1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

The objectives of this standard operating procedure are: 1) to provide a basic understanding of the principles of operating the atomic absorption spectrophotometer (AAS); 2) to describe routine analysis for trace metals (i.e., Na^{+}, Mg^{++}, K^{+}, Ca^{++}) in aqueous filter extracts or precipitation samples using the Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer; and 3) to codify the actions which are taken to implement a state-of-the-art atomic absorption spectrophotometric measurement process. This procedure is to 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

Atomic absorption spectrophotometry resembles emission flame photometry in that a sample is aspirated into a flame and atomized. In flame photometry, the amount of light emitted is measured, whereas in atomic absorption spectrophotometry, the amount of light absorbed is measured. A light beam from a hollow cathode lamp is directed through the flame, into a monochromator, and onto a photoelectric detector that measures the amount of light absorbed by the atomized element in the flame. The cathode of a hollow cathode lamp contains the pure metal which results in a line source emission spectrum. Since each element has its own characteristic absorption wavelength, the source lamp composed of that element is used. The amount of energy of the characteristic wavelength absorbed in the flame is proportional to the concentration of the element in the sample. Both atomic absorption and atomic emission can be measured using Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer.

1.3 Measurement Interferences and Their Minimization

1.3.1 Chemical Interferences

Major interferences can be caused by competition between molecular association and dissociation in the flame. This occurs when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidized immediately to a compound that will not dissociate further at the flame temperature. A high temperature flame provides additional energy to break down the compounds. Alternatively, this type of chemical interference can be controlled by the addition of a releasing agent to the sample and standard solutions. The releasing agent (or competing cation) added to the

sample solution will preferentially react with the interferant and remove the interference.

Lanthanum can be added to the aqueous sample or sample extract before aspiration to eliminate the interference of phosphate and silicates in the calcium (Ca^{++}) determination. Because nitric acid enhances the signal for the determination of calcium, this acid must also be added to both the sample extracts and calibration standards. Lanthanum is also used to eliminate the interference of phosphorus, silicon, titanium and aluminum sulfate in the determination of magnesium (Mg^{++}).

1.3.2 Ionization Interferences

Ionization interferences occur when the flame temperature has enough energy to remove an electron from the atom, creating an ion. This depletes the number of ground state atoms which are absorbing the incident light, thus reducing the absorption if the incident light by the atoms. The overall effect is to reduce the sensitivity of the method. The addition of easily ionized elements, in much higher concentrations than the ion to be analyzed, to both calibration standard solutions and sample extracts can eliminate the ionization interferences. The addition of cesium chloride to the aqueous sample or sample extract before aspiration is necessary to overcome ionization interferences in the determination of sodium (Na^{+}) and potassium (K^{+}).

1.3.3 Matrix Interferences

Matrix interferences occur when the physical characteristics (i.e., viscosity, surface tension, burning characteristics) between the sample solutions and calibration standard solutions differ substantially. This is common when there are high concentrations of dissolved salts or acids in the sample solutions.

Diluting the sample, matching the matrix components in both sample and calibration standard solutions (i.e., adding the same reagent to both sample and calibration standard solutions), or adding methanol to the solutions are procedures which may eliminate matrix interferences.

1.3.4 Calibration standard solutions must be matched as nearly as possible to the sample solutions in important matrix components such as additives and pH.

1.4 Ranges and Typical Values of Measurement Obtained by this Procedure

A wide range of ambient concentrations can be found in both the filter extracts and precipitation samples. Table 1-1 summarizes the ranges and typical values of measurement obtained from the past studies.

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

The minimum detection limits of Na^+, K^+, Mg^{++}, and Ca^{++} are 0.005, 0.010, 0.003, and 0.025 μg/ml, respectively. The Lower Quantifiable Limits (LQLs) for each species listed in Table 1-1 is equal to three times the standard deviation of blank filter analysis or the minimum detection limit [ACS, 1983], whichever is greater.

Accuracy and precision of AAS depend on the sample and standard matrix, element of interest, and other instrument parameters such as the wavelength selected, the purity of the gases as well as the flame type and conditions. In general, the accuracy of AAS is primarily limited by the uncertainties in the standard solution preparation, typically within ±10%. Precisions depend on the species analyzed because sensitivity varies with analyte. Sodium and potassium have approximately the same sensitivity, so the expected precisions for these two elements are the same: ±30% for concentrations less than 0.100 μg/ml; ±20% for concentrations between 0.100 and 0.150 μg/ml; and ±10% for concentrations greater than 0.150 μg/ml. Calcium is approximately ten times less sensitive under the instrument conditions currently used, so the precision ranges would be expected to shift by that factor: ±30% for concentrations less than 1.000 μg/ml; ±20% for concentrations between 1.000 and 1.500 μg/ml; and ±10% for concentrations greater than 1.500 μg/ml. Magnesium is roughly twice as sensitive, so the precision ranges would shift correspondingly: ±30% for concentrations less than 0.050 μg/ml; ±20% for concentrations between 0.050 and 0.100 μg/ml; and ±10% for concentrations greater than 0.100 μg/ml.

1.6 Responsibilities of Personnel for Carrying Out Portions of This Procedure

All analysts in the laboratory should read and understand the entire standard operating procedure prior to performing AA analysis. The analyst must follow the procedure for routine system calibrations, chemical analysis, and performance tests.

It is the responsibility of the laboratory manager to ensure that the AA analysis procedures are properly followed, to examine all replicate, standard, and blank performance test data, to designate samples for

Table 1-1

Typical Ranges and Values of Atomic Absorption Measurements with Minimum Detectable[a] and Quantifiable[b] Limits

Chemical Species	Concentrations in $\mu g/m^3$			
	Range of Urban Concentrations	Range of Non-Urban Concentrations	Minimum Detectable Limit[a]	Lower Quantifiable Limit[b]
Soluble Na^+	0.2 to 5[c]	0.07 to 0.3[c]	0.05[d]	0.005[d]
Soluble Mg^{++}	0.07 to 0.7[c]	0.03 to 0.1[c]	0.0008[d]	0.010[d]
Soluble K^+	0.07 to 0.7[c]	0.07 to 0.5[c]	0.07[d]	0.003[d]
Soluble Ca^{++}	0.11 to 1.3[c]	0.1 to 0.4[c]	0.05[d]	0.025[d]

[a] Minimum Detectable Limit (MDL) is the concentration at which instrument response equals three times the standard deviation of the response to a known concentration of zero

[b] Lower Quantifiable Limit (LDL) equals three times the standard deviation of dynamic field blanks as determined from previous monitoring programs

[c] Preliminary data from CADMP sites for PM_{10} samples

[d] Assumes extraction of half filter in 15 ml and 15 m^3 air volume

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 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:

Atomic Emission: The flame converts the sample aerosol into an atomic vapor and then thermally elevates the atoms to an excited state. When these atoms return to the ground state, they emit light which is detected by the instrument. The intensity of light emitted is proportional to the concentration of the element of interest in the sample.

Atomic Absorption: The flame converts the sample aerosol into an atomic vapor which can absorb light from the primary light source. The amount of light absorbed is proportional to the concentration of the element in the sample.

Hollow Cathode Lamp: The primary light source which emits high intensity narrow-line spectra of the element of interest. The cathode of a hollow cathode lamp is constructed with a pure metal of the selected element. Two elements can be used in one lamp to reduce time spent changing lamps. DRI laboratory uses a K/Na lamp and a Ca/Mg lamp.

Double-Beam System: The light from the source lamp is divided into a sample beam, which is focused through the sample cell, and a reference beam, which is directed around the sample cell. The read out represents the ratio of the sample and reference beams. Thus, fluctuations in source intensity do not become fluctuations in instrument readout and a more stable baseline can be achieved.

Nebulizer:	A system in which the sample is aspirated into the instrument and broken into tiny droplets for delivery into the flame.
Burner chamber:	The area in which the flame gases are mixed with the sample and swept up into the burner head.
Burner head:	The section of the burner at which the flame is generated. One burner head is required for use with the air/acetylene flame (10 cm, PE # 0040-0266) and another for use with the nitrous oxide/acetylene flame (5 cm, PE #0040-0277).
Autosampler:	A microprocessor controlled carousel and probe which automatically delivers up to 50 samples to the nebulizer.
Optimum Concentration Range:	Defined by limits expressed as concentrations, below which background noise swamps the analyte signal and above which curve correction should be used. This range varies with the sensitivity of the method for the analyte.
Sensitivity:	The sensitivity is defined as the concentration of the metal analyte in μg/ml which produces an absorbance of 1% (approximately 0.0044 absorbance units). For the Perkin-Elmer 2380, the sensitivity for sodium is 0.006 μg/ml; for potassium, it is 0.01 μg/ml; for magnesium, 0.003 μg/ml; for calcium, 0.05 μg/ml.
Detection Limit:	The concentration of an element which would yield an absorbance equal to three times the standard deviation of the response to a known concentration of zero [ACS, 1983].

1.8 Related Procedures

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

DRI SOP 13 Sectioning of Filter Samples
DRI SOP 14 Extraction of Ionic Species from Filter Samples Materials Safety Data Sheets

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

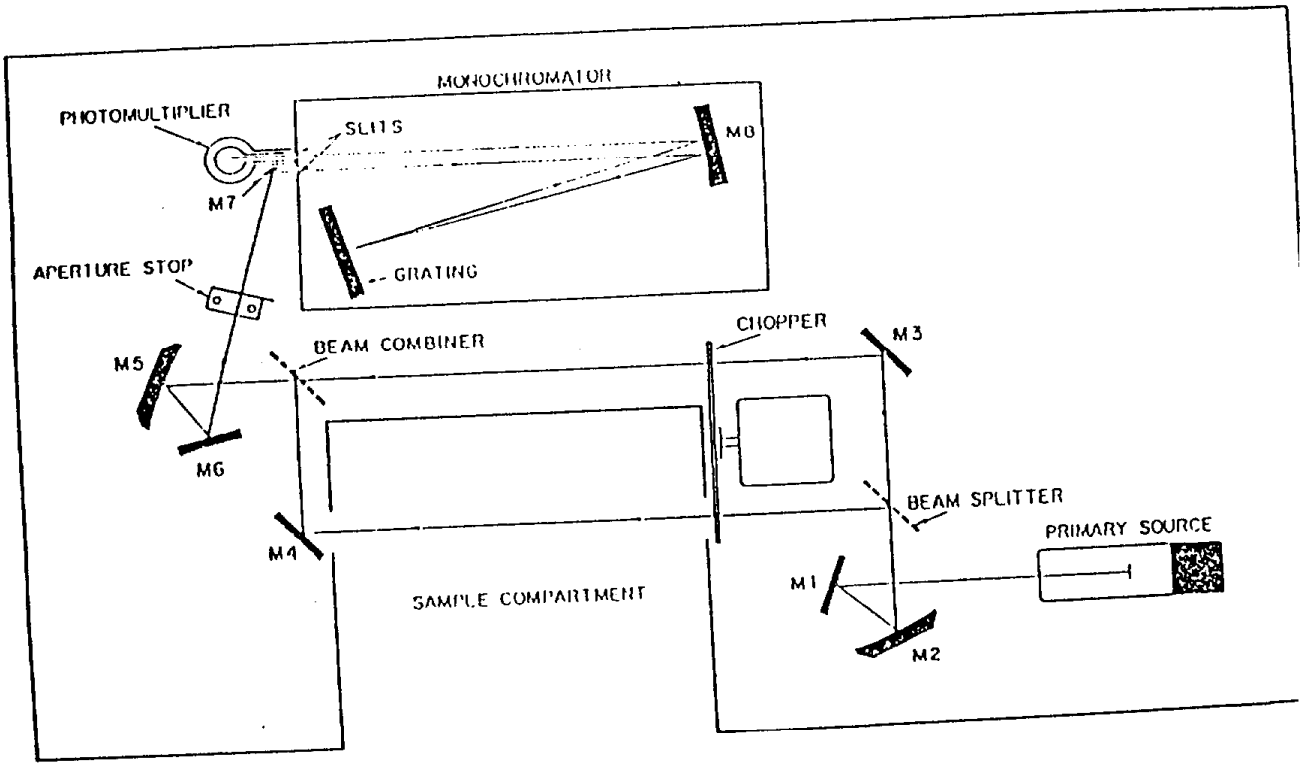
The Perkin Elmer (PE) Atomic 2380 Absorption Spectrophotometer (AAS) double beam instrument consists of 5 main parts as shown in Figure 2-1.

- Light Source: Emits the line-spectrum of the element of interest.
- Absorption Cell: Cell in which atoms of the sample are produced via a flame.
- Monochromator: A grating used for isolating an emission line from the lamp to be used for absorption.
- Photoelectric Detector: Measures the light intensity and amplifies the signal.
- Display: Shows the reading after it has been processed by the instrument electronics.

Additional required equipment include the exhaust vent, autosampler, recorder, computer, and printer.

- A venting system is required to remove the fumes and vapors from the flame or furnace of atomic absorption instruments. A flow rate of 5400-5800 lpm is used for the AAS venting system. The exhaust vent is used to: 1) protect laboratory personnel from toxic vapors produced by some samples; 2) protect the instrument from corrosive vapors from aspiration of the sample; 3) improve flame stability by removing laboratory drafts; and 4) remove heat generated from the flame.
- The Perkin Elmer Model AS-50 Flame Auto Sampler is used for analysis using the flame. This consists of a transport mechanism (sample carousel) and a control unit. The sample carousel holds up to fifty 15 ml sample tubes, three standards and a wash beaker. Sampling is performed by a probe which is connected to the nebulizer.

Figure 2-1. Perkin Elmer Model 2380 AA Optical Schematic.



- A chart recorder is used to continuously monitor the absorbance and to provide a visual graph of the absorbance peaks of the samples.

- An IBM compatible personal computer (PC) is used to automatically record the absorbance data of the calibration standards and samples in order as they are analyzed.

- A printer connected to the PC generates a hard copy of the absorbance data as the samples are analyzed.

2.1.2 Instrument Characterization

The PE 2380 AAS and AS-50 autosampler analyzes the contents of as many as 50 sample tubes per run, including an auto zero and up to 3 calibration standards if the instrument is used in the CONCENTRATION mode. In the ABSORBANCE mode, as many standards as desired are used to establish the calibration curve. Currently, one blank and 7 standards are used.

The autosampler controller is used to set a read delay time to allow time for the sample to travel through the sample tube into the flame and for the subsequent signal to stabilize. The read time is also set at a level long enough to permit the required number of readings to be taken.

The PE 2380 AAS instrument controls are used to select the proper lamp current, gain and wavelength. The flame gases are controlled from the Interlocked Gas Control System. The signal resulting from the samples can be received in Absorbance, or Concentration. Absorbance is used since this permits the original signal to be captured on the computer.

The integration time, numbers of readings to be taken per sample, and reporting of average and standard deviation can be selected on the PE 2380 AAS.

The location of the burner head and flow rate through the nebulizer must be optimized. Since the samples analyzed are all aqueous solution, these adjustments are performed only after the burner system is cleaned.

2.1.3 Maintenance

Regular maintenance of the PE 2380 includes the following:

- The burner chamber must be rinsed with water after each set of analyses by aspirating water through the system with the flame lit for 5 minutes after analysis is complete.

- At the end of each full week of analyses, the burner chamber and burner head must be rinsed more thoroughly by removing the burner head, sonicating it for one hour and gently scraping any salt deposits off the burner surface. While the head is off, the chamber itself is cleaned by pouring 250 ml DDW through the top of the chamber.

- Occasionally, a sputtering sound can be heard when the flame is first lit after thorough cleaning. This indicates either incorrect seating of the burner head or water in the system. Water may be at the nebulizer outlet after washing. Allow the air to vent through the burner chamber for 15 minutes without the flame being lit to aid in drying. If the system is expected to be dry after sitting for an extended period, check for incorrect seating by removing the burner head and reseating it. If the sputtering sound persists, the O-ring at the top of the chamber which seals the burner head seat may need to be replaced (PE #303-6095).

- The drain bottle under the instrument must be checked at the beginning of each analysis day. If the level of waste is at the shoulder of the bottle, the bottle must be emptied to the 8 liter mark on the side. Because the samples are all aqueous, without significant adjustment of pH or other characteristics, the waste may be poured directly down the sink.

- The nebulizer is cleaned after 6 months of use, according to the maintenance manual (PE, 0993-9575, 1977, Section 12C)

- If the signal seems noisy, the burner head is cleaned as above, the chamber location is readjusted. If the signal suddenly drops, a clog in the nebulizer or sample delivery tube is suspected. The nebulizer can be cleaned with the brass cleaning wire provided with the nebulizer.

- Printer paper should be checked before the beginning of each analysis run to ensure that a sufficient quantity is in place for the run.

- The printer ribbon should be checked and changed when the print quality changes from dark black to light black.

- Work areas should be kept clean.

- Additional maintenance and trouble shooting information can be found in the Perkin Elmer 2380 Instruction Manual (PE, 1977).

2.1.4 Laboratory Supplies and Spare Parts

- Compressed air supply: minimum of 28 lpm flow rate at a minimum pressure of 40 PSI. DRI's building compressed air supply is used after it has passed through an oil trap, a particulate filter, and a regulator set at 75 psi. The compressed air is used as the oxidant for the air/acetylene flame.

- Acetylene: Obtained in size 1B cylinders containing about 9000 liters (STP) of gas dissolved in acetone. The acetylene flow is 4 lpm with a heat combustion value of 1450 BTU per cubic foot. Suitable acetylene has a minimum purity of 99.6 to 99.8%. Air/acetylene is the preferred flame for the determination of approximately 35 elements by atomic absorption. Replace the acetylene tank when the pressure is at 520 PSI. This residual pressure is due to the acetone solvent.

- Nitrous Oxide: Obtained in size 1A cylinders containing about 15,000 liters (STP). The nitrous oxide is in a liquid state with an initial pressure at 750 psi. The gas above the liquid is drawn off for use in the instrument. After all the liquid has evaporated, the pressure falls rapidly as the remaining gas in the cylinder is drawn off. Nitrous oxide/acetylene flame requires a flow rate of 20 lpm nitrous oxide. The size 1A cylinder of nitrous oxide lasts for about 12 hours of operation.

- Volumetric flasks: Class B polymethylpentene volumetric flasks, 100 ml (±0.16 ml accuracy). (Fisher Scientific, 2170 Martin Ave., Santa Clara, CA. Cat. # 10-198-52C)

- Pipettes: volumetric in 1, 2, 3, 5, and 10 ml sizes. Class A.
- Micropipettes: Eppendorf pipets in 1000 µl, 500 µl, 200 µl and 100 µl with disposable pipet tips. (Fisher Scientific, 2170 Martin Ave., Santa Clara, CA. Cat. # 21-371 and 21-372)

- Volumetric micro syringe: Hamilton 50 μl (Hamilton, Reno, NV 89510 #705, 50μl)
- Wide mouth bottles: Polyethylene, 125 ml. Used for storage of calibration and working standards.
- Polyethylene centrifuge tubes: 15 ml, used in the autosampler. (Cole Parmer Instrument Co., 7425 N. Oak Park Ave, Chicago, IL, 60648. Catalog # J06334-21)
- Disposable beakers: Polystyrene, 10 ml. (American Scientific Products, McGaw Park, IL 60085 Cat. # B2718-10)
- Spare lamps: Na-K, PE# 303-6095; Ca-Mg, PE# 303-6092 (Perkin Elmer, Norwalk, CT)
- Spare burner head O-rings: PE# 990-2219 (Perkin Elmer, Norwalk, CT)
- Spare probes: Stainless Steel PE# 047-1422 (Perkin Elmer, Norwalk, CT)
- Spare sample tubing: Polyethylene PE# 990-8265 (Perkin Elmer, Norwalk, CT)
- Spare impact beads: Glass, PE# 0057-2615 (Perkin Elmer, Norwalk, CT)
- Spare flow spoiler: polyethylene, PE# 0057-2561 (Perkin Elmer, Norwalk, CT)
- Printer ribbons
- Printer paper

2.2 Reagents

2.2.1 Use analytical grade chemicals for all solutions.

Use distilled-deionized water (DDW) conforming to ASTM specification D1193, Type II (Annual Book of ASTM Standard, 1983)

Nitric Acid (HNO_3): Concentrated, ACS reagent grade (#A200-212, 2.5 liter, Fisher Scientific, Fair Lawn, NJ 07410).

Cesium Chloride (CsCl): Certified reagent grade (#C-24, 25 g, Fisher Scientific, Fair Lawn, NJ 07410). Used as ionization suppressant for sodium and potassium analysis.

Lanthanum Nitrate Hexahydrate ($La(NO_3)_3 \cdot 6H_2O$): Reagent grade (#P354-05, J. T. Baker Chemical Co., Phillipsburg, NJ 08865). Used as releasing agent in analysis of Ca and Mg.

Stock calibration standard solutions: Certified, Fisher Scientific, Fair Lawn, NJ 07410

Na, 1000 μg/ml #SS139-500
K, 1000 μg/ml #SS351-500
Ca, 1000 μg/ml #SC191-500
Mg, 1000 μg/ml #SM51-500

Ethanol: #A962S-4 Fisher Scientific, Fair Lawn, NJ 07410

2.2.2 Preparation of Solutions

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

In transferring solutions for dilutions, pour the concentrated solution into a disposable beaker. Rinse the volumetric pipet to be used from this solution in the beaker. Pour a new aliquot of solution into a different disposable beaker and pipet from this beaker using the volumetric pipet rinsed with the solution into the volumetric flask. This procedure minimizes contamination due to inserting pipets or other objects into the solution.

Use glassware and plasticware which has been properly washed using a dilute Alconox solution (0.1 g in approximately 4 liters distilled water) and rinsed with DDW until the detergent is no longer visible, then rinsed with DDW at least three more times.

- Cesium Chloride Stock Solution (1% w/v Cs):
  Before preparing the Cs Stock Solution from a new batch of reagent, test the new batch of reagent for the presence of the elements to be analyzed by preparing at least two 10 ml test samples at different concentrations as follows:

%Cs	Weight CsCl/10 ml DDW
Blank	0
0.1%	0.01268 g
2.5%	0.3167 g
5.0%	0.6333 g

Test these solutions for the presence of the element of interest using the AAS. An absorbance of less than 0.010 absorbance units at the 0.1% level is acceptable since the standards and samples will be matched in Cs concentration.

To prepare the Cesium Stock Solution (1% w/v), weigh into a weighing boat 6.335g ± 0.001 g CsCl (99.9% pure, ACS reagent grade) which has been tested for sodium contamination by elements to be analyzed. Quantitatively transfer the solid into a 500.00 ml flask, using DDW. Fill to the 500.00 ml mark with DDW. This solution is used to produce standards and samples of 0.1% Cs concentration. The Cs acts as an ionization suppressant in the K and Na analyses.

- Lanthanum Nitrate Hexahydrate ($La(NO_3)_3.6H_2O$) (1% w/v La) Stock Solution: Before preparing the La Stock Solution, test the new batch of reagent for the presence of the elements to be analyzed by preparing at least two 10 ml test samples at different concentrations as follows:

%La	Weight $La(NO_3)_3 \cdot 6H_2O$/10 ml DDW
Blank	0
0.1%	0.03116 g
2.5%	0.7791 g
5.0%	1.5581 g

Test for the presence of any elements of interest by measuring the absorbance on the AAS. An absorbance of less than 0.010 units at the 0.1% level is acceptable since the standards and samples will be matched in La concentration.

To prepare the Lanthanum Stock Solution (1% w/v), weigh 15.600 ± 0.001 g lanthanum nitrate hexahydrate (99.9% pure, ACS reagent grade) which has been tested for contamination by elements of interest into a weighing boat. Quantitatively transfer the solid into a 500.00

ml flask, using DDW. Fill to the 500.00 ml mark with DDW. This solution is used to produce standards and samples 0.1% in La. The La acts as an interference suppressant for phosphate, aluminum and silicate in the Mg^{++} and Ca^{++} analyses.

- Combined Lanthanum/Cesium stock solution (1% La w/v and 1% Cs w/v)

  To prepare the Lanthanum/Cesium combined Stock Solution (1% w/v La and 1% w/v Cs), weigh 15.600 ± 0.001 g lanthanum nitrate hexahydrate (99.9% pure, ACS reagent grade) which has been tested for contamination by elements of interest into a weighing boat. Quantitatively transfer the solid into a 500.00 ml volumetric flask using DDW. Then, weigh 6.335 ± 0.001 g CsCl (99.9% pure, ACS reagent grade) which has been tested for contamination by elements of interest into a weighing boat. Quantitatively transfer the solid into a 500.00 ml volumetric flask using DDW. Dissolve the combined solids in about 250 ml DDW. Fill to the 500.00 ml mark with DDW and mix thoroughly by inverting the flask at least 10 times and swirling each time. Transfer the solution into a 500 ml high density polypropylene bottle by rinsing the clean bottle three times with small portions of the solution and discarding the rinses, then pouring the solution into the storage bottle. Store in the refrigerator. This solution is stable indefinitely, so prepare as needed when the solution is depleted. Before using, check for any contamination by preparing the AA BLANK as described below in Section 3.1.6.

  This solution is used to produce standards and samples 0.1% in La and Cs. The La acts as an interference suppressant from phosphate, aluminum and silicate in the Mg^{++} and Ca^{++} analyses, and the Cs acts as an ionization suppressant in the analysis of Na^{+} and K^{+}.

- Nitric acid (HNO_3), 1.6M: Dilute concentrated nitric acid (16M) by pipetting 10.00 ml into a 100.00 ml volumetric flask. Dilute to the mark with DDW. This solution is used to prepare standards and samples with concentrations of 0.016 N HNO_3 for the analysis of Ca.

2.3 Forms and Paperwork

A sample analysis list will be prepared by the laboratory manager indicating which samples will be analyzed and any special instructions (Figure 2-2). Samples designated for atomic absorption spectrophotometry (AA) analysis are logged into the "AA Analysis Logbook," as are notes concerning the preparation of standards and maintenance (Figure 2-3).

The samples are listed in a run list (Figure 2-4) (see also section 4.3.1). The samples are loaded into the autosampler from this list. The sample ID's are correlated with the absorbencies generated in the computer print out of the absorbencies by recording the number of the analysis (Computer Run #) on the run list next to the Sample ID in the column indicated. Using this run list, the sample ID's are finally combined with the computer run numbers in the data base of the absorbance and concentrations produced in the calculations (Section 5).

3.0 CALIBRATION STANDARDS

3.1 Preparation of Standard Solutions

Stock Standard Solutions are either purchased as certified solutions or prepared from ACS reagent grade materials. These solutions are properly labeled with the name of the chemicals in the solution, the concentrations, the initials of the person making them, and stored in the refrigerator in high density polyethylene or polypropylene containers. Discard the solutions after a year.

In transferring solutions for dilutions, pour the concentrated solution into a disposable beaker. Rinse the volumetric pipet to be used from this solution in the beaker. Pour a new aliquot of solution into a different disposable beaker and pipet from this beaker using the volumetric pipet rinsed with the solution into the volumetric flask.

Use glassware and plasticware which has been properly washed using a dilute Alconox solution (0.1 g in approximately 4 liters distilled water) and rinsed with DDW until the detergent is no longer visible, then rinsed with DDW at least three more times.

3.1.1 Stock Solutions

Stock Standard Solutions for Na^+, Mg^{++}, K^+, and Ca^{++} are purchased as certified, ACS reagent grade material from Fisher in 1000 μg/ml concentrations.

Figure 2-2. DRI Sample Analysis List.

Bullhead City Ambient Quartz Filters

****

Date: 11/28/89
From: L.Pritchett
To : J.Chow
J.Watson
B.Price

Total number of samples: 63

Species to be analyzed:
Na/K/Ca/Mg : by AA
NH4 : by AC

Instructions:

1. This is a set of selected ambient filters from Bullhead City. Follow the list carefully to analyze only those filters designated for analysis.

2. Filters will be quantitatively halved and extracted in 10 ml DDW on Wednesday, 11/29/89; extracts will be sonicated for 30 minutes and shaken for 30 minutes.

3. NH4 analysis will be performed Thursday, 11/30/89. Data entry and Level I validation will be completed by Wednesday, 12/13/89.

4. AA analysis will be performed as analysis load allows in the next 2 weeks. Data entry and Level I validation will be completed by Wednesday, 12/13/89.

5. Deposit area for the filters is 12.6 cm2.

6. dBase III files will be named:

NH4 data : BCN401A.DBF
Na data : BCNa01A.DBF
Mg data : BCMg01A.DBF
K data : BCKP01A.DBF
Ca data : BCCa01A.DBF

Filter	Description	NH4	Na	K	Ca	Mg
BCQ0047	Ambient	Y ____	Y ____	Y ____	Y ____	Y ____
BCQ0048	Ambient	Y ____	Y ____	Y ____	Y ____	Y ____
BCQ0052	Ambient	Y ____	Y ____	Y ____	Y ____	Y ____
BCQ0053	Ambient	Y ____	Y ____	Y ____	Y ____	Y ____
BCQ0054	Ambient	Y ____	Y ____	Y ____	Y ____	Y ____
BCQ0056	Ambient	Y ____	Y ____	Y ____	Y ____	Y ____

Figure 2-3. DRI AA Analysis Logbook Format.

ANALYSIS DATE	PROJECT	SAMPLE ID	#	SPECIES ANAL'D	BY	COMMENTS
7/13/89	CARB II	AQ070227-657	40	K^+	LCP	
7/14/89	CARB II	AQ070227-657	40	Na^+	LCP	
8/26/89	CCHD	FQF 740-834	20	Ca^{2+}	LCP	
		FQC 740-834	20	Ca^{2+}		
9/1/89	ACCEPT	Q 414-419	6	K^+	LCP	
		Q 450-457	8	K^+	LCP	
9/2/89	ACCEPT	Q 420-449	20	Na^+	LCP	

Figure 2-4. DRI AA Run List.

DRI IE2380 ATOMIC ABSORPTION

Standards

Std Curve	µg/ml	Initial	
	Blank		
	.025		
	.050		
	.100		
	.250		
	.500		
	1.000		
	1.500		
	QA		

File:

Date:

Computer Run #	Sample I.D.	Conc. µg/ml	% Diff.

3.1.2 Working Standards (WS) (50 and 5 μg/ml)
These are intermediate standard solutions used for calibration of AAS. WS are prepared from the stock solutions for use within one month and stored in the refrigerator in 125 ml high density polyethylene or polypropylene bottles. Make up two working standard solutions: one 50.00 μg/ml in Na^+ and K^+, and one 50.00 μg/ml in Ca^{++} and Mg^{++}.

- Preparation of 50.00 μg/ml Na/K Working Standard (50 Na/K WS)

  Pipet 5.00 ml (using a 5.00 ml volumetric pipet which has been rinsed with the solution to be pipetted as described in section 3.1) of each of the stock solutions of Na^+ and K^+ from disposable beakers filled with the solutions into a 100.00 ml polyethylene volumetric flask and fill to volume with DDW. Mix well by inverting the flask 10 times and swirling each time.

  The final concentration of the solution is 50.00 μg/ml in Na^+ and K^+. Transfer the 50 WS solution to a clean 125 ml wide mouth high density polyethylene bottle for storage by rinsing the bottle three times with small amounts of the 50 WS solution and pouring the solution into the bottle.

- Preparation of 50.00 μg/ml Ca/Mg Working Standard (50 Ca/Mg WS)

  Pipet 5.00 ml (using a 5.00 ml volumetric pipet which has been rinsed with the solution to be pipetted as described in section 3.1) of each of the stock solutions of Ca^{++} and Mg^{++} from disposable beakers filled with the solutions into a 100.00 ml polyethylene volumetric flask and fill to volume with DDW. Mix well by inverting the flask 10 times and swirling each time.

  The final concentration of the solution is 50.00 μg/ml in Ca^{++} and Mg^{++}. Transfer the 50 WS solution to a clean 125 ml wide mouth high density polyethylene bottle for storage by rinsing the bottle three times with small amounts of the 50 WS solution and pouring the solution into the bottle.

- Preparation of 5.00 μg/ml Na/K Working Standard (5 Na/K WS)

A second working standard is needed for dilute standards. Make a 5.00 μg/ml WS by pipetting from a disposable beaker filled with the 50 Na/K WS (with a 10.00 ml volumetric pipet which has been rinsed with the solution to be pipetted as described in section 3.1) 10.00 ml of the 50.00 μg/ml Na/K WS into a 100.00 ml polyethylene volumetric and fill to volume with DDW. Mix thoroughly by inverting the stoppered flask 10 times and swirling each time.

- Preparation of 5.00 μg/ml Ca/Mg Working Standard (5 Ca/Mg WS)

  A second working standard is needed for dilute standards. Make a 5.00 μg/ml WS by pipetting 10.00 ml (with a 10.00 ml volumetric pipet prepared by rinsing with the solution to be pipetted as described in section 3.1) of the 50.00 μg/ml Ca/Mg WS from a disposable beaker filled with the solution into a 100.00 ml polyethylene volumetric and fill to volume with DDW. Mix thoroughly by inverting the stoppered flask 10 times and swirling.

3.1.3 Calibration Standards for atomic absorption analysis for sodium and potassium ONLY

Prepare calibration standards in concentrations of sodium and potassium of 0, 0.025, 0.050, 0.100, 0.250, 0.500, 1.000, and 1.500 μg/ml. Use 100.00 ml polymethylpentene volumetric flasks. Store calibration standards in 125 ml high density polypropylene bottles in the refrigerator. Prepare as needed as the solutions are depleted. Prepare one new standard to compare with the old ones each time analyses are run to check for contamination or degradation.

In preparing to pipet, proceed with rinsing the volumetric pipets with the appropriate WS from a disposable beaker. Pipet from another disposable beaker filled with a second portion of the solution to be pipetted.

After the volumetric flasks are filled to volume with DDW, stopper the flasks and mix each one thoroughly by inverting each one 10 times and swirling each time.

- Sodium and potassium calibration standards. (0.025, 0.050, 0.100, 0.250, 0.500, 1.000, 1.500 μg/ml)

Blank Solution: Add 10.00 ml 1% w/v Cs Stock Solution (using a 10.00 ml volumetric pipet) to 100.00 ml polymethypentene volumetric flask and bring to volume with DDW.

0.025 μg/ml: Add 10.00 ml 1% w/v Cs Stock Solution to 100.00 ml polymethypentene volumetric flask; then using a 0.500 ml Eppendorf pipet (use the balance to confirm the volume by weight, pipette 0.500 ml 5 μg/ml Na/K WS into the flask and bring to volume with DDW.

0.050 μg/ml: Add 10.00 ml 1% w/v Cs Stock Solution to 100.00 ml polyethylene volumetric flask, then pipette 1.00 ml 5 μg/ml Na/K WS into the flask and bring to volume with DDW.

