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THE BROOKHAVEN NATIONAL LABORATORY FILTER PACK SYSTEM FOR COLLECTION AND DETERMINATION OF AIR POLLUTANTS

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ABSTRACT

A filter pack system for sampling trace constituents in the atmosphere from aircraft and ground-based measurement platforms has been developed. The system simultaneously and quantitatively collects atmospheric aerosol, nitric acid, and sulfur dioxide using three sequential filter stages. The quartz aerosol filter is routinely analyzed for sulfate, nitrate, ammonium, and hydrogen ions, and specifically for sulfuric acid. The sodium chloride filter is analyzed for nitrate ion (from collected nitric acid), and the carbonate-glycerine filter for sulfate ion (from collected sulfur dioxide). Details of the procedures used for filter preparation, sampling, extraction and analysis are given.

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INTRODUCTION

One of the most reliable and adaptable methods for determining concentrations of trace materials in the atmosphere is the use of a filter pack sampling system. In these methods, a measured quantity of air is passed through a series of filter elements each designed to capture a different species. The exposed filters are then extracted and analyzed in the laboratory to determine the quantity of materials collected. Atmospheric concentrations are then computed by dividing the amount of material collected by the volume of air passed through the filter system during the sampling period.

The filter pack method has many advantages which make it useful for both ground and aircraft-based measurements. The technique is quite sensitive, is inexpensive to set up and operate, and can be designed to measure the concentrations of specific chemical components in the atmosphere. The major disadvantage of the technique is that the sample size required by the analytical techniques can limit the spacial and temporal resolution of the measurements.

A number of considerations are involved in the design of a filter pack sampling system for collection of trace atmospheric species. Collection elements must be treated appropriately so that each collects the desired component(s) efficiently while passing others. When collected by the designated filter, the component must not be lost by volatilization as the composition of the air sample passing through the system changes nor should either the filter material or the collected species chemically interact with other components in the air sample to produce artifact species. The collected samples also must maintain their chemical integrity during storage so that meaningful results can be obtained. Finally, the air inlet system must be designed which will deliver a representative air sample to the system without changing the composition of the sample.

The current BNL filter pack sampling system consists of a five element sequential aerosol, nitric acid, and sulfur dioxide sampler as illustrated in Figure 1 (Romano et al., 1976; Daum et al., 1982). The system is suitable for aircraft and ground-based sampling. The first filter is quartz fiber and is designed to collect aerosol particles (Leahy et al., 1980). The second and third filter elements collect nitric acid on NaCl-impregnated fast-flow cellulose paper (Forrest et al., 1980). Two filter elements are used to obtain a collection efficiency for nitric acid of approximately 95%. The fourth and fifth stages are K_2CO_3-glycerine-impregnated fast-flow cellulose circles designed to absorb sulfur dioxide at an efficiency of greater than 95% (Forrest and Newman, 1973; Johnson and Atkins, 1975).

The elements are arranged as described to obtain appropriate speciation and to avoid contamination. The quartz filter is placed first to collect the aerosol particles for analysis and to prevent their collection on the subsequent impregnated filters and being mistakenly interpreted as vapor-phase material. Sodium chloride filters, which trap nitric acid, are placed second to allow sulfur dioxide to pass through for collection by the carbonate impregnated filters.

At present, the filters are analyzed for a number of species. The aerosol sample collected on the quartz filter is analyzed for sulfate, nitrate, ammonium ions and strong acid (H^+) and can be specifically analyzed for sulfuric acid. The second and third elements are combined and analyzed for nitrate to determine nitric acid. Sulfur dioxide is determined as sulfate from the combined carbonate impregnated filters.

The methods currently used for analyzing of the filter extracts are listed in Table 1. As shown in this table, the ion chromatographic method is used for most of the filter pack analyses because it is ideally suited for analyzing the species of interest and also due to the continuing significant improvements in this technique. Also given in Table 1 are limits of detection for determination of the various species in the atmosphere. Depending on species, the detection limit is determined by either variability in the filter blank values or by the analytical method. Lower detection limits can be achieved by extending the sampling time in excess of the two hour example used in the table.

This report describes improvements that have been incorporated into the procedures which have been utilized for a number of years. The most tedious step, using an ultrasonic bath during the quartz filter preparation, has been simplified. A higher purity filter circle is now used in the sodium chloride and potassium carbonate filter preparation. The strong acid titration procedure has been modified by upgrading the computer used in the instrument assembly.

Improvements in the ion chromatographic analyses and data processing have been achieved by using a Dionex DX-300 gradient chromatography system in conjunction with a Gateway 2000 PC utilizing Dionex AI-450 software.

Table 1. Limits of Detection of Methods for the BNL 47 mm Filter Pack

			Limit of Detection(a)		
Filter	Species	Method	Analytical Method	Ambient Atmosphere(b)	Factor Limiting Sensitivity
Quartz(c)	$SO_4^=$	Ion Chromatography	0.03 µg mL^{-1} $SO_4^=$	0.06 - 1 µg m^{-3} $SO_4^=$ = 0.02 - 0.3 ppb	Blank Variability
Quartz(c)	NH_4^+	Indophenol/ Autoanalyzer	0.1 µg mL^{-1} NH_4^+	0.3 µg m^{-3} NH_4^+ = 0.4 ppb	Analytical Method
Quartz(c)	NO_3^-	Ion Chromatography	0.02 µg mL^{-1} NO_3^-	0.04 µg m^{-3} NO_3^- = 0.02 ppb	Analytical Method
Quartz(c)	Cl^-	Ion Chromatography	0.001 µg mL^{-1} Cl^-	.002 µg m^{-3} Cl^- = .001 ppb	Analytical Method
Quartz(d)	Strong Acid	H^+/Coulometric Titration	0.005 µeq mL^{-1} H^+	0.01 eq m^{-3} H^+ = 0.3 ppb	Blank Variability
Sodium Chloride(e)	HNO_3	As NO_3^-/Ion Chromatography	0.006 µg mL^{-1} NO_3^-	0.01 µg m^{-3} HNO_3 = 0.005 ppb	Analytical Method
Carbonate(f)	SO_2	As $SO_4^=$/Ion Chromatography	0.01 µg mL^{-1} SO_2	0.2 µg m^{-3} SO_2 = .008 ppb	Analytical Method

(a) Twice expected error
(b) 2-h sampling time at 60 L min^{-1}. Longer sampling times will reduce the detection limits where the analytical method error predominates. Parts per billion (ppb = 10^{-9}) units for aerosol constituents represent mole fraction.
(c) 1/2 filter circle extracted with 7 mL
(d) 1/4 filter circle extracted with 5 mL
(e) Entire filter circle extracted with 15 mL
(f) Entire filter circle extracted with 20 mL

The limit of detection for the analytical method is given as the minimum concentration detectable in the filter extract. Detection limits which are controlled by blank variability are subject to revision based on the results of blanks taken during an individual program. The limits of detection which are controlled by the analytical method are further subject to improvement not yet reflected in this table based on periodic enhancements of instrumentation.

These methods have been applied extensively with three filter sizes: 47-mm, 4-inch and 5-inch diameters. Filter size selection has been governed primarily by the availability of filter holders and flow capacities. Table 1 lists the detection limits for 47 mm filters. These limits are applicable within a factor of two for other diameters because the extraction volume is adjusted for other filter sizes.

SAMPLING

Cassettes. The BNL filter pack cassette system usually consists of a series of 4- or 5-inch diameter threaded rings as shown in Figure 1 covered with coarse stainless steel mesh which serves to provide physical support to the filter elements. The rings are provided with an "O" ring gasket which seals against a Teflon washer on the bottom of the ring above, eliminating air leakage when the system is operated. As the system is modular, any number of filter elements can be placed in series.

The five-inch system is most often used for ground-based sampling, as it gives optimum operating conditions for our needs (flow rate, collection area, ease of filter preparation). It is locally manufactured. A four-inch system (available from several manufacturers) is occasionally used. Currently, aircraft sampling operations are conducted using a 47-mm sampling system. This filter pack consists of a series of plastic filter holders, such as Nuclepore Stock Number 470410 (Nuclepore Corp., Pleasanton, CA).

