1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

The objectives of this standard operating procedure are to:

Provide a basic understanding of the principles of conductivity measurement.

Describe routine analysis of wet deposition samples using a YSI Model 32FL Conductivity Meter.

Describe routine maintenance of the YSI Model 32FL Conductivity Meter.

This procedure will be followed by all analysts in the Environmental Analysis Facility of the Energy and Environmental Engineering Center of the Desert Research Institute.

1.2 Measurement Principle

Conductivity is the measure of an aqueous solution's ability to conduct electricity. It depends on the concentration of ions present in the solution, their mobilities and valences, and the temperature at which the measurement is made. Conductance is determined by measuring the ratio of electrical current through a cell immersed in the aqueous sample to the applied voltage. The standard unit of electrical conductance is the siemens (or the mho), which is the inverse of electrical resistance in ohms (R). Specific conductance (designated by lower case k) is the conductance measured between opposite faces of a 1 cm cube of liquid at a specified temperature. The observed conductance of a solution depends inversely on the distance (d) between the electrodes and directly upon their area (A):

$$\frac{1}{R} = k \frac{A}{d}$$

The ratio d/A is the cell constant (K) for a cell with fixed electrodes. Therefore, conductivity is determined by multiplying the measured solution conductance by the cell constant K.

$$k = K \times 1/R$$

YSI Model 32FL Conductivity Meter.

Conductivity Cell, Dip cell (YSI 3403), cell constant K=1.0/cm.

Thermistor Temperature Sensor (YSI 3220 series).

Swing arm cell holder.

Graduated cylinder, 25 ml.

2 volumetric flasks, class A glass, 1000 ml.

Volumetric pipette, class A, 5 ml.

Wash bottle, polyethylene, 500 ml.

Sample storage bottles, Nalgene polyethylene, narrow mouth screw top, 250 ml.

Kimwipe paper towels.

10 ml polystyrene disposable beakers.

2.1.2 Characterization

2.1.2.1 Corrected Cell Constant

Due to lack of a large sample volume (20 ml or greater), it is not always possible to immerse the conductivity cell in the sample solution. Therefore the immersion cell is converted into a sample cup by sealing the vent slot with Parafilm. The model 3403 cell requires a minimum of 3 ml to cover the cell electrodes within the sealed sample cup. The electrical conduction field within a sealed, inverted dip cell differs from the electrical field present when the cell is immersed in a solution. When used as a sealed cup, the cell constant (K) must be corrected. The corrected cell constant is specific for each cell. The following is the procedure to determine the cell constant:

1. Before sealing the vent slot, immerse the cell in room temperature standard solution and measure conductance.

2. Multiply by the cell constant to determine conductivity.

3. Seal the vent slot with Parafilm and fill the electrode chamber with some of the same solution and again measure conductance. Take care to ensure that neither solution temperature nor composition change during these steps.

4. Multiply by the cell constant to determine conductivity.

5. Divide the difference between the two conductivity determinations by the conductivity obtained in step 4.

6. The result of step 5 is a percent variation of cell constant. Add this variation to the constant marked on the cell. This result is the cell constant to use whenever the vent slot is closed.

2.1.2.2 Determination of Temperature Compensation Setting

The temperature coefficient (percent change in conductance per degree change in temperature) is a function of ions present and their concentrations. Tabulated values of temperature coefficients for dilute solutions of various ions range from 1.21 to 2.28 (YSI). The dominant ion is likely to be NO_3^-, so the temperature compensation setting is determined from a KNO_3 solution. The temperature compensation setting of 1.85 was determined by following the steps listed below:

1. Prepare a 0.1M KNO_3 solution and divide into two parts.

2. Heat one part to 25°C and cool the other part to 20°C.

3. Measure the conductance of the 25°C solution with temperature compensation turned off.

4. Measure the conductivity of the 20°C solution with temperature compensation turned on. Adjust the temperature compensation dial until the indicated reading agrees exactly with that obtained for the 25°C sample.

5. Repeat again at a lower temperature to confirm the temperature coefficient setting. Record this temperature coefficient setting for use in routine measurements.

2.1.3 Maintenance

Any one of the foaming acid tile cleaners, such as Dow Chemical "Bathroom Cleaner", will clean the cell adequately. If a stronger cleaning solution is needed use a 1:1 isopropyl alcohol and 10 N HCl solution. Dip the cell into the solution, making sure it is submerged beyond the vent slot. Agitate for one to two minutes. Remove the cell from the solution and rinse with several changes of DDW. Inspect the platinum black on the electrodes for signs of wearing to see if replatinizing is required.

Store the conductivity cell by filling with DDW and sealing with Parafilm.

2.2 Reagents

Potassium Chloride (KCl), ACS reagent grade or better.

DDW- Use DDW conforming to ASTM Specification D 1193, Type II (ASTM 1982). DDW having a conductivity reading of less than 1.5 μmhos/cm is required for all analyses. If conductivity is higher than this, notify water supplier immediately, so fresh water can be sent. DDW is supplied in 4 liter collapsible polyethylene containers.

3.0 CALIBRATION STANDARDS

3.1 Preparation of Standard Solutions

3.1.1 Preparation of Stock Solution (0.100M KCL)

Place approximately 10-12 g of KCl into a clean glass petri dish, cover lightly with aluminum foil, and dry in an oven at 105°C for approximately 1 hour. Cool to room temperature.

Using a disposable weighing boat, weigh out 7.455 g of the KCL. Transfer volumetrically to a 1 liter volumetric flask using DDW. Rinse weighing boat at least 3 times. Dilute to volume with DDW. This solution may be stored in a 1 liter Nalgene bottle which has been soaked in DDW for 24 hours, store at room temperature.

3.1.2 Preparation of Working Standard Solution (0.0005M KCl)

Pour a 10 ml aliquot of the Stock solution into a disposable 10ml beaker. Rinse a 5ml volumetric pipette with this solution. Add more stock solution to the dispoBeaker, and pipet 5 ml into a 1 liter volumetric flask. Dilute to volume with DDW. This solution has an immersion cell conductivity of 73.9 μmhos/cm at 25°C.

Store working standard solution at room temperature and remake every 2 months or if standard no longer reads 73.9 ±5% at 25°C. If standard is out of range, notify lab supplier immediately and fresh working standard solution will be made and sent.

4.0 PROCEDURES

4.1 General Flow Diagram- Not applicable.

4.2 Instrument Start Up

1. Set the Function switch to OFF, and connect the instrument to a 110/220V power source. If a power source is not available, the Model 32FL can be operated in battery mode. A full battery charge will provide about 24 hours of continuous operation but will require 15 hours of battery charging before it can be used in the portable mode again.

2. Connect the two cell leads to the terminals. If cell has been stored dry, it must be soaked in DDW for 24 hours before use.

3. Connect the temperature probe jack to its receptacle.

4. If immersion cell has not already be converted to a sealed sample cup, do so by placing a piece of Parafilm around the outside on the cell and stretching it around the outside to seal the vent slots. Place the inverted cell into its holder.

5. Fill wash bottle with fresh DDW.

6. Set the temperature coefficient dial to 1.85. Record the temperature coefficient setting on the Data Sheet.

7. Record the corrected cell constant written on a tag attached to the conductivity cell on the Data Sheet.

4.3 Routine Operation

1. Rinse a 25 ml graduated cylinder twice with DDW, then fill with DDW. Rinse temperature probe with DDW and immerse into water sample in cylinder. Move function switch to Temperature setting and allow 20-30 seconds for a stable reading. Record temperature on the Data Sheet.

2. Rinse the sample cup twice with DDW and then fill with DDW. Move the function switch to the Conductance setting. Move range switch to lowest range setting that does not give an overrange indication (a 1 followed by blanks). Let reading stabilize for 60 seconds and record value to three significant figures on the Data Sheet in the cv column. This is the conductance value which is not compensated for temperature variation from 25°C. This reading is used as a comparison value only.

3. Move function switch to the Conductance - Temperature Coefficient setting. Allow to stabilize. Record reading on the Data Sheet in

Desert Research Institute
Energy and Environmental Engineering Center

WET DEPOSITION MEASUREMENT FORM

Barton Flats Field Technician: _____ Sample ID: _____

Start: __/__/__ __:__ Stop: __/__/__ __:__ (MM/DD/YY, HH:MM 00:00-24:00)

RAIN GAUGE:

	Tue	Wed	Thu	Fri	Sat	Sun	Mon	Tue	Week Total
Amount (inches)	.	.	.	.	.	.	.	.	.
Type (R,S,M,U)									

R = Rain, S = Snow, M = Mixed, U = Uncertain

WET BUCKET: Rinse Blank (Y/N)? ___ Volume DDW Added: ____ml

Bucket Weight (grams): Final - Initial = Net
_____ _____ _____

Graduated Cylinder Volume: _____ ml

Inches of Precipitation (ml or grams X 0.0006)= _____

Dry Bucket Cleaned (Y/N)? ___

CONDUCTANCE (µs/cm): Temperature Coefficient Setting: ____

	Temp, °C	cv	cv(t)	X	K	=	C(t)
Bucket Rinse:	___.___	_____	_____		_____		_____
DDW:	___.___	_____	_____		_____		_____
Working Std:	___.___	_____	_____		_____		_____
Sample:	___.___	_____	_____		_____		_____

pH:
Slope: ___.___ Calib. Std. (pH4): ___.___ (pH7): ___.___ Sample: ___.___

COMMENTS:

Revised November 17, 1994

Figure 4-1. DRI Wet Deposition Measurement Form

the cv(t) column. This is the temperature compensated-conductance value.

4. Calculate and record the temperature compensated conductivity C(t) on the Data Sheet,

$$C(t) = cv(t) \times K.$$

5. Repeat steps 2 to 4 with the standard working solution. Substitute the standard whenever DDW is referred to in the procedure.

6. Pour the standard solution out of the sample cup and rinse sample cup three times with DDW. Shake the sample cup gently to remove DDW. If there is enough sample, rinse the sample cup with the sample. Repeat steps 2 to 4 with the sample. Substitute the sample whenever DDW is referred to in the procedure.

4.4 Shut-Down

To store cell, rinse several times with DDW. Fill sample cup to the brim with DDW and stretch a piece of Parafilm over top making sure it seals tightly.

Turn Conductivity Meter off. Do not unplug meter unless moving to another location.

5.0 QUANTIFICATION

The YSI Model 32FL conductivity meter is calibrated from the factory before shipment. If components are replaced, or the instrument has been in service for a long time, a calibration check may be done. The YSI service department at the factory can provide this service. Section 2.1.2 describes procedures for determination of cell constant and temperature coefficient setting.

6.0 QUALITY CONTROL

To ensure that the conductivity meter is working properly the working standard solution is analyzed with every batch of samples. If the result is off by more than ±10%, the solution needs to be remade and checked before continuing with analysis of the samples.

7.0 QUALITY ASSURANCE

The performance and system audits are scheduled on a biannual basis by the QA officer to ensure that all procedures are followed properly and to verify the precision, accuracy and validity of the data.

8.0 REFERENCES

California Air Resources Board (1990). Procedure for the Preparation and Physical Measurements of Wet Deposition Samples. SOP No. MLD 109.

YSI Model 32 Conductance Meter Instruction Manual. Yellow Springs Instrument Company, Yellow Springs, Ohio.

ASTM, 1982. Annual Book of ASTM Standards, 1982.

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

The objectives of this standard operating procedure are to:

- Provide a basic understanding of the principles of operating an Orion Model 720A pH Meter.
- Describe routine operation of the Orion Model 720A pH Meter.

This procedure will be followed by all technicians in the Environmental Analysis Facility of the Energy and Environmental Engineering Center of the Desert Research Institute.

1.2 Measurement Principle

The pH meter uses the difference in electrical potential occurring between the sample solution and the electrode solution to measure the [H+]. The pH meter consists of a pair of electrodes connected to a meter capable of measuring small voltages, on the order of millivolts. A voltage, which will vary with the pH, is measured when the electrodes are placed in a solution this is then converted into pH units in which the meter is calibrated. Acidic solutions have a pH less than 7.00, Basic solutions have a pH greater than 7.00 and neutral solution have a pH of 7.00. Normal rain pH is about 5.60. pH measurement is temperature dependent, therefore it is important that all solutions used in pH measurement be at the same temperature. The pH value should be reported to three significant figures.

1.3 Measurement Interferences and Their Minimization

pH measurements are temperature dependent. Make sure all solutions, including the sample are equilibrated to room temperature before taking any readings or calibrating the pH meter.

The pH electrode will leak K^+ and Cl^- into the sample solution, therefore if the same aliquot is to be used for both conductivity and pH measurements, always do the conductivity measurement first. This aliquot should never be used for ion analysis.

High levels of Na^+, NH_4^+, and high ionic strength solutions will cause interfences and give erroneous readings. Dehydration of the glass

electrode is caused by letting the electrode air dry or by putting it in a hydrophilic solution such as alcohol. This is to be avoided.

The electrode used for acid rain deposition work should never be used for any other pH measurements.

1.4 Ranges and Typical Values of Measurements

pH is generally measured on a scale of 0 to 14 pH units. The smaller the number the more acidic; the larger the number the more basic. Normal rain pH is about 5.60 pH.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

pH range of the Orion Model 720A is -2.000 to 19.999. The resolution can be from 1 decimal point to 3 decimal points with a relative accuracy of ±0.002. The slope of the curve should be between 80% to 120%.

1.6 Personnel Responsibilities

All field technicians should read and understand the entire standard operating procedure before performing pH measurements. The technician is expected to follow this procedure step by step to perform routine system calibration and measurements. The field manager is responsible for ensuring that the pH measurement procedures are properly followed, to examine all data and to deliver analyses results to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center (EEEC) is responsible for determining the extent and methods of quality assurance to be applied to each project, for estimating the level of effort involved in this quality assurance, for identifying the appropriate personnel to perform these QA tasks, for updating this procedure periodically, and for ascertaining that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

The following terms are used:

pH	The negative log in base 10 of the molar hydrogen-ion concentration.

Combination pH Electrode	The measuring glass electrode and the reference electrode (AgCl, KCl, Calomel etc.) together in one probe.
Glass Electrode	Electrode made out of special composition glass which is sensitive to small diameter cations, specifically H^+. This is the half-cell whose potential depends on the concentration of H^+.
Reference Electrode	The electrode which contains an electrochemical half-cell whose potential is known that completes the measurement circuit and provides a reference voltage.
Reference Cell Solution	Solution that the reference electrode is filled with to provide the half-cell reaction and electrical connection.
Acid	A substance that is able to donate a H^+ ion. The solution will have a pH value < 7.0. The smaller the number, the stronger the acid.
Base	A substance that produces an excess of OH^- ions when dissolved in water or will readily accept an H^+ ion. The solution will have a pH value > 7.0. The larger the number, the stronger the base.
pH Buffer	An aqueous solution the resists pH changes upon addition of small amounts of acid or base. These contain a mixture of either a weak acid and its salt or a weak base and its salt. By choosing appropriate components and adjusting their relative concentrations, buffer solutions at virtually any pH can be made.

Nernstian Slope	The change in pH electrode output with changes in pH values.
Temperature Compensation	Corrects for changes in the Nernstian slope due to changes in temperature.

1.8 Related Procedures

Related field procedures are specified in the following DRI Standard Operating Procedures:

DRI SOP 04 Operation of the Aerochem Metrics Model 301 Wet/Dry Precipitation Collector.

2.0 APPARATUS, INSTRUMENTATION, REAGENTS AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The Orion Model 720A pH Meter consists of a microprocessor controlled unit which will measure pH, mV, RMV, Conc, and if an Automatic Temperature Probe is attached display temperature. It can also measure dissolved oxygen with an oxygen electrode. It features pH autocalibration, concentration calibration, sealed keypads, simultaneous temperature display, two color vacuum fluorescent display with a separate prompt line which explains each step during calibration and measurement. The Orion ROSS Combination pH electrode Model 81-15 uses a 3 M KCl solution as the refence electrode solution. This is a semi-micro probe with an epoxy body.

2.1.2 Characterization

The Orion 720A Model has the capability to display from 1 to 3 significant figures. The more significant figures, the longer the stabilization time. In the three significant figure resolution, the final figure will vary by ±0.002 pH units. A stable reading will usually occur within 5 minutes when going from a highly buffered solution to a weakly buffered solution.

2.1.3 Maintenance

For routine maintenance the following steps need to be followed:

1. Inspect the electrode for scratches, cracks, salt crystal build-up or membrane/junction deposits.

2. Clean any salt deposits from exterior by rinsing with DDW. Avoid rubbing or wiping electrode bulb, to reduce chance of error due to polarization.

3. Drain the reference chamber, flush with fresh ROSS filling solution, Orion Cat. No. 810007, and refill the chamber. Do not use any filling solution which may contain silver.

4. Between measurements, rinse electrode with DDW, then either blot excess moisture or shake gently to remove excess moisture.

5. After final measurement, make sure electrode is immersed in the pH electrode storage solution and the filling hole is covered. Wrap a piece of Parafilm around top opening of storage bottle to prevent evaporation of storage solution.

6. Consult Orion Instruction Manuals for further maintenance and trouble-shooting guides.

2.1.4 Spare Parts List

Not applicable.

2.2 Reagents

The following reagents should be kept on hand:

1. VWR Buffer Solution pH 4, Cat. No. 34180-243.
2. VWR Buffer Solution pH 7, Cat. No. 34180-286.
3. VWR Buffer Solution pH 10, Cat. No. 34180-300.
4. Orion ROSS Reference Electrode Filling Solution, Orion Cat. No. 81-00-07.
5. pH Electrode Storage Solution, Orion Cat. No. 910001.

2.3 Forms

Figure 2.1 shows the Acid Deposition Report Form. This is the form on which pH values will be reported.

Desert Research Institute
Energy and Environmental Engineering Center

WET DEPOSITION MEASUREMENT FORM

Barton Flats Field Technician: _____ Sample ID: _____

Start: __/__/__ __:__ Stop: __/__/__ __:__ (MM/DD/YY, HH:MM 00:00-24:00)

RAIN GAUGE:

	Tue	Wed	Thu	Fri	Sat	Sun	Mon	Tue	Week Total
Amount (inches)	.	.	.	.	.	.	.	.	.
Type (R,S,M,U)									

R = Rain, S = Snow, M = Mixed, U = Uncertain

WET BUCKET: Rinse Blank (Y/N)? ___ Volume DDW Added: ___ml

Bucket Weight (grams): Final - Initial = Net Graduated Cylinder Volume: _____ ml

Inches of Precipitation (ml or grams X 0.0006)= _____

Dry Bucket Cleaned (Y/N)? ___

CONDUCTANCE (μs/cm): Temperature Coefficient Setting: .

	Temp, °C	cv	cv(t) X K	= C(t)
Bucket Rinse:	.			
DDW:	.			
Working Std:	.			
Sample:	.			

pH:
Slope: . Calib. Std. (pH4): . (pH7): . Sample: .

COMMENTS:

Revised November 17, 1994

Figure 2.1. Wet deposition measurement form.

3.0 CALIBRATION STANDARDS

3.1 Preparation of Calibration Standards

VWR Buffer Solutions pH 4, pH 7, and pH 10 are used as is to calibrate the pH meter.

In the laboratory, for rain water samples, prepare a 1:10 dilution of the VWR Buffered pH 4 and pH 7 solutions. This is done by measuring 9 ml of DDW into a blue-capped test tube using a wash bottle. Add 1 ml of the Buffer by pouring a small amount of the buffer into a disposable 10 ml beaker and using a disposable pastuer pipet to bring the volume in the test tube to the 10 ml mark. Clearly label both test tubes. This is done because the buffer solutions have a higher ionic strength than normal rain water samples and this affects the pH readings. By diluting the buffer solutions, you more closely match the sample matrix.

3.2 Use (What is Compared to the Standards)

In the Laboratory, after the pH meter has been calibrated with the above diluted pH buffers, the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 2694a-I or 2694a-II should be read as a QC check. The pH values are 4.30 ± 0.03 and 3.60 ± 0.03 respectively.

3.3 The Accuracy of Calibration Standards

The accuracy of the VWR pH 4 Buffer Solution is traceable to the National Institute of Standards and Technology (NIST) Standard Reference Material (SRM) 185, VWR Buffer Solution pH 7 is traceable to NIST SRM 186 I&II, and VWR Buffer Solution pH 10 is traceable to NIST SRM 191 & 192. All three buffers are accurate to ± 0.01 pH units at 25°C.

4.0 PROCEDURE

4.1 General Flow Diagram

Not applicable

4.2 Start Up

Plug the Orion Model 720A pH Meter into electrical outlet. Allow to warm up for at least 5 minutes. The following parameters need to be set before initial calibration.

1. Date and Time. To enter date press, the key +/-,(Date/Time and Beep). Follow the prompts to enter the correct date and time. See Instruction Manual for more details.

2. Resolution. To enter the number of decimal places for the display to read out, press key 5, (resolution and channel). Press the key until the desired read out is obtained, 2 decimal places.

3. The ready function, standby function and autoshutoff function are default values. The ready function will display RDY in the prompt line when a stable reading is obtained, it will also beep. The standby function prolongs display life by illuminating the display at half intensity when not in use. The autoshutoff function also prolongs the meter life by activating standby when no keys have been pressed for 10 minutes.

4. Remove seal from filling hole and check level of refence filling solution. Follow the procedure in Section 2.1.3 for rinsing and refilling the electrode.

5. Allow the electrode to soak in pH Electrode Storage Solution for at least one hour if electrode has not been stored in this solution.

4.3 Routine Operation

4.3.1 Calibration Procedure

Before measurement of pH in samples can be done a two point calibration of the pH meter needs to be performed. This is done by rinsing a blue-capped test tube with an aliquot of pH 4 buffer and then pouring in a fresh aliquot of the buffer. This is repeated for the pH 7 buffer. Label both tubes clearly. Place in a wire test tube rack. <u>Important: Make sure that all solutions and samples are at room temperature before proceeding.</u>

Remove the electrode from the storage solution and holding over a beaker, rinse the electrode with fresh DDW in a wash bottle. Gently shake excess water off the electrode. <u>Caution: handle the electrode gently as it is very fragile.</u> Place the electrode in the pH 4 buffer solution and press Key 2 (calibrate) on the meter. It will display date and time of last calibration and then ask for

number of calibration buffers. Enter 2 then press "Yes". It will then measure the pH of the first buffer solution and when a stable reading is obtained, beep and in the prompt line Rdy Cal As 4.01 will appear. Press "Yes". Take the electrode out of the pH 4 buffer and holding over the beaker, rinse with DDW and remove excess DDW.

Place electrode in the pH 7 buffer and repeat the process. The prompt line will display Rdy Cal As 6.997, press "Yes". It will then display the slope of the curve in percent. Record this value on the data sheet. The range of the slope should be between 92 to 102%. The meter will then go into the measure mode.

4.3.2 Routine pH measurements

Take electrode out of the pH 7 buffer, rinse with DDW. Place in the electrode storage solution while preparing samples for measurement. If the same sample is to be used for both conductivity and pH measurement, perform the conductivity reading first. After the conductivity reading has been taken, carefully pour the sample into a blue-capped test tube. The minimum amount required for a pH reading is 3 ml. This will allow the reference junction to be adequately covered .

After the last sample has been read or after the 10th sample measurement, check the calibration by measuring the pH 4 and pH 7 buffers, record these values along with the sample values. If the buffers have drifted by more than ± 5% redo the calibration and redo the pH measurements on the samples.

4.4 Shut-Down

When all samples have been analyzed and standard buffers checked. Put the pH meter in the stand-by mode, rinse the electrode off with DDW and place in storage bottle containing pH Electrode Storage Solution. Wrap a piece of parafilm around top of container to help prevent evaporation. Make sure the electrode is sufficiently immersed in the storage solution.

5.0 QUANTIFICATION

5.1 Calibration

See section 4.3.1

5.2 Calculations

pH values are calculated based on the slope obtained from the two point calibration curve. Values above and below the standard buffers are calculated based on extrapolation of this curve. The Model 720A pH meter automatically recognizes five buffers; 1.68, 4.01, 7.00, 10.01 and 12.46 within a range of ± 0.5 pH units and up to a five point calibration can be performed. A three point calibration curve using the 1.68 pH buffer can also be used if it is determined that a large number of samples are significantly below the 4.01 pH buffer.

The E° values used in the calibration curve are based on the Nernst Equation :

$$E = E^\circ - \frac{0.0591}{n} \log Q \qquad (T=298K)$$

E = Electromotive force (emf) or cell potential
E°= Standard emf or standard cell potential
Q = ratio of half-cell ions in solution

6.0 QUALITY CONTROL

6.1 Performance Testing

Standard pH buffers used in the calibration of the pH meter are measured after every 10 samples and at the end of the set of samples. The values obtained should be within ± 0.5% of the value of the pH buffer.

6.2 Reproducibility Testing

Replicates will be based upon amount of sample available. pH and conductivity measurements are done in the field when the sample is collected and also in the laboratory. If there is sufficient sample available, one replicate will be performed for every ten samples or sample set if less than ten.

7.0 QUALITY ASSURANCE

Not applicable

8.0 REFERENCES

Brown, T, LeMay, H.E., and Bursten, B. (1991). "Chemistry the Central Science" 5th Ed., Prentice Hall, Englewood Cliffs, NJ.

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure provides the methods for performing gravimetric analysis of 37 and 47 mm diameter polyolefin ring mounted Teflon membrane filters. It also covers the assignment of IDs to Teflon filters.

1.2 Measurement Principle

The Cahn C-31 Microbalance is used to weigh filters to the nearest 0.001 milligram. The balance measures the difference between the gravitational weights on two ends of a pivoted beam. A sample pan is suspended from one end of the beam and a tare pan from the other. The pivot point of the balance beam passes through a torque motor, and an optical sensor at one end of the beam determines when the beam is horizontal. The beam is a low mass, equal arm design supported by a platinum taut band. The equal arm beam minimizes calibration drift due to temperature change, and the taut band suspension minimizes effects of vibration and eliminates problems of knife edge wear and friction.

In operation, a filter is placed on the sample pan which forces the sample side of the beam down. The balance supplies an electric current through the torque motor sufficient to rotate the beam to a horizontal position. The amount of electrical current necessary to balance the beam is proportional to its weight.

1.3 Measurement Interferences and Their Minimization

Humidity changes affect the mass of filters and their deposits by changing the amount of absorbed water on the sample. To minimize this effect, filters are equilibrated and weighed in a temperature and humidity controlled environment (20 ± 5° C and 30 ± 5% RH).

Contamination from airborne particles or from particles that have accumulated on instrument and workbench surfaces is possible. Cross contamination from one sample to another is also possible. A sample can be significantly contaminated without any visible indication. The balance resides in a laminar flow hood and filters are handled only with clean tweezers to reduce the likelihood of contamination.

The microbalance is extremely sensitive to static electricity, from effects of accumulated static charge on the pan and balance beam as well as from interaction of electrically charged samples with parts of the balance. Static electrical charge on the filters, which may be significant after air is pulled through the filters during sampling, is dissipated by placing the filters over a radioactive ^{210}Po ionizing radiation source for 30 to 60 seconds prior to weighing. Static charge accumulations in the balance itself are reduced by electrically grounding the balance and periodically cleaning the weighing chamber with anti-static wipes.

Some Teflon filters exhibit a loss of weight for a period of time after they are removed from their original shipping containers. Weight loss of up to 150 μg has been observed. The magnitude of weight loss varies from batch to batch and may be due to loss of volatile components from the polyolefin support ring. New filters are removed from their sealed packages and equilibrated in a clean, open atmosphere for a sufficient time to allow the filter weights to stabilize before use.

1.4 Ranges and Typical Values of Measurements

Unexposed filters vary considerably in mass depending on filter media and size. The 37 mm diameter filters generally weigh between 80 and 130 mg, while 47 mm diameter filters generally weigh between 110 and 160 mg.

Deposit mass depends on the air-borne particle concentration, air flow rate through the filter, sample collection time, and the particle size cut device employed. All of these factors are considered and adjusted during the development of program plans to yield optimal loading for mass measurement and subsequent chemical analyses. Most deposits range from 0 to 5 mg. Deposits greater than about 1 mg/cm^2 tend to be physically unstable.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The sensitivity of the Cahn C-31 Microbalance is 1 μg in the 0 - 250 mg range. The 0 - 25 mg range sensitivity is 0.1 μg, but this more sensitive range is not routinely used for filter measurements.

The precision of mass measurements for unsampled filters based on replicate weighings is typically 3 to 5 μg/filter. The precision on sampled filters is typically 5 to 8 μg/filter. Precision on filters with deposits heavier than 1 mg/cm^2 may approach $\pm$ 2% of the deposit mass. Deposit mass precision is the square root of the sum of the squares of the pre and post sampling precision (typically 6 - 9 μg/filter).

The lower quantifiable limit is determined as the standard deviation of field blank deposit weights. In the absence of field blanks, lower quantifiable limit can be estimated as the deposit mass precision.

Measurement accuracy is limited by the accuracy of the calibration weight and the linearity of the balance. Balance linearity is 1 μg, or 0.0001% of the load on the beam, including sample pans. The accuracy of the 200 mg Class 1.1 calibration weight is ± 5 μg. Since deposit mass is determined by difference, the maximum error introduced from the calibration weight error is 5 μg/200 mg x 0.001 mg/μg x deposit weight (μg). In effect, accuracy is 1 μg.

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand this entire standard operating procedure prior to performing filter weighing.

The laboratory manager is responsible for insuring that the weighing procedures are properly followed, maintaining the supplies necessary to insure uninterrupted weighing, and insuring proper chain-of-custody documentation.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center has the following responsibilities: 1) to determine the extent and methods of quality assurance applied to each project; 2) to estimate the level of effort involved in the quality assurance; 3) to update this procedure periodically; and 4) to verify that the budgeted tasks are carried out as specified in each contract.

1.7 Definitions

The following terms are used in this document:

Suspension wire	The stainless steel wires with a loop at the bottom that hang down from the balance beam. There is one on each end of the beam to support sample and tare stirrups. A third suspension wire mid way between the beam center point and the left end of the beam is used for higher capacity weighing (not for filter weighing).
Stirrup	The nichrome wire frame that supports the sample and tare pans and hangs from the suspension wire on each end of the balance beam. The sample stirrup is on the left side of the beam and the tare stirrup is on the right side of the beam.
Sample pan	The 38 mm diameter flat aluminum platform part of the sample stirrup.
Tare pan	A 13 mm diameter aluminum pan super-glued to the tare stirrup.
Tare weight	A 20 - 50 mg weight that is kept on the tare pan to balance the weight of the larger sample pan.

1.8 Related Procedures

Sample Shipping, Receiving, and Chain-of-Custody (DRI SOP 2-209.3)
X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples (DRI SOP 2-205.3)

2.0 APPARATUS, INSTRUMENTATION, AND FORMS

2.1 Apparatus and Supplies

2.1.1 Description

The Cahn C-31 Microbalance is depicted in Figures 2-1 and 2-2. This microbalance is designed to measure weights ranging from 0.1 μg to 3.5 grams. It resides in the Energy and Environmental Engineering Center's Environmental Analysis Facility clean room, which provides a temperature and humidity controlled environment. The balance sits inside a laminar flow hood on a large block of marble providing vibration isolation.

