the 25 μL automatic pipet to add 1 N stock H<sub>2</sub>SO<sub>4</sub> to flasks #1-3. Use the 100 μL pipet to add 1 N stock H<sub>2</sub>SO<sub>4</sub> to flasks #4-7. Dilute all flasks to the 25 mL mark with absolute ethanol. Cap with stoppers or parafilm and mix well.

**19.1.2 2 M Potassium Chloride (KCl) Solution.**

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

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

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

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

**19.1.3 0.1 N Perchloric Acid (HClO<sub>4</sub>) Solution.**

19.1.3.1 Fill a 1 L graduated cylinder about ½ full with DDW. Transfer 10 ± 0.1 mL of 60-62% HClO<sub>4</sub> into the 1 L cylinder with a 10 mL pipet.

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

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

**19.1.4 0.01 N HClO<sub>4</sub> Solution.**

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

19.1.4.2 Measure 100 mL of the 0.1 N HClO<sub>4</sub> solution with the 100 mL graduated cylinder. Add solution to the 1 L cylinder.

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

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

**19.1.5 Extraction Solution (0.0001 N HClO<sub>4</sub>).**

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

19.1.5.1 Using a 5 mL calibrated automatic pipet, add 10 ± 0.1 mL of 0.01 N perchloric acid (HClO<sub>4</sub>) to a 2L Erlenmeyer flask of water. Add 990 ± 10 mL of DDW to the flask.



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

**19.1.6 EA Solution.**

19.1.6.1 Measure  $150 \pm 2$  mL of 0.0001 N  $\text{HClO}_4$  (prepared in Section 19.1.5) into a 250 mL graduated cylinder. Transfer to a 250 mL Erlenmeyer flask.

19.1.6.2 Using a 5 mL graduated cylinder, add  $5 \pm 0.1$  mL of ethanol (from the same fresh bottle of ethanol that was used to prepare the standards in 19.1.1) to the flask.

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

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

**19.1.7 Working Standard Test Solutions.**

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

19.1.7.2 Using the displacement pipet, add 50  $\mu\text{L}$  of absolute ethanol to each cup. Pour about 3 mL of standard ( $\text{H}_2\text{SO}_4$  solution) #1 into a labeled 4 mL cup.

19.1.7.3 Immediately pipet 50  $\mu\text{L}$  of this standard into the 4 mL cups labeled 1 and 1\* containing the EA solution and ethanol.

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

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

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

**19.2 Calibration of pH Meter**

The pH meter requires temperature calibration whenever a new electrode is used. Use the manufacturer's procedure in the instrument manual. This calibration should be repeated every 3 months when not in use. The pH meter is left with the power cord plugged into the AC outlet, the mode control knob is left in the standby position, the electrode lead is partially disconnected by pressing the plastic ring on its outer edge, and the combination electrode is immersed in a 4 M KCl solution (a slit rubber stopper seals the bottle with the electrode in it). Keep a record of the temperature calibrations in a lab notebook.

**19.3 Pre-Analysis Calibration**

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

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



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

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

19.3.4 Test the pH by turning to the pH mode of the meter. Allow the reading to stabilize for at least 30 s. Record the result on the log for "1st cup."

19.3.5 Turn to standby mode, and then test the last cup of pH 7 buffer. Record the results on the log for the "2nd cup." If the pH value for the 2nd cup is not  $7.00 \pm 0.01$ , adjust the "calib." knob to obtain a reading of 7.00. Note this adjustment on the log.

19.3.6 Fill three 4 mL cups with pH 4 buffer. With the meter in the standby mode, remove the cup containing pH 7 buffer, wipe the tip of the electrode gently with a Kimwipe® and then rinse the electrode with the first cup of pH 4 buffer.

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

#### 19.4 pH Test 0.01 N HClO<sub>4</sub> Solution

*[Note: The 0.01 N HClO<sub>4</sub> solution is used to prepare the ES solution, which is used to prepare the EA solution. The pH value for the EA solution must be  $4.09 \pm 0.04$ . If this pH value is not achieved, the 0.01 N HClO<sub>4</sub> solution must be reprepared.]*

19.4.1 Calibrate the pH meter with pH 4 buffer.

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

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

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

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

#### 19.5 Analysis of Working Standard

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

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

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

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

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



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

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

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

19.5.6 Use the mode control knob in the "temp." position to measure the temperature of the test solutions every 5-10 samples and record the results on the logsheet.

#### 19.6 Analysis of Filter Extracts

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

### 20. Atmospheric Species Concentration Calculations

The system described in the previous sections collects nitric acid ( $\text{HNO}_3$ ), sulfur dioxide ( $\text{SO}_2$ ), ammonia ( $\text{NH}_3$ ), particulate sulfate ( $\text{SO}_4^{2-}$ ), particulate nitrate ( $\text{NO}_3^-$ ), particulate ammonium ( $\text{NH}_4^+$ ), and acidic ( $\text{H}^+$ ) particles. The collection of each of these species is illustrated in Figure 1. Nitric acid and sulfur dioxide gases are collected on denuder one. Ammonia gas is collected on denuder two. Particulate sulfate, nitrate, and ammonium are collected on the first (Teflon®) filter, while some of the particulate nitrate collected on the Teflon® filter evaporates and collects on the second (nylon) filter. Also collected on the Teflon® filter are fine particles that contain hydrogen ions ( $\text{H}^+$ ), though probably not free  $\text{H}^+$ . Hydrogen ions are most likely present in the  $\text{H}_3\text{O}^+$  form. The concentration of these  $\text{H}^+$  ions indicates the atmospheric acid aerosol content and is collected on the nylon filter. Prepare the Teflon® filter extracts for pH analysis prior to IC analysis for the particulate sulfate contents. Special precautions must be taken to prevent contamination of the Teflon® filters by ammonia before either of the analyses.

#### 20.1 Assumptions of the Annular Denuder System

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

- The first denuder stage collects 100% of sampled  $\text{HNO}_3$  as nitrate. (Since the diffusivity of  $\text{HNO}_3$  is high, diffusion to the side walls is assumed to be very quick.)
- The first denuder collects 100% of the  $\text{SO}_2$  as sulfite, which can oxidize to sulfate.



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*[Note: Before analysis, add hydrogen peroxide ( $H_2O_2$ ) to oxidize the sulfite ( $SO_3$ ) to sulfate ( $SO_4^{2-}$ ) to simplify the calculations.]*

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

20.1.2 Analytical results from the IC and technician autoanalysis are given in units of  $\mu g/mL$  from  $NO_3^-$ ,  $SO_4^{2-}$ , and  $NH_4^+$ , respectively.

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

## 20.2 Calculation of Air Volume Sampled, Corrected to Standard Conditions

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

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

where:

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

t = net elapsed time, min.

$V_t$  = total sample volume, L.

20.2.2 Convert L to  $m^3$  by:

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

where:

$V_s$  = total sampling volume,  $m^3$ .

$10^{-3}$  = conversion factor,  $m^3/L$ .

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



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

where:

- $V_{std}$  = volume of sample at EPA-reference conditions, m<sup>3</sup>.
- $V_s$  = volume of gas sample through the dry gas meter, or calculated volume sampled as indicated by rotameter (see Section 20.2.2), m<sup>3</sup>.
- $T_{std}$  = absolute EPA-reference temperature, 298EK.
- $T_m$  = average flowmeter or dry gas meter temperature, EK.
- $P_{bar}$  = barometric pressure of flow or volume measurement condition, mm Hg.
- $P_{std}$  = EPA-reference barometric pressure, 760 mm Hg.
- $Y$  = dry gas meter calibration factor (if applicable), dimensionless.

**20.3 Calculations of Concentration Using Results from IC and Technicon Autoanalysis**

**20.3.1 Analytical Results for HNO<sub>3</sub> from Na<sub>2</sub>CO<sub>3</sub> Denuder**

$$C_g(\text{HNO}_3), \mu\text{g}/\text{m}^3 = 1.016 [\text{NO}_3^- (\mu\text{g}/\text{mL}) \times 10 \text{ mL}] / V_{std}$$

This factor 1.016 represents the ratio of molecular weights of HNO<sub>3</sub> and NO<sub>3</sub><sup>-</sup>. Subscript "g" denotes "gas."

**20.3.2 Analytical Results for SO<sub>2</sub> from Na<sub>2</sub>CO<sub>3</sub> Denuder**

$$C_g(\text{SO}_2), \mu\text{g}/\text{m}^3 = 0.667 [\text{SO}_4^{2-} (\mu\text{g}/\text{mL}) \times 10 \text{ mL}] / V_{std}$$

The factor 0.667 represents the ratio of molecular weights of SO<sub>2</sub> and SO<sub>4</sub><sup>2-</sup>. Subscript "g" denotes "gas."

**20.3.3 Analytical Results for NH<sub>3</sub> from Citric Acid Denuder**

$$C_g(\text{NH}_3), \mu\text{g}/\text{m}^3 = 0.944 [\text{NH}_4^+ (\mu\text{g}/\text{mL}) \times 10 \text{ mL}] / V_{std}$$

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

**20.3.4 Analytical Results for Particulate SO<sub>4</sub><sup>2-</sup> Captured on Teflon® Filter**

$$C_p(\text{SO}_4), \mu\text{g}/\text{m}^3 = [\text{SO}_4^{2-} (\mu\text{g}/\text{mL}) \times 6.2 \text{ mL}] / V_{std}$$

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

**20.3.5 Analytical Results for Particulate NH<sub>4</sub><sup>+</sup> Captured on Teflon® Filter**

$$C_p(\text{NH}_4^+), \mu\text{g}/\text{m}^3 = [\text{NH}_4^+ (\mu\text{g}/\text{mL}) \times 6.2 \text{ mL}] / V_{std}$$



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

**20.3.6 Analytical Results for Particulate NO<sub>3</sub>G Captured on Teflon® Filter**

$$C_{pt} (\text{NO}_3\text{G}), \mu\text{g}/\text{m}^3 = [\text{NO}_3\text{G}(\mu\text{g}/\text{mL}) \times 6.2 \text{ mL}] / V_{std}$$

Nitrates evaporator from the Teflon® filter during sampling, so one must also calculate the NO<sub>3</sub>G on the nylon filter. The subscript "pn" denotes particles on Teflon® filters.

$$C_{pn} (\text{NO}_3\text{G}), \mu\text{g}/\text{m}^3 = [\text{NO}_3\text{G}(\mu\text{g}/\text{mL}) \times 10 \text{ mL}] / V_{std}$$

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

$$C_p (\text{NO}_3\text{G}) = C_{pt} (\text{NO}_3\text{G}) + C_{pn} (\text{NO}_3\text{G})$$

**20.4 Calculations Using Results from pH Analysis**

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

**20.4.1 Adjustment for Filter vs. Non-Filter Standards.** This adjustment is necessary because experiments showed that the measured acid concentration from filters doped with H<sub>2</sub>SO<sub>4</sub> stock standards yielded concentrations, as measured by the difference from EA solution, that were about 3% lower than the values found for working standards (prepared without filters from the same stock standards). The results gave the following relation (by linear regression):

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

where:

C<sub>f</sub> = calculated net strong acid concentration as would be obtained from filter standards doped with H<sub>2</sub>SO<sub>4</sub>.