0.100 μg/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml polyethylene volumetric flask, then pipette 2.00 ml 5 μg/ml Na/K WS into the flask and bring to volume with DDW.

0.250 μg/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml polyethylene volumetric flask, then pipette 5.00 ml 5 μg/ml Na/K WS into the flask and bring to volume with DDW.

0.500 μg/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml polyethylene volumetric flask, then pipette 10.00 ml 5 μg/ml Na/K WS into the flask and bring to volume with DDW.

1.000 μg/ml: Add 10.00 ml 1% Cs Stock Solution to 100.00 ml polyethylene volumetric flask, then pipette 2.00 ml 50 μg/ml Na/K WS into the flask and bring to volume with DDW.

1.500 μg/ml: Add 10 ml 1% Cs Stock Solution to 100.00 ml polyethylene volumetric flask, then pipette 3.00 ml 50 μg/ml Na/K WS into the flask and bring to volume with DDW.

3.1.4 Preparation of calibration standards for analysis for calcium and magnesium ONLY

Prepare calibration standards in concentrations of calcium and magnesium of 0, 0.025, 0.050, 0.100, 0.250, 0.500, 1.000, and 1.500 μg/ml. Use 100.00 ml polymethylpentene volumetric flasks. Store

calibration standards in 125 ml polypropylene bottles in the refrigerator. Prepare as needed as the solutions are depleted. Prepare one new calibration standard each time analyses are done to check for contamination or degradation.

- Calcium/Magnesium Standards (0.025, 0.050, 0.100, 0.250, 0.500, 1.000, 1.500 μg/ml)

  Prepare as for Sodium/Potassium standards, but add 10 ml 1% La Stock Solution to 100.00 ml polyethylene volumetric flasks, add 1 ml 1.6N HNO_3, then pipette in the appropriate amounts of the Calcium/Magnesium 5 μg/ml and 50 μg/ml WS as above.

3.1.5 Preparation of calibration standards for analysis for calcium, magnesium, sodium and potassium (CADMP)

For CADMP, the samples are teflon (or teflon type) filters which are first wetted with 200 μl ethanol and extracted in 10 ml matrix solution of 0.1% La, 0.1% Cs and 0.016 N HNO_3 in DDW. The standards must match the sampled in matrix, including the addition of 200 μl ethanol per 10 ml solution. This means preparing the standards for CADMP with 2.00 ml ethanol added into the solution.

For other projects in which all four elements are to be analyzed, and if other types of filters are used, prepare the standards so they duplicate the samples in all matrix components. For analysis, the samples and standards must contain the matrix modifiers (Cs ionization suppressant, La releasing agent, nitric acid for the Ca analysis). Matching the samples and standards may require preparation of standards as required for the analysis and modifying the matrices of the samples to match.

Prepare calibration standards with concentrations of calcium, magnesium, sodium and potassium of 0, 0.025, 0.050, 0.100, 0.250, 0.500, 1.000, and 1.500 μg/ml. Use 100.00 ml polymethylpentene volumetric flasks. Store calibration standards in 125 ml polypropylene bottles in the refrigerator. Prepare as needed as the solutions are depleted. Calibration standards prepared in acidic solutions, stored in high density polypropylene bottles are stable for at least 3 months if kept uncontaminated. If these older calibration standards are to be used, prepare at least two new calibration standards just prior to analysis to check that the calibration standards have not become contaminated.

- Calcium/Magnesium/Sodium/Potassium standards (0.025, 0.050, 0.100, 0.250, 0.500, 1.000, 1.500 μg/ml)

Prepare as for Sodium/Potassium standards, but add 10 ml 1% La/Cs Stock Solution, 2.00 ml ethanol and 1.00 ml 1.6N HNO_3, to each 100.00 ml polyethylene volumetric flask. Then pipette in the appropriate amounts of the calcium/magnesium 5 μg/ml and 50 μg/ml WS and the appropriate amounts of the sodium/potassium 5 μg/ml and 50 μg/ml WS as above. Before diluting to the mark, check Special Standards section below for any extra matrix requirements.

3.1.6 Special Standards

The standards must be treated exactly as the samples. If the samples are extracted by first wetting the filter with ethanol (EtOH) as is routine for teflon filters, the corresponding amount of ethanol must be added to the standards. For example, if 200 μl EtOH is added to a 10 ml extraction volume, then 2.000 ml EtOH must be added to each 100.00 ml of the calibration or audit standards. If 200 μl EtOH is added to 10 ml extraction volume, add 2.0 ml EtOH to each calibration standard.

NOTE: calcium must be analyzed in an acid matrix when the air/acetylene flame is used. The samples to be analyzed for calcium must be acidified to 0.016N HNO_3 to match the standards.

Audit standards prepared in DDW must also be adjusted to match the samples and standards. These matrix modifications are carried out in the AAS autosampler tube just prior to analysis.

For analysis of Na^+ or K^+ only, this requires the addition of 0.100 ml 1% Cs Stock Solution to each ml of audit standard, NBS rainwater or other reference standard. Since this solution is added to 1.00 ml, making a total volume of 1.10 ml, a dilution factor of 1.1 must be included in subsequent calculations. This dilution factor will apply to samples treated in this manner, also.

For analysis for Ca^{++} or Mg^{++} only, 0.100 ml of 1% La Stock Solution plus 0.010 ml 1.6N HNO3 are added to each 1.00 ml audit standard, NBS rainwater or other reference standard. This makes the dilution factor 1.11 for these two modifiers: La Stock Solution and HNO3.

For the analysis of all 4 elements, 0.100 ml of the combined 1% La/Cs stock solution plus the 0.010 ml 1.6 N HNO3 must be added to each 1.00 ml audit standard, NBS rainwater or other reference standard. The corresponding dilution factor is be 1.11.

Notice that if the audit standard must be diluted for analysis (as the case for the ERA Ca standard), the matrix modifiers can be added to the dilution flask as for the preparation of the calibration standards.

- Preparation of NBS rainwater audit standard for use:

  SRM 2694I contains Na, K, and Mg in certified concentrations (See Table 3-1). When this SRM is used as a quality control check, it must be adjusted to contain the same additives as the samples and calibration standards.

  For analysis for Na and K only, add 0.100 ml (using the 100 1 Eppendorf pipet) 1% Cs stock for each 1.00 ml of rain water to the AAS autosampler tube, then add the corresponding amount of the SRM 2694I (1.000 ml for each element, using the 1000 1 Eppendorf pipet.)

  For analysis for Na, K, and Mg, add 0.100 ml 1% Cs/La combined stock (using the 100 1 Eppendorf pipet for 0.100 ml, or the 200 1 Eppendorf pipet for 0.200 ml or 0.400 ml) plus 0.010 ml 1.6 N HNO3 (using the 50 μl syringe) for each 1.00 ml of rainwater to the AAS autosampler tube, then add the corresponding amount ofSRM 2694I (1.000 ml for each element, using the 1000 μl Eppendorf pipet).

  Prepare the AA BLANK at the same time. This blank reflects the concentration of the audit standard in matrix components, but DDW is used instead of the NBS simulated rainwater. Prepare exactly as the rainwater was prepared, using DDW.

- Preparation of ERA Ca audit standard

  The ERA Ca stock solution is 100.00 μg/ml in Ca. Because this needs dilution to 1.000 μg/ml, the modifiers can be added at the time of dilution.

Table 3-1
Quality Control Standards

(I) NIST Simulated Rainwater Standards

Species	Concentrations in µg/ml NBS 2694-1	NBS 2694-11
Fluoride	0.054 ± 0.002	0.098 ± 0.007
Chloride*	0.24	1.0
Nitrate	---	7.06 ± 0.15
Sulfate	2.75 ± 0.05	10.9 ± 0.2
Sodium	0.205 ± 0.009	0.419 ± 0.015
Potassium	0.052 ± 0.007	0.106 ± 0.008
Ammonium*	---	1.0
Calcium	0.014 ± 0.003	0.049 ± 0.011
Magnesium	0.024 ± 0.002	0.051 ± 0.003

I. WasteWatR Quality Control Standards

Parameter	Lot No. 9927 ERA Certified Value mg/l	Advisory Range mg/l
Potassium	230	207 - 253
Berilium	230	207 - 253

III. Hardness WasteWatR

Parameter	Lot No. 9927 ERA Certified Value mg/l	Advisory Range mg/l
Calcium	68	54 - 82
Magnesium	35	28 - 42

*Values are not certified

Using a 10.00 ml volumetric pipet prepared by rinsing with the solution to be pipetted, pipet 10.00 ml 1% combined Cs/La stock solution into a 100.00 ml polymethylpentene volumetric flask. Using a 1000 µl Eppendorf pipet, add 1.00 ml 1.6 N HNO3 to the same 100.00 ml flask. Using the 1000 µl Eppendorf pipet and the balance to confirm a 1.000 g weight, pipet 1.00 mlERA Ca stock solution into the same flask. Fill to the 100.00 ml mark with DDW and mix by inverting and swirling at least 10 times.

Prepare a Ca audit blank at the same time, using another 100.00 ml polymethylpentene volumetric flask, adding 10.00 ml 1% combined Cs/La stock solution and 1.00 ml 1.6 N HNO3 and filling to volume with DDW.

Store these solutions in 125 ml high density polyethylene bottles, labeled with the concentrations of components, date of preparation and initials of the preparer, as for the calibration standards.

- Preparation of ERA Quality Control Standard

The ERA quality control standards used for AAS analysis are the Minerals WasteWatR (for Na and K) and Hazardous WasteWatR (for Ca and Mg). The Minerals WasteWatR is diluted 1:1000 to get the coponents in range for analysis by putting 1.00 ml stock solution (using a 1000 µl Eppendorf pipet) into a 1000 ml volumetric flask. Fill to volume with DDW.

The concentrations of both Na and K are 0.230 µg/ml in the resulting standard.

The Hazardous WasteWatR stock is duluted 1:100 by putting 100 ml (using a 1000 µl Eppendorf pipet) stock into a 1000 ml volumetric flask. Fill to volume with DDW and mix thoroughly. The resulting QC standard has concentrations as follows: Ca = 0.680 µg/ml, Mg -= 0.350 µg/ml.

3.2 Use (What is compared with standards)

Standard Reference Material (SRM) 2694, simulated rain water, from the National Bureau of Standards is used as a cross audit check. SRM 2694 has

been developed to aid in the analysis of acidic rainwater by providing homogeneous materials as control standards at each of two levels of acidity. The standard was prepared by the dissolution of high-purity salts and acids in high-purity distilled-deionized water. Certified values for SRM 2694-I and 2694-II are listed in Table 3-1. The laboratory analyst should verify the SRM for each element daily for every 50 samples as external quality control checks.

Presently, ERA quality control standards are used. The working standards as well as selected calibration standards should be prepared and analyzed by the laboratory manager or an external quality assurance auditor quarterly as an independent check. All unused working standards should be kept in the laboratory as a backup tracer until data has been properly examined and reported.

3.3 The Accuracy of Calibration Standards

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

4.0 PROCEDURES

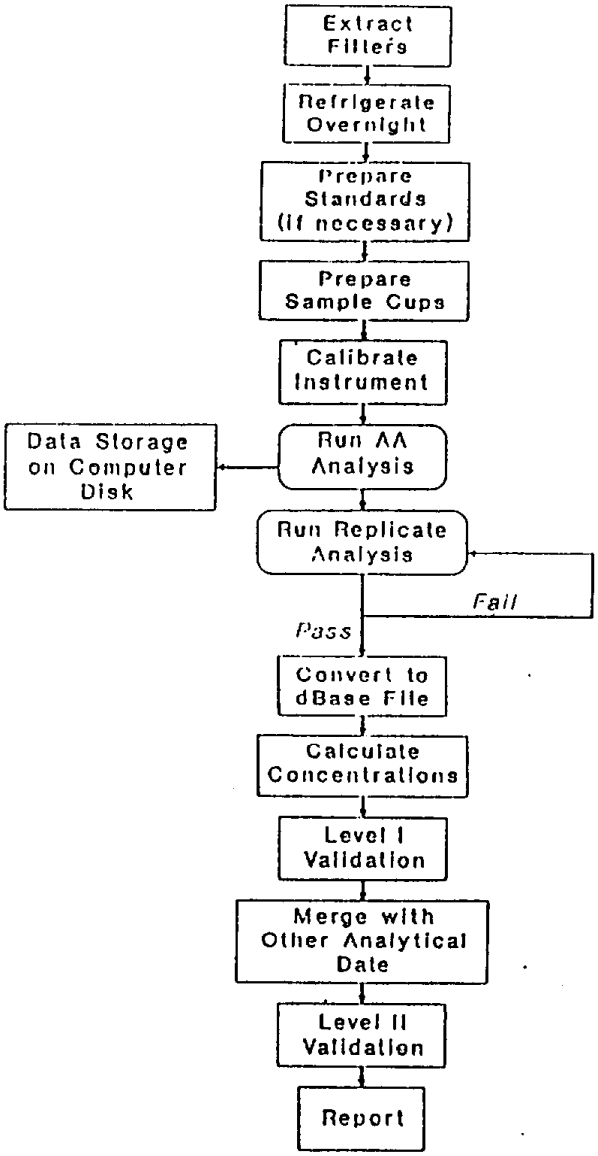
4.1 General Flow Diagram

A general flow diagram of routine atomic absorption spectrophotometry analysis is illustrated in Figure 4-1. It starts with the selection of standard operating conditions and analysis parameter set up. The samples and replicates are analyzed after the standard calibration.

4.2 Sample preparation

Make sure samples, standards and reference materials are all at room temperature. Cold samples seem to produce low signals, probably becauseless sample is being delivered to the flame since some of the nebulizing energy is absorbed in warming the sample.
Set up a test tube rack of AAS sample tubes labeled to correspond to the sample ID's, in the order to be analyzed as specified on the run list (see Figure 2-4, and Section 4.3). Pipet into the tubes any necessary

Figure 4-1. DRI AA Analysis Flow Diagram.



additives (modifiers) in the amounts indicated above in section 3.1. Note the required dilution factors from the use of the additives on the run list. Then, pipet the required amount of sample for the analysis, checking both the sample test tube and the AAS sample tube for ID. One ml is needed for each element to be analyzed, with generally 0.100 ml 1% Cs and/or 0.100ml 1% La Stock Solution per ml sample.

4.2.1 Preparation of samples for analysis for Na and K

Samples will have been extracted as indicated on the analysis list (Figure 2-2). If the samples were teflon filters, they will have been wetted with 200 μl ethanol before extraction. Standards may need to be modified to correspond to the samples (see Section 3.1). Generally, samples to be analyzed only for Na and K are extracted in DDW. Because the sample extracts are used for additional analyses, the matrix modifiers cannot be added to the samples except in the AAS auto sampler tubes.

Pipet 0.100 ml (using a 0.100 ml Eppendorf pipet for 0.100 ml and the 0.200 ml Eppendorf pipet for 0.200 ml) 1% Cs stock solution for each ml of sample to be analyzed into the autosampler tube. Then pipet (using the 1.00 ml Eppendorf pipet for 1 ml sample and repeat for 2.00 ml) the corresponding sample in the correct amount into the same autosampler tube. Use 1.00 ml sample for 1 element and 2.00 ml sample for 2 elements. The pipetting of the sample from the extraction tube into the autosampler tube is done by pouring roughly the correct amount of sample into a 10 ml disposable beaker and pipetting from the beaker. This procedure maintains the sample integrity. Necessary sample dilutions can be carried out directly in the AAS sample tube if the dilution will not exceed the capacity of the tube. Matrix modifiers are added in the amount of 0.100 ml per 1.00 ml sample analyzed (or, final volume of the sample in the AAS autosampler tube). Note any dilutions on the run list and maintain the correct ratio of matrix modifiers to sample.

4.2.2 Preparation of samples for analysis for Ca

The samples will be pipetted into the autosampler tubes as for the Na, K case, but the modifiers are different. In the case of CADMP, the samples are extracted in the correct matrix, so modification is not necessary. The need to pipet the sample into the AAS autosampler tube is also eliminated for CADMP samples, so the appropriate amount of sample can be merely poured from the extraction tube into the autosampler tube.

If the samples were extracted in water only, pipet 0.100 ml 1% La stock solution and 0.010 ml (using the Hamilton 50 µl syringe) 1.6 N HNO_3 per 1.00 ml sample into the labeled autosampler tube. Then,pipet the sample into the autosampler tube using the procedure described in section 4.2.1.

4.2.3 Preparation of samples for analysis for Mg

Occasionally, requests are made for Mg analysis only. If possible,extract these in the matrix used for CADMP to minimize matrix modification. If the samples are in DDW, the sample matrix must be modified to correspond to the standards as used in the calibration of the AAS. Although nitric acid matrix is not necessary for the Mg analysis, generally the standards are made up in nitric acid, so the samples must be modified. The La interference suppressant must be added.

Pipet into the labeled autosampler tube 0.100 ml (using the 0.100 ml Eppendorf pipet for 0.100 ml or the 0.200 ml Eppendorf pipet for 0.200 ml) 1% La stock solution and 0.010 ml (using the Hamilton 50 µl syringe) 1.6 N HNO_3 per 1.00 ml sample. Add the nitric acid only if the samples were extracted in water. Pipet the corresponding sample and sample amount using Eppendorf pipets as described abovein Section 4.2.1.

4.3 Instrument start-up

Start with all instrument parameter knobs on right front panel at farthest point counterclockwise:

Signal---------Lamp
Mode----------Cont
Recorder-------Abs
Gain at farthest counterclockwise position
Lamp at farthest counterclockwise position
BG Corrector---AA.

Install lamp for element to be analyzed by removing lamp and loosening the holder screws in the lamp chamber. Remove the holder with the lamp. Replace with the correct lamp in its holder. Each lamp has its own holder, so a lamp should need to be removed from a holder only when the lamp needs to be replaced. This procedure minimizes time spent aligning the lamp since it remains aligned in the holder. The alignment needs to be checked when a lamp in its holder is placed in the lamp chamber since it may have been moved.

Turn power to instrument on by pushing POWER switch on the far lower right corner of the instrument.

See Table 4-1 for Standard Operating Conditions.

Turn lamp to proper current as written on lamp for continuous operation, as indicated in LAMP/ENERGY window on right front panel of instrument by rotating the LAMP knob in a clockwise direction, watching the indicator LAMP/ENERGY window. (For Na/K lamp, current should be 12 ma; for Ca/Mg lamp, current should be 15 ma.)

Select proper wavelength using the COARSE ADJUST knob and slit width for the element of interest (refer to the standard operating conditions as provided by Perkin-Elmer for the element of interest), as listed on the instrument left front panel The slit width is selected from the SLIT, nm, NORMAL side of the dial.

Set the SIGNAL control on the right hand control panel to SET UP.

Set the GAIN so a value of roughly 50 is shown in the LAMP/ENERGY window by rotating the GAIN knob gently in a clockwise direction.

Maximize the signal from the lamp by adjusting the FINE ADJUST knob to get a maximum lamp energy reading as indicated on the LAMP/ENERGY window on the right control panel. Align the lamp in the holder by adjusting the two large alignment screws on the holder and watching the LAMP/ENERGY reading. (This needs to be done only when the lamp has been changed. The adjustment should be minimal, so turn the knobs only slightly.) Readjust the GAIN to get an energy reading of approximately 75.

Set the SIGNAL control to ABS by turning the knob clockwise to the ABS position.

Position the burner head only if it has been removed for cleaning and replaced. With the burner head clearly not interfering with the path of the light from the lamp to the signal receiver, press AZ to zero the reading. (The location of the burner head can be seen by placing a piece of paper between the burner head and the left hand wall of the burner compartment and observing the lamp image.) Find the maximum height of the burner head by rotating the BURNER HEAD VERTICAL ADJUST KNOB (marked with a V) so the head rises until a reading greater than zero is seen. Subsequent burner head adjustments must not raise the burner head above this level.

Table 4-1

Standard Conditions for Atomic Absorption

Chemical Species	Wavelength (nm)	Slit Width (nm)	Flame Gases
Na^+	589.0	0.7	Air-Acetylene
Mg^{++}	285.2	0.7	Air-Acetylene
K^+	766.5	2.0	Air-Acetylene
Ca^{++}	422.7	0.7	Air-Acetylene

Check the level of liquid in the drain jug, empty if too high, fill up to the line drawn on the jug. Check the acetylene level (replace tank if pressure falls below 520 kPa). Turn on exhaust fan. Turn on AIR valve (left front panel of instrument), check that flow rate is 40. (Adjust with OXIDANT FLOW knob, if necessary.) Turn on FUEL using toggle switch to point straight out, check that flow rate is 20. (Adjust with FUEL FLOW knob, if necessary.) Ignite flame with lighter by holding the lighter flame near the opening of the burner head. Lower probe into water beaker by pressing MANUAL on the AUTOSAMPLER CONTROLLER. Always turn on air first, then fuel and light. When flame is lit, aspirate water or sample. To warm up instrument, let water aspirate through flame for about 15-30 minutes.

Adjust the location of the burner head only after it has been removed for cleaning and replaced. To adjust burner head location, aspirate the standard which produces an absorbance of about 0.200 absorbance units while moving the burner head horizontally by turning the left hand knob marked H and watching the READOUT window until maximum absorbance is observed; then, rotate the burner head to achieve maximum absorbance using the knob located back in the burner chamber to the right of the burner head assembly; then, lower the burner head from its maximum position by turning the right knob at the bottom of the burner head assembly marked V to check if absorbance increases. The sensitivity of the signal to burner headlocation for one element compared to another for the four elements presently analyzed using these procedures is small, so these adjustments do not have to be made when changing from analysis for one element to another.

Adjust nebulizer only after it has been removed and taken apart for cleaning. This cleaning is done only if necessary, probably about once per year. To adjust nebulizer to maximize absorbance, aspirate the standard which produces an absorbance of 0.200 and rotate the front nut of the nebulizer until bubbles come into the tube. Then tighten the knob again until a maximum absorbance is observed.

On the right control panel, set MODE to HOLD. Set integration TIME to 0.4 by pressing "0.4", "t". (This sets integration time at 0.4 seconds.) Average 8 readings by pressing "8", "AVE". Set Standard Deviation (SD) and PRINT on by pressing these buttons.

4.3.1 Data Collection

Turn on chart recorder, chart speed at 2.5 cm/min, 0.01 volts fullscale.

Select computer settings to accumulate data:

Turn computer on by flipping the power switch located at the back left side of the computer, insert a disc to collect absorbance readings.

Select the proper directory by typing
"DIR/p" return
This lists the directories one page at a time. Select any key to get the next page.

Switch to the proper directory by typing
"CD\xxxxx" return
This selects the main directory, where xxxxx is the name of that directory.

Select a proper subdirectory (if necessary, usually AA) by typing
"CD\xxxxx\AA" return

Call up data accumulation program by typing

"AACOM" at the DOS prompt (C:\>), return.

The AACOM program accumulates data in the computer and prints the absorbencies as they are read by the AA.

- Run list (See section 2.3)

The run list (see Figure 2-4) must be maintained on a written sheet since there is no way to enter a sample ID into the data collection program at this time. The run list is prepared before the run is started and samples and standards are run in the order indicated. Standards in increasing order from blank to 1.500 µg/ml, QA standard (usually NBS simulated rainwater 2694I), AA BLANK, other QA standards and blanks.

Samples, replicates and standards in this order:

10	Samples
1	Replicate
1	Standard (approximating expected value, or range)
1	Blank (as used in Auto Zero)

10	Samples
1	Replicate
1	Standard (Page 2 of run list)
10	Samples
1	Replicate
1	Standard
1	Blank
10	Samples
1	Replicate
1	Standard

This sampling order maintains the recommendation of one blank every 20 samples, one replicate every 10 samples, one standard every 10 samples. If any dilutions are made, a dilution blank should be analyzed as one of the samples. An AA BLANK consisting of any modifiers and a volume of DDW corresponding to the volume of sample should also be prepared and run as a sample. This last is to check any possible deviation of the AA standard blank with the actual preparation of the samples.

Any additional dilutions must be entered on the run list as the samples are prepared. The computer run number must be entered on the list as the samples are run, but absorbencies do not need to be recorded as this can be recovered from the printed copy of the collected data.

Label the run list with the name of the file, the date, the element and the analyst's initials.

Generally, the sample tray is filled with samples and QA standards, so the calibration is done by aspirating the calibration standards manually. Aspirate the blank by lifting the probe from the DDW beaker by pressing MANUAL on the autosampler control box. Press AUTO ZERO. This will be entered as #1 on the data in the computer. Read standards and samples in ABSORBANCE,

use the computer to convert the data into concentration during data entry. Read the blank by pressing READ. This will be #2 in the data file. Read the standards in increasing order by removing the tube from the probe and aspirating another. Watch the absorbance on the recorder until it levels out, then press the READ button. After the AVERAGE is printed out, the sample can be removed from the probe. Refer to previous runs to check if standards are yielding a similar absorbance. Even if the standards yield different absorbencies than previously, if a plot of absorbance vs. concentration gives a smooth curve (not linear at higher concentrations), the readings may be used. Read the absorbance of the NBS simulated rainwater prepared with any necessary modifiers as outlined in 3.1.2. Compare the readings with previous readings and with the calibration plot, using the dilution correction to see if the result is within the permitted range (±10%).

If the calibration curve and audit standard are acceptable, proceed with analysis using autosampler.

4.4 Routine operation with Autosampler

Samples can be introduced into the AAS manually by holding a sample tube up to the probe, or using the autosampler. The autosampler can calibrate using 3 standards if the AAS is in the CONCENTRATION MODE. In the ABSORBANCE MODE, it seems easiest to auto zero and read standards manually so there is maximum space in the autosampler for samples. Note that when the AAS is not being used for analysis (as in warm-up or while loading trays), the probe should be in the rinse beaker so water is being aspirated at all times. The auto sampler is returned to this rest position by pressing RESET, then MANUAL to lower the probe into the beaker. This position is used when samples are introduced manually, as at the beginning when the standards are read.

4.4.1 Autosampler settings

Since measurements are made in the ABSORBANCE MODE, the number of standards (# STD) is zero. In routine analysis, the AZ, S1, S2 and S3 spaces at the beginning of the analysis are not used. The autosampler is advanced to position 1 by pressing "1, MANUAL", then the START/STOP button is pressed for routine analysis. (If the autosampler is not advanced to position 1, in the absorbance mode, the Auto Zero will be reset (AZ). In general, this is undesirable since the standards were read before the auto sampler was set in

use. If the standards are included as the first several samples, this option could be used.)

Set READ DELAY to 3 (3 seconds), READ TIME to 5 (5 seconds). This read delay allows time for the preceding sample to be washed through before readings are taken on the current sample. The read time is long enough to let all 8 readings to be taken. This sampling time requires about one ml of sample.

Load the auto sampler tray from the run list, enter the number of the last sample by typing "number of last sample", LAST SAMPLE.

4.4.2 Sampling Sequence

The order of samples and standards in the autosampler carousel is as in the run list, as follows:

Positions 1-10	: Samples
Position 11	: Replicate
Position 12	: Standard (approximating expected value, or range)
Position 13	: Blank (as used in Auto Zero)
Positions 14-23	: Samples
Position 24	: Replicate
Position 25	: Standard

(Page 2 of analysis list)

Positions 26-35	: Samples
Position 36	: Replicate
Position 37	: Standard
Position 38	: Blank
Positions 39-48	: Samples
Position 49	: Replicate
Position 50	: Standard

This sampling order maintains the recommendation of one blank every 20 samples, one replicate every 10 samples, one standard every 10 samples. If any dilutions are made, a dilution blank should be analyzed as one of the samples. An AA blank consisting of any modifiers and a volume of DDW corresponding to the volume of sample should also be prepared and run as a sample. This last is to check any possible deviation of the AA standard blank with the actual preparation of the samples.

4.4.3 When data collection is complete, press "ESC" to get out of the data accumulation program. The program then prompts for the name of a file to save the data. The data are saved to the C: drive at the end of data collection by typing "projdate.element" (where "projdate"= 2 letter symbol for the project name, four digit month and date) and the "element" extension is a two letter symbol for the element and the number of the analysis run (example: SB0516.Na1 = Santa Barbara samples run 05/16, sodium 1) when requested.

These data are transferred to a floppy disc to be used in calculating the concentrations from this absorbance data using dBase.

Type "copy 'projdate.ele' a:" to copy the file to a floppydisc.

4.4.4 If another element on the same lamp is to be analyzed, the sample tubes must have been loaded with the appropriate amount of sample (1 ml per element). It is necessary to merely change the wavelength, recall the data collection program on the computer (AACOM), read the standards for the second element and proceed with the analysis on the autosampler (see Section 4.3.1). If other elements are to be analyzed on the same samples, it is most efficient to change the lamp and proceed with the analysis of all elements on the samples before reloading the tray. Thus, the order of analysis on two trays of samples for four elements (two lamps) would be as follows: Tray 1, element A, element B (lamp 1), element C, element D (lamp 2); Tray2, element D, element C (lamp 2), element A, element B (lamp 1).

While the analysis on the AAS is taking place, the next rack of samples can be prepared.

4.5 Shut-Down

After all analyses are complete and checked for reproducibility and accuracy (QA standards), water is aspirated through the burner chamber for 5 minutes to clean the chamber by pressing the MANUAL button on the autosampler to lower the probe into the rinse beaker. Then, the probe is lifted from the rinse beaker by again pressing the MANUAL button on the autosampler.

The flame is turned off from the left hand control panel of the instrument by flipping the FUEL toggle to the up position. After the flame goes out, the air is turned off by turning the oxidant valve to the OFF position. The exhaust fan can now be turned off by slipping the switch mounted on the wall to the left of the instrument.

The instrument is turned off from the right hand control panel by turning the SIGNAL knob to the SET UP position and rotating the GAIN knob to its furthest counterclockwise position. Next, the SIGNAL knob is turned to the LAMP position, and the LAMP knob is rotated to its furthest counterclockwise position. The MODE knob is returned to the CONTINUOUS setting. The POWER switch is now turned to the OFF position.

The computer is turned off by flipping the POWER switch.

The printer is turned off by flipping the POWER switch.

The recorder is turned off by turning the POWER knob to OFF.

The autosampler is left on.

5.0 QUANTIFICATION

5.1 Calculations

5.1.1 Since the measurements are taken in Absorbance, the readings must be converted to concentrations based on the standards. This is presently performed using a combination of manual and computer calculations.

The absorbencies are entered into a data base as follows:

From the MS-DOS prompt (C:\>) select the proper directory.

To get a listing of directories, one page at a time, type "dir/p" (return)

To view additional pages, press any key.

Change to the proper directory (selected from the listing according to the project) by typing "cd\xxxxxx" (return) where xxxxx is the name of the directory.

Often a subdirectory is used to store AAS data, so obtain a listing of the sub directories of the selected directory by typing

"dir/p" (return)

AAS data are stored in the subdirectory called "AA"

Change to the AA subdirectory by typing

"cd\xxxxx\aa" (return)

(This can be done at the first step if an AA directory does not need to be made)

If an AA subdirectory does not already exist, create one by typing

"md aa" (return)

Once the correct directory is being used, go into dBase by typing

"dbase" (return)

Load the floppy disc with the data into the a: drive.

List the files on the disc in a: drive by typing

"run dir a:"

Call up the data entry program to enter the data into a database by typing one of the following:

"do inputna" to input sodium data,
"do inputk" to input potassium data,
"do inputca" to input calcium data,
"do inputmg" to input magnesium data.

At the prompt "NAME OF INPUT FILE", type

"a:yyyyyy.ee"

where yyyyy.ee is the name of the input file to be used for the element to be entered in a data base.

At the prompt "NAME OF OUTPUT FILE", type

" zzzzzz "

where zzzzz is the name of the database file already named in the analysis list.

The absorbance data are now read from the floppy disc into the database created by the program on the c: drive.

Next, the analysis dates (ADATE), area factors (AREAF), extraction volumes (EXTVOL), dilution factors (NAADILF,KPADILF, CAADILF or MGADILF) are entered as follows:

Type: "replace all adate with ctod('mm/dd/yy')" (return)
"replace all extvol with nn" (return)
where nn is the extraction volume in milliliters
"replace all areaf with aa" (return)
where aa is the inverse of the fraction of filter used in the extraction
"replace all naadilf with dd" (return)
where dd is the dilution factor applied to the majority ofthe analyses in the set, as described on the run list notes.

To enter the sample ID (QID), flags (NAAF, KPAF, MGAF, or CAAF), and check the dilution factors, and absorbencies (NAABS, KPAABS, MGAABS, or CAAABS), type
"brow fields qid, naaf, naadilf, naaabs" (return)

In the BROWSE mode, enter the sample ID's from the run list checking the computer run number with the file number and the absorbance from the hard copy of the original data.

At the same time, enter the flags to identify the standards, replicates, blanks and quality assurance standards as follows:

q1 standard check
q4 standard used in calibration
r1 replicate samples (further replicates, use r2,etc.)
b1 field/dynamic blank
b2 laboratory control blank
b3 distilled water blank
b4 method blank
q2 or q3 extract/solution blank, AAblank
q2 QA standard other than NBS
q3 NBS QA standard
q5 spike tests
v void

After the sample ID's and flags have been entered, press CONTROL and END simultaneously to exit from the browse mode and save the changes made.

After the flags have been entered, any changes in extraction volume, area factors and dilution factors can be made by reference to the flags, for example

"replace extvol with 1 for naaf='q1'.or.naaf='q2'"(return)

For example, the standards will have a dilution factor of 1, while the samples and NBS rainwater will have dilution factors dependent on the additives or subsequent dilutions. Extraction volumes and area factors for standards and rainwater are 1.

The description of the curve must be entered manually at this time. A plot is manually generated using a hand calculator and a linear regression function; concentration of the y axis, absorbance on the x axis will correspond to the calculations. The plot will generally begin to curve such that less absorbance than expected based on a linear response is observed. The curving generally begins at an absorbance of about 0.2. This means, a linear description can be entered up to the point where curving of the plot is observed, then linear sections between pairs of standards are entered. A linear regression is performed on the data in the linear region (using a calculator), and the slope and intercept are entered into the data base for absorbencies in that region. The slope and intercept for each of the piecewise sections are similarly entered for the absorbencies involved in each section.

Proceed as follows: After the calibration curve with slopes and intercepts according to the absorbencies has been generated and written in a listing, the data are entered:

"replace naaint with -0.xxxxx for naaabs<=0.0aa" (return) where -0.xxxxx is the calculated intercept with 5 decimal places for the absorbance area less than the upper bound of the linear region.

Press the up arrow to recall the last command (up to 20 previous commands) type over the numbers for the entry of the next intercept and absorbance range to produce:

"replace naaint with -0.qqqqq for naaabs>0.0aa.and.naaabs<=0.bbb" (return)

Continue entering the intercept data for the various regions by pressing the up arrow and typing over the required numbers.