The sample stirrup is 57 mm wide and has a 38 mm diameter flat platform. It is used on the far left position (A position) on the balance beam. The tare stirrup is the 19 mm wide open (no platform) type and has a 13 mm aluminum pan super-glued in place. It is used on the right side of the balance beam, along with a tare weight (accuracy not critical) of 20 to 50 mg, sufficient to balance the sample pan. The smaller tare stirrup minimizes effects of air currents and the possibility of stirrup frame from coming close to the chamber walls.

Static charge on samples is removed using ^{210}Po ionizing radiation sources mounted inside a small plastic box (6 cm H x 7 cm W x 8 cm D). Three sources are mounted on both the top and bottom, and one on each side, all facing towards the center of the box. The front of the box is open and the back is covered with aluminum foil. Filters are placed inside the box before weighing. A ^{210}Po source in the weighing chamber minimizes accumulation of static charges in the balance as samples are processed.

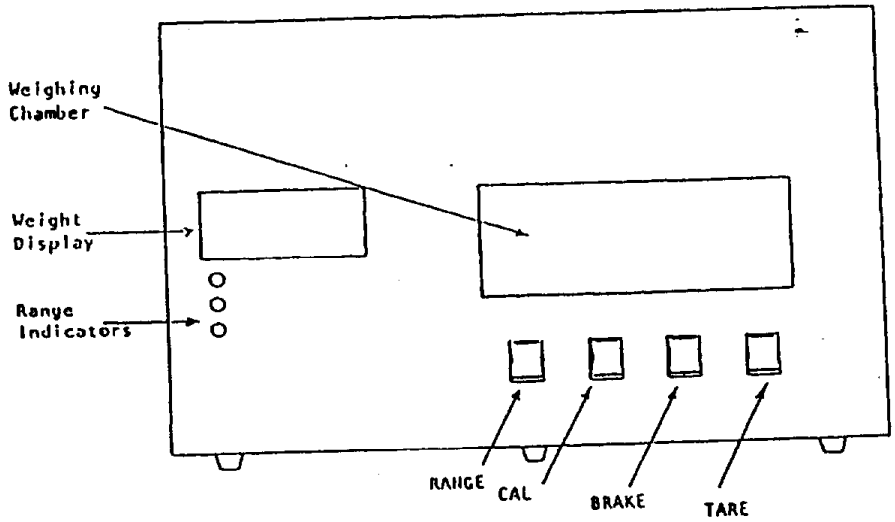


Figure 2-1. Overview of Cahn C-31 Microbalance.

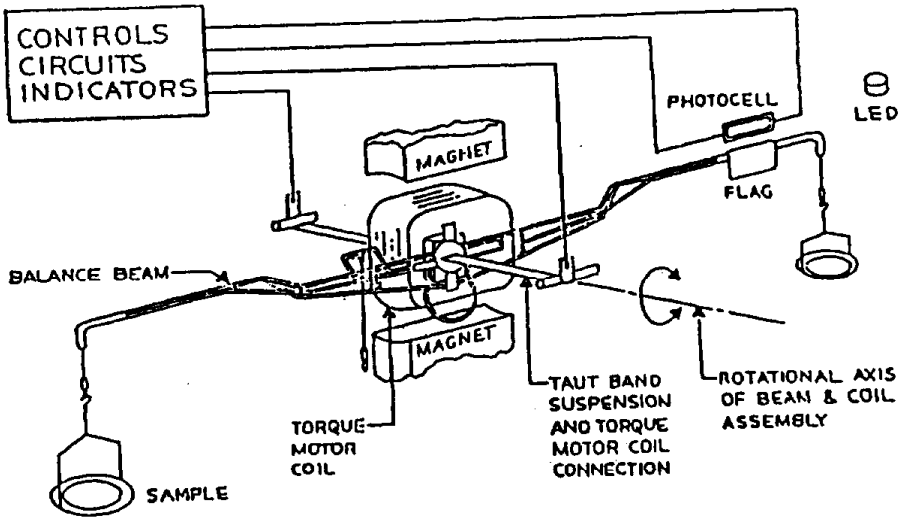


Figure 2-2. Schematic diagram of Cahn C-31 Microbalance weighing mechanism

The balance is connected to a light pen equipped PC/XT compatible computer using the balance's built in serial interface. The MSDOS program CAHN.EXE records sample IDs from the keyboard or light pen, automatically records sample weight after a stable reading is obtained, and controls movement of the balance pan brakes. It records sample flags and comments entered by the operator as well as weights for initial, final, replicate and re-analysis weighings, calculates net weight and constructs dBase III compatible files of completed weighing sets.

2.1.2 Characterization

The Cahn C-31 Microbalance has a response time which averages 30-40 seconds. However, static electricity effects, humidity changes, and loss of volatile species from particle deposits may extend the time to more than one minute. The weighing program takes the mass reading 60 seconds after lowering the pan brakes to ensure uniform measurements.

The suspension wires are easily kinked or broken and the operator must take care to avoid exerting excess force on them. The balance is equipped with two brakes, one under each pan. The brakes are activated prior to adding or removing a filter from the balance to reduce the possibility of suspension wire bending or breakage and reduce the tendency of the pans to swing.

2.1.3 Maintenance

Maintenance on the Cahn C-31 Microbalance consists of periodically cleaning the weighing chamber with isopropanol impregnated anti-static wipes to remove accumulated dust and static charge. This maintenance should be performed only by trained personnel, since the weighing pans must be removed and special precautions must be taken to avoid damaging the suspension wires. Compressed air should never be used to clean the chamber because dust and dirt particles may be forced into the torque motor and electronics.

The ^{210}Po source has a half life of 138 days. Change sources every six months and dispose of old sources according to manufacturer's recommendations.

Annual cleaning and calibration and operation checks are performed by QA Services. Any additional maintenance that is required is completed at this time.

All maintenance and calibration activities are logged into the DRI Weighing Logbook (Figure 2-3).

For additional maintenance procedures, refer to the Instruction Manual for the Cahn C-31 Microbalance.

2.1.4 Parts List

- Two Class 1.1 (formerly Class M) 200 mg calibration weights , one for use as a primary standard and one for use as a working standard during routine analysis (Cahn Instruments, #01540-01).
- Sample stirrup (Cahn part no. 01567-01).
- Tare stirrup (Cahn part no. 02011-01).

DATE	PROJECT	SAMPLE RANGE	#	I/F CK/AW	INITIALS
11/17/89	CADMP	TKAZ0070-89	20	CK	LCP
11/17/89	ADEQ	AZT013471-540	70	I	LCP
11/19/89	ADEQ	AZT013471-540	21	CK	BAH
11/20/89	PBC	CATT161-180	1	CK	LCP
		WPTT161-170	10	I	LCP
		WPFT161-170	10	I	LCP
		SCFT161-170	10	I	LCP
		CAFT161-170	10	I	LCP
		VAFT161-180	20	I	LCP
11/20/89	PBC	Selected from above	21	CK	BAH

Figure 2-3. Example page from Filter Weighing Logbook.

- Aluminum tare pan (Cahn part no. 01187-01).
- Two flat tipped stainless steel non-serrated tweezers, one for calibration and one for routine weighing (Millipore, #62-00006).
- Teflon filters: 47 mm, 2 μm pore size (Gelman, R2PJ047) and 37 mm, 2 μm pore size (Gelman, R2PJ037).
- Deionizers (StaticMaster - VWR cat. no. 58580-041).
- Vinyl gloves, non-powdered (Fisher, #11-393-25).
- Kimwipes (VWR, #21905-025).
- Anti-Static Wipes (Global, #C8165).
- Glass petri dishes, 15 mm x 150 mm (Fisher, Falcon #2045).
- Disposable Petri dishes, 50 mm x 9 mm (Fisher, Falcon #1006).
- Disposable petrislides (Millipore, #PD15-047-00).
- Light table.
- Equilibration trays: two stainless steel trays hinged along one edge. Holes are drilled in the bottom tray and short rubber legs are attached to the outside of the bottom tray to provide air circulation.
- Grounding wires having alligator clips on one end to attach to the equilibration trays and banana clips on the other end to insert into a grounded electrical outlet.
- Mini-drum Hygrothermograph (Cole-Parmer, #G-08369-70).
- Rubber bulb to blow foreign particles off of the filters (VWR, #56341-406).

2.1.5. Spare Parts list

- Chamber lamp.

2.2 Reagents

Methanol in squeeze bottle

2.3 Forms

- Filter Weighing Logbook (Figure 2-3).
- Laboratory Blanks Logbook (Figure 2-4).

PROJECT : Cyprus

Filter ID Saved	Date	Filter ID Used	Date
RIDT 099	4/17/92	RIDT 099	7/13/92
RIDT 100	↓	RIDT 100	↓
CODT 199	4/16/92	CODT 199	7/13/92
CODT 200	↓	CODT 200	↓
GCDT 199	4/16/92	GCDT 199	7/13/92
GCDT 200	↓	GCDT 200	↓

Figure 2-4. Example page from Laboratory Blanks Logbook.

- Filter Equilibration Logbook (Figure 2-5).
- Filter Assignment Logbook (Figure 2-6).
- Data Sheet for Filter Weight (Figure 2-7).
- Data Sheet for Replicate Weights (Figure 2-8).
- Data Sheet for Filter Reweight (Figure 2-9).

3.0 CALIBRATION STANDARDS

3.1 Traceability of Standards

Calibration standards are 200 mg Class 1.1 calibration weights. Traceability to primary standards is maintained by the calibration weight manufacturer. An annual external calibration check makes use of standards traceable to primary standards. Two separate calibration weights are used at DRI. A reference calibration standard is used semi-annually to check the working standard. A working calibration standard is used for routine filter weighing. The weight of the working calibration standard as measured against the reference calibration standard is posted next to the balance and is used to calibrate the balance.

3.2 Use of the Standards

The microbalance is operated with a 20 - 50 mg tare weight in the tare pan. The balance is electronically tared to 0.000 mg at the beginning of each weighing session. The span of the balance is set with the working standard on the sample pan, using the working standard's most recently determined weight. The balance zero and span are set before and after each set of 10 filters are weighed.

The standards are handled <u>only</u> with a pair of tweezers that has been permanently labeled "CAL". These tweezers are not used for any other purpose. The working standard is kept next to the balance in a petri dish that has been lined with aluminum foil. The reference standard is stored in a plastic vial and used only semi-annually to calibrate the working standard.

4.0 PROCEDURES

4.1 General Flow Diagram

A general flow diagram for this procedure is shown in Figure 4-1.

4.2 Filter Equilibration

This section provides procedures for equilibrating pre-sampling and post-sampling filters. The pair of tweezers to be used for routine measurements should be permanently marked "FILTER" so that it is not switched with the calibration tweezers which have been marked "CAL".

Lot #	Size	Date Equilibrated	Date Weighed
452	37mm	8/27/93	11/16/93
453	37mm	8/27/93	11/17/93
454	47mm	9/14/93	11/30/93

Figure 2-5. Example page from Filter Equilibration Logbook.

DRI FILTER ASSIGNMENT LOGSHEET

Date	Project	Manufacturer	Filter Size	DRI Lot #	Assigned Filter ID#

Figure 2-6. Format of Filter Assignment Logbook.

DATA SHEET FOR FILTER WEIGHT

Network Name:
Network Code:
Sampling Site:
Site Code:
Filter Type:
Filter Code:
Filter Lot No.:

Initial Weight

Date:
Time:
Temp (°C)
Rel. Humidity (%):
Technician:

Final Weight

Date:
Time:
Temp (°C)
Rel. Humidity (%):
Technician:

	Filter ID	Tare Weight (mg)	Initial Weight (mg)	Flag	Final Weight (mg)	Flag	Comments
1	T						
2	C						
3							
4							
5							
6							
7							
8							
9							
10							
1	T						
2	C						
3							
4							
5							
6							
7							
8							
9							
10	T						
	C						

Figure 2-7. Data sheet for filter weight.

DATA SHEET FOR REPLICATE WEIGHTS

	Filter ID	Tare Weight (mg)	Original Weight (mg)	Initial or Final Weight	Check Weight (mg)	Weight Diff. (mg)	Tech	Date (YYMMDD)	Comments
1									
2									
3									
4									
5									
6									
7									
8									
9									
10									
11									
12									
13									
14									
15									
16									
17									
18									
19									
20									
21									
22									
23									
24									
25									
26									
27									
28									
29									
30									

Figure 2-8. Data sheet for replicate weights.

DATA SHEET FOR FILTER REWEIGHT

Network Name:
Network Code:
Sampling Site:
Site Code:
Filter Type:
Filter Code:
Filter Lot No.:

Initial Weight

Date:
Time:
Temp (°C)
Rel. Humidity (%):
Technician:

Final Weight

Date:
Time:
Temp (°C)
Rel. Humidity (%):
Technician:

	Filter ID	Tare Weight (mg)	Initial Weight (mg)	Flag	Final Weight (mg)	Flag	Comments
1	T						
2	C						
3							
4							
5							
6							
7							
8							
9							
10							
1	T						
2	C						
3							
4							
5							
6							
7							
8							
9							
10	T						
	C						

Figure 2-9. Data sheet for filter reweight.

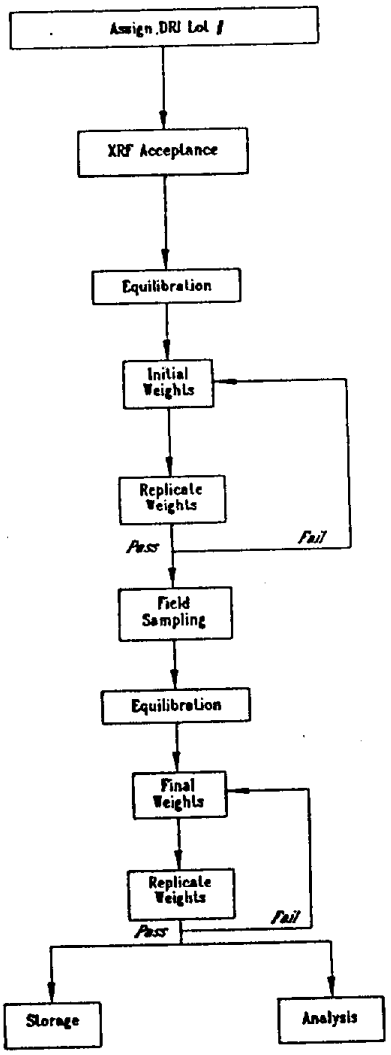


Figure 4-1. Filter weighing flow diagram.

4.2.1 Equilibration of Unexposed Filters

Equilibrate filters for weighing only after they pass acceptance testing by XRF. Equilibrate Gelman filters for a minimum of four weeks and Sierra Andersen filters for a minimum of six weeks before performing initial weights.

- Wearing gloves, clean an equilibration tray with methanol-moistened Kimwipes. Also clean two 15 mm x 150 mm glass petri dishes for each lot. Label each dish with the lot number assigned during acceptance testing using a small gummed label. The first dish is labeled [Lot #]-1 and the second is [Lot #]-2. (The -1 and -2 designations provide a weighing order and have no other function.) Be sure that all particles or fingerprints are removed from all surfaces.

- Open a box of filters that have passed XRF acceptance testing. Using the flat tipped tweezers that have been labeled for filter use, hold the filters one by one over the light table, examining each for holes or filter defects. If there are any foreign particles on the filter, remove them by blowing the surface of the filter with a rubber bulb. Filter defects include separation of the Teflon from the support ring, particles that can not be blown off with the rubber bulb, and drastic variations in density across the surface of the Teflon membrane. Note that some variation in density of the Teflon membrane is normal; reject only those that would result in non-uniform deposits.

- Place rejected filters into a container marked "Rejects".

- Place filters not rejected in an overlapping circular pattern in the petri dish creating a rosette design. Place approximately 50 filters in each petri dish. Set the full dish in the equilibration tray. Ground the equilibration tray by attaching the alligator clip to the tray and putting the jack in the ground hole of a 3 prong wall plug socket.

- Record the lot number and date of equilibration in the proper section of the Filter Equilibration Logbook (Figure 2-5). The date weighed will be recorded when the filters are first used for a project. This will provide a record of the equilibration time and help determine an actual minimum equilibration time.

4.2.2 Equilibration of Exposed Filters

- Confirm that the samples have been properly logged in (DRI SOP 2-209.3).

- Equilibrate exposed filters for a minimum of 24 hours before weighing.

- Wearing gloves, clean the work surface of the laminar flow hood (or and equilibration tray if the laminar flow hood if full) with methanol moistened Kimwipes.

- Place the slides or dishes containing the exposed filters on the counter of the laminar flow hood or in the equilibration tray. Arrange them sequentially in rows of ten. This arrangement allows the technician to more easily estimate the time required for weighing a batch of filters, since the calibration checks are performed after each set of ten. Place the first row about two inches from the back of the laminar flow hood. To prevent any cross

contamination; do not equilibrate or set both exposed and unexposed filters in the same area or tray.

- Open the lids and set them slightly ajar on the bottom half of the dish so that the filters can come to equilibrium with the temperature and humidity controlled air in the room. Take care that the lid is not so far ajar that it can tip and contact the filter. The Petrislides have a tweezers access opening in the front of the holder, so that the lid does not have to be opened very far.

- Post a note indicating the project, date, and time equilibrated on each set of equilibrating filters. If the filters are in a tray, the end of the tray should be labeled with the same information using a permanent marker. Do not weigh filters until 24 hours of equilibration time has elapsed.

- Close the lids of the equilibration trays, if used, and attach the grounding wires.

4.3 Routine Operation

4.3.1 General Remarks

No food is allowed in the clean room. Drinks are allowed in order to prevent dehydration and drowsiness; keep them away from the computer and do not put them inside of the laminar flow hood.

Use black ball-point pen for all recording purposes. Blue pen does not copy well. Red pen is used for validation and correction. Pencil is erasable and felt tip pens can smear so neither of these can be used when a permanent record is necessary.

Make corrections by drawing a single line through the entry and then posting the correction in the Comments column. NO BOO-BOO GOO (white-out).

Do not begin weighing unless there is enough time to complete a set of ten filters and two sets of calibrations.

If the tweezers ever touch the exposed area of the filter, clean them with the anti-static wipes. Stringently avoid cross contamination.

4.3.2 Assigning IDs to Unexposed Filters

Obtain a Filter Weigh Sheet (Figure 2-7) for the project. For ongoing projects, check the weighing binder to determine if additional entries can be made to a previous sheet or if a new sheet is required.

Obtain labels for the petri dishes or Petrislides. The labels for ongoing projects are filed in the weighing room. To generate labels for a new project, use the analysis program found in DRI SOP 2-209.3: "Sample Shipping, Receiving, and Chain-of-Custody".

Obtain the Filter Assignment Logbook (Figure 2-6) located to the left of the weighing platform. Record the size of the filters and corresponding IDs assigned to each DRI lot number. If a new

lot is being weighed, record the date in the proper section of the Filter Equilibration Logbook (Figure 2-5).

Occasionally, it is necessary to reassign filters from one project to another. This occurs if the scope of work for a project changes and too many filters have already been weighed. Ideally, all reassigned filters should be reweighed. If time does not allow this, perform the 3% replicate weighing. For reassignment without reweighing, use the sheet with the original IDs and record new IDs next to the old in RED pen. Place the new barcode label over the top of the old in case there is any question about reassignment.

4.3.3 Weighing Unexposed Filters

Verify that filters to be weighed have been equilibrated for at least four weeks (Gelman) or six weeks (Sierra Anderson) before proceeding.

Wear gloves while performing all weighing procedures.

Clean the top of the balance, the marble support, and the work surface of the laminar flow hood near the balance with methanol moistened Kimwipes. Clean the deionizer box by blowing it out with the rubber bulb. Clean the CAL and FILTER tweezers with anti-static wipes.

Place a small Kimwipe on the marble block just outside of the chamber door of the balance. Carefully remove the sample and tare stirrups by positioning both tines of the open tweezers underneath the upper portion of the stirrup frame and lifting the stirrup off the suspension wire. DO NOT GRAB THE WIRES of the stirrup, since deformation could occur. Place the stirrups on the Kimwipe and clean them and the inside of the chamber with an anti-static wipe. Do not use compressed air in the chamber because particles could be forced into the torque mechanism. Using the rubber bulb, blow gently on the tare weight to remove dust. Carefully replace the stirrups using the same technique, being careful not to put stress on the suspension wires. Replace the tare weight on the tare stirrup pan.

Remove a petri dish containing equilibrated filters from the equilibration tray and place it on the weighing platform. Assemble the Petrislides or petri dishes and the barcode labels that are needed. Petrislides are used for 47 mm filters and petri dishes are used for 37 mm filters.

Use the following step-by-step instructions for the CAHN program to weigh filters:

- At the C:> prompt, type CAHN. The weighing program menu will appear on the screen.
- Use option 6, "Directory Functions", followed by option 2, "Change Directory", to access the list of directories available. Use the arrow keys to highlight the proper directory. Touch the <Enter> key to select the project to be weighed. Return to the main menu using the <Esc> key.
- Choose weighing option #3, initial weight. Enter all requested information. The program automatically sets the balance to the 250 mg range. After the header has printed, a prompt will appear indicating that it is time for the tare check.
- Make sure that the weighing pan is empty. Push the <Enter> key. The weighing program

will activate the brake release and the one minute countdown will begin. The time is displayed in the lower right hand corner of the monitor screen. While the balance is zeroing, remove a filter from the glass petri dish and put it in the deionizer box. Put a petrislide or dish with the barcode label on it in front of the box.

- At the end of the weighing, a quiet beep will indicate a tare weight that is within limits. Enter the tare weight on the weighing sheet. A loud beep will indicate if the tare is outside of the limits. If it is, tare the balance by pushing "T". Record 0.000 on the weighing sheet. During tare and calibration, the program will automatically reset itself to begin the determinations.

- Place the working calibration standard on the sample pan. Close the door and press the<Enter> key. The weighing program will begin. While the weighing is proceeding, fill out the top section of the weighing sheet (Fig 2-5) with the required project and filter media information. Record date, time, humidity, temperature, and technician information in the Initial Weight section. After one minute, the calibration weight should be within ± 0.002 mg of the posted value. If it is not, the loud beep will sound. Calibrate the balance by pushing "C". The balance will then be calibrated by the program. Record the calibration weight on the weighing sheet. Return the calibration standard to its container

- Move the filter from the deionizing box and place it on the sample pan, centering it carefully. Close the weighing chamber door. Activate the weighing program by scanning the barcode label attached to the slide or dish. Verify that the ID displayed on the computer screen is the correct ID. If it is not, abort the run by pushing the <Esc> key. Re-enter the correct ID. Place the dish or slide corresponding to this filter in front of the weighing chamber.

- Place the next filter into the deionizer box. Put its corresponding dish in front of the chamber. By having only two dishes and two filters on the weighing platform, there will be little chance of switching filters.

- At the end of 30 seconds, record the first three digits of the display on the Filter Weigh Sheet. At the end of one minute, record the final mass of the filter. The manual entry of th mass is meant to be a check on the computer determination. DO NOT simply copy the digit from the screen display. Hit the <Esc> key to reset the fields for the next mass determination.

- Remove the filter and put it in the prepared dish or slide and place the slide in the laminar flow hood. Leave the lid ajar, proceed to the next filter, and arrange the weighed filters in rows of ten for replicate weighing.

- Tare and calibration checks are performed after each set of ten samples. Post the values in the "T" or "C" row on the weighing sheet. If the tare and calibration values are within ±0.002 mg, proceed to weigh the next set of filters. If either reading differs from its specified value by more than 0.002 but less than 0.005 mg, place a check mark next to the recorded value, re-Tare or re-Calibrate, and proceed to the next set of ten filters. If the ta and/or calibration weights differ by more than ± 0.005 mg from their true values, the previous set of ten must be reweighed after retaring and recalibration. See Section 6.2 for reweighing procedure.

4.3.4 Weighing Exposed Filters

Follow the cleaning, project directory access, recording and calibrating procedures described in Section 4.3.3., then proceed with the following instructions:

- While the machine is weighing the calibration standard, open the petri dish containing the first exposed filter to be weighed. Take care that any static electricity that may have built up in the dish does not cause the filter to jump out. Examine the filter. If there is anything strange about the deposit or the appearance of the filter, note it on the weighing sheet with the correct flag(s) and/or comments columns (see Section 6.3). Any loose foreign particles should be removed by using the rubber bulb or tweezers. Do not blow on resuspension samples, however, because the deposits are not well fixed on the filter. After the visual examination, place the filter in the deionization box.

- When the tare and calibration are completed, the exposed filters can be weighed. Remove the filter from the deionization box and place it on the sample pan, being careful to center it. Close the weighing chamber door. Activate the weighing program by scanning the barcode label attached to the slide or dish. Verify that the ID displayed on the computer screen is the correct ID. If it is not, abort the run by pushing the <Esc> key. Re-enter the correct ID. Place the dish or slide corresponding to this filter in front of the weighing chamber.

- Place the next filter into the deionizer box. Put its corresponding dish in front of the chamber. By having only two dishes and two filters on the weighing platform, there will be little chance of switching filters.

- At the end of 30 seconds record the first three digits of the display on the Filter Weigh Sheet. At the end of one minute record the final mass of the filter. The manual entry of the mass is meant to be a check on the computer determination. DO NOT simply copy the digits from the screen display.

- After the normal beep indicating the end of the weighing time (one minute), the cursor will be in the field for analysis flags. Refer to Section 6.4 for a list of the most commonly used flags and, if required, enter the appropriate flag. The last field is for any comments that are not covered by the flag (e.g., the location of a hole or scrape, whether or not a particle was removed before weighing, etc.). After this information is entered, the program will then put the cursor in the field for barcode entry. If there are no flags or comments, the <Esc> key will cause the program to skip those two fields and the barcode entry field will be highlighted.

- Tare and calibration checks are performed after each set of ten samples. Post the values in the "T" or "C" row on the weighing sheet. If the tare and calibration values are within ±0.002 mg, proceed to weigh the next set of filters. If either reading differs from its specified value by more than 0.002 but less than 0.005 mg, place a check mark next to the recorded value, re-Tare or re-Calibrate, and proceed to the next set of ten filters. If the tare and/or calibration weights differ by more than ± 0.005 mg from their true values, the previous set of ten must be reweighed after retaring and recalibration. See Section 6.2 for reweighing procedure.

- After weighing, the filters are returned to the equilibration area with the lids ajar, awaiting replicate testing (see Section 6). Push the <Esc> key twice to end the weighing session.

4.3.4 Replicate Weighing and Reweight Weighing

Replicate initial and final weights are collected by a second technician according to the following procedure:

- Wearing gloves, tare and calibrate the machine as described in Section 4.3.3.
- From each set of ten weighed filters, select three at random.
- Turn to the Replicate Weigh Sheet (Figure 2-8) which is on the back of the Weigh Sheet and record the first selected filter ID in the first column. Note whether the weights measured are initial or final replicates in the fourth column.
- Weigh the filters as described in Section 4.3. Record the weights in the column marked Check Weight. Record the original and net weights in the appropriate columns. Fill in the technician and date columns.
- If the three replicate weights are within the specifications stated above, the set of ten has passed; mark "OK" in the final column.
- If the replicate weights are outside of the appropriate criteria, the corresponding set of ten filters must be reweighed. Cross out the initial weights with two diagonal lines, forming an X through the data, but not obliterating it. Obtain a Reweigh Sheet (Figure 2-9) and staple it to the back of the Weigh and Replicate Weigh Sheet. Reweigh the set of ten, making sure that the new values are recorded in the same area of the reweigh sheet as on the original weight sheet.. Place them in the hood, with the lids ajar, for replicate weights. Be sure that the headings of the form are completed because these reweights become the active weights and will automatically replace the original weights when the INPCAHN (merge) program is used.
- Notify the supervisor that there were samples to be reweighed and that another replicate weighing is required.
- When unexposed filters are being weighed, if there is a consistent negative replication (>0.010 mg), is usually a sign that the filters have not equilibrated long enough. In this case, notify the supervisor.
- If the set has passed, replace the container lids, being careful not to bend or tear the filters. Put these filters in a tray marked with the project and the ID range and place them in the designated storage area. NOTE: all resuspension filters must be stored flat to minimize the chance of particles falling off of the filters after mass determination. If additional analyses will be performed, notify the Laboratory Supervisor that the filters are ready for analysis.
- Record all activities in the DRI Weighing Logbook.

4.4 Shut-Down

At the C: prompt, type INPCAHN. This command activates the merge program, which is used to take the sequential (YYMMDD.seq) file from the weighing program and merge it into a dBase file. Follow the on-screen directions to merge the data. Enter 00 for the batch number and X for the sampler type. All merged database files will have the filename ppMSG00X.dbf, where pp is the assigned project code.

After merging, if there is more than one project to be weighed, proceed with the next one.

After all weighing is complete, insure that the weighing chamber door is closed and the brake is engaged. Be sure that all maintenance activities and weighing activities are recorded in the proper books.

The printer that generates the data is located in an adjacent room because of the paper dust that is generated by the dot matrix printer. When the printouts are removed, they are clamped together as a batch and the inclusive dates are posted on the top sheet. All computer printouts of the mass are kept in a box next to the printer, labeled "CAHN PRINTOUTS - do not discard". These are kept as a permanent hard copy record of the computer analysis, in case there is any question about the results during validation.

4.5 Abbreviated Checklist

- Equilibration of unexposed filters
  - Verify acceptance testing results.
  - Clean equilibration trays and glass petri dishes.
  - Label petri dishes.
  - Light check and arrange filters in petri dishes.
  - Place in equilibration trays.
  - Attach alligator clips.
  - Label tray with filter size and date of equilibration.
  - Record information in the Filter Equilibration Logbook.
- Routine Weighing
  - Clean Area.
  - Use the CAHN program to access the correct directory.
  - Obtain weighing sheet.
  - Choose CAHN option for initial, final, or replicate weighing.
  - Replicate weighing performed by another technician.
  - Use INPCAHN to merge the data.
  - Record information in the proper logbooks.

5.0 QUANTIFICATION

5.1 Calibration Procedures

Routine calibration checks are performed before and after each set of ten filters as described in Section 4.3.

The working calibration standard is checked against a second Class 1.1 primary calibration standard every six months by the Laboratory Supervisor. This check consists of ten replicate weighings of the working standard after the balance is calibrated against the primary standard using a calibration value of 200.000 mg. The average and standard deviation of these multiple weighings are calculated, and the posted calibration value is updated if necessary. It is best to perform the calibration check procedure after a project has ended and before a new one begins, since the validation procedures (see Section 5.2) would be affected by the difference in the calibration weight.

5.2 Calculations

The weights are input into a dBase file using an input program called INPCAHN which is run as part of the weighing procedure (see Section 4.3). This program automatically calculates the net weights. The mass file that is generated, ppMSG00X.dbf, serves as a reservoir from which project batch mass files are removed. The raw data files, YYMMDD.seq are never deleted from the CAHN project directories.