C<sub>nr</sub> = the apparent net strong acid concentration of H<sub>2</sub>SO<sub>4</sub> based on standards prepared without filters.

For each working standard (non-filter), on a given analysis day, calculate the "apparent net strong acid concentration of H<sub>2</sub>SO<sub>4</sub>" as follows:

$$C_{nr} = 10^{-pEWS} - 10^{-pBEA}$$





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where:

pH<sub>WS</sub> = measured pH for a working standard (or apparent strong acid concentration for non-filter H<sub>2</sub>SO<sub>4</sub> doped standards).

pH<sub>EA</sub> = measured pH for the EA solution (or apparent strong acid concentration for non-filter, non-H<sub>2</sub>SO<sub>4</sub> doped standard).

After calculating the C<sub>nr</sub> values for each working standard, use the above equation to calculate the adjusted values of C<sub>r</sub> for each.

**20.4.2 Determination of Nominal Strong Acid Concentration for Filter Samples.** The apparent net strong acid concentration of each sample filter extract, C<sub>s</sub>, is calculated as with the working standards:

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

where:

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

pHEA = measured pH for the EA solution (or apparent strong acid concentration for non-filter, non-H<sub>2</sub>SO<sub>4</sub> standards).

*[Note: The C<sub>s</sub> values for the filter extracts are directly comparable to the C<sub>r</sub> values for the working standards, since the C<sub>r</sub> values have been adjusted for the difference in apparent acid concentration for tests made with filters and tests made without filters.]*

**20.4.3 Calculation of Strong Acidity Aerosol Concentration.** Calculate the final concentration of apparent net fine particle (<2.5 Fm) strong acidity (as H<sub>2</sub>SO<sub>4</sub>):

$$C(\text{H}^+) = C_r / V_{sd}$$

where:

C<sub>gr</sub> = apparent net fine particle strong acidity concentration, Fg/m<sup>3</sup>.

C<sub>r</sub> = apparent net strong acid, Fg, as calculated from standard curve.

V<sub>sd</sub> = volume of sampled gas at EPA-referenced conditions (see Section 17.2.3), m<sup>3</sup>.

**21. Variations of Annular Denuder System Usage**

As described in Sections 3 and 4, the ADS is used to measure reactive acidic (SO<sub>2</sub> and HNO<sub>3</sub>) and basic (NH<sub>3</sub>) gases, particulate sulfates and nitrates, and strong acidity of atmospheric particles (<2.5 μm) found in ambient air. The unique features of the ADS that separate it from established air monitoring methods are the ability of sampling artifacts to be eliminated from the collected gases and particles and preservation of the samples for subsequent analysis, which is accomplished by removing NH<sub>3</sub> in the gas stream with a citric acid coated denuder, thus reducing the probability of the particulate acid sulfates (SO<sub>4</sub><sup>-</sup>) captured on the Teflon® filter from being neutralized. The ADS configuration described in this methodology clearly illustrates these unique features. The elutriator is designed to allow only particles with <2.5 μm diameter into the system. The impactor is designed to reduce the possibility of coarse particle infiltration even further. And finally, the sequence of the



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

21.1 Today, the ADS is being used in intercomparison studies to assess  $\text{NH}_3$  concentration differences indoors and outdoors. The assembly used here consists of an elutriator-impactor assembly, an annular denuder, and a filter pack assembly. The elutriator-impactor assembly and the annular denuder are both smaller than those described earlier. The filter pack is available in the smaller size, but an adaptor is also available to assemble the smaller annular denuder to the larger filter pack assembly. This system is referred to as the personal sampler (see Figure 18). It is designed for sampling while attached to the shirt of a worker. The personal sampler can be used to measure other chemical species in indoor air by simply changing the reactive surface (coating) of the annular denuder or the types of filters used.

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

21.3 If one has interest in quantitations  $\text{HNO}_2$  utilizing the ADS, special sampling and analytical concerns must be addressed. As identified in Section 24, Citation 14, guidance is given for accurate quantitation of  $\text{HNO}_2$  in ambient air.

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

## 22. Method Safety

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

## 23. Performance Criteria and Quality Assurance (QA)

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



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### 23.1 Standard Operating Procedures (SOPs)

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

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

### 23.2 QA Program

The user should develop, implement, and maintain a quality assurance program to ensure that the sampling system is operating properly and collecting accurate data. Established calibration, operation, and maintenance procedures should be conducted regularly and should be part of the QA program. Calibration procedures provided in Sections 17 and 19, operation procedures in Sections 14 and 17, and maintenance procedures in Section 17 of this method and the manufacturer's instruction manual should be followed and included in the QA program. Additional QA measures (e.g., trouble shooting) and further guidance in maintaining the sampling system are provided by the manufacturer. For detailed guidance in setting up a quality assurance program, the user is referred to the *Code of Federal Regulations* (Section 24, Citation 12) and the *U. S. EPA Handbook on Quality Assurance* (Section 24, Citation 13).

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

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

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

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

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

### 24. References

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12. 40 CFR Part 58, Appendix A, B.
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**TABLE 1. ESTIMATED DETECTION AND QUANTIFICATION LIMITS  
 FOR THE ANNULAR DENUDER SYSTEM<sup>1</sup>**

Detection limits, $\mu\text{g}/\text{m}^3$	Sampling period		
	1 hour	1 day	1 week
<i>Gaseous species</i>			
SO <sub>2</sub>	3.1	0.13	0.02
HNO <sub>3</sub>	2.0	0.08	0.01
NH <sub>3</sub>	5.6	0.25	0.04
<i>Particulate matter</i>			
SO <sub>4</sub> <sup>2-</sup>	1.6	0.07	0.01
NO <sub>3</sub> <sup>-</sup>	1.8	0.08	0.01
H <sup>+</sup>	1.0	0.05	0.001
<b>Quantification limits, <math>\text{Fg}/\text{m}^3</math></b>			
<i>Gaseous species</i>			
SO <sub>2</sub>	10.4	0.43	0.06
HNO <sub>3</sub>	6.8	0.28	0.04
NH <sub>3</sub>	20.0	0.83	0.12
<i>Particulate matter</i>			
SO <sub>4</sub> <sup>2-</sup>	5.3	0.22	0.03
NO <sub>3</sub> <sup>-</sup>	6.1	0.25	0.04
H <sup>+</sup>	2.1	0.15	0.01

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



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TABLE 2. ACCELERATOR JET DIAMETERS AND CORRESPONDING REYNOLDS NUMBER (RE) FOR SELECTED FLOW RATES TO OBTAIN 2.5  $\mu\text{m}$  DIAMETER (AERODYNAMIC) PARTICLES SEPARATION

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



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

Factor	Criteria
Vertical spacing above ground	<ul style="list-style-type: none"> <li>• 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.</li> <li>• About 1 m or more above the structure where the sampler is located.</li> </ul>
Horizontal spacing from obstruction and obstacles	<ul style="list-style-type: none"> <li>• Minimum horizontal separation from obstructions such as trees should be &gt; 20 m from the dripline and must be 10 m from the dripline when the trees act as an obstruction.</li> <li>• Distance from sampler inlet to an obstacle such as a building must be at least twice the height the obstacle protrudes above the sampler.</li> <li>• 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.</li> <li>• 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.</li> </ul>
Unrestricted airflow  Spacing from roads	<ul style="list-style-type: none"> <li>• 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.</li> <li>• 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.</li> <li>• 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.</li> </ul>



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TABLE 4. DILUTION RATES

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

<sup>a</sup>Based on 6.2 mL extraction volume.

TABLE 5. OTHER CHEMICAL SPECIES  
 AMENDABLE TO ANNULAR DENUDER TECHNOLOGY

Symbol	Chemical Species Collected on Annular Denuder	Coating	Comments
O <sub>3</sub>	Ozone	1% (wt/wt) NaHCO <sub>3</sub> /glycerin	Analysis by IC or colorimetry
HCl HF	Hydrogen Chloride Hydrogen Fluoride	Na <sub>2</sub> CO <sub>3</sub> -alkali coating	Extracted with water/ analyzed by IC
PAHs SVOCs	Semi-volatile polycyclic aromatic hydrocarbons	Ground XAD-4/glycerin	Soxhlet extraction/GC/MS analysis





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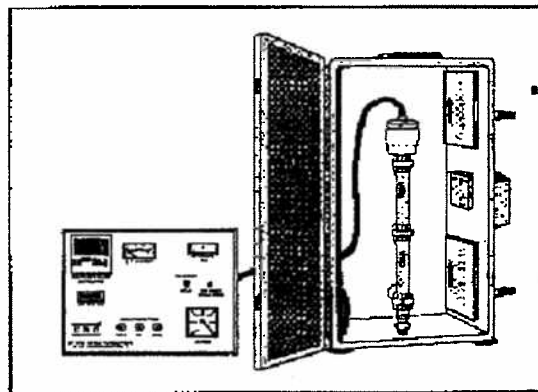
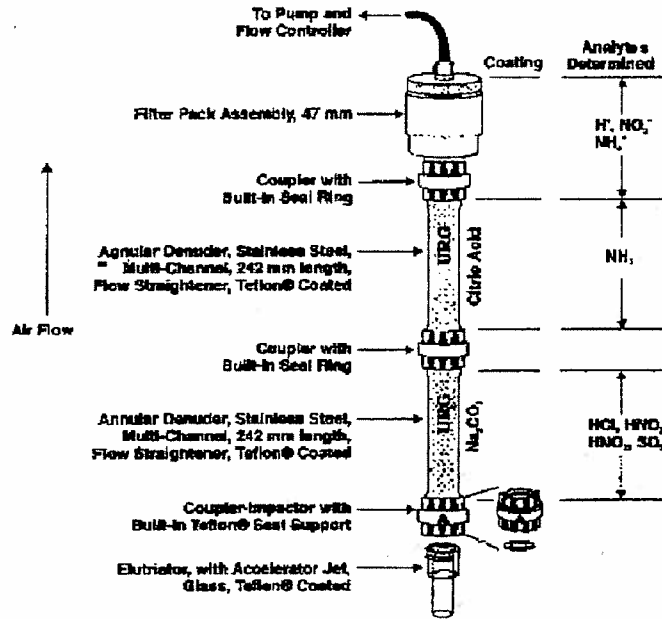


Figure 1. Schematic view of Annular Denuder showing species collected.