Air Samplers. 110 VAC or 24 VDC Hi-Vol blowers (Staplex Co., New York, NY) are employed to provide air samples for the 4 or 5-inch filter packs. The 24 VDC model is used for aircraft sampling and is powered by the airplane's DC electrical generating system. Flow rates of ~17cfm are attained using the 5-inch cassette system. Typical flow rates for ground sampling using 110 VAC units are ~25 cfm (4-inch system) and ~35 cfm (5-inch system). A 4-inch to 5-inch adapter for the samples is necessary when the 5-inch system is used. Vacuum pumps such as Metal Bellows MB 158 (Metal Bellows Corp., Sharon, MA) are used with the 47 mm cassettes. 110 VAC or 24 VDC models are available for ground or aircraft sampling. Flow rates of 25 to 60 liters/min are commonly observed.

Loading and Unloading. Shortly before use, the filter pack cassette system is assembled, filters inserted in the prescribed order using tweezers, and the individual rings screwed together (Fig. 2). To avoid cross-contamination of filters, the same ring is always used for a specific type filter, and separate dedicated tweezers used for each type of filter circle. For example, carbonate contamination of the quartz filter could adversely affect strong acid determinations. Prepared filter packs are sealed in polyethylene bags until use and again after sampling prior to unloading. When the filters are unloaded after sampling, the exposed quartz filter is folded over (protecting the sample-exposed surface), placed in a 5" x 6" poly bag, heat sealed (Seal-N-Save Model 259659001, Sears Roebuck and Co.) and identifed with a label. The two exposed NaCl circles are placed in another 5" x 6" poly bag, sealed and labeled. The two exposed CO_3 filters are placed in a third 5" x 6" poly bag, sealed and labeled. The sealed bags are stored in separate desiccators to await extraction and analysis. A set of blank filters is obtained for each sampling episode. This involves loading and packaging a filter cassette unit as described, carrying it to the sampling location and treating the unit in an identical fashion as the exposed filters. The blank filters are analyzed and results used as a blank correction.

Aircraft Sampling. Aircraft from various agencies are currently being used in our atmospheric studies. Because of this, each aircraft filter pack installation is somewhat unique. However, any of the three filter sizes available can be adapted for use.

Ground Sampling. Ground sample filter packs can be attached directly to a high volume air sampler (open face) or in an in-line configuration using a suitable inlet sample tube. A number of aluminum shelter housings capable of semi-automatic operation are available for use. Sampling times and flow rates are recorded. One unit can be programmed to sequentially sample four filter cassettes at pre-designated time intervals. Care must be taken so that the high volume discharge does not contaminate the incoming air sample. 20 to 30 minute sampling periods are sufficient for analysis.

FILTER PREPARATION

The following methods are for the preparation of 5-inch filters. If needed, smaller diameter filters are cut from these filters.

Quartz Filters

Commercially available quartz material is not suitable as received for use in sampling of ambient aerosols by the methods described here. Before acceptable and consistent blank values can be obtained, this material must first be subjected to a series of washes and acid baths, ignited and dried. A 10% HCl acid treatment helps in lowering the background $SO_4^=$ value by dissolving acid-soluble salts and neutralizing alkaline sites. Ignition at 750°C eliminates residual HCl, destroys organic binder material that could interfere with specific H_2SO_4 determination and strengthens the quartz material.

The final ultrasonic bath treatment with deionized H_2O is to assure uniform blank values for each batch of circles processed.

Reagents: HCl, conc. Reagent Grade

Equipment: Funnel, Büchner, Nalgene 4280, 150 mm
Bath, ultrasonic Cole Palmer 8845-60
Dish, crystallizing, Pyrex 190 x 100 mm
Hot plate
Muffle furnace
Vacuum oven
Filter circles, Whatman 41, 15 cm
Quartz filter material, 12" x 12"
(QAO 2500 Pallflex Corp., Putnam, CT)
Cutting dies
Suction flask, 2 liter

Procedure:

1. Cut 5 1/2" circles from the 12" x 12" Quartz filter material.

2. Place 15 circles in a plastic Büchner funnel lined with two Whatman 41 filter circles and wash with slight suction using 500 mL deionized H_2O.

3. Detach the top section of the Büchner funnel containing the damp circles and immerse into the deep crystallizing dish containing 1-1/2 liters of hot 10% v/v (~1.2 M) HCl. Allow to soak for 15 minutes.

4. Lift the plastic Büchner section from the HCl solution and allow excess to drain back into the crystallizing dish. Place the plastic section into a pan of deionized H_2O for a preliminary rinse and again lift and drain off excess H_2O.

5. Re-connect the plastic Büchner funnel and rinse the circles using one liter of deionized H_2O per group of 15 and slight suction.

6. Remove the quartz circles (discard Whatman 41 liners) and ignite to 750°C. Sandwich the filters between scrap quartz material to prevent contamination.

7. After cooling, wash the filters (in groups of 15) using one liter of deionized water and a plastic Büchner funnel lined with a Whatman 41 circle. Full vacuum can be applied to the funnel assembly.

8. Dry the filters in a vacuum oven at 100°C.

9. Cut the cool filters to 4 or 5 inches and place (in groups of ~50) in a Whatman 41-lined upper section plastic Büchner funnel and suspend in ultrasonic bath containing deionized H_2O. Sonicate for 30 minutes.

10. Lift the Büchner funnel section from the bath, allow excess H_2O to drain into the bath, reassemble the funnel apparatus and remove remaining H_2O by gradually increasing the suction on the assembly. Repeat the ultrasonic bath and drying procedure using a fresh supply of deionized H_2O.

11. Final drying is carried out by stacking the filters on a Whatman 41 circle resting on a small beaker and drying in a vacuum oven at 100°C.

12. Store each group of circles in a sealed poly bag and place in a desiccator.

Notes:

Stack 5 sheets of filter material on a cutting board to give a total of 20 circles/5 sheets. The cutter can be tapped with a hammer. 60 circles are processed as one group.

Quartz circles are initially cut oversize as some shrinkage occurs during the treatment, most likely during the ignition step.

The inside of the plastic Büchner funnel must be sanded smooth. When received, the units contain sharp rough spots that could possibly puncture the quartz material during processing.

Slight suction is defined as 1/2 turn of the house vacuum system knob. Too high a setting causes excessive "dimpling" (sometimes even pinholes) of the bottom quartz circles.

All rinsing steps involving quartz material must be conducted carefully to avoid physical damage to the filters. Pouring should be done from a 50 mL beaker at the minimum practical distance above the filter circles. The force of pouring water in some cases is sufficient to cause damage.

The temperature of the HCl bath is between 75-90°C.

Ignition to 750°C for 30 to 60 minutes is sufficient. Prolonged exposure to the ignition temperature causes the filters to become brittle.

The washing procedure described in step 7 can be facilitated by soaking the filters (groups of 15) in a dish of deionized water for a minute or so prior to placing them in the Büchner funnel assembly. The result is increased suction on the filters during rinsing.

Drying in the vacuum oven can be facilitated by bleeding a small amount of air into the unit during operation. This allows water vapor to be withdrawn as it develops.

S&S Fast Flow 2W circles, 5 1/2-inch (14 cm) may be substituted if Whatman Filters are not available (Schleicher and Schuell, Keene, NH).

Sodium Chloride Filters

FF#2 cellulose papers were selected for this method as they allow high flow rates and collection efficiencies. As received, these papers contain impurities that interfere with analysis and, therefore, must be soaked in hot deionized water and thoroughly rinsed in order to reduce the impurities to acceptable levels. After impregnation with NaCl solution, the filters must be thoroughly dried as moisture might trap gaseous contaminants.

Reagents:	Sodium Chloride Reagent Grade
Equipment:	Dish, crystallizing, Pyrex 190 x 100 mm
	Funnel, Büchner, Nalgene 4280, 150 mm
	Filter circles, FF#2 Analytical Paper, 13.2 cm or 4 1/4 inches (Schleicher and Schuell, Keen, NH)
	Filter circles, Whatman 41, 15.0 cm
	Flask, suction, 2 liter

Procedure:

1. Place FF#2 circles (100) in the deep crystallizing dish containing ~1000 ml deionized H_2O and heat (70 to 80°C) on a hot plate for about 30 minutes.
2. Using gloves, remove cooled circles from the dish (in groups of 20 to 25) and give a preliminary rinse using one liter deionized H_2O, a Whatman 41 lined plastic Büchner funnel and suction.
3. Divide the circles into groups of 10 and rinse each group thoroughly using 500 ml deionized H_2O, a Whatman 41 lined plastic Büchner funnel and suction.
4. Dry the circles in the vacuum oven at 40°C and full vacuum.
5. Place circles (in groups of 5) in a dish containing NaCl-impregnating solution (50 grams NaCl per liter). Excess solution is removed by placing in a Whatman 41 lined Büchner funnel and using full suction.
6. Dry the impregnated circles in the vacuum oven at 40°C and full vacuum.
7. Place impregnated circles in a poly bag, seal, and store in a desiccator.