The project database file is created by indexing the ppMSG00X.dbf file on SAMPLEID and copying the appropriate range to the ppMSGnns.dbf, where "pp" is the assigned project code, "nn" is the assigned batch number, and "s" is the sampler type. After verifying that the created database does indeed have the correct range of IDs in it, the copied range of data is deleted from the ppMSG00X.dbf. After the project batch file is created, validate the data according to section 6.5.

After the mass data is validated, from FoxPro type "do MSSREP". This program will ask for the project code and the batch number. Uncertainties are then calculated from the replicate data. The program will display the uncertainties and maximum and minimum deviations. It will ask if the calculated uncertainties should be added to the mass file, ppMSGnns. If there is a large minimum or maximum deviation (> ± 0.015 mg) there is probably some mass replicate data that has been included which should be made void. The INPCAHN program will overwrite any data in which the same SAMPLEID appears. However, unless the technician has chosen the same filters for replicate weighing, the replicate data will include both the ou of range data and the reweighed data. The invalid mass concentrations are deleted from the project file at this point. All sequential files are kept on the CAHN, and the printouts as well as the handwritten weighing sheets are kept, so if there are questions at a later date, the raw data can be accessed.

The end result of these calculations is a batch file in the EAFMAIN project directory, a project batch file in the CAHN subdirectory that is identical to the file in the project subdirectory, and a ppMSG00X.dbf fil in the CAHN that no longer contains the batch file data.

6.0 QUALITY CONTROL

6.1 Performance Testing

Laboratory blanks are weighed and retained at the rate of 2% of the total number of filters assigned to a given project. Filter IDs xxxx050 and xxxx100 are kept for non-dichot sampling and xxxx049, xxxx050 xxxx099 and xxxx100 for dichotomous sampling. The reason for keeping more dichotomous filters is so that the even/odd numbering/sampling sequence integrity is maintained. All lab blanks assigned to a project are logged in and out of the weighing room using the Filter Equilibration Logbook.

Field blanks are normally supplied and collected at the rate of 10% of the total number of samples for every project. Field blanks are weighed to provide background levels present in the field during samplin

Laboratory blanks are removed from storage and weighed when the range of samples returned include the archived filter IDs. The use of lab blanks provides a measure of filter mass stability and weighing room cleanliness. While weighing laboratory blanks, the technician should calculate the difference between the initial and final weights. If the resulting lab blank weights are > ± 0.015mg, the supervisor should be notified.

6.2 Reproducibility Testing

Replicate weighings are performed on 30% of the filters weighed.

Replicate pre-sampling (initial) weights must be within ± 0.010 mg of the original weights. Replicate post-sampling weights (final) on ambient samples must be within ± 0.015 mg; post-sampling weights on heavily loaded samples and for resuspensions must be within 2% of the net weight.

6.3 Control Charts

Control charts are not currently prepared. All calibration (zero and span) and replicate data points are checked. If any measurement is not within specified limits, samples are reweighed as described in section 4.3.

6.4 Flags for Non-Standard Procedures

The technician should record any unusual deposit appearances or filter damage in the comments sections of the weigh sheets and the CAHN program. Flags are applied during weighing into the YYMMDD.seq file, and follow the current DRI analysis flags definitions.

The most commonly used flags are:

b1	field blank
b2	laboratory blank
f2	filter damaged, inside analysis area*
f3	Teflon membrane substrate separated from the support ring
f4	filter loaded in PetriSlide deposit side down
f5	filter dropped during handling
f6	filter stuck to PetriSlide
i1	inhomogeneous filter deposit
i2	deposit smeared or scraped after sampling*
i3	deposit appears to have fallen off
i4	foreign particles on the filter*
i6	particles larger than the inlet device allows
i8	deposit on back of filter
w1	pre-weight is questionable
w2	post-weight is questionable

When the flags with an asterisk (*) are applied, an explanation of the damage or particle type should be made in the comments section as well as whether or not the particles were successfully removed.

A complete list of validation flags can be found in EAFMAIN D:\PROTOCOL under the filename CHEMFLAG.

6.5 Validation

After the project file is created (Section 5.2), it must be validated. Check all mass concentrations and verify any large outliers by using the computer printouts and written data. If the data is verified and there is still a large outlier, check for possible switches of filters or use of replacement filters. Discuss any changes with the Laboratory Supervisor before taking action. It may be necessary to reweigh the filter. If the filter is reweighed, use the proper validation flag to indicate whether the weight has changed. (See section 6.4). If all attempts at reconciling the data fail, the mass data is flagged suspect and all supporting evidence is listed and given to the Project Manager. Supporting evidence includes, but is not limited to, reweights, damage to the filter, foreign particles on the filter, or evidence of air leaks. Final disposition of the data will be made in Level II Validation.

After the mass data is validated, copy the file to the EAFMAIN F:\project\batchnn\data subdirectory.

7.0 REFERENCES

"Instruction Manual for CAHN 30 and 31", Cahn Instruments, Inc., Cerritos, CA, Manual #10918-01, 3/86.

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This standard operating procedure describes the procedure for the inspection, impregnation, freeze or vacuum drying, storage, and acceptance testing of filters impregnated with citric acid, potassium carbonate (K_2CO_3), and triethanolamine (TEA) for collecting ammonia (NH_3), sulfur dioxide (SO_2), and nitrogen dioxide (NO_2), respectively. This procedure will be followed by all analysts at the Environmental Analysis Facility of the Energy and Environmental Engineering Center of the Desert Research Institute (DRI).

1.2 Measure Principle

Selected filter substrate is impregnated with gas-absorbing solution to collect gaseous species in the atmosphere. The impregnation solutions differ with respect to their reactive components and with respect to their formulations. The criteria must be met by the impregnation solutions are:

- Availability of pure reagent;
- Stability of the impregnation solution composition before and after impregnation;
- Low degree of hazard or toxicity;
- Lack of interferences with other pollutants being sampled or with analytical methods; and
- Minimal effects of environmental factors such as temperature and water vapor content.

After extensive laboratory testing, potassium carbonate with glycerine has been used to impregnate filters for sulfur dioxide (SO_2) sampling. Citric acid with glycerine has been used to impregnate filters for ammonia (NH_3) sampling, and triethanolamine has been used to impregnate filters for nitrogen dioxide (NO_2) sampling.

The impregnation solutions consist of:

- 15% K_2CO_3 and 5% glycerol solution (balance being DDW) for SO_2 sampling.
- 25% citric acid and 5% glycerol (balance being DDW) for NH_3 sampling.

- 25% triethanolamine, 4% ethylene glycol, (balance being DDW) for NO_2 sampling.

1.3 Measurement Interference and Their Minimization

All filters are used for collecting minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters during the inspection and impregnation procedures. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges. Touching the tweezers to the central portion can damage a filter.
- Human breath contains ammonia. Therefore, avoid breathing on any filters; particularly the citric acid-impregnated filters, since they will collect ammonia from human breath.
- Impregnating procedures should be carried out under the laminar flow-hood or in clean room with HEPA filter filtration.

1.4 Ranges and Typical Values of Measurements

All gaseous concentrations will usually be in the range of 0.01 to 500 $\mu g/m^3$.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The acceptance test criteria are:

- <1.0 μg/filter of SO_4^- for 47mm K_2CO_3 impregnated filter
- <0.35 μg/filter of SO_4^- for 25mm K_2CO_3 impregnated filter
- >19.0 mg/filter of K^+ for 47mm K_2CO_3 impregnated filter
- >5.2 mg/filter of K^+ for 25mm K_2CO_3 impregnated filter
- <1.0 μg/filter of NH_4^+ for 47mm citric acid impregnated filter
- <1.0 μg/filter of NO_3^- for 47mm TEA impregnated filter

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing filter impregnation, which includes solution preparation, filter impregnation, assigning of blanks, and acceptance testing of filters.

It is the responsibility of the laboratory manager or supervisor to insure the impregnation procedures are properly followed, to verify that filter blanks have been assigned, to maintain the supplies necessary to insure uninterrupted impregnation, and to oversee proper chain-of-custody documentation.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center is responsible to determine the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

(Not Applicable)

1.8 Related Procedures

- DRI SOP 15 — Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography
- DRI SOP 17 — Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetry

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus

2.1.1 Filter Supplies

- Pallflex 2500 QAT-UP quartz-fiber filters, 47mm or 25mm for K_2CO_3 impregnation. (Putnam, CT)
- Whatman 41, cellulose-fiber filters, 47mm for citric acid or K_2CO_3 impregnation. (CHEMTREX, Hillsboro, OR)
- Whatman 31ET chromatography paper, 47mm for TEA impregnation. (CHEMTREX, Hillsboro, OR)

2.1.2 Filter Batch Labels

The impregnated filters and the impregnation solutions are prepared in batches. The containers for these batches are labeled with DRI labels that identify the batches. All of the labels needed during the impregnation procedures are produced on one or more sheets of pregummed labels.

2.1.3 Sartorius R160D Analytical Balance

2.1.4 Spatula

2.1.5 Plastic weighing boats

2.1.6 Parafilm

2.1.7 PVC gloves, non-powdered

2.1.8 500 ml volumetric flask for each solution to be prepared

2.1.9 500 ml glass or plastic bottles with screw tops for storage of impregnating solutions. (CAUTION: TEA SOLUTION SHOULD BE STORED IN AN AMBER BOTTLE.)

2.1.10 Teflon impregnation container with lid. (Savillex, Minnetonka, MN)

2.1.11 Flat-tipped tweezers. (Millipore, San Francisco, CA.)

2.1.12 Sonicator (Branson Model 5200)

2.1.13 GLAS-COL Shaker (Fisher #14-258) with Test Tube Rack holder (#14-259-3)

2.1.14 Drying apparatus

- Labconco Corp. Model 77500 bench-top freeze dryer, Lyph-Lock Freeze Dry System (45L)
- 250 ml freeze-drying flasks (Kontes #562800-0250)
- Ultra high vacuum pump, minimum 200 ℓ/min
- Glass elbow joint adaptor
- Vacuum oven (VWR Mode 1410)

2.1.15 Water aspirator

2.1.16 5 cm Hirsch funnel and vacuum flask (500 ml)

2.1.17 Light Table

2.2 Reagents

All chemicals should be reagent grade.

- Citric acid monohydrate crystals (Fisher Certified ACS A104-500)
- Potassium carbonate, 1-1/2 hydrate crystals (Fisher Certified ACS P179-500)
- Triethanolamine (Fisher Certified T407-500)
- Glycerol (Anhydrous, Baker Analyzed Reagent 2136-01)
- Ethylene glycol (Fisher Certified E178-500)
- Methanol (Fisher absolute acetone free Certified ACS A412-20)

2.3 Forms

Filter Impregnation Log Sheet (Table 2-1).

Table 2-1

Log Sheet for Filter Impregnation

LOG SHEET FOR FILTER WASHING, IMPREGNATION, AND ACCEPTANCE TESTING

Filter Type_____ Manufacturer_____

Filter Size_____ Manufacturer Lot ID_____

DRI Lot ID	Date of Washing	Wash Solution	Tech	Date of Impregnation	Impregnation Solution	Tech	Acceptance Testing Species	Date of Analysis	Tech	Concentration µg/filter	Pass/Fai
							Cl^-				
							NO_2^-				
							NO_3^-				
							$SO_4^=$				
							NH_4^+				
							K^+				
							Na^+				
							Ca^{++}				
							Mg^{++}				
							Cl^-				
							NO_2^-				
							NO_3^-				
							$SO_4^=$				
							NH_4^+				
							K^+				
							Na^+				
							Ca^{++}				
							Mg^{++}				
							Cl^-				
							NO_2^-				
							NO_3^-				
							$SO_4^=$				
							NH_4^+				
							K^+				
							Na^+				
							Ca^{++}				
							Mg^{++}				

3.0 CALIBRATION STANDARDS

(Not Applicable)

4.0 PROCEDURES

4.1 General Flow Diagram

A general flow diagram for this procedure is shown in Figure 4-1.

4.2 Preparation of Impregnating Solutions

4.2.1 Potassium Carbonate Impregnation Solution (15% K_2CO_3, 5% Glycerol, and 80% DDW)

- Using an analytical balance, weigh 100 g of potassium carbonate, 1-1/2 of hydrate, into a weighing boat. Transfer quantitatively into a 500 ml volumetric flask.
- Add about 200 ml distilled-deionized water (DDW) to dissolve crystals. Sonicate until completely dissolved.
- Weight 25 g of glycerol and add to the solution. Add DDW to the 500 ml mark and mix well.
- Obtain a 500 ml plastic bottle with a tight fitting screw lid. Rinse bottle at least three times with DDW prior to solution transfer.
- Label bottle clearly with the contents, date of preparation, and the initials of the preparer. Transfer the K_2CO_3 solution to the bottle.

4.2.2 Citric Acid Impregnation Solution (25% citric acid, 5% Glycerol, and 70% DDW)

- Using an analytical balance, weigh 125 g of citric acid monohydrate into a weighing boat. Transfer quantitatively into a 500 ml volumetric flask.
- Add about 200 ml DDW to dissolve crystals and sonicate until completely dissolved.

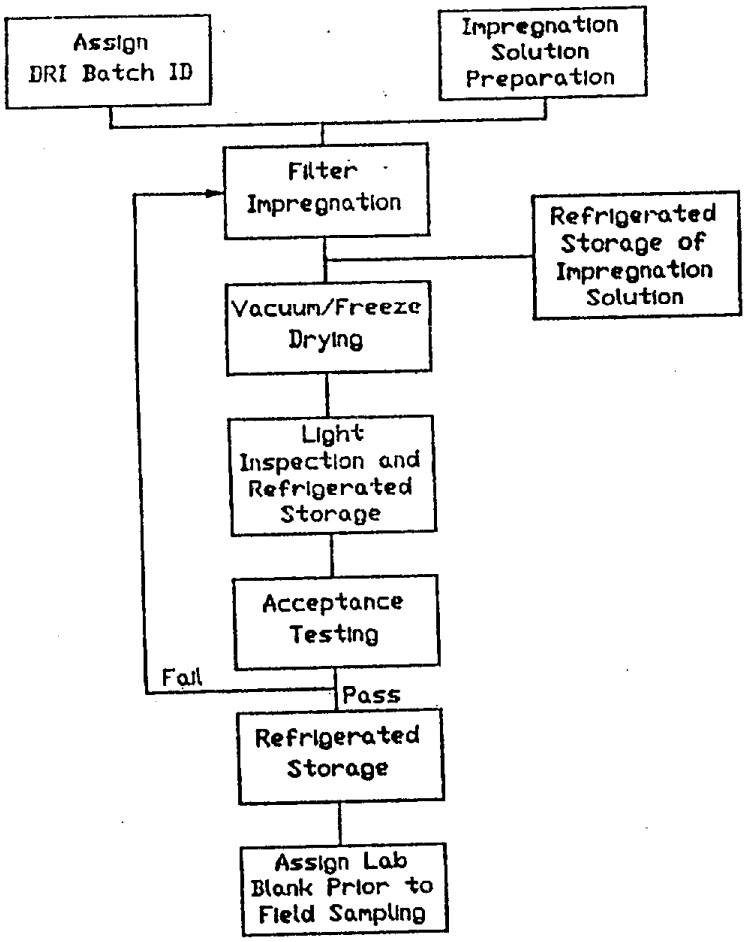


Figure 4-1. Flow Diagram of Filter Impregnation Procedure.

- Weigh 25 g of glycerol and add to the citric acid solution. Add DDW to bring to the 500 ml mark and mix well.

- Obtain a 500 ml plastic bottle with a tight-fitting screw lid. Rinse bottle at least three times with DDW prior to solution transfer.

- Label bottle clearly with the contents, date of preparation, and the initials of the preparer. Apply an appropriate barcode label. Transfer the citric acid solution to the bottle.

4.2.3 TEA Impregnation Solution (25% Triethanolamine, 4% Ethylene glycol, and 46 % DDW)

- Using an analytical balance, weigh 125 g of triethanolamine into a weighing boat.

- Transfer quantitatively into a 500 ml volumetric flask.

- Add 125 ml of methanol to the flask.

- Weigh 20 g of ethylene-glycol and add to flask. Bring up to the 500 ml volume mark with DDW and sonicate until solution is clear.

- Obtain a 500 ml amber plastic bottle with a tight-fitting screw lid. Rinse bottle at least three times with DDW prior to solution transfer. (CAUTION: TEA SOLUTION MUST BE STORED IN AN AMBER PLASTIC BOTTLE.)

- Label bottle clearly with the contents, date of preparation, and the initials of the preparer. Transfer the TEA solution to the bottle.

4.3 Inspection and Impregnation of Potassium Carbonate Filters

4.3.1 Open one box of 47 mm Whatman 41 filters or four boxes of 47 mm Pallflex 2500 QAT-UP or one box of 25mm Pallflex quartz-fiber filters. (Whatman 47 mm and Pallflex 25 mm filters are 100 filters/box, Pallflex 47 mm filters are 25 filters/box.)

4.3.2 Assign DRI batch ID and place filters in the Teflon impregnation jar. Approximately 100 filters can be impregnated in this container.

4.3.3 Add approximately 100 ml of the impregnation solution, making sure there is enough solution to totally submerge the filters. Place the lid on the container and tightly seal.

4.3.4 Clamp the container to the test tube shaker and immobilize the impregnation container in the shaker using a piece of foam rubber and clamp bar. Agitate slowly by adjusting the speed to 60 cycles per minute (knob setting at 3) and leave it on for 30 minutes.

4.3.5 Remove the impregnation container from the shaker and decant the impregnation solution. Transfer the stack of filters to a 5 cm Hirsch funnel and place a sheet of parafilm on the top of the funnel.

4.3.6 Place the funnel into a 500 ml vacuum flask and apply a vacuum with a water aspirator. Allow the vacuum to draw off all of the excess wash solution from the stack of filters. The parafilm will be drawn into the funnel and will press over the filter stack to press out excess liquid. When the solution is dripping at a rate of 2 drops/sec., transfer the stack of filters back to the impregnation container and continue with Drying Procedure in Section 4.6 or 4.7.

4.3.7 Set up the vacuum oven or freeze dryer as described in Section 4.6 or 4.7. The drying precedure takes 5 to 10 minutes. As the filters color change to semi-transparent, remove impregnated filters from the vacuum oven. (CAUTION: DO NOT OVER DRY THE FILTERS.)

4.3.8 With gloved hands and using tweezers, remove each filter individually and inspect each filter using a bright light table. Make sure there are no holes, wrinkles, torn edges, or foreign materials. Make sure that each filter is uniform in thickness and appearance and that each one is a perfect circle.

4.3.9 Place dried impregnated filters, 100 per batch, into plastic boxes with assigned DRI batch ID and impregnation date. Place any "reject" filters in a clearly marked box to be saved and returned to the supplier for reimbursement.

4.3.10 Place filter batches in ziplock bags and store in the refrigerator.

4.4 Inspection and Impregnation of Citric Acid Filters

4.4.1 Open a box of 100 47 mm Whatman 41 filters.

4.4.2 Place the filters in the Teflon impregnating container.

4.4.3 Add approximately 100 ml of the impregnation solution, making sure that there is enough solution to totally submerge the filters. Place the lid on the container and tightly seal.

4.4.4 Clamp the container to the test tube shaker and immobilize the impregnation container in the shaker using a piece of foam rubber and clamp bar. Agitate slowly by adjusting the speed to 60 cycles per minute (knob setting at 3) and leave on for 30 minutes.

4.4.5 Remove the impregnation container from the shaker and decant the impregnation solution. Transfer the stack of filters to a 5 cm Hirsch funnel and place a sheet of parafilm on the top of the funnel.

4.4.6 Place the funnel into a 500 ml vacuum flask and apply a vacuum with a water aspirator. Allow the vacuum to draw off all of the excess wash solution from the stack of filters. The parafilm will be drawn into the funnel and will press over the filter stack to press out excess liquid. When this solution is dripping at a rate of 2 drops/sec., transfer the stack of filters back to the impregnation container and continue with Drying Procedure on Section 4.6 or 4.7.

4.4.7 Set up the vacuum oven or freeze dryer as described in Section 4.6 or 4.7. The drying procedure takes 5 to 10 minutes. As the filters color change to semi-transparent, remove impregnated filters from the vacuum oven. (CAUTION: DO NOT OVER DRY THE FILTERS.)

4.4.8 With gloved hands and using tweezers, remove each filter individually and inspect each filter using a bright light table. Make sure there are no holes, wrinkles, torn edges, or foreign materials. Make sure that each filter is uniform in thickness and appearance and that each one is a perfect circle.

4.4.9 Place dried impregnated filters, 100 per batch, into plastic boxes with assigned DRI batch ID and impregnation date.

4.4.10 Place filter batches in ziplock bags and store in the refrigerator.

4.5 Inspection and Impregnation of TEA filters

4.5.1 Open a box of 47 mm 100 Whatman 31ET Chromatography filters.

4.5.2 Prior to actual impregnation, the TEA filters are washed in a solution of 50% methanol and 50% DDW. Prepare this solution and add approximately 100 ml to the Teflon impregnation container with approximately 50 filters (make sure it is enough to submerge the filters). Place the lid on the container and seal tightly.

4.5.3 Clamp the container to the test tube shaker and immobilize the impregnation container in the shaker using a piece of foam rubber and clamp bar. Agitate slowly by adjusting the speed to 60 cycles per minute (knob setting at 3) and leave on for 30 minutes.

4.5.4 Remove the impregnation container from the shaker and decant the impregnation solution. Transfer the stack of filters to a 5 cm Hirsch funnel and place a sheet of parafilm on the top of the funnel.

4.5.5 Place the funnel into a 500 ml vacuum flask and apply a vacuum with a water aspirator. Allow the vacuum to draw off all of the excess wash solution from the stack of filters. The parafilm will be drawn into the funnel and will press over the filter stack to press out excess liquid. When this solvent solution is completely sqeezed out, transfer the stack of filters back to the impregnation container.

4.5.6 Add approximately 100 ml of TEA impregnation solution, making sure there is enough solution to totally submerge the filters. Place the lid on the container and tightly seal.

4.5.7 Clamp the container to the shaker as in step 4.5.3 and follow the same procedure to agitate the container.

4.5.8 Follow the same procedure in 4.5.4 and 4.5.5 WITH ONE IMPORTANT EXCEPTION. Instead of aspirating all of the impregnation solution from the stack of filters, some residual solution should remain on the filters. Only apply the vacuum on the filters until the liquid stream exiting the funnel reaches approximately 4 drops per second. DO NOT OVER-SQUEEZE THESE IMPREGNATED FILTERS.

4.5.9 Set up the vacuum oven or freeze dryer as described in Section 4.6 or 4.7. Dry for 5 minutes and remove impregnated filters from the vacuum oven. (CAUTION: DO NOT OVER DRY THE FILTERS.)

4.5.10 With gloved hands and using tweezers, remove each filter individually and inspect each filter using a bright light table. Make sure there are no holes, wrinkles, torn edges, or foreign materials. Make sure that each filter is uniform in thickness and appearance and that each one is a perfect circle.

4.5.11 Place dried impregnated filters in stacks of 100 per batch into plastic boxes with assigned DRI batch ID and impregnation date.

4.5.12 Place filter batches in the ziplock bags and store in the refrigerator.

4.6 Vacuum Oven Drying Procedure

4.6.1 Preheat oven to proper temperature: 30-35°C for citric acid and TEA filters; 60-70°C for K_2CO_3. Turn on vacuum pump. Make sure inlet valve is closed and that there is ice in the trap when drying TEA and Citric Acid filters.

4.6.2 Load filters on top of inverted Petri Dishes. Approximately 5 47mm filters and 10 25mm filters can be arranged per Petri Dish. Place Petri dishes into the vacuum oven. Close and latch the door.

4.6.3 Open Vacuum inlet until pressure reaches 20-25 mm Hz. Dry the impregnated filters until they are translucent. This process takes 5 to 10 minutes for K_2CO_3 and Citric Acid filters and 5 minutes for TEA filters. The TEA do not change in appearance. Remove them after 5 minutes.

4.6.4 Close Vacuum inlet and open the air inlet. When the vacuum pressure has decreased to zero (this process takes approximately 2 minutes), remove the petri dishes and filters. Follow the light inspection procedure stated in Section 4.3.8, 4.4.8, and 4.5.10. Place filters in proper air-tight containers for refrigerated storage.

4.7 Freeze-Drying Procedure

4.7.1 Transfer stacks of no more than 50 Whatman 41 filters or 25 31ET Chromatography filters to each of the four freeze-drying flasks.

4.7.2 Turn on power to freeze dryer.

4.7.3 Turn on refrigeration when the temperature is -40 °C or lower. Turn on the vacuum pump.

4.7.4 Make certain that all valves are in the "VENT" position to achieve a vacuum.

4.7.5 Connect a flask when the vacuum is 25 microns or less. After connection, turn the valve to the "VAC" position. Allow the system pressure to return to a vacuum of approximately 100 microns or less before adding additional flasks to the unit.

4.7.6 When all the frost has disappeared from the outer surface of the flasks and no cold spots can be detected by handling the container, the filters are nearly dry.

4.7.7 To remove a flask after drying is complete, turn the plastic knob on the vacuum valve to the "VENT" position.

4.7.8 Place dried filters in stacks into plastic petri dishes appropriately labeled with DRI filter batch ID and impregnation date.

4.8 Data Recording

Complete the first five sections of a Filter Impregnation Log Sheet (Table 2-1) for each batch of filters. The final sections will be completed after the batches are acceptance tested.

5.0 QUANTIFICATION

(Not applicable)

6.0 QUALITY CONTROL

6.1 Appearance Check

Check for uniform appearance, even color (white), off color, excessive wetness or dryness, stiff or brittle appearance. Place rejects into a petri dish labeled "rejects" and mark with the batch number.

6.2 Acceptance Testing

One percent of the filters in each batch of impregnated and dried filters are analyzed for background levels. If filters are stored in separate containers of less than 100 filters, analyze at least one filter from each container.

All of the filters analyzed must contain less than the following levels of ions for acceptance of the batch:

- 47mm K_2CO_3 impregnated < 1 μg SO_4^{2-}/filter
- 45mm K_2CO_3 impregnated < 0.35 μg SO_4^{2-}/filter
- 47mm K_2CO_3 impregnated > 19.0 mg K^+/filter
- 25mm K_2CO_3 impregnated > 5.2 mg K^+/filter
- 47mm Citric Acid impregnated < 1 μg NH_4^+/filter
- 47mm TEA impregnated < 1 μg NO_3^-/filter

Results of the blank analyses are summarized in the last 2 sections of the Filter Impregnation Log Sheet (Table 2-1).

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

Nylon filters absorb nitric acid over time. This procedure describes the inspection, washing, and drying procedures for nylon filters to be used in ambient sampling of nitric acid or total particulate nitrate.

1.2 Measurement Principle

(Not Applicable)

1.3 Measurement Interferences and Their Minimization

Nylon filter washing procedures can also ensure the removal of that other contaminants (i.e., Cl^-, $SO_4^=$) which might be present in the filter during filter manufacturing are removed.

1.4 Ranges of Typical Values of Measurements

(Not Applicable)

1.5 Typical Lower Quantifiable Limits. Precision and Accuracy

The acceptance criteria for washed nylon filters is <1.0 μg/filter for Cl, NO_2^-, NO_3^-, and $SO_4^=$

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing nylon washing, which includes washing, rinsing, and drying of filters as well as assignment of acceptance test filters and laboratory blanks.

It is the responsibility of the laboratory manager or supervisor to ensure the nylon filter washing procedures are properly followed, to maintain the supplies necessary to insure uninterrupted analysis, and to verify that the acceptance test filters and laboratory blanks have been documented and are stored in the proper place.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center is responsible to determine the extent and methods of

quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

(Not applicable)

1.8 Related Procedures

DRI SOP 14 Extraction of Ionic Species from Filter Samples

2.0 APPARATUS INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Supplies

2.1.1 Filter Media

- Nylosorb, 1.0 μm, 47 mm, Gelman Scientific (Ann Arbor, MI)

Nylon filters are prepared in batches of 100. The containers for these batches bear labels that identify them.

2.1.2 1-liter glass beaker

2.1.3 Large watch glass or glass petri dish (cover for beaker)

2.1.4 1-liter volumetric flask

2.1.5 Sartorius R160D Analytical Balance and weighing boat

2.1.6 Drying vacuum oven (VWR Model 1410)

2.1.7 Petri dishes (4" x 1/2")

2.1.8 PVC Gloves, non-powdered

2.1.9 Flat-tipped Tweezers (Millipore, San Francisco, CA)

2.1.10 Light Table

2.1.11 Plastic containers for clean filter storage

2.1.12 Kaydry Towels

2.1.13 Nylon Filter Log Sheet (Table 2-1)

2.2 Reagent

2.2.1 Sodium carbonate, Na_2CO_3 (Baker Analyzed Reagent 3604-01)

2.3 Forms

Log Sheet for Filter Washing, Impregnation and Acceptance Testing.

3.0 CALIBRATION STANDARDS

(Not Applicable)

4.0 PROCEDURES

4.1 General Flow Diagram

Figure 4-1 shows the general flow diagram for washing nylon filters

4.2 Preparation of Washing Solution (0.015 M Na_2CO_3)

4.2.1 Using the analytical balance, weigh 1.6 g of Na_2CO_3 into a weighing boat.

4.2.2 Transfer the Na_2CO_3 into the 1-liter volumetric flask and add approximately 700 ml DDW. Place stopper into flask and shake to dissolve. If necessary, sonicate. Fill to 1 liter with DDW upon complete dissolution. Label the concentration (0.015 M Na_2CO_3) and date on the volumetric flask.