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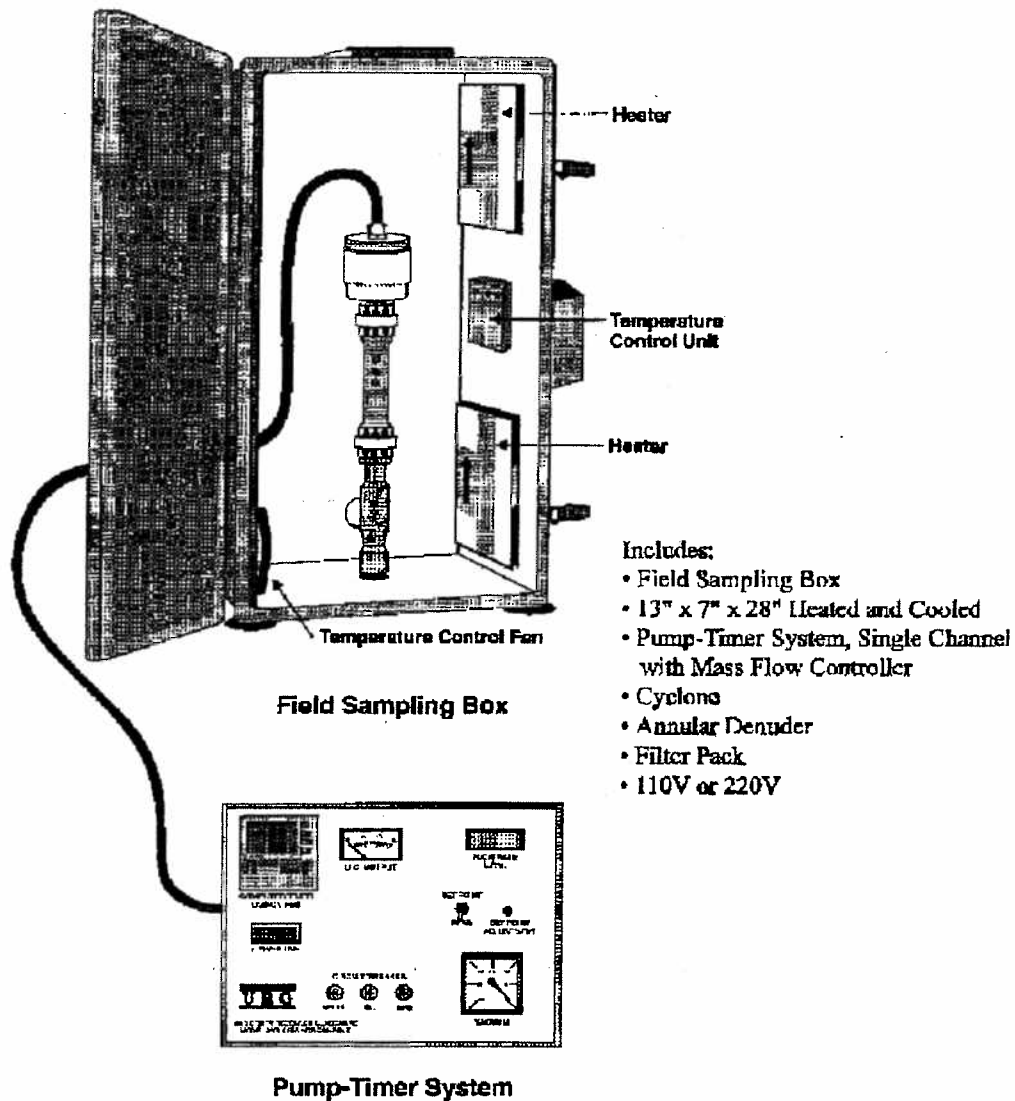


Figure 2. Annular Denuder system in field sampling box.



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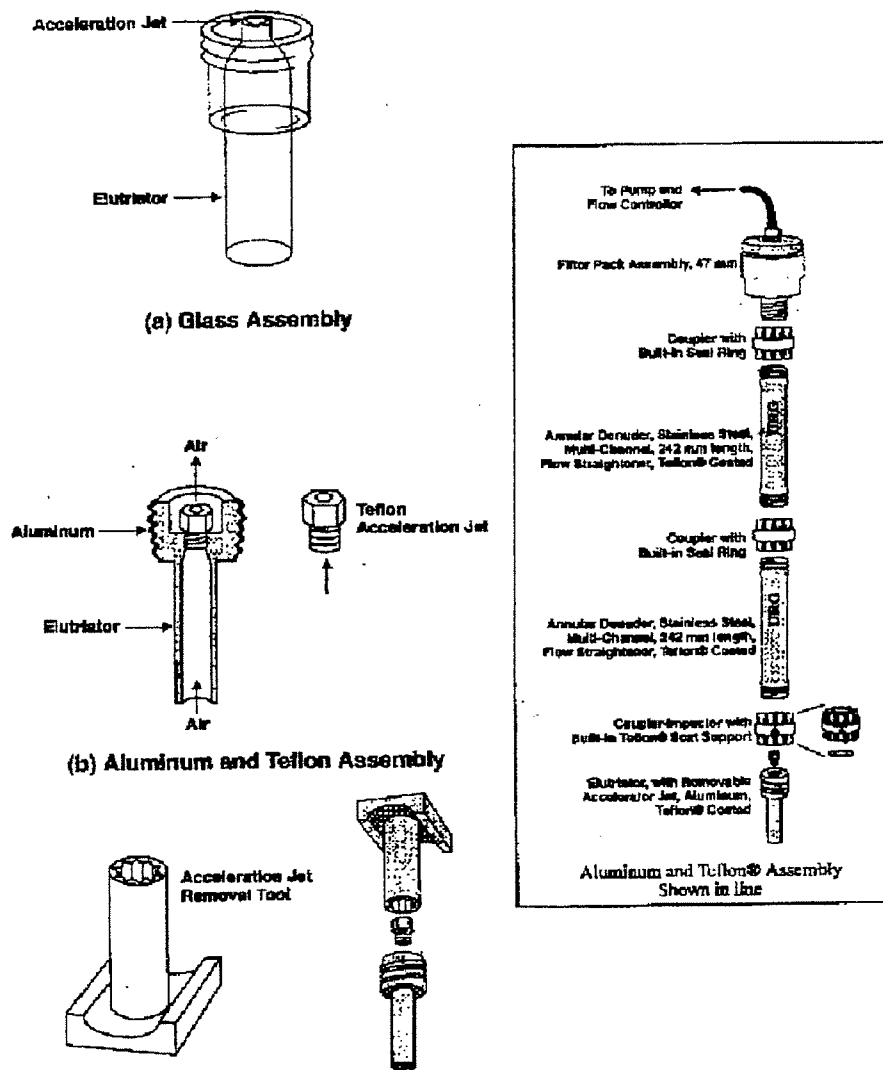


Figure 3. Available elutriator and acceleration jet assemblies.



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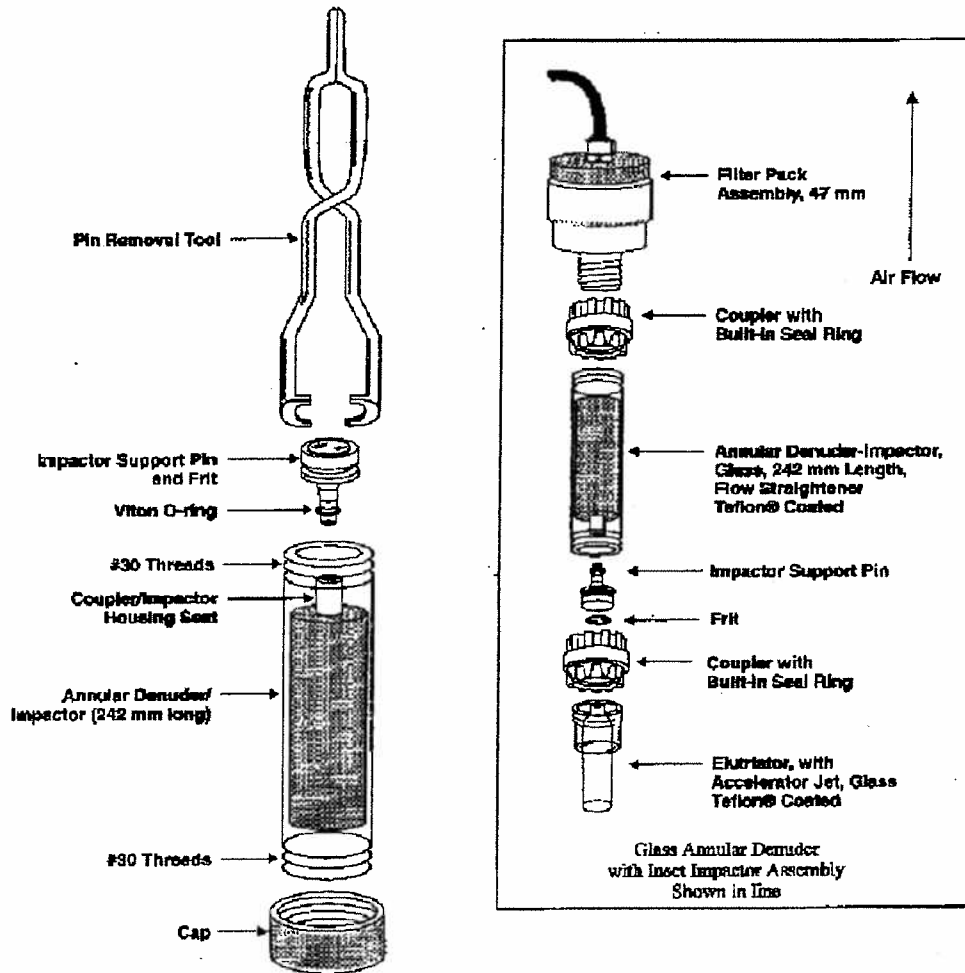


Figure 4. Glass Annular Denuder with inset impactor assembly.