After the intercept data are entered, use the up arrow to change to the slope and enter slope data

"replace naaslope with 2.sssss for naaabs>0.ppp.and.naaabs<=0.kkk" (return)

After the slopes and intercepts are entered, the concentration (NAAML, KPAML, MGAML or CAAML) can be calculated according to

Concentration = Slope*Abs + intercept

(Note, the Y variable must be concentration while the X variable is absorbance for the equation to have this form.)

type: "replace all naaml with naaabs*naaslope+naaint" (return)

Calculate the concentration (NAAC, KPAC, MGAC or CAAC) on the filter as follows:

type: "replace all naac with naaml*naadilf*areaf*extvol" (return)

Then, the concentration of the element of interest on the filter is:

[filter] - [solution]*extvol*areaf*dilf.

Finally, after the data are all entered, get a hard copy of the data by typing

"run copy\compr prn" (return) to change the printer to compressed print

"list to print" (return)

Make a copy on a disk by typing

"run copy zzzzz.dbf a:" where zzzzz.dbf is the name of the database file.

5.2 Precision Estimates

The precision for samples analyzed over selected time periods is calculated by the methods described in Watson et al.(1983). For replicate analyses, the precision of the ionic species C, on each sample extract is

$$C = \left[\frac{1}{n-1} \sum_{i=1}^{n} (C_1 - C_2)^2\right]^{1/2}$$

where:

n = number of replicates

Cl = ionic concentration derived from routine analysis

Cr = ionic concentrations derived from replicate analyses

This precision contains the uncertainty due to the inhomogeneity of the deposit across the filter surface as well the uncertainty of the ion analysis. For dynamic blanks, the uncertainty of the blank subtraction, B is:

$$\underline{B} = [\frac{1}{m} \sum_{j=1}^{M} B_j$$

where:

M = the number of blanks

B_j = the value of the jth blank

B = the average blank value

The average blank value, $\bar{B}$, is normally subtracted from each ion measurement if it exceeds $\bar{B}$. Both C and B are combined with the precision of the sample volume measurement to determine the precision of the ambient concentrations.

6.0 QUALITY CONTROL

The quality control procedures serves two purposes: 1) to identify the possible problems with the measurement process, and 2) to calculate the precision of the ion measurements.

6.1 Performance Testing

Besides the daily start-up described in Section 4.0, the analysis sequence for standards, blanks, and replicates should be followed as specified in Section 4.3. After every ten samples, one replicate sample will be analyzed. The replicate should be from the previous day's run. In the case of a new project starting, with no previous analysis of the samples, the replicates can be chosen from the set of 10 just run, the next replicate would also be from that first set, and the ones after that from the set preceding the current one by two.

After each group of ten, a standard will be run. The standard and replicate will be evaluated, and the data recorded on a QA chart, kept by the instrument for this purpose. Figure 6-1 is an example of the QA chart

to be used. The equation for the calculation of the replicate percent error is as follows:

$$\text{Error } \% = \frac{(R_{1i} - R_{2i}) \times 100}{(R_{1i} + R_{2i}) \div 2}$$

Where:

R_{1i} = concentration of sample i
R_{2i} = concentration of the replicate analysis of sample i

For calculation of the standard percent error:

$$\text{Error } \% = \frac{(S_i - S) \times 100}{S}$$

Where:

S = concentration of the working standard
S_i = concentration of standard obtained from the replicate analysis

6.2 Control Charts, Tolerance and Actions to be Taken

Maintain a QC chart of the absorbencies of selected standards and the NBS rainwater to monitor the performance of the instrument. An absorbance suddenly way off would indicate a contamination. Gradual change in the absorbance would indicate the growing need to reset instrument parameters to readjust absorbance to the maximum.

The permissible range of error is a function of concentration and the element to be analyzed as stated in section 1.5 with a larger percent error range tolerated for lower concentrations. Ranges of errors depend on the species analyzed because sensitivity varies with analyte. Sodium and potassium have approximately the same sensitivity, so the expected ranges of error for these two elements are the same: ±30% for concentrations less than 0.100 μg/ml; ±20% for concentrations between 0.100 and 0.150 μg/ml; and ±10% for concentrations greater than 0.150 μg/ml. Calcium is approximately ten times less sensitive under the instrument conditions currently used, so the ranges of error would be expected to shift by that factor: ±30% for concentrations less than 1.000 μg/ml; ±20% for concentrations between 1.000 and 1.500 μg/ml; and ±10% for concentrations greater than 1.500 μg/ml. Magnesium is roughly twice as sensitive, so the range of error would shift correspondingly: ±30% for

Figure 6-1. DRI AA Quality Control Chart.

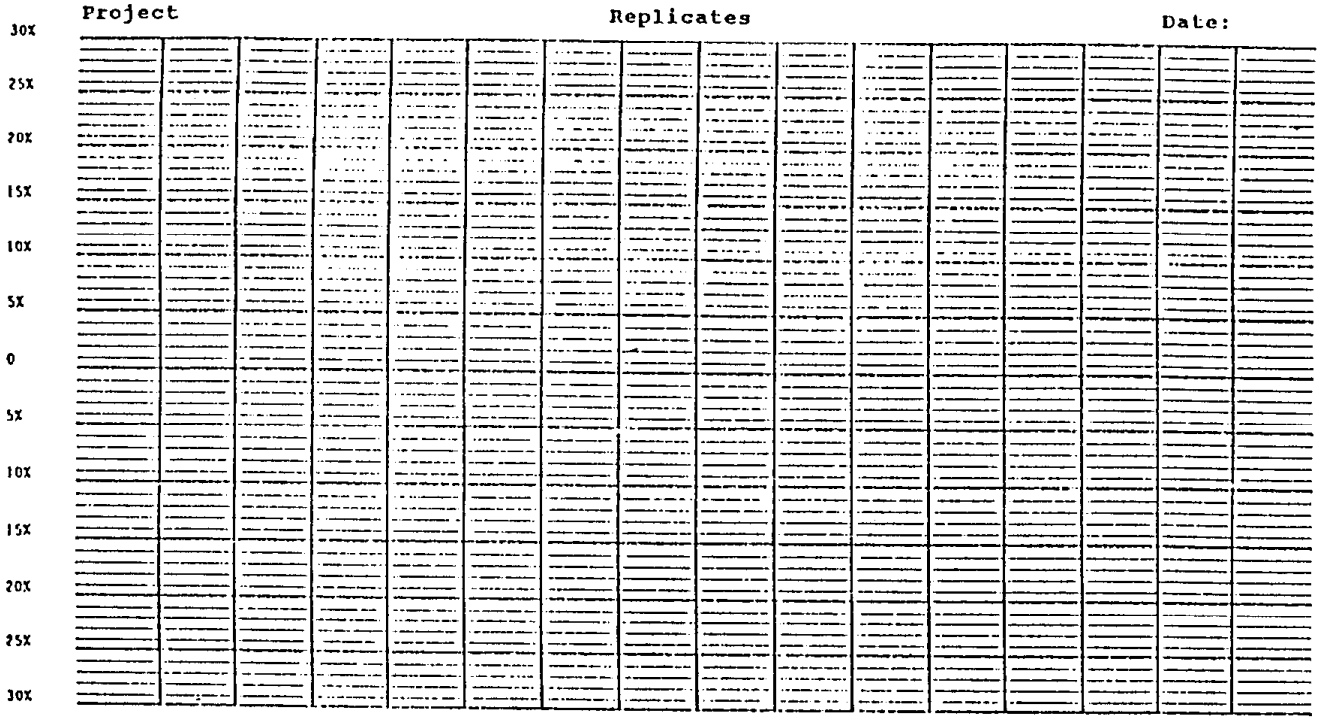
.030 - .100 µg/ml	30%
.100 - .150 µg/ml	20%
> 150 µg/ml	10%

Control Chart

Project

Replicates

Date:



concentrations less than 0.050 μg/ml; ±20% for concentrations between 0.050 and 0.100 μg/ml; and ±10% for concentrations greater than 0.100 μg/ml.

If replicates exceed the tolerances as calculated in section 6.1, the sample will be rerun to check for a spurious result. If the replicate is still in variance, standards should be rechecked, any dilutions redone and appropriate blanks checked. After the reason for error is discovered, samples analyzed after the replicate preceding the one in variance must be reanalyzed using the corrected procedure.

6.3 Record Keeping

A manila folder, with clips, will be used to keep the analyses records together. Data in the folder will be organized in the following sequences:

- The original analysis list request, containing sample numbers, priority of analyses, and other pertinent information.
- The sample run list, the order in which the samples were analyzed, including replicates and standards.
- The method used for the analysis.
- Calibration curves for the analyzed species.
- Original recorder charts.
- QA charts for replicates.
- QA charts for Standards.

The manila folder will be dated and labelled with the project name and filed in the proper cabinet.

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:

- Flagging samples when significant deviations from measurement assumptions have occurred.

- Verifying computer file entries against data sheets.

- Eliminating values from measurements which are known to be invalid because of instrument malfunctions.

- Replacing date when re-analysis have been performed.

- 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 the 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 the 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 project manager 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:

American Chemical Society (ACS) Committee on Environmental Quality (1983). Principles of Environmental Analysis. Analytical Chemistry 55: p. 2217.

Perkin Elmer Manuals

PE, 1980 #047-0096, 047-0097 Model AS-50 Flame Auto Sampler for Atomic Absorption, December, 1980. Perkin Elmer, Norwalk, CT.

PE, 1987 #0993-9575 Instructions, Model 2380 Atomic Absorption Spectrophotometer, September, 1987. Perkin Elmer, Norwalk CT.

PE, 1982 #0303-0152 Analytical Methods for Atomic Absorption Spectrophotometry, January, 1982. Perkin Elmer, Norwalk, CT.

Mueller, P. K., G.M. Hidy, J.G. Watson, R.L. Baskett, K.K. Fung, R.C. Henry, T.F. Lavery, and K.K. Waren (1983). "The Sulfate Regional Experiment: Report of Findings, Volumes 1, 2, and 3." Report EA-1901, Electric Power Research Institute, Palo Alto, CA.

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 the Technicon Random Access Automated Colorimetry System (TRAACS) 800 Continuous Flow Analyzer,
- describe routine analysis of ammonium ion (NH_4^+) in aqueous filter extracts or precipitation samples using the Technicon TRAACS 800,
- detail the concerns and procedures which will insure a state-of-the-art measurement process.

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

1.2 Measurement Principles

The measurement of ammonium ion in water and waste water by the Technicon TRAACS 800 is based on the Berthelot reaction (Berthelot, 1855). Indophenol blue, a blue dye, is formed when phenol and hypochlorite react with ammonia in an alkaline solution. Sodium nitroprusside is added to intensify the color.

The sample is drawn into the reaction coils by a peristaltic pump, mixed with alkaline phenol, nitroprusside (sodium nitroferricyanide), sodium hypochlorite, and the disodium salt of ethylenediaminetetracetic acid (EDTA), passed through a heated zone (37 °C for two minutes), and passed through a photocell detector. The absorbance at 660 nm is measured and converted to μg/ml. Brij-35 is added as a surfactant to the EDTA solution to aid in bubble formation. Bubbles are introduced into the sample tubing to aid in mixing the reagents and to serve as delimiters between samples.

1.3 Measurement Interferences and their Minimization

- The presence of alkali metals in the sample will cause precipitates to form at high pH (high alkalinity). The resulting opacity will interfere with the colorimetric detection. The formation of these precipitates can be prevented by the addition of EDTA to the sample stream as a complexing agent.

- Metals such as copper and aluminum can compete with the indophenol reaction, causing a decrease in sensitivity (Berthelot, 1855). The EDTA will complex with these metals also, decreasing the interference.

1.4 Ranges and Typical Values of Measurements

A wide range of ambient concentrations can be found in both the filter extracts and precipitation samples. NH_4^+ concentrations ranged from 0.00 to 10.06 $\mu g/m^3$ in ambient samples from the Denver airshed (Watson, 1988) with a median value of 1.03 $\mu g/m^3$. In general, "typical" ranges are difficult to express except in terms of ranges, because $\mu g/ml$ 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 minimum detectable limit of ammonia with the Technicon TRAACS 800 is 0.050 $\mu g/ml$ based on the manufacturer's specifications. The precision and accuracy of the Technicon measurement of ammonia depend on the sample matrix and individual techniques. In general, the accuracy of the TRAACS 800 is dominated by the uncertainties in the standard solution preparation and is typically within ±10%. Precision as estimated by replicate analyses is in the range of ±10 to ±30%, depending on the concentration.

1.6 Responsibilities of Personnel

All analysts in the laboratory should read and understand the entire standard operating procedure before performing the ammonia analysis on the TRAACS 800. The analyst must follow the procedure for routine system calibrations, chemical analysis and performance tests.

It is the responsibility of the laboratory manager to ensure that the colorimetric analysis 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 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 assuring 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:

Berthelot Reaction:	Berthelot (1855) first reported that a blue color is produced when phenol and hypochlorite react with ammonia in an alkaline reaction.
Bubble Pattern:	Air is injected into the sample stream to aid in mixing and separating samples, allowing steeper concentration gradients by keeping the samples separate. The bubbles should be oblong, well separated, present a repetitive pattern. A change in the bubble pattern is an indication of possible trouble.
Carry Over Adjustment:	In the analyzer tubing, samples can be contaminated by previous samples due to carry over. To calculate the amount of contamination, the protocol comment 'H,2L' will cause one high sample (usually the 2.00 μg/ml standard) to be analyzed and one low sample (usually DDW) to be analyzed twice. The difference between the two low analyses are then used to calculate the carry over. This correction is used in the final calculation of the data.
Detection Limit:	The concentration of an analyte which would yield an absorbance equal to twice the standard deviation of a series of measurements of a solution with a concentration distinctly detectable above, but close to a blank solution (ACS, 1983).

Gain Peak Number: The number of the sample peak used to correct for possible drift in analytical response during an analysis run. A sample early in the run is reanalyzed as the last sample in the run, and the gain is adjusted to minimize the difference in the responses. The sample to be reanalyzed is designated by the tray protocol command "G@x", where x is the sample cup number. The gain peak number is the peak number used for comparison with the last peak of the run. The convention is to designate the third peak (gain peak number = 3), which corresponds to the 2.00 μg/ml standard in the second cup, as the gain peak and to include the command "G@2" in the tray protocol as the last cup analyzed. The sample used for gain adjustment must have a response of greater than 50% full scale.

Peristaltic Pump: The pump squeezes flexible, small diameter tubing between a rotating set of rollers and a platen, causing the fluids to be pumped. Flow rates are governed by the interior diameter of the tubing.

Pump Tubing: The tubing used in the peristaltic pump to carry the liquids. These are color coded according to their inner diameters.

Tray Protocol: The commands which define the order in which the autosampler will access the sample cups. These commands include naming the type of sample in the cup and the number of times it will be analyzed. Commands consist of a one letter code followed by the cup number. For example, "C@9" means calibrant (standard) has been placed in cup number nine; "S2@6" means that there is a sample in cup number 6 and that separate statistics (average, standard deviation, and coefficient of variation) will be collected for all samples labelled "S2."

1.8 Related Procedures

Related procedures are specified in the following:

DRI SOP 13 Sectioning of Filter Samples

DRI SOP 14 Extraction of Ionic Species from Filter Samples

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

2.1.1 Description

The Technicon TRAACS 800 is an automated, continuous flow spectrophotometric instrument. It consists of the analytical console (peristaltic pump, reagent mixing coils, heating coil, and detector), a random access linear autosampler, an IBM-XT microcomputer, and a dot matrix printer (Figure 2-1).

An overall flow schematic appears in Figure 2-2. A schematic of sample flow through the colorimetric detector cell and of associated detector signal process is depicted in Figure 2-3.

The linear autosampler is a random access sampler, capable of accessing samples in any order specified, with sampling rates as high as 240 samples per hour. The autosampler provides positions for 120 4 ml polystyrene sample cups, as shown in Figure 2-4.

The Technicon TRAACS 800 instrument is controlled by the GATEWAY computer program. This software controls the flow of the reagents, the base and gain of the photometric signal amplifier, the sampling interval, the type of sample, the order of the samples, the concentration of the standards, and the name of the samples. The software also plots absorbencies as the samples are analyzed (in a strip chart format), plots the calibration data, calculates the concentrations of the samples, and saves the data in both chart and text file formats on a hard disk. The text file is then transferred to a data base and further manipulated to produce a report.

Figure 2-1. Technicon TRAACS 800 System Overview.

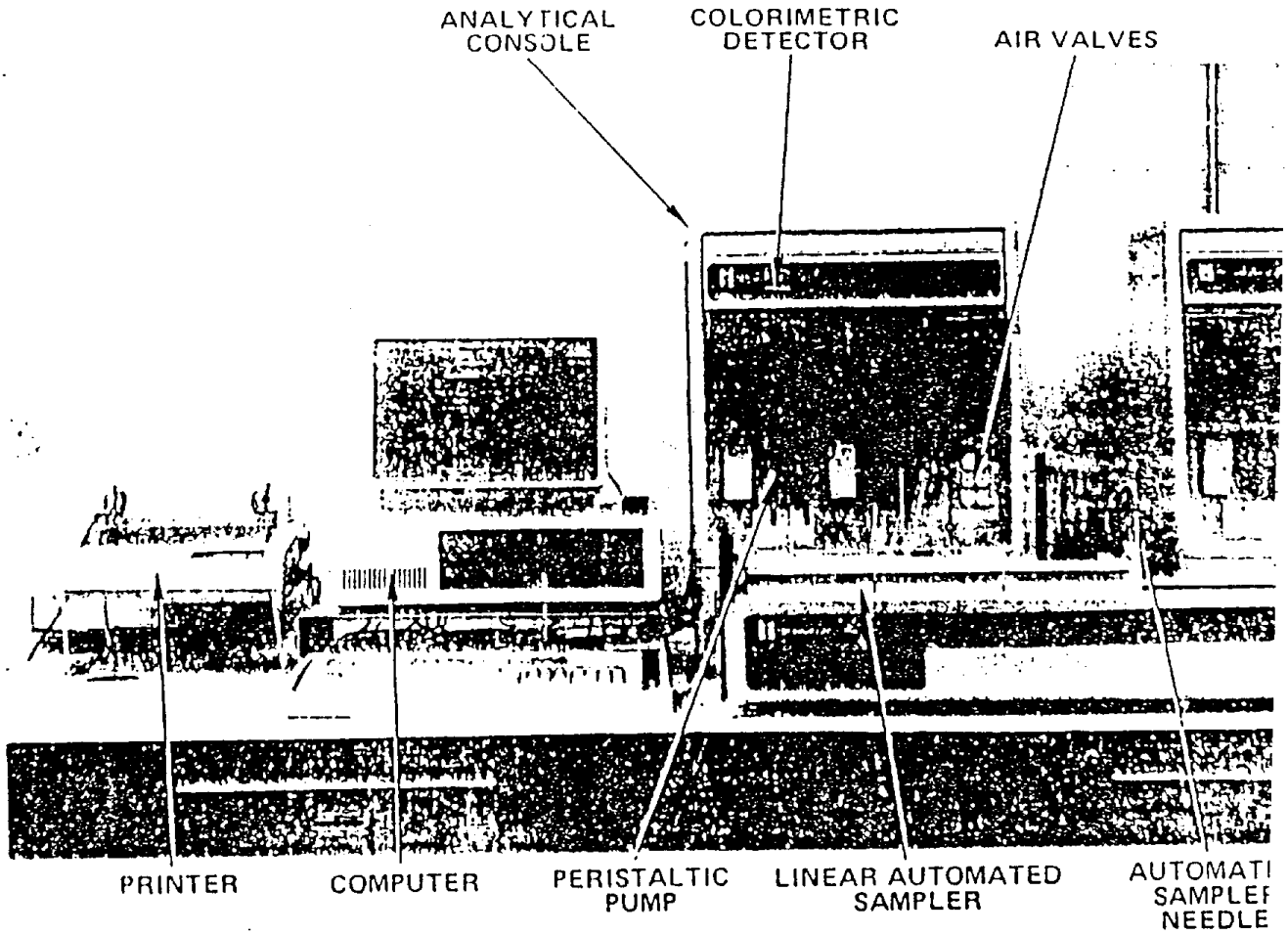


Figure 2-2. Technicon TRAACS 800 Flow Schematic.

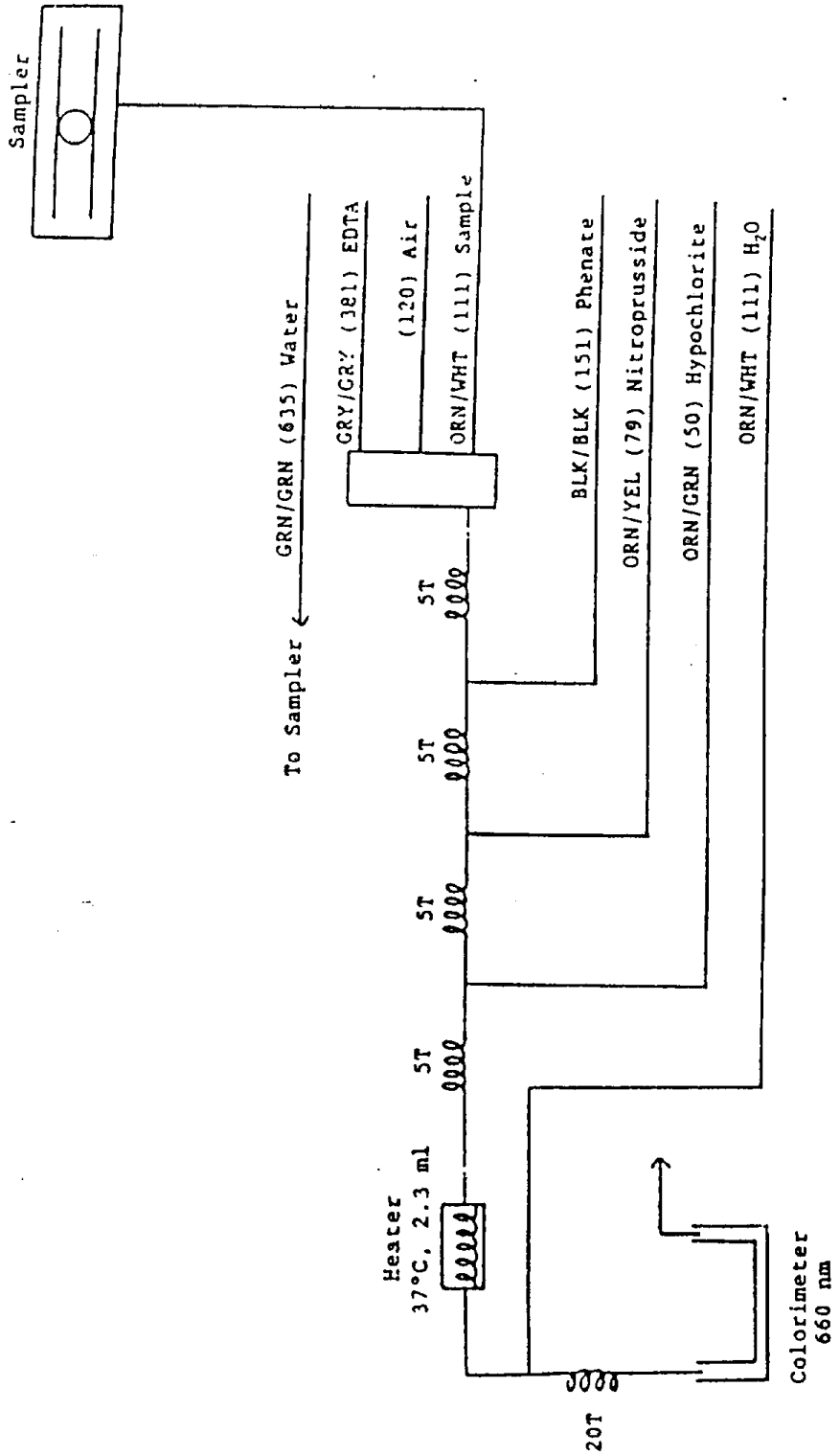


Figure 2-3. Technicon TRAACS 800 Detector Schematic.

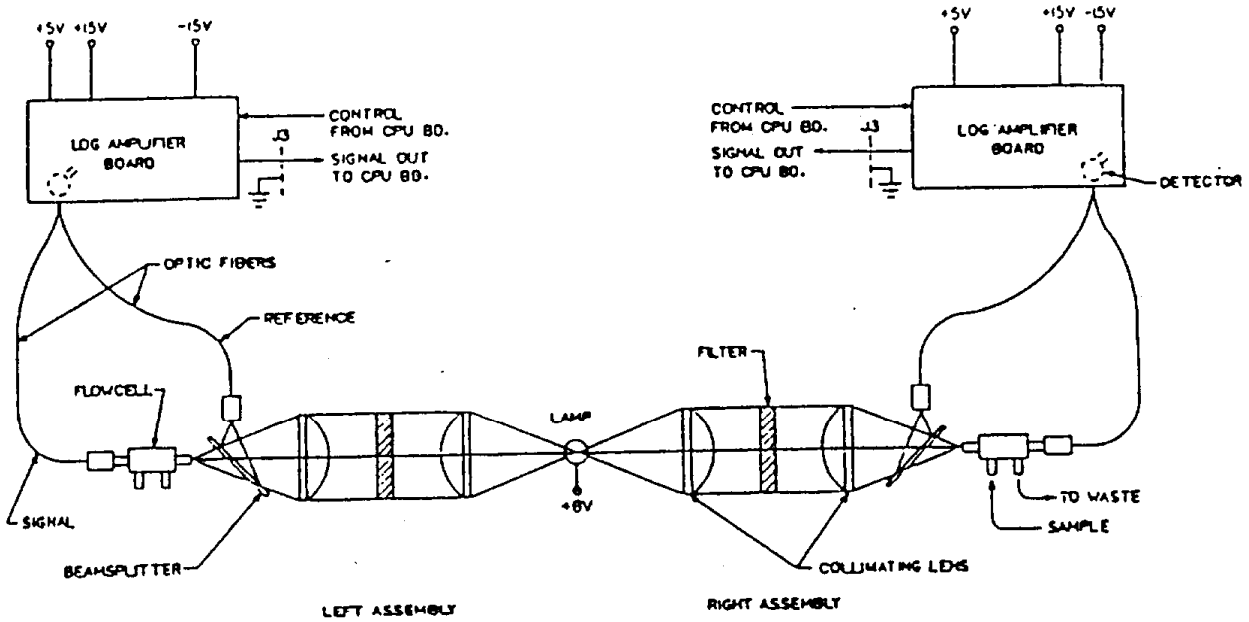
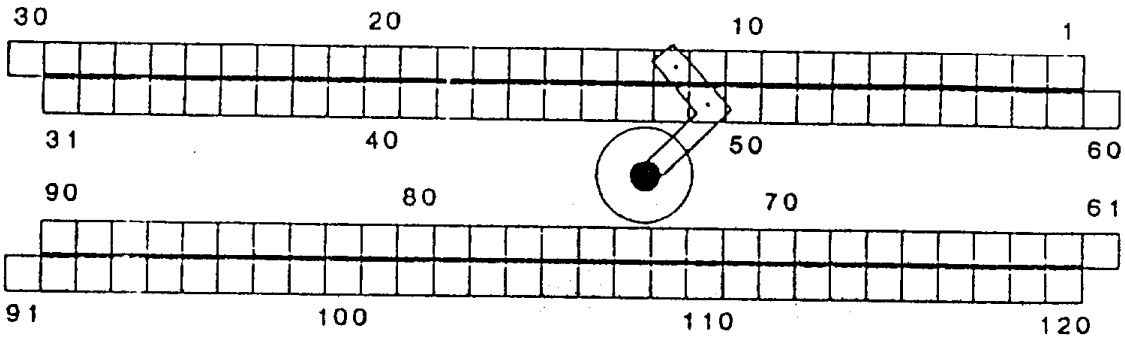


Figure 2-4. Technicon TRAACS 800 Linear Autosampler Cup Positions.



The GATEWAY program consists of five main modules, each containing submodules (Figure 2-5). The modules most commonly used are Chart and Run (press <F4>), Edit (press <F2>), Retrieve (press <F5>), and Exit to DOS (press <F1>).

Chart and Run is used to start the pumps, and perform calibration and analysis runs.

Edit is used to prepare the input file to be used for the analysis runs.

Retrieve is used to retrieve a text file (or chart file), usually to generate a calibration curve.

Exit to DOS is used to produce a hard copy of the tray protocol and to produce a report using DBase III.

The **Base and Gain** option automatically sets the base and gain, but this can be done easily manually, so this feature is usually not used.

The **Reanalyze** option can be used if input parameters need to be changed after the samples have been analyzed.

2.1.2 Instrument Characterization

The Technicon TRAACS 800 analyzes the contents of as many as 120 sample cups per run, including 10 standards, 10% replicate samples, and 5% distilled-deionized water (DDW) blanks. One ml of each sample is placed in the 4 ml sample cups; replicates are sampled from different aliquots. The sampling rate is adjustable, but is currently set at 80 samples/hour.

The analyzer maintains a 2:1 ratio of sample volume to wash volume to reduce cross-sample interferences. In addition, the autosampler probe is rinsed between each sample at its home position. Transit time for a sample aliquot to travel from the sample cup to the colorimetric detector is approximately seven minutes.

The GATEWAY program automatically established a five minute baseline response at the beginning of each run and a four minute baseline at the end of each run to characterize instrument stability.

Figure 2-5. Technicon GATEWAY Software: Main Menu.

Technicon TrMcs System

F1 DOS

F2 Edit

F3 Base & Gain

F4 Chart and Run

F5 Retrieve

F6 Reanalyze

?Return to Disk Operating System (DOS)

The TRAACS 800 Analytical Console contains a dedicated microprocessor which operates on software downloaded from the IBM-XT. This program is lost whenever the Analytical Console is turned off or experiences a power failure. After such interruptions in electrical power, the program must be downloaded to allow the Analytical Console to operate properly (see Section 4.2).

CAUTION: THE PHENOLIC WASTES GENERATED BY THE COLORIMETRIC TECHNIQUE ARE HEALTH HAZARDS AND MUST BE HANDLED APPROPRIATELY. WASTE CONTAINERS SHOULD BE CAPPED, CLEARLY LABELLED, AND PROPERLY STORED WHEN FULL.

Additional information on health effects and proper handling procedures may be found in the Material Safety Data Sheets (MSDS) binder located in DRI's Environmental Analysis Laboratory or in the laboratory supervisor's office.

2.1.3 Maintenance

Regular maintenance of the TRAACS 800 includes the following:

- The tubing passing through the air valves (refer to Figure 2-1) should be adjusted on a monthly basis. This involves pulling the tubing through the retainer clips so the pinch valves are operating on a fresh section of tubing.

- The peristaltic pump tubing has a rated lifetime of approximately 200 hours. This tubing should be replaced at least once per month under conditions of constant use. The tubing sections are color coded based on their inside diameters and consequently on their pumping capacities; tubing sections must be replaced with identically coded tubing. These sections may also require replacing if bubble patterns change, extra bubbles appear, peak shapes are no longer flat on the top, or if the calculated carry over exceeds its normal range of 0.2 to 1.1%.

- The waste containers must be checked regularly and replaced when full. Refer to Section 2.1.2 for additional details.

- The analyzer should be cleaned every six months by sampling a 5 N sulfuric acid (H_2SO_4) solution for 30 to 60 minutes, followed by DDW for two to three hours.

- Printer paper should be checked before beginning each analysis run to insure a sufficient quantity is in place for the run.

- The printer ribbon should be checked and changed when the print quality changes from dark black to light blue.

- The work areas should be kept clean.

- Additional maintenance and troubleshooting information may be found in the Technicon TRAACS 800 Operation Manual (Technicon, 1988).

2.1.4 Laboratory Supplies and Spare Parts

The following items must be kept in the laboratory to insure minimal interruptions to the colorimetric analysis:

- Compressed air supply: minimum of 28 liters/minutes flow rate a minimum pressure of 40 psi. DRI's building air supply is used after it has passed through an oil trap, a particulate filter, and a regulator set at 75 psi.

- Volumetric flasks: glass, 100.0 ml, Class A (±0.01 % accuracy)

- Pipettes: volumetric in 1, 2, 3, 10, 20, and 30 ml sizes, Class A

- Micropipettes: Eppendorf in 100, 200, 500, and 1,000 ul sizes, with appropriate disposable plastic tips

- Sample cups: polystyrene, conical bottom, 4 ml capacity (Fisher, #02-544-4)

- Peristaltic pump tubing:

  0.635 ml/min tubing, GRN/GRN (Technicon, #178-3748P14)
  0.381 ml/min tubing, GRY/GRY (Technicon, #178-3748P11)
  0.111 ml/min tubing, ORN/WHT (Technicon, #178-3748P06)
  0.151 ml/min tubing, BLK/BLK (Technicon, #178-3748P07)
  0.574 ml/min tubing, ORN/YEL (Technicon, #178-3748P05)
  0.050 ml/min tubing, ORN/GRN (Technicon, #178-3748P07)

- Printer ribbons

- Printer paper

2.2 Reagents

2.2.1 Use analytical grade chemicals for all solutions.

Use DDW conforming to ASTM specification D1193, Type II (Annual Book of ASTM Standards, 1983).

Ammonium sulfate: $(NH_4)_2SO_4$, reagent grade (#A-938, Fisher Scientific, primary standard).

Brij-35, 30% solution: (P/N T21-0110, Technicon, Tarrytown, NY, Phone 914-333-6142). A surfactant.

Chloroform: UV grade (#1-9183, J. T. Baker, Phillipsburg, N. J., 1-800-JTBAKER). Used as a preservative for the primary standard solution.

EDTA, disodium salt: disodium salt of ethylenediaminetetraacetic acid, $Na_2C_{10}H_{14}O_8N_2 \cdot 2H_2O$ (#8993-01, J. T. Baker, Phillipsburg, N. J., 1-800-JTBAKER). Used as a complexing agent for interferences from metals.

Phenol, crystalline: C_6H_5OH, Reagent grade (#A92-500, Fisher Scientific). Used to produce the colored complex with ammonia and hypochlorite.

Sodium hypochlorite: NaOCl, 5% aqueous solution, 'Chlorox' (local grocery store). Used to produce the colored complex with ammonia and phenol.

Sodium hydroxide, 50% w/w solution: NaOH, (#SS254-1, Fisher Scientific)

Sodium nitroferricyanide: sodium nitroprusside, $Na_2Fe(CN)_5NO \cdot 2H_2O$, Reagent grade, (#SX675 CB737; Matheson, Coleman and Bell). Used to enhance the blue color of the ammonia/phenol/hypochlorite complex.