4.3 Washing Procedure

4.3.1 Fill the 1 liter glass beaker with the 0.015 M Na_2CO_3 solution to about the 800 ml mark. Open a new box of 100 Nylon filters and separate the Nylon filter one by one and throw away the blue or yellow insert paper between each filter (CAUTION: DO NOT THROW AWAY THE NYLON FILTERS. NYLON FILTERS ARE WHITE AND HAVE A VERY SMOOTH SURFACE. INSERT PAPERS ARE LIGHT BLUE OR YELLOW). Assign

Table 2-1

Log Sheet for Nylon Filter Washing and Acceptance Testing

Manufacturer	Manufacturer ID Lot	DRI ID Lot	Date of Washing/ Inspection	Acceptance Testing Species	Date of Analysis	Concen-tration (µg/filter)	Filter Size (mm)	Pass	Fail	Comments
				Cl^- NO_2^- NO_3^- $SO_4^=$ NH_4^+						
				Cl^- NO_2^- NO_3^- $SO_4^=$ NH_4^+						
				Cl^- NO_2^- NO_3^- $SO_4^=$ NH_4^+						

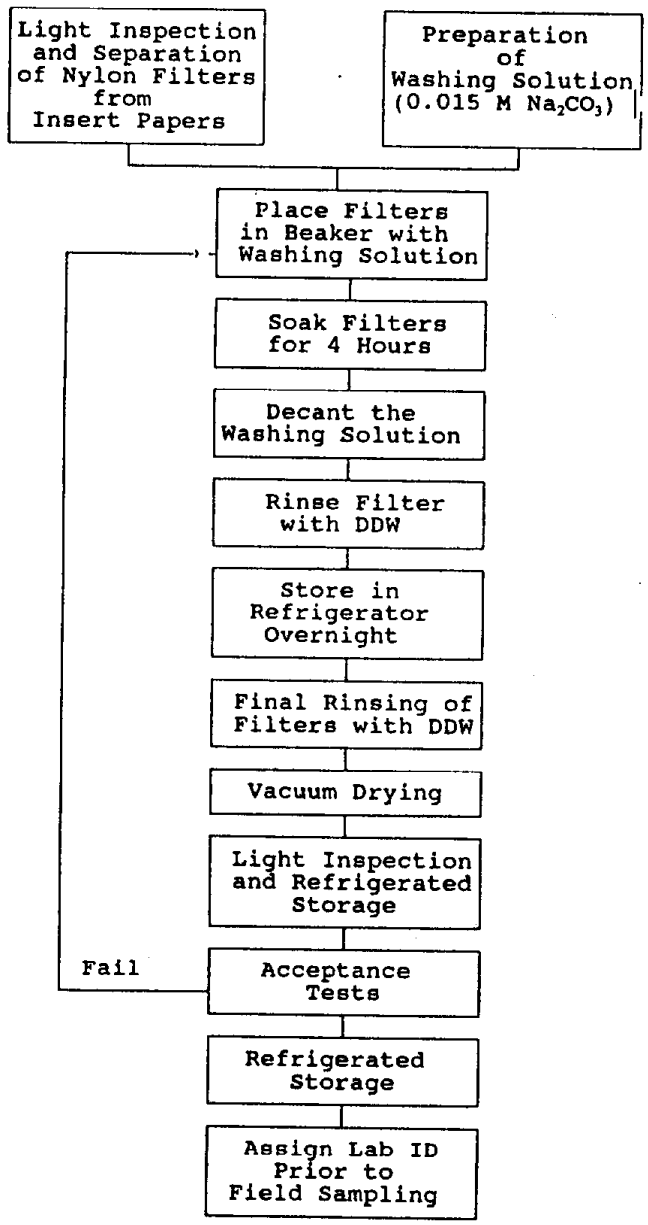


Figure 4-1. Flow Diagram of Nylon Filter Pre-Washing Procedure

DRI Batch ID. Place a batch of 100 nylon filters in the beaker. Cover the beaker with a watch glass or glass petri dish. Soak for 4 hours.

4.3.2 Decant the sodium carbonate solution, and place the beaker in the sink. Tilt the beaker and turn on the DDW faucet. Swirl the beaker so that the DDW causes turbulence and agitates the filters. Decant as much DDW as possiblew and repeat the rinsing process for 10 minutes. (CAUTION: BE CAREFUL NOT TO WASH ANY FILTERS OUT OF THE BEAKER.) Decant as much DDW as possible.

4.3.3 Fill the beaker with DDW to 800 ml level, cover beaker and store in the refrigerator overnight.

4.3.4 Decant the DDW as much as possilbe. Transfer several filters into a cleaned large glass Petri dish that is filled with DDW/ This will act as a final rinse before drying.

4.4 Drying Procedure

4.4.1 Place three of the filters in a single layer on clean inverted petri dishes. Dry in preheated air oven at 60 degrees Centigrade. Check filters every 5 minutes and remove filters from oven as soon as they are dry (after 5 to 10 minutes.) (CAUTION: OVERDRYING WILL CAUSE FILTERS TO CURL AND RUIN THEM FOR USE.)

4.4.2 Light inspect each filter, discard any filter that has holes or scratches that were made during the washing procedure.

4.4.3 Store filters in a plastic box labelled with DRI batch ID and Nylon filter washing date. The storage box should be rinsed with DDW and dried with a Kaydry towel before use.

4.4.4 Place the box in an air tight ziplock bag and store cleansed filters in the refrigerator. (CAUTION: IT IS IMPORTANT TO STORE NYLON FILTERS IN AN AIR-TIGHT BAG)

4.5 Acceptance Testing and Storage

4.5.1 Randomly select one filter per batch and acceptance test for Cl^-, NO_2^-, NO_3^- and $SO_4^=$. Ensure the blank level is <1.0 μg/filter. Reject the entire batch if the blank level exceeded the criteria and repeat steps 4.2 to 4.4.

4.5.2 Refrigerate until sampling. Remember to assign laboratory blanks prior to filter shipment.

4.6 Data Recording

Complete the first three sections of a Nylon Filter Log Sheet (Table 2-1) for each batch. Circle the appropriate species listed under Acceptance Testing Species. The final four sections will be completed after the species are acceptance tested.

5.0 QUALIFICATION

5.1 Calibration Procedures

(Not Applicable)

5.2 Calculations

(Not Applicable)

6.0 QUALITY CONTROL

6.1 Complete documentation is kept for:

- Light Inspection of the filters
- Washing of the filters
- Drying of the filters
- Acceptance testing.

6.2 One percent of each batch of 100 filters prepared are to be analyzed for background levels of Chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), and sulfate ($SO_4^=$). If the level on any 47 mm filter exceeds 1 μg, the entire batch is rewashed and resubmitted for acceptance testing.

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure describes the quantitative sectioning of exposed Teflon filter samples. One half of the filter is used for atomic absorption spectrophotometry (AA) analysis; the other half is used for ion chromatography (IC) analysis.

1.2 Measurement Principle

(Not applicable)

1.3 Measurement Interferences and Their Minimization

(Not applicable)

1.4 Ranges and Typical Values

(Not applicable)

1.5 Lower Quantifiable Limits, Precision, and Accuracy

(Not applicable)

1.6 Responsibilities of Personnel

All technicians in the laboratory should read and understand this operating procedure before handling or sectioning any samples related to analysis work performed in the laboratory.

The Laboratory Manager or Supervisor is responsible for insuring that the procedures are followed.

1.7 Definitions

No terms used in this procedure require definition.

1.8 Related Procedures

DRI SOP 18	Filter Pack Assembling, Disassembling, and Cleaning Procedure.
DRI SOP 2-209.2	Sample Shipping, Receiving, and Chain-of-Custody.

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Equipment and Supplies

- Exposed Teflon filters (Gelman Zefluor or Gelman Teflon) in plastic petri dishes or PetriSlides.
- Paper cutter with 37 or 47 mm half-circle plastic template attached.
- Kaydry towels (Van Watus & Rogers, #52857-120).
- Kimwipe towels (Van Watus & Rogers, #21905-025).
- Extraction tubes with screw-on caps (Galcon, #2045).
- Test tube racks.
- PVC gloves, non-powdered (Fisher, #11-393-26).
- Flat-tipped tweezers (Millipore, #XX62-000-06).
- Barcode labels, generated in-house using the CADMPBAR.EXE or BARCODES.EXE program and Avery #5354 adhesive labels.

2.2 Reagents

- Methanol (Fisher #A412-20).

2.3 Forms

(Not applicable)

3.0 Calibration Procedure

(Not applicable)

4.0 PROCEDURE

4.1 Setup

- Clean and cover the work area with Kaydry towels.
- Place the paper cutter on the towels.
- Place the petri dishes or PetriSlides containing the Teflon filters to the right of the paper cutter outside the towelled surface.
- Label the extraction tubes with barcode labels, placing the tubes destined for IC analysis in one rack and the tubes destined for AA analysis in another rack.

4.2 Sectioning

- Place the first sample container and the corresponding empty IC and AA extraction tubes on the towelled surface.
- Verify the barcode labels with the DRI analysis list.
- Wipe the surface of the half-circle template and the cutting blade of the paper cutter with KimWipes moistened with methanol.
- With gloved hands, open the first petri dish containing the Teflon filter to be cut.
- Raise the blade of the paper cutter. Remove the filter from the sample container using the flat-tipped tweezers, making sure to touch only the outer, unexposed edge of the filter with the tweezers. Place the filter into the semi-circular template/holder. Make sure the filter is snug against the circular edge and that the clamp is firmly in place. One half of the filter will stick out over the edge of the paper cutter. Hold this half with the tweezers.
- Lower the blade slowly with your left hand (the filter is being held with your right) until the blade is about 1 inch from the filter. Then cut the filter with one quick motion.
- Place the filter half into an extraction tube by pushing one end of the filter support ring into the tube and twisting the tube so the ring spirals into the tube. The filter must be inserted past the 10 ml mark on the extraction tube. Use a glass rod if necessary.

- Repeat the procedure above with the second half of the filter. Make sure the sample ID's correspond correctly.
- Cap the tubes. Replace the IC tube in the IC rack and the AA tube in the AA rack.
- Clean the tweezers, glass rod, petri dish, paper cutter surface, paper cutter blade, and filter holder/template with a KimWipe moistened with methanol before proceeding to the next filter.
- Repeat the above procedure with subsequent filters.
- The racks of sectioned filters are stored in the refrigerator until chemical analysis is scheduled.

4.4 Shut-Down

Return all equipment to its normal storage area. Store the empty sample containers in an area designated by the Laboratory Supervisor.

5.0 QUANTIFICATION

(Not applicable)

6.0 QUALITY CONTROL

(Not applicable)

7.0 QUALITY ASSURANCE

(Not applicable)

8.0 REFERENCES

(None)

1.0 GENERAL DISCUSSIONS

1.1 Purpose of Procedure

This method describes the procedures for the extraction of ions from Teflon and nylon filters as well as impregnated filters samples. These filters are used in the various ambient and source monitoring programs at DRI.

1.2 Measurement Principle

(Not Applicable)

1.3 Measurement Interferences and their Minimization

One blank extraction vial should be extracted with extraction solution for a batch of 49 samples to ensure there is no background contamination from the extraction vials.

1.4 Ranges and Typical Values of Measurements

(Not Applicable)

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

(Not Applicable)

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing filter extraction, which includes solution preparation and filter extraction.

It is the responsibility of the laboratory manager or supervisor to insure the extraction procedures are properly followed, to maintain the supplies necessary to insure uninterrupted extraction, and to oversee proper chain-of-custody documentation.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center is responsible to determine the extent and methods of quality assurance to be applied to each project, to estimate the level of effort involved in this quality assurance, to update this procedure

periodically, and to ascertain that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

(Not Applicable)

1.8 Related Procedures

- DRI SOP 11 Impregnating, Drying, and Acceptance Testing of Filters for Sampling Gas in Air
- DRI SOP 13 Sectioning of Filter Samples
- DRI SOP 15 Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography
- DRI SOP 17 Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetry

2.0 APPARATUS INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Supplies

2.1.1 Filter Media

- Teflon membrane filters, Teflon 2 μm, 47 mm (#R2PJ047); Teflon 2 μm, 37 mm (#R2PJ037); or Zeflour 2 μm, 47 mm (#P5TJ047); Gelman Scientific, Inc.; (Ann Arbor, MI). (Teflon filters used for most ambient sampling programs are weighed before and after sample collection.
- Quartz fiber filters, 25 mm or 47 mm, Pallflex 2500 QAT-UP quartz-fiber filters, Pallflex Inc.; (Putnam, CT).
- Nylon 66 filters, 2.0 μm, 47 mm, Schleicher & Schuell, Inc.; (Keene, NH).
- Nylasorb filters, 1.0 μm, 47 mm, Gelman Scientific, Inc.; (Ann Arbor, MI).
- K_2CO_3 -impregnated, 47 mm, Whatman 41 cellulose fiber filters, CHEMTREX; (Hillsboro, OR).

- K_2CO_3 -impregnated, 25 mm or 47 mm, Pallflex 2500 QAT-UP quartz-fiber filters, Pallflex Inc.; (Putnam, CT).
- Citric Acid-impregnated, 47 mm, Whatman 41 Cellulose fiber filters, CHEMTREX; (Hillsboro, OR).
- Triethanolamine-impregnated, 47 mm, Whatman 31ET Chromatography filter, CHEMTREX; (Hillsboro, OR).

These filters are placed in a 15 ml sterile polystyrene tube with twist seal cap (17 mm x 120 mm, Intermountain Scientific #374624) when they are removed from filters holders. The samples are extracted in batches of 50 or less. The extraction tubes are labelled with barcode labels that identify the samples. (CAUTION: VERIFY THE BARCODE LABEL AGAINST THE DRI CHEMICAL ANALYSIS LIST.)

2.1.2 2 Flat-tipped Tweezers (Millipore, San Francisco, CA)

2.1.3 PVC Gloves, non-powdered

2.1.4 Repipet II - 10 ml and 20 ml (Van Waters and Rogers, #53523-460 and #53523-506, respectively)

2.1.5 Polystyrene, 15 ml conical extraction tubes, 17 mm x 120 mm (Intermountain Scientific #374624)

2.1.6 Eppendorf Pipet 200 μl (Fisher 21-278-20)

2.1.7 Sonicator (Branson Model 5200)

2.1.9 GLAS-COL Shaker (Fisher #14-258) with Test Tube Rack holder (Fisher #14-259-3)

2.2 Reagents

2.2.1 All chemicals should be Reagent Grade for Extraction Solutions.

- Sodium carbonate anhydrous (Baker analyzed 3604-1)
- Sodium bicarbonate (Fisher certified, S233-500)
- H_2O_2, 30% (Fisher certified, H325-500)
- Sodium citrate dihydrate (Fisher Certified S279)
- Cesium chloride (Fisher Certified C-24)

- Lanthanum Nitrate, 6 Hydrate (Baker P354-05)
- Nitric Acid (Fisher ACS, A200-212)

2.2.2 Solutions

- Sodium carbonate/bicarbonate (0.0035 M/0.0017 M) made from dilution of 10 ml of 0.1 M Na_2CO_3 and 0.1 M $NaHCO_3$ (140 ml NA_2CO_3 + 68 ml $NaHCO_3$, diluted to 4.0 liters) .
- Sodium citrate dihydrate (0.1 M, 29 g in 1 liter)
- H_2O_2: 0.1% solution (3.33 ml 30% H_2O_2 dilutes to 1 liter with distilled-deionized water (DDW).
- Cesium chloride/lanthanum nitrate solution (0.1% CsCl, 0.1% $La(NO_3)_3$, 0.016 M HNO_3) made from 1.266 g cesium chloride, 3.116 g lanthanum nitrate, and 1.0 ml nitric acid, diluted to 1 liter with DDW.

2.3 Forms

- DRI Filter Extraction Data Log Sheet (Table 2-1)
- DRI Sample Chain-of-Custody for Filter Extraction and Chemical Analysis (Table 2-2)
- DRI SO_2 Extract Dilution Data Log Sheet (Table 2-3)

3.0 CALIBRATION STANDARDS

(Not Applicable)

4.0 PROCEDURES

4.1 General Flow Diagram

A general flow diagram for this procedure is shown in Figure 4-1

Table 2-1

DRI Filter Extraction Data Log Sheet

Extraction Date	Project	Inclusive Lab ID	Filter Size	Area of Filter Used	Solution Type (conc.)	Solution Volume (ml)	Sonication				Shaking		Tech. Init.	Comments
							Start Time	Start Temp (°C)	Stop Time	Stop Temp (°C)	Start Time	Stop Time		

Table 2-2

DRI Sample Chain-of-Custody for Filter Extraction and Chemical Analysis

Date Submitted	Project	Inclusive Lab ID	Number of Samples	Analysis Method	Species	Date Analyzed	Tech Initials	Comments

Table 2-3

DRI SO_2 Extract Dilution Data Log Sheet

Project	Inclusive Labe ID	Extraction Date	Extract Volume (ml)	Extract Solution Type (conc.)	Dilution Date	Dilution Volume (ml)	Dilution Solution Type	Sonication				Tech Init	Comments
								Start Time	Start Temp (°C)	End Time	End Temp (°C)		

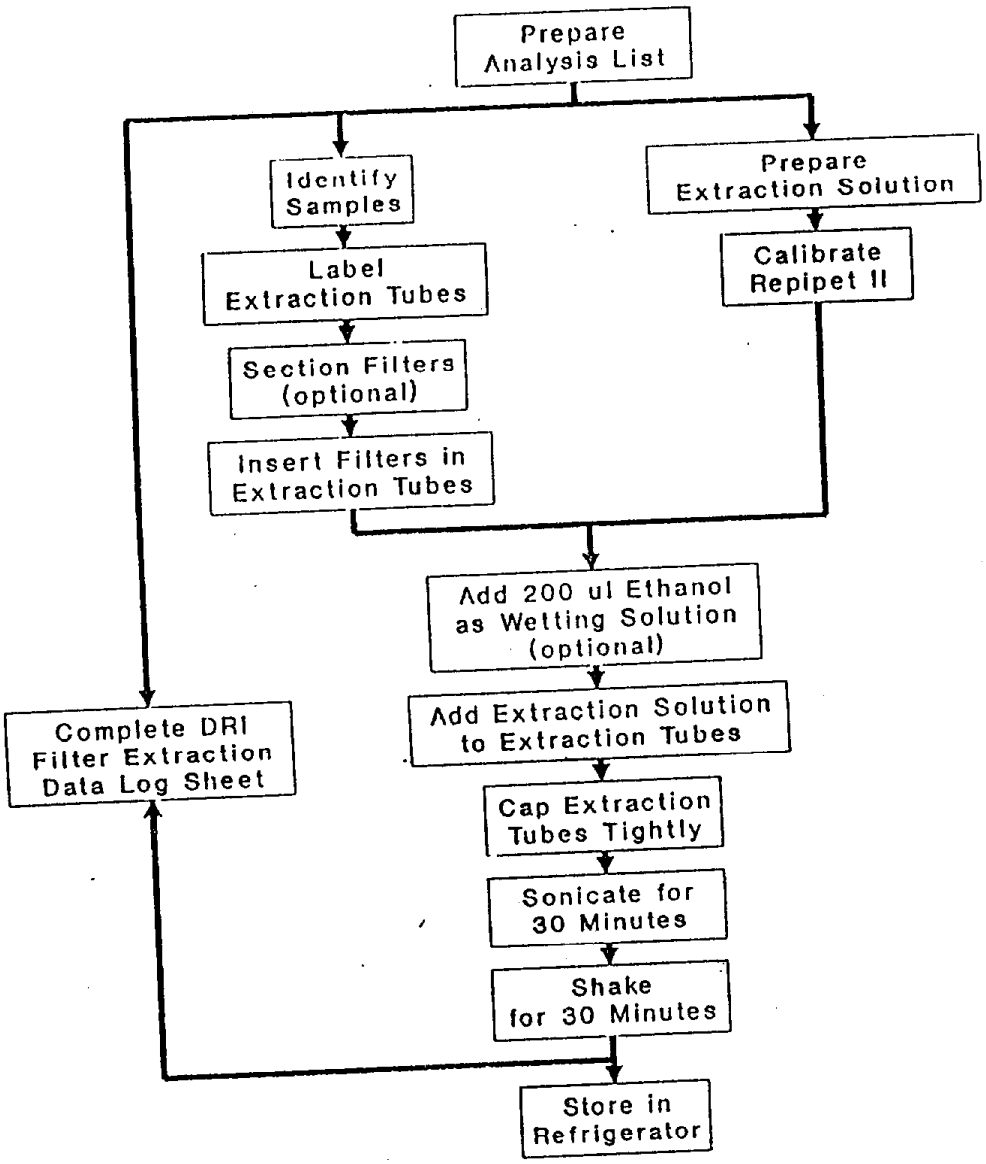


Figure 4-1. Flow Diagram of Filter Extraction Procedure.

4.2 Extraction of Teflon Filters for Ion Chromatographic and Automated Colorimetric Analyses

4.2.1 Before extracting Teflon filters, confirm that they have been weighed.

4.2.2 The following procedure is used for extracting the filters for analyses of chloride (Cl^-), nitrate (NO_2^-), nitrite (NO_3^-), and sulfate ($SO_4^=$) by ion chromatography (IC), and ammonium (NH_4^+) by automated colorimetry (AC).

4.2.3 Filters must be removed from petri slides and placed in extraction tubes prior to extraction. To perform this operation, set up polystyrene tubes in test tube racks and label with the appropriate barcode labels for the filters to be extracted. (CAUTION: VERIFY THE BARCODE LABELS AGAINST THE DRI ANALYSIS LIST.)

4.2.4 With gloved hands, open a petri slide and an extraction tube. Using tweezers, remove the filter from the petri slide. With help from a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside the fold and place it into the corresponding polystyrene tube.

4.2.5 Calibrate the Repipet II filled with DDW to 10.0 ml by weighing.

4.2.6 Using an Eppendorf pipet, add 200 μl ethanol onto Teflon filter surface as wetting solution. Make sure the ethanol directly contacts the Teflon filter surface. Shake the tube, if necessary, to wet the filter.

4.2.7 Add 10.0 ml DDW to each filter sample in the extraction tube using the Repipet II.

4.2.8 Place 200 μl ethanol in an empty extraction tube, add 10.0 ml DDW and mark the tube as reagent blank.

4.2.9 Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.

4.2.10 Fill the ultrasonic bath approximately 80% full with distilled water. Measure the temperature.

4.2.11 Place the extraction rack in the ultrasonic bath. Make sure that all filters are submerged in the extraction solution and that the water level of the ultrasonic bath is higher than the extraction solution level.

4.2.12 Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at the end of 30 minutes and at the end of 60 minutes. If the temperature exceeds 27°, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (CAUTION: THE WATER IN THE BATH SHOULD BE KEPT AT AMBIENT TEMPERATURE DURING THE EXTRACTION.)

4.2.13 Install the extraction rack on the GLAS-COL test tube shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).

4.2.14 Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1)

4.2.15 Store the extracted samples in the refrigerator prior to chemical analyses.

4.2.16 Fill in the entries of DRI Sample Chain-of-Custody for Filter Extraction and Chemical Analysis form (Table 2-2) and inform the laboratory supervisor as extraction is completed.

4.3 Extraction of Teflon Filters for Atomic Absorption Analysis

4.3.1 Before extracting Teflon filters, confirm that they have been weighed.

4.3.2 The following procedure is used for extracting the filters for analyses of potassium, (K^+), sodium (Na^+), calcium (Ca^{++}), and magnesium (Mg^{++}) by atomic absorption spectrophotometry.

4.3.3 Section the filters according to the procedure in DRI SOP 13.

4.3.4 Calibrate the Repipet II filled with cesium chloride/lanthanum nitrate extraction solution to 15.0 ml by weighing.

4.3.5 Using an Eppendorf pipet, add 200 µl ethanol onto Teflon filter surface as wetting solution. Make sure the ethanol directly contacts the Teflon filter surface. Shake the tube, if necessary, to wet the filter.

4.3.6 Add 15.0 ml cesium chloride/lanthanum nitrate extraction to each filter sample in the extraction tube using the Repipet II.

4.3.7 Place 200 µl ethanol in an empty extraction tube, add 15.0 ml cesium chloride/lanthanum nitrate extraction solution and mark the tube as reagent blank.

4.3.8 Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.

4.3.9 Fill the ultrasonic bath approximately 80% full with distilled water. Measure the temperature.

4.3.10 Place the extraction rack in the ultrasonic bath. Make sure that all filters are submerged in the extraction solution and that the water level of the ultrasonic bath is higher than the extraction solution level.

4.3.11 Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at the end of 30 minutes and at the end of 60 minutes. If the temperature exceeds 27°, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (CAUTION: THE WATER IN THE BATH SHOULD BE KEPT AT AMBIENT TEMPERATURE DURING THE EXTRACTION.)

4.3.12 Install the extraction rack on the GLAS-COL test tube shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).

4.3.13 Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1)

4.3.14 Store the extracted samples in the refrigerator prior to chemical analyses.

4.3.15 Fill in the entries of DRI Sample Chain-of-Custody for Filter Extraction and Chemical Analysis form (Table 2-2) and inform the laboratory supervisor as extraction is completed.

4.4 Extraction of Nylon Filters

4.4.1 The following procedure is used for extracting the filters for the analyses of chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), sulfate ($SO_4^=$) by ion chromatography, and ammonium (NH_4^+) by automated colorimetry.

4.4.2 Filters must be removed from petri slides and placed in extraction tubes prior to extraction. To perform this operation, set up polystyrene tubes in test tube racks and label with the appropriate barcode labels for the filters to be extracted. (CAUTION: VERIFY THE BARCODE LABELS AGAINST THE DRI ANALYSIS LIST.)

4.4.3 With gloved hands, open a petri slide and an extraction tube. Using tweezers, remove the filter from the petri slide. With help

from a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside the fold. Place the filter into the corresponding polystyrene tube.

4.4.4 Calibrate the Repipet II filled with sodium carbonate/bicarbonate eluent to 10.0 ml by weighing.

4.4.5 Add 10.0 ml of sodium carbonate/bicarbonate eluent (0.0020 M/0.0010 M) to each filter sample in the extraction tube using the Repipet II.

4.4.6 Add 10.0 ml extraction solution to an empty extraction tube and label this tube as reagent blank.

4.4.7 Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.

4.4.8 Fill the ultrasonic bath approximately 80% full with distilled water. Measure the temperature.

4.4.9 Place the extraction rack in the ultrasonic bath. Make sure that all filters are submerged in the extraction solution and that the water level of the ultrasonic bath is higher than the extraction solution level.

4.4.10 Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at the end of 30 minutes and at the end of 60 minutes. If the temperature exceeds 27°, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (CAUTION: THE WATER IN THE BATH SHOULD BE KEPT AT AMBIENT TEMPERATURE DURING THE EXTRACTION.)

4.4.11 Install the extraction rack on the GLAS-COL test tube shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).

4.4.12 Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1)

4.4.13 Store the extracted samples in the refrigerator prior to chemical analyses.

4.4.14 Fill in the entries of DRI Sample Chain-of-Custody for Filter Extraction and Chemical Analysis form (Table 2-2) and inform the laboratory supervisor as extraction is completed.

4.5 Extraction of Quartz Filters

4.5.1 This procedure is used for extraction for analyses of Chloride (Cl^-), nitrite (NO_2^-), nitrate (NO_3^-), sulfate ($SO_4^=$) by ion chromatography, and ammonium (NH_4^+) by automated colorimetry.

4.5.2 Filters must be removed from petri slides and placed in extraction tubes prior to extraction. To perform this operation, set up polystyrene tubes in test tube racks and label with the appropriate barcode labels for the filters to be extracted. (CAUTION: VERIFY THE BARCODE LABELS AGAINST THE DRI ANALYSIS LIST.)

4.5.3 With gloved hands, open a petri slide and an extraction tube. Using tweezers, remove the filter from the petri slide. With help from a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside the fold, and place the filter into the corresponding polystyrene tube.

4.5.4 Calibrate the Repipet II filled with DDW to 10.0 ml by weighing.

4.5.5 Add 10.0 ml DDW to each filter sample in the extraction tube using the Repipet II.

4.5.6 Add 10.0 ml of DDW to one empty extraction tube. Mark this tube as reagent blank.

4.5.7 Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.

4.5.8 Fill the ultrasonic bath approximately 80% full with distilled water. Measure the temperature.

4.5.9 Place the extraction rack in the ultrasonic bath. Make sure that all filters are submerged in the extraction solution and that the water level of the ultrasonic bath is higher than the extraction solution level.

4.5.10 Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at the end of 30 minutes and at the end of 60 minutes. If the temperature exceeds 27°, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (CAUTION: THE WATER IN THE BATH SHOULD BE KEPT AT AMBIENT TEMPERATURE DURING THE EXTRACTION.)

4.5.11 Install the extraction rack on the GLAS-COL test tube shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).

4.5.12 Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1)

4.5.13 Store the extracted samples in the refrigerator prior to chemical analyses.

4.5.14 Fill in the entries of DRI Sample Chain-of-Custody for Filter Extraction and Chemical Analysis form (Table 2-2) and inform the laboratory supervisor as extraction is completed.

4.6 Extraction of K_2CO_3-Impregnated Whatman 41 Cellulose Filters or K_2CO_3-Impregnated Pallflex 2500 QAT-UP Quartz Fiber Filters.

4.6.1 This procedure is used for extracting the filters and for the analyses of sulfur dioxide (SO_2) as sulfate ($SO_4^=$) by ion chromatography.

4.6.2 Filters must be removed from petri slides and placed in extraction tubes prior to extraction. To perform this operation, set up polystyrene tubes in test tube racks and label with the appropriate barcode labels for the filters to be extracted. (CAUTION: VERIFY THE BARCODE LABELS AGAINST THE DRI ANALYSIS LIST.)

4.6.3 With gloved hands, open a petri slide and an extraction tube. Using tweezers, remove the filter from the petri slide. With help from a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside the fold, and place the filter into the corresponding polystyrene tube.

4.6.4 Calibrate the Repipet II filled with 0.1% H_2O_2 extraction solution to 10.0 ml by weighing.

4.6.5 Add 10.0 ml extraction solution to each extraction tube using a Repipet II.

4.6.6 Add 10.0 ml extraction solution to one empty extraction tube and mark the empty tube as reagent blank.

4.6.7 Store the extraction tubes in the refrigerator for two days. (CAUTION: IT IS IMPORTANT TO STORE THE SAMPLES IN 0.1% H_2O_2 SOLUTION FOR TWO DAYS TO INSURE ALL SO_2 AND SO_3 ARE OXIDIZED TO $SO_4^=$.)

4.6.8 Fill in all entries on the DRI SO_2 Extract Dilution Data Log Sheet (Table 2-3).

4.6.9 Calibrate a Repipet II filled with DDW to 10.0 ml by weighing.

4.6.10 Prepare a new set of extraction vials having the identical label IDs as those extracted two days previously.

4.6.11 Pipet 1.0 ml of each extract into its corresponding empty extraction tube. Using the calibrated Repipet II, add 10.0 ml DDW to each tube.

4.6.12 Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.

4.6.13 Fill the ultrasonic bath approximately 80% full with distilled water. Measure the temperature.

4.6.14 Place the extraction rack in the ultrasonic bath. Make sure that all filters are submerged in the extraction solution and that the water level of the ultrasonic bath is higher than the extraction solution level.

4.6.15 Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at the end of 30 minutes and at the end of 60 minutes. If the temperature exceeds 27°, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (CAUTION: THE WATER IN THE BATH SHOULD BE KEPT AT AMBIENT TEMPERATURE DURING THE EXTRACTION.)

4.6.16 Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1) and complete information on DRI SO_2 Extract Dilution Data Log Sheet (Table 2-3).

4.6.17 Install the extraction rack on the GLAS-COL test tube shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).

4.6.18 Store the extracted samples in the refrigerator prior to chemical analyses.

4.6.19 Fill in the entries of DRI Sample Chain-of-Custody for Filter Extract and Chemical Analysis form (Table 2-2) and inform the laboratory supervisor as extraction is completed.

4.7 Extraction of Citric Acid-Impregnated Whatman 41 cellulose fiber filters.

4.7.1 This procedure is used for extracting the impregnated filters and for the analysis of ammonium (NH_4^+) by Technicon automated colorimetry (AC) or by ion chromatography (IC).

4.7.2 Filters must be removed from petri slides and placed in extraction tubes prior to extraction. To perform this operation, set up polystyrene tubes in test tube racks and label with the appropriate barcode labels for the filters to be extracted. (CAUTION: VERIFY THE BARCODE LABELS AGAINST THE DRI ANALYSIS LIST.)

4.7.3 With gloved hands, open a petri slide and an extraction tube. Using tweezers, remove the filter from the petri slide. With help from a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside the fold, and place it into the corresponding polystyrene tube.