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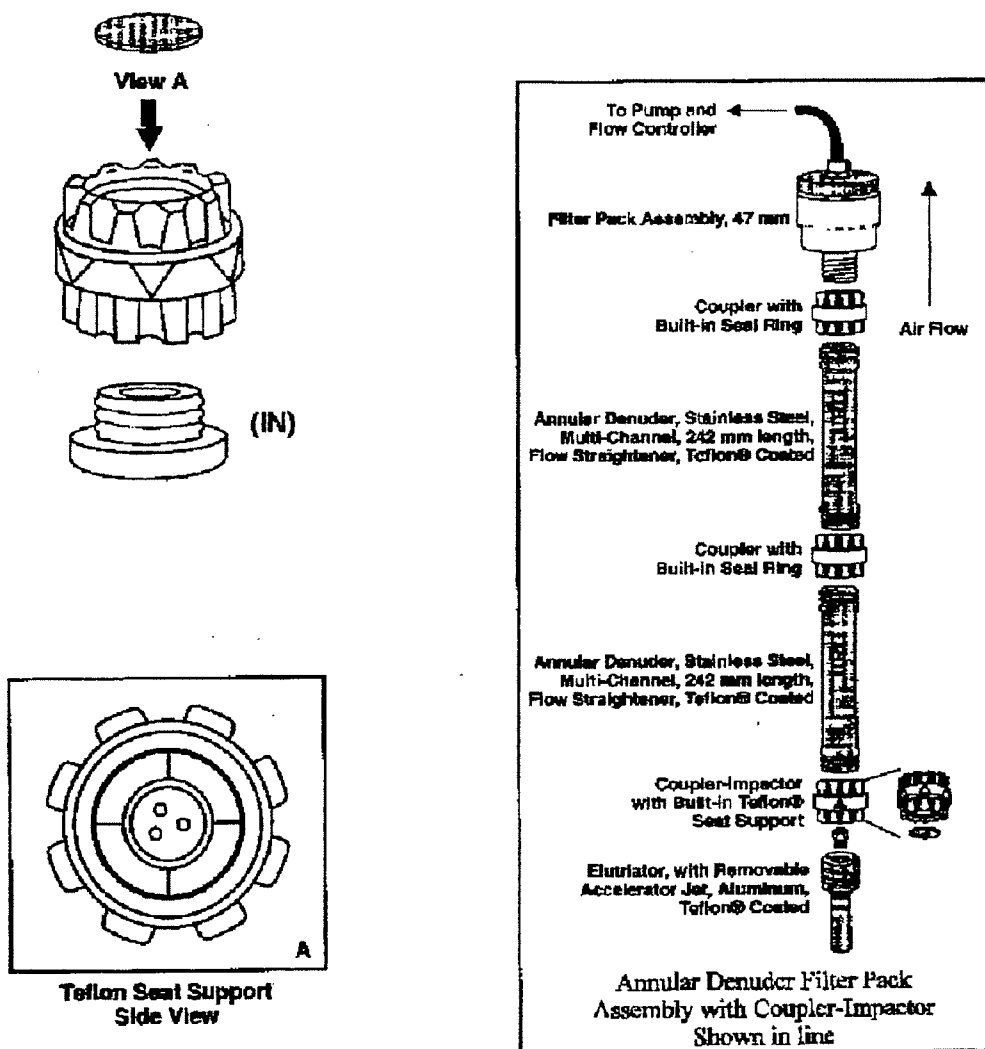


Figure 5. Side view impactor/coupler assembly.



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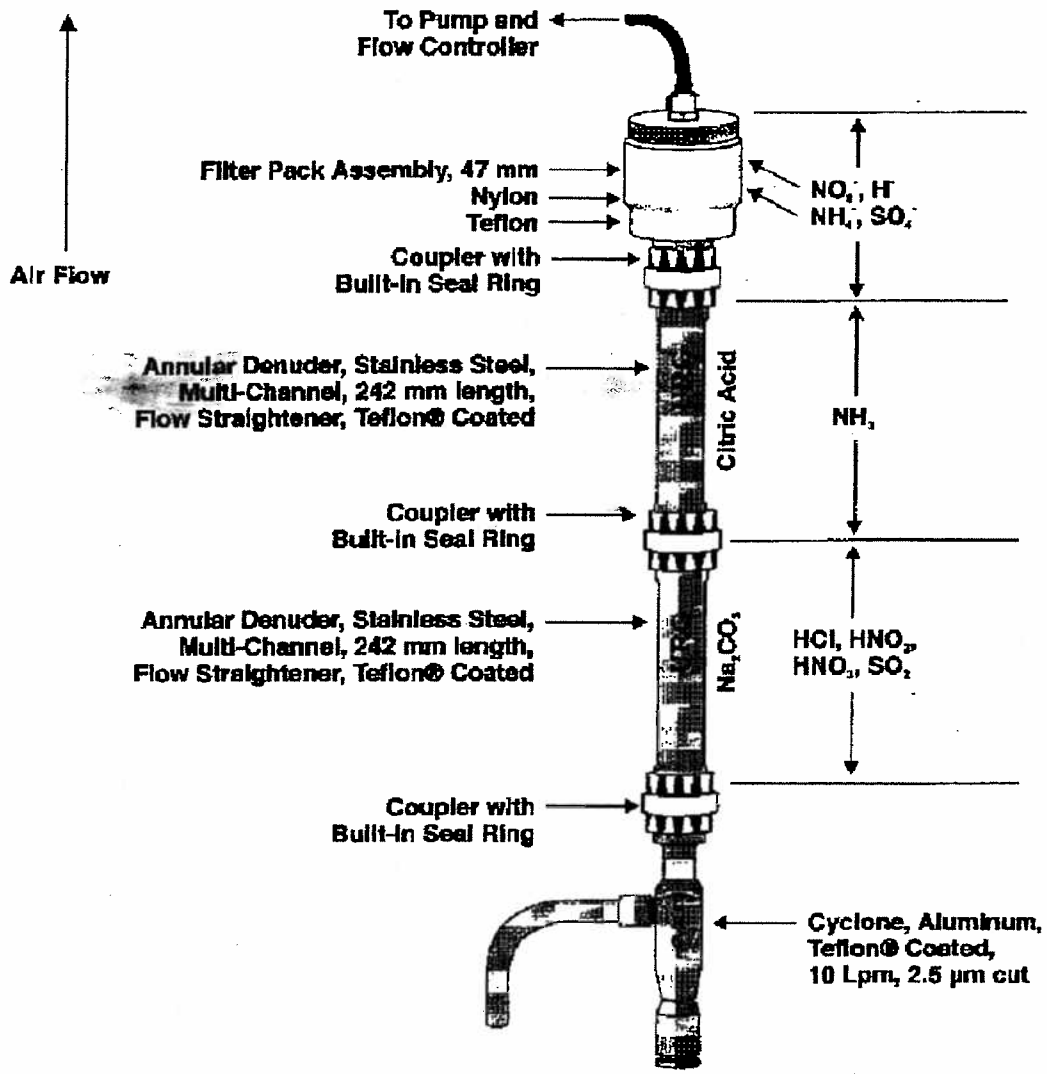


Figure 6. Schematic view of Annular Denuder with cyclone adaptor for removal of coarse particles.



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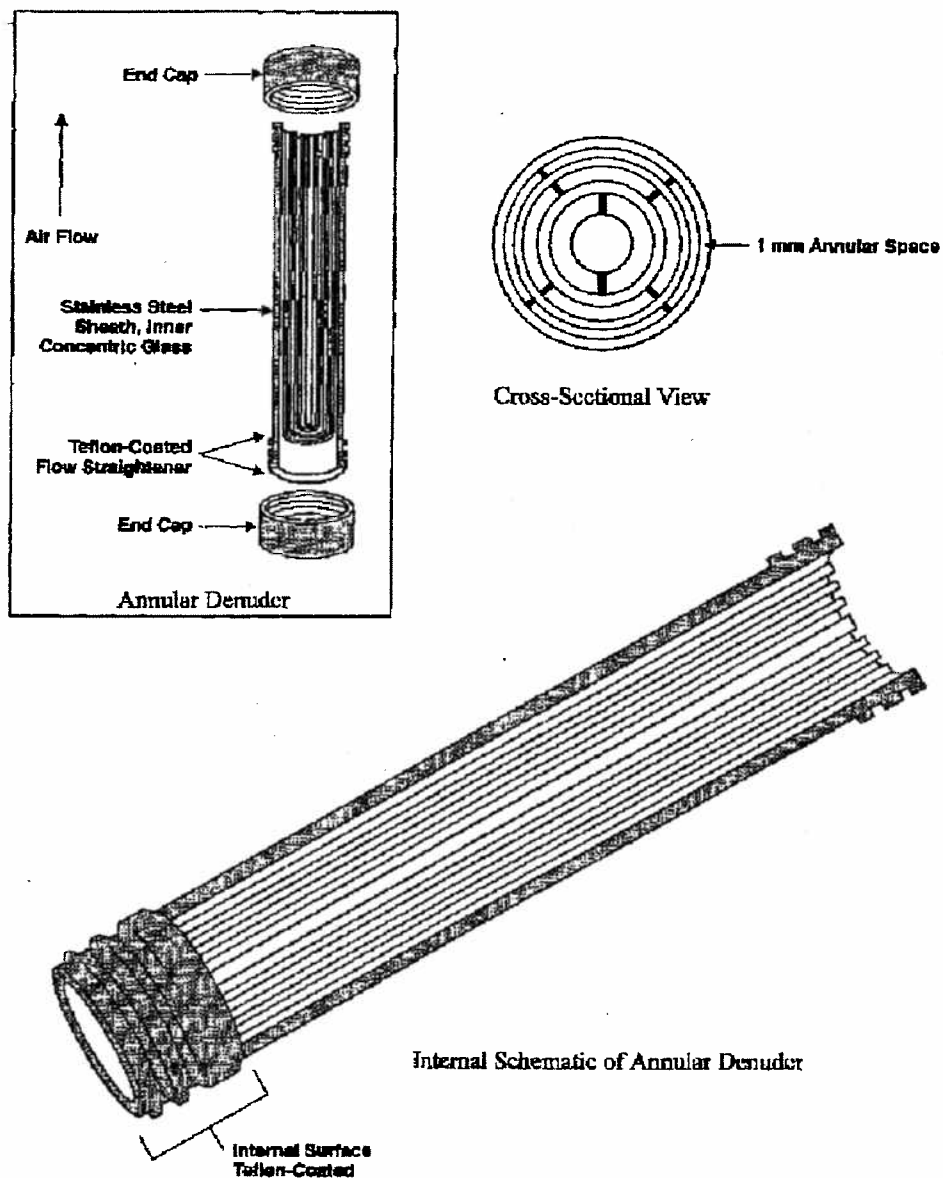


Figure 7. Internal schematic of Annular Denuder.