Standard Solution of ammonia, to be used as a reference standard.

Sodium Citrate: $Na_3C_6H_5O_7 \cdot 2H_2O$, reagent grade, (#3646.01, Baker Analyzed Reagent). Used in filter extraction of citric acid impregnated filters and in matrix matching of standards.

Citric acid: $C_6H_8O_7 \cdot H_2O$, reagent grade, (#A104-500 Fisher Scientific). Used in impregnating filters and matrix matching of standards.

Glycerol: $HOCH_2CHOHCH_2OH$, anhydrous, reagent grade (#2136-01, Baker Analyzed Reagent). Used in impregnating filters and matrix matching of standards.

2.2.2 Preparation of Solutions

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

2.2.2a Alkaline Phenol: Weigh out into a clean glass beaker 42.0 g of crystalline phenol to the nearest 0.1 g. Add DDW to dissolve some and carefully pour into a 500 ml volumetric flask. Repeat the addition of small amounts of DDW until all the phenol has been transferred into the flask. Weigh out 48 g of 50% w/w sodium hydroxide solution (or measure out 31.5 ml in a graduated cylinder), and add very slowly to the phenol solution, with swirling, cooling under running tap water or in an ice bath if necessary. Rinse the boat used for the NaOH to ensure complete transferral. After the solution cools, dilute to the mark with DDW. Transfer to a dark plastic bottle, store in the refrigerator. The solution is stable for about two weeks. {Note differences between Technicon method and CADMP method: Technicon=38.6 g phenol, 21 ml 50% NaOH, 500 ml DDW, stability 2 weeks, no refrigeration; CADMP=42 g phenol, 48 ml 50% NaOH, 500 ml water, stability 3 months, no refrigeration; DRI=41 g phenol, 48 g (31.5 ml) 50% NaOH, 500 ml DDW, stability 2 weeks, refrigerate.}

CAUTION: BOTH INGREDIENTS ARE CORROSIVE. Wash with copious amounts of water if either contacts the skin. Clean bench area carefully after making this reagent.

2.2.2b Sodium hypochlorite solution: The sodium hypochlorite (Chlorox) is used as received. {Note differences from Technicon method and CADMP method: DRI=use as received; Technicon and CADMP=dilute 86 ml to 100 ml with DDW (1%), stability one week, and one day, respectively.} Readjust Base and Gain whenever the reagent bottle is refilled (Section 4.2).

2.2.2c Sodium nitroferricyanide solution (called nitroprusside solution): Weigh out 1.10 g of sodium nitroferricyanide to

the nearest 0.01 g. Transfer to a 1000 ml volumetric flask and fill to mark with DDW. Store in amber container in refrigerator. Stable for one month.

2.2.2d EDTA solution: Weigh out 41.00 g of disodium EDTA to the nearest 0.01 g. Transfer quantitatively into a 1000 ml volumetric flask. Add 1.0 g sodium hydroxide (50% w/w) solution and add DDW to approximately 800 ml. Dissolve the EDTA (using hot plate if necessary), then dilute to near the mark with DDW. Add 3 ml Brij-35 and carefully dilute to mark with DDW. Mix very gently but thoroughly. Stability about six months. (CADMP method uses plastic storage bottle.) Note: the Brij-35 causes severe foaming if added before the water.

2.3 Forms and Paperwork

A sample analysis list will be prepared by the laboratory manager indicating which samples will be analyzed and any special instructions (Figure 2-6). Samples designated for automated colorimetry (AC) analysis are logged into the "TRAACS Analysis Logbook," as are notes concerning preparation of standards and maintenance (Figure 2-7).

3.0 CALIBRATION STANDARDS

3.1 Preparation of Standard Solutions

The stock standard solutions should either be purchased as certified solutions or prepared from ACS reagent grade materials. These solutions should be properly labelled with the name of the chemical, concentration, initials of the person making it, and the date it was made.

3.1.1 Stock Standard Solution, 100μg/ml:

The standard stock solution is prepared from ACS reagent grade ammonium sulfate {$(NH_4)_2SO_4$}. Weigh out 0.3667g ammonium sulfate to the nearest 0.0001 g into a weighing boat. Quantitatively transfer to a 1000 ml glass volumetric flask, add 1.0 ml chloroform as a preservative and dilute to volume with DDW. The final concentration of ammonium ion is 100.0 μg/ml. Store in refrigerator. This solution is stable for one month without a chloroform preservative.

Figure 2-6. Example of DRI TRAACS Analysis List.

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

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

Total number of samples: 92
Species to be analyzed:
NH_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. Analysis for NH_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:
NH_4^+ data : SAN403A.DBF

Filter	Description	NH_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 ____
AQ6038	Ambient	Y ____

Figure 2-7. DRI TRAACS Analysis Logbook Format.

ANALYSIS DATE	PROJECT	# of SAMPLES	TECH	COMMENTS
890901	SJV	60	SFC	NH_4^+
890901			SFC	prepared new EDTA solution
890906	SJV	35	SFC	2QI4059-6068 NH_4^+
890906	ACCEPT	3	SFC	Q576-579
890907			SFC	prepared new stds
890907	SJV	60	SFC	7QQ1008-4025 NH_4^+
891018	Santa Barb.	94	EMP	3rd quarter NH_4^+, new stds
891025			SFC	prepared new NO_2^- stds
891025	CADMP	80	SFC	April TEA filters for NO_2^-
891025	Kochy	10	SFC	TEA filters for NO_2^-

3.1.2 Working Standard (WS), 10 μg/ml:

This is an intermediate standard solution used for the preparation of calibration standards. Pipette 10 ml of Standard Stock Solution into a 100.00 ml glass volumetric flask and dilute to volume with DDW. The final concentration is 10.00 μg/ml. Store in refrigerator. This WS is stable for 3 days.

3.1.3 Calibration Standards for routine ammonia analysis:

Prepare calibration standards in concentrations of 0.050, 0.100, 0.300, 0.500, 1.000, 2.000 and 3.000 μg/ml. Use 100.00 ml glass volumetric flasks, and store in refrigerator. These may be used for two consecutive days.

0.050 μg/ml: Pipette 0.500 ml (using the analytical balance) of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

0.100 μg/ml: Pipette 1.000 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

0.300 μg/ml: Pipette 3.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

0.500 μg/ml: Pipette 5.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

1.000 μg/ml: Pipette 10.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

2.000 μg/ml: Pipette 20.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

3.000 μg/ml: Pipette 30.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

(Alternately:

2.000 μg/ml: Pipette 2.00 ml of the 100.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

3.000 μg/ml: Pipette 3.00 ml of the 100.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.)

ERA Reference Standards:

A single component calibration standard 10 mg/l ammonia as NH_3 is used as a quality control check. This is diluted as follows:

2.00 μg/ml: Pipet 2.00 ml stock ERA calibration standard into a 100 ml volumetric flask. Fill to volume with DDW and mix thoroughly.

0.100 μg/ml: Pipet 5.00 ml of the ERA 2.00 μg/ml calibration standard (above) into a 100.00 ml volumetric flask. Fill to volume with DDW and mix thoroughly.

3.1.4 Calibration Standards for filters impregnated with citric acid (Laboratory Operations Manual for CADMP, SOP Ammonium Analysis by Technicon, Number 2260-403)

Prepare calibration standards in concentrations of 0.050, 0.100, 0.300, 0.500, 1.000, 2.000 and 3.000 μg/ml. Use 100.00 ml glass volumetric flasks and store in refrigerator. These may be used for two consecutive days.

Match the standard matrix solutions with the sample matrix by adding 10.00 ml 1M sodium citrate stock and 2 ml 25% citric acid/5% glycerol stock to each 100.00 ml flask. Prepare a blank in addition to the standards.

1 M Sodium Citrate Stock Solution: Dissolve 294.1 g of sodium citrate in 800 ml DDW. Dilute to 1 liter and mix thoroughly. Store at room temperature.

25% Citric Acid/5% Glycerol Stock Solution: dissolve 25 g citric acid in 80 ml DDW. Add 5 ml glycerol and dilute to 100 ml with DDW. Mix thoroughly and store at room temperature.

Prepare standards as for the routine standard preparation.

0.050 μg/ml: Pipette 0.500 ml (using the balance) of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

0.100 μg/ml: Pipette 1.000 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

0.300 μg/ml: Pipette 3.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

0.500 μg/ml: Pipette 5.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

1.000 μg/ml: Pipette 10.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

2.000 μg/ml: Pipette 20.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

3.000 μg/ml: Pipette 30.00 ml of the 10.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

(Alternately:

2.000 μg/ml: Pipette 2.00 ml of the 100.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.

3.000 μg/ml: Pipette 3.00 ml of the 100.00 μg/ml WS into a 100.00 ml glass volumetric flask. Fill to volume with DDW.)

3.2 Use

Standard reference material (SRM) 2694, simulated rainwater, from the National Institute of Standards and Technology (NIST) is used as a cross audit check. However, since the value for ammonia in SRM 2694 II is not certified, this is only an approximate check. An additional audit check is the use of other commercially available standards or standard reference materials. Presently, Environmental Resource Associate Calibration and WasteWatR ™ quality control standards are used as shown in Table 3-1.

ERA Quality Control Standard:

ERA Nutrients WasteWatR is used as a quality control check for ammonia. The stock has a concentration of 10.174 mg/l ammonia as NH_4^+. Dilute this 1:10 to get the concentration in range for the instrument by pipetting 10.00 ml of the ERA stock into a 100.00 ml glass volumetric flask. Dilute to volume with DDW and mix thoroughly.

For analysis of samples from citrate impregnated filters, the rainwater matrix must be adjusted to match the matrix of the samples and standards. This requires the addition of 0.1 ml sodium citrate (1 M), and 0.020 ml 25% citric acid/5% glycerol to each 1 ml NIST rainwater. The concentration of the sample is thus altered and must be corrected by a dilution factor of 1.12.

Table 3-1

Environmental Resource Associates WasteWatR Quality Control Standards

Constituent Elements/ Parameters	Lot No. 9927 ERA Certified	Advisory Range
NUTRIENTS WasteWatRTM		
Ammonia as N, mg/L	7.9	6.9 - 8.9
Nitrate plus Nitrite as N, mg/L	10.4	9.4 - 11.4
Phosphate as P, mg/L	4.0	3.6 - 4.4

The laboratory analyst verifies the SRM daily as a first level of validation. The working standards as well as selected calibration standards are prepared and analyzed by the laboratory manager or an external quality assurance auditor quarterly as an independent check. All working standards are kept in the laboratory as back up tracers until the data have been properly examined and reported.

3.3 Accuracy of Calibration Standards

The accuracy of calibration standards is primarily limited by variations in standard solution preparation and is typically within 10% of the nominal standard concentrations.

4.0 PROCEDURES

Routine analysis involves establishing a baseline with the reagents, analyzing standards to check if they produce a linear and reproducible instrument response, analyzing the standards and samples in the analysis run, and rinsing the tubes with water before shutting down. The instrument is controlled by a computer, using the GATEWAY computer program.

4.1 General Flow Diagram

The typical flow of samples and data for TRAACS 800 analysis is depicted in Figure 4-1.

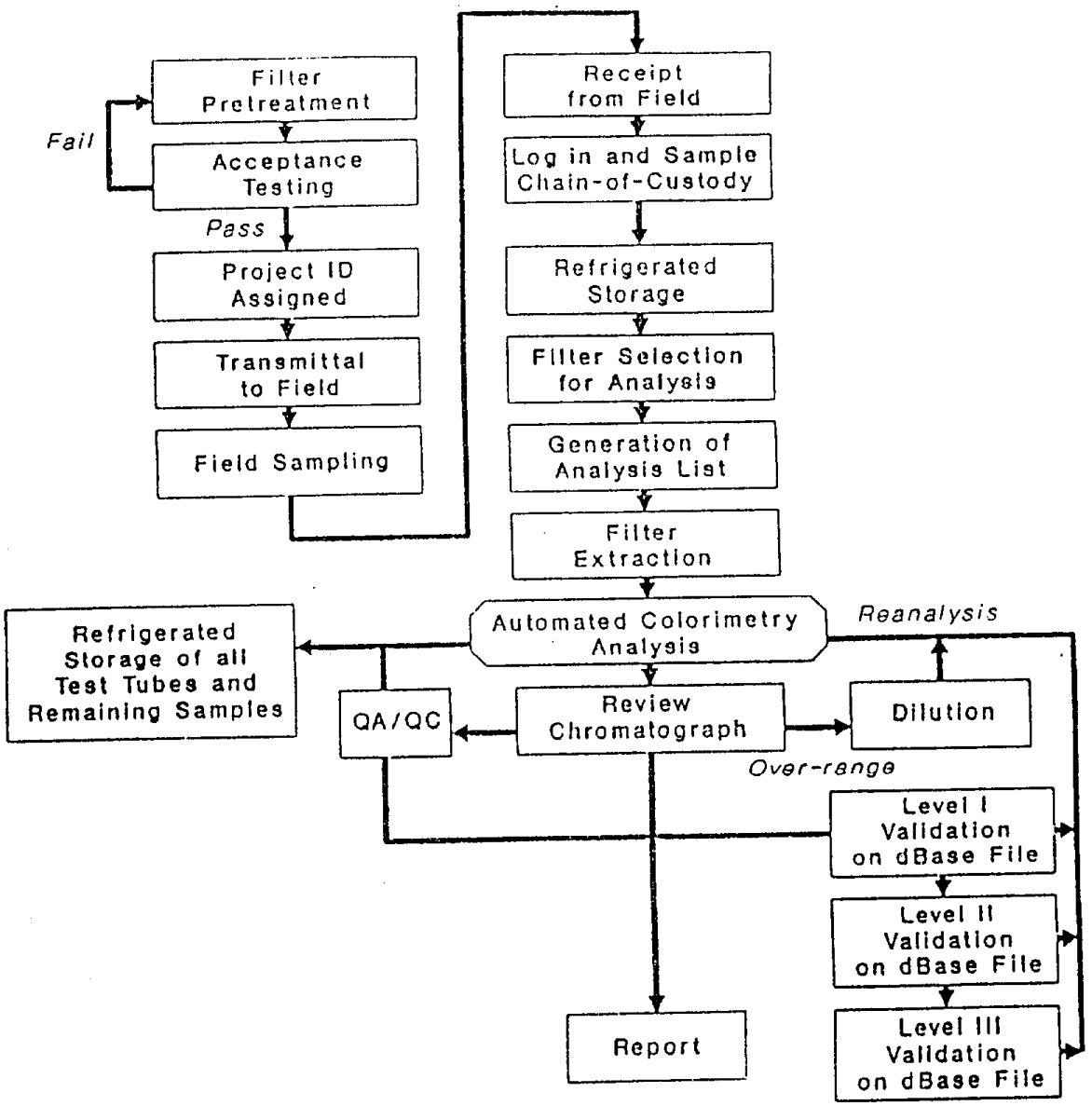
4.2 Instrument Start-Up

Rinse out the DDW water bottle thoroughly and fill with fresh DDW. Place all tubes into the water bottle so the system can be rinsed before analysis starts.

Turn on the computer, printer and auto sampler. NOTE: If electrical power to the TRAACS 800 Analytical Console has been interrupted the software will need to be downloaded before the Analytical Console will respond properly to the GATEWAY program. This is accomplished by the following:

- Apply power to the Analytical Console.

Figure 4-1. DRI TRAACS Analysis Flow Diagram.



- After the IBM-XT has been turned on and has booted, return to the DOS C> prompt by pressing <F1>.
- Place the TRAACS boot disk in drive A:.
- Type A: <CR>
- Type EDOWNL <CR>
- At the prompt "Enter name of binary file:", type EPSLON2.COM <CR>.
- At the prompt "Baud rate (3,12,24,48,96):", type 24 <CR>.
- Press the red reset button located on the bottom of the CPU circuit board on the left side of the Analytical Console.
- Press <CR> to begin the transfer.
- Verify that the red LED labelled "DS7" is flashing, indicating that the transfer is underway.
- When the A:> prompt reappears, type C: <CR>.
- At the C:> prompt type GATEWAY <CR>.
- At the main menu press <F4>.
- Type the following in sequence:

  B1 <CR>
  CK <CR>
  DM0 <CR>
  DL0 <CR>

When the GATEWAY program displays the main menu (Figure 2-5), select <F4> (Chart and Run). Check the computer by selecting <F4> (response 'Command?') and typing CK. A response of '0' means the computer is OK. Set up the bubbling algorithm by pressing <F4> again (response 'Command?') and typing DL0 so the low bubble algorithm is not used; select F4 and type DM0 to debubble using software.

Carefully stretch the tubes across the rollers of the peristaltic pump to the lower holder so each of the tubes goes straight down from the upper holder to the lower holder catching the colored clip in the lower holder (tubes must not cross each other). Close the platen by pushing it down and

raising the black handled clips located at the bottom edge of the pump. Start the pump for the ammonia analysis (in channel 1) by selecting <F4> and typing OP1 (open pump 1). The rollers will start turning and the clicking of the air valves will be heard. (If either does not happen, check the TRAACS 800 operating manual and get assistance if needed.) Let water pump through for about five minutes. While the system is rinsing, get out the reagents, stored in the refrigerator. If the standards were recently made, these will be in the refrigerator and can be retrieved at this time. If standards need to be made, they can be made at this point, or before the pump is turned on.

After the system is rinsed, place the tubes in the correct reagent as follows (refer to Figure 2-2):

EDTA	Grey/Grey (381 µl/min)
Phenate	Black/Black (151 µl/min) (Note that the sample tube which goes to the sampler is also black/black.)
Nitroprusside	Orange/Yellow (79 µl/min)
Hypochlorite	Orange/Green (111 µl/min)
Water	Orange/White (50 µl/min)
Water (sampler)	Green/Green (635 µl/min)

To monitor the baseline, select <F9> (Start/Stop Charting), (response 'Which channels?') type 1 to select channel 1, (response 'What chart speed (60,30,20,15,12,6 or 4 inches per hour?') type 4 to select the slow chart speed. The base reading will be displayed at the bottom of the screen and charted on the printer. When the baseline has come to a constant reading, adjust to 5% full scale if necessary by selecting <F4> and typing VB1 to view base of channel 1. To raise the base line, select <F4> and type CB1 nn (change base 1), where nn is a number greater than the response from the VB1 query. Lowering the base line is achieved by <F4>, CB1 nn, where nn is a number less than the response from the VB1 query. The adjustment is iterative and there is a slight delay in the reading response.

Next, the gain is adjusted so the high standard gives a response of 95% full scale. To sample the high standard, pour the 3.0 (µg/ml) standard into a sample cup at least up to the second line, select <F4> and type SS1 (response -128) to sample the first cup. Sample for about 5 minutes, then select <F4> and type SI1 to return the probe to the rinse cup. There is approximately an 8 minute delay until the sample reaches the detection cell from the beginning of sampling. After the response has leveled off, adjust the gain by selecting <F4> and typing VG1 to view the gain of channel 1. Increase the response to 95% by selecting F4 and typing CG1 nn, where nn is an integer greater than the response from the VG1 query. The adjustment is iterative, and there is a slight delay in the reading response.

Reduction in the response can be achieved by <F4>, CG1 nn, where nn is a number less than the last setting.

4.3 Routine Operations

4.3.1 Calibration check

This step merely checks the standards and analytical system before analysis proceeds. The calibration curve generated here is reestablished in the analysis run.

Place cups in the sampling tray according to the tray protocol of Calibrat or Calshort input files:

Cup Number	Standard Concentration (μg/ml)
1	3.0
2	2.0
3	1.0
4	0.5
5	0.3
6	0.1 Fisher
7	0.05
8	2.0 Fisher
9	Blank/DDW
10	1.0 NBS 2694II

Note that the standard concentrations in the list above are approximate. The actual concentration of the standards must be entered into the protocol.

Stop the gain check by selecting <F9>, <4>, <ENTER>. Begin the calibration check run by selecting <F9> (Start/Stop Charting). Response 'Which Channels?', type 1; response 'What chart speed (60,30,20,15,12,6 or 4 inches per hour)?', type 30 to select a faster chart speed. Select <F7> (Start/Stop a run). Response 'Enter a run program filename', type Calibrat; response 'Please enter operator's name', type initials; response comment from input file--'Do you wish to modify this comment (Y/N), type N to leave comment as is; response 'Enter filename to save chart', type [Date]CAL1 (Date is month and day numbers, such as 830). (If using Calshort, use DateCALS1 as the filename.) After this point, the Calibrat run will start, first sampling the baseline for several minutes.

There are two programs presently available for the calibration check: Calibrat, which samples standards and reference materials in cups 8, 10, 6, 7 and 9 five times each and checks the calibration curve at the end; and Calshort, which samples the standard in cup 6 five times and the calibration curve twice. Calibrat takes approximately 1 hour to run while Calshort takes approximately 1/2 hour. Either of the two input files can be used as the basis for an analysis run.

When the calibration check is complete, check the reported values of the standards and reference materials. The measured values should be within ±10% of the known values. If there are deviations, the calibration curve should be plotted to check for one or two standards far from the known value.

To retrieve the calibration curve, select <F2> (Return to DOS/GATEWAY) to return to the GATEWAY main menu. Then, select <F5> (Retrieve). Response 'Retrieve chart data from which file?', type filename of calibration check: [Date]Cal1. The heading of the file will appear on the screen when it has been retrieved. Next, select <F9> (Plot a calibration curve). Response 'Cal. curve for which analysis (1,2)?', type 2 to get the linear plot. As indicated on the screen, press <ENTER> to get the curve. To return to the menu from the curve, press <ENTER> again. To get a hard copy of the curve, press <Print Scrn> <1>, simultaneously. A plot similar to Figure 4-2 will be printed. The calibration curve is linear over the range of the standards above. If one standard is clearly out of line, it can be remade. Sometimes, rerunning the calibration check program improves results. If several standards are out of line, remake the whole set.

When the calibration curve check is satisfactory, prepare for the analysis run.

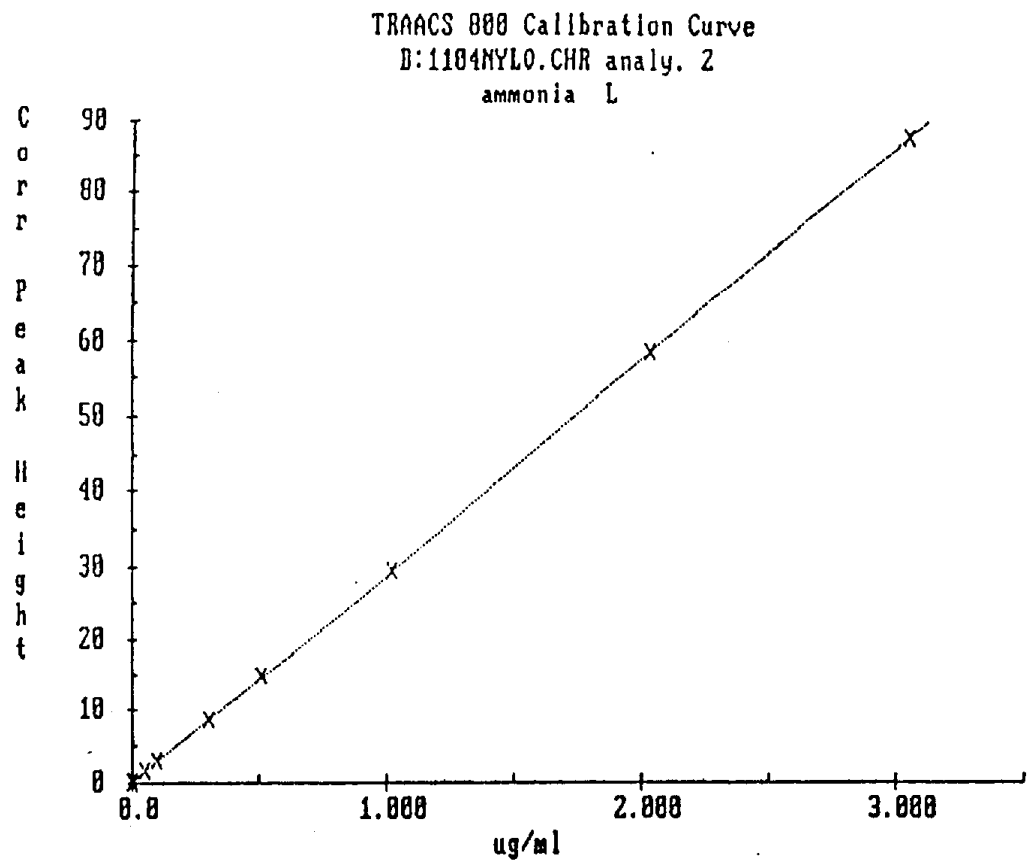
To return to the main menu from retrieve, press <F2>, <4>, <ENTER>.

4.3.2 Routine Analysis

4.3.2a Preparation of the input file for analysis

The input file for the analytical run is based on the Calibrat or Calshort input files. From the main GATEWAY menu, select <F2> (Edit). A blank protocol form appears on the screen. Type 'Calibrat', enter, <F5> to read the Calibrat input file. The input file can now be altered. The file consists of three screens: the first includes

Figure 4-2. Example of TRAACS 800 NH_4^+ Calibration Plot.



the file name, sampling times and calibrant values (Figure 4-3); the second screen includes the Run Comment, the Tray Protocol and the Gain Peak # (Figure 4-4); and the third screen, which may be several pages long, consists of the list of samples in the sampling cups and the sample identifications (Figure 4-5). To access the three screens, page up or page down is pressed. To access the several pages in screen three, <F7> (Sc Up) is selected to bring up the previous page and <F8> (Sc Dn) is selected to bring up a succeeding page.

The Tray Protocol is located on the second screen. For Calibrat, the tray protocol is as follows:

P,1C@1,6C,1C@9,H,2L@9,5S1@8,5S2@10,5S3@6,5S4@7,5S5@9, 10S>1,G@2,E.

This means the first sample and cup is the primer cup (P), 1 calibration at cup 1, (1C@1), 6 calibration cups following (6C) (the sampler is now sampling cup 7), one calibration at cup 9 (1C@9--this is the blank), high (H, at the next cup, 8, before the skip to cup 9), 2 low samples at cup 9 (these two values, H,2L are used to calculate carryover), 5 replicate analyses of cups 8, 10, 6, 7, 8, and 9 with results accumulated in statistics files 1 through 5 respectively (5S1@8, etc.), then 10 samples starting with 1 (10S>1, a resampling of the whole calibration curve with reference materials), the gain cup at 2 (G@2) and the end (E).

Note that the sampler can access any cup, but that sending the sampler to a specific cup with the @ symbol does not interrupt the incremental order of unspecified cups. That is, the incremental sampling starts at 1 and proceeds through cup 8 in the above tray protocol.

To prepare the tray protocol for the analysis of samples, modify the Tray Protocol by deleting the repetitive sampling of cup 9 using the delete key. Press <F10> to confirm deletion, then, with the keyboard in insert mode, type 2S to sample 9 and 10. Then insert the sampling of cups after the repeated sampling of the standards, but before the resampling of the whole set of standards. The samples are interspersed with blanks, standards and replicate samples as follows:

Figure 4-3. Technicon GATEWAY Software: Editor, First Screen.

Technicon TRAACS 800 System Editor

First Screen

File Name D:CALIBRAT.INP Analysis 1 2 3 4
# of anal. 2 Channel 1 1 3 4

Samples/hr 080 Sample/wash 2.0000 Pecking N
Sample time 0030 Wash time 0015 Base Corr Y
Raw output N

Anal	Fit	Inv Chem	Base Concent.	Dilution Carryover	Carryover	Chem Name		Units	Base in Calib
1	P	N	.000000	.000000	.000000	ammonia	P	ug/ml	Y
2	L	N	.000000	.000000	.000000	ammonia	L	ug/ml	Y
3	L	N	.000000	.000000	.000000				Y
4	L	N	.000000	.000000	.000000				Y

Calibrant values

Anal	1	2	3	4	5	6	7	8
1	3.061000	2.041000	1.020000	.510000	.306000	.100000	.051000	.000000
2	3.061000	2.041000	1.020000	.510000	.306000	.100000	.051000	.000000
3	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000
4	.000000	.000000	.000000	.000000	.000000	.000000	.000000	.000000

Name of file to be read or written (8 characters,no spaces).
2 Edone 3 Res E 4 Exit 5 Rd fl 6 Wr fl 9 DIR 0 ConDel

Figure 4-4. Technicon GATEWAY Software: Editor, Second Screen.

```
                    Technicon TRAACS 800 System Editor
                                                          Second Screen

# to resample   0   Old cal file name                 Dual Probe System  N

Run Comment
CALIBRATION CURVE CHECK FOR AMMONIA STANDARDS IN DDW

Tray Protocol
P,1C01,6C,1C09,H,2L09,5S100,5S2010,5S306,5S407,5S509,10S>1,G02,E



Gain peak #   003


# of cups to resample after offscale (0-2), 0=NO RESAMPLE/AUTODILUTION
      2 Edone 3 Res E 4 Exit  5 Rd fi 6 Wr fi                 9 DIR  0 ConDel
```

Figure 4-5. Technicon GATEWAY Software: Editor, Third Screen.

Technicon TRAACS 800 System Editor

Goto --> 000

Third Screen

Cup#	Peak#	Count	Type	Sample ID	Weight	Dilution	Spike
1	1	3	P	STD-3.0612	1.000000	1.000000	N
2	3	3	C	STD-2.0408	1.000000	1.000000	N
3	4	2	C	STD-1.0204	1.000000	1.000000	N
4	5	2	C	STD-0.5102	1.000000	1.000000	N
5	6	2	C	STD-0.30612	1.000000	1.000000	N
6	7	7	C	ERA 0.100	1.000000	1.000000	N
7	8	7	C	STD-0.05102	1.000000	1.000000	N
8	10	7	N	ERA 2.0	1.000000	1.000000	N
9	9	9	C	BLANK	1.000000	1.000000	N
10	18	6	S	ERA NUTRIENT WW	1.000000	1.000000	N
11					1.000000	1.000000	N
12					1.000000	1.000000	N
13					1.000000	1.000000	N
14					1.000000	1.000000	N
15					1.000000	1.000000	N
16					1.000000	1.000000	N
17					1.000000	1.000000	N
18					1.000000	1.000000	N
19					1.000000	1.000000	N
20					1.000000	1.000000	N

Cup number to move to

1 Copy 2 Edone 3 Res E 4 Exit 5 Rd fl 6 Wr fl 7 Sc Up 8 Sc Dn 9 DIR 0 ConDel

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

etc.

This results in the analysis of a standard after ten analyses, a blank after every 20 samples and a replicate after every 10 samples. The samples are grouped in units of ten to aid in entering the samples into the autosampler.

The modified tray protocol for the above list would be:

P,1C@1,6C,1C@9,H,2L@9,5S1@8,5S2@10,5S3@6,5S4@7,2S,11S,1S@6,12S,1S@5,11S,1S@4,12S, 10S>1,G@2,E

This permits the addition of 40 samples, plus the replicates and blanks. The tray protocol generates the listing of samples in the third screen (Figure 4-5). After the tray protocol is entered, the samples must be listed.

In estimating the number of sets of 10 to include to cover all samples, enter at least 10 extra samples. Any unused cups which were entered into the protocol can be filled with blanks initially. The sample ID on the third screen can be left blank. During the analysis, if any samples are over range, they can be diluted and replaced in one of the blank spots at the end. The sample ID and dilution must then be entered by hand on the hard copy of the tray protocol input file.

To enter these sample ID's on the third screen, the <F1> key can be used to copy the preceding entry. Changes can then be made simply by typing over the undesired entry. Succeeding pages of the third screen can be accessed by the <F8> key, preceding by the <F7> key.

When the tray protocol and sample ID's are all entered, change the name of the input file by paging up to the first screen. The input file should be named as [Date]Proj, leaving the B: and extension .INP alone: for example, B:829SJV.INP would be the input file for San Joaquin Valley run 8/29.

After all modifications of the input file are complete, <F2> (Editing Done) can be selected. Note that any deletions must be confirmed with the <F10> key or they will not be carried out. Selection of <F2> will return the computer to the main GATEWAY menu.

4.3.2b Hard copy of the input file for the analysis run

Since samples must be loaded according to the input file tray protocol, it is easiest to work from a hard copy of the listing of the samples and cup numbers. This is generated by selecting <F1> (DOS) from the main GATEWAY menu. Then, type the command 'copy B:[date]proj.inp lpt1' (the complete input file name) is given to get a hard copy. This lists all the parameters, the tray protocol as well as the listing of samples and cups on the last page (Figure 4-6). Type GATEWAY <CR> to restart the program.

4.3.3 Loading samples and running the analysis

Load new standards since the first set will have been sitting out for a while at this point. After the standards are loaded, the run can be started since there is about a 5 minute delay for sampling baseline before starting on the calibration curve.

Start the run by selecting <F4>. From this menu (Figure 4-7), select <F9>, channel 1, chart speed 30; <F7>, input file name just developed, operator initials, modify comment to reflect the project being analyzed (Y, Ammonia, San Joaquin, 4th quarter; for example). Save the chart to a file with the same name as the input file.

Load samples according to the hard copy of the protocol. Remember to load any blanks with DDW and fill any space at the end with blanks until that space might be used for dilutions.

As the run progresses, a strip-chart-style plot of the sample peaks will be produced similar to Figure 4-8.