4.7.4 Calibrate the Repipet II filled with DDW to 10.0 ml by weighing if analysis is performed by IC; calibrate the Repipet II filled with 0.1 M sodium citrate to 10.0 ml by weighing if analysis is performed by AC. This creation of buffer retards the absorption if ambient NH_3 is present while the sample is in the autosampler.

4.7.5 Using the Repipet II, add 10.0 ml of DDW to each filter sample in the extraction tube if the analysis is performed by IC; add 10.0 ml of 0.1 sodium citrate to each filter sample in the extraction tube if analysis is performed by AC.

4.7.6 Add 10.0 ml of DDW to one empty extraction tube and mark this tube as reagent blank if analysis is performed by IC; add 10.0 ml of 0.1 M sodium citrate to one empty extraction tube if analysis is performed by AC.

4.7.7 Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.

4.7.8 Fill the ultrasonic bath approximately 80% full with distilled water. Measure the temperature.

4.7.9 Place the extraction rack in the ultrasonic bath. Make sure that all filters are submerged in the extraction solution and that the water level of the ultrasonic bath is higher than the extraction solution level.

4.7.10 Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at the end of 30 minutes and at the end of 60 minutes. If the temperature exceeds 27°, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (CAUTION: THE WATER IN THE BATH SHOULD BE KEPT AT AMBIENT TEMPERATURE DURING THE EXTRACTION.)

4.7.11 Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1)

4.7.12 Install the extraction rack on the GLAS-COL test tube shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).

4.7.13 Store the extracted samples in the refrigerator prior to chemical analyses.

4.7.14 Fill in the entries of DRI Sample Chain-of-Custody for Filter Extracts and Chemical Analysis form (Table 2-2) and inform the laboratory supervisor as extraction is completed.

4.7.15 Make sure the extracted samples are stored in the refrigerator for 24 hours before analysis.

4.8 Extraction of Triethanolamine (TEA) Impregnated Whatman 31ET Chromatography Filters.

4.8.1 This procedure is used for extracting the impregnated filters and for the analysis of nitrite (NO_2^-) by Technicon automated colorimetry (AC), and analysis of nitrite (NO_2^-) and nitrate (NO_3^-) by ion chromatography (IC).

4.8.2 Filters must be removed from petri slides and placed in extraction tubes prior to extraction. To perform this operation, set up polystyrene tubes in test tube racks and label with the appropriate barcode labels for the filters to be extracted. (CAUTION: VERIFY THE BARCODE LABELS AGAINST THE DRI ANALYSIS LIST.)

4.8.3 With gloved hands, open a petri slide and an extraction tube. Using tweezers, remove the filter from the petri slide. With the help from a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside of the fold, and place the filter into the corresponding polystyrene tube.

4.8.4 Calibrate the Repipet II filled with DDW to 10.0 ml by weighing.

4.8.5 Add 10.0 ml DDW to each filter sample in the extraction tube using the Repipet II.

4.8.6 Add 10.0 ml of DDW to one empty extraction tube, and mark the tube as reagent blank.

4.8.7 Cap the tubes tightly. Be sure that the exposed area on the filter is completely and continually immersed in the extraction solution.

4.8.8 Fill the ultrasonic bath approximately 80% full with distilled water. Measure the temperature.

4.8.9 Place the extraction rack in the ultrasonic bath. Make sure that all filters are submerged in the extraction solution and that the water level of the ultrasonic bath is higher than the extraction solution level.

4.8.10 Sonicate for 60 minutes. Measure the temperature of the ultrasonic bath at the end of 30 minutes and at the end of 60 minutes. If the temperature exceeds 27°, add ice to bring the temperature down. An alternate method is to circulate the water continuously. (CAUTION: THE WATER IN THE BATH SHOULD BE KEPT AT AMBIENT TEMPERATURE DURING THE EXTRACTION.)

4.8.11 Install the extraction rack on the GLAS-COL test tube shaker and shake for 60 minutes at 60 cycles per minute (knob setting at 3).

4.8.12 Fill in all entries on the DRI Filter Extraction Data Log Sheet (Table 2-1)

4.8.13 Store the extracted samples in the refrigerator prior to chemical analyses.

4.8.14 Fill in the entries of DRI Sample Chain-of-Custody for Filter Extracts and Chemical Analysis form (Table 2-2) and inform the laboratory supervisor as extraction is completed.

5.0 QUANTIFICATION

(Not applicable)

6.0 QUALITY CONTROL

For each batch of 50 samples being analyzed, one extraction tube with extraction solution will be analyzed as reagent blank. If reagent blank is greater than the field blanks, the analyst should stop the analyses and inform the laboratory supervisor immediately.

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

The objectives of this standard operating procedure are to:

- provide a basic understanding of the principles of operating ion chromatography (IC)
- describe routine analysis of aqueous filter extracts of precipitation samples using the Dionex 2020i or 4000i Ion Chromatograph for the following anions:

  Fluoride (F^-)
  Chloride (Cl^-)
  Nitrite (NO_2^-)
  Nitrate (NO_3^-)
  Sulfate ($SO_4^=$)
  Bromide (Br^-)
  Phosphate ($PO_4^{\equiv}$)
  Formate (Fo^-)
  Acetate (Ac^-)

- specify the implementation of a state-of-the-art ion chromatography measurement process

This procedure will be followed by all analysts in the Environmental Analysis Facility of the Energy and Environmental Engineering Center of the Desert Research Institute.

1.2 Measurement Principle

Ion Chromatography using the Dionex 2020i or 4000i is a liquid chromatographic technique based on an ion exchange mechanism and suppressed conductivity detection for the separation and determination of anions. Its separation principle is similar to that of all chromatographic methods. Each ion's affinity for the exchange site, known as its selectivity quotient, is largely determined by its radius and its valence. As a consequence of differences in the equilibrium distribution of sample components between the mobile (sample/eluent flow) and stationary (ion exchange column) phases, the sample ions elute from the column as discrete bands based upon their migration velocities. Each ion is identified by its retention time within the ion exchange column.

During routine operation, a filtered aliquot of sample is pumped through an ion exchange column where the ions are separated. The eluent ions from this separator column are then neutralized in the succeeding micro-membrane suppressor and the sample ions are converted to their corresponding strong acids for detection with a conductivity detector. The conductivity responses are associated with ionic species by their elution times. Ionic concentrations are quantitatively determined from conductivity peak heights or area (Small et al., 1975).

1.3 Measurement Interferences and their Minimization

- Water from the sample injection will introduce a negative peak or dip in the chromatogram when it elutes since its conductance is less than that of the suppressed eluent. Any ion of interest eluting near the water dip (such as F^- or Cl^-) must be sufficiently resolved from the dip in order to be accurately quantified. This can be achieved by changing the eluent concentration or decreasing the flow rate. Alternatively, the negative peak can be reduced by adding an equivalent of 100 μl of a prepared eluent concentrate (solution that is 100 times more concentrated than the eluent used for analysis) per 10.0 ml of sample. Proportionate eluent additions must also be included in calibration and quality control solutions (Bachman et al., 1986). Increasing the eluent concentration may, however, result in unresolved peaks or peak overlap.

- The presence of air bubbles in the columns, tubing, or conductivity detector cell may cause baseline and peak variability. Avoid introducing air into the system when injecting samples and standards. The Eluent Degas Module equipped with the Dionex Series 2020i or 4000i Ion Chromatography should minimize the introduction of air bubbles through the system.

- Unresolved peaks will result when the ion concentration of one of the sample components is 10 to 20 times higher than another component that appears in the chromatogram as an adjacent peak. Decreasing the eluent concentration or the flow rate may correct this problem. Decreasing the flow rate will, however, lengthen the retention time.

- Interferences may be caused by ions with retention times that are similar to each other, resulting in overlapping peaks. Decreasing the eluent concentration or the flow rate may result in improved peak resolution and minimize the positive interferences (Bachman et al., 1986).

- Injection of samples with total ionic concentrations greater than 50 ppm or the use of sample loop volumes greater than 250 μl may result in column overloading, in turn causing loss of the sample since it cannot be retained on an overloaded column. Non-quantifiable responses will also occur. Dilution of samples or decreasing the sample loop volume will prevent column overloading.

- Deterioration in column performance can result from the accumulation of contaminants on the exchange resin. Changes in retention times and in resolution are symptoms of column deterioration. Refer to the manufacturer's guidelines (Dionex, 1986) for instructions on cleaning the column resin.

1.4 Ranges and Typical Values of Measurements

A wide range of ambient concentrations are found in both filter extracts and precipitation samples. Table 1-1 summarizes the ranges of anion concentrations from past DRI studies. "Typical" values are difficult to express except in terms of ranges, because μg/ml measurements depend on volume of extract or sample, amount of filter extracted, type of sample (i.e., urban or rural ambient, direct or diluted source), volume of air sampled, and filter deposit area. All of these factors may be adjusted to compensate for unusually low or high concentrations.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The Dionex Series 2020i or 4000i Ion Chromatography System is capable of measuring the anions for F^-, Cl^-, NO_2^-, NO_3^-, $SO_3^=$, $SO_4^=$, Br^-, $PO_4^{\equiv}$, Fo^-, and Ac^- down to the 10 - 30 ppb range. The lower quantifiable limit (LQL) for each of the ionic species is determined by variability in blank analyses or the minimum detection limit -- whichever is greater. Table 1-2 lists the LQLs resulting from various ion chromatography analyses. The accuracy is primarily limited by the uncertainties in the standard solution preparation and is typically within ± 5%. Precision as estimated by replicate analyses is in the range of ± 10 to ± 30%, depending on the analyte and the concentration of the analyte.

1.6 Personnel Responsibilities

All analysts in the laboratory should read and understand the entire standard operating procedure before performing IC analysis. The analyst is expected to follow this procedure step by step to perform routine system calibrations, chemical analyses, and performance tests. The

Table 1-1

Ranges and Typical Concentrations of Anions Determined by Ion Chromatography

Ionic Species	Dry Deposition ($\mu g/m^3$) Ambient Concentration Range	Wet Deposition ($\mu mole/l$) Ambient Concentration Range	Wet Deposition ($\mu mole/l$) Typical Value
Cl^-	0.15 to 0.22[b]	0.1 to 75[a]	0.5[a]
NO_2^-	3.0 to 44.0[c]		
NO_3^-	0.7 to 13.0[c]	0.2 to 14[a]	2.5[a]
$SO_4^=$	1.0 to 20.0[c]	0.1 TO 8[a]	0.8[a]
SO_2	0.5 to 13.0[c]		

[a] From Hidy et al. (1974)
[b] Range of average fine particle values at urban and nonurban sites from Watson et al. (1981)
[c] Preliminary data from CADMP sites for PM_{10} samples from Watson et al. (1981)

Table 1-2

Lower Quatifiable Limits of Anions
Determined by Ion Chromatography

Ionic Species	Lower Quantifiable Limits ($\mu g/m^3$)*	$\mu g/ml$
F^-	0.0017	0.05
Cl^-	0.0017	0.05
NO_2^-	0.0017	0.05
NO_3^-	0.0017	0.05
SO_2^-	0.0017	0.05
$SO_4^=$	0.0017	0.05
Br^-	0.0017	0.05
$PO_4^=$	0.0017	0.05
OCH^-	0.0017	0.05
OAC^-	0.0017	0.05

* Values given are per filter assuming no dilution factor, 10 ml extraction volume, sampling at 33 l/min for 24 hours.

laboratory manager is responsible for ensuring that the IC procedures are properly followed, to examine all replicate, standard, and blank performance test data, to designate samples for re-analysis, and to deliver the analysis results to the project manager within the specified time period.

The quality assurance (QA) officer of DRI's Energy and Environmental Engineering Center (EEEC) is responsible for determining the extent and methods of quality assurance to be applied to each project, for estimating the level of effort involved in this quality assurance, for identifying the appropriate personnel to perform these QA tasks, for updating this procedure periodically, and for ascertaining that these tasks are budgeted and carried out as part of the performance on each contract.

1.7 Definitions

The following terms are used in this document:

Analytical Column/ Separator Column	The column used to perform the actual chromatographic separation.
Column Capacity	Related to the total ionic strength of the sample, it is the maximum concentration of sample that may be loaded onto a separator column before overloading.
Conductivity	A measure of the characteristic of ions in solution to carry electrical current through a liquid between two oppositely charged electrodes. Absolute conductivity is a function of flow rate of the regenerate and eluent strength.
Eluent	The ionic liquid mobile phase used to transport the sample through the exchange column.
Guard Column/Pre-Column	A small column which prevents poisoning and contamination of the separator column by removing particles and absorbing organic compounds.

Ion Exchange	The reversible process by which ions are interchanged between an insoluble material and a liquid with no substantial structural changes of materials (Annual Book of ASTM Standard, 1982).
Ion Exchange Capacity	The number of active ion-exchange sites in a given weight or volume of resin, often expressed in meq/g or meq/ml.
Ion Exchange Resin	An insoluble carbon-based polymer matrix containing charged exchange sites (anionic or cationic). The resin used in IC are formed into small spherical particles (i.e., beads).
MicroMembrane Suppressor	A device used to continuously minimize eluent conductivity and convert sample species to a high conductivity form, thus increasing detection sensitivity.
Regenerant	A solution that converts and maintains active ion exchange sites in a suppressor. Suppressors (i.e., Micro Membrane and Fiber Suppressors) can be regenerated continuously to minimize the system down time.
Resolution	A measure of the ability of a column to separate constituents under specified test conditions. Peak resolution is a function of column efficiency, selectivity, and capacity.
Retention Time	The interval measured from the point of sample injection to the point of maximum peak height or area; the basis for identification of a species in chromatography.
Theoretical Plates/ Column Efficiency	A measure of peak dispersion as flow moves through a column proportional to column length for a given column diameter and resin.

1.8 Related Procedures

Related laboratory procedures are specified in the following DRI Standard Operating Procedures:

DRI SOP 11 Impregnation and Drying of Filters for Sampling Gases in Air

DRI SOP 13 Filter Sectioning

DRI SOP 14 Extraction of Ionic Species from Filter Samples

2.0 APPARATUS, INSTRUMENTATION, AND REAGENTS

2.1 Apparatus and Instrumentation

2.1.1 Description

Table 2-1 and Table 2-2 list the description and catalog numbers of the components accompanying the Dionex Series 2020i and 4000i IC Systems, respectively.

The components of the Dionex Series 2020i or 4000i Ion Chromatography Systems are illustrated in Figures 2-1 and 2-2. The Dionex Series Ion Chromatographs are completely inert and metal free analytical systems.

The Dionex 2020i system contains two isocratic pumps, two chromatographic columns, two detector systems, and two autosamplers. The two systems, designated System 1 and System 2, are controlled by one computer, but operate independently.

The 2020i IC system includes:

- Pump Module: A microprocessor-based eluent delivery system designed to provide isocratic elution capability at precisely controlled flow rates. It is a dual-piston, direct current (DC) motor pump which can be operated with flow rates ranging from 0.1 to 9.9 ml/min (in increments of 0.1 ml/min) and pressures ranging from 0 to 1900 psi (in increments of 10 psi). A constant pressure, constant flow pump is necessary for baseline stability.

- Eluent Degas Module: Provides continuous on-line purging, degassing, and pressurization of as many as four eluent reservoirs with helium (He) gas. The regenerant reservoirs

Table 2-1

Components of the Dionex Series 2020i Ion Chromatograph

Item	Description	Catalog No.
1.	Dionex Series 2020i Ion Chromatograph • Advanced Chromatography Module for Series 2020i (CMA-6) • Conductivity Detector (CDM-II)	35209
2.	Series 2020i Spare Parts Kit	37144
3.	Advanced Computer Interface (ACI)	39678
4.	Cable	38831
5.	5.0 ml Polyvials and filter caps (Poly Val Vial)	38141
6.	5.0 ml Cassettes (sample vial holders)	38016
7.	Automated Sampler	37077
8.	Anion Separator Column (AS4a)	35395
9.	Anion Guard Column (AG4a)	35396
10.	Anion MicroMembrane Suppressor (AMMS)	38019
11.	Anion MicroMembrane Suppressor Installation Kit	38018
12.	Controlled Air Module	37125
13.	Eluant Degas Module	37124
14.	Eluant Degas Module (EDM) Eluent Container Set, Plastic	37179
15.	AI-450 Ion Chromatography Software	SP1423

Table 2-2

Components of the Dionex Series 4000i Ion Chromatograph

Item	Description	Catalog No.
1.	Dionex Series 4000i Ion Chromatograph	37113
	• Conductivity Detector (CDM-I)	
2.	Basic High Pressure Chromatography Module (CMB-2) for Series 4000i	38659
3.	Series 4000i Spare Parts Kit	37144
4.	Advanced Computer Interface (ACI)	39678
5.	Cable	38831
6.	Anion Separator Column (AS4a)	35395
7.	Anion Guard Column (AG4a)	35396
8.	Anion MicroMembrane Suppressor (AMMS)	38019
9.	MicroMembrane Suppressor Installation Kit	38018
10.	Cation Separator Column (CS5)	37028
11.	Cation Guard Column (CG5)	37029
12.	HPIC Separator Column (AS7)	35393
13.	MPIC Guard Column (NG1)	35320
14.	Controlled Air Module	37125
15.	Eluant Degas Module	37124
16.	Eluant Degas Module (EDM) Eluent Container Set, Plastic	37179
17.	AI-450 Ion Chromatography Software	SP1423
18.	Reagent Delivery Module (RDM)	37030
19.	Membrane Reactor	35354

Table 2-2 (continued)

Components of the Dionex Series 4000i Ion Chromatograph

Item	Description	Catalog No.
20.	Packed-Bead Reaction Coil	36036
21.	Variable Wavelength UV/VIS Detector (VDM-II)	39646
22.	Automated Sampler (ASM)	37077
23.	5.0 ml Polyvials + Filter Caps	38141
24.	5.0 ml Cassettes (sample vial holders)	38016

Figure 2-1. Dionex 2020i Ion Chromatography System Overview.

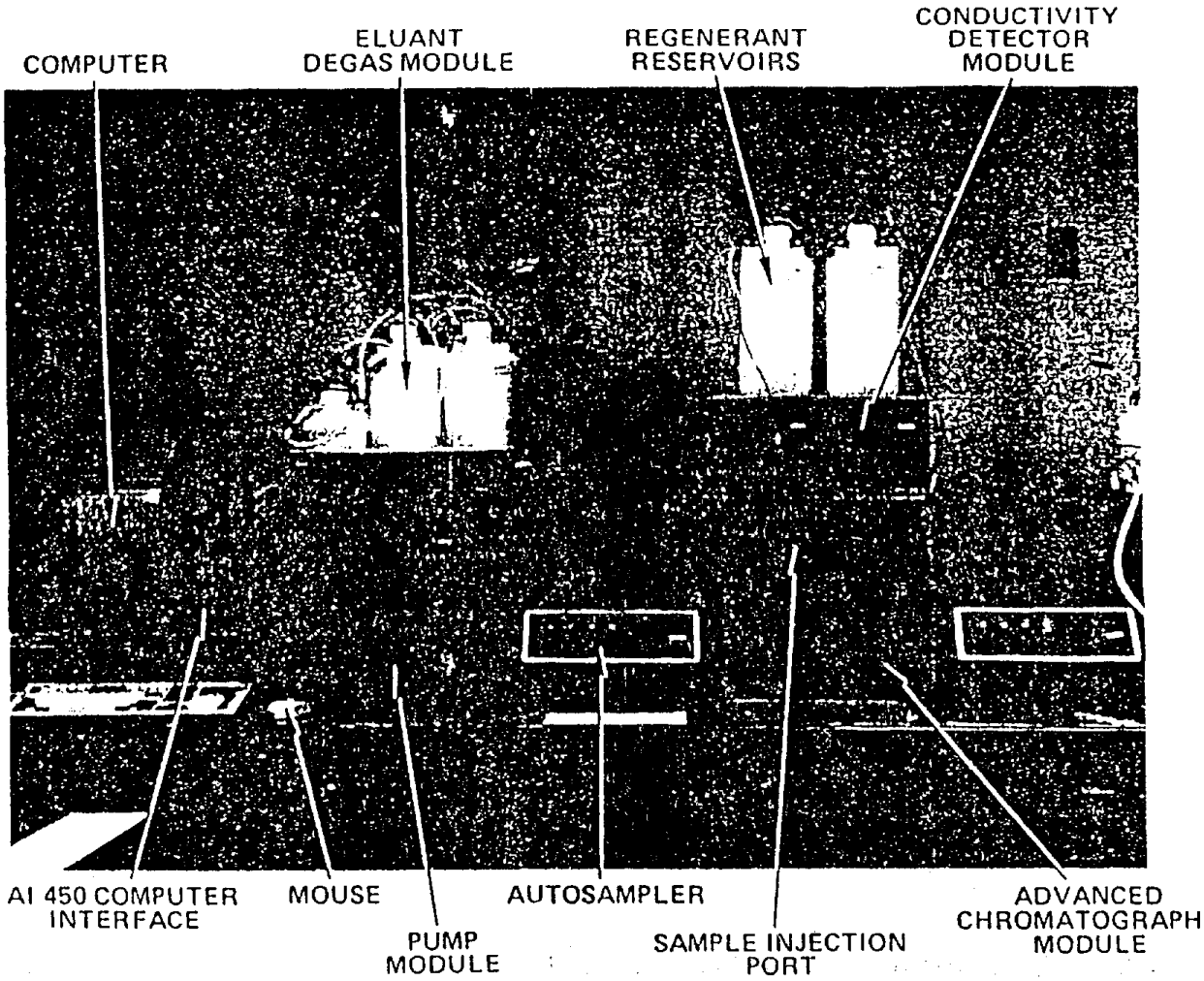
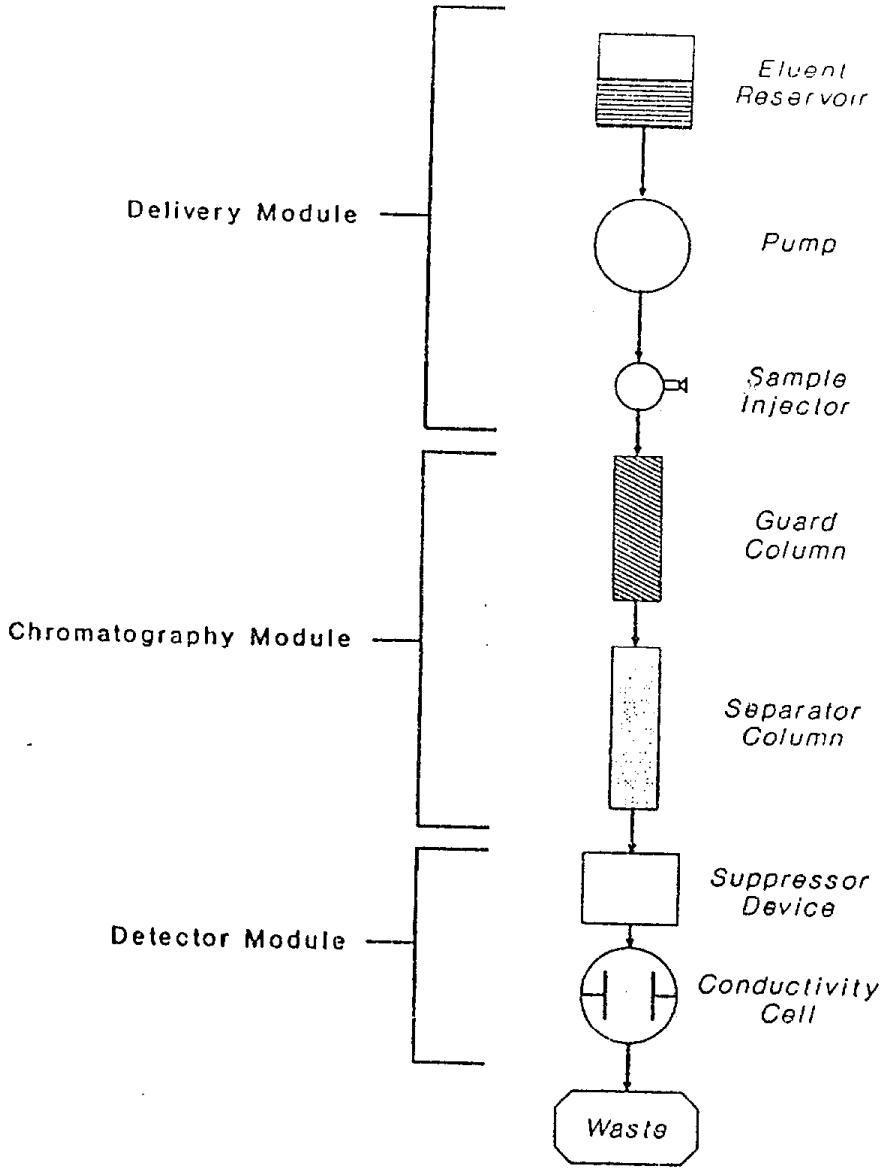


Figure 2-2. Dionex 2020i Ion Chromatography System Schematic.



are pressurized with 5 to 10 psi compressed gas (i.e., nitrogen, air, or helium) to ensure constant delivery to the micromembrane suppressor.

- Sampling System: Samples are introduced into the analyzer with either an automated sampler or hand-operated syringe.

  -- Automated Sampler (Figure 2-3): Can be operated manually from the front panel or remotely from the computer. In routine operation, the automated sampler system is used to deliver between 2.5 and 5.0 ml of sample through the 250 µl sample loop. The sampler tray can hold up to 66 samples (including quality control samples). Each PolyVial sample vial is equipped with a 20 µm filter cap to remove particulates from the sample before injection and to prevent contamination or loss of the sample through evaporation or spills. The filter cap also serves as a piston to force samples out of the vial.

  -- Syringe: A polyethylene syringe with a minimum capacity of 1 ml is used for manual injection of samples. The syringe is equipped with a pre-filter for use with samples which contain particles.

- Advanced Chromatography Module: A single hydraulic system which includes an Injection Valve (a high-pressure pneumatically operated 6 port valve with a 250 µl sample loop), a Column Selection Valve (a high-pressure 6 port valve which provides switching between two columns), and interconnecting tubing.

  Figure 2-4 illustrates the flow through the Advanced Chromatography Module. Pumped eluent and the sample are mixed at the Injection Valve. The mixture of eluent and sample then flows through the Column Selection Valve (valve A), through the Guard Column, through the Separator Column, through the corresponding MicroMembrane Suppressor, and finally through the Detector Cell to waste.

- Conductivity Detector: A microprocessor-controlled detection system which is based on electronic signal processing to increase the signal-to-noise ratio and enhance sensitivity at low concentrations. The system displays conductivities over the full-scale range of 0.01 to 1,000 µS (micro siemen) and

Figure 2-3. Dionex Autosampler.

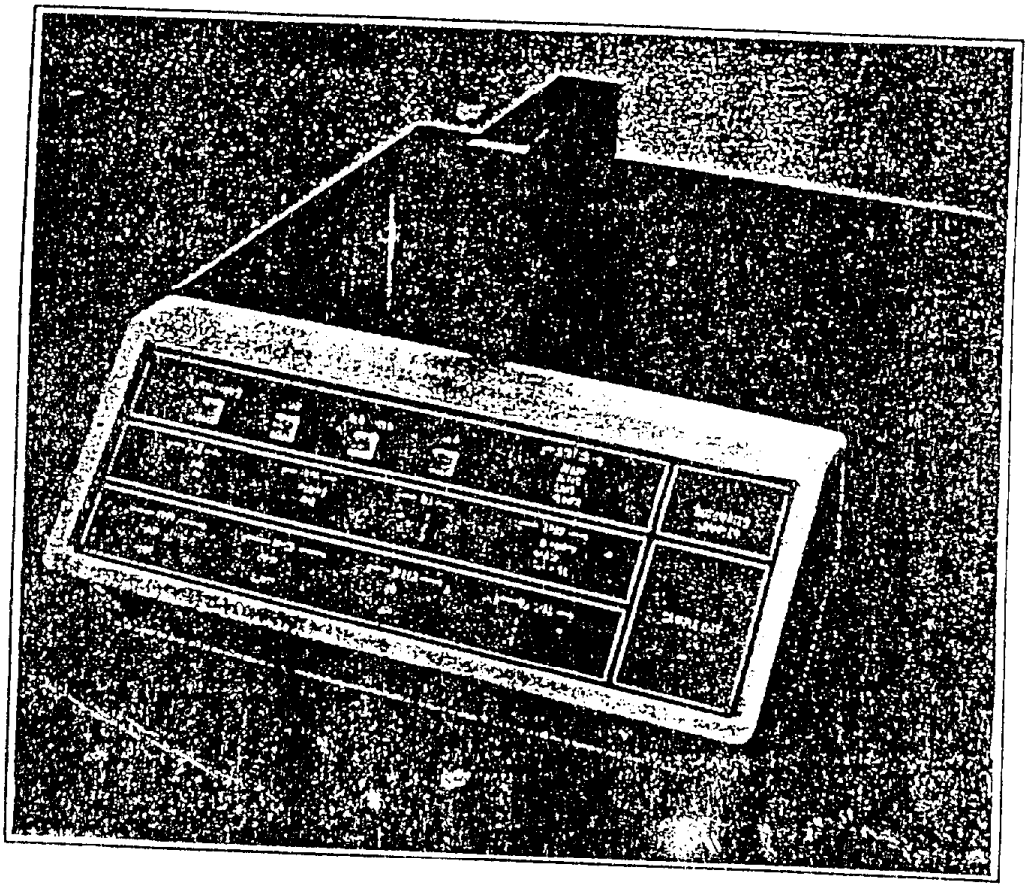
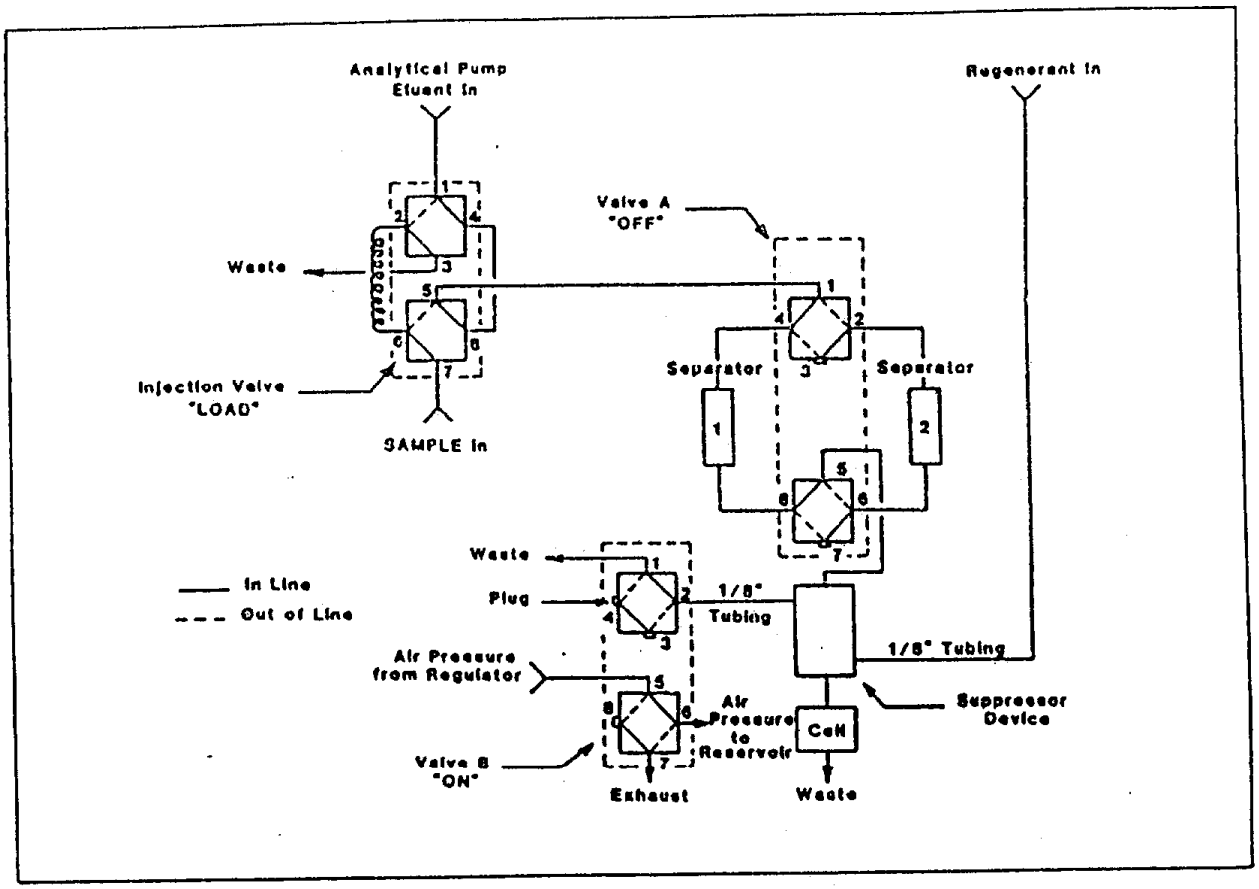


Figure 2-4. Dionex Advanced Chromatography Module Schematic.



compensates for temperature induced-conductivity variations, with correction factors between 0.0 and 9.9% per °C.