Notes:

Insides of plastic Büchner funnels should be sanded smooth. When received, they contain sharp rough spots that could possibly puncture filters during processing.

Filter circles dried at high temperatures (80-100°C) in the vacuum oven are difficult to "wet" during the impregnating step.

For filter storage, use self-sealing "zip-lock" poly bags or regular poly bags sealed by masking tape.

S&S Fast Flow 2W circles, 5 1/2 inch (14 cm) may be substituted if Whatman are not available (Schleicher and Schuell, Keene, NH).

Use 13.2 cm circles for the 5" system, 4.25 in circles for the 4" set-up.

Drying in the vacuum oven can be facilitated by bleeding a small amount of air into the unit during operation. This allows water vapor to be withdrawn as it develops.

Old unused impregnated filters need not be discarded, they can be recycled. Start at step 3 and carry through the procedure.

Wear plastic gloves (disposable) when handling filters.

Carbonate-Glycerine Filters

FF#2 cellulose papers were selected for this method as they allow high flow rates and collection efficiencies. As received, these papers contain high levels of sulfate impurities that can be reduced considerably by impregnating, storing in the moist condition for a period of time, then rinsed and dried. The finished impregnated filter as used is moist, not dry.

Reagents:	Potassium Carbonate Reagent Grade Glycerine
Equipment:	Dish, crystallizing, pyrex, 190 x 100 mm Funnel, Büchner, Nalgene 4280, 150 mm Filter circles, FF#2 Analytical Paper, 13.2 cm or 4 1/4" inches (Schleicher and Schuell, Keene, NH) Filter circles, Whatman 41, 15.0 cm Flask, suction, 2 liter

Procedure:

1. Place FF#2 circles in a deep crystallizing dish containing $CO_3^=$ impregnating solution (250 grams K_2CO_3 and 100 ml glycerine per liter). Take the wetted filters from the solution (in

groups of ~10) and remove excess solution using a Whatman 41 lined plastic Büchner funnel and suction.

2. Seal the moist filters in a poly bag and store in a desiccator for at least 30 days.

3. Filters are thoroughly rinsed with deionized H_2O using a Whatman 41 lined Büchner funnel and suction.

4. Dry the circles in the vacuum oven at 40°C and full vacuum.

5. Impregnate the circles by placing in a deep crystallizing dish containing $CO_3^=$ solution (250 grams K_2CO_3 and 100 ml glycerine per liter). Excess solution is removed by placing the filters (in groups of ~10) in a Whatman 41 lined plastic Büchner funnel and suction.

6. Place the moist impregnated filters in a poly bag, seal, and store in a desiccator.

Notes:

Insides of plastic Büchner funnels should be sanded smooth. When received, they contain sharp rough spots that could possibly puncture filters during processing.

Filter circles dried at higher temperatures (80-100°C) in the vacuum oven are difficult to "wet" during the impregnating step.

For filter storage, use self-sealing "zip-lock" poly bags or regular poly bags sealed by masking tape.

Use 13.2 cm circles for the 5" system, 4.25 in circles for the 4" set-up.

A "second-hand" solution can be used for the initial impregnating treatment (step 1). Solution left over from the final impregnating procedure (step 5) is combined with that collected in the suction flask and saved for this purpose.

Drying in the vacuum oven can be facilitated by bleeding a small amount of air into the unit during operation. This allows water vapor to be withdrawn as it develops.

Impregnated filters show a tendency to increase in blank value about 30 days after preparation. They need not be discarded, they can be recycled. Start at step 3 and carry through the procedure.

Wear plastic gloves (disposable) when handling filters.

S&S Fast Flow 2W circles, 5 1/2 inch (14 cm) may be substituted if Whatman are not available (schleicher and Schuell, Keene, NH).

EXTRACTION OF FILTER ELEMENTS

The following extraction volumes are specifically for five-inch aircraft samples. Volumes should be adjusted for different diameter filters and for filters exposed to markedly different than "normal" conditions.

Quartz. The folded quartz circle is placed on a clean plastic sheet in a laminar flow hood and with the aid of a guide, cut into two equal (1/2) portions. One section is folded small enough and placed into a clean one-ounce poly bottle. 15 ml of deionized H_2O is pipetted into the bottle, cap secured and the assembly agitated in an ultrasonic bath at 40°C for 20 minutes, The extract is stored in a refrigerator while awaiting analysis for sulfate by ion chromatography, nitrate by ion chromatography and ammonium ion by Auto Analyzer technique.

The remaining 1/2 section of quartz is divided into two equal (1/4) sections. One 1/4 section is used to determine strong acid by coulometric titration while the remaining 1/4 section is reserved as a contingency sample or is used to determine sulfuric acid by benzaldehyde extraction.

Sodium Chloride. Fold the filters and place into a clean two-ounce poly bottle, add 30.0 ml of deionized H_2O from a pipette, cap tightly and agitate in an ultrasonic bath at 40°C for 20 minutes. Agitate in a wrist-action shaker for an additional 20 minutes, Store the extract in a refrigerator while awaiting analysis for nitrate by ion chromatography.

Carbonate. Do not extract filters unless they are to be analyzed within 24 hrs. Fold the filters and place into a clean two-ounce poly bottle. 40 ml of dilute H_2O_2 solution (1:500 dilution of 30% H_2O_2 - freshly prepared) is added by pipet, the bottle capped and agitated for 20 minutes in an ultrasonic bath. Plume and extended-period ground samples are leached using a 4-ounce poly bottle and 100 ml of the dilute H_2O_2 solution. Let stand overnight. Samples must be analyzed the following day. Sulfate is determined by ion chromatography.

ANALYTICAL PROCEDURES

Quartz Extract

Sulfate, Nitrate and Chloride Analyses by Ion Chromatography[1]

The Dionex Ion Chromatograph separates ions by conventional ion exchange elution chromatography using a "separator" column. The eluent is then passed through a "suppression" system which converts eluted and eluent anions into their corresponding acids thereby decreasing the background conductivity due to the eluent and increasing the conductivity of the eluted anions. The concentration of the eluted ions is, therefore, measured using a conductivity detector.

Apparatus and Equipment:	Dionex DX-300 Ion Chromatograph equipped with Ion Pac AG4 and AS4 Columns, Anion self-regenerating suppressor and eluent Degas Module.
	Precleaned Vials Micropipette filter tips 0.45 µm Ion Chromatography "acrodisc" filters (Gelman Sciences) One ml disposable syringes
Instrument Control and Data Processing:	Gateway 2000 PC with AI-450 Software and Interface HP Laserjet 4 printer
Reagents:	Reagent grade anyhdrous Na_2SO_4, $NaNO_3$, NaCl, Na_2CO_3, and $NaHCO_3$ Deionized H_2O

Preparation of required solutions:

The stock and standard solutions are prepared as shown in the accompanying table from anhydrous reagents which are dried at 110°C for two hours and cooled in a desiccator for one hour prior to weighing.

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[1] Small, H., Stevens, T. S., and Bowman, W. C. Novel ion exchange chromatographic method using conductimetric detection. Anal. Chem. 47, 1801-1809 (1975).