Figure 4-6. Example of Technicon TRAACS 800 Tray Protocol Listing.

```
 10                    VERSION NUMBER.
  2                    NO. OF ANALYSES.
  2  2  3  4           ANALYZED COLORIMETER CHANNELS
  4  0                 CHANNELS FOR SAMPLER 1 AND 2
  80  80               SAMPLES/HR FOR EACH SAMPLER
2.0000 2.0000          SAMPLE/WASH FOR EACH SAMPLER
   0.000    4.028    3.021    2.014    1.007    0.503    0.101    0.050    0.000
   0.000    4.028    3.021    2.014    1.007    0.503    0.101    0.050    0.000
   0.000    0.000    0.000    0.000    0.000    0.000    0.000    0.000    0.000
   0.000    0.000    0.000    0.000    0.000    0.000    0.000    0.000    0.000
   0.000     0.000     0.000     0.000       CARRYOVER FACTORS (%)
   0.000     0.000     0.000     0.000       DILUTION CARRYOVER FACTORS (%)
Nitrite P     Nitrite L
ug/ml         ug/ml
 2  1  1  1         CAL TYPE: 0->QUAD, 1->LIN, 2->PIECEW, 3->CUB
 0  0  0  0           INVERSE CHEMISTRY IF NOT 0.
C                     C-> CONCENTRATION OUTPUT,  R-> RAW.
P0                    SET # OF PECKS TO 0 OR 2.
B                     B -> BASE DRIFT CORRECTION  N-> NONE.
  24   24    0   0    NOISE TOLERANCE IN A/D UNITS. 0 -> 24.
 3                    GAIN REFERENCE PEAK NUMBER.
 0                    NUMBER OF PEAKS TO RESAMPLE.
                                        OLD CAL RUN CHART FILE NAME.
cal. curve, carryover, gain adj., Aud. std 2.0@8, .10@6, HBS 1.00@10
P,1C@1,6C,1C@9,H,2L@9,3S1@8,3S2@10,3S3@6,3S4@7,2S,11S,1S@6,12S,1S@5,
11S,1S@4,12S,1S@3,11S,1S@2,12S,1S@6,11S,1S@5,12S,1S@4,11S,1S@3,7S,10S>1,
G@2,E


   TRAY PROTOCOL MUST END IN E AND START WITH P.
 0                    RUN MODE (0=120CUPS, 1=Dual Probe).

  1    1    3  P     1.0000     1.0000  N  SD4028
  2    3    4  C     1.0000     1.0000  N  SD3021
  3    4    4  C     1.0000     1.0000  N  SD2014
  4    5    4  C     1.0000     1.0000  N  SD1007
  5    6    4  C     1.0000     1.0000  N  SD05035
  6    7    7  C     1.0000     1.0000  N  SD01007
  7    8    5  C     1.0000     1.0000  N  SD005035
  9    9    5  C     1.0000     1.0000  N  BS0000
  8   10    5  H     1.0000     1.0000  N  SD2014
 10   16    5  S     1.0000     1.0000  N  ICSTD-G
 10   16    5  S     1.0000     1.0000  N  ICSTD-G
 11   27    1  S     1.0000     1.0000  N  GTAZ00021(1:3)
 12   28    1  S     1.0000     1.0000  N  GTAZ00022(1:3)
 13   29    1  S     1.0000     1.0000  N  GTAZ00023(1:3)
 14   30    1  S     1.0000     1.0000  N  GTAZ00024(1:3)
 15   31    1  S     1.0000     1.0000  N  GTAZ00026
 16   32    1  S     1.0000     1.0000  N  GTAZ00027(1:3)
 17   33    1  S     1.0000     1.0000  N  GTAZ00028(1:3)
 18   34    1  S     1.0000     1.0000  N  GTAZ00029(1:3)
 19   35    1  S     1.0000     1.0000  N  GTAZ00030(1:3)
 20   36    1  S     1.0000     1.0000  N  GTAZ00031(1:3)
```

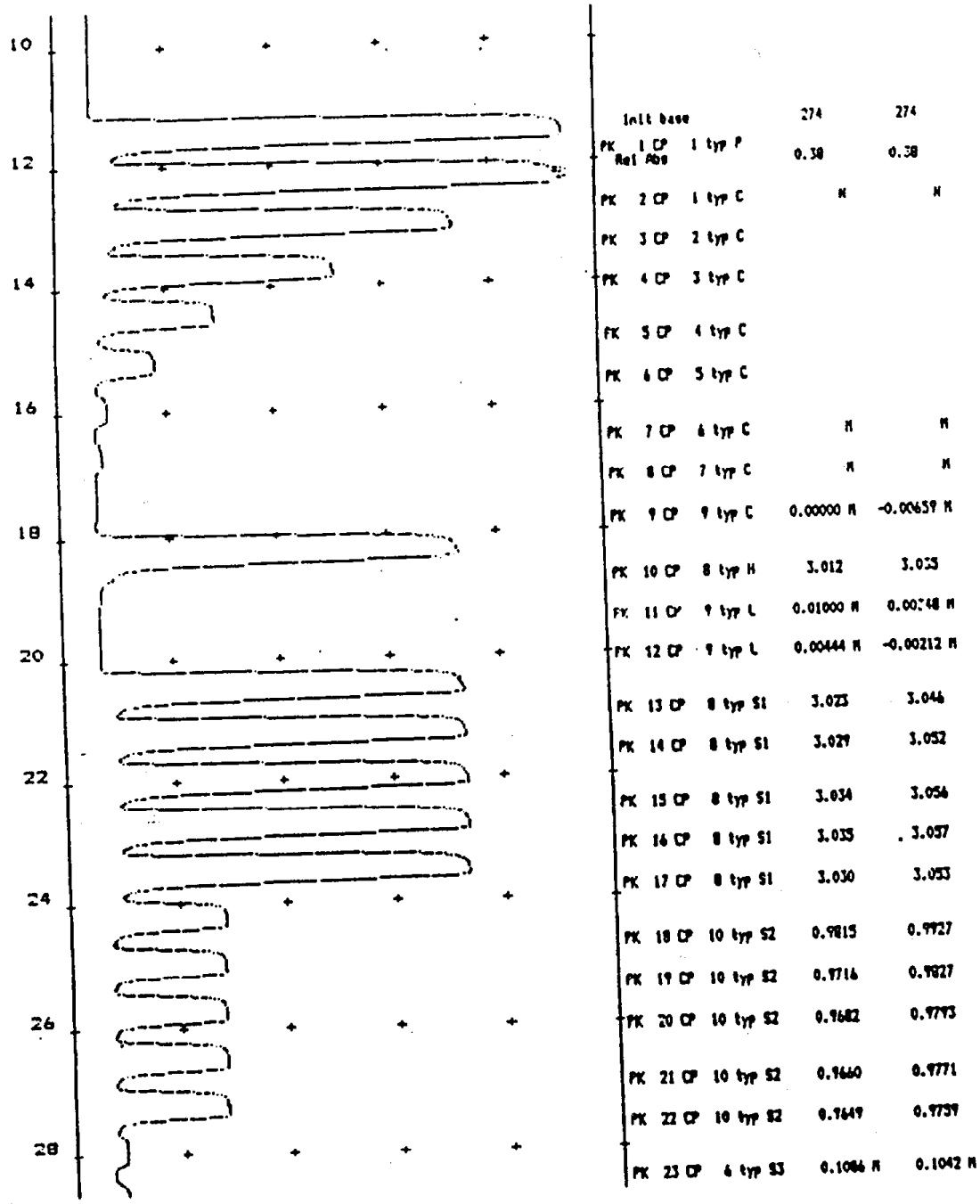
Figure 4-7. Technicon GATEWAY Software: Run/Chart Menu.

```
CHART and RUN. MAIN MENU.                          PRN STATUS: On Line.

     F1   Display Help screen.        F2   Go to DOS/TrAAcs Main Menu.
                                      F4   TrAAcs command & response.
     F5   Options, Run parms.         F6   Save Chart file to disk.
     F7   Start/Stop a Run.           F8   Start/Stop Digital display.
     F9   Start/Stop Charting.        F10  Display data directory.
Text  YES                                        Chr Min    0  Chr Max  100

 1 Help  2 Quit  3      4 Commd 5 Opts  6 Sav C 7 Run   8 Dg on 9 C on  0 Dir
```

Figure 4-8. Example of TRAACS 800 Runtime Plot.



4.4 Shut-down

After the analysis is complete and the Technicon data has been stored to the text file, the reagent tubes can be moved to the rinse bottle filled with DDW. Cap all the reagent bottles and store in the refrigerator. Let the system rinse for one hour. Then, select <F4>, type QP1 to turn off the pumps for system 1. The instrument and computer are generally left on during routine analysis.

For prolonged shut-down (more than 2 days), turn off the computer. Leave the instrument and autosampler on.

5.0 QUANTIFICATION

5.1 Get a hard copy of the calibration curve actually used in the analytical run by returning to the GATEWAY main menu by selecting <F2> from the Chart and Run menu (Figure 4-7). Select <F5> (Retrieve), retrieve the chart file from the analysis just completed 'DateProj,' select <F9> (Plot) to plot the calibration curve for analysis 2 (linear plot) <ENTER>. Press <ENTER> again to get the curve (Figure 5-1). Print a hard copy of this calibration curve by pressing <Print Scrn> followed by a <1>. After printing press <ENTER> to get back to the Retrieve menu.

After the analysis run is complete, the data will be stored to the chart and text file named in the beginning of the run. The text file will then be converted to a DBase III file for report generation. This is achieved by returning to the GATEWAY main menu by selecting <F2> from the Chart and Run or Retrieve menu. Select <F1> (DOS). From DOS, type db to call up DBase III. After the introductory remarks, the choice of converting a text file to a data base file is presented (a 1 is selected for conversion), the complete list of text files is generated so the one desired can be selected. The name of the desired file is entered and the text file is converted to a data base file. At the second option, select the 0 to remain in DBase.

The program to generate the report is called Finish. To initiate the program, type 'do finish' at the dot prompt. A Modify Structure screen will come up. The weight, spike and dilute fields need to be deleted by pressing 'control,' U for each of these. A new field, RatioPL, numeric, width 10, Decimal 4 needs to be added. To do this, move to the next open field line with the down arrow. Type the name in the Field Name space, press <ENTER>. The cursor moves to the Type space. Press <spacebar> to change to numeric, then <ENTER>. At the Width space, type "10", then

Figure 5-1. Technicon GATEWAY Software: Retrieve Menu.

```
RETRIEVE. MAIN MENU.                                PRN STATUS: On Line.

    F1   Display  Help screen.      F2   Go to DOS/TrAAcs Main Menu.
                                    F4   Display .CHR file directory.
    F5   Options, Run  parms.       F6   Retrieve a .CHR file from disk.
    F7   Choose Printer or Screen.  F8   Display CAL curve coefficients.
    F9   Plot calibration curve.    F10  Plot chart.
Chr Speed  60  Start Time      0   End Time      0  Chr Min    0  Chr Max  100


 To activate a function key, press Enter and the function key, OR
 Enter the chart file name to be retrieved and press Enter:
1 Help  2 Quit  3       4 Dir   5 Opts  6 Get F 7 To pr 8 Coeff 9 Cal   0 Chart
```

<ENTER>. At the Decimal space, type "4", then <ENTER>. Save the change by pressing <CTRL><End> and <ENTER>.

Next, a report screen appears in which the title needs to be changed. Press <CR> on the title and type the new title reflecting the analysis, the project and the date. Save the changes as indicated in the menu at the top of the screen.

The report is automatically generated from this point.

5.2 Reanalysis of Data

If the calibration curve is in error due to one standard being incorrect, it is possible to reanalyze the data after that incorrect point has been deleted.

- Adjust tray protocol and calibrant list to reflect deletion of standard in error.

  Enter the Edit Mode (<F2>), calling up the input file of the analysis to be reanalyzed. Edit the calibrant list (first screen) by deleting the calibrant in error and moving any subsequent standards up in the listing so there are no voids in the middle of the listing.

  Edit the tray protocol (second screen) so the standard which has been deleted is now called a sample in the analysis run list. For example, if standard 2.0 (in cup 2) were eliminated in the normal tray protocol, the new tray protocol would be:

  P, 1C@1, 1S, 5C, 1C@9, H, 2L@9,...G@2, E

- Save these changes to a new name, DateProjI or similar notation. If the changes were stored to the same file, the original data would be hard to retrieve.

- Select Reanalyze by pressing <F6> from the GATEWAY main menu (Figure 5-2). At the prompt, enter the chart file name for the original analysis, then the input file name as the new file just created with the revised tray protocol and calibrant listing. Following the prompts, enter new names for the new chart file name and text file. Continuing to follow the prompts, the report based on the reanalyzed data will be generated.

Figure 5-2. Technicon GATEWAY Software: Reanalyze Menu.

```
REANALYZE. MAIN MENU.                          PRN STATUS: On Line.

  F1  Display Help screen.          F2  Go to DOS/TrAAcs Main Menu.
  F3  Retrieve a .CHR file from disk.
  F5  Options, Run parms.           F6  Save Chart file to disk.
  F7  Start/Stop a Run.             F8  Start/Stop Digital display.
  F9  Start/Stop Charting.          F10 Display data directory.
Text  YES     Picking  OFF                   Chr Min    0  Chr Max  100


 To activate a function key, press Enter and the function key, OR
 Enter the chart file name to be reanalyzed and press Enter:
 1 Help  2 Quit  3 Get F 4      5 Opts  6 Sav C 7 Run   8 Dg on 9 C on  0 Dir
```

- The new calibration curve can be printed by selecting retrieve, calib curve, 2 (linear curve), <Shift><Print Scr> followed by <1>.
- A new dBase report can be generated using the procedure outlined above in Section 5.1

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 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 after that first spurious replicate and should be 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 samples after the last acceptable replicate must be reanalyzed. Notify the laboratory supervisor immediately if sample rerun is to be performed.

6.2 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

Berthelot, M.P. Rep. Chim. Appl. 1855, p. 284

American Chemical Society (ACS) Committee on Environmental Quality (1983). Principles of Environmental Analysis. Analytical Chemistry 55: 2210-2218.

Bran+Luebbe Analyzing Technologies, Technicon Industrial Systems, "TRAACS 800 Continuous-Flow Analytical System: Operation Manual," Technical Publication DSM-0005-00.5, Version 3.03, August, 1988.

CADMP, "Laboratory Operations Manual for the California Acid Deposition Monitoring Program: Sample Pretreatment, Sample Preparation, and Chemical Analysis," DRI Document # 8068.3DI, February 28, 1989.

Watson, J.G., J.C. Chow, L.W. Richards, S.R. Anderson, J. E. Houck, and D.L. Dietrich (1988). "The 1987-88 Metro Denver Brown Cloud Air Pollution Study, Volume II: Measurement." DRI Document No. 8810.1F2, prepared for the Greater Denver Chamber of Commerce, Denver, CO, by Desert Research Institute, Reno, NV.

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure describes the assembly, shipping, and disassembly of filter packs used for aerosol sampling. It also covers the cleaning and storage of the filter holder parts after disassembly.

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 Typical Lower Quantifiable Limits, Precision, and Accuracy

(Not applicable)

1.6 Responsibilities of Personnel

All technicians in the laboratory should read and understand the entire standard operating procedure before performing assembly, disassembly, or cleaning of filter packs.

The Laboratory Manager is responsible for ensuring that the procedures are properly followed and to deliver the filters for shipping or assembly within the specified time period.

The Quality Assurance Officer of DRI's Energy and Environmental Engineering Center is responsible for determining 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

No terms used in this procedure require definitions.

1.8 Related Procedures

DRI SOP 11	Impregnating, Drying, and Acceptance Testing of Filters for Sampling Gases in Air.
DRI SOP 12	Preparation of Nylon Filters for Nitric Acid or Total Nitrate Sampling.
DRI SOP #2-106.2	Pre-firing of Quartz Fiber Filters for Carbonaceous Material Sampling.
DRI SOP 10	Gravimetric Analysis Procedures.
DRI SOP #2-107.2	Procedures for Light Transmission Analysis.
DRI SOP #2-209.2	Sample Shipping, Receiving, and Chain-of-Custody.

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Materials

2.1.1 Filter Holders

- Injection molded Teflon support grids with grooves for o-rings (Atmospheric Technology Inc.).
- Viton o-rings to fit the groove in the support grid.
- Injection molded Teflon open face inlet (Savillex Corp, Minnetonka, MN).
- Two-part injection molded Teflon inline outlet with a 3/8" fitting and a polypropylene clampnut (Savillex Corp, Minnetonka, MN).
- Wired cardboard mailing tags, approximately 1" X 2".

2.1.2 Filter Media

- Teflon 2 μm pore size, 47 mm (Gelman Scientific, Ann Arbor, MI).

- Teflon, Zefluor 2 μm pore size, 47 mm (Gelman Scientific, Ann Arbor, MI)
- Citric acid-impregnated Whatman 41 cellulose, 47 mm (Chemtrex, Hillsboro, OR; impregnation performed at DRI).
- K_2CO_3-impregnated Whatman 41 cellulose, 47 mm (Chemtrex, Hillsboro, OR; impregnation performed at DRI).
- Glass fiber filters, Pallflex TX40HI20-WW, 47 mm (Pallflex, Putnam, CT).
- TEA-impregnated, chromatography 31ET filters, 47 mm (Chemtrex, Hillsboro, OR; impregnation performed at DRI).

2.1.3 Barcode Labels

The filter holders and containers are labeled with barcode labels generated in-house using the CADMPBAR.EXE or BARCODES.EXE programs. As shown in Figure 2-1, these labels contain both human- and machine-readable versions of the ID number. The first two characters of the ID number signify the site. The following two digits indicate the filter pack type:

"GT" for TEA impregnated filter packs.

"DN" for denuded nylon filter packs.

"TN" for Teflon-nylon filter packs.

"TK" for Teflon+citric acid+potassium carbonate filter packs.

2.1.4 Equipment

- Flat-tipped tweezers (Millipore, South San Francisco, CA)
- PVC gloves, non-powdered (Fisher, #11-393-26).
- Kay Dry towels (Van Waters and Rogers, Brisbane, CA).
- Petri Slides, 47 mm (Millipore, #PD15004700).

Figure 2-1. Example of DRI Filter Holder Barcode Labels.

TAGK066	TAGK067	TAGK068	TAGK069
TAGK066	TAGK067	TAGK068	TAGK069
TAGK070	TAGK071	TAGK072	TAGK073
TAGK070	TAGK071	TAGK072	TAGK073
TAGK074	TAGK075	TAGK076	TAGK077
TAGK074	TAGK075	TAGK076	TAGK077
TAGK078	TAGK079	TAGK080	XXX
TAGK078	TAGK079	TAGK080	XXX

- Polystyrene extraction tubes with screw-cap lids in racks (Intermountain Scientific).
- Automatic dishwasher.
- Test tube racks.
- Mesh bags (type used for washing lingerie).
- Drying racks or towels.

2.2 Reagents

(Not Applicable)

2.3 Forms

Chain-of-Custody form is depicted in Figure 2-2.

3.0 CALIBRATION STANDARDS

(Not Applicable)

4.0 PROCEDURES

4.1 General Flow Diagrams

4.1.1 Assembly (Figure 4-1).

4.1.2 Disassembly (Figure 4-2).

4.1.3 Cleaning (Figure 4-3).

4.2 Procedure for Assembly of TK filter packs (Figure 4-4).

Teflon filters used for sampling are weighed before and after sampling. They are stored in labeled petri dishes before assembly into filter holders, and are returned to the same petri dishes during filter pack disassembly. All other filters are placed into extraction tubes during disassembly.

Figure 2-2. DRI Filter Assignment Logsheet.

DRI Filter Assignment Logsheet					
Date	Project	Manufacturer	Filter Size	DRI Lot #	Assigned Filter IDs

Figure 4-1. DRI Filter Pack Assembly Flow Diagram.

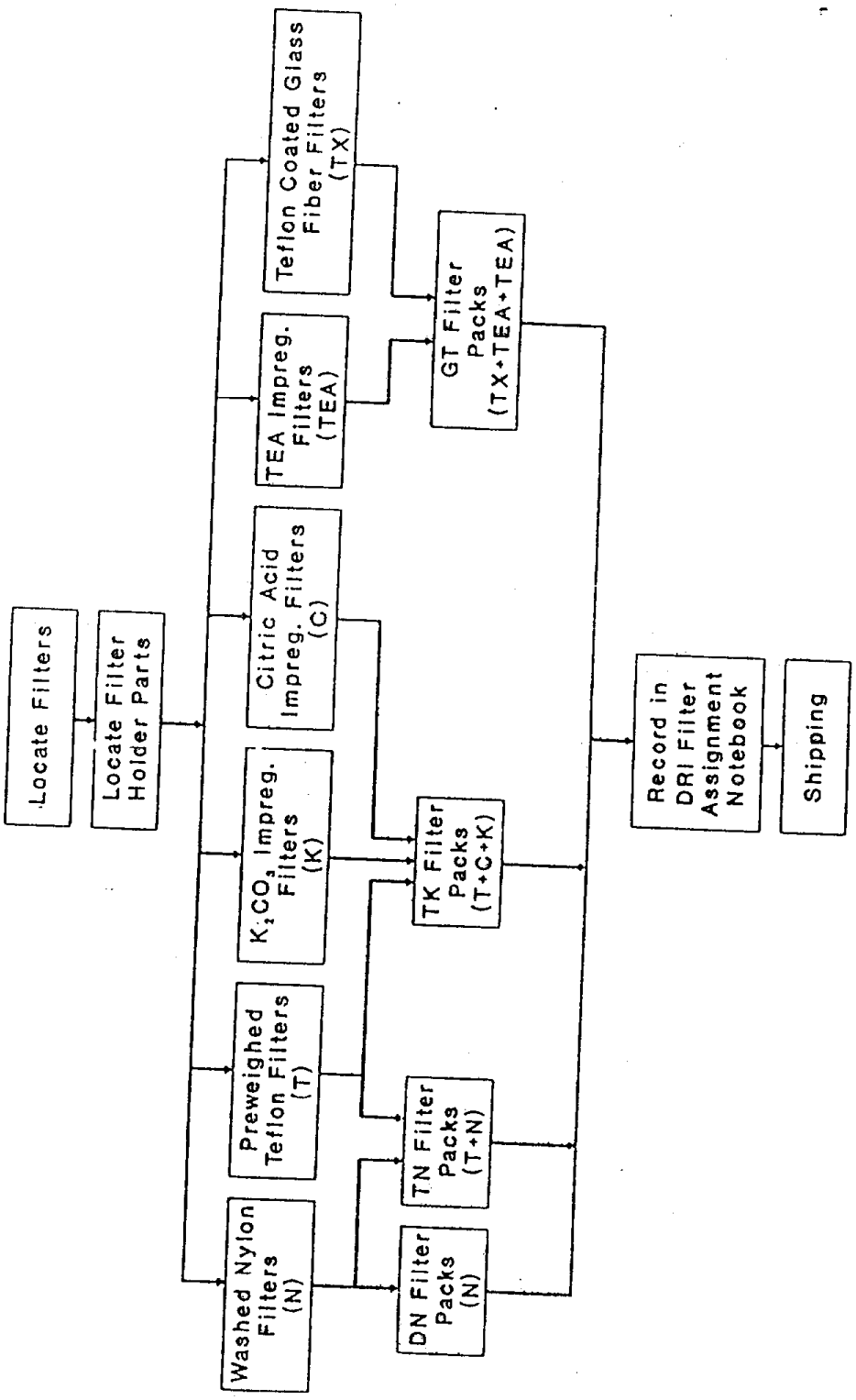


Figure 4-2. DRI Filter Pack Disassembly Flow Diagram.

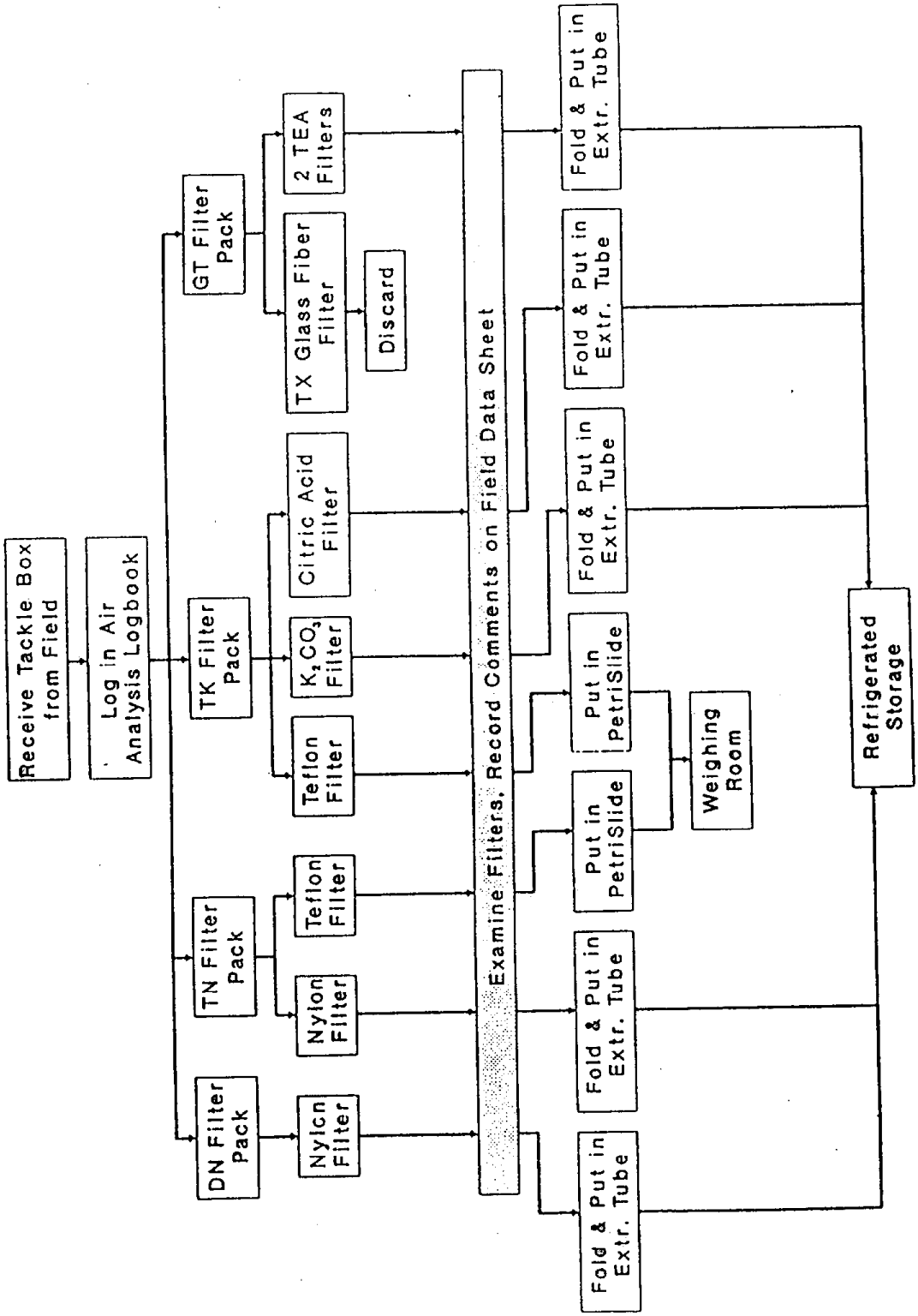


Figure 4-3. DRI Filter Holder Cleaning and Storage.

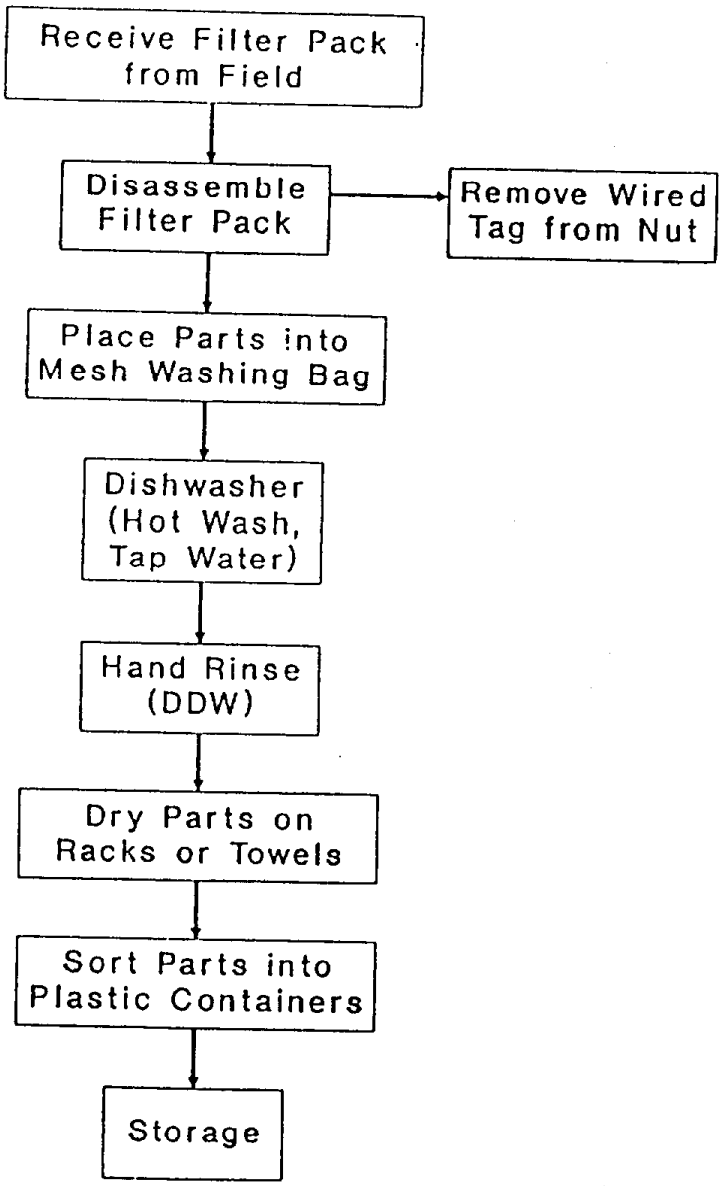
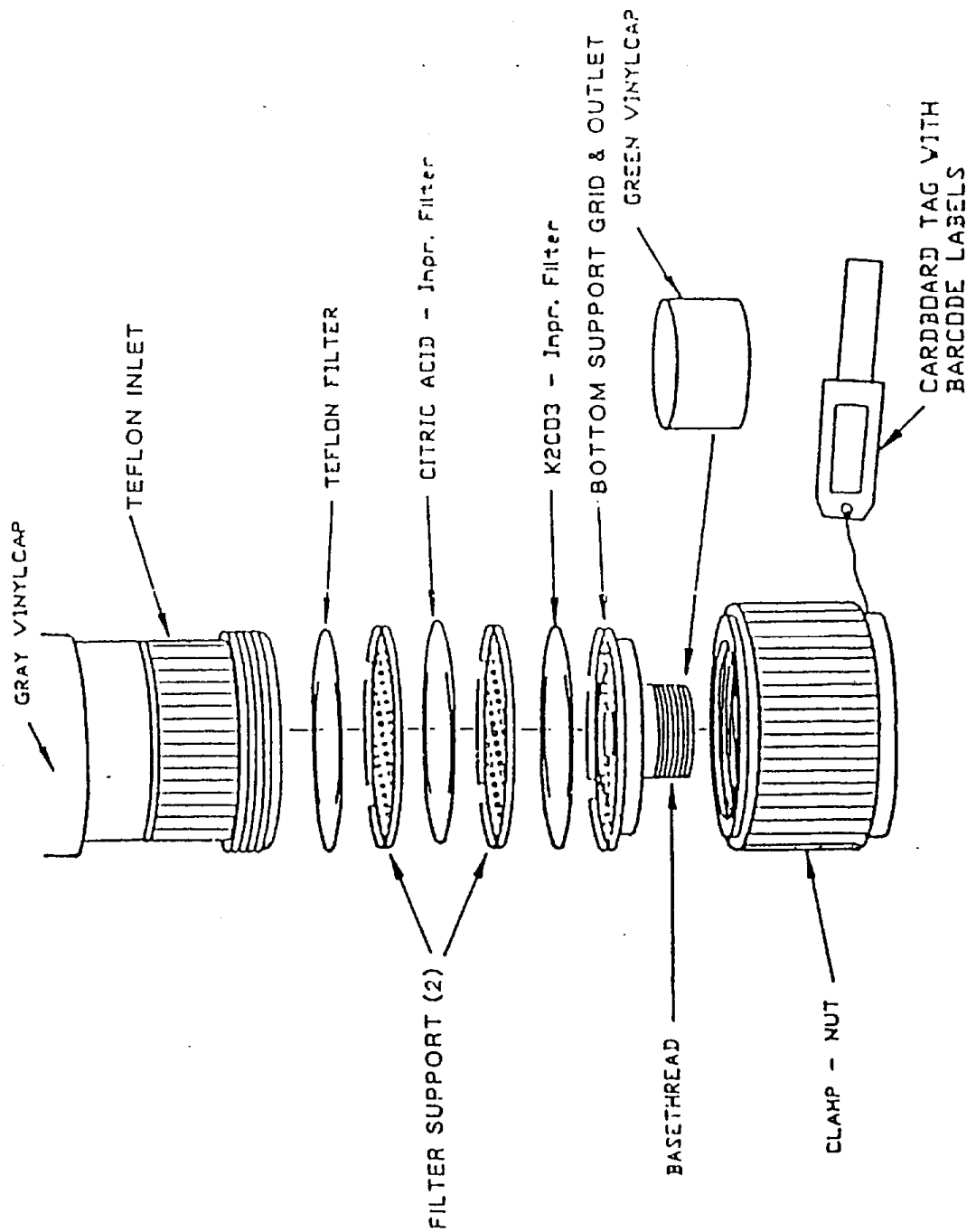


Figure 4-4. Assembly Diagram for TK Filter Packs.



4.2.1 Cover area with Kay-Dry towels

4.2.2 Place the tray containing pre-weighed Teflon filters, the box of K_2CO_3 impregnated filters and the box containing citric acid impregnated filters in the work area.

4.2.3 Place the required filter parts in the work area (see Figure 4-4), attach wire tags, with the barcode label on them, to the complete set of nuts.

4.2.4 Snap the flat grid into the base.

4.2.5 Wearing gloves, hold the outlet in one hand and use the flat tipped tweezers to place one potassium carbonate impregnated filter on the outlet. Be sure that the filter fits within the "ears" of the outlet. Snap the support grid, with the O-ring down, into the outlet. Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly).

4.2.6 Put the finished first stage on the Key-Dry towel. Complete the whole set of filter packs using the potassium carbonate impregnated filters before proceeding with citric acid impregnated filters. (This is to ensure that the citric acid and potassium carbonate impregnated filters do not get switched).

4.2.7 Using the tweezers, place a citric acid impregnated filter on the support grid again, being sure that the filter fits within the "ears".

4.2.8 Snap another grid into place, as in 4.2.6.

4.2.9 Hold the assembly tightly with one thumb on the top grid and a finger on the bottom. Insert this assembly into the prelabeled nut, make sure that the outlet is seated in the nut. Complete the whole set of nuts.

4.2.10 Using the tweezers, carefully place the Teflon filter on the top support grid. (CAUTION: BE SURE THAT THE ID ON THE WIRE TAG AND THE PETRI SLIDE LABEL ARE IDENTICAL).

4.2.11 Screw the inlet into the nut, being careful not to tear the filter. Look down at the filter to make sure alignment is correct.

4.2.12 Place the grey cap on the top end of the inlet.

4.2.13 Place the green cap on the grooved outlet on the bottom of the pack. If the green cap is put on first, air pressure may force the top filter out of position.

4.2.14 Place the filter pack in the shipping container.

4.2.15 Record the project, type of filter, lot number of the filter(s) used and the filter ID on the chain-of-custody sheet (Figure 2-2).

4.3 Procedure for Disassembly of TK Filter Packs (Figure 4-4):

4.3.1 Filter Handling Precautions: These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges.
- Always wear PVC gloves.
- Your breath contains ammonia. Therefore, avoid breathing on any filters, particularly the citric acid-impregnated filters, since they will collect ammonia from your breath.