The Dionex 4000i IC System is a gradient pump system operated by its own computer. It operates under the same software as the 2020i system, with appropriate changes for the gradient system. The basic 4000i system includes:

- Gradient Pump Module: A microprocessor based eluent delivery system designed to provide gradient or isocratic capability with mixtures of as many as four solvents at precisely controlled flow rates. It delivers the same flows and pressures as the isocratic pump.

- Eluant Degas Module: this module provides purging, degassing, and pressurization of as many as 6 eluent reservoirs with helium gas. The regenerate system is also pressurized with helium gas.

- Sampling System: Either an automated sampler or syringe may be used for sampling. A polyethylene syringe with a minimum capacity of 1 ml is used for manual injections of samples. The syringe is equipped with a filter cap as a pre-filter for use with samples which contain particles. The automated sampler uses 5 ml vials with filter caps.

- Basic Chromatography Module: A single hydraulic system which includes an Injection Valve (a high-pressure 6 port valve with a 250 μl sample loop), a Column Selection Valve (a high-pressure 6 port valve which provides switching between two columns), and inter-connecting tubing. Figure 2-4 illustrates the fluid schematic for the Basic Chromatography Module.

- Conductivity Detector: A microprocessor-controlled detection system which is based on electronic signal processing to increase the signal-to-noise ratio and enhance sensitivity at low concentrations. The system displays conductivities over the full-scale range of 0.01 to 1,000 mS and compensates for temperature induced-conductivity variations, with correction factors between 0.0 and 9.9% per °C.

- Variable Wavelength Detector: A microprocessor-controlled detection system which measures the absorbance of light by the sample according to Beer's Law. The system displays absorbances over a range of 0.002 to 2 absorbance units.

This colorimetric detector uses a Reagent Delivery Module to deliver post-column reagents to the eluent coming from the column. The resulting colored compounds are quantified by the Variable Wavelength Detector. The Reagent Delivery Module is capable of delivering two different reagents simultaneously.

2.1.2 Characterization

The Dionex 2020i and the Dionex 4000i systems both equilibrate about 30 minutes after the appropriate method has been entered and the pumps and regenerate have started. The instruments are very stable and will produce area counts within ±10% of previous readings dependent upon the primary standard used to make up the calibration standards and the eluent solution used.

2.1.3 Maintenance

Routine maintenance of the Dionex systems consists of periodic cleaning of the columns and the conductivity cells. When retention times of the components change significantly this is an indication that the columns need to be cleaned. This is done by the following.

Column Cleaning Solutions:

The columns are cleaned with the following two solutions:

1 M HCl/0.1 M KCl solution:

Weigh out in a disposable weighing boat, 7.46 g KCl to the nearest 0.01 g. Quantitatively transfer to a 1000.0 ml volumetric flask using DDW from a wash bottle. Bring to about 500 ml volume with DDW. Using a grade A graduated cylinder, measure 83.3 ml concentrated HCl (Baker, Instra-Analyzed for trace metals, only). Carefully add to the 1000.0 ml volumtetric flask containing the KCl and 500 ml DDW. Allow to cool if necessasry and bring to volume with DDW.

0.1 M NaOH solution:

Weigh into a disposable weighing boat, 8.0 g of 50% NaOH solution. Quantitatively transfer to a 1000.0 ml volumetric flask containing about 500 ml DDW. Bring to volume with DDW.

Disconnect the column from the Anion MicroMembrane Suppressor. Connect the container of 1 M HCl + 0.1 M KCl directly into the bottom of the pump's priming block, set flow rate to 1 ml/min and

pump 60 ml of the HCl/KCl solution through the column, followed by 30 ml of DDW. Make sure to have an appropriate waste container for the column effluent. After the DDW rinse, remove the HCl/KCl container and connect the container of 0.1 M NaOH to the pump. At 1 ml/min wash the column for 30-60 minutes with the NaOH solution. After treatment, rinse the column for 30 minutes with DDW at 2 ml/min.

Routine maintenance of the Conductivity Detectors requires periodic checks of the liquid line connections to the cells for leaks and every six months to clean the cell electrodes and calibrate the cell. This is done by the following.

Cleaning Solution:

3 M HNO_3: Measure 200 ml concentrated HNO_3 into a 1000.0 ml volumeetric flask containing about 600 ml DDW. Bring to volume with DDW.

Disconnect the conductivity cell from the suppressor outlet and connect a length of 0.5 mm ID tubing with fittings on both ends to the cell inlet. Connect a female luer adaptor to the tubing using a union. Fill a 10 ml syringe with the 3 M HNO_3 solution and attach to the luer adaptor. Turn the cell off and inject 5 ml of the 3 M HNO_3 through the cell. Wait two minutes then push the remaining 5 ml of 3 M HNO_3 through the cell and wait an additional 2 minutes. Rinse the syringe well with DDW and fill with 10 ml DDW. Inject the DDW through the cell. Check the calibration of the cell constant as follows.

Cell Calibration Solution:

0.01 M KCl: Weigh into a disposable weighing boat, 0.7456 g KCl, quantitatively transfer into a 1000.0 ml volumetric flask using DDW in a wash bottle. Bring to volume with DDW.

0.001 M KCl: Using a class A graduated cylinder, measure 100.0 ml of the 0.01 M KCl solution into a 1000.0 ml volumetric flask. Bring to volume with DDW.

Connect the container containing the 0.001 M KCl solution to one of the eluent panel fittings. Disconnect the pump eluent line from the Chromatography module. Disconnect the syringe and luer adaptor from the union and connect the eluent line from the pump to the union. Pump the 0.001 M KCl calibration solution throught the cell at 8.0 ml/min. After 2 minutes reduce the flow rate to 2.0 ml/min. Turn

the cell on. Turn the Auto Offset off. Set the Temperature Compensation to 1.7. Check the Conductivity Display. The conductivity of the calibration solution is 147 μS ± 2 μS. If the reading is incorrect recalibrate according to the instructions in the Dionex manual. After making any adjustments necessary, pump DDW through the cell at 8 ml/min for at least 15 minutes to flush the calibration solution from the system. Disconnect the liquid line from the cell inlet and reconnect the liquid line from the suppressor outlet to the cell inlet. Reconnect the pump to the panel fitting to which it was originally connected.

2.2 Reagents

The following chemicals should be ACS reagent grade or better:

Sodium Bicarbonate ($NaHCO_3$)
Sodium Carbonate (Na_2CO_3)
Sulfuric Acid (H_2SO_4)
Sodium Floride (NaF)
Sodium Chloride ($NaCl$)
Sodium Nitrite ($NaNO_2$)
Sodium Bromide ($NaBr$)
Sodium Nitrate ($NaNO_3$)
Sodium Phosphate (Na_2HPO_4)
Sodium Sulfate ($NaSO_4$)
Sodium Acetate ($NaCH_3COO$)
Sodium Formate ($NaHCOO$)
Sodium Tetraborate•10 H_2O ($Na_2B_4O_7$)

2.2.1 Water

Use water conforming to ASTM Specification D 1193, Type II (Annual Book of ASTM Standards, 1982). Deionized-distilled water (DDW) having a conductivity reading of less than 1 μmho per cm, or a resistance of at least 18 megohm per cm, is required for all analyses.

2.2.2 Eluent Solutions

These solutions are used to elute ions from the separator/analytical column. The compositions of the eluent solutions are determined by the ions to be analyzed. In general, alkaline eluents are used to elute anions.

- For analysis of Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-} and SO_4^{2-} the following eluent solution is used:
  0.0017 M $NaHCO_3$/0.0035 M Na_2CO_3

- For analysis which includes F^- the following eluent solution is used:
  0.0018 M $NaHCO_3$/0.0015 M Na_2CO_3

- For analysis of Ac^- and Fo^- the following eluent solution is used:
  0.005 M Sodium Tetraborate

These are prepared by using the following procedures:

0.1 M $NaHCO_3$ stock solution:

Weigh out into a disposable weighing boat 8.40 g $NaHCO_3$ (to the nearest 0.01 g). Transfer quantitatively, to a 1000.0 ml volumetric flask using degassed DDW in a wash bottle to wash the solid sodium bicarbonate into the volumetric flask. Dilute to 1000.0 ml with DDW.

0.1 M Na_2CO_3 stock solution:

Weigh out into a disposable weighing boat 10.60 g Na_2CO_3 (to the nearest 0.01 g). Transfer quantitatively, to a 1000.0 ml volumetric flask using DDW in a wash bottle to wash the solid sodium carbonate into the volumetric flask. Dilute to 1000.0 ml with DDW.

0.1 M Sodium Tetraborate solution:

Weigh out into a disposable weighing boat 38.14 g $Na_2B_4O_7$ (to the nearest 0.01g). Transfer quantitatively to a 1000.0 ml volumetric flask using DDW in a wash bottle to wash the solid sodium tetraborate into the volumetric flask. Dilute to 1000.0 ml with DDW.

0.0017 M $NaHCO_3$ and 0.0035 M Na_2CO_3 combined eluent:

Using a grade A graduated cylinder measure 136.0 ml 0.1 M $NaHCO_3$ into the 10 L carboy. Then using a grade A graduated cylinder, measure 280.0 ml of 0.1 M Na_2CO_3 into the same carboy. Fill to the 8 L mark with DDW. This solution (0.0017 M $NaHCO_3$ and 0.0035 M Na_2CO_3) is poured directly into the eluent reservoirs on top of the Eluant Degas Module.

0.0018 M $NaHCO_3$ and 0.0015 M Na_2CO_3 combined eluent:

Using a grade A graduated cylinder measure 144.0 ml 0.1 M $NaHCO_3$ into the 10 L carboy. Then using a grade A graduated cylinder, measure 120.0 ml of 0.1 M Na_2CO_3 into the same carboy. Fill to the 8 L mark with DDW. This solution (0.0018 M $NaHCO_3$/0.0015 M Na_2CO_3) is poured directly into the eluent reservoirs on top of the Eluant Degas Module.

0.005 M $Na_2B_4O_7$ eluent:

Using a grade A graduated cylinder measure 400.0 ml 0.1 M $Na_2B_4O_7$ into the 10 L carboy. Fill to the 8 L mark with DDW. This solution (0.005 M sodium tetraborate) is poured directly into the eluent reservoirs on top of the Eluant Degas Module.

(2) 4000i IC System

Because this system uses a gradient pump, the sodium carbonate and bicarbonate do not need to be mixed in the reservoir. Instead, they are mixed by selecting the proper conditions in the gradient pump module (GPM) section of the chromatography method.

- The same eluent stocks used for the 2020i IC are used to prepare the eluents used for the 4000i IC.

  0.01 M $NaHCO_3$ eluent solution:

  Measure 100 ml of the 0.1M $NaHCO_3$ stock solution into a grade A graduated cylinder. Pour it quantitatively into a 1000.00 ml volumetric flask. Fill to the 1000.00 mark with DDW. Mix well by inverting and shaking the flask. Pour the 0.01 M sodium bicarbonate solution directly into the 0.01 M sodium bicarbonate reservoir on the top of the 4000i Eluant Degas Module.

  0.01 M Na_2CO_3 eluent solution:

  Measure 100 ml of the 0.1M Na_2CO_3 stock solution into a grade A graduated cylinder. Pour it quantitatively into a 1000.00 ml volumetric flask. Fill to the 1000.00 mark with degassed DDW. Mix well by inverting and shaking the flask. Pour the 0.01 M sodium carbonate directly into the 0.01 M sodium carbonate reservoir on the top of the 4000i Eluant Degas Module.

2.2.3 Regenerant Solution

A solution which converts and maintains active ion exchange sites in the suppressor column. This solution is used for both the 2020i and 4000i IC instruments. Prepare as follows:

0.0125 M H_2SO_4 regenerant solution:

For the determination of anions with the anion micromembrane suppressor, use 0.0125 M sulfuric acid (H_2SO_4). Add 7.0 ml reagent grade concentrated H_2SO_4 to about 2 liters DDW in the 0.0125 M sulfuric acid reservoir. Dilute to the 10 liter line on the reservoir with DDW. Mix well by swirling the reservoir. Add the 0.0125 M sulfuric acid directly to the regenerant solution reservoir on the top of the IC.

3.0 CALIBRATION STANDARDS

3.1 Preparation of Standard Solutions

3.1.1 Preparation of Stock Solutions (1000 μg/ml)

A combined stock solution containing the analytes of interest is prepared from ACS reagent grade chemicals. The stock solution should be made up to be approximately 1000 μg/ml in each of the components of interest, to four significant figures. Discard solutions after 1 year.

The solid reagent chemicals should be dried at 105°C for 1 hour and cooled. Care must be taken when weighing chemicals not to loose solid reagent because of static electricity.

- Chloride (to be 1000 μg/ml in the combined stock):

  Use NaCl, assaying at 100%. (Sodium Chloride, Baker Analyzed Reagent, #3624-1, 500 g bottle. J. T. Baker Chemical Co. Phillipsburg, N. N.J. 08865)

  Weigh out to the nearest 0.1 mg 0.8243 g NaCl into a weighing boat and transfer quantitatively to a 500.00 ml volumetric flask by rinsing the boat with DDW from a wash bottle into the 500.00 ml volumetric flask. Record the weight actually used and calculate the actual concentration using the formula below.

- Nitrite (to be 1000 μg/ml in the combined stock):

  Use $NaNO_2$, (Sodium Nitrite, Fisher Scientific Company, #S-347, 500 g bottle, Fisher Scientific Company, Chemical Manufacturing Division, Fair Lawn, N.J. 07410)

  Correct the weight used for the assay value for nitrite. If the assay were 100%, 0.7535 g would be needed. Divide this value by the fraction assay to calculate the required amount.

  97.4% pure $NaNO_2$ requires 0.7535/0.97 g = 0.7768 g $NaNO_2$

  Weigh out into a weighing boat the calculated amount to the nearest 0.1 mg. Transfer quantitatively to the same 500.00 ml volumetric flask as used for the chloride by washing the solid into the flask using DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

- Nitrate (to be 1000 μg/ml in the combined stock):

  Use $NaNO_3$ assaying at 100%. (Sodium Nitrate, Matheson Coleman and Bell, Manufacturing Chemists, #SX655. MCB, Norwood, Ohio 45212.)

  Weigh out to the nearest 0.1 mg 0.6854 g $NaNO_3$ into a weighing boat and transfer quantitatively to the same 500.00 ml volumetric flask by washing the solid sodium nitrate into the flask using DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

- Sulfate (to be 1000 μg/ml in the combined stock):

  Use Na_2SO_4, assaying at 100%. (Sodium Sulfate (Anhydrous), Fisher Scientific #S421-500, 500 g bottle. Fisher, Fair Lawn, N.J. 07410.)

  Weigh out into a weighing boat to the nearest 0.1 mg 0.7425 g Na_2SO_4. Transfer quantitatively to the same 500.00 ml flask used for the preceding chemicals by washing the solid into the 500.00 ml volumetric flask using DDW from a wash bottle. Record the weight actually used and calculate the actual concentration using the formula below.

Dissolve the combined salts in approximately 200 ml DDW and dilute to the 500.00 ml mark with DDW. Mix thoroughly by inverting the 500.00 ml flask at least 10 times and swirling.

Store the stock solution in a clean plastic 500 ml bottle by rinsing the bottle three times with the stock solution to remove any water or other contaminants from the storage bottle. Rinse the screw cap with stock solution also. After rinsing is completed, pour the stock solution into the plastic storage bottle. Label the storage bottle clearly with the contents, the date of preparation and the initials of the person who prepared it. Store the stock solution in the refrigerator.

Concentrations are calculated according to the formula:

$$W_s = (C_s)(10^6\ g/\mu g)(10^3\ ml/l)(0.500\ l) \times \frac{(FW)_s}{(FW)_x} \times \frac{100}{\%assay}$$

where:

W_s = the weight of the salt in stock standard in g.

C_s = the concentration of the stock solution in $\mu g/ml$.

$(FW)_s$ = the formula weight of the salt s in grams.

$(FW)_x$ = the formula weight of ion x in grams.

% assay = the purity of the salts of an ion x in percent.

0.500 l = the volume of combined stock prepared.

3.1.2 Preparation of Working Standards (100 $\mu g/ml$ and 10 $\mu g/ml$)

These are the working standard solutions from which calibration standard solutions are prepared. These are prepared once a month or more frequently if needed.

- 100.00 $\mu g/ml$ working standard: Pipet 10.00 ml (using grade A pipet) of the combined stock solution (1000.00 $\mu g/ml$) into a 100.00 ml volumetric flask. Dilute to volume with DDW. Actual concentrations are calculated by dividing the actual concentration of the stock (C_s) by 10.

- 10 $\mu g/ml$ working standard: Using an grade A pipet, pipet 10.00 ml of the 100.00 $\mu g/ml$ working solution into a 100.00 ml volumetric flask. Dilute to volume with DDW. Actual

concentrations are calculated by dividing the concentration of the stock (C_s) by 100.

3.1.3 Preparation of Calibration Standards

These are the standard solutions used to create the calibration curves for the analysis. The concentrations are as follows:

Concentration	Working Standard	Volume of Working Standard	Final Volume
0.05 μg/ml	10 μg/ml	0.05 ml	100 ml
0.1 μg/ml	10 μg/ml	1.00 ml	100 ml
0.2 μg/ml	10 μg/ml	2.00 ml	100 ml
0.5 μg/ml	10 μg/ml	5.00 ml	100 ml
1.0 μg/ml	10 μg/ml	10.00 ml	100 ml
2.0 μg/ml	100 μg/ml	2.00 ml	100 ml
5.0 μg/ml	100 μg/ml	5.00 ml	100 ml

The calibration standards are prepared biweekly in routine operation.

3.2 Use (What is compared to the Standards)

Stock solutions prepared from ACS reagent grade materials should be cross examined with certified solutions as a quality control (QC) check. Quality control standards from Environmental Resources Associates (ERA), National Institute of Standards and Technology (NIST, formerly National Bureau of Standards), and Alltech Associates, Inc., shown in Table 3-1, are used as independent checks for daily operation.

3.2.1 ERA Quality Control standards (Stock standards are custom ordered from Environmental Resource Associates, Arvada, Colorado.) Stocks are valid for one year.

Alltech, Associates, Inc. Quality Control standards. Stocks are valid for one year.

Either the ERA QC standards or the Alltech QC standards are used for all analyses involving the analytes covered by the standards.

Table 3-1

Summary of Quality Control Standards

(I) National Institute of Standards and Technology

Constituents Elements/ Parameters	Simulated Rainwater Standard[a]	
	SRM 2694-I	SRM 2694-II
pH @ 25°C	4.27 ± 0.03	3.59 ± 0.02
Specific Conductance (μS/cm @ 25°C)	26 ± 2	130 ± 2
Acidity (meq/l)	0.050 ± 0.002	0.284 ± 0.005
Fluoride (μg/ml)	0.054 ± 0.002	0.098 ± 0.007
Chloride (μg/ml)	(0.24)	(1.0)
Nitrate (μg/ml)	----[b]	7.06 ± 0.15
Sulfate (μg/ml)	2.75 ± 0.05	10.9 ± 0.2
Sodium (μg/ml)	0.205 ± 0.009	0.419 ± 0.015
Potassium (μg/ml)	0.052 ± 0.007	0.106 ± 0.008
Ammonium (μg/ml)	----	(1.0)
Calcium (μg/ml)	0.014 ± 0.003	0.049 ± 0.011
Magnesium (μg/ml)	0.024 ± 0.002	0.051 ± 0.001

Table 3-1 (continued)

Summary of Quality Control Standards

(II) Environmental Resource Associates WasteWatR Quality Control Standards

Constituent Elements/ Parameters	Lot No. 9927 ERA Certified	Advisory Range
MINERALS WasteWatR™		
Total solids at 105°C (μg/ml)	1270	1140-1400
Dissolved solids at 180°C (μg/ml)	1270	1140-1400
Conductivity at 25°C (micromhos)	1650	1490-1810
Alkalinity (μg/ml)	157	144-160
Chloride (μg/ml)	243	224-262
Fluoride (μg/ml)	13.5	11.6-15.4
Sulfate (μg/ml)	249	224-274
Potassium (μg/ml)	230	207-253
Sodium (μg/ml)	230	207-253
pH	9.1	8.9-9.3
NUTRIENTS WasteWatR™		
Ammonia as N (μg/ml)	7.9	6.9-8.9
Nitrate as N (μg/ml)	10.4	9.4-11.4
Phosphate as P (μg/ml)	4.0	3.6-4.4
COMBINED MIXED STANDARDS		
Chloride, Nitrate, Sulfate (μg/ml)	100.0	
Fluoride, Bromide, Phosphate (μg/ml)	100.0	

Table 3-1 (continued)

Summary of Quality Control Standards

(III) Alltech Associates, Inc. Quality Control Standards

Constituent Elements	Lot No.	Certified Value
Chloride (μg/ml)	3200	200.0
Nitrite (μg/ml)	1101	200.0
Nitrate (μg/ml)	1081	200.0
Sulfate (μg/ml)	2107	200.0

[a] The certified values are based on proven reliable methods of analysis. the estimated uncertainties are 2 standard deviations of the certified values except for uncertainties associated with sulfate, acidity, pH, and specific conductance which are based on scientific judgement and are roughly equivalent to 2 standard deviations of the certified value.

[b] Note: The nitrate value for 2694-I is not certified because of instability. it is believed that bacterial or fungal activity contributes to that instability.

Quality control standards are prepared from ERA stocks (100 µg/ml of chloride, nitrate and sulfate, and/or 100 µg/ml fluoride, phosphate and bromide) or from the Alltech stocks (individual standards of chloride, nitrite, nitrate and sulfate at 200 µg/ml) in the concentrations of 1.00 µg/ml and 0.100 µg/ml as follows:

- Prepare a secondary stock solution at 10 µg/ml by diluting the ERA stock solution 1:10 or the Alltech stock solution 1:20. Using a class A pipet, pipet 10.0 ml ERA stock into a 100 ml volumetric flask and bring to volume with DDW. Using a class A pipet, pipet 5.0 ml Alltech stock into a 100 ml volumetric flask and bring to volume with DDW.
- 1.00 µg/ml QC, ERA or Alltech:

  Using a 10.0 ml class A pipet, pipet 10..00 ml of the 10 µg/ml secondary stock into a 100.00 ml volumetric flask. Bring to volume with DDW and mix thoroughly.

- 0.100 µg/ml QC, ERA or Alltech:

  Using a class A pipet, pipet 1.0 ml of the 10 µg/ml secondary stock solution into a 100 ml volumetric flask and bring to volume with DDW.

- ERA Minerals WasteWatR standard is used as a quality control check for routine analysis of chloride and sulfate. To get the concentrations of anions in range, dilute the Minerals standard 1:500 by pipetting 1.0 ml ERA Minerals WasteWatR stock solution using a class A pipet into a 500 ml volumetric flask. Fill to volume with DDW and mix thoroughly.

- ERA Nutrients WasteWatR standard is used for routine analysis of nitrate and phosphate. To get the concentrations of anions in range, dilute the Nutrients WasteWatR as instructed then dilute further 1:100 by pipetting 1.0 ml, using a class A pipet, into a 100 ml volumetric flask. Fill to volume with DDW and mix thoroughly.

3.2.2 NIST Quality Control standards:

- NIST 2694I simulated rainwater is used as a quality control for the sulfur dioxide analysis. To get the concentration of sulfate into range, dilute the NIST 2694I simulated rainwater 1:5 directly in a sample vial by pipetting 0.500 ml DDW four times into a sample vial with a 0.500 ml Eppendorf pipet. Then pipet 0.500 ml NBS 2694I into the same vial and mix well.

- NIST simulated rainwater 2694II is used as another quality control check for routine anion analysis. To get the concentrations of anions in range, dilute the NIST 2694II simulated rainwater 1:10 by pipetting directly into the sample vial, 0.200 ml DDW into the sample vial nine times with the Eppendorf pipet, then pipetting 0.200 ml NIST 2694II into the same vial and mixing well.

3.3 The Accuracy of Calibration Standards

The accuracy of calibration standards is primarily limited by the uncertainties or variabilities of the standard solution preparation and is typically within ±10%.

4.0 PROCEDURES

4.1 General Flow Diagram for the 2020i and 4000i system.

Figure 4-1 describes the general flow diagram for filter chain-of-custody, chemical analysis and data processing/validation. Figure 4-2 shows an example of DRI's analysis list. Figure 4-3 describes the general flow diagram of the routine ion chromatography analysis. It starts with the initial chromatography adjustment and analysis parameter set up. The samples and replicates are analyzed after the calibration curve is established.

4.2 Start-Up for the 2020i instrument.

Systems 1 and 2 are independent, so each must be started up individually. During routine daily operation, the instrument is left on, so start-up procedures are minimal. If the instrument has been turned off and the columns removed, the columns must be reconnected and purged with eluent and the system observed to be stable for 15 minutes before samples are analyzed.

4.2.1 Start-up (assuming the instrument has been turned off)

- Turn on the power to the instrument by pressing the power switch.

- Turn the Eluant Degas Module power on. Eluent reservoir switches should be set to pressurize, with the pressure set at 7 psi. On the 2020i Dionex, System 1 uses eluent switch 1,

Figure 4-1. General Sample Chain-of-Custody Flow Diagram.

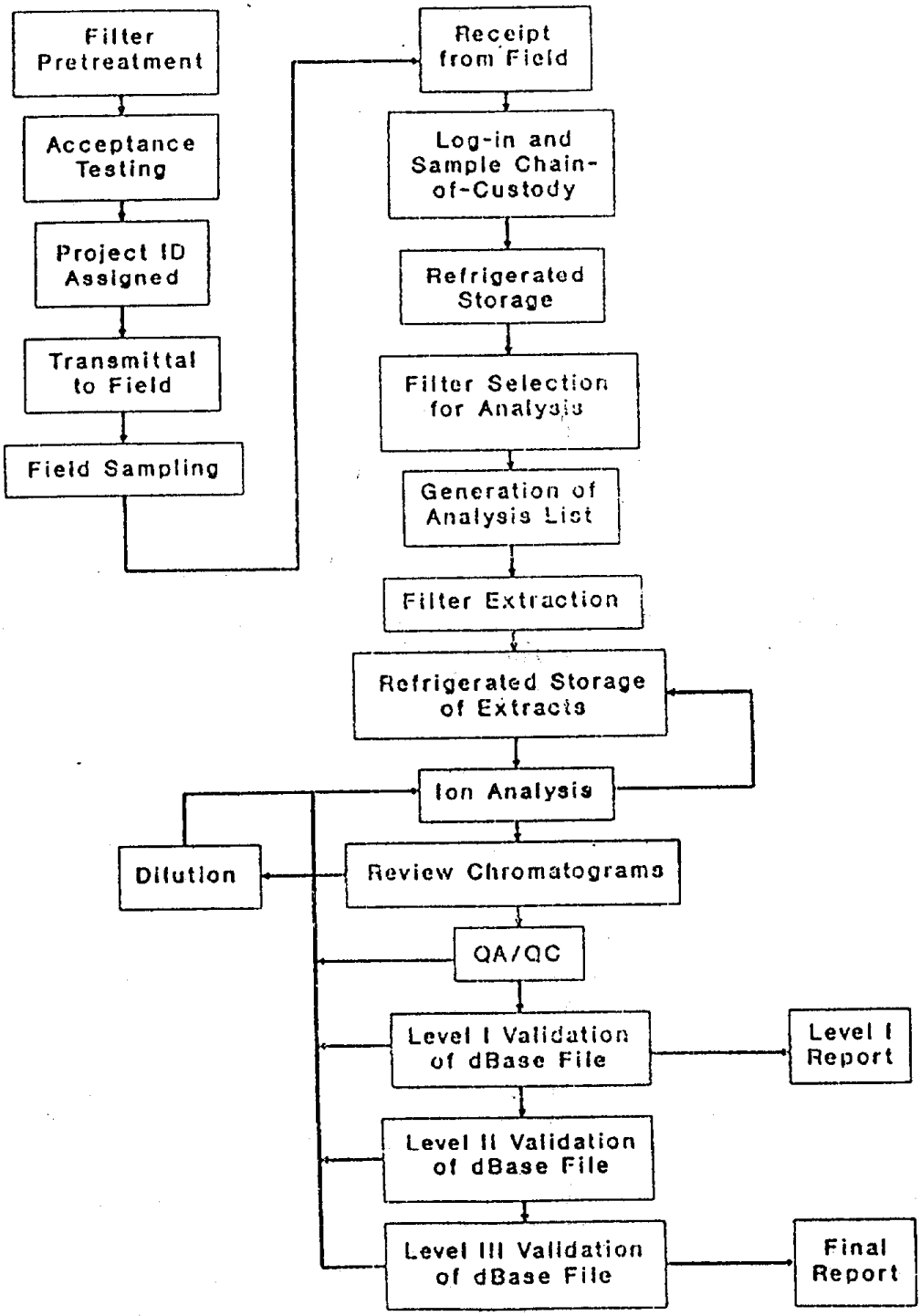


Figure 4-2. Example of DRI Ion Chromatography Analysis List.