Anion Stock Solution			
Reagent	M.W.	Stock Conc.	To Prepare 1L
Na_2SO_4	142.04	7.50 mM	1.0653 g
$NaNO_3$	84.99	9.00	0.7649
NaCl	58.44	3.75	0.2191

Working Standards					
	#1	#2	#3	#4	#5
Stock Dilution Factor	2500	1000	300	150	100
Take X mL Stock Dilute to One Liter	0.4	1.0	3.33	6.67	10.0

Anion Concentrations in Working Standards (µM)					
Anion	#1	#2	#3	#4	#5
$SO_4^=$	3.0	7.5	25	50	75
NO_3^-	3.6	9.0	30	60	90
Cl^-	1.5	3.75	12.5	25	37.5

a. Concentrated eluent solution: (0.224 M $NaHCO_3$ + 0.176 M Na_2CO_3)

18.82 g $NaHCO_3$ + 18.65 g Na_2CO_3 diluted to 1000 ml with deionized H_2O.

b. Dilute eluent solution: (2.8 mM $NaHCO_3$ + 2.2 mM Na_2CO_3)

50.0 ml of concentrated eluent solution diluted to 4000 ml with deionized H_2O.

Procedure:

1. Fill reagent reservoirs with appropriate solutions (as labeled) and tighten caps.
2. Turn air and helium gas cylinders on. Air is preset at 100 psi and helium at 40 psi.
3. Computer and printer turned on (Interface and Ion Chromatograph are always on).
4. Sparge eluents using "Degas" module.
    - (a) Turn the system switch to "on".
    - (b) Switch the appropriate reservoir toggles to "on".
    - (c) Degas the eluents for five minutes.
    - (d) Switch the "mode" toggles to the pressurize position.
    - (e) Let pressure equilibrate for five minutes before turning pump on.

5. Turn pump and conductivity cell on simultaneously. Should the pump need priming, follow procedure in accompanying manual.

6. Examine and modify AI-450 method file as needed. Put conductivity cell and pump modules in the "Remote" mode.

7. Calibrate system and perform analyses using Run Program.

8. Filter 5 ml of filter extract by drawing it through a micropipette filter tip using a five ml Finnpipette. Place filtered extract into a clean vial. This is done to remove any filter paper fibers or insoluble particles which may be present.

9. Flush lines and sample loop by injecting 2 ml of deionized H_2O by flushing twice with a 1-ml disposable syringe.

10. Sample injection is done in two steps. First, the sample loop is rinsed and filled by two or three separate 1-ml injections using a 1-ml disposable syringe in conjunction with a 0.45 μM "Acrodisc" filter. The contents of the 50 μl sample loop are then introduced into the eluent stream by initiating the Run Program.

11. The various anionic species present in the sample are separated on the anion exchange column using the dilute eluent solution. Under these conditions, the order of elution is F^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, NO_3^-, and SO_4^{2-}. The resolution between species and their retention time will vary depending on the condition of the column.

12. The system is calibrated using the five working standards in conjunction with the "Autocal" feature of the AI-450 software. Quality assurance is maintained by injecting one standard for every ten or less samples analyzed.

13. Calculation of results:

Based on the standard curves generated using the five working standards, the Cl^-, NO_3^- and $SO_4^=$ concentrations are automatically calculated employing peak area.

14. Shut Down:

Return conductivity cell and pump modules to local mode. Turn off pump and conductivity cell simultaneously. Shut down computer and printer. Eluent "Degas" module must be shut down in order: (a) Toggles switched to sparge position; (b) Caps on eluent reservoirs loosened; (c) Main switch off; and, (d) Shut air and helium cylinders off.

Quartz Extract

Ammonium Analysis by Auto Analyzer[2,3]

The automated procedure for the determination of ammonia in water utilizes the Berthelot reaction. The formation of a green-colored compound believed to be closely related to indophenol occurs when the solution of an ammonium salt is added to sodium phenoxide, followed by the addition of sodium hypochlorite. A solution of potassium tartrate (Rochelle Salt) is added to the sample stream to eliminate hydroxide precipitation of heavy metals,

Apparatus and Equipment:	Auto Analyzer II (Technicon, Tarrytown, NY) Filter Tips (Supelco Inc., Bellefonte, PA)
Reagents:	Sodium Hydroxide (NaOH) Phenol (C_6H_5OH) Brij-35 Sodium Hypochlorite (Clorox) Potassium Sodium Tartrate ($KNaC_4H_4O_64H_2O$) Ammonium Sulfate ($(NH_4)_2SO_4$) Chloroform

Solutions:

a. Alkaline Phenol

To 500 ml of distilled water, dissolve 200 g of sodium hydroxide contained in a vessel surrounded by circulating cold water. While cooling, slowly add 276 ml liquified phenol (88%) stirring continuously. Dilute to one liter with distilled water and store in a brown bottle. Add

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[2] Tellow, J. A. and Wilson, A. L. An absorptiometric method for determining ammonia in boiler feed water. Analyst 89, 453-465 (1965).

[3] Bolleter, W. T., Bushman, C.J ., and Tidwell, P. W. Spectrophotometric determination of ammonia as indophenol. Anal. Chem 33, 592-594 (1961).

0.5 ml of Brij-35 per liter. The alkaline phenol reagent should be filtered through a glass wool filter prior to use.

b. Sodium Hypochlorite (Clorox)

Any good commercially available household bleach having 5.25% available chlorine may be used. Store bleach in refrigerator.

c. Potassium Sodium Tartrate

Dissolve 150 g of potassium sodium tartrate in 850 ml de-ionized H_2O and dilute to one liter. Add 0.5 ml Brij and mix.

Standards:

a. Stock solution - 1000 µg N/ml

Dissolve 2.3643 g $(NH_4)_2SO_4$ (oven dried at 105°C and stored in desiccator) in 200 ml deionized H_2O. Add 1 ml chloroform and dilute to 500 ml with de-ionized H_2O. Prepare every 6 months.

b. Working standards: Make up standards from stock and dilute with deionized H_2O. Prepare working standards weekly.

Procedure:

1. Quartz filter sample extract is filtered through a 45-µM filter tip.
2. Filtrate is analyzed by Auto Analyzer in accordance with Technicon Industrial Method 98-70W.

Operating Notes:

1. Chloroform is added to the standard stock solution as a preservative.
2. For best results, the sample cups should be washed in de-ionized water and stored in plastic bags in an ammonia-free environment.
3. Where particulate matter is present, the solution must be filtered prior to the determination.
4. If the system is being run in an ammonia-contaminated environment, the air for segmenting the stream should be scrubbed through 10% v/v H_2SO_4 prior to its introduction into the system.

5. Various concentration ranges may be obtained by utilization of the Std Cal control on the Colorimeter and changing the sample tubing.

6. All effluent solutions from this Auto Analyzer technique are collected and disposed of as hazardous waste (contains ~2% Phenol).

Quartz Filter Section

Determination of Strong Acid[4]

A portion of the quartz aerosol filter is leached in dilute sulfuric acid and the strong acid in the leachate is titrated by coulometrically generated hydroxide ion. The titration apparatus is automated and consists of a pH meter, precision coulometer, and a personal computer (Fig. 4). The equivalence point of the titration is determined by the computer using a Gran plot. The contribution of the sulfuric acid leach solution is subtracted from the total amount of strong acid when measuring the concentration of strong acid on the filter. The magnitude of the correction is determined by titration of a blank filter.

Apparatus and Equipment:

Polypropylene vessels 15-ml (Radiometer/Copenhagen, The London Co., Cleveland, OH)
Dispensing pipette "Re-pipette" (Markson Scientific, New York, NY)
Ultra-Sonic Bath Model 8845-3 (Cole Parmer, Chicago IL)
Adjustable automatic pipette 1-5 ml FinnPipette
Filter tips, 45-µM no. 58474 (Supelco, Bellfonte, PA)
Micro Pipette, 500-µl, Centaur (Markson Scientific, New York, NY)
Digital pH Meter, Model 4500 (Beckman Instruments, Irvine, CA)
PAR Digital Coulometer, Model 179 (Princeton Applied Research, Princeton, NJ)
Star Head Magnetic Stir Bar, Cat. No. 6600-0010, Teflon (Nalge Company, Rochester, NY)

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[4] Phillips, M. F., Gaffney, J. S., Goodrich, R, W., and Tanner, R. L. Computer-assisted Gran titration procedure for strong acid determination. Informal Report, BNL 35734, Oct. 1984.