4.3.2 Cover work area with Kay Dry towels.

4.3.3 Place a filter holder awaiting disassembly on one side of work area.

4.3.4 Place the corresponding empty, prelabeled petri slide and prelabeled extraction tube on the work area.

4.3.5 Remove the green cap from the outlet and the grey cap from the inlet. Inspect the top filter, recording any damage or unusual appearance on the Field Data Sheet returned with the shipment (Figure 4-5).

Figure 4-5. Filter Pack Field Data Sheet.

Site _____ Run Number _____ Sample Run Date _____

ELAPSED TIME

Chan 3 Load _____ Remove _____ Total _____

FILTER I.D. Port	Type	PM_{10} Number
1	GT	
3	GT	
4	GT or no filter Blank	
5	TCK	
7	TCK	
8	TCK or no filter Blank	

Chan 4 Load _____ Remove _____ Total _____

Port	Type	$PM_{2.5}$ Number
1	DN	
3	DN	
4	DN or no filter Blank	
5	DN	
7	DN	
8	DN or no filter Blank	

4.3.6 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet.

4.3.7 Remove the Teflon filter from the top grid. Inspect the filter for the presence of any other unusual conditions. Note these conditions on the Field Data Sheet returned with the shipment of filters (Figure 4-5).

4.3.8 Place the Teflon filter in the appropriate petri slide. Place the cover on the container. Remove the remaining assembly from the nut by placing a finger on the top and a thumb on the bottom.

4.3.9 Remove the top grid from which the Teflon filter was removed. The citric acid filter is now exposed. To insert the filter into the tube, place it sample side up, on an inverted petri slide. Using a second pair of tweezers, carefully fold the filter, keeping the exposed side of the filter inside of the fold. Then insert it into the tube. Cap the tube. Clean inverted petri slide, glass rod and tweezers before continuing on with next filter.

4.3.10 Repeat step 4.3.9 for the potassium carbonate filter. (CAUTION: MAKE SURE THE FILTERS ARE PLACED IN THE CORRECT TEST TUBES SINCE CITRIC ACID AND K_2CO_3-IMPREGNATED FILTERS LOOK ALIKE.)

4.3.11 Store the containers with the filters in a refrigerator as instructed by your supervisor.

4.3.12 Remove wire tags from the nuts and put all filter parts into a mesh bag to be washed.

4.4 Procedure for Assembly of DN Filter Pack (Figure 4-6)

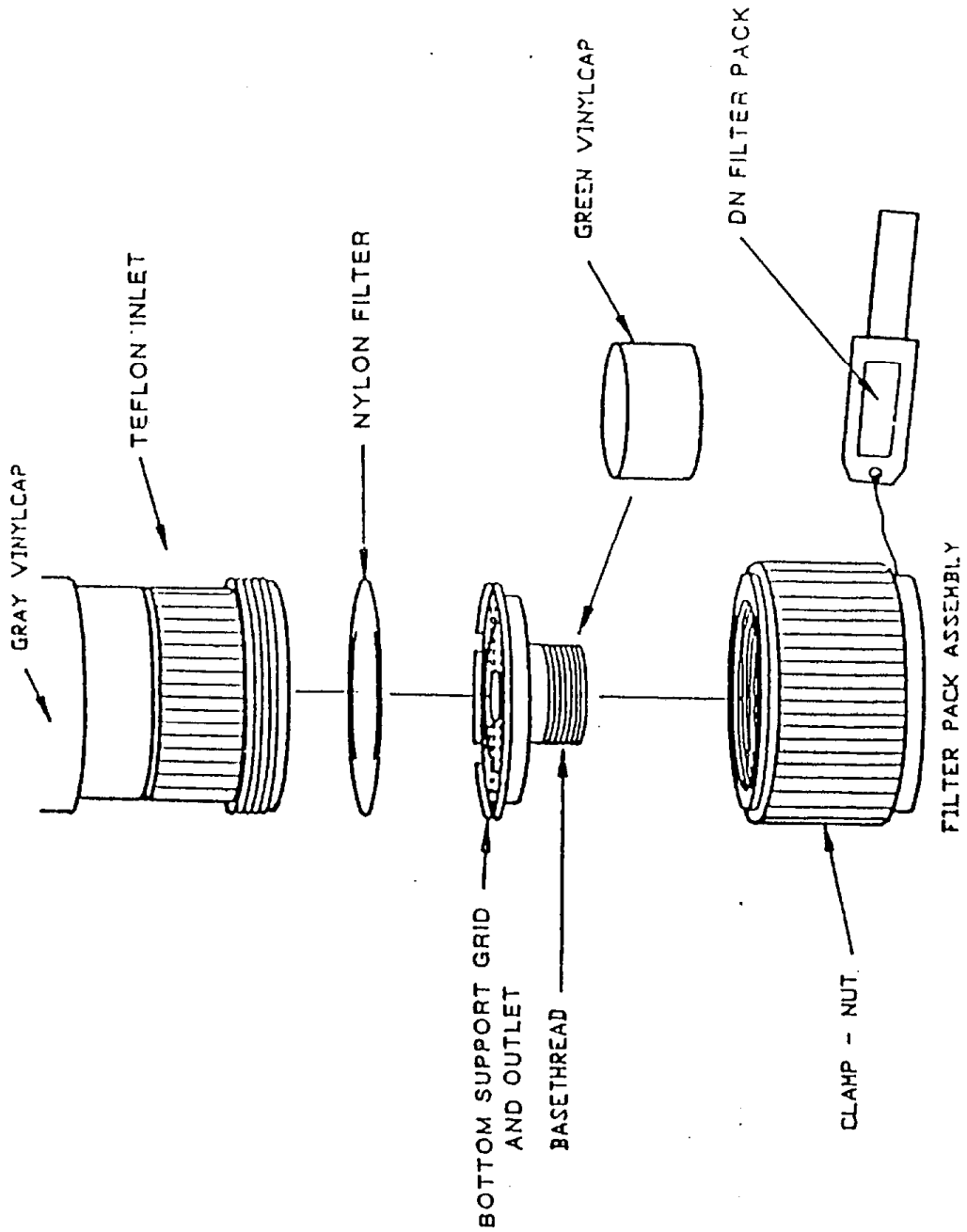
4.4.1 Cover area with Kay Dry towels.

4.4.2 Place the box of prewashed nylon filters on the work area.

4.4.3 Place the required filter parts on the work area (see Figure 4-6). Attach wire tags, with the barcode labels on them, to all nuts in the set.

4.4.4 Wearing gloves, snap a support grid, o-ring down, into the outlet. (CAUTION: BE SURE THERE IS NO FLAT GRID IN THE BASE). Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade

Figure 4-6. Assembly Diagram for DN Filter Packs.



to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly.)

4.4.5 Insert the outlet and grid into the prelabeled nut, being sure that the outlet is seated in the nut.

4.4.6 Using flat-tipped tweezers, place one nylon filter on the support grid, being sure that it fits down within the "ears". Finish the assembly of the filter pack as in steps 4.2.11 to 4.2.15.

4.5 Procedure for Disassembly of DN Filters (Figure 4-6)

4.5.1 These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edge.
- Always wear PVC gloves when disassembling filter holders.

4.5.2 Cover work area with Kay Dry towels.

4.5.3 Place a filter holder awaiting disassembly on one side of work area.

4.5.4 Place a prelabeled extraction tube to hold the filter on the work area.

4.5.5 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet. Push the outlet from the bottom until the nylon filter can be accessed.

4.5.6 Remove the single nylon filter from the grid. Inspect the filter for the presence of any unusual conditions. Note these conditions on the Field Data Sheet returned with the shipment (Figure 4-5).

4.5.7 Place the nylon filter into the appropriate test tube as in 4.3.9, and cap the tube.

4.5.8 Store the container with the filter in a refrigerator as instructed by your supervisor.

4.5.9 Remove the wire tags from the nuts and put all filter parts in mesh bags to be washed.

4.6 Procedure for Assembling TN Filter Pack (Figure 4-7)

4.6.1 Cover area with Kay Dry Towels.

4.6.2 Place the box of prewashed nylon filters and the tray of preweighed Teflon filters on the work area.

4.6.3 Place the required filter parts on the work area (Figure 4-7).

4.6.4 Wearing gloves, snap a support grid, o-ring down, into the outlet. (CAUTION: BE SURE THERE IS NO FLAT GRID IN THE BASE). Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly.)

4.6.5 Using flat-tipped tweezers, carefully place one nylon filter on the support grid being sure that it fits down between the "ears".

4.6.6 Snap another support grid, O-ring down, on top of the outlet and nylon filter. Hold the assembly tightly with one thumb on the top grid and a finger on the bottom. Insert this assembly into the prelabled nut.

4.6.7 Load the Teflon filter and finish the assembly as in 4.2.11 to 4.2.15. (CAUTION: BE SURE THAT THE ID ON THE WIRE TAG AND THE PETRI SLIDE ARE IDENTICAL).

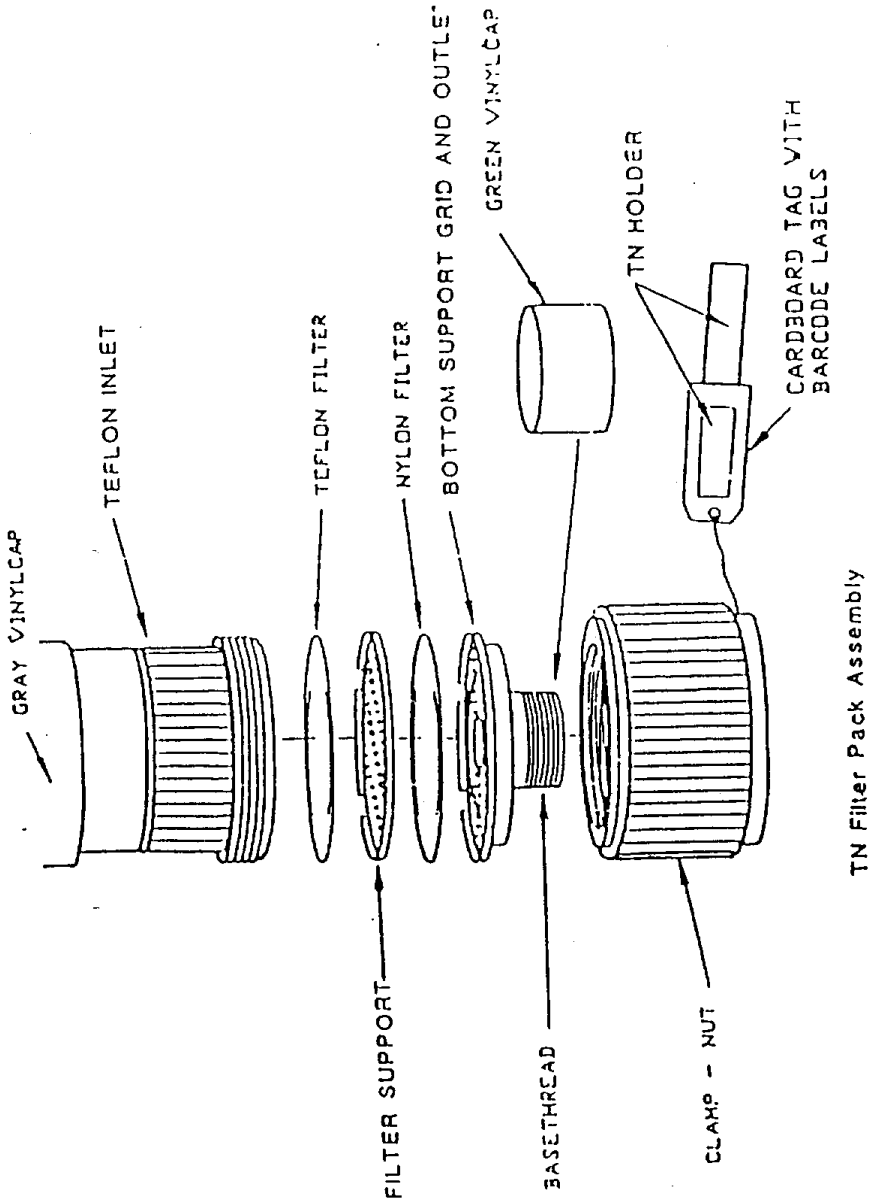
4.7 Procedure for Disassembling TN Filter Pack (Figure 4-7)

4.7.1 Filter Handling Precautions

These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme care must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edges.

Figure 4-7. Assembly Diagram for TN Filter Packs.



- Your breath contains ammonia. Therefore, avoid breathing on any filters.

- Always wear PVC gloves when disassembling filter packs.

4.7.2 Cover work area with Kay Dry towels.

4.7.3 Place a filter holder awaiting disassembly on one side of work area.

4.7.4 Place the corresponding empty petri dish and prelabeled extraction tube on the work area.

4.7.5 Remove the green cap from the outlet and the grey cap from the inlet. Inspect the top filter, recording any damage or unusual appearance on the Field Data Sheet returned with the shipment. (Figure 4-5)

4.7.6 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet.

4.7.7 Remove the Teflon filter from the top grid. Inspect the filter for the presence of any unusual conditions. Note these conditions on the Field Data Sheet that was returned with the shipment. (Figure 4-5)

4.7.8 Place the filter in the appropriate petri slide. Place the cover on the container. (CAUTION: BE SURE THAT THE ID ON THE WIRE TAG AND THE PETRI SLIDE ARE IDENTICAL).

4.7.9 Remove the grid and outlet in one piece from the nut. This is accomplished by putting a thumb on the threaded outlet and a finger on the support grid. Push the assembly up out of the nut until it can be taken out in one piece.

4.7.10 Separate the support grid from the outlet, exposing the nylon filter.

4.7.11 Place the nylon filter into the appropriate extraction tube as in 4.3.7.

4.7.12 Store the containers with the filters in a refrigerator as instructed by your supervisor.

4.7.13 Remove wire tags from nuts and put all parts into mesh bags to be washed.

4.8 Procedure for Assembly of GT Filter Packs (Figure 4-8)

4.8.1 Cover the work area with Kay Dry towels.

4.8.2 Place the box of TX40HI20 filters and the box of TEA-impregnated filters on the work area.

4.8.3 Place the required filter parts on the work area (see Figure 4-8). Attach the wire tags, with the barcode label on them, to all the nuts in the set.

4.8.4 Wearing gloves, snap the flat grid into the outlet.

4.8.5 Holding the outlet in one hand, use flat-tipped tweezers to place two TEA-impregnated filters on the outlet, making sure that they sit down between the "ears".

4.8.6 Snap the support grid, with the o-ring down, into the outlet. Be sure that the "ears" of the support grid and the outlet do not overlap, since this will cause leakage. If necessary, use a razor blade to cut a piece of the "ear" off of the outlet. (It is all right if the "ears" do not meet exactly).

4.8.7 Hold the assembly firmly with a thumb on the top grid and a finger on the bottom. Insert this assembly into the prelabeled nut, being sure that the base is seated in the nut.

4.8.8 Using the tweezers, place one TX40HI20 filter on the support grid. The Teflon (non-shiny) side should be facing upward.

4.8.9 Finish the assembly of the filter pack as in steps 4.2.11 to 4.2.15.

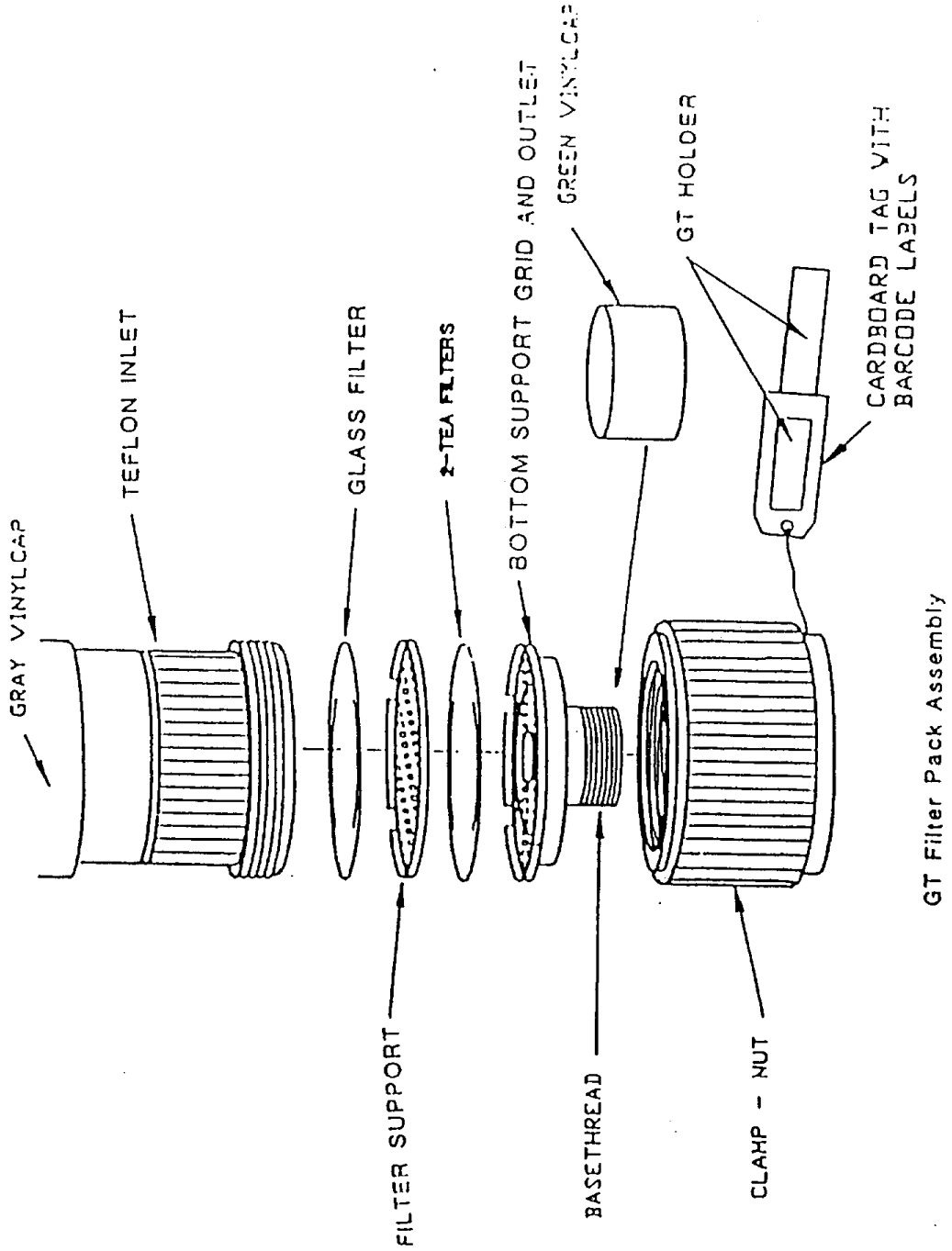
4.9 Procedure for Disassembly of GT Filter Packs (Figure 4-8)

4.9.1 Filter Handling Precautions.

These filters have collected minute quantities of materials from the atmosphere. Therefore, extreme caution must be used to avoid contamination of the filters when they are handled during filter pack disassembly. Special precautions include:

- Never handle a filter with anything other than flat-tipped tweezers.
- Handle the filters only on the edge.

Figure 4-8. Assembly Diagram for GT Filter Packs.



- Always wear nylon gloves when disassembling filter holders.

4.9.2 Cover work area with Kay Dry towels.

4.9.3 Place a filter holder awaiting disassembly on one side of work area.

4.9.4 Place the prelabeled extraction tubes on the work area.

4.9.5 Remove the green cap from the outlet and the grey cap from the inlet. Inspect the top filter, recording any damage or unusual appearance on the Field Data Sheet returned with the shipment. (Figure 4-5)

4.9.6 Carefully unscrew the clampnut from the filter holder inlet and remove the inlet.

4.9.7 Remove the single glass filter from the top grid and dispose of properly. Remove the remaining assembly from the nut while holding firmly to the top and bottom.

4.9.8 Separate the support grid from the outlet, exposing the two TEA-impregnated filters.

4.9.9 Remove the TEA filters from the bottom grid. Inspect the filters for any unusual conditions. Note these conditions on the Field Data Sheet returned with the shipment.

4.9.10 Fold the two TEA filters together, do not separate them. Place into the appropriate test tube as in 4.3.7.

4.9.11 Store the containers with the filters in a refrigerator as instructed by your supervisor.

4.10 Cleaning and Storage of Filter Holders

4.10.1 Place mesh bags containing filter parts into the trays of the dishwasher.

4.10.2 Wash parts using hot water and no soap. Do not use a dry cycle or else set it to COLD.

4.10.3 Fill three plastic dishpans with DDW. Wearing gloves, rinse a bag of parts in the first, then the second, then the third.

4.10.4 Repeat for all bags, using the same dishpans in the same order.

4.10.5 Empty the bags onto the drying area, separating the parts for faster drying.

4.10.6 Store dried parts in the containers provided, either Zip-Lock bags or plasticware containers.

5.0 QUANTIFICATION

(Not Applicable)

6.0 QUALITY CONTROL

(Not Applicable)

7.0 QUALITY ASSURANCE

(Not Applicable)

8.0 REFERENCES

(Not Applicable)

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure describes the data processing operations required for producing aerosol and gas concentration data from analysis of samples collected using the DRI sequential filter sampler, DRI MEDVOL, dichotomous sampler, DRI resuspension sampler, MOUDI sampler or portable sampler. Operations include the following six steps.

- Transmittal of data from field data sheets into database files,
- Calculation of measurement precision for each chemical species,
- Integration of data from the various measurements into a unified data base,
- Calculation of field blank concentrations,
- Calculation of ambient concentrations, and
- Preparation of validation summaries.

1.2 Measurement Principle

(Not applicable)

1.3 Measurement Interferences and Their Minimization

(Not applicable)

1.4 Ranges and Typical Values of Measurements Obtained by this Procedure

(Not applicable)

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

(Not applicable)

1.6 Responsibilities of Personnel

The Analytical Chemists are responsible for Level I chemical data validation and calculating analytical precision.

The Data Processing Technician is responsible for entering field data, merging chemical data into a data base, calculating field blank values, calculating concentrations and preparing Level II data validation summaries.

The Project Manager is responsible for reviewing all data processing operations, Level II chemical data validation, and submittal of samples for re-analysis.

The Quality Assurance Officer is responsible for auditing the data processing procedures.

1.7 Definitions

Level I data validation	Level I data validation consists of the following: 1) flagging samples when significant deviations from measurement assumptions have occurred; 2) verifying computer file entries against data sheets; 3) eliminating values for measurement which are known to be invalid because of instrument malfunctions; 4) replacement of data from a backup data acquisition system in the event of failure of the primary system; and 5) adjustment of measurement values of quantifiable calibration or interference biases.
Level II data validation	Level II data validation takes place after data from field sampling and laboratory analyses have been assembled in a common data set. Level II validation applies consistency tests based on known physical relationships between variables to the assembled data. Examples of these tests include the following: 1) the sum of chemical species in a particulate matter sample should be less than or equal to the gravimetric mass of that sample; 2) size segregated particle concentrations should be less than total particle concentrations (e.g. $PM_{2.5} < PM_{10}$); 3) the sum of all major species (with oxide forms included) should exceed 75% of the measured mass; and 4) analyses of the same species by different methods should yield compatible results (e.g., sulfur by XRF and sulfate by IC); 5) collocated measurements should yield comparable results; 6) the ratio of anion concentrations in $\mu eq/m^3$ to cation concentrations should be 0.8 to 1.2.

1.8 Related Procedures

Related procedures include:

- Sequential Filter Sampler for PM_{10} or $PM_{2.5}$: Operation, Maintenance, and Field Calibration (DRI SOP #1-207.11)

- Micro-Orifice Uniform Deposit Impactor (MOUDI) Field and Laboratory Operations (DRI SOP #1-208.3)
- Portable PM_{10} Survey Sampler II (DRI SOP #1-210.3)
- DRI MEDVOL Gas/Particle Sampler for Simultaneous Collection of Gases and $PM_{2.5}$ or PM_{10} on Four Filter Packs (DRI SOP #1-231.1)
- Resuspension of Bulk Samples onto Teflon and quartz Filters (DRI SOP #1-250.1)
- Gravimetric Analysis Procedure (DRI 10)
- Light Transmission Analysis Procedure (DRI SOP #2-107.2)
- Anion Analysis of Filter Extracts and Precipitation Samples by Ion Chromatography (DRI 15)
- Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples (DRI SOP #2-204.4)
- X-Ray Fluorescence (XRF) Analysis of Aerosol Filter Samples (SOP #2-205.2)
- Analysis of Filter Extracts and Precipitation Samples by Atomic Absorption Spectroscopy (DRI 16)
- Analysis of Filter Extracts and Precipitation Samples by Automated Colorimetric Analysis (DRI 17)
- Analysis of Filter Extracts and Precipitation Samples for Nitrite by Automated Colorimetric Analysis (DRI SOP #2-213.1)

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

- Computer: An MSDOS based microcomputer with an 80386 or higher processor, math co-processor, I Mbytes of RAM, and hard disk.
- Printer: HP LaserJet or Epson dot matrix compatible.

- Operating System Software: MS-DOS, version 6.2 or later, Microsoft Windows, version 3.1 or later (Microsoft Corp).
- Database software: FoxPro 2.5 for Windows (Microsoft Corp.).
- Plotting software: Excel 5.0 (Microsoft Corp.) or similar.
- FILTER program software: FILTER.APP is a FoxPro application which is used to perform all of the procedures in this document. It is compiled from a FoxPro project file (FILTER.PJX) which contains all the necessary menu files, screen files, program files, format files, database structures and report files.

2.2 Reagents

(Not applicable)

2.3 FORMS

(Not applicable)

3.0 CALIBRATION STANDARDS

(Not applicable)

4.0 PROCEDURES

4.1 General Flow Diagram

All of the data processing operations described in this procedure are initiated by running application FILTER.APP and making selections from the FILTER pull down menu bar or by entering commands in the command window. By making menu item selections and providing appropriate input to interactive parts of the program, data is processed in a flow pattern as shown in Figure 4-1.

Field and flow calibration data are used to build a field data file. An analysis data file, which contain species concentrations in μg/filter is created for each analysis method. Replicate measurements contained in the analytical data file are used to calculate analytical precision. Replicate results are saved in a replicate file and concentration uncertainties are saved back in the original analysis files.

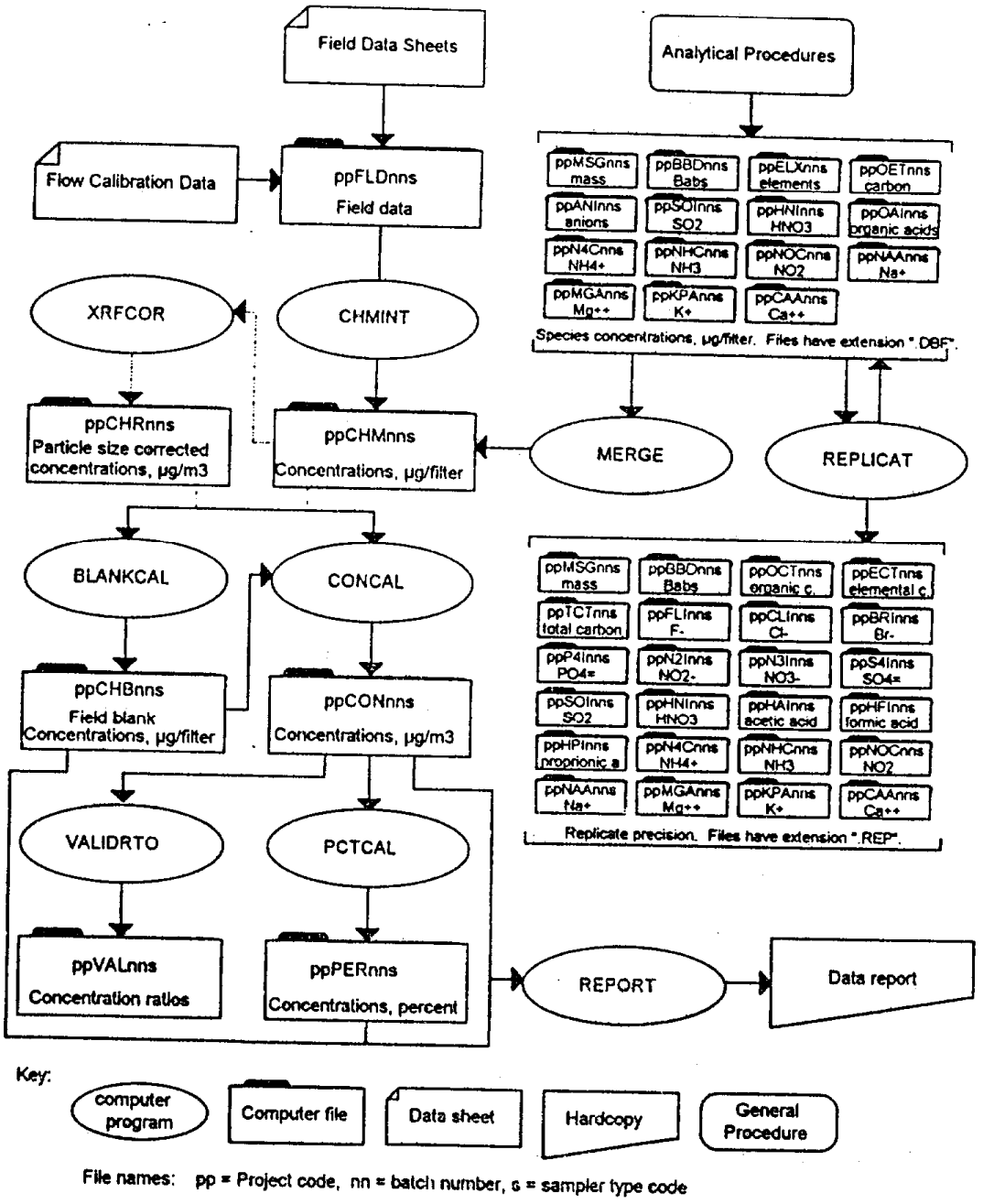


Figure 4-1. Data processing flow diagram.

A CHM (pronounced "chem") file is created from the field data file; it contains relevant field data and concentration place holders for each measured chemical species. Analysis concentrations and associated uncertainties are merged from individual analysis files into the CHM file by sample ID. Each record in the CHM file now contains all the data for a single sample. If necessary, XRF particle size corrections are made and corrected data stored in corrected concentration (CHR) file. Field blank concentration and variability for each species are calculated and saved in the blank (CHB) file. Concentrations in $\mu g/m^3$ are calculated by subtracting the field blank values in the CHB file from the CHM or CHR file concentrations and dividing by sampling volume. Concentrations are saved in the CON file. For source samples, concentrations are converted to mass percent and saved in a percent (PER) file. Concentration ratios of selected species are calculated from the CON file data and saved in a validation (VAL) file. A data report is generated from the CHB, VAL and CON or PER data files.

All files created and used in data processing operations follow the file naming conventions specified in Table 4-1.

4.2 Start-Up

Data processing programs are stored on the Environmental Analysis Facility's main file server, EAFMAIN. Login to EAFMAIN from your workstation and re-direct your local P: drive to EAFMAIN's P-DRIVE. Your workstation must have drive P:\ in its DOS PATH statement. You must have a CONFIG.FPW file in your DOS path that contains the following line.

PATH = P:\FOXPRO25.WIN;P:\PROG.FP2;P:\STRU.FP2

Project related files are also stored on EAFMAIN. Most projects are stored on F-DRIVE with each project having its own subdirectory. Some large projects are stored on drives other than F-DRIVE. The laboratory manager has drive locations for these projects. Redirect one of your local drives (a good choice is F:) to EAFMAIN's F-DRIVE, or to the proper drive if the project is not on F-DRIVE.

Data files are organized by subdirectories below the project directory. Each analysis batch has its own directory named BATCHnn, where nn is the batch number. Files for each batch are further divided into DATA and REPORT directories. Completed analytical data files are saved in the <PROJECT>\BATCHnn\DATA directory by the analysts after Level I validation of the data is completed. Files created during data processing and validating procedures are saved in the <PROJECT>\BATCHnn\REPORT PATH directory. Do not change the files in the DATA directory; they should remain as they were originally submitted.

Copy all analysis files from the DATA directory to the REPORT directory before beginning data processing procedure.

Table 4-1
Database File Naming Conventions

Generalized file name: ppDDDnns.DBF

- pp — two character project code (assigned by laboratory coordinator)
- DDD — three character data type (see below)
- nn — two digit analysis batch number (01 through 99)
- s — one character sampler type code (see below)

File Type	Data Type Code[a]	Definition
Analytical	MSG	Mass by gravimetry
	BBD	B_{abs} by densitomitry
	ELX	Elements by XRF[b]
	OET	Organic/elemental carbon by TOR[c]
	ANI	Anions by IC[d]
	SOI	SO_2 as SO_4 by IC
	HNI	HNO_3 on nylon filters by IC
	OAI	Organic acids by IC
	N4C	NH_4^+ by AC[e]
	NHC	NH_3 as NH_4^+ on citric acid-impregnated filters by AC
	NOC	NO_2 as NO_2^- on TEA impregnated filters by AC
	NAA	Na^+ by AA[f]
	MGA	Mg^{2+} by AA
	KPA	K^+ by AA
	CAA	Ca^{2+} by AA
Replicate[g]	OCT	Organic carbon by TOR
	ECT	Elemental carbon by TOR
	TCT	Total carbon by TOR
	FLI	F^- by IC
	CLI	Cl^- by IC
	BRI	Br^- by IC
	P4I	PO_4^{2-} by IC
	N2I	NO_2^- by IC
	N3I	NO_3^- by IC
	S4I	SO_4^{2-} by IC
	HAI	Acetic acid by IC
	HFI	Formic acid by IC
	HPI	Proprionic acid by IC
Data Processing	FLD	Field data, volume in m^3
	CHM	Concentrations in μg/filter, not blank subtracted
	CHB	Concentrations in μg/filter, blank subtracted
	CHR	Concentrations in μg/filter, XRF particle size corrected
	CON	Concentrations in $\mu g/m^3$, blank subtracted and XRF particle size corrected
	PER	Concentrations, mass percent
	VAL	Concentration ratios of selected species

Table 4-1 (continued)
Database File Naming Conventions

File Type	Sampler Type Code	Definition
Analytical, replicate and database	A	Agricultural burn emissions dilution sampler
	C	DRI Medvol sampler, combination particle/gaseous
	D	Dichotomous sampler
	G	DRI Medvol sampler, gaseous
	H	Hivol sampler
	I	IMPROVE/NPS sampler
	M	DRI Medvol sampler, particle
	P	Portable survey sampler
	R	Resuspension chamber sampler
	S	Sequential Filter Sampler (SFS)
	U	Multiple Orifice Uniform Deposit Impactor (MOUDI) sampler
	W	Wet deposition (bucket) sampler
	X	Unknown sampler
	Y	DRI Y source sampler

[a] For analytical and replicate file types, the first two characters of the data type code indicate species, and the third character indicates analysis method.
[b] XRF = x-ray fluorescence
[c] TOR = thermal/optical reflectance
[d] IC = ion chromatography
[e] AC = automated colorimetry
[f] AA = atomic absorption spectrophotometry
[g] Replicate file names are the same as analytical data file names except, 1) file extensions are REP instead of DBF, and 2) the data type codes listed in the table are used instead of data type codes OET, ANI and OAI.