Santa Barbara Quartz Samples: 3rd Quarter
****

Date: 10/12/89
From: L.Pritchett
To : J.Chow
J.Watson
C.Frazier
S.Chandra
B.Price

Total number of samples: 92
Species to be analyzed:
NO_3^-, $SO_4^=$ by AC

Instructions:

1. This list includes the filters designated for analysis from the third quarter of sampling for the Santa Barbara project.

2. The deposit area is 13.8 cm^2 for the 47 mm quartz filters.

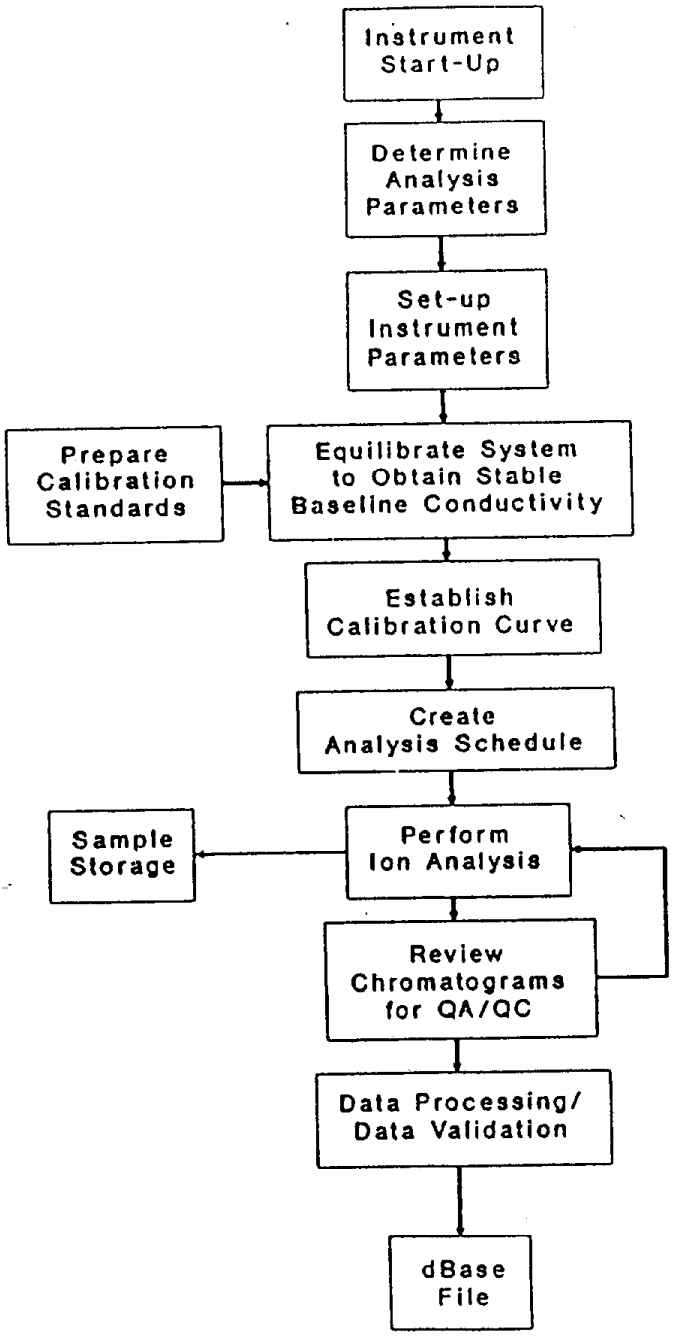
3. Filter halves will be extracted in 15 ml DDW for 1 hour and allowed to sit overnight before analyzing. Extraction will be performed Monday, October 16.

4. IC analysis for NO_3^- and $SO_4^=$ will begin Tuesday, Oct. 18, and data entry and validation will be completed by Friday, Oct. 27.

5. dBase file name conventions will be:
IC data : SAAF03A.DBF

Filter	Description	$NO_3^-/SO_4^=$
AQ6027	Ambient	Y ____
AQ6028	Ambient	Y ____
AQ6029	Ambient	Y ____
AQ6030	Field blank	Y ____
AQ6031	Ambient	Y ____
AQ6032	Ambient	Y ____
AQ6033	Ambient	Y ____
AQ6034	Ambient	Y ____
AQ6035	Ambient	Y ____
AQ6036	Ambient	Y ____
AQ6037	Ambient	Y ____

Figure 4-3. General Flow Diagram for Ion Chromatographic Analysis.



while System 2 uses eluent switch 4. On the 4000i Dionex, the switches correspond to the eluent reservoirs you wish to use.

Reconnect the columns if they were removed for storage (follow the Dionex manual which is included in each new column purchased). Pump eluent for a few minutes through the columns before connecting the columns to the micro-membrane suppressors. This can be done by manually selecting a flow rate of 2.0 ml/minute at the pump module. After the column is fully connected, allow the system to equilibrate as outlined below.

4.2.2 Initial Chromatograph Adjustment--Daily Operation

- Check all reservoir levels.

  Dionex 2020i Systems:

  Generally, Systems 1 and 2 on the Dionex 2020i are used for the same analysis, depending on the project. The eluent for routine anion analysis is 0.0017 M sodium bicarbonate and 0.0035 M sodium carbonate. The eluent for sulfur dioxide analysis is 0.0025 M sodium carbonate and 0.0030M sodium bicarbonate. A minimum of 3 liters of eluent is required for analyses which will take 24 hours. The sulfuric acid regenerate (0.0125 M) requires 4 liters for a whole 24 hour day of analysis.

  Dionex 4000i System:

  The 0.01 M sodium bicarbonate and the 0.01M sodium carbonate reservoirs each should have at least 2 liters of eluent solution for 24 hours of analysis.

  If the waste reservoir is half full, neutralize the contents of the waste reservoir with solid baking soda ($NaHCO_3$) by adding small amounts to the waste reservoir and swirling to dissolve, use pH paper to determine neutrality and empty into sink.

- Get the calibration working standards out of refrigerator, or prepare if the quantities are too low.

- Make sure all components of the IC instrument are in "remote."

- Turn on computer if necessary. The computer is generally left on, except during periods when analyses are not done for several days. The main menu of the AI-450 software will appear after the computer has booted (Figure 4-4). To allow the IC instrument to equilibrate, load the method for the analysis to be performed on that day by selecting (using the mouse) the "run icon" from the main menu, select the method to be used as follows:

  (If the computer is at some spot other than the main menu, the main menu can be retrieved by double clicking on the close box in the upper left hand corner.)

  (1) 2020i Systems:

  Double click on "run icon"
  Click on "load"
  Click on "method"
  Highlight "Anion1.met" (or the method to be used)
  Click on "Open"

  Anion1.met is used for routine anions analysis on System 1; Anion2.met is the corresponding method for System 2 on the Dionex 2020i.

  (2) 4000i System:

  The procedure for loading the method is the same; however, because it is only a single channel system, only one method can be selected at a time.

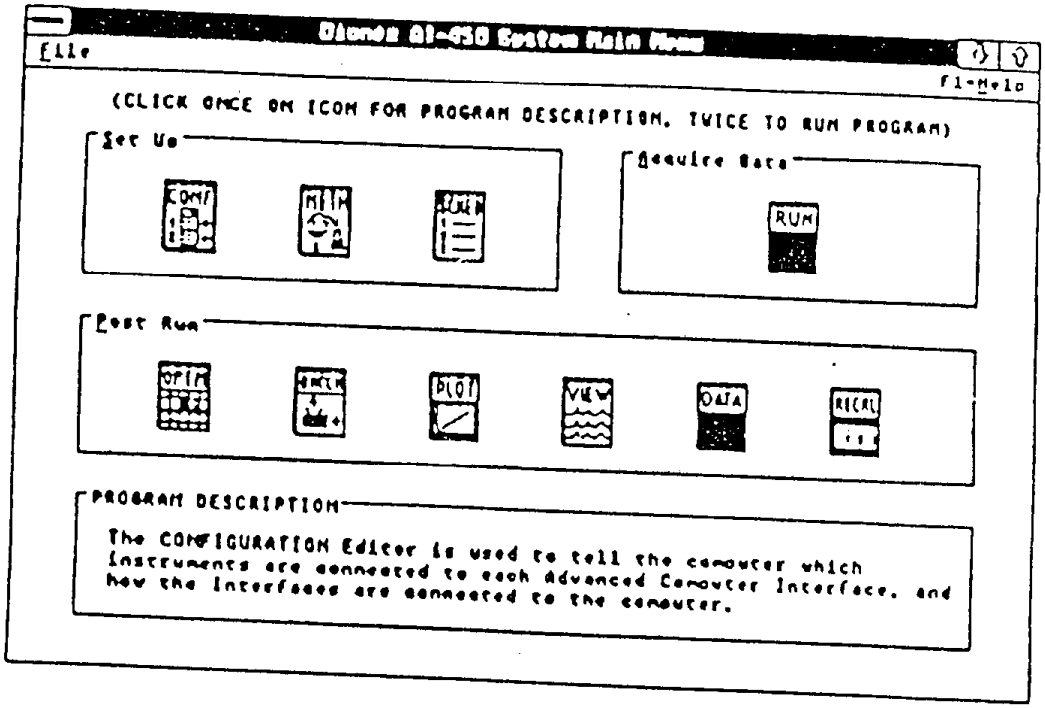
  Either 2020i or 4000i System:

  Type the data file name requested by clicking at the data file box, back spacing until any former names are removed, and typing "dateproj" where "dateproj" is the date of analysis (4 characters) and the 4 character abbreviation of the project.

  The other options at this window are selected by the method and do not need to be changed: For System 1, the ACI is 1, System is 1, System name is Anion 1, no sample name, Data file (as selected).

- Allow the eluents to pump for approximately one half hour until the conductivity stabilizes at about 15.0 to 21.0 μS.

Figure 4-4. Dionex Ion Chromatography AI-450 Software: Program Menu.



If the conductivity is way off, the regenerant solution was probably made up incorrectly. Pump malfunction also causes conductivity problems.

- While the IC instrument is stabilizing, and if data are to be transferred from the hard disk to a floppy, format a new datadisc by inserting the new disk into the floppy drive and proceeding as follows, using the "mouse" to select options:

  Double click on the "program manager" (at the bottom of the main menu screen)
  Double click on "main"
  Double click on "file manager"
  Click on "disk" and choose "format diskette"
  click on "format" and "ok"

  After the computer is done formatting, put the window back down into the "icon" as follows:

  Close File Manager by double clicking on upper left hand box the "ok".
  Single click on the "down arrow" in the upper right hand corner.

- Data are transferred after each night's run to save disk space on the hard drive. While the instrument is stabilizing, the folder for the previous day's analyses can be assembled, calibration standards made if necessary, samples loaded into autosampler vials, etc.
- The methods for analysis are stored in the "Method editor."

  - Figures 4-5a and 4-5b list the method parameters for anion ion chromatographic analysis on system 1 and system 2, respectively.

4.3 Routine Operation

4.3.1 Analysis of Standards

- Standard schedules called Std1.sch and Std2.sch have been created. These are used to run the calibration curves at the beginning of the week for each system. This curve is then used for the rest of the week.

Figure 4-5a. List of Dionex Method Parameters for Anion Chromatographic Analysis on System 1 (ANION1.MET).

DIONEX METHOD PARAMETERS - ANION1.MET

System Parameters

System Name : ANION1
Number of Detectors..... 1
Detector 1 Type..... Conc
Detector 1 real time plot scale (nS)..... 10000.00
Run Time (minutes)..... 8.0
Sampling Rate (seconds)..... 0.1

-- DETECTOR 1 PARAMETERS --

Report Options

Save Data File..... Yes
Data File Name: C:\DI\DATA\020SAU11.DS7
Create ASCII Report File..... No
Print Report..... Yes
List Peaks Not Found in this run..... No
Report Unknowns Found in this run..... Yes
Print Chromatogram..... Yes
AutoScale Chromatogram to Highest Peak..... No
Fill Peaks with Color ..... No
Draw Grid Lines on Chromatogram..... No
Label with Peak Number..... No
Label with Retention Times on Chromatogram..... Yes
Label with Component Name..... No
Format File Name: c:\dx\method\default.prf

Integration Parameters

Starting Peak Width (seconds)..... 10.0
Peak Threshold (mV or uS/data pt interval)..... 200.000
Peak Area Reject..... 100
Area Reject for Reference Peaks..... 100
Percent Retention Time Window for Reference Peaks..... 10.0

Data Events

Time	Description
0.00	Start peak detection
0.90	Void volume treatment for this peak
1.50	Force baseline at start of all peaks
6.50	Stop peak detection

Calibration Parameters

Number Of Levels for Calibration..... 6
Calibration Fit Type..... Linear
Replace Or Average Calibrations..... Replace
External or Internal Calibration..... External
Calibrate by Area or Height..... Area
Default Injection Volume..... 1.0
Default Dilution Factor..... 1.0
Response Factor for Unknown Peaks..... 0.0
Calibration Standard Volume 1.0
Internal Standard Volume 1.0

Figure 4-5a (cont). List of Dionex Method Parameters for Anion Chromatographic Analysis on System 1 (ANION1.MET).

Component # 1 CHLORIDE Retention Time [illegible]
Reference Peak CHLORIDE Window Size [illegible]
Amount = K0 + K1*Area
K0 = 2.94419E-002
K1 = 1.30789E-008

Level	Amount	Area	Height
1	[illegible]	[illegible]	0
2	1.01300E-001	[illegible]	0
3	[illegible]	[illegible]	0
4	5.09500E-001	[illegible]	0
5	1.01900E+000	[illegible]	0
6	2.03800E+000	154985720	0

Component # 2 NITRITE Retention Time 1.75
Reference Peak NITRITE Window Size 5.00%
Amount = K0 + K1*Area
K0 = 1.96667E-002
K1 = 2.25139E-008

Level	Amount	Area	Height
1	0.00000E+000	0	0
2	1.03800E-001	3635617	0
3	2.07600E-001	8018186	0
4	5.19000E-001	21646352	0
5	1.03800E+000	45094957	0
6	2.07600E+000	91562028	0

Component # 3 NITRATE Retention Time 2.87
Reference Peak NITRATE Window Size 10.00%
Amount = K0 + K1*Area
K0 = 2.11179E-002
K1 = 2.47803E-008

Level	Amount	Area	Height
1	0.00000E+000	0	0
2	1.05300E-001	3681860	0
3	2.10600E-001	7680986	0
4	5.26500E-001	19614713	0
5	1.05300E+000	40574280	0
6	2.10600E+000	84809947	0

Component # 4 SULFATE Retention Time 4.07
Reference Peak SULFATE Window Size 10.00%
Amount = K0 + K1*Area
K0 = 1.41290E-002
K1 = 1.91535E-008

Level	Amount	Area	Height
1	0.00000E+000	0	0
2	9.64000E-002	4776505	0
3	1.92800E-001	9444000	0
4	4.82000E-001	23442111	0
5	9.64000E-001	48539665	0
6	1.92800E+000	100626465	0

Figure 4-5a (cont). List of Dionex Method Parameters for Anion Chromatographic Analysis on System 1 (ANION1.MET).

Timed Events File: C:\DX\METHOD\ANION1.TE

Step	Time	Description
Init		AFM Flow = 2.0 mL/min
Init		Eluant 1 ON
Init		Eluant 2 OFF
Init		Eluant 3 OFF
Init		Eluant 4 OFF
Init		Eluant 5 OFF
Init		Eluant 6 OFF
Init		CDM-2 AutoOffset Off
Init		CDM-2 Recorder Mark OFF
Init		CDM-2 Temp. Comp. = 1.7 / Deg C
Init		CDM-2 Recorder Range = 30.00 uS
Init		CDM-2 Cell ON
Init		CHA Heater = 25 Deg. C
Init		Valve A OFF
Init		Valve B ON
Init		Inject Valve OFF
Init		ACI Autosmp OFF
Init		ACI RLY 2 OFF
Init		ACI TTL 1 OFF
Init		ACI TTL 2 OFF
Init		ACI Regen OFF
1	0.0	ACI Autosmp ON
2	0.1	ACI Autosmp OFF
3	2.4	CDM-2 AutoOffset ON
4	2.5	Inject Valve ON
4	2.5	Start Sampling
5	7.5	CDM-2 AutoOffset Off
5	7.5	Inject Valve OFF

Figure 4-5b. List of Dionex Method Parameters for Anion Chromatographic Analysis on System 2 (ANION2.MET).

DIONEX METHOD PARAMETERS - ANION2.MET

System Parameters

System Name : ANION2	
Number of Detectors.....	1
Detector 1 Type.....	CDM-2
Detector 1 real time plot scale (nS).....	10000.00
Run Time (minutes).....	5.00
Sampling Rate (seconds).....	0.10

-- DETECTOR 1 PARAMETERS --

Report Options

Save Data File.....	yes
Data File Name: C:\DX\DATA\DATA.D01	
Create ASCII Report File.....	No
Print Report.....	yes
List Peaks Not Found in this run.....	No
Report Unknowns Found in this run.....	yes
Print Chromatogram.....	yes
AutoScale Chromatogram to Highest Peak.....	No
Fill Peaks with Color	No
Draw Grid Lines on Chromatogram.....	No
Label with Peak Number.....	No
Label with Retention Times on Chromatogram.....	Yes
Label with Component Name.....	No
Format File Name: c:\dx\method\default.prf	

Integration Parameters

Starting Peak Width (seconds).....	10.0
Peak Threshold (mV or uS/data pt interval).....	200.000
Peak Area Reject.....	100
Area Reject for Reference Peaks.....	100
Percent Retention Time Window for Reference Peaks.....	5.0

Data Events

Time	Description
0.00	Start peak detection
0.90	Void volume treatment for this peak
1.50	Force baseline at start of all peaks
9.00	Stop peak detection

Calibration Parameters

Number Of Levels for Calibration.....	6
Calibration Fit Type.....	Linear
Replace Or Average Calibrations.....	Replace
External or Internal Calibration.....	External
Calibrate by Area or Height.....	Area
Default Injection Volume.....	1.0
Default Dilution Factor.....	1.0
Response Factor for Unknown Peaks.....	0.0
Calibration Standard Volume	1.0
Internal Standard Volume	1.0
Sample Unit	

Figure 4-5b (cont). List of Dionex Method Parameters for Anion Chromatographic Analysis on System 2 (ANION2.MET).

Component # 1 CHLORIDE
Reference Peak CHLORIDE
Amount = K0 + K1*Area
K0 = 3.61924E-002
K1 = 1.70157E-008

Retention Time 1.48
Window Size 5.00%

Level	Amount	Area	Height
1	0.00000E+000	0	0
2	1.01900E-001	4402125	0
3	2.03800E-001	9689496	0
4	5.09500E-001	26745448	0
5	1.01900E+000	54679450	0
6	2.03800E+000	119293040	0

Component # 2 NITRITE
Reference Peak NITRITE
Amount = K0 + K1*Area
K0 = 2.95532E-002
K1 = 2.79988E-008

Retention Time 1.72
Window Size 5.00%

Level	Amount	Area	Height
1	0.00000E+000	0	0
2	1.03800E-001	2945219	0
3	2.07600E-001	6254749	0
4	5.19000E-001	16666489	0
5	1.03800E+000	34859613	0
6	2.07600E+000	73818457	0

Component # 3 NITRATE
Reference Peak NITRATE
Amount = K0 + K1*Area
K0 = 2.26980E-002
K1 = 3.14933E-008

Retention Time 2.72
Window Size 10.00%

Level	Amount	Area	Height
1	0.00000E+000	0	0
2	1.05300E-001	2749014	0
3	2.10600E-001	6004049	0
4	5.26500E-001	15435186	0
5	1.05300E+000	31864325	0
6	2.10600E+000	66678523	0

Component # 4 SULFATE
Reference Peak SULFATE
Amount = K0 + K1*Area
K0 = 1.64130E-002
K1 = 2.41038E-008

Retention Time 3.83
Window Size 10.00%

Level	Amount	Area	Height
1	0.00000E+000	0	0
2	9.64000E-002	2740922	0
3	1.92800E-001	7409339	0
4	4.82000E-001	19478748	0
5	9.64000E-001	38308792	0
6	1.92800E+000	79952945	0

Figure 4-5b (cont). List of Dionex Method Parameters for Anion Chromatographic Analysis on System 2 (ANION2.MET).

Timed Events File: C:\DX\METHOD\ANION2.TE

Step	Time	Description
Init		APM Flow = 2.0 mL/min
Init		Eluant 1 ON
Init		Eluant 2 OFF
Init		Eluant 3 OFF
Init		Eluant 4 OFF
Init		Eluant 5 OFF
Init		Eluant 6 OFF
Init		CDM-2 AutoOffset Off
Init		CDM-2 Recorder Mark OFF
Init		CDM-2 Temp. Comp. = 1.7 / Deg C
Init		CDM-2 Recorder Range = 30.00 uS
Init		CDM-2 Cell ON
Init		CHA Heater = 25 Deg. C
Init		Valve A OFF
Init		Valve B ON
Init		Inject Valve OFF
Init		ACI Autosmp OFF
Init		ACI RLY 4 OFF
Init		ACI TTL 3 OFF
Init		ACI TTL 4 OFF
Init		ACI AC 2 OFF
1	0.0	ACI Autosmp ON
2	0.1	ACI Autosmp OFF
3	2.4	CDM-2 AutoOffset ON
4	2.5	Inject Valve ON
4	2.5	Start Sampling
5	7.5	CDM-2 AutoOffset Off
5	7.5	Inject Valve OFF

- The standards are run in the following order:
  1. Blank
  2. Std-0.1 μg/ml
  3. Std-0.2 μg/ml
  4. Std-0.5 μg/ml
  5. Std-1.0 μg/ml
  6. Std-2.0 μg/ml

- Load the schedule into the "Run.exe" program using the "mouse" as follows:

  Double click on the "run icon" from the "main menu".
  Click on "load"
  Click on "schedule"
  Highlight the schedule to be used by clicking on the schedule of interest
  Click on "open".

  At the next window, the "ACI address", "system" and "system name" as in the schedule appear. These are left unchanged. The "number of loops" is one (1), the default value.
  Since the "Start Inj # 1" remains at 1 at this point,
  Click on "OK".

- Fill sample vials with 2 ml of sample, referring to the marked sample vial for the approximate level. Put on the vial filter cap by inserting the cap gently into the tube with the narrow part up. Push the filter cap into the tube using the filter cap insertion tool provided.

  First, push down with the narrow part of the cap inserted into the hole in the tool. After the tool is pushed down to the top of the vial, reverse the tool to the flat side and push the cap into the tube until the narrow part is flush with the top of the tube. Load the vials into the sample cassettes, 6 per cassette, such that the white dot is to the right. The sample next to the white dot is sampled first. Place the cassettes into the autosampler by sliding the "spring loaded cassette pusher" back and inserting the cassette into the autosampler tray with the white dot to the right.

- Set the autosampler controls as follows:
  Local
  Run
  Type = Loop
  Mode = Prop (proportional)

Bleed = On
Inj/vial = 1 (one injection/vial).
Other lights are indicators and cannot be selected.

- Start the run from the computer using the "mouse" as follows:
  Click on "Run"
  Click on "Start"
  Click on "OK".

  The autosampler bleeds off the first 2.5 ml volume (air), then slowly injects the rest of the sample. It takes approximately 2 minutes for the probe to go all the way down.

4.3.2 Calibration

The areas of the analyte peaks are generated in the standard calibration run (Figure 4-6). These data must then be entered into the CalPlot calibration program so they can be used to convert areas to concentrations (entered in μg/ml) on the sample chromatograms. This is done only when a new calibration curve is to be used, or new standards are made up. A curve is good for one week, so if the QC samples give acceptable results, the curve does not need to be changed.

- To enter a new curve into the CalPlot program, close the Run.Exe as follows:

  Double click on the box in the upper left hand corner of the "run" window. This brings up the "main menu".
  Double click on the "CalPlot icon" from the main menu.
  Click on "File"
  Click on "Open Method"
  Highlight the method to be updated by clicking on that file from the list
  Click on "Open" to retrieve the file
  Click on "Edit" from the active menu bar at the top of the window
  Click on "calibration". Check that it is on level 6, if not choose level 6.
  Click on "ok".
  Click on "Edit" again and choose "component table".

  Select the desired component as follows:

  Using the mouse highlight the component name that you want to update the area counts. (The components in the

Figure 4-6. Example of Ion Chromatogram for Calibration Standard at 0.5 ug/ml.

Sample Name: STD-0.5_UG/ML
Data File : C:\DX\DATA\STDTE111.D28
Method : C:\DX\METHOD\ANION1.met
ACI Address: 1 System : 1 Inject#: 28 Detector: CDM-2
Date: Sun Jun 30 16:30:18 1991

EPORT	VOLUME	DILUTION	POINTS	RATE	START	STOP	AREA	REJ
xternal	1	1	3910	10Hz	0.00	6.52		100

?k. Num	Ret Time	Component Name	Concentration	Height	Area	Bl. Code	%Delta
1	2.02	CHLORIDE	0.509	11637107	51440626	1	0.00
2	2.33	NITRITE	0.503	5231611	30184349	1	0.00
3	3.80	NITRATE	0.499	3182255	26201062	1	0.00
4	5.58	SULFATE	0.506	2716991	31963577	1	0.00

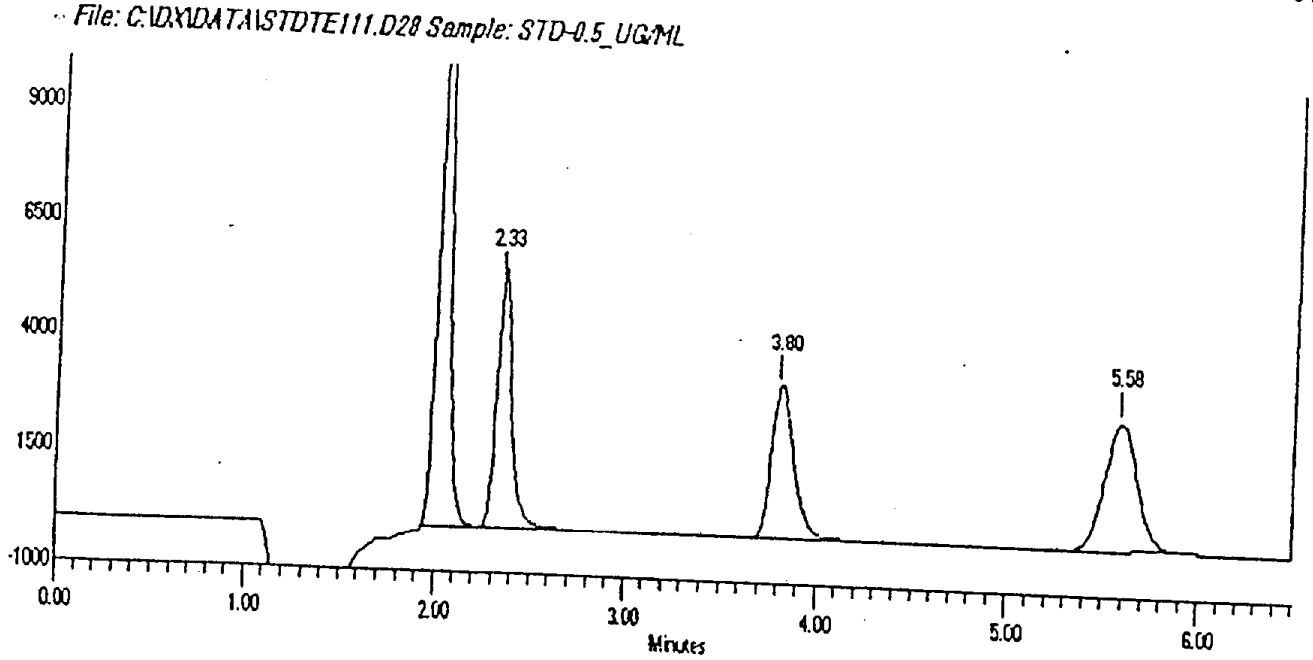


table are entered in the order of their elution, for example: chloride, nitrite, nitrate and sulfate).

Click on the end of desired area count and backspace to erase the number.

Enter the new area count.

For each anion of the analysis, enter the 6 data points corresponding to the 6 concentrations of the calibration standards. The retention times are also entered in the component table, with a range in retention time given as a percentage (i.e., 1.68 minutes ± 5%). Generally these retention times and ranges do not change, although the area counts do. If the retention times do change significantly, there may be a problem with the eluent if new eluent was used or the column is deteriorating. Adjust the retention time in the component table or if peak shapes or resolution of peaks changes too much replace both the guard column and the separator column.

- When all 6 calibration data points for the analyte have been entered, close the component table editor as follows:
  Click on "enter".

- Go to the next component and repeat the procedure for the rest of the components. When all components have new area counts close the component table by clicking on "exit".

- The equations for the curves are shown on the plots of the curves (Figure 4-7). Access different calibration curves as follows:

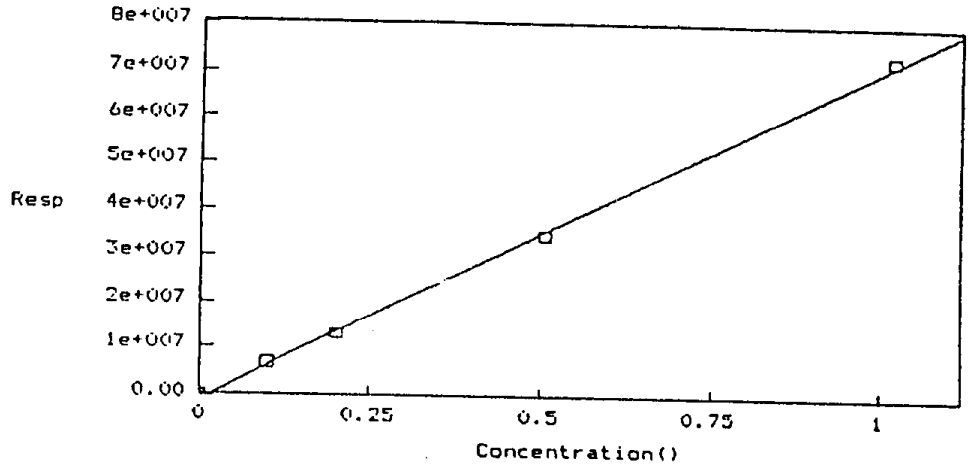
  Click on the scroll arrows at the bottom of the window.
  The window can be expanded to full screen as follows:
  Click on the up arrow (↑) in the upper right hand corner of the window. This may be necessary to bring the scroll arrows at the bottom of the window into view.

- Save the 6 point curve to the method as follows:

  Click on "file" from the active menu bar at the top of the window Click on "Save Method As ..."
  Check the name of the method listed in the window to make sure it is correct (name of method opened)
  Click on "OK"

Figure 4-7a. Examples of Dionex Ion Chromatography Calibration Curves.