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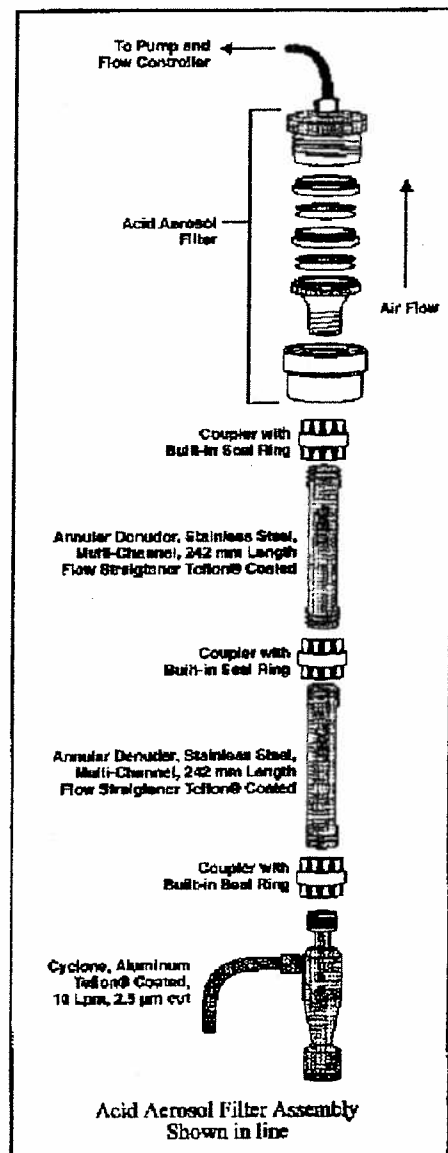
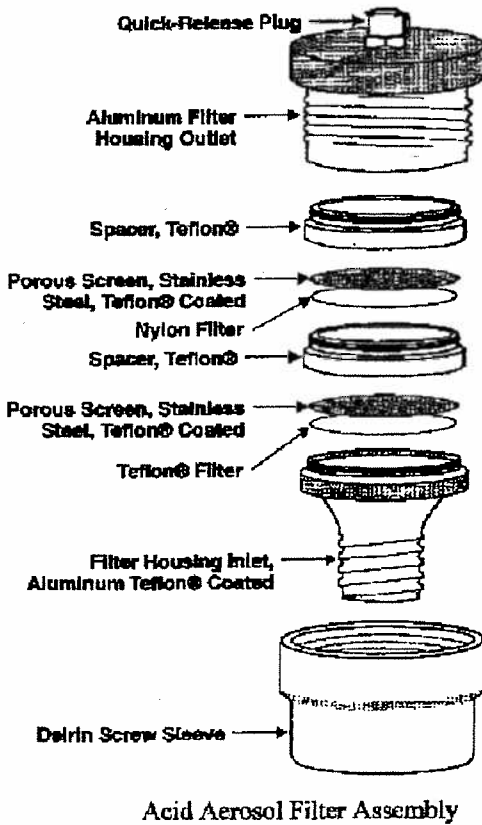


Figure 8. Filter pack assembly.





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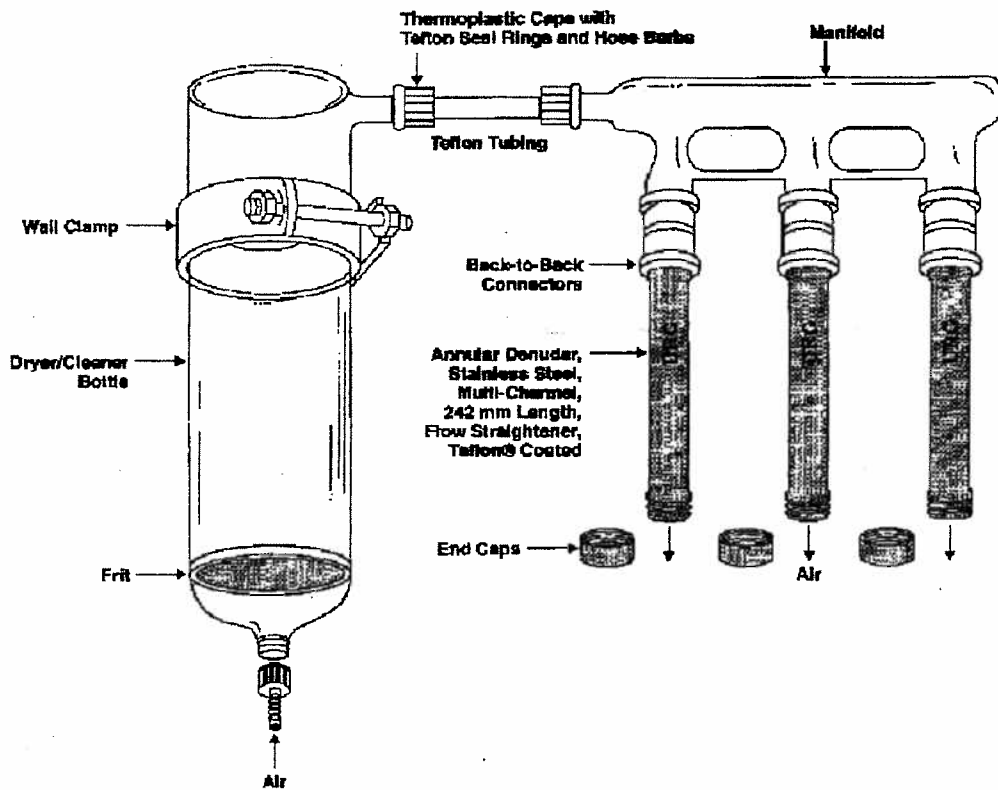


Figure 9. Drying train and manifold.



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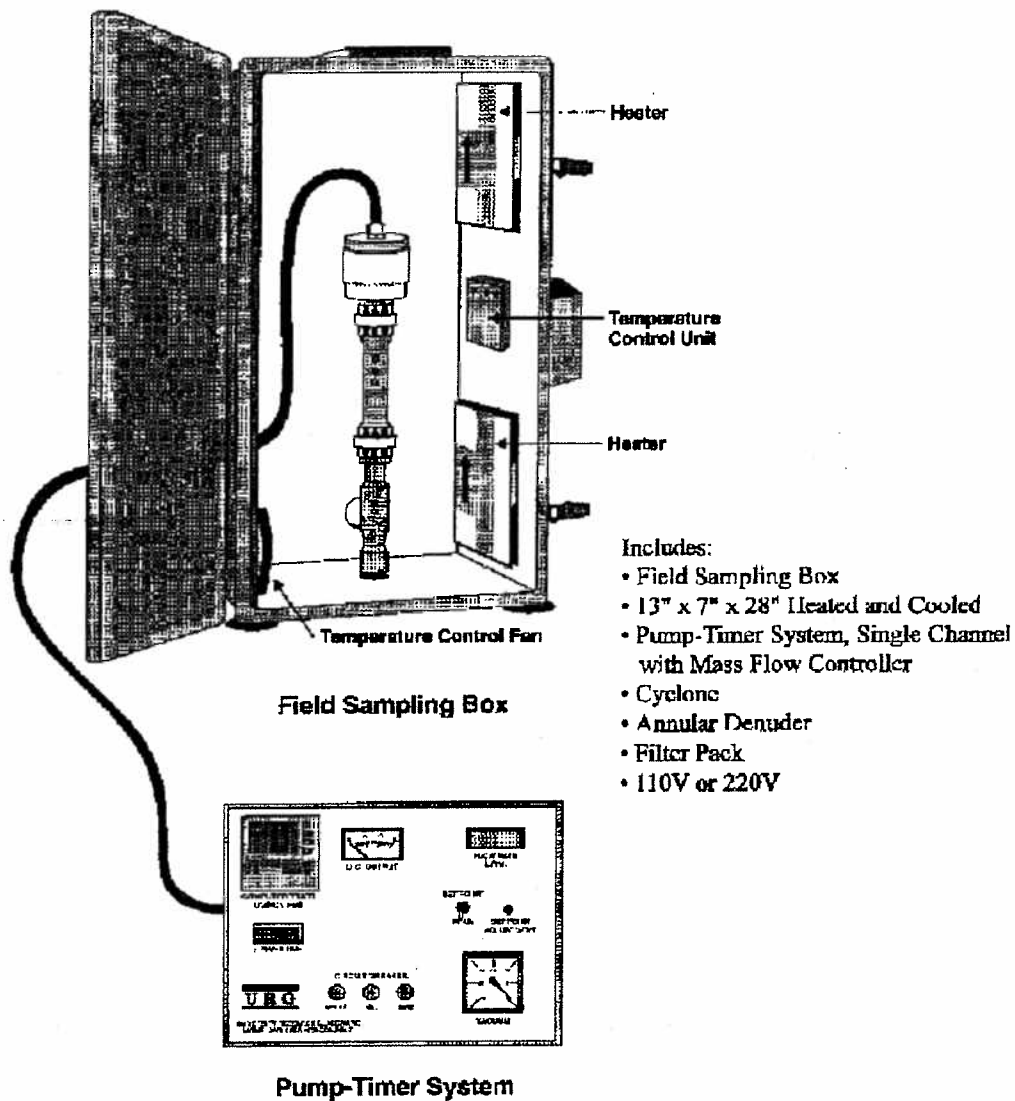


Figure 10. Annular Denuder system with cyclone in heated sampling case.



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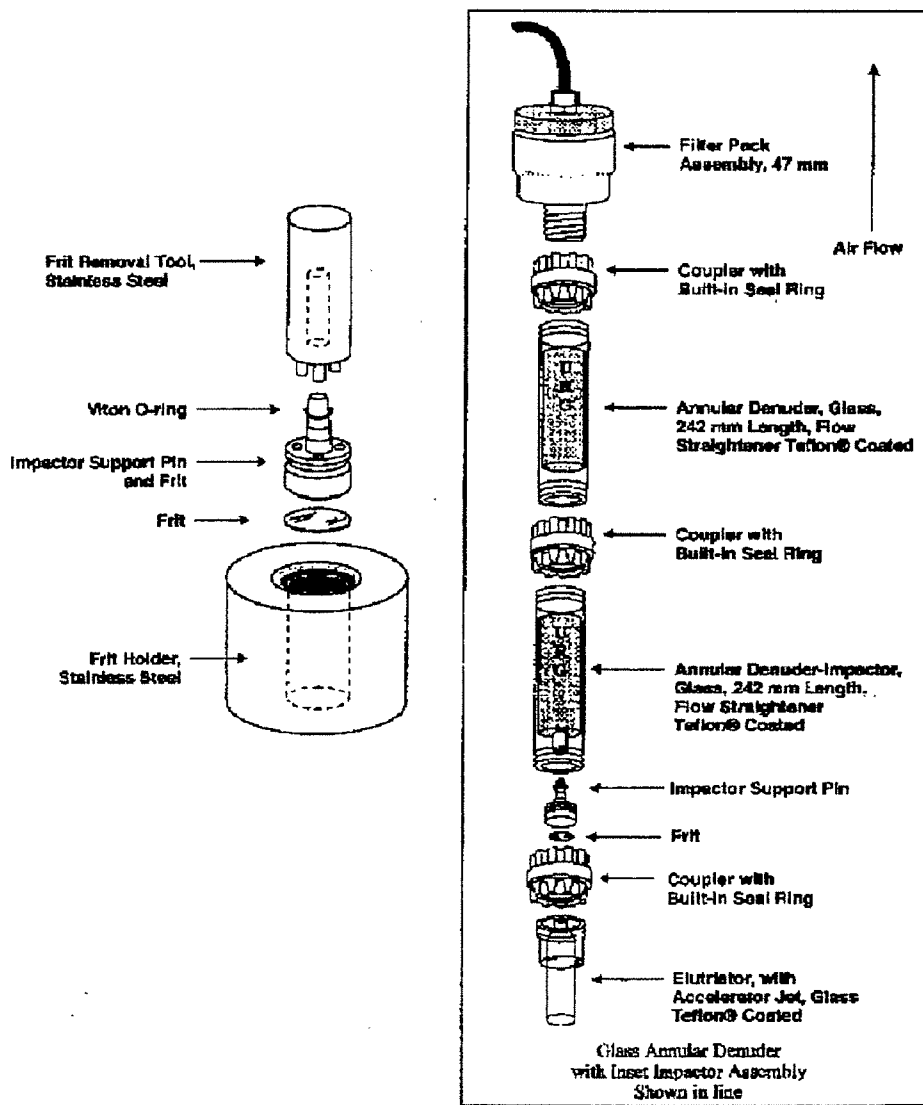


Figure 11. Frit removal from pin.