Start Windows if it is not already running. Start FoxPro by double-clicking its icon. Open a new text file and save it with the file name DPnns.DOC, where nn is the batch number and s is the sampler type. The purpose of this file is to document all data processing operations performed on a data set. Keep this file open throughout data processing operations and record all data processing operations performed as they are completed in this file. Record programs run, the input and output file names processed by those programs, parameters used in the programs, etc. The level of detail in the file should be sufficient to allow someone else to duplicate the final database starting from the raw data. It is easy to enter most of the information into the file by cutting and pasting from the command window, and adding explanatory material where necessary.

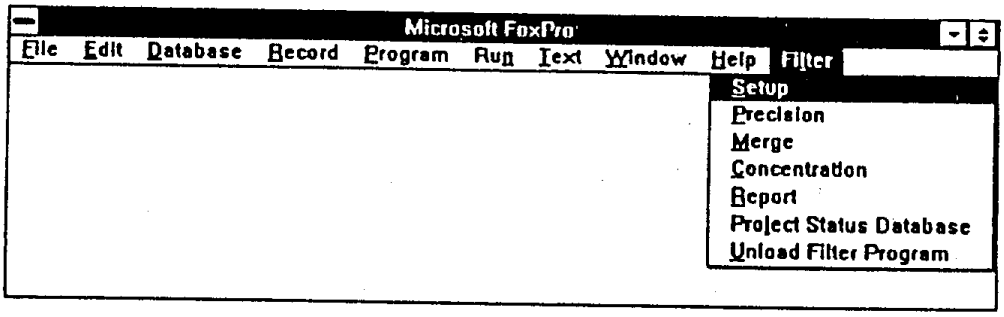
Run the FILTER.APP by typing

do filter

in the command window. This adds the FILTER menu pad to the FoxPro menu bar. Note: throughout this procedure, commands to be typed in the command window will be indicated by underlining, as above, and must be followed by pressing the Enter or Return key. Case is not important.

4.3 Routine Operation

Click the Filter menu pad or press Alt-L. This displays the Filter program pull down menu, shown in screen 4-1.



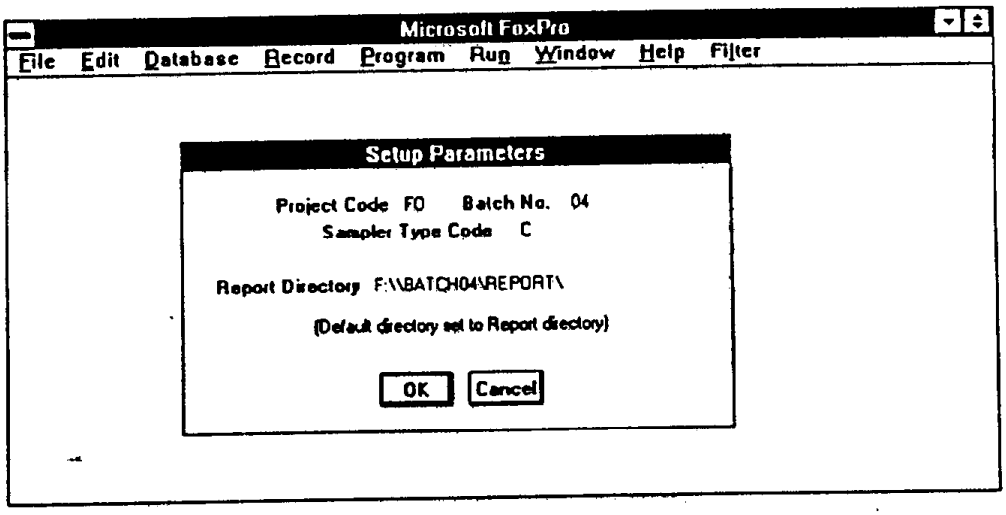
Screen 4-1. Filter pull-down menu.

Select menu items by clicking with the mouse, moving the highlight bar with arrow keys and pressing return, or by pressing the key of an underlined letter. The "Project Status Database" option starts the application that tracks project status. You may select this option anytime to query the status of a project, or to enter new status information as portions of a project are completed.

4.3.1 Setup

Select "Setup." Enter the two-character project code, two-digit batch number, and one-character sampler type code. Sampler type codes are given in Table 4-1. The program creates a partial report directory pathname as shown in Screen 4-2 based on the batch number you enter, and assuming the file is on drive F:. Edit the pathname as needed and select OK. If the pathname cannot be found on disk, the program will display an error message and reset the path to the current directory. You may cancel the program or use Alt-Tab to switch to the file manager to determine the correct report directory pathname.

Other parts of the FILTER program use the project code, batch number and sampler type code to construct default file names.



Screen 4-2. Filter program setup dialog.

4.3.2 Field Data

Create a field file with the correct file structure by typing

```
use xxfld00s
copy to ..\DATA\ppfldnns
use ..\DATA\ppfldnns
browse
```

in the command window. Substitute the project code for pp, the batch number for nn and the sampler type for s in filenames in the lines above. Field file structure definitions are given in Tables 4-2 through 4-8.

For sampler configurations with multiple filter packs other than simple Teflon and quartz pairs, it is necessary to create a new field file structure by adding new sample ID, field flag, flow and volume fields for the additional filter packs to one of the existing field file structures. For example, to create a DRI Medvol field data file, start with the SFS field file using the first three commands above, then type

modify structure

and add/change the necessary ID and other fields.

Enter data from field data sheets; press Ctrl-N for each new record of data. Be sure to enter all field flags and appropriate comments listed on the field data sheets. Additional flags and comments may be listed in the sample login file as well. Edit the comments so that they are consistent in quality and wording. A comment should be entered only if it provides additional information beyond the definition of any applied flag. Enter flags as necessary for sampling time and flow rate deviations, and for any other abnormal conditions that are not already flagged. A list of field data flags is given in Table 4-9. Consult the field sampling technician and/or the sample login technician in cases where any field data are ambiguous, or if the data sheets appear to be in error.

After all data are entered, check all data entries by comparing data sheets to a printout of the file or to the file displayed on screen. Correct any data entry errors before proceeding.

Enter data to calculated fields by giving the appropriate REPLACE commands. Examples are shown below; actual field names may differ depending on the file structure you are using.

```
replace duration with (timef - timei) * 60
replace tflowavg with (tflowf - tflowi) / 2
replace tflowact with tflowavg * <slope> + <intercept>
replace tvoc with tflowact * (timef - timei) * <TP corr> / 1000
replace all tvou with tvoc * 0.05
```

Slope and intercept to convert indicated flow rate to actual flow rate are indicated on the rotometer calibration data sheet. The formula to calculate the temperature/pressure correction factor is likewise indicated on the rotometer calibration data sheet. This factor converts measured flow rate to flow rate at actual site conditions. Note that

Table 4-2
Database Structure for Sequential Filter Sampler Field Data

Structure for table: XXFLD00S.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Sampling site name
2	DATE	Date	8	Sampling start date
3	SIZE	Character	3	Particle size code: 2.5 = $PM_{2.5}$, 10 = PM_{10}
4	STRTHHMM	Character	4	Nominal sample start time, HHMM
5	STOPHHMM	Character	4	Nominal sample stop time, HHMM
6	PERIOD	Character	1	Sample period code, defined for each project
7	TID	Character	10	Teflon filter pack ID
8	QID	Character	10	Quartz filter pack ID
9	TIMEI	Numeric	7.1	Initial elapsed time meter reading
10	TIMEF	Numeric	7.1	Final elapsed time meter reading
11	DURATION	Numeric	5.1	Actual sample duration, hours
12	TFLOWI	Numeric	5.1	Initial Teflon filter flow reading from rotometer
13	TFLOWF	Numeric	5.1	Final Teflon filter flow reading from rotometer
14	TFLOWAVG	Numeric	5.1	(TFLOWI + TFLOWF) / 2
15	TFLOWACT	Numeric	5.1	Average Teflon filter flow rate, lpm
16	TVOC	Numeric	10.4	Teflon filter volume, m^3
17	TVOU	Numeric	10.4	Teflon filter volume uncertainty, m^3
18	TFFLG	Character	5	Teflon filter field flag
19	QFLOWI	Numeric	5.1	Initial quartz filter flow reading from rotometer
20	QFLOWF	Numeric	5.1	Final quartz filter flow reading from rotometer
21	QFLOWAVG	Numeric	5.1	(QFLOWI + QFLOWF) / 2
22	QFLOWACT	Numeric	5.1	Average quartz filter flow rate, lpm
23	QVOC	Numeric	10.4	Quartz filter volume, m^3
24	QVOU	Numeric	10.4	Quartz filter volume uncertainty, m^3
25	QFFLG	Character	5	Quartz filter field flag
26	COMMENT	Character	100	Comments applied during field sampling or sample login

Table 4-3
Database Structure for Dichotomous Sampler Field Data

Structure for table: XXFLD00D.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Sampling site name
2	DATE	Date	8	Sampling start date
3	SIZE	Character	3	Particle size code: F = $PM_{2.5}$, C = 2.5 - 10 μm
4	STRTHHMM	Character	4	Nominal sample start time, HHMM
5	STOPHHMM	Character	4	Nominal sample stop time, HHMM
6	PERIOD	Character	1	Sample period code, defined for each project
7	TID	Character	10	Teflon filter ID
8	QID	Character	10	Quartz filter ID
9	TTIMEI	Numeric	8.2	Teflon Initial elapsed time meter reading
10	TTIMEF	Numeric	8.2	Teflon Final elapsed time meter reading
11	TTIMEUNIT	Character	1	Teflon elapsed timer units: M = minutes, H = hours
12	TDURATION	Numeric	5.1	Actual Teflon sample duration, hours
13	TFLOWI	Numeric	5.2	Initial Teflon filter flow reading. Fine records: total channel rotometer. Coarse records: coarse channel rotometer.
14	TFLOWF	Numeric	5.2	Final Teflon filter flow reading. Fine records: total channel rotometer. Coarse records: coarse channel rotometer.
15	TFLOWAVG	Numeric	5.2	(TFLOWI + TFLOWF) / 2
16	TFLOWACT	Numeric	5.2	Average Teflon filter flow rate, lpm. Fine records: total channel flow rate. Coarse records: coarse channel flow rate.
17	TVOC	Numeric	10.4	Teflon filter volume, m^3. Fine records: fine channel volume. Coarse records: total sampler volume.
18	TVOU	Numeric	10.4	Teflon filter volume uncertainty, m^3
19	TFFLG	Character	5	Teflon filter field flag
20	QTIMEI	Numeric	8.2	Quartz Initial elapsed time meter reading
21	QTIMEF	Numeric	8.2	Quartz Final elapsed time meter reading
22	QTIMEUNIT	Character	1	Quartz elapsed timer units: M = minutes, H = hours
23	QDURATION	Numeric	5.1	Actual quartz sample duration, hours
24	QFLOWI	Numeric	5.2	Initial quartz filter flow reading. Fine records: total channel rotometer. Coarse records: coarse channel rotometer.
25	QFLOWF	Numeric	5.2	Final quartz filter flow reading. Fine records: total channel rotometer. Coarse records: coarse channel rotometer.
26	QFLOWAVG	Numeric	5.2	(QFLOWI + QFLOWF) / 2
27	QFLOWACT	Numeric	5.2	Average quartz filter flow rate, lpm. Fine records: total channel flow rate. Coarse records: coarse channel flow rate.
28	QVOC	Numeric	10.4	Quartz filter volume, m^3. Fine records: fine channel volume. Coarse records: total sampler volume.
29	QVOU	Numeric	10.4	Quartz filter volume uncertainty, m^3
30	QFFLG	Character	5	Quartz filter field flag
31	COMMENT	Character	100	Comments applied during field sampling or sample login

Table 4-4
Database Structure for Hivol Sampler Field Data

Structure for table: XXFLD00H.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Sampling site name
2	DATE	Date	8	Sampling start date
3	SIZE	Character	3	Particle size code: 10 = PM_{10}, TSP = total suspended particulate
4	STRTHHMM	Character	4	Nominal sample start time, HHMM
5	STOPHHMM	Character	4	Nominal sample stop time, HHMM
6	PERIOD	Character	1	Sample period code, defined for each project
7	QID	Character	10	Quartz filter ID
8	TIMEI	Numeric	8.2	Initial elapsed time meter reading
9	TIMEF	Numeric	8.2	Final elapsed time meter reading
10	TIMEUNIT	Character	1	Elapsed timer units: M = minutes, H = hours
11	DURATION	Numeric	5.1	Actual sample duration, hours
12	QVOC	Numeric	10.4	Quartz filter volume, m^3
13	QVOU	Numeric	10.4	Quartz filter volume uncertainty, m^3
14	QFFLG	Character	5	Quartz filter field flag
15	COMMENT	Character	100	Comments applied during field sampling or sample login

Table 4-5
Database Structure for Multiple Orifice Uniform Deposit Impactor (MOUDI) Sampler Field Data

Structure for table: XXFLD00U.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Sampling site name
2	DATE	Date	8	Sampling start date
3	STAGE	Character	2	Sampler stage, 1 through 8 and BU (backup)
4	STRTHHMM	Character	4	Nominal sample start time, HHMM
5	STOPHHMM	Character	4	Nominal sample stop time, HHMM
6	PERIOD	Character	1	Sample period code, defined for each project
7	XID	Character	10	Filter ID
8	XTIMEI	Numeric	7.1	Initial elapsed time meter reading
9	XTIMEF	Numeric	7.1	Final elapsed time meter reading
10	DURATION	Numeric	5.1	Actual sample duration, hours
11	XFLOWI	Numeric	5.1	Initial flow reading from rotometer
12	XFLOWF	Numeric	5.1	Final flow reading from rotometer
13	XFLOWAVG	Numeric	5.1	(XFLOWI + XFLOWF) / 2
14	XFLOWACT	Numeric	5.1	Average flow rate, lpm
15	PUPPERI	Numeric	5.1	Initial upper magnehelic reading, inches H_2O
16	PUPPERF	Numeric	5.1	Final upper magnehelic reading, inches H_2O
17	PLOWERI	Numeric	5.1	Initial lower magnehelic reading, inches H_2O
18	PLOWERF	Numeric	5.1	Final lower magnehelic reading, inches H_2O
19	XVOC	Numeric	10.4	Sample volume, m^3
20	XVOU	Numeric	10.4	Sample volume uncertainty, m^3
21	XFFLG	Character	5	Field flag
22	COMMENT	Character	100	Comments applied during field sampling or sample login

Table 4-6
Database Structure for Resuspension Sampler Field Data

Structure for table: XXFLD00R.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Name of ambient sampling site if resuspension sample was collected nearby
2	DATE	Date	8	Sample collection date
3	SIZE	Character	3	Particle size code: 1.0 = $PM_{1.0}$, 2.5 = $PM_{2.5}$, 10 = PM_{10}, TSP = 0 - ~30 μm
4	SOURCETYPE	Character	20	Source type, eg. Paved road dust, Unpaved road dust, Storage pile, Tailings, Soil, Coal, Coal fly ash, Lime, Parking lot dust, etc.
5	LOCATION	Character	50	Description of sample collection location.
6	CUSTID	Character	10	Client designated sample ID
7	SID	Character	10	DRI source sample ID
8	REP	Numeric	1	Replicate number for multiple resuspensions of same sample
9	TID	Character	10	Teflon filter ID
10	QID	Character	10	Quartz filter ID
11	SEQ	Numeric	1	Resuspension sequence number: 1 = initial, 2 = 1st replacement, 3 = 2nd replacement, etc.
12	RESUSDATE	Date	8	Date of resuspension
13	TTIMEI	Numeric	7.1	Initial Teflon filter elapsed time meter reading
14	TTIMEF	Numeric	7.1	Final Teflon filter elapsed time meter reading
15	TDURATION	Numeric	5.1	Teflon sample duration, minutes
16	TFLOWACT	Numeric	4.1	Average Teflon filter flow rate, lpm
17	TVOC	Numeric	7.4	Teflon filter volume, m^3
18	TVOU	Numeric	7.4	Teflon filter volume uncertainty, m^3
19	TFFLG	Character	5	Teflon filter field flag
20	QTIMEI	Numeric	7.1	Initial quartz filter elapsed time meter reading
21	QTIMEF	Numeric	7.1	Final quartz filter elapsed time meter reading
22	QDURATION	Numeric	5.1	Quartz sample duration, minutes
23	QFLOWACT	Numeric	4.1	Average quartz filter flow rate, lpm
24	QVOC	Numeric	7.4	Quartz filter volume, m^3
25	QVOU	Numeric	7.4	Quartz filter volume uncertainty, m^3
26	QFFLG	Character	5	Quartz filter field flag
27	COMMENT	Character	100	Comments applied during resuspension or sample unloading

Table 4-7
Database Structure for Portable Sampler Field Data

Structure for table: XXFLD00P.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Sampling site name
2	DATE	Date	8	Sampling start date
3	SIZE	Character	3	Particle size code: 10 = PM_{10}
4	STRTHHMM	Character	4	Nominal sample start time, HHMM
5	STOPHHMM	Character	4	Nominal sample stop time, HHMM
6	PERIOD	Character	1	Sample period code, defined for each project
7	TSAMPLERID	Character	5	Teflon filter sampler ID
8	QSAMPLERID	Character	5	Quartz filter sampler ID
9	TID	Character	10	Teflon filter pack ID
10	QID	Character	10	Quartz filter pack ID
11	TTIMEI	Numeric	7.1	Initial Teflon filter elapsed time meter reading
12	TTIMEF	Numeric	7.1	Final Teflon filter elapsed time meter reading
13	TDURATION	Numeric	5.1	Actual Teflon filter sample duration, hours
14	TFLOWI	Numeric	5.1	Initial Teflon filter flow reading from rotometer
15	TFLOWF	Numeric	5.1	Final Teflon filter flow reading from rotometer
16	TFLOWAVG	Numeric	5.1	(TFLOWI + TFLOWF) / 2
17	TFLOWACT	Numeric	5.1	Average Teflon filter flow rate, lpm
18	TVOC	Numeric	10.4	Teflon filter volume, m^3
19	TVOU	Numeric	10.4	Teflon filter volume uncertainty, m^3
20	TFFLG	Character	5	Teflon filter field flag
21	QTIMEI	Numeric	7.1	Initial quartz filter elapsed time meter reading
22	QTIMEF	Numeric	7.1	Final quartz filter elapsed time meter reading
23	QDURATION	Numeric	5.1	Actual quartz filter sample duration, hours
24	QFLOWI	Numeric	5.1	Initial quartz filter flow reading from rotometer
25	QFLOWF	Numeric	5.1	Final quartz filter flow reading from rotometer
26	QFLOWAVG	Numeric	5.1	(QFLOWI + QFLOWF) / 2
27	QFLOWACT	Numeric	5.1	Average quartz filter flow rate, lpm
28	QVOC	Numeric	10.4	Quartz filter volume, m^3
29	QVOU	Numeric	10.4	Quartz filter volume uncertainty, m^3
30	QFFLG	Character	5	Quartz filter field flag
31	COMMENT	Character	100	Comments applied during field sampling or sample login

Table 4-8
Database Structure for DRI Y Source Sampler Field Data

Structure for table: XXFLD00Y.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Name of ambient sampling site if source sample was collected nearby
2	DATE	Date	8	Sample collection date
3	SIZE	Character	3	Particle size code: 2.5 = $PM_{2.5}$, 10 = PM_{10}, TSP = total suspended particulate
4	STRTHHMM	Character	4	Sample start time, HHMM
5	STOPHHMM	Character	4	Sample stop time, HHMM
6	SOURCETYPE	Character	20	Source type, eg. Roadside, Residential wood combustion, Agricultural field burn, etc.
7	LOCATION	Character	50	Description of sample collection location.
8	SID	Character	10	DRI source sample ID
9	TID	Character	10	Teflon filter ID
10	QID	Character	10	Quartz filter ID
11	DURATION	Numeric	6.1	Sample duration, minutes
12	TFLOWI	Numeric	5.1	Initial Teflon filter flow reading from rotometer
13	TFLOWF	Numeric	5.1	Final Teflon filter flow reading from rotometer
14	TFLOWAVG	Numeric	5.1	(TFLOWI + TFLOWF) / 2
15	TFLOWACT	Numeric	5.1	Average Teflon filter flow rate, lpm
16	TVOC	Numeric	10.4	Teflon filter volume, m^3
17	TVOU	Numeric	10.4	Teflon filter volume uncertainty, m^3
18	TFFLG	Character	5	Teflon filter field flag
19	QFLOWI	Numeric	5.1	Initial quartz filter flow reading from rotometer
20	QFLOWF	Numeric	5.1	Final quartz filter flow reading from rotometer
21	QFLOWAVG	Numeric	5.1	(QFLOWI + QFLOWF) / 2
22	QFLOWACT	Numeric	5.1	Average quartz filter flow rate, lpm
23	QVOC	Numeric	10.4	Quartz filter volume, m^3
24	QVOU	Numeric	10.4	Quartz filter volume uncertainty, m^3
25	QFFLG	Character	5	Quartz filter field flag
26	COMMENT	Character	100	Comments applied during field sampling or sample login

Table 4-9

Ambient and Source Field Sampling Data Validation Flags*

Validation Flag	Sub Flag	Description
A		Sampler adjustment or maintenance.
	A1	Sampler audit during sample period.
	A2	Sampler cleaned prior to sample period.
	A3	Particle size cut device regreased or replaced prior to sample period.
B		Field Blank.
D		Sample dropped.
	D1	Sample dropped after sampling.
	D2	Filter dropped during unloading.
F		Filter damaged or ripped.
	F1	Filter damaged in the field.
	F2	Filter damaged when removed from holder.
	F3	Filter wrinkled.
	F4	Filter torn due to over-tightened filter holder.
	F5	Teflon membrane separated from support ring.
	F6	Pinholes in filter.
G		Filter deposit damaged.
	G1	Deposit scratched or scraped, causing a thin line in the deposit.
	G2	Deposit smudged, causing a large area of deposit to be displaced.
	G3	Filter returned to lab with deposit side down in PetriSlide.
	G4	Evidence that part of deposit has fallen off filter.
	G5	Finger touched filter in the field (without gloves).
	G6	Finger touched filter in the lab (with gloves).
H		Filter holder assembly problem.
	H1	Filter misaligned in holder - possible air leak.
	H2	Filter holder loose in sampler - possible air leak.
	H3	Filter holder not tightened sufficiently - possible air leak.
	H4	Filter support grid upside down.
	H5	Two substrates loaded in place of one.
I		Inhomogeneous sample deposit.
	I1	Evidence of impaction - deposit heavier in center of filter.
	I2	Random areas of darker or lighter deposit on filter.
	I3	Light colored deposit with dark specks.
	I4	Non-uniform deposit near edge - possible air leak.

Table 4-9 (continued)

Ambient and Source Field Sampling Data Validation Flags[a]

Validation Flag	Sub Flag	Description
L		Sample loading error.
	L1	Teflon and quartz filters were loaded reversely in SFS.
	L2	$PM_{2.5}$ and PM_{10} filter pack switched.
	L3	Fine and Coarse filters were loaded reversely in dichotomous sampler.
	L4	Filter loaded in wrong port.
M		Sampler malfunction.
N		Foreign substance on sample.
	N1	Insects on deposit, removed before analysis.
	N2	Insects on deposit, not all removed.
	N3	Metallic particles observed on deposit.
	N4	Many particles on deposit much larger than cut point of inlet.
	N5	Fibers or fuzz on filter.
	N6	Oily-looking droplets on filter.
	N7	Shiny substance on filter.
	N8	Particles on back of filter.
	N9	Discoloration on deposit.
O		Sampler operation error.
	O1	Pump was not switched on after changing samples.
	O2	Timer set incorrectly.
	O3	Dichotomous sampler assembled with virtual impactor 180° out of phase; only PM_{10} data reported.
P		Power failure during sampling.
Q		Flow rate error.
	Q1	Initial or final flow rate differed from nominal by > ±10%.
	Q2	Initial or final flow rate differed from nominal by > ±15%.
	Q3	Final flow rate differed from initial by > ±15%.
	Q4	Initial or final flow rate not recorded, used estimated flow rate.
	Q5	Nominal flow rate assumed.
R		Replacement filter used.
	R1	Filter that failed flow rate or QC checks replaced with spare.
	R2	Filter sampling sequence changed from order designated on field data sheet.
S		Sample validity is "suspect", but not invalid.

Table 4-9 (continued)

Ambient and Source Field Sampling Data Validation Flags*

Validation Flag	Sub Flag	Description
T		Sampling time error.
	T1	Sampling duration error of > ±10%.
	T2	Sample start time error of > ±10% of sample duration.
	T3	Elapsed time meter reading not recorded or recorded incorrectly. Sample duration estimated based on readings from previous or subsequent sample.
	T4	Nominal sample duration assumed.
	T5	Sample ran during prescribed period, plus part of next period.
	T6	More than one sample was run to account for the prescribed period.
U		Unusual local particulate sources during sample period.
	U1	Local construction activity.
	U2	Forest fire or slash or field burning.
V		Invalid sample (Void).
W		Wet Sample.
	W1	Deposit spotted from water drops.
	W2	Filter damp when unloaded.
	W3	Filter holder contained water when unloaded.
X		No sample was taken this period, sample run was skipped.

* Samples are categorized as valid, suspect, or invalid. All field flags except 'S' and 'V', or no flags at all indicate valid samples. The 'S' flag in combination with any other flag indicates samples of suspect validity. The 'V' flag in combination with any other flag indicates invalid samples.

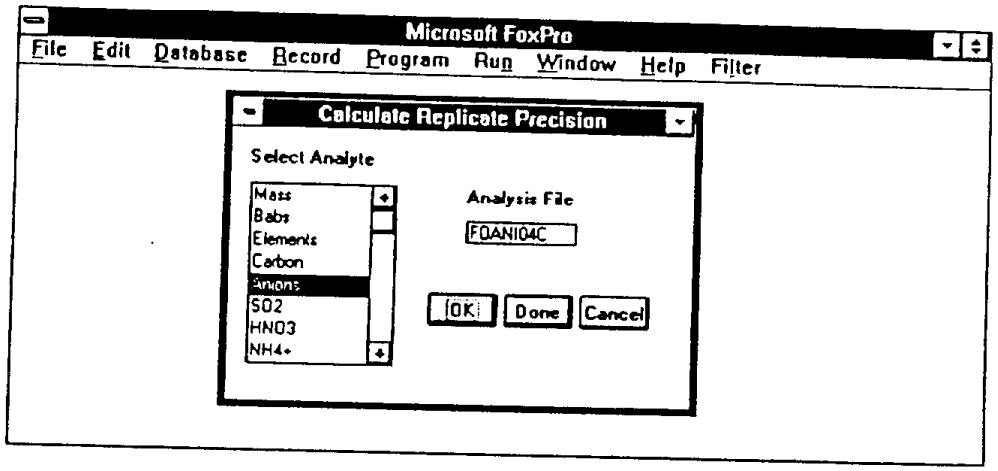
elapsed timer readings are sometimes in hours rather than minutes; adjust your calculations accordingly. Projects with multiple sites may have a different rotometer set with different slope and intercept values for each site. Volume uncertainty is estimated as a percentage of volume, usually 5%. If flow audit data are available, use the standard deviation of the difference between site rotometer and audit flow rates as the volume uncertainty.

Field data may be available in disk file format for some projects. In those cases, import data into a FoxPro FLD file of the correct structure. Spot check several records, including the first and last record of the file to make sure that data is translated correctly.
After all field data are entered and checked, and all calculated fields entered, perform a final quality check of the field data. Run a query on the field file with output set to a browse window. Set the order to each field in turn to check for out of range or typographic errors. For character fields such as site and sample ID, any errors will appear at the top or bottom of the browse window, or between records where the site name changes. For numeric records such as flow, errors or questionable values will appear at the top or bottom. Resolve all questionable data; consult with the project manager, field data technician and sample login technician if necessary. Complete all Level I validation of the field file. Obtain approval of the project manager on field data before creating the CHM file. Copy the completed file from the DATA subdirectory to the REPORT subdirectory.

4.3.3 Calculate Replicate Precision

Precision is determined from replicate measurements. Precision for the chemical measurement methods is calculated as the average fractional difference between original and replicate analysis concentrations. Concentration uncertainty is the fractional precision times sample concentration. If sample concentration times fractional precision is less than the method detection limit, then the detection limit is used as concentration uncertainty. For mass and B_{abs}, precision is calculated as the square root of the sum of the squares of the pre-exposure and post-exposure precisions. Pre-exposure precision is calculated as the standard deviation of the replicate differences (pre-exposure replicate minus pre-exposure original measurement). Post-exposure precision is calculated the same way, except that post-sampling measurements are used. Mass and B_{abs} uncertainties are simply the calculated precisions.

Select "Precision" from the "Filter" menu. The dialog in Screen 4-3 appears. Select the analyte; the default analysis file name appears. Edit the file name if necessary and select "OK" to begin precision calculation.



Screen 4-3. Precision calculation dialog.

The precision calculation program for chemical analysis methods allows rejection of outliers and selection of concentration ranges for precision calculations. Outliers are usually defined as those values outside the range of ± 3 times the standard deviation. The capability to calculate precision based on concentration range allows reasonable precisions to be applied for measurement values where measurement precision depends on concentration. Replicate statistics are calculated and displayed along with the name of the replicate file as shown in screen 4-4.

In this example, the average difference (AVE) for SO_4^- is 0.1655 μg/filter and the standard deviation of the differences (STD) is 0.2453 μg/filter. If the absolute value of the average is greater than the standard deviation, that indicates a systematic bias in the measurement. Other statistics shown include the root mean square (RMS), fractional standard deviation (FSTD, standard deviation divided by average concentration), fractional difference (FDIFF), the maximum difference (MAX), the minimum difference (MIN), and the total number of replicates (NUM).

To view individual replicate values, sorted in order of concentration, and to eliminate outliers, select "Scan Replicate Data/Eliminate Outliers" (option 1). Sample ID, analysis flag, and original and replicate concentrations are displayed as shown in Screen 4-5. Also displayed are fields for replicate difference (DIFF), fractional difference (FDIFF), and ideal percentage difference (FIDEAL), along with average difference, standard deviation of differences, and average fractional difference in the record labeled "ALL" near the bottom of the screen. Use the up and down arrow keys, PgUp and PgDn keys or scroll bars to view the contents of the file. Press Ctrl-End or double click the close box to exit the browse screen and return to Screen 4-4.

```
Replicate data in file foS4i04c.REP
Calculating precision for:

 ALL Replicates...
   AVE     STD     RMS     FSTD    FDIFF     MAX     MIN     NUM
   0.1655  0.2453  0.2865  0.0322  0.0246  0.6400  -0.0600  11
Press any key to continue...

Plot precision versus concentration (Y/N)? n _

    1   Scan Replicate Data/ Eliminate Outliers
    2   Define 2 Concentration Ranges
    3   Define 3 Concentration Ranges
    4   Restore Values Designated as Outliers ("undo" Option 1)
    5   Delete Defined Concentration Ranges ("undo" Options 2 or 3)
    6   Precision Calculation Complete

        Select Option:
```

Screen 4-4. Example of precision calculation results.

You may need to eliminate outliers to avoid biasing precision values too high. Exclude outliers from precision calculation by highlighting the outlier and pressing function key F2. This replaces the DIFF field with a value of -99.0000, which is not used in the precision calculation. Exercise caution before you designate samples as outliers, particularly with small data sets. Designate samples as outliers only in extreme cases where a replicate result is clearly much poorer than others in the data set. Quality control measures for analysis methods rarely allow replicates that are outliers.

If concentrations span a large range, and there are a large number of replicates in the data set, you should divide the precision calculation into 2 or 3 concentration ranges, so that precision for the lower concentration samples is not dominated by replicate measurements for high concentration samples.

Microsoft FoxPro

File Edit Database Record Program Run Window Help Filter

Fos4i04c

Qid	Anif	Orig	S4ic	Diff	Fdiff	Fideal
BFFQ173	r7	1.3000	1.4000	0.1000	0.0741	30.0000
BFFQ210	r1	2.9200	2.9000	-0.0200	0.0069	20.0000
BFFQ175	r1	3.0200	2.9600	-0.0600	0.0201	10.0000
BFFQ164	r1	3.3000	3.3000	0.0000	0.0000	10.0000
BFFQ194	r7	5.1600	5.3400	0.1800	0.0343	10.0000
BFFQ193	r1	5.4000	5.4400	0.0400	0.0074	10.0000
BFFQ156	r1	5.5400	5.5200	-0.0200	0.0036	10.0000
BFFQ197	r7	8.6200	9.1800	0.5600	0.0629	10.0000
BFFQ214	r1	10.4200	10.4600	0.0400	0.0038	10.0000
BFFQ214	r7	10.4200	10.7800	0.3600	0.0340	10.0000
BFFQ203	r7	26.7400	27.3800	0.6400	0.0237	10.0000
ALL			0.1655	0.2453	0.0246	
LOW		-99.0000	-99.0000	-99.0000	-99.0000	
MID		-99.0000	-99.0000	-99.0000	-99.0000	
HIGH		-99.0000	-99.0000	-99.0000	-99.0000	

Screen 4-5. Example replicate precision file browse screen.

Select option 2 or 3 from Screen 4-4 to calculate precision based on concentration range. Enter concentration(s) as prompted to use for the LO range (and MID range if 3 ranges selected). Precision is calculated and displayed as before, except that precision data is calculated separately for ALL samples, for LO concentration samples, and for HIGH concentration samples (and for MID concentration samples if 3 ranges selected).