Method: ANION1.MET
Component: CHLORIDE
Fit Type: Linear
r^2: 0.998982
Conc = Resp * 1.388e-008 + 0.01228
Resp = Conc * 7.202e+007 + -8.842e+005
Standardization: External
Calibration: Area



Method: ANION1.MET
Component: NITRITE
Fit Type: Linear
r^2: 0.999381
Conc = Resp * 2.269e-008 + 0.01272
Resp = Conc * 4.408e+007 + -5.607e+005
Standardization: External
Calibration: Area

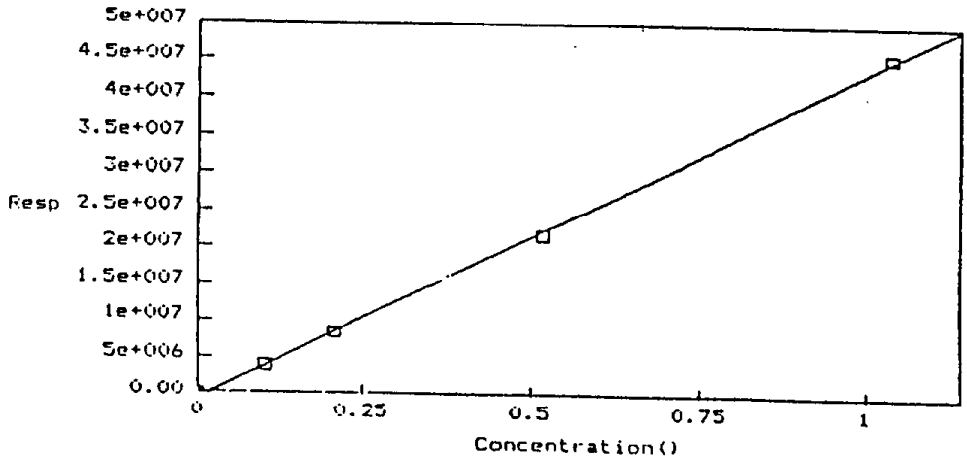
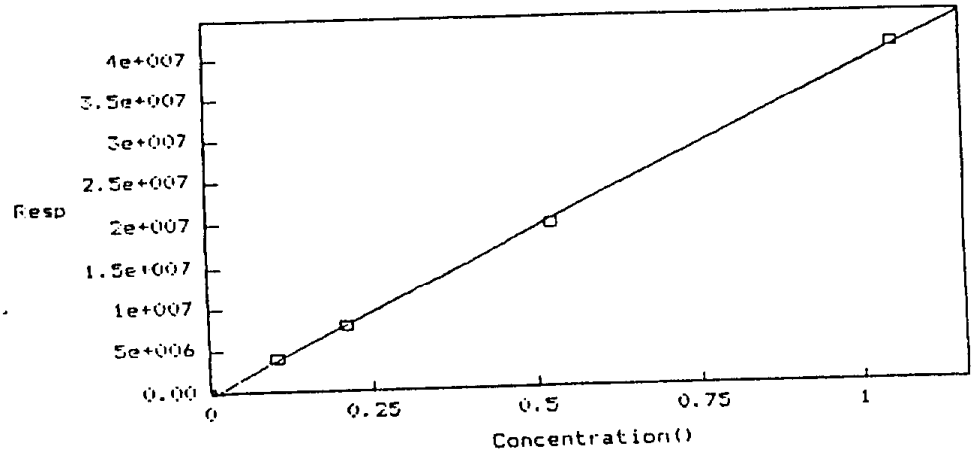
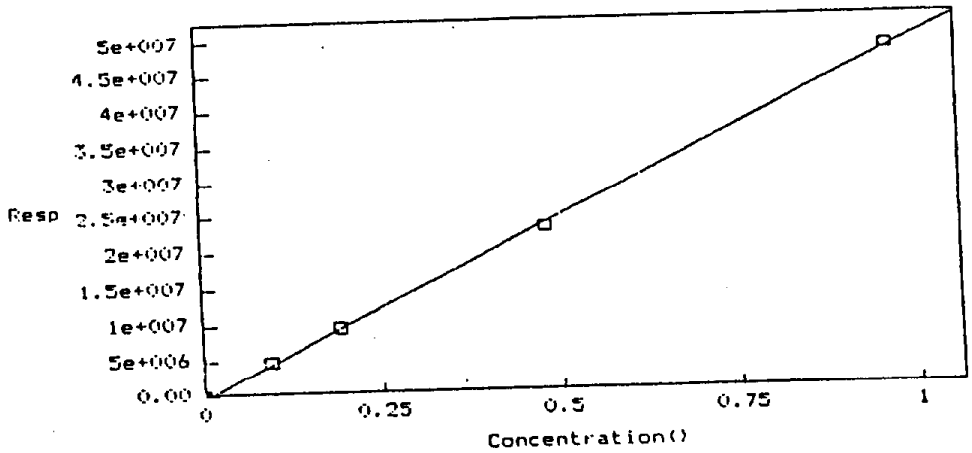


Figure 4-7b. Examples of Dionex Ion Chromatography Calibration Curves.

Method: ANION1.MET
Component: NITRATE
Fit Type: Linear
r^2: 0.999510
Conc = Resp * 2.594e-008 + 0.00767
Resp = Conc * 3.856e+007 + -2.957e+005
Standardization: External
Calibration: Area



Method: ANION1.MET
Component: SULFATE
Fit Type: Linear
r^2: 0.999482
Conc = Resp * 2.01e-008 + 0.006733
Resp = Conc * 4.976e+007 + -3.35e+005
Standardization: External
Calibration: Area



- Print out the 6 point calibration curve as follows:

  Click on "File"
  Click on "Print"
  Select any print options desired by clicking on the circle in front of the option. A darkened circle means the option has been selected. This is usually "all components" and "half page".
  Click on "OK" when the print options are correct.

- After printing out the 6 point curves, click on "edit" then click on "calibration". Change the 6 point curve to a 5 point curve. Check the calculated values of the standards used for the calibration curves as follows:

  Click on "Edit" from the active menu bar
  Click on "calculator"
  Click on the individual areas from the table at the right side of the window ("Level Response")

  The concentration from the 5 point calibration curve will be calculated and appear in the field "Concentration". Check that the percent difference of the calculated result versus the known value is within ±10%. To access different anions, select the appropriate arrow on the scroll bar at the bottom of the plot window behind the calculate window. Click again on the box on the bottom scroll bar to change the areas to match the component.

- Save the 5 point curve to the Method as described previously and print out the calibration curves.

- Print out the areas used to generate the curve as follows:

  Double click on the box in the upper left hand corner to close "CalPlot". This will return to the "main menu".
  Double click on the "method icon" from the "main menu"
  Click on "File"
  Click on "Open", highlight the method by clicking on the name
  Click on "Open"
  Click on "Detector 1"
  Click on "Calibration", change to 6 points, click on "ok"
  Click on "Component Table"
  Click on "Print".

Date and initialize the printed table and place in the calibration curve folder.

The six point curve is not accurate enough for lower concentrations. Because the lower concentrations are usually encountered most frequently, a five point calibration curve using only the lower 5 concentrations of the calibration standards is stored to the method for normal analysis. If samples are higher in concentration than 1 μg/ml but less than 2 μg/ml, the results are recalculated using "CalPlot" and the 6 point calibration curve. The regression coefficient should be 0.998 or better, except for chloride, which may be as low as 0.995. For all anions, the slope should be comparable to that of the calibration curve being replaced.

- If the samples require, a calibration curve covering higher ranges can be generated. Only 6 data points can be accommodated in any single calibration curve.

4.3.3 Quality Control

The quality control samples are analyzed at the beginning of each sample run. Quality control samples that have a concentration above 0.150 μg/ml should be within ±10% of the certified value, while the quality control samples that have a concentration of 0.1 μg/ml should be within ±15% of the certified value.

4.4.4 Analysis of Samples

After the calibration curves are generated, a schedule for the sample run is created. Figure 4-8 is an example of a typical sample run schedule.

- Samples are run in groups of 10, followed by a replicate and a standard. After 20 samples, a replicate and a standard, a blank is analyzed. Thus, after the QC entries in the schedule, the sample schedule will have the format:

10 samples
1 replicate
1 standard
10 samples
1 replicate
1 blank
1 standard

Figure 4-8. Example of Dionex Analysis Schedule.

DIONEX SCHEDULE - C:\DX\SCHEDULE\0924PRO1.SCH

Inj#	Sample Name	Method	Data File	Vol.	Dil.	Int.Std.
1	BLANK	..\ANION1.m	..\0924PRO1	1	1	1
2	STD-0.05_UG/ML	..\ANION1.m	..\0924PRO1	1	1	1
3	EPA-0.1_UG/ML	..\ANION1.m	..\0924PRO1	1	1	1
4	EPA-1.0_UG/ML	..\ANION1.m	..\0924PRO1	1	1	1
5	EPA-MINERAL_WW	..\ANION1.m	..\0924PRO1	1	1	1
6	EPA-NUTRIENT_WW	..\ANION1.m	..\0924PRO1	1	1	1
7	SAMPLE 1	..\ANION1.m	..\0924PRO1	1	1	1
8	SAMPLE 2	..\ANION1.m	..\0924PRO1	1	1	1
9	SAMPLE 3	..\ANION1.m	..\0924PRO1	1	1	1
10	SAMPLE 4	..\ANION1.m	..\0924PRO1	1	1	1
11	SAMPLE 5	..\ANION1.m	..\0924PRO1	1	1	1
12	SAMPLE 6	..\ANION1.m	..\0924PRO1	1	1	1
13	SAMPLE 7	..\ANION1.m	..\0924PRO1	1	1	1
14	SAMPLE 8	..\ANION1.m	..\0924PRO1	1	1	1
15	SAMPLE 9	..\ANION1.m	..\0924PRO1	1	1	1
16	SAMPLE 10	..\ANION1.m	..\0924PRO1	1	1	1
17	PREV. DAY REPLICATE	..\ANION1.m	..\0924PRO1	1	1	1
18	STD-0.1_UG/ML	..\ANION1.m	..\0924PRO1	1	1	1
19	SAMPLE 11	..\ANION1.m	..\0924PRO1	1	1	1
20	SAMPLE 12	..\ANION1.m	..\0924PRO1	1	1	1
21	SAMPLE 13	..\ANION1.m	..\0924PRO1	1	1	1
22	SAMPLE 14	..\ANION1.m	..\0924PRO1	1	1	1
23	SAMPLE 15	..\ANION1.m	..\0924PRO1	1	1	1
24	SAMPLE 16	..\ANION1.m	..\0924PRO1	1	1	1
25	SAMPLE 17	..\ANION1.m	..\0924PRO1	1	1	1
26	SAMPLE 18	..\ANION1.m	..\0924PRO1	1	1	1
27	SAMPLE 19	..\ANION1.m	..\0924PRO1	1	1	1
28	SAMPLE 20	..\ANION1.m	..\0924PRO1	1	1	1
29	PREV. DAY REPLICATE	..\ANION1.m	..\0924PRO1	1	1	1
30	BLANK	..\ANION1.m	..\0924PRO1	1	1	1
31	STD-0.2_UG/ML	..\ANION1.m	..\0924PRO1	1	1	1
32	SAMPLE 21	..\ANION1.m	..\0924PRO1	1	1	1
33	SAMPLE 22	..\ANION1.m	..\0924PRO1	1	1	1
34	SAMPLE 23	..\ANION1.m	..\0924PRO1	1	1	1
35	SAMPLE 24	..\ANION1.m	..\0924PRO1	1	1	1
36	SAMPLE 25	..\ANION1.m	..\0924PRO1	1	1	1
37	SAMPLE 26	..\ANION1.m	..\0924PRO1	1	1	1
38	SAMPLE 27	..\ANION1.m	..\0924PRO1	1	1	1
39	SAMPLE 28	..\ANION1.m	..\0924PRO1	1	1	1
40	SAMPLE 29	..\ANION1.m	..\0924PRO1	1	1	1
41	SAMPLE 30	..\ANION1.m	..\0924PRO1	1	1	1
42	PREV. DAY REPLICATE	..\ANION1.m	..\0924PRO1	1	1	1
43	STD-0.5_UG/ML	..\ANION1.m	..\0924PRO1	1	1	1
44	STOP	..\STOP1.me	..\0924PRO1	1	1	1

This pattern repeats until all of the samples have been analyzed. The replicates should be selected from the previous day's samples. If a new analysis set is to be started and there are no previous day replicates to be run, leave out the replicates in the schedule and run replicates the next day.

- To create a schedule from the "main menu" double click on the schedule icon.

- Sample #1 is highlighted, type in "Blank" then press "enter". Using the down arrow key, move to sample #2. Type in the next sample name, "enter", down arrow key, continue to do this until all QC standards, samples and QA standards have been entered. After all sample names have been entered, go to the top of the list using the "page up" key. Using the arrow key move over to the "method" column. Type in "Anion1" or "Anion2" depending on which system you making the schedule for. Using the arrow key move over to the "Data File" column. Type in "DateProjSyst" where date is current date (4 digit), proj is current project abbreviation (2 digit), and system is 1 or 2 with a 1 after it (2 digit); i.e. 0804AZ11 or 0804AZ21. This information needs to be copied to the end of the schedule. To do this:

  Click on "Edit" from the active menu bar
  Click on "Copy"
  Mark only "Method" and "Data File Name" as in Section 4.3.1
  Set the "Source injection" From: 1 To:1
  Set the "Destination injection" From 1 To:"S_{last}"; where "S_{last}" is the injection number of the last sample.

  After the method and data file have been copied, go to the last entry using the "page down" key. The last entry will be the stop entry -- Sample name: Stop, Method name: Stop1.met or Stop2.met, Data file name: same as rest of schedule. This sample will be a DDW blank. The stop method shuts down the system by turning off the eluent valve, the pump, the conductivity cell, and the regenerate valve.

Save the schedule as follows:

  Click on "File" from the active menu bar
  Click on "Save"

Type the name of the file as "dateprojsyst"; following the same convention as above.
Click on "OK".

Print a hard copy of the schedule to use for loading the samples as follows:

Click on "File"
Click on "Print".

Close the "schedule executive" to return to the "main menu" as follows:

Double click on the "close box" in the upper left hand corner of the window.

- Load the schedule into the "Run.Exe" program as follows:

  Double click on the "run icon" from the "main menu"
  Click on "load"
  Click on "schedule", highlight the schedule to be used by clicking on it
  Click on "open"
  Click on "ok"

- After the schedule is loaded, load the samples into the auto sampler vials according to the schedule. Use the procedure outlined in 4.3.1 above.

- Put the autosampler in run mode, check all reservoirs. Start the run from the computer as follows:

  Click on "run" from the active menu bar
  Click on "start"
  Click on "OK".

  Check to see that the first sample has been injected.

- If the run needs to be interrupted for some reason, before the chromatogram of a sample finishes do the following:

  Click on "run" from the active menu bar
  Click on "End".
  Choose which system to end. Click on "ok"

  Leave the auto sampler in the run mode.

To begin sampling again, reload the schedule and select the start injection number desired. Start the analysis from the computer as follows:

Click on "Run"
Click on "Start"
Click on "OK".

4.5 Shut-Down

4.5.1 Routine Instrument Shut-Down

Under routine operation, the instrument is used daily with a run that goes overnight. In this case, the instrument power is left on, but the pumps, E1 valves, conductivity cells, and B valves are turned off by the stop methods.

4.5.2 Long Term Shut-Down (longer than two days)

For long term shut-down turn the main power off. This is the blue "power" button on the front of the instrument. Turn the eluent degas module off. On the computer, close all .exe files by clicking once on the icon and choosing "close". When only the main menu and the program manager icon remain, double click on the box in the top left hand corner of the main menu. It will ask if you really want to leave AI-450, click on "yes". Double click on the program manager icon to open and do the same. It will tell you that this will end you "windows session", save changes, click on "ok".

Then, turn off the power to the computer by pressing the Master switch on the power director.

- If the system is to be shut down for more than one week, the column should be disconnected from the conductivity module and sodium hydroxide (0.1 M) should be pumped through the column for a few minutes to drive off the eluent. The column is then capped on both ends with the plugs provided with the column. Refer to the Installation Instructions and Troubleshooting Guide provided with the column.

5.0 CALCULATIONS AND COMPUTER ENTRY

5.1 Calibration

Calibration is performed by the instrument computer using the "CalPlot" program, as outlined in section 4.3.2.

5.2 Calculation of Concentrations in the Extraction Solution

The peaks in the chromatograms are identified and area counts are converted to concentrations in µg/ml directly on the print out of the chromatogram. An example of a typical ion chromatogram for ambient samples is illustrated in Figure 5-1. Area counts that are above those of the highest standard on the calibration curve stored to the method (5 point calibration curve) can be calculated using a different calibration curve that extends to a higher concentration (6 point calibration curve) using the "CalPlot" program as follows:

Double click on the "CalPlot icon" to bring up the calibration curve. If the curve shown is the one covering the wider concentration range,

Click on "edit"
Click on "calculator".

Enter the area counts of the peak which is beyond the range of the lower range curve (5 point calibration curve) as follows:

Type in the area count
Press "enter".

The concentration calculated from the curve shown behind the calculator window is returned. Calibration curves for the various components may be selected by clicking on the arrows at the bottom left and right hand corners of the calibration curve plots without closing the calculate window.

After recalculations are complete, exit as follows:

Click on "Exit" in the "calculator window"
Double click on the "close box" in the upper left hand corner to close "CalPlot".

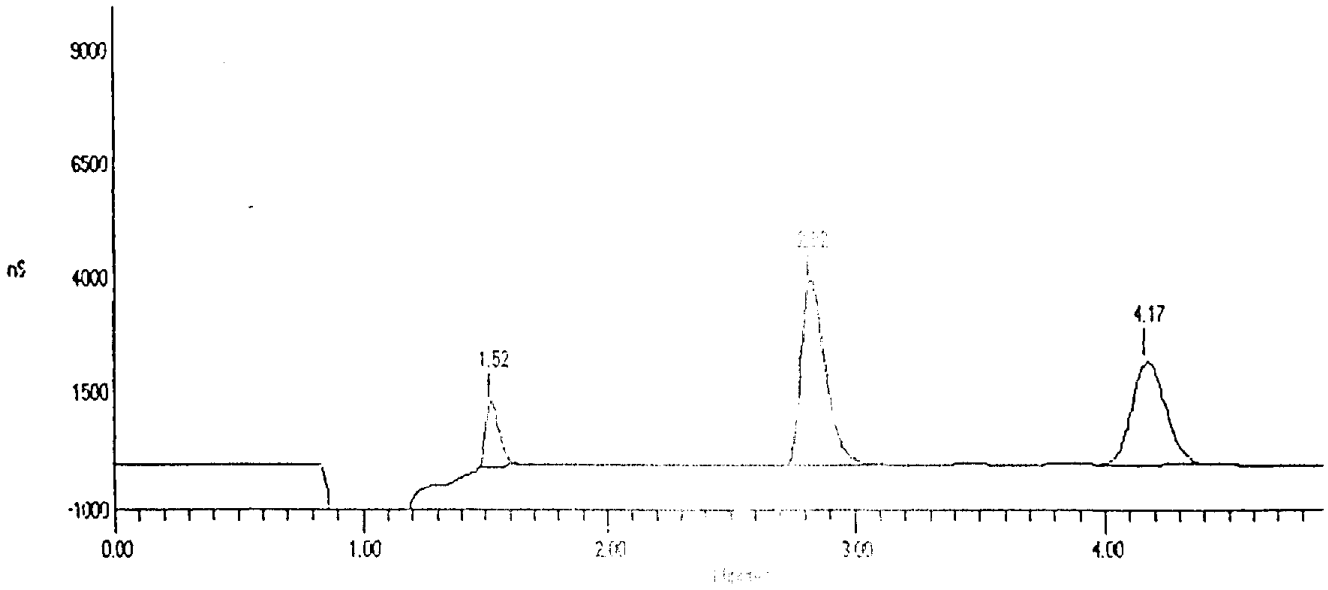
Samples which have area counts above the highest standard in the wider range calibration curve must be diluted and analyzed again because the calibration curve does not extend indefinitely in a linear manner.

Figure 5-1. Example of Ion Chromatogram [illegible] of Health Sample.

```
==========================================================================
| Sample Name: 90FCS70                          Date: Wed Aug 07 16:49:24 19
| Data File   : C:\DX\DATA\0807CO11.D35
| Method      : C:\DX\METHOD\ANION1.met
| ACI Address: 1        System : 1        Inject#:  35  Detector: CDM-2
==========================================================================
```

REPORT	VOLUME	DILUTION	POINTS	RATE	START	STOP	AREA	REJ
External	1	1	3010	[illegible]	0.00	5.02	100	

Pk. Num	Ret Time	Component Name	Concentration	Height	Area	Bl. Code	%De
1	1.52	CHLORIDE	[illegible]	1263900	5442624	1	[illegible]
2	2.82	NITRATE	0.[illegible]	3777816	26165868	1	[illegible]
3	4.17	SULFATE	0.413	2119402	20232563	1	[illegible]



5.3 Calculation of Concentrations on the Filter

Concentrations of the ionic species on the filter are calculated using dBaseIII+ on a separate computer. An example data base structure for ion chromatographic analysis is shown in Table 5-1. The following are the steps necessary to convert the AI-450 data into a dBase format:

- Batch process the individual runs into a Parse.PRN file:

  Double click on the Batch icon from the AI-450 main menu to open.
  Click on "File".
  Click on "Select existing schedule file", choose the schedule you want to batch process.
  Click on "open". A "Batch Reprocessing Options" menu will appear.
  Click on "print report text", "print chromatograms", and "update methods from autocal's" to turn these options off.
  Click on "ok".
  Click on "options" on the active menu bar.
  Click on "export options". From the export options menu choose "Export to File", ".PRN", "Full", and type in the file name "parse.prn".
  Click on "ok".
  Click on "priority" on the active menu bar and choose "high".
  Click on "controls" and choose "start".

- The program will then open each individual run file, reintegrate, then write the results to the parse.prn file. For a run of 60 samples this takes about 15 minutes.

- Transfer the Parse.prn file to a floppy disk:

  Insert floppy disk into drive A.
  Double click on "program manager" icon.
  Double click on "file manager".
  Double click on "DX".
  Double click on "Data".
  Highlight "Parse.prn", which will usually be on the end of the list of files.
  Click on "File" on the active menu bar at the very top.
  Click on "Copy", type "a:".
  Click on "Copy" or press enter.

Table 5-1
Data Base Structure for Ion Chromatographic Analysis
(File XXANOOT.STR)

Number of data records:	0
Date of last update:	9/19/91
Missing value code:	-99
Precision:	Reported
with values	

Field	Data Name	Type	Width	Description
1	QID	Character	10	Sample ID
2	ANIF	Character	5	Anion Flag
3	FLIC	Numeric	10.4	Fluoride, µg/filter
4	FLIU	Numeric	10.4	Fluoride Uncertainty, µg/filter
5	CLIC	Numeric	10.4	Chloride, µg/filter
6	CLIU	Numeric	10.4	Chloride Uncertainty, µg/filter
7	N2IC	Numeric	10.4	Nitrite, µg/filter
8	N2IU	Numeric	10.4	Nitrite Uncertainty, µg/filter
9	BRIC	Numeric	10.4	Bromide, µg/filter
10	BRIU	Numeric	10.4	Bromide Uncertainty, µg/filter
11	N3IC	Numeric	10.4	Nitrate, µg/filter
12	N3IU	Numeric	10.4	Nitrate Uncertainty, µg/filter
13	P4IC	Numeric	10.4	Phosphate, µg/filter
14	P4IU	Numeric	10.4	Phosphate Uncertainty, µg/filter
15	S4IC	Numeric	10.4	Sulfate, µg/filter
16	S4IU	Numeric	10.4	Sulfate Uncertainty, µg/filter
17	FLIML	Numeric	10.4	Fluoride, µg/ml
18	CLIML	Numeric	10.4	Chloride, µg/ml
19	N2IML	Numeric	10.4	Nitrite, µg/ml
20	BRIML	Numeric	10.4	Bromide, µg/ml
21	N3IML	Numeric	10.4	Nitrate, µg/ml
22	P4IML	Numeric	10.4	Phosphate, µg/ml
23	S4IML	Numeric	10.4	Sulfate, µg/ml
24	FLIDILF	Numeric	5.1	Fluoride, Dilution Factor
25	CLIDILF	Numeric	5.1	Chloride, Dilution Factor
26	N2IDILF	Numeric	5.1	Nitrite, Dilution Factor
27	BRIDILF	Numeric	5.1	Bromide, Dilution Factor
28	N3IDILF	Numeric	5.1	Nitrate, Dilution Factor
29	P4IDILF	Numeric	5.1	Phosphate, Dilution Factor
30	S4IDILF	Numeric	5.1	Sulfate, Dilution Factor
31	EXTVOL	Numeric	5.1	Extraction Volume, ml
32	AREAF	Numeric	8.4	Area Factor, Exposed Area/Extracted Area
33	ADATE	Date	8	Analysis Date
34	NOTE	Character	60	Comments and Observations

- After copying the Parse.prn file, close out the "file manager" by double clicking on the box in the top left hand corner. Put the "program manager" icon back down by clicking on the down arrow box in the upper right hand corner.

- On a computer which has had the PARSE program loaded onto the hard drive, change to the appropriate project directory or create one. At the D> prompt type "DBASE" <return>. This will put you in the dBase program.

- At the dot prompt type "Do Parse" <return>. The computer will then tell you to insert the floppy disk into drive a: and press any key to continue.

- The computer will then ask for a dbase file name, date of analysis, and extraction volume. Enter the dbase file name using the same naming conventions used for schedules, i.e. "dateprojsyst".

- The next step is to modify the structure to include only the species required for the project.

- Replace extvol and areaf with 1 for QA/QC standards and blanks.

- Replace dilution factors as needed.

- Replace μg/ml concentrations with recalculated values as needed.

- Recalculate μg/filter concentrations as needed.

5.4 Calculations

5.4.1. These steps should be followed if manual calculation of concentrations is necessary.

1. Determine the linear regression of the calibration curve for each ionic species. The calibration equation is given by the following relationship.

   μg/ml = SLOPE (integrator reading) + intercept (5-1)

2. Calculate concentrations of sample extract corresponding to the area counts according to the calibration curve.

3. Calculate the total amount of ionic species in precipitations samples or in the filter by using the appropriate factors and record on the data sheet.

$$\mu g/filter = \mu g/ml \times V \times D \times F \qquad (5\text{-}2)$$

where:

V = volume of extract

D = dilution factor

F = scaling factor, determined by ratio of filter size to the fraction analyzed

5.4.2 Precision Estimates

To serve the second purpose, IMPROVE aerosol precisions reported in the data bases are propagated from the precision of the replicated analysis and the field blank variability using the methods of Bevington (1969). The following formulae describe the calculation of the precision propagation:

$$B_i = \frac{1}{n} \sum_{j=1}^{n} B_{ij} \qquad \text{for } B_i > \sigma_{Bi} \qquad (5\text{-}3)$$

$$B_i = 0 \qquad \text{for } B_i <= \sigma_{Bi} \qquad (5\text{-}4)$$

$$\sigma_{Bi} = STD_{Bi} = \left[\frac{1}{n-1} \sum_{j=1}^{n} (B_{ij} - B_i)^2\right]^{1/2} \qquad \text{for } STD_{Bi} > SIG_{Bi} \qquad (5\text{-}5)$$

$$\sigma_{Bi} = SIG_{Bi} = \left[\frac{1}{n-1} \sum_{j=1}^{n} (\sigma_{Bij})^2\right]^{1/2} \qquad \text{for } STD_{Bi} <= SIG_{Bi} \text{ and } B_i >= SIG_{Bi} \qquad (5\text{-}6)$$

$$\sigma_{Bi} = 0 \qquad \text{for } Bi < SIG_{Bi} \qquad (5\text{-}7)$$

$$D_{Mij} = M_{ijr} - M_{ijr} \qquad (5\text{-}8)$$

$$D_{Mi} = \frac{1}{n} \sum_{j=1}^{n} D_{Mij} \qquad (5\text{-}9)$$

$$\sigma_{Mi} = \left[\frac{1}{n-1} \sum_{j=1}^{n} (D_{Mij} - D_{Mi})^2\right]^{1/2} \qquad (5\text{-}10)$$

where:

M_i = amount of species i on the substrate
M_{ijf} = amount of species i on sample j from routine analysis
M_{ijr} = amount of species i on sample j from replicate analysis
B_i = average amount of species i on field blanks
B_{ij} = the amount of species i found on field blank j
σ_{Bi} = blank precision for species j
σ_{Mi} = precision of amount of species i on substrate

6.0 QUALITY CONTROL

The quality control procedures serves two purposes: 1) to identify possible problems with measurement process, and 2) to calculate the precision of ion measurements.

6.1 Performance Testing

In addition to the daily start-up described in section 4, the analysis sequence for standards, blanks and replicates should be followed as described in Section 4.3.4. This results in approximately 10% standards check, 10% replicates and 5% blank checks.

6.2 Reproducibility Testing

Reproducibility is examined with the 10% replicate analyses during the routine sample analysis. The samples are extracted only once, so the replicate analysis refers only to the IC analysis of the extract. The precision of the replicate analysis will be calculated as stated in Section 5.4.2.

6.3 Tolerances and Actions to be Taken

Tolerances are generally ±30% at levels between 0.030 and 0.100 μg/ml; ±20% at levels between 0.100 and 0.150 μg/ml; and ±10% at levels above 0.150 μg/ml. If replicates exceed these tolerances, analyses beyond the last acceptable replicate are suspected to be incorrect. The replicate analysis on the same sample should be repeated again. If the second replicate duplicates, the original sample result, the first replicate result can be taken as spurious. Another replicate should be selected from samples within the same set of 10, after that first spurious replicate, and analyzed to verify that assumption. If the second replicate analysis exceeds the tolerance criteria, the cause of the error (probably in the instrument or the chemistry of the analysis) must be determined. Then, the whole set of 10 samples must be reanalyzed. Notify the laboratory supervisor immediately if sample rerun is to be performed.

6.4 Data Validation Feedback

The sample validation philosophy follows the three-level approach devised by Mueller and Hidy et al., (1983) in the Sulfate Regional Experiment (SURE). Level I sample validation takes place in the field or laboratory and consists of: 1) flagging samples when significant deviations from measurement assumptions have occurred, 2) verifying computer file entries against data sheets, 3) eliminating values from measurements which are known to be invalid because of instrument malfunctions, 4) replacing data when re-analyses have been performed, and 5) adjusting measurement values for quantifiable calibration of interference biases.

Level II sample validation takes place after data from various measurement methods have been assembled in the master data base. Level II applies consistency tests based on known physical relationships between these variables in the assembled data.

Level III sample validation is part of the data interpretation process and will be performed by each project manager and subsequent data users. The first assumption upon finding a measurement which is inconsistent with physical expectations is that the unusual value is due to a measurement error. If, upon tracing the path of the measurement, nothing unusual is found, the value can be assumed to be a valid result of an environmental cause.

The laboratory supervisor should review all the QC data as soon as it becomes available and ensure the feedback from the QC results to the routine operations. The project manager should consult with the QA

officer to initiate and document changes to the data base as they are needed.

7.0 QUALITY ASSURANCE

The performance and system audits are scheduled on a biannual basis by the QA officer to ensure that all procedures are followed properly and to verify the precision, accuracy and validity of the data.

8.0 REFERENCES

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