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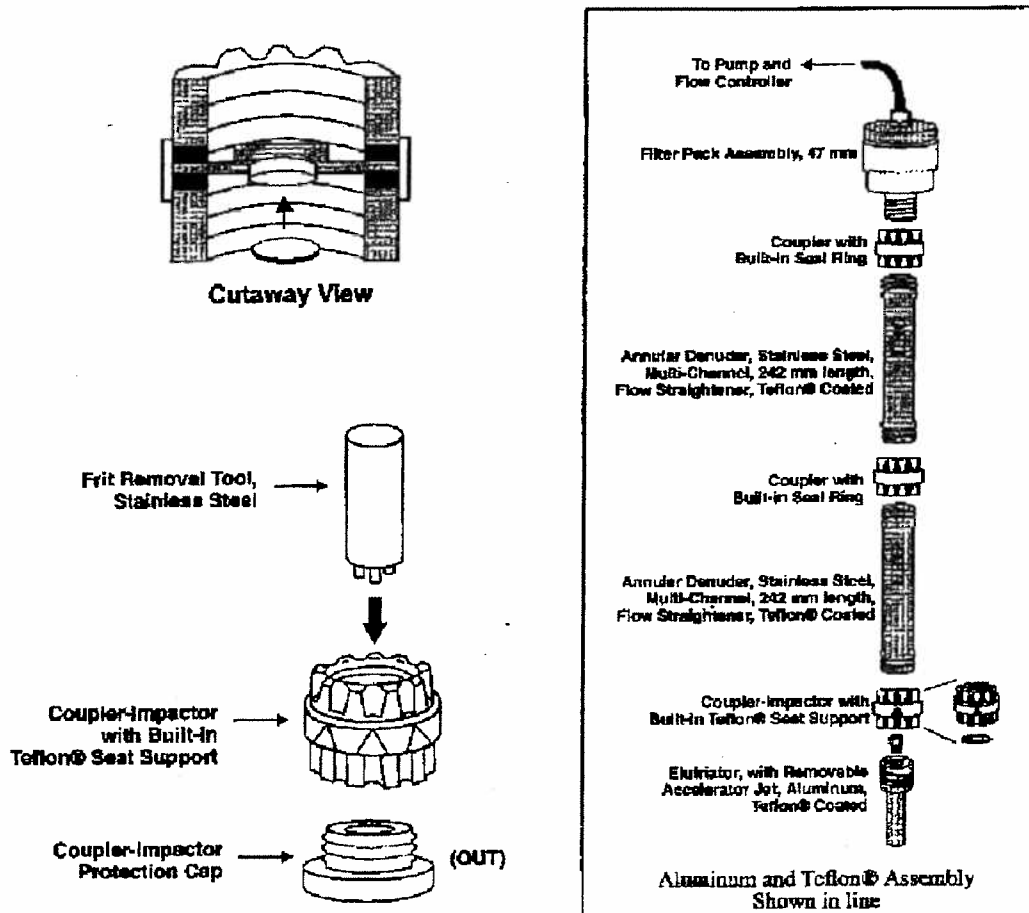


Figure 12. Side view impactor/coupler assembly with disc removal tools.



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**GENERAL**

Project: \_\_\_\_\_  
 Site: \_\_\_\_\_  
 Location: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 Sample Code: \_\_\_\_\_

Date: \_\_\_\_\_  
 Location of Sampler: \_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_  
 Operator: \_\_\_\_\_  
 \_\_\_\_\_

**EQUIPMENT**

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

**Sampler**

Sodium Carbonate Denuder No. \_\_\_\_\_  
 Citric Acid Denuder No.: \_\_\_\_\_  
 Filter Assembly No.: \_\_\_\_\_

**SAMPLING DATA**

Time

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

Stop

\_\_\_\_\_  
 \_\_\_\_\_  
 \_\_\_\_\_

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

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

Figure 13. Annular Denuder Field Test Data Sheet.



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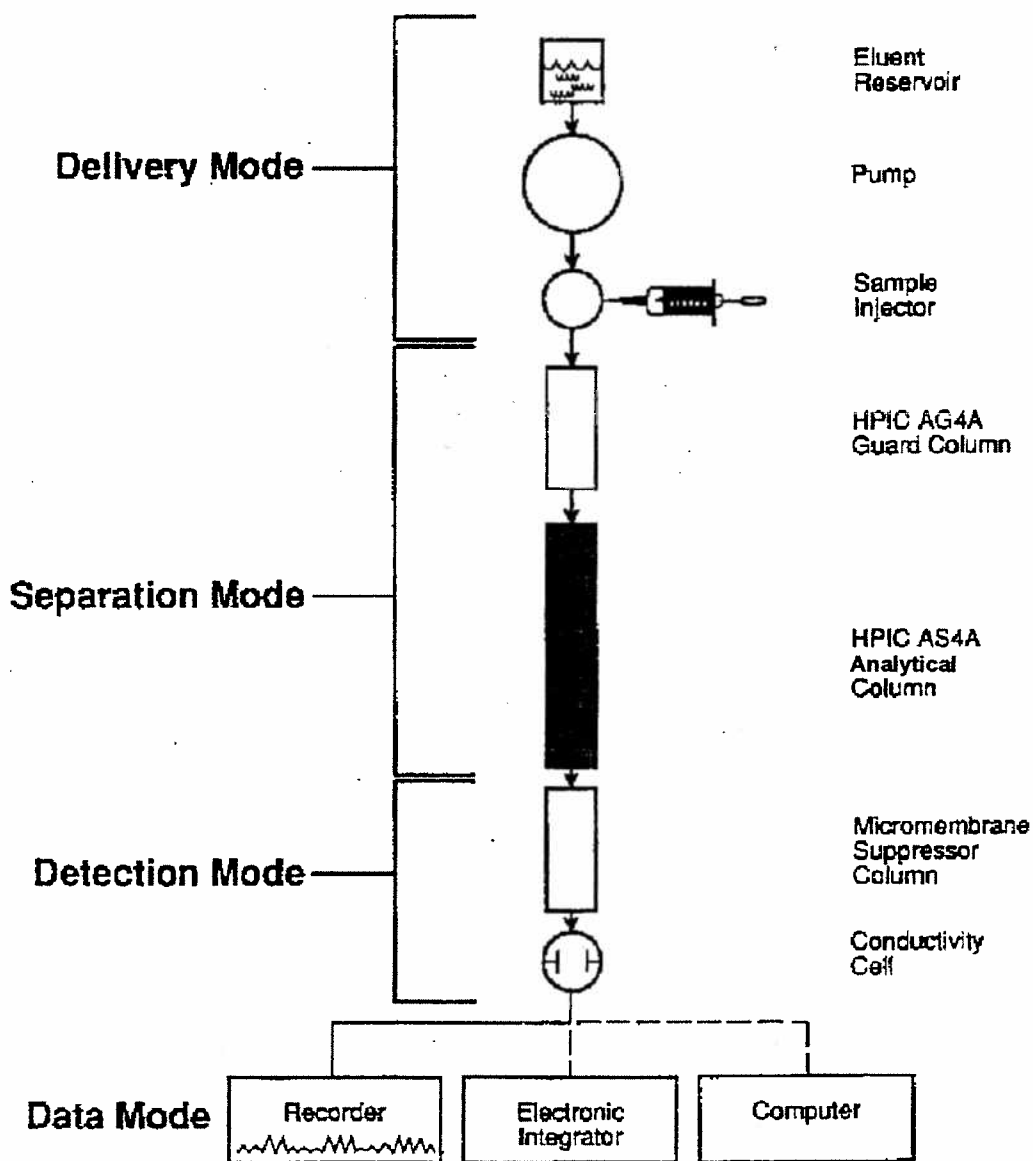


Figure 14. Major components of a commercially available ion chromatograph.



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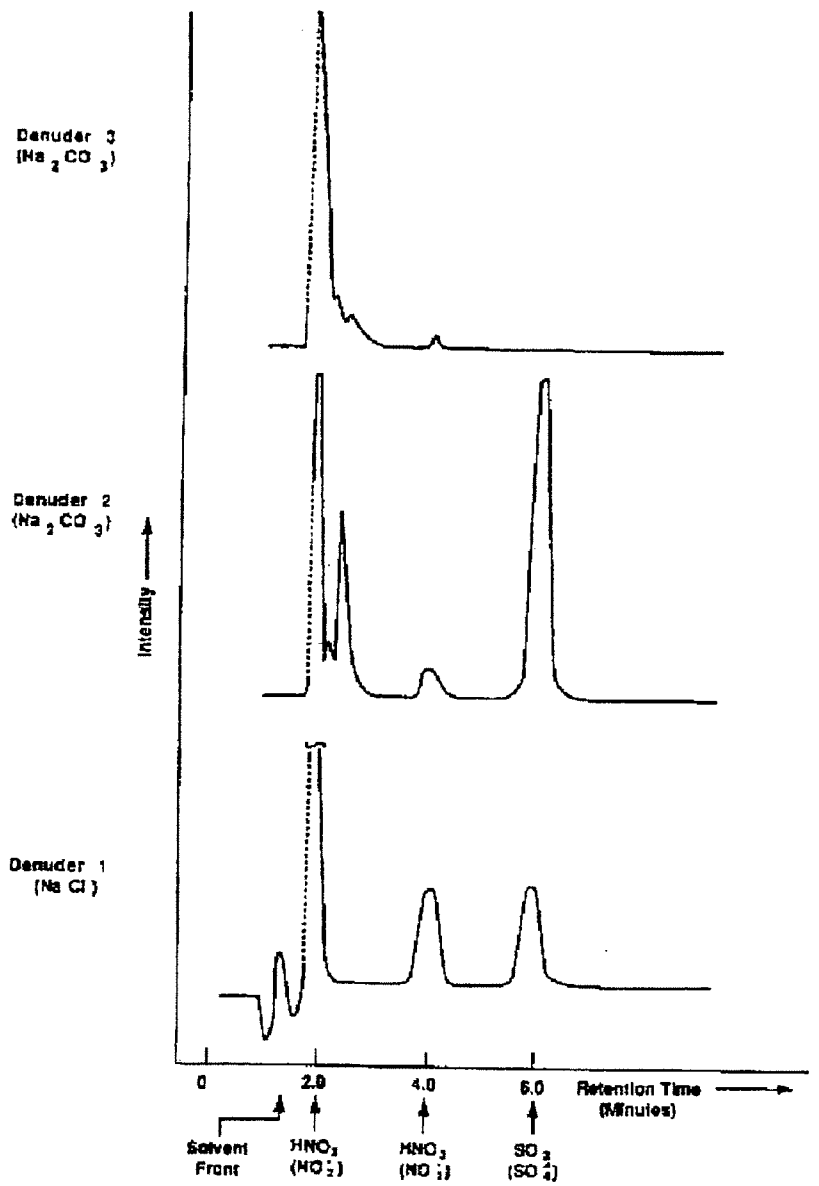


Figure 15. Chromatograms of denuder/filter extract performed by the ion chromatography.