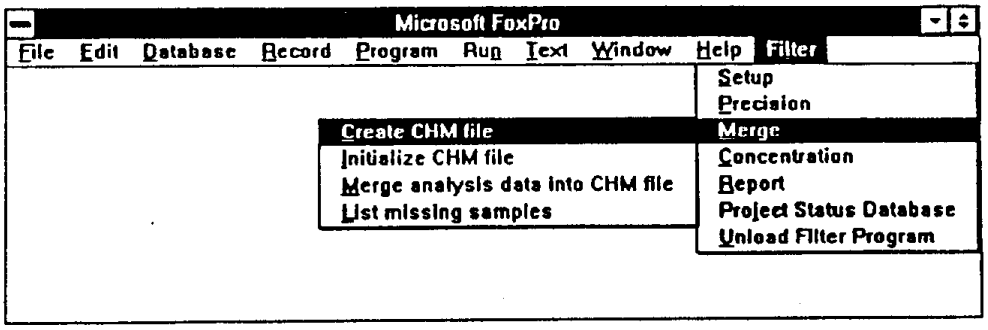
If, after defining 2 or 3 ranges for precision calculation, you find that there is little difference in fractional precision between ALL Replicates and the defined ranges, you may "undo" the precision ranges by selecting "Delete Defined Concentration Ranges" (option 5). Likewise you may "undo" an outlier by selection option 4.

Select "Precision Calculation Complete" (option 6) to exit. You are prompted to save calculated precision values to the analysis file.

Precision for mass and B_{abs} measurements is accomplished as for chemical analysis, except that there are no options to exclude outliers or subdivide concentration ranges.

4.3.4 Merge Field, Mass, and Chemical Data

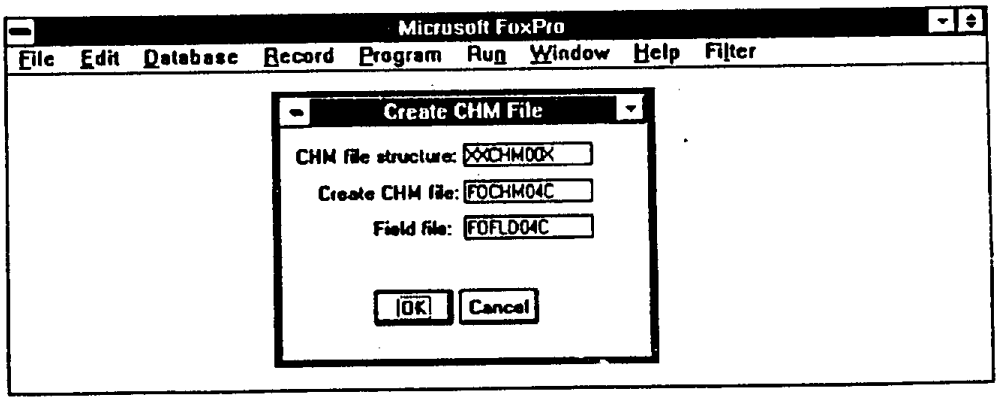
Select "Merge" from the filter menu. The Merge submenu appears as shown in Screen 4-6.



Screen 4-6. Merge submenu.

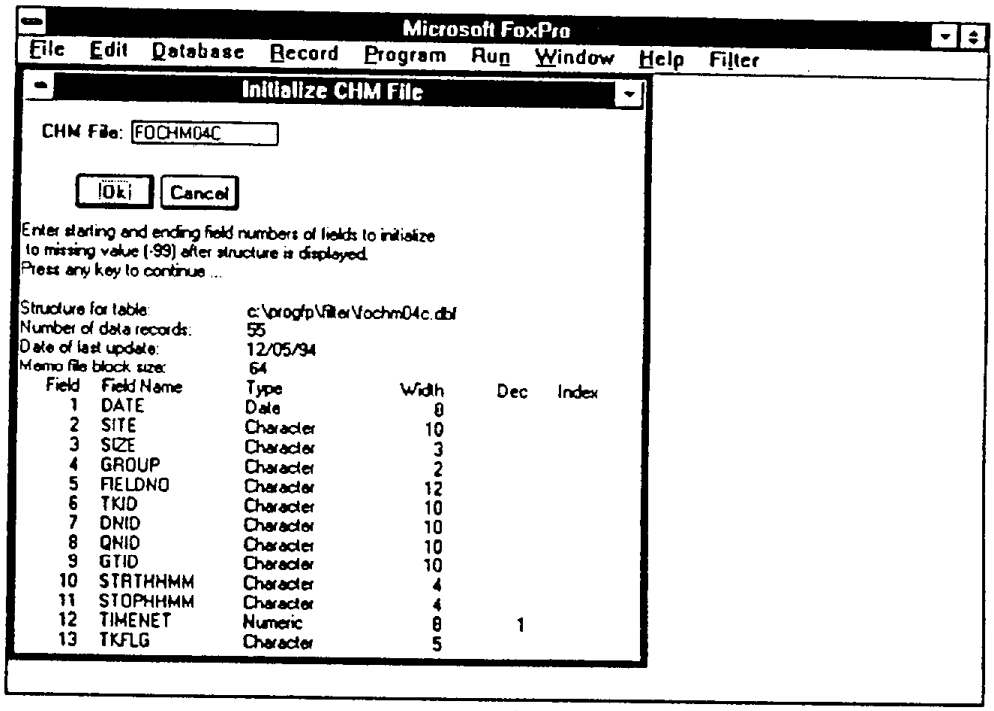
Select "Create CHM file". Default file names for the CHM structure file, the created CHM file and the field file are displayed in a dialog as shown in Screen 4-7. Use the default CHM file structure unless a CHM file of the proper structure has already been created. In that case, enter the pathname of the CHM file you wish to use as a structure. The default CHM and field file names are derived from the project code, batch number and sampler type code entered earlier. Select "OK" to create a new CHM file. The program copies the generic CHM file structure to the new CHM file, then starts the modify structure dialog. Delete flag and species fields that are not used in the project, make other changes as necessary, and save the new CHM file structure.

The program then appends contents of the field file into the CHM file, adds a "Field:" prefix to any text in the COMMENTS field, and deletes all white space in the COMMENTS field.



Screen 4-7. Create CHM file dialog.

Select "Initialize CHM File." Enter CHM file name (default is provided) and select "OK" to list the file structure. Screen 4-8 shows the result. Note the starting file number and ending field number of fields to initialize. You should initialize all mass, B_{abs} and chemical measurement fields, but not field data such as sample volumes. All numeric data in the selected fields are initialized to -99, which is the code for missing data value.



Screen 4-8. Example of CHM file initialization dialog.

Table 4-10 shows the default CHM file structure definitions. Define starting and ending fields to use during calculation operations by entering a 12 character code in the FIELDNO field. The format of the field is QQQqqqTTTttt, where QQQ is a 3 digit number that specifies the field number where quartz filter analysis species starts, qqq is a 3 digit number that specifies the field number where quartz filter analysis species end, and TTT and ttt specify where Teflon filter analysis species (including mass) begin and end. Mass is the first analysis species in any CHM file and uranium is the last (if XRF data is included), so TTT and ttt will be the highest and lowest numbers in the code since these are Teflon filter species. Quartz filter species usually start after mass, and end before the XRF species. Enter the FIELDNO code into the CHM file by typing the following commands in the command window.

Table 4-10
Database Structure for Default CHM File

Structure for table: XXCHM00X.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Sampling site name
2	DATE	Date	8	Sampling start date
3	SIZE	Character	3	Particle size code: 2.5 = $PM_{2.5}$, 10 = PM_{10}, F = $PM_{2.5}$, C = 2.5 - 10 μm, TSP = total suspended particulate
4	STRTHHMM	Character	4	Nominal sample start time, HHMM
5	STOPHHMM	Character	4	Nominal sample stop time, HHMM
6	DURATION	Numeric	5.1	Actual sample duration, hours
7	PERIOD	Character	1	Sample period code, defined for each project
8	GROUP	Character	2	XRF particle size correction code
9	FIELDNO	Character	12	Internal processing code
10	TID	Character	10	Teflon filter pack ID
11	QID	Character	10	Quartz filter pack ID
12	TFFLG	Character	5	Teflon filter field flag
13	QFFLG	Character	5	Quartz filter field flag
14	MSGF	Character	5	Mass analysis flag
15	BBDF	Character	5	B_{abs} analysis flag
16	NHCF	Character	5	NH_3 analysis flag
17	HCIF	Character	5	HCl analysis flag
18	NOCF	Character	5	NO_2 analysis flag
19	HNIF	Character	5	HNO_3 analysis flag
20	SOIF	Character	5	SO_2 analysis flag
21	OAIF	Character	5	Organic acids analysis flag
22	ANIF	Character	5	Anion analysis flag
23	N4CF	Character	5	NH_4^+ analysis flag
24	NAAF	Character	5	Na^+ analysis flag
25	MGAF	Character	5	Mg^{2+} analysis flag
26	KPAF	Character	5	K^+ analysis flag
27	CAAF	Character	5	Ca^{2+} analysis flag
28	OETF	Character	5	Carbon analysis flag
29	ELXF	Character	5	XRF analysis flag
30	TVOC	Numeric	10.4	Teflon filter volume, m^3
31	TVOU	Numeric	10.4	Teflon filter volume uncertainty, m^3
32	QVOC	Numeric	10.4	Quartz filter volume, m^3
33	QVOU	Numeric	10.4	Quartz filter volume uncertainty, m^3
34	MSGC	Numeric	10.4	Deposit mass, μg/filter
35	MSGU	Numeric	10.4	Deposit mass uncertainty, μg/filter
36	BBDC	Numeric	10.4	B_{abs}, optical density units
37	BBDU	Numeric	10.4	B_{abs} uncertainty, optical density units
38	NHCC	Numeric	10.4	NH_3 concentration, μg/filter
39	NHCU	Numeric	10.4	NH_3 concentration uncertainty, μg/filter
40	HCIC	Numeric	10.4	HCl concentration, μg/filter

Table 4-10 (continued)
Database Structure for Default CHM File

Field	Field Name	Type	Width	Description
41	HCIU	Numeric	10.4	HCl concentration uncertainty, μg/filter
42	NOCC	Numeric	10.4	NO_2 concentration, μg/filter
43	NOCU	Numeric	10.4	NO_2 concentration uncertainty, μg/filter
44	HNIC	Numeric	10.4	HNO_3 concentration, μg/filter
45	HNIU	Numeric	10.4	HNO_3 concentration uncertainty, μg/filter
46	SOIC	Numeric	10.4	SO_2 concentration, μg/filter
47	SOIU	Numeric	10.4	SO_2 concentration uncertainty, μg/filter
48	HAIC	Numeric	10.4	Acetic acid concentration, μg/filter
49	HAIU	Numeric	10.4	Acetic acid concentration uncertainty, μg/filter
50	HFIC	Numeric	10.4	Formic acid concentration, μg/filter
51	HFIU	Numeric	10.4	Formic acid concentration uncertainty, μg/filter
52	HPIC	Numeric	10.4	Proprionic acid concentration, μg/filter
53	HPIU	Numeric	10.4	Proprionic acid concentration uncertainty, μg/filter
54	FLIC	Numeric	10.4	F^- concentration, μg/filter
55	FLIU	Numeric	10.4	F^-concentration uncertainty, μg/filter
56	CLIC	Numeric	10.4	Cl^- concentration, μg/filter
57	CLIU	Numeric	10.4	Cl^- concentration uncertainty, μg/filter
58	N2IC	Numeric	10.4	NO_2^- concentration, μg/filter
59	N2IU	Numeric	10.4	NO_2^- concentration uncertainty, μg/filter
60	N3IC	Numeric	10.4	NO_3^- concentration, μg/filter
61	N3IU	Numeric	10.4	NO_3^- concentration uncertainty, μg/filter
62	P4IC	Numeric	10.4	PO_4^{2-} concentration, μg/filter
63	P4IU	Numeric	10.4	PO_4^{2-} concentration uncertainty, μg/filter
64	S4IC	Numeric	10.4	SO_4^{2-} concentration, μg/filter
65	S4IU	Numeric	10.4	SO_4^{2-} concentration uncertainty, μg/filter
66	N4CC	Numeric	10.4	NH_4^+ concentration, μg/filter
67	N4CU	Numeric	10.4	NH_4^+ concentration uncertainty, μg/filter
68	NAAC	Numeric	10.4	Na^+ concentration, μg/filter
69	NAAU	Numeric	10.4	Na^+ concentration uncertainty, μg/filter
70	MGAC	Numeric	10.4	Mg^{2+} concentration, μg/filter
71	MGAU	Numeric	10.4	Mg^{2+} concentration uncertainty, μg/filter
72	KPAC	Numeric	10.4	K^+ concentration, μg/filter
73	KPAU	Numeric	10.4	K^+ concentration uncertainty, μg/filter
74	CAAC	Numeric	10.4	Ca^{2+} concentration, μg/filter
75	CAAU	Numeric	10.4	Ca^{2+} concentration uncertainty, μg/filter
76	OCTC	Numeric	10.4	Organic carbon concentration, μg/filter
77	OCTU	Numeric	10.4	Organic carbon concentration uncertainty, μg/filter
78	ECTC	Numeric	10.4	Elemental carbon concentration, μg/filter
79	ECTU	Numeric	10.4	Elemental carbon concentration uncertainty, μg/filter
80	TCTC	Numeric	10.4	Total carbon concentration, μg/filter
81	TCTU	Numeric	10.4	Total carbon concentration uncertainty, μg/filter
82	C3TC	Numeric	10.4	Carbonate concentration, μg/filter
83	C3TU	Numeric	10.4	Carbonate concentration uncertainty, μg/filter

Table 4-10 (continued)
Database Structure for Default CHM File

Field	Field Name	Type	Width	Description
84	NAXC	Numeric	10.4	Na concentration, μg/filter
85	NAXU	Numeric	10.4	Na concentration uncertainty, μg/filter
86	MGXC	Numeric	10.4	Mg concentration, μg/filter
87	MGXU	Numeric	10.4	Mg concentration uncertainty, μg/filter
88	ALXC	Numeric	10.4	Al concentration, μg/filter
89	ALXU	Numeric	10.4	Al concentration uncertainty, μg/filter
90	SIXC	Numeric	10.4	Si concentration, μg/filter
91	SIXU	Numeric	10.4	Si concentration uncertainty, μg/filter
92	PHXC	Numeric	10.4	P concentration, μg/filter
93	PHXU	Numeric	10.4	P concentration uncertainty, μg/filter
94	SUXC	Numeric	10.4	S concentration, μg/filter
95	SUXU	Numeric	10.4	S concentration uncertainty, μg/filter
96	CLXC	Numeric	10.4	Cl concentration, μg/filter
97	CLXU	Numeric	10.4	Cl concentration uncertainty, μg/filter
98	KPXC	Numeric	10.4	K concentration, μg/filter
99	KPXU	Numeric	10.4	K concentration uncertainty, μg/filter
100	CAXC	Numeric	10.4	Ca concentration, μg/filter
101	CAXU	Numeric	10.4	Ca concentration uncertainty, μg/filter
102	TIXC	Numeric	10.4	Ti concentration, μg/filter
103	TIXU	Numeric	10.4	Ti concentration uncertainty, μg/filter
104	VAXC	Numeric	10.4	V concentration, μg/filter
105	VAXU	Numeric	10.4	V concentration uncertainty, μg/filter
106	CRXC	Numeric	10.4	Cr concentration, μg/filter
107	CRXU	Numeric	10.4	Cr concentration uncertainty, μg/filter
108	MNXC	Numeric	10.4	Mn concentration, μg/filter
109	MNXU	Numeric	10.4	Mn concentration uncertainty, μg/filter
110	FEXC	Numeric	10.4	Fe concentration, μg/filter
111	FEXU	Numeric	10.4	Fe concentration uncertainty, μg/filter
112	COXC	Numeric	10.4	Co concentration, μg/filter
113	COXU	Numeric	10.4	Co concentration uncertainty, μg/filter
114	NIXC	Numeric	10.4	Ni concentration, μg/filter
115	NIXU	Numeric	10.4	Ni concentration uncertainty, μg/filter
116	CUXC	Numeric	10.4	Cu concentration, μg/filter
117	CUXU	Numeric	10.4	Cu concentration uncertainty, μg/filter
118	ZNXC	Numeric	10.4	Zn concentration, μg/filter
119	ZNXU	Numeric	10.4	Zn concentration uncertainty, μg/filter
120	GAXC	Numeric	10.4	Ga concentration, μg/filter
121	GAXU	Numeric	10.4	Ga concentration uncertainty, μg/filter
122	ASXC	Numeric	10.4	As concentration, μg/filter
123	ASXU	Numeric	10.4	As concentration uncertainty, μg/filter
124	SEXC	Numeric	10.4	Se concentration, μg/filter
125	SEXU	Numeric	10.4	Se concentration uncertainty, μg/filter
126	BRXC	Numeric	10.4	Br concentration, μg/filter

Table 4-10 (continued)
Database Structure for Default CHM File

Field	Field Name	Type	Width	Description
127	BRXU	Numeric	10.4	Br concentration uncertainty, μg/filter
128	RBXC	Numeric	10.4	Rb concentration, μg/filter
129	RBXU	Numeric	10.4	Rb concentration uncertainty, μg/filter
130	SRXC	Numeric	10.4	Sr concentration, μg/filter
131	SRXU	Numeric	10.4	Sr concentration uncertainty, μg/filter
132	YTXC	Numeric	10.4	Y concentration, μg/filter
133	YTXU	Numeric	10.4	Y concentration uncertainty, μg/filter
134	ZRXC	Numeric	10.4	Zr concentration, μg/filter
135	ZRXU	Numeric	10.4	Zr concentration uncertainty, μg/filter
136	MOXC	Numeric	10.4	Mo concentration, μg/filter
137	MOXU	Numeric	10.4	Mo concentration uncertainty, μg/filter
138	PDXC	Numeric	10.4	Pd concentration, μg/filter
139	PDXU	Numeric	10.4	Pd concentration uncertainty, μg/filter
140	AGXC	Numeric	10.4	Ag concentration, μg/filter
141	AGXU	Numeric	10.4	Ag concentration uncertainty, μg/filter
142	CDXC	Numeric	10.4	Cd concentration, μg/filter
143	CDXU	Numeric	10.4	Cd concentration uncertainty, μg/filter
144	INXC	Numeric	10.4	In concentration, μg/filter
145	INXU	Numeric	10.4	In concentration uncertainty, μg/filter
146	SNXC	Numeric	10.4	Sn concentration, μg/filter
147	SNXU	Numeric	10.4	Sn concentration uncertainty, μg/filter
148	SBXC	Numeric	10.4	Sb concentration, μg/filter
149	SBXU	Numeric	10.4	Sb concentration uncertainty, μg/filter
150	BAXC	Numeric	10.4	Ba concentration, μg/filter
151	BAXU	Numeric	10.4	Ba concentration uncertainty, μg/filter
152	LAXC	Numeric	10.4	La concentration, μg/filter
153	LAXU	Numeric	10.4	La concentration uncertainty, μg/filter
154	AUXC	Numeric	10.4	Au concentration, μg/filter
155	AUXU	Numeric	10.4	Au concentration uncertainty, μg/filter
156	HGXC	Numeric	10.4	Hg concentration, μg/filter
157	HGXU	Numeric	10.4	Hg concentration uncertainty, μg/filter
158	TLXC	Numeric	10.4	Tl concentration, μg/filter
159	TLXU	Numeric	10.4	Tl concentration uncertainty, μg/filter
160	PBXC	Numeric	10.4	Pb concentration, μg/filter
161	PBXU	Numeric	10.4	Pb concentration uncertainty, μg/filter
162	URXC	Numeric	10.4	U concentration, μg/filter
163	URXU	Numeric	10.4	U concentration uncertainty, μg/filter
164	SPSUMC	Numeric	10.4	Sum of species concentration, μg/filter
165	SPSUMU	Numeric	10.4	Sum of species concentration uncertainty, μg/filter
166	COMMENT	Memo	10	Comments

list structure to print

Determine field code numbers as described above.

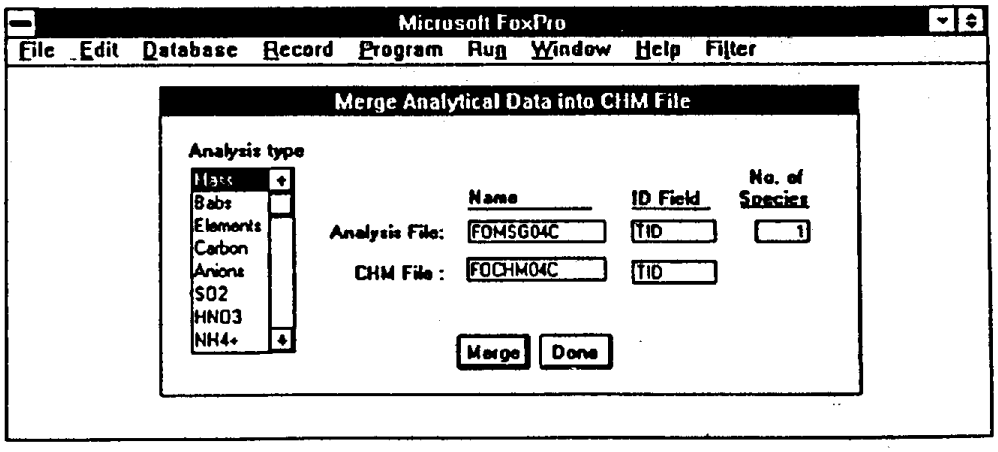
replace all FIELDNO with "QOOqqqTTTttt"

If particulate samples are PM_{10} or coarse fraction, XRF data needs to be corrected for particle size effects. For coarse fraction (2.5 - 10 μm) and PM_{10} samples, use XRF group code 9. For PM_{10} samples that do not require correction for sulfur (assuming that most sulfur is $PM_{2.5}$ in sulfate form) use group code 10. for PM_{10} samples that do not require correction for sulfur or potassium (assuming most potassium is $PM_{2.5}$ from wood combustion), use group code 8. Enter group number by typing the following command in the command window.

replace all GROUP with "GG"

where GG is the group number. If the group number is 8 or 9, enter just one digit. Include the quote marks.

Select "Merge analytical data into CHM file." The merge dialog appears. Select the analysis type. Default values for analysis file, CHM file, ID field names, and number of species are displayed as shown in Screen 4-9. Edit the default values if needed and select "Merge." The program copies data from the analytical measurement file into the CHM file based sample ID. If a data value has already been merged (concentration < > -99), the program displays both values and asks for confirmation before merging the new data. Analysis flags and contents of the COMMENT field (preceded by a prefix indicating the analysis type) are also copied to the CHM file.

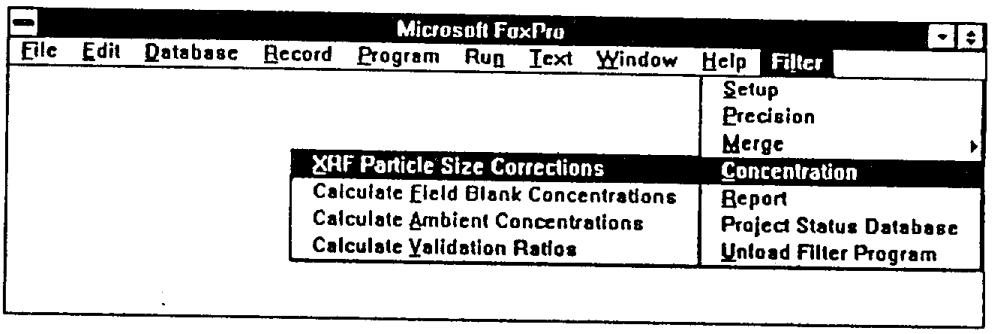


Screen 4-9. Example data merge dialog.

After the merge is complete, select another analysis type or "Done" if all files have been merged. Select "List missing samples from the "Merge" menu to identify data that has not yet been merged.

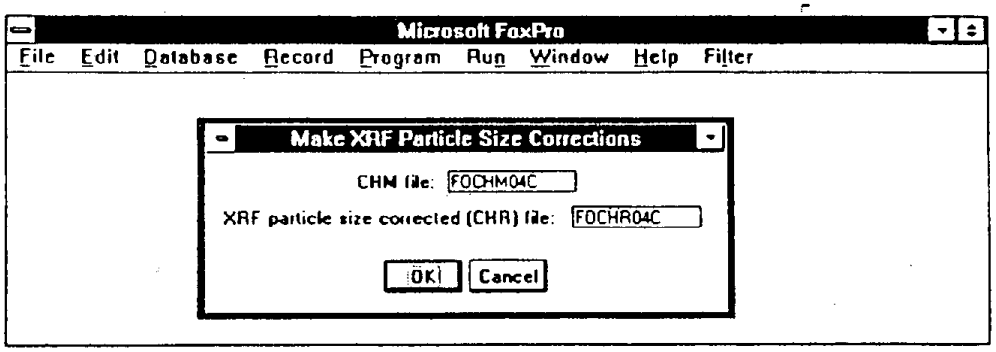
4.3.5 Calculate Concentrations

Concentrations are calculated by dividing μg/filter concentrations in the CHM or CHR file by volume in m^3 after first making XRF particle size corrections and subtracting field blank concentrations. The result is a CON file with the same structure as the CHM file, but with concentrations in $\mu g/m^3$. Gaseous species concentrations are converted at the same time from the analyte ion to the gaseous species concentration. Select "Concentration" from the "Filter" menu. The Concentration submenu appears as in Screen 4-10.



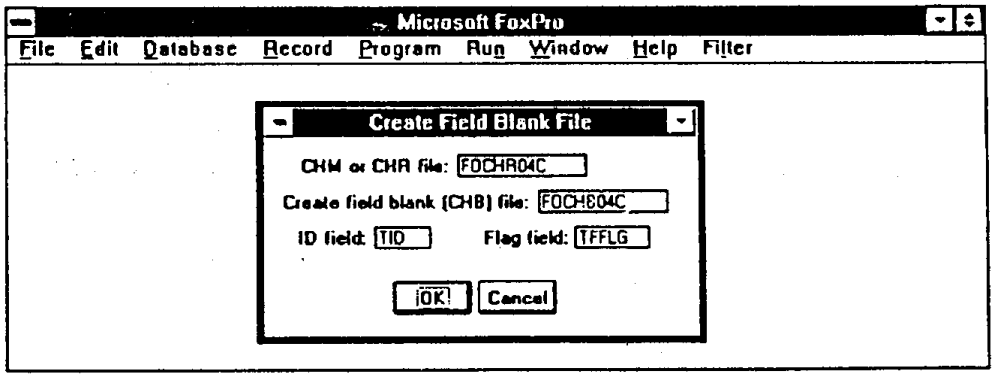
Screen 4-10. Concentration calculation submenu.

If some samples in the data set are PM_{10}, and if they were analyzed by XRF, corrections for x-ray absorption in particles must be made. Select "XRF Particle Size Corrections" if corrections are needed. The particle size correction dialog (Screen 4-10) is displayed. Make changes to the default CHM and CHR file names if necessary and select "OK." The program copies the CHM file to the CHR file, then corrects concentrations in the CHR file using correction factors in XRFCOR.DBF. Structure of the CHR file is the same as the CHM file. Data are corrected based on GROUP and SIZE fields.



Screen 4-11. XRF particle size correction dialog.

Select "Calculate Field Blank Concentrations." Default CHR or CHM and field blank (CHB) file names along with default ID and field flag field names are displayed in a dialog as shown in Screen 4-12. Use the CHR file, if it exists, rather than the CHM file for creating the blank file. Make any corrections to the defaults if needed and select "OK." The program copies all field blank records (all records with "B" in the flag field), from the CHM to the CHB file. It calculates statistics for field blank concentrations and appends them to the end of the CHB file. The CHB file is opened in a BROWSE window as shown in Screen 4-13. Structure of the CHB file is the same as the CHM file.



Screen 4-12. Calculate field blanks dialog.

Microsoft FoxPro

File Edit Database Record Program Run Browse Window Help Filter

Fochb04c

Tkid	Msgc	Msgu	Clic	Cliu	N3ic	N3iu	S4ic	S4iu
BFTK166	7.0000	4.7450	0.4400	0.3333	0.0000	0.3333	0.3600	0.3333
BFTK179	5.0000	4.7450	0.3400	0.3333	0.0000	0.3333	0.0000	0.3333
BFTK190	5.0000	4.7450	0.3400	0.3333	0.0000	0.3333	0.0000	0.3333
BFTK202	2.0000	4.7450	0.3800	0.3333	0.0000	0.3333	0.2400	0.3333
BFTK213	0.0000	4.7450	0.6600	0.3333	0.3000	0.3333	0.3200	0.3333
AVE +- STD	1.8000	4.6583	0.4320	0.1339	0.0600	0.1342	0.1840	0.1734
RT MN SQ	-99.0000	4.7450	-99.0000	0.3333	-99.0000	0.3333	-99.0000	0.3333
AVE+3*STD	15.7750		0.8336		0.4625		0.7043	
AVE-3*STD	-12.1750		0.0304		-0.3425		-0.3363	
BLNK+-UNC	0.0000	4.7450	0.4320	0.3333	0.0000	0.3333	0.0000	0.3333

Screen 4-13. Field file BROWSE screen.

Records for each field blank are shown along with records for statistical parameters. Names of the calculated parameters are in the ID field; split the BROWSE window so that the ID field is in the left window, and the rest of the data can be scrolled in the right hand window. All of the flag fields are displayed, as flags may be necessary to interpret validity of field blank concentrations.

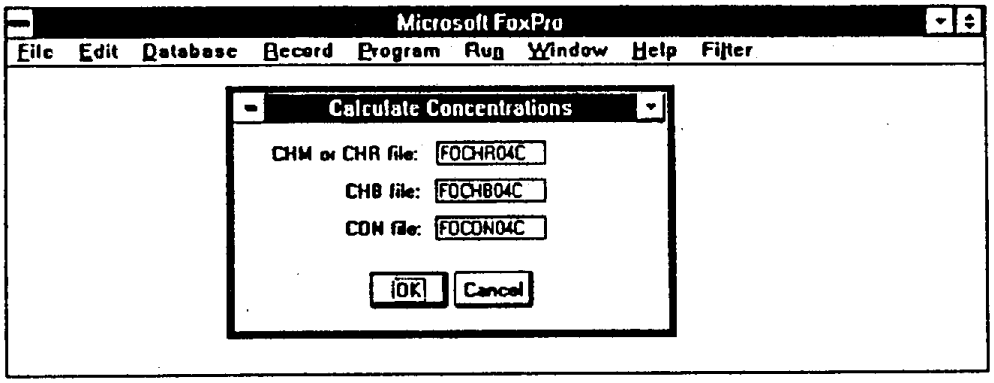
The average and standard deviation of blank concentrations for each species are shown in the concentration and uncertainty fields, respectively. The blank concentration and blank uncertainty to be subtracted from ambient samples is shown on the bottom record. The blank uncertainty is the larger of the standard deviation or the root mean square. The blank concentration is equal to the average, unless the average is less than the uncertainty, in which case it is set to zero.

As with replicate precision procedure, it may be necessary to exclude outliers from the blank calculation. As a general guide, values outside the range of the average $\pm$ 3 times the standard deviation may be outliers. Consider results from past studies when designating outliers. Mark outliers by placing the cursor on the uncertainty field associated with the outlying concentration value, and press function key F2. Uncertainties are replaced by -99.9999. Be sure not to press function key F2 when the cursor is on a concentration field, or the program will exit when calculating concentrations. Exit the BROWSE screen by double-clicking the close box.

If you excluded outliers, answer the recalculate prompt with "Y." Blank statistics are calculated again. Examine recalculated values in the BROWSE screen. To "undo" an outlier designation, use the same procedure as for designating outliers, except press function key F3. Make sure cursor is on the uncertainty field, not the concentration field, otherwise the program will stop when re-calculating blank values. Uncertainty

will be replaced by -98.0000 after pressing function key F3. Close the BROWSE window and recalculate blank values after "undoing" outliers.

Select "Calculate Ambient Concentrations" from the "Concentration" submenu. Default CHR or CHM, field blank (CHB) and concentration (CON) file names are displayed as shown in Screen 4-14. Correct default names, if necessary, then select "OK." Concentrations in $\mu g/m^3$ are calculated and saved in the CON file. The file structure and field definitions for the CON file are the same as the CHM file, except concentrations are in $\mu g/m^3$.



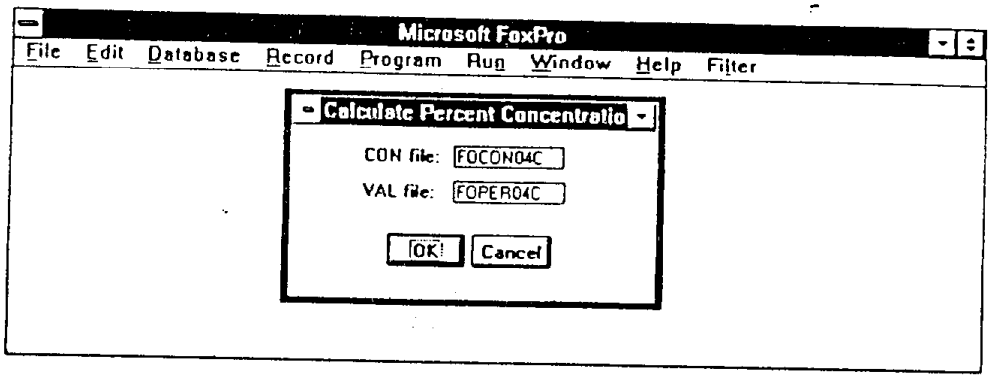
Screen 4-14. Concentration calculation dialog.

If the data set includes B_{abs} data, values must be converted from optical density units divided by volume to inverse megameters (Mm^{-1}). From the command window, run the conversion program by typing the following line.

do babscon

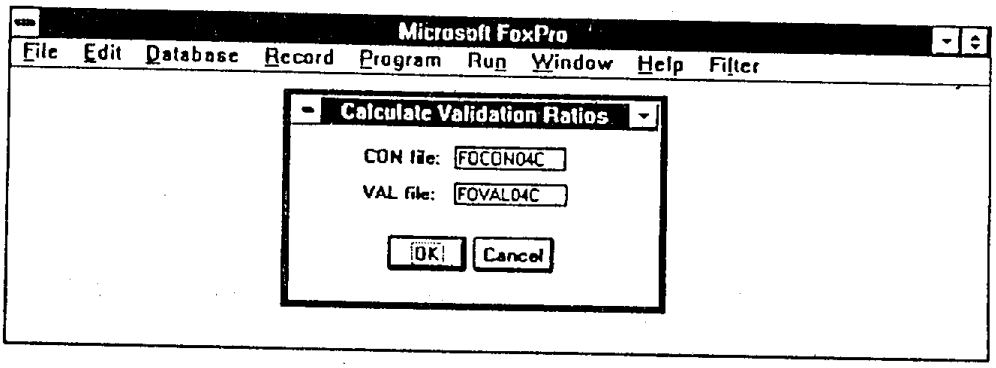
Enter the filter deposit area and CON file name as prompted by the program. B_{abs} data are now converted to