Sensorex Combination pH/Reference Electrode, Miramark 15 cm x 6 mm (Markson Scientific, New York, NY)
Ag/AgBr Counter Electrode (BNL Mfg.)
Constant Temperature Water Bath, Haake E52 (Polyscience Corp., Evanston, IL)
IBM PC-XT (IBM, Armonk, NY)
Epson FX 86e Printer (Epson, Torrance, CA)

Reagents: H_2SO_4 1×10^{-4} M
KBr 0.8 M

Sample Preparation:

1. The quartz filter section (usually 1/4 circle) is folded and placed in a 1-ounce poly bottle.
2. Add 5.0 ml H_2O and 5.0 ml 1×10^{-4}M H_2SO_4 to each sample using the "Re-pipette" brand dispensing pipette bottles.
3. Suspend in the ultrasonic bath for 15 minutes.
4. Transfer the leachate to a clean vessel using a Finnpipette with filter tip. At least 8 ml should be recovered.
5. Transfer 7.0 ml to a clean titrating vessel. A Finnpipette set at 3.50 ml is used for the transfer.
6. Add 0.5 ml 0.8 M KBr to each sample.
7. Place a stirring bar in each titrating vessel and equilibrate in a jacketed beaker supplied with 25°C water from a constant temperature bath.

Titration Procedure:

1. Standardize the pH meter. Follow the procedure outlined in the Beckman manual. This should be done on a weekly basis or more frequently if a daily pH buffer check indicates a significant change.
2. Place the electrodes in the sample to be titrated and activate the magnetic stirrer.

3. Read the response of the solution to be titrated. If the response is in excess of 200 mv, set the coulometer current at 500 µA, 170-200 mv at 250 µA, below 170 mv set at 125 µA. Settings must be made manually.

4. Initiate the titration using the IBM XT. Detailed instructions are given in the appendix. The "A" button on the coulometer triggers the start, "ZERO I" button will end the titration.

5. To print the titration curve and pertinent information, hold down the shift key on the keyboard, press "PRTSC*", release the shift and press (number) 0.

Operating Notes:

1. All titration vessels, pipette tips, and filter tips should be rinsed in deionized water and dried in a vacuum oven at 30°C. It is convenient to store cleaned items in a one gallon round can with friction top.

2. 45-µM external filter tips (Cat. # FT6006) may also be obtained from Centaur West, Inc. 587 Dunn Circle, Sparks, NV 89431, (702) 331-1890.

3. An Orion 910300 semi-micro pH electrode (Cole-Parmer, Chicago, IL) may be used as a replacement for the Sensorex electrode.

Quartz Filter Section

Sulfuric Acid Analysis[5,6]

(Benzaldehyde Extraction)

Sulfuric acid is extracted from the quartz filter section by contacting it with benzaldehyde in a special tube. After mixing, the tube assembly is centrifuged and the benzaldehyde separates from the pulpy mass of quartz material which collects in the bottom of the tube. An aliquot of

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[5] Leahy, D., Siegel, R., Klotz, P., and Newman, L. The separation and characterization of sulfate aerosol. Atmos. Envir. 9, 219-229 (1975).

[6] Tanner, R. L., Cederwall, R., Garber, B., Leahy, D., Marlow, W., Meyers, R., Phillips, M., and Newman, L. The separation and analysis of aerosol sulfate species at ambient concentrations. Atmos. Envir. 11, 955-966 (1977).

the benzaldehyde is washed with a known quantity of water and the sulfuric acid is extracted into the aqueous phase. A portion of the aqueous phase is removed and the sulfate concentration is determined by ion chromatography.

Apparatus and Equipment: Centrifuge, Model 7514H (International, Boston, MA)
Ultrasonic Bath 8845-3 (Cole-Palmer, Chicago, IL)
Automatic Pipettor "Dispensette" (Brinkmann, Westbury, NY)
Automatic Pipette P-5000D (Rainin, Brighton, MA)
Tefzel Tubes, 50 ml (Markson Scientific, New York, NY)
Gelman Centrifugal Filter Holders, 4662-610 (Markson Scientific, New York, NY)

Reagents: Benzaldehyde (Fisher Scientific, Springfield, NJ)

Procedure:

1. Place the sample (1/4 section quartz filter) into a 50 ml Tefzel tube and store in a vacuum desiccator over silica gel overnight or until dry.
2. Remove sample from the desiccator and add 10.0 ml benzaldehyde.
3. Cap the tube, shake manually, then place in an ultrasonic bath for 5 minutes.
4. Transfer contents to a Gelman Centrifugal filter holder and centrifuge for 2 minutes (maximum speed).
5. Pipette 8.0 ml of the benzaldehyde into a screw top, 30-ml polypropylene centrifuge tube.
6. Add 6.0 ml H_2O, shake manually for 1 minute then centrifuge for 10 minutes at maximum speed.
7. Transfer 3.0 ml of the H_2O phase to a 20 ml stoppered flat bottom polyethylene vial using a Rainin pipette.
8. Evaporate to dryness on a steam bath.
9. Dissolve residue in 2.0 ml H_2O, stopper, and save for sulfate analysis by ion chromatography.

Operating Notes:

1. The quartz filter section and benzaldehyde reagent must be dry if a successful extraction is to be conducted. Moisture causes water soluble sulfates other than sulfuric acid to be carried through the procedure.

2. Vacuum drying of the quartz filter section is required as heat may cause some loss of sulfuric acid by volatilization.

3. Pure benzaldehyde reagent must be used. Benzoic acid causes an interfering peak in the ion chromatograph determination.

Sodium Chloride Filter Extract

Nitrate by Ion Chromatography

The same Ion Chromatographic procedure used to analyze the quartz filter extracts for NO_3^- is utilized here with one exception. The sodium chloride filter extracts are not doubly filtered before injection; only the 0.45 µm "Acrodisc" filter is used during injection.

Carbonate Filter Extract

Ion Chromatographic Analysis of Sulfur Dioxide as Sulfate in Potassium Carbonate, Glycerol, Hydrogen Peroxide Matrices

The same Ion Chromatographic procedure used to analyze the quartz filter extracts for $SO_4^=$ is utilized here with one exception. The carbonate filter extracts are not doubly filtered before injection; only the 0.45 µm "Acrodisc" filter is used during injection.

COMPUTATION OF RESULTS

Results of filter pack analysis are reported in units of µg/m^3 where the volume is referred to 760 mm of Hg at 20°C. The following equation is used to compute the results:

$$C = \frac{(\text{extract conc. } (\mu g/ml) - \text{blank conc. } (\mu g/ml)) \times \text{extract vol (ml)} \times \frac{1}{f}}{\text{Volume of air sample } (m^3)}$$

where f is the fraction of the filter analyzed and the blank correction is determined by analysis of the unexposed blank filter.

SO_2 concentration from the carbonate filter is obtained by multiplying the sulfate concentration by 0.667 to convert $SO_4^=$ to SO_2 and by 1.11 to account for incomplete extraction. Nitrate analyses from the nitric acid filters are combined with nitrate analyses from the quartz filter and reported as total inorganic nitrate.

Quality Assurance

A. Flowmeters - flow meters are calibrated semi-annually using a volume displacement meter.

B. Chemical Analysis Procedures - Pertinent quality assurance procedures are included in each method.

C. Collection Efficiency and Artifact Formation - Results of experiments performed with the BNL filter pack system have been described previously.[7,8,9]

D. Pipets gravimetrically calibrated annually.

E. Balances serviced and calibrated every year.

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[7] Forrest, J., and Newman, L. Sampling and analysis of atmospheric sulfur compounds for isotope ratio studies. Atmos. Environ. 7, 561-573 (1973).

[8] Forrest, J., Tanner, R. L., Spandau, D., D'Ottavio, T., and Newman, L. Determinations of total inorganic nitrate utilizing collection of nitric acid on NaCl-impregnated filters. Atmos. Environ. 11, 955 (1980).

[9] Leahy, D. F., Phillips, M. F., Garber, R. W., and Tanner, R. L. Filter material for sampling of ambient aerosols. Anal. Chem. 52, 1779 (1980).

REFERENCES

Daum, P. H., Forrest, J., and Newman, L. Application of filter pack measurements to airborne monitoring systems. In Proceedings of the Air Pollution Control Association Specialty Conference on In-Situ Air Quality Monitoring from Moving Platforms, San Diego, CA, pp. 299-310, 1982.

Forrest, J. and Newman, L. Sampling and analysis of atmospheric sulfur compounds for isotope ratio studies. Atmos. Environ. 7, 561-573 (1973).