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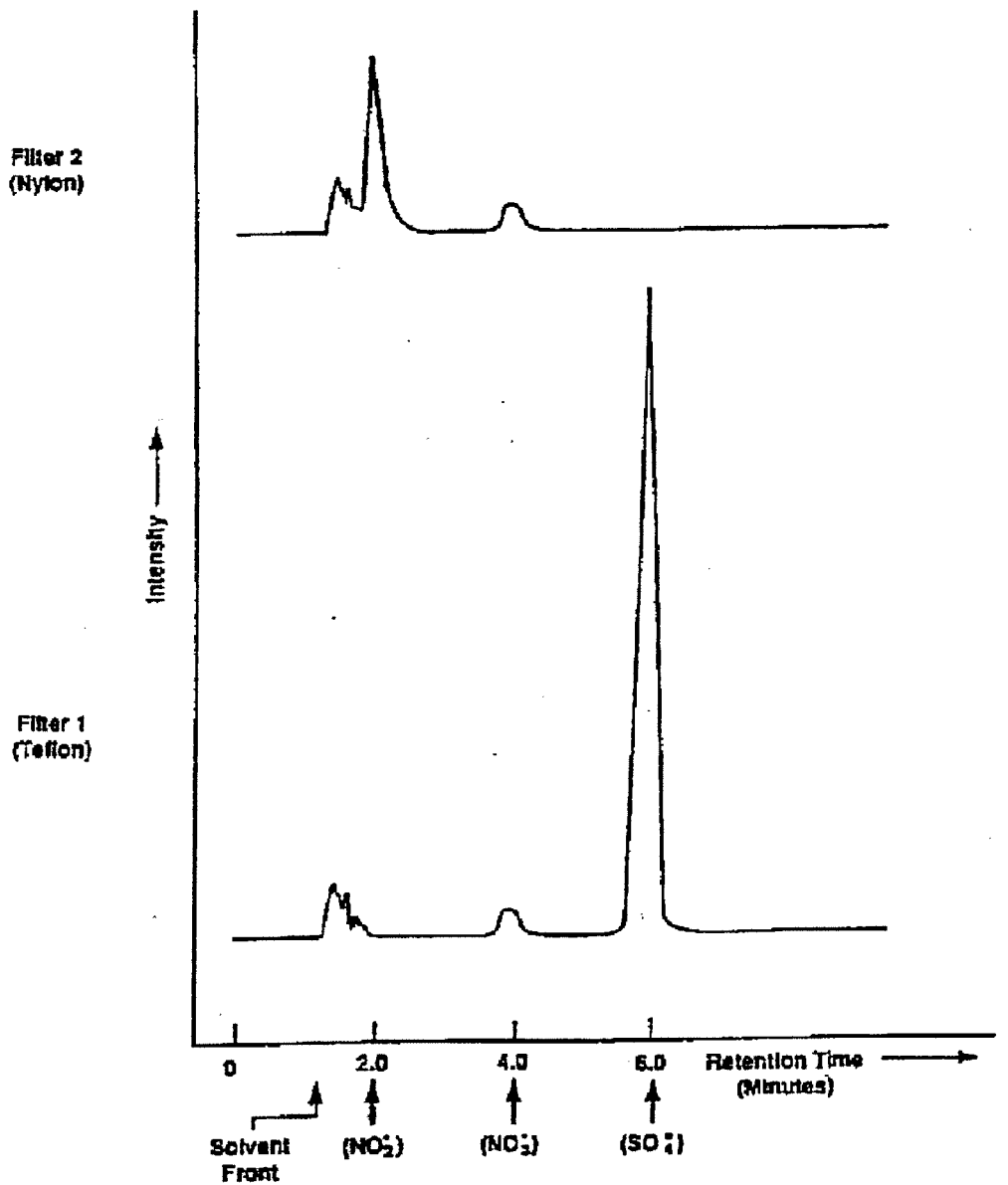


Figure 15 (Cont'd). Chromatograms of denuder/filter extract performed by the ion chromatography.





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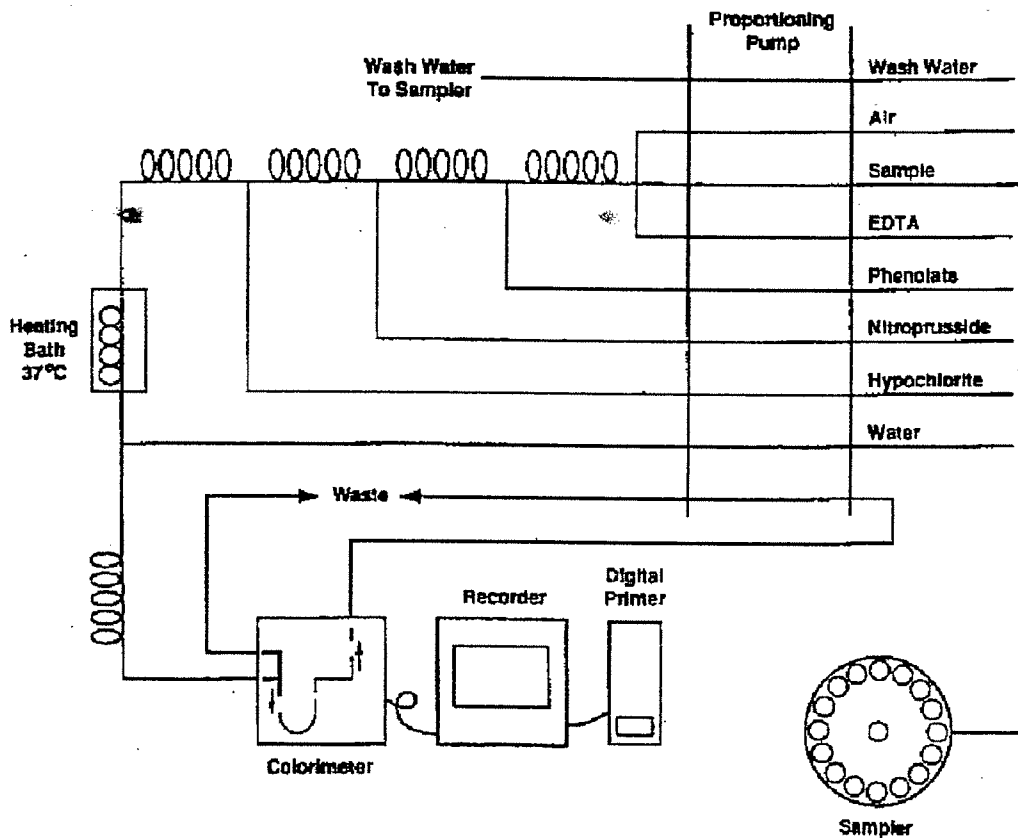


Figure 16. Technicon autoanalyzer flow diagram for ammonia analysis.



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

Name: \_\_\_\_\_  
 Date: \_\_\_\_\_  
 LAB: \_\_\_\_\_

Sample I.D.: \_\_\_\_\_  
 Location: \_\_\_\_\_

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

Figure 17. pH Analytical Laboratory Log Form



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

Figure 17 (cont). pH Analytical Laboratory Log Form



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Chapter IO-4  
Atmospheric Acidic