Forrest, J., Tanner, R. L., Spandau, D., D'Ottavio, T., and Newman, L. Determination of total inorganic nitrate utilizing collection of nitric acid on NaCl-impregnated filters. Atmos. Environ. 14, 137-144 (1980).

Johnson, D. A. and Atkins, D. H. F. An airborne system for the sampling and analysis of sulfur dioxide and atmospheric aerosols. Atmos. Environ. 9, 825-829 (1975).

Leahy, D. F. The Brookhaven National Laboratory Atmospheric Sciences Aircraft. Informal Report, BNL 28102R, July 1981.

Leahy, D. F., Phillips, M. F., Garber, R. W., and Tanner, R. L. Filter material for sampling of ambient aerosols. Anal. Chem. 52, 1779-1780 (1980).

Romano, A., Klein, J. H., and Newman, L. An air sampling system to measure power plant effluents using a lightweight aircraft. J. Environ. Sys. 5, 271-289 (1975).

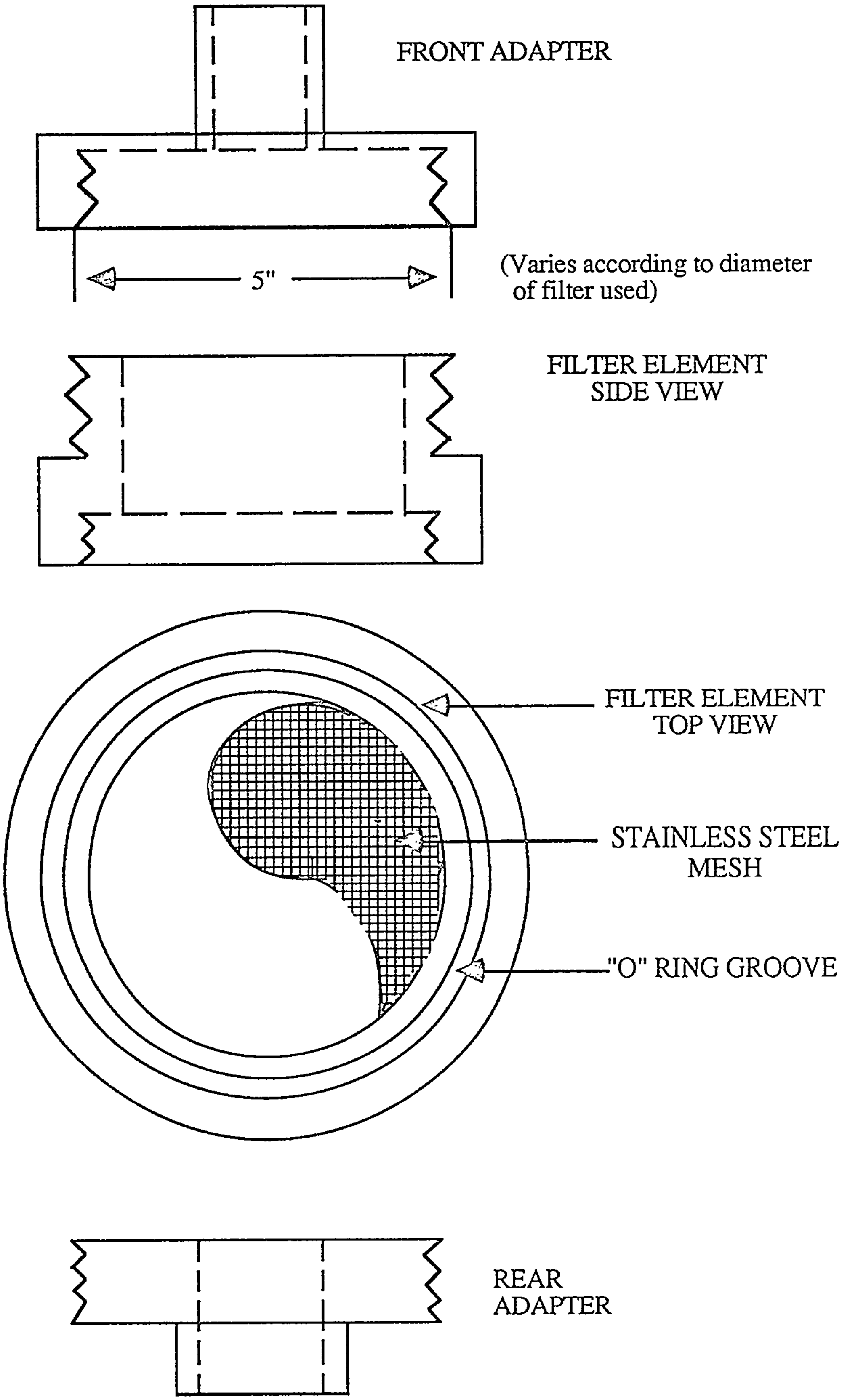


Figure 1. Elements of filter pack sampler.

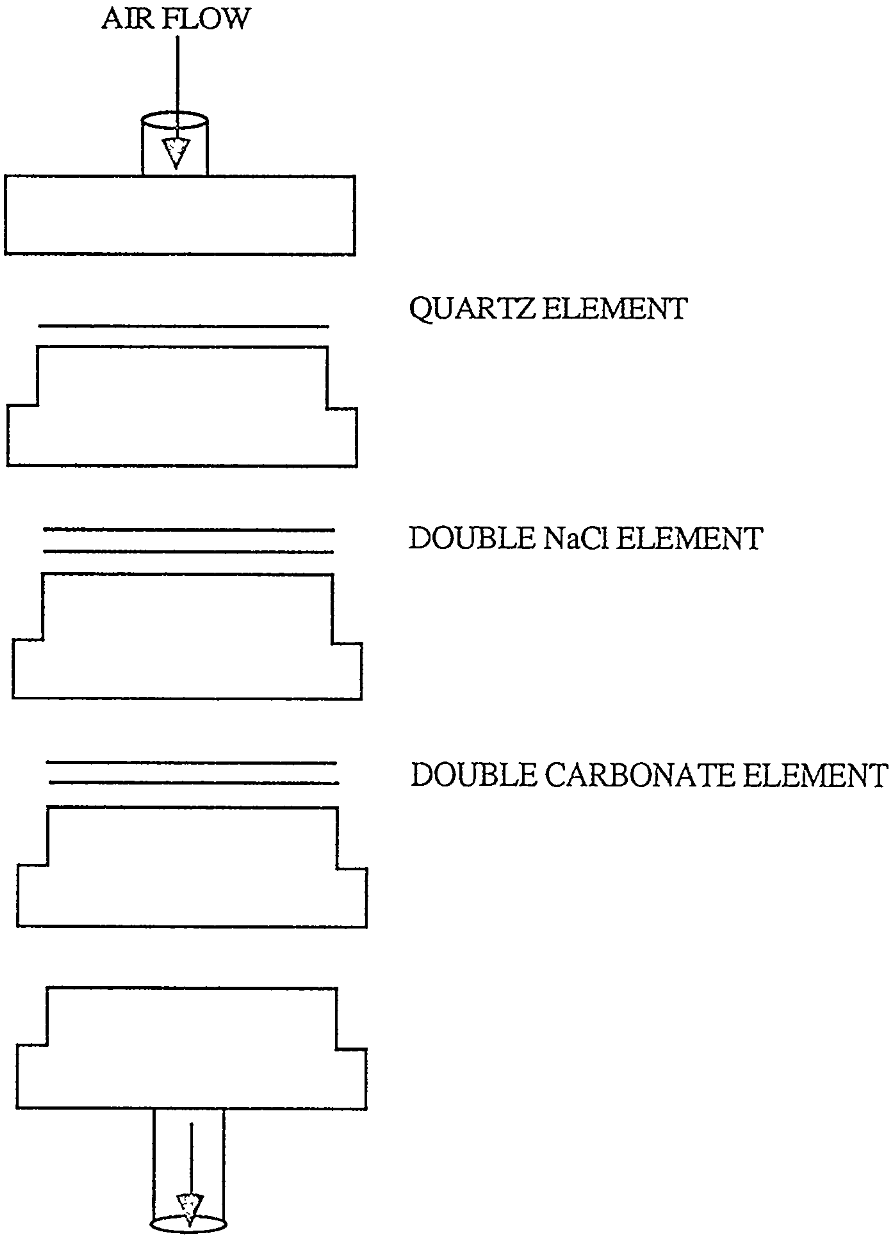


Figure 2. Schematic diagram of BNL filter pack sampler.

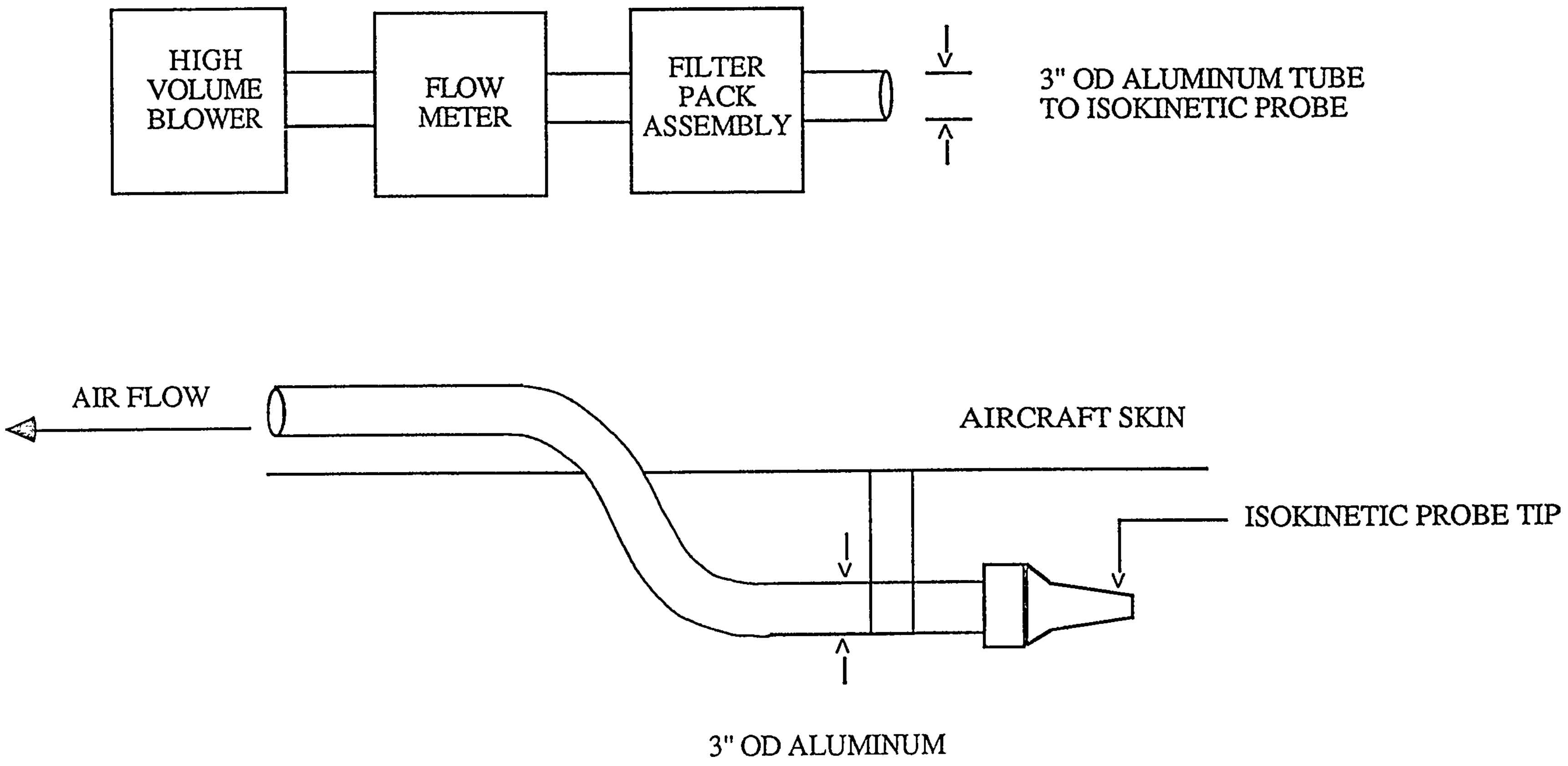
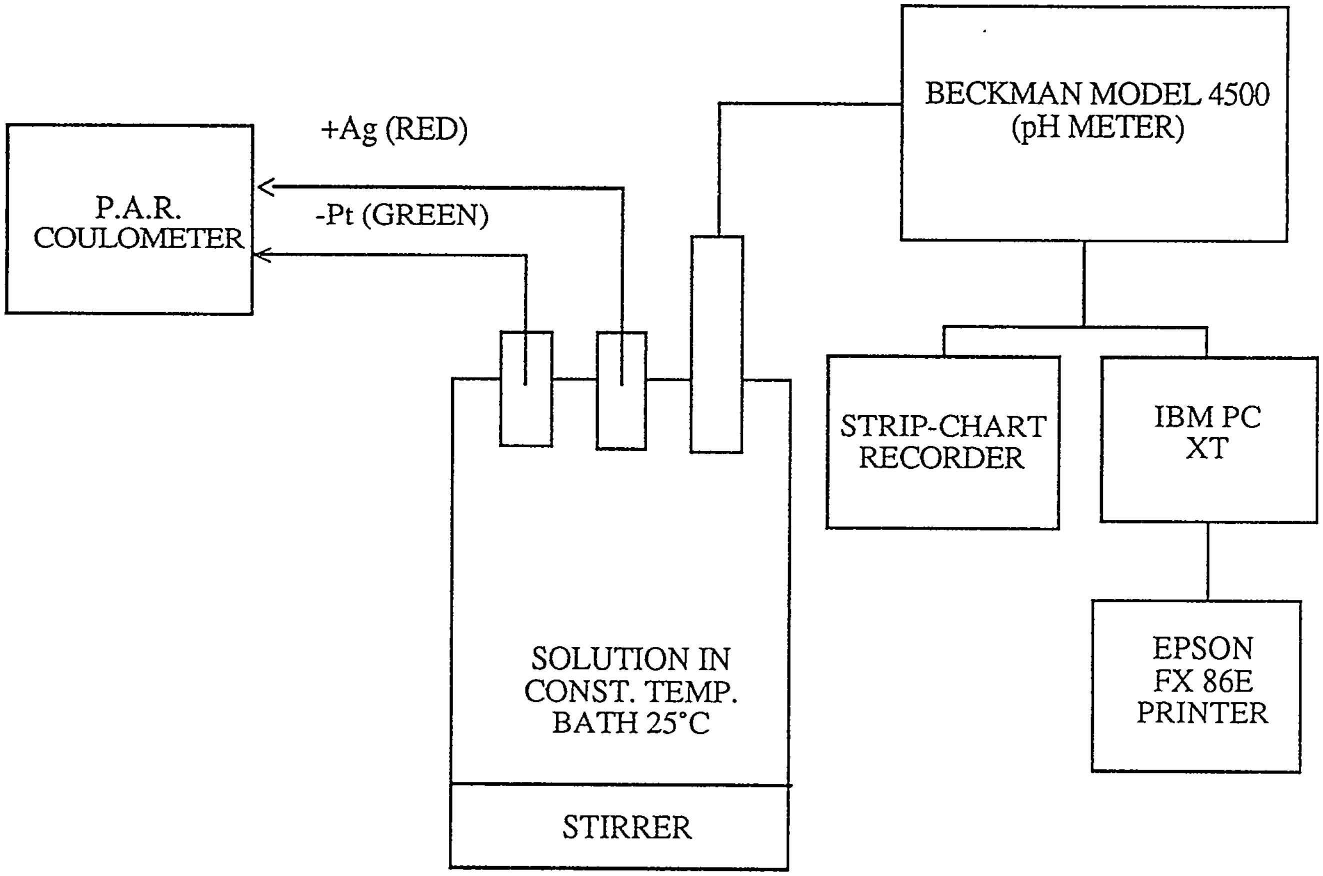


Figure 3. Block diagram of typical aircraft filter pack sampling system.