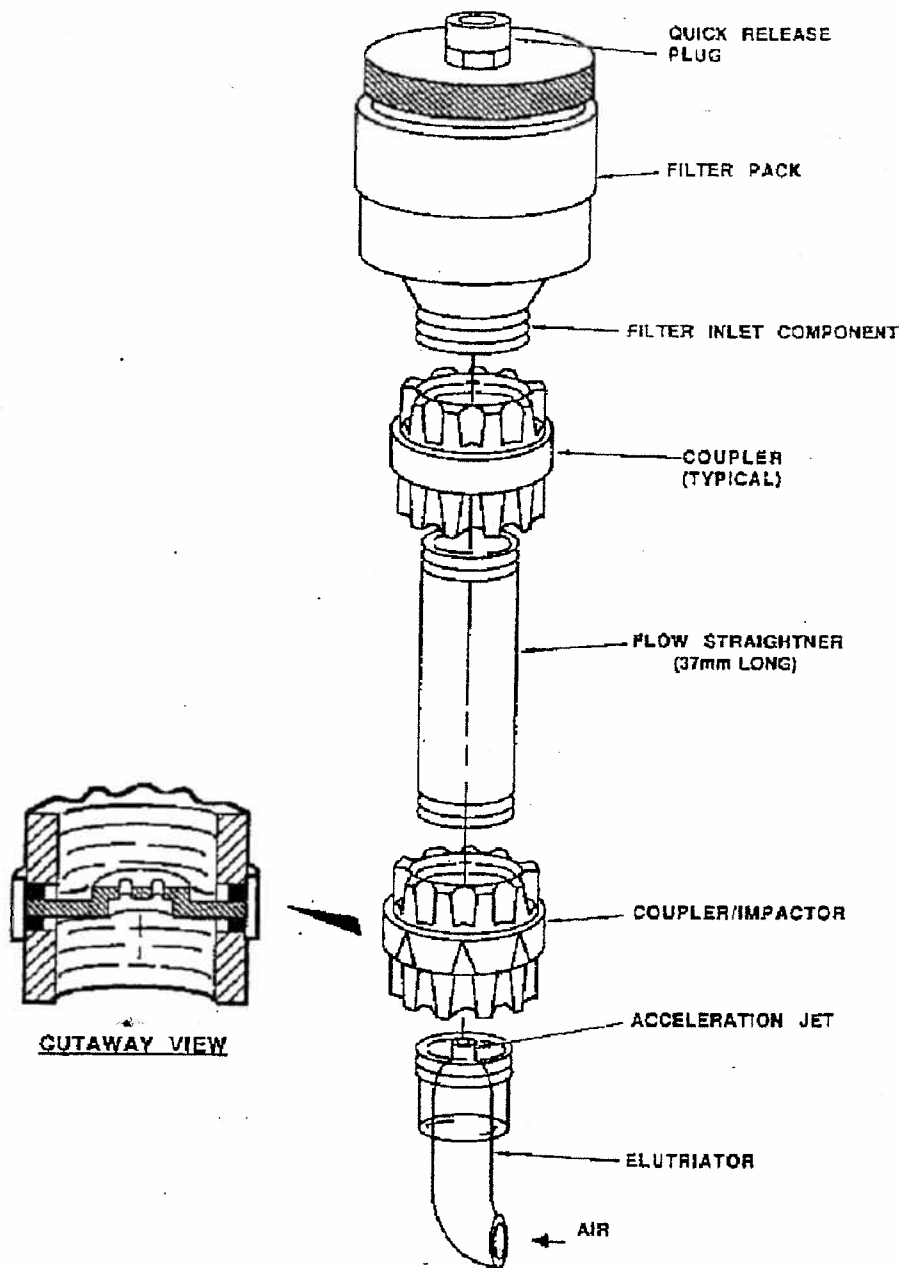


Figure 18. Field Particle personal sampler.



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Chapter IO-4  
Atmospheric Acidic

Method IO-4.2  
Acidic/Basic Constituents

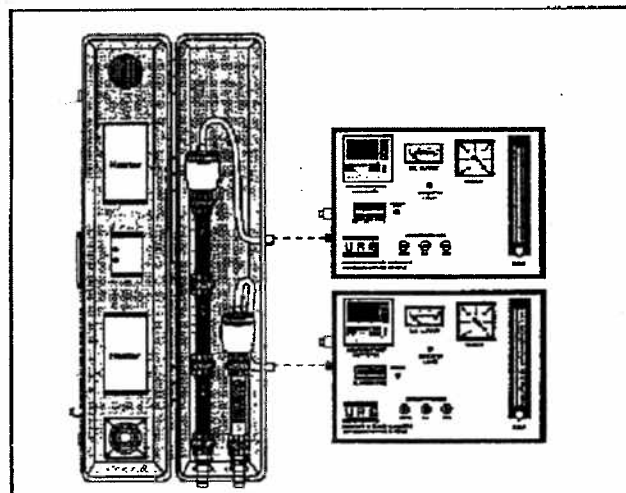
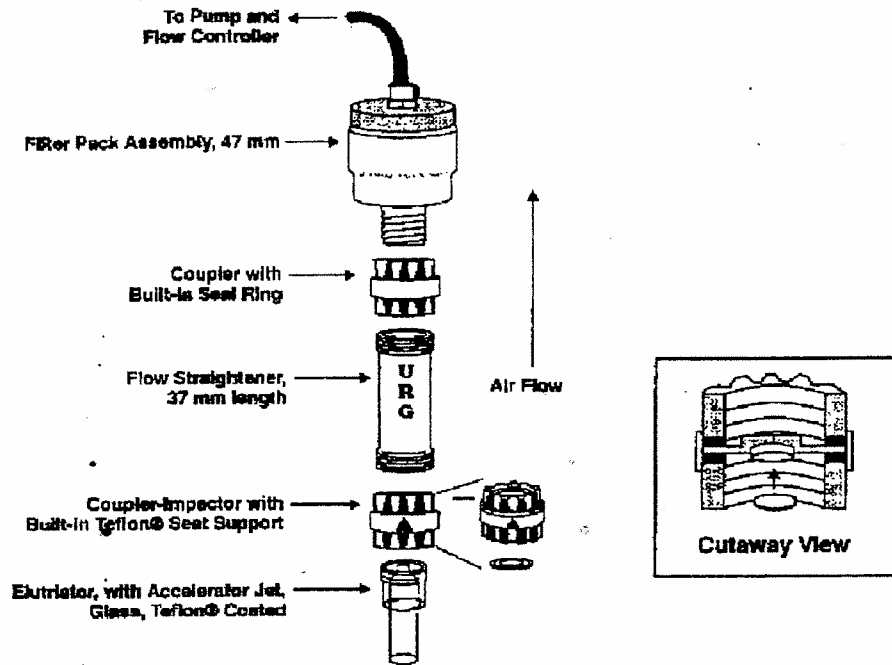


Figure 19. Annular Denuder system with parallel fine particle sampler.



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# Appendix E



Quality Assurance Project Plan  
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**CORROSION CLASSIFICATION COUPON  
 Environmental Monitoring Procedure**



**About Purafil**

Purafil is the leading manufacturer of air purification systems for the removal of corrosive, toxic, and odorous pollutants. Airborne pollutants are the biggest threat to the reliability of your electronics. Even trace levels of these pollutants can cause irreversible damage to integrated circuits, pin connectors, and other electrical and electronic components.

**Environmental Assessment**

Corrosive pollutants are invisible to the human eye and are 10 times smaller than the smallest particulate matter. Purafil's Corrosion Test Kit will enable you to determine the air quality in your facility. The test kit is part of Purafil's Environmental Assessment Program, an analytical service designed to characterize the corrosive potential of an environment as defined by the Instrumentation Society of America (ISA) Standard S71.04-1985.

**The Corrosion Classification Coupon (CCC)**

As part of the environmental monitoring procedure, place the CCC in the environment to be tested for a period of 30 to 90 days. Over time, the copper strip will tarnish. The amount of corrosion forming on the strip, over a given period, is a primary indicator of how well controlled an environment may be.

Upon immediate return to Purafil, the CCC is analyzed to identify the levels of corrosive contaminants present in the control room or other protected space.

**Coupon Placement**

The copper strip is mounted on a Plexiglas support panel. *Touching the copper strip will invalidate the test results.*

Follow these steps carefully to insure the validity of the test results:

1. Within 30 days of receipt, place the CCC in the space of concern.

2. Remove the CCC from the plastic packing bag. Keep the bag for return mailing to Purafil's laboratory.

3. Completely fill in the blank spaces on the label affixed to the CCC:

- Company Name & Address
- Room/area identification
- Date and time installed

**DO NOT...**

- Touch the copper strip
- Affix the coupon outdoors
- Affix the coupon inside the control cabinet

**IMPORTANT: A report cannot be provided without a date and time of installation.**

4. Place the CCC in the area of concern with the label side up.

5. Corrosion is defined in terms of corrosion film thickness, which builds up within one month of exposure. However, due to varying environmental conditions, a visual inspection of the coupon should be made.

In a harsh environment, a coupon may become highly tarnished before 30 days, and should be returned sooner to Purafil for analysis. If a CCC shows little to no discoloration, it should remain in place for an additional period of time up to 90 days. If visual inspection is not possible and the severity of the environment is unknown, return the CCC at 90 days.

6. After the specified time has passed, remove the coupon from the test area. Mark the label with the date and time of removal. *This information is critical - the lab cannot produce an analysis without it!*

7. Place the CCC in the plastic bag being careful to seal the bag. Return to the following address:

Attn: Laboratory  
 Purafil, Inc.  
 2654 Weaver Way  
 Doraville, GA 30340 USA

8. Purafil will issue a report classifying the corrosivity of your environment.



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### Reactivity Monitoring

Reactivity Monitoring is a widely accepted technique used to characterize the destructive potential of an environment. Because many of the contaminants targeted for control are corrosive in nature (i.e., hydrogen sulfide and sulfur dioxide), reactivity monitors have long been used to gauge the quality of ambient air and to indicate the effectiveness of pollution control strategies.

Purafil's reactivity monitoring technique is passive in nature and involves the use of copper and silver Corrosion Classification Coupons (CCCs).

CCCs are typically employed in industrial environments, to determine the effect of corrosion on sensitive electronics, or in museums, to determine whether or not artifacts are safe from decay.

CCCs are a reliable yet cost-effective means of classifying the external and internal environments. As part of the Purafil's monitoring strategy, individual CCCs are placed in the following areas:

#### Industrial Environments

- Control Rooms
- Rack Rooms
- Motor Control Centers
- Laboratories
- Critical Parts Storage Rooms
- Mainframe Computer Rooms

#### Museum Environments

- Outside air intakes
- Inlet of Recirculation Air Handlers
- Storage Rooms
- Display Cases

Following a period of 30 to 90 days, the CCCs are collected and sent to Purafil's laboratory. Field exposed CCCs are analyzed to determine the level of contamination in the environment.

### CCC Analysis

The purpose of CCC Analysis is to determine the type and thickness of corrosion buildup on the surface of each CCC. CCCs are analyzed via Coulometric Reduction, which allows the contaminant type to be easily identified. Knowing the period of time during which the coupon was exposed and the thickness of corrosion present, a corrosion reactivity rate can be calculated. This method of reactivity monitoring has been extensively researched by Batelle Laboratories and Bell Telephone.

### Corrosion Potential Industrial

#### Environments:

Knowing an environment's corrosion potential is important to industrial facilities. Purafil's laboratory analysis provides a quantitative measure of an environment's overall corrosion potential and details the environmental class as defined by Instrumentation Society of America (ISA) Standard S71.04-1985, titled "Environmental Conditions For Process Measurement and Control Systems: Airborne Contaminants." This standard requires that rooms containing back plane wired equipment, instrumentation, process control systems or computers, must have a G1 environmental classification, defined in terms of corrosion thickness as 0-299 Angstroms per 30 days. A G1 classification is characterized by ISA as "Mild"; G2, "Moderate"; G3, "Harsh"; and GX, "Severe".

**Museum Environments:** In museums corrosion is caused by the burning of fuels in power-stations, factories, commercial and domestic buildings, and automobiles. Purafil offers CCCs to test multiple locations within the local environment. The environmental classifications for both copper and silver corrosion is provided.

### Air Purity

#### Recommendations

- **Class S1/C1:** Archives, Metal Collections, Rare Books
- **Class S2/C2:** Museums, Museum Storage, Libraries
- **Class S3/C3:** Historic Houses
- **Class S4/C4:** Short Term Acceptable
- **Class S5/C5:** Not Acceptable

### CCC Comprehensive Report

The results of Purafil's environmental analysis are reported and made accessible to your local Purafil representative via Purafil's online Installed Tracking System. Included in the report are the general classes of gases present, estimated concentration levels, and humidity effects.





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