- Pt: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
+ Ag: $Ag + Br^- \rightarrow AgBr + e^-$

Figure 4. Automated Coulometric Titration Apparatus

APPENDIX

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Internet yaya@bnl.gov

Memorandum

To: Files
From: HJB
Subject: Preliminary Operation Instructions for NGRAN
Date: 26 August 1991

These are the preliminary operating instructions for the program NGRAN for Coulometric Titration. The program in written for Basic version 6, and must be operated from the compiled version only. The QB version cannot access the interface board.

0. Power up all equipment

1. Go to the directory containing the program and data files:

```
CD \NGRAN
```

2. Start the program

```
NGRAN
```

The display should now show

```
                 COULOMETRIC TITRATION PROGRAM 7/23/91

Use Arrow keys to Highlight an Option.  Enter to Select it

RUN  CONFIGURE  PLOT  TEST  EXIT

Acquire data
```

3. Use the arrow keys to select the "CONFIGURE" option and verify the configuration, especially the length of the run, the current, and the minimum and maximum axis values.

4. ESC from the configure option and select the "RUN" option. Answer the questions (see next page) and wait. The machine will spend 6 seconds on an autocalibration and then wait for the trigger specified. If the trigger is being done manually, hit any key to start the run.

```
RUN or TEST
Sample ID #? 001
Do you want to plot data on screen (Y/N)? y

Do you want to print data on printer (Y/N)? y

Do you want to dump data to file (Y/N)? y

File name (default extension is .DAT): run001
```

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2. Start the program

```
NGRAN
```

The display should now show

```
                    COULOMETRIC TITRATION PROGRAM 7/23/91

Use Arrow keys to Highlight an Option.  Enter to Select it

RUN  CONFIGURE  PLOT  TEST  EXIT

Acquire data
```

3. Use the arrow keys to select the "CONFIGURE" option and verify the configuration, especially the length of the run, the current, and the minimum and maximum axis values.

4. ESC from the configure option and select the "RUN" option. Answer the questions (see next page) and wait. The machine will spend 6 seconds on an autocalibration and then wait for the trigger specified. If the trigger is being done manually, hit any key to start the run.

```
RUN or TEST
Sample ID #? 001
Do you want to plot data on screen (Y/N)? y

Do you want to print data on printer (Y/N)? y

Do you want to dump data to file (Y/N)? y

File name (default extension is .DAT): run001
```

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1. Go to the directory containing the program and data files:

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CD \NGRAN
```

2. Start the program

```
NGRAN
```

The display should now show

```
                    COULOMETRIC TITRATION PROGRAM 7/23/91

Use Arrow keys to Highlight an Option.  Enter to Select it

RUN  CONFIGURE  PLOT  TEST  EXIT

Acquire data
```

3. Use the arrow keys to select the "CONFIGURE" option and verify the configuration, especially the length of the run, the current, and the minimum and maximum axis values.

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```
RUN or TEST
Sample ID #? 001
Do you want to plot data on screen (Y/N)? y

Do you want to print data on printer (Y/N)? y

Do you want to dump data to file (Y/N)? y

File name (default extension is .DAT): run001
```

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```
CD \NGRAN
```

2. Start the program

```
NGRAN
```

The display should now show

```
                    COULOMETRIC TITRATION PROGRAM 7/23/91

Use Arrow keys to Highlight an Option.  Enter to Select it

RUN  CONFIGURE  PLOT  TEST  EXIT

Acquire data
```

3. Use the arrow keys to select the "CONFIGURE" option and verify the configuration, especially the length of the run, the current, and the minimum and maximum axis values.

4. ESC from the configure option and select the "RUN" option. Answer the questions (see next page) and wait. The machine will spend 6 seconds on an autocalibration and then wait for the trigger specified. If the trigger is being done manually, hit any key to start the run.

```
RUN or TEST
Sample ID #? 001
Do you want to plot data on screen (Y/N)? y

Do you want to print data on printer (Y/N)? y

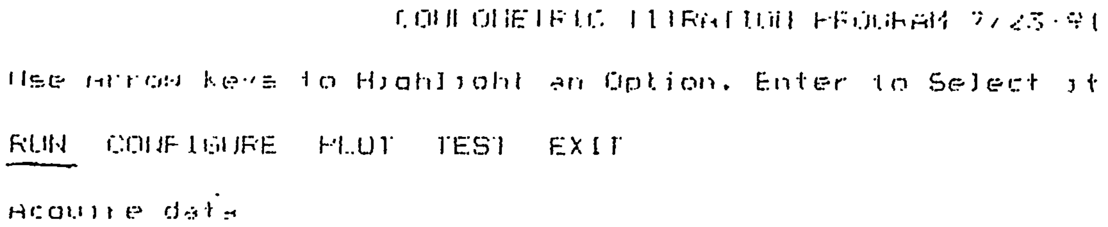
Do you want to dump data to file (Y/N)? y

File name (default extension is .DAT): run001
```

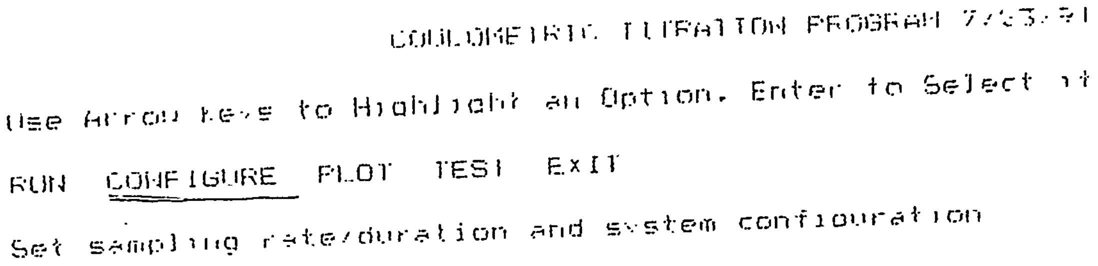
```
CONFIGURE
 Sample rate - readings per second:  .1    .2    .5    1    2    5    10
           Run duration - minutes: 10
                    Input channel:  CH0   CH1
                 Full scale range:  1v    2v    5v    10v
  Trigger code to start on (0 - 15): 0
                    Relay 0 start:  off   on
                      Relay 0 end:  off   on
                    Relay 1 start:  off   on
                      Relay 1 end:  off   on
          CROM-1 board I/O address: &H330
CROM-1 board interrupt level (2-7): 5
                         Operator: Operator
                 Site Information: BNL ECD
               Current (microAmps): 500
                      Temperature: 17 C
         Minimum X-axis (ueq OH-): 0
         Maximum X-axis (ueq OH-): 3
          Minimum Y-axis (10 E/6): 0
          Maximum Y-axis (10 E/6): 4000



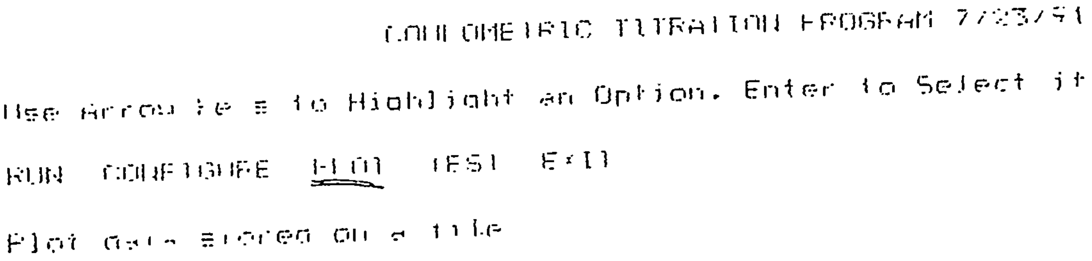
Press <ESC> to return to command menu
```



```
                         COULOMETRIC TITRATION PROGRAM 7/23/91
Use Arrow keys to Highlight an Option. Enter to Select it
RUN  CONFIGURE  PLOT  TEST  EXIT
Acquire data
```



```
                         COULOMETRIC TITRATION PROGRAM 7/23/91
Use Arrow keys to Highlight an Option. Enter to Select it
RUN  CONFIGURE  PLOT  TEST  EXIT
Set sampling rate/duration and system configuration
```



```
                         COULOMETRIC TITRATION PROGRAM 7/23/91
Use Arrow keys to Highlight an Option. Enter to Select it
RUN  CONFIGURE  PLOT  TEST  EXIT
Plot data stored on a file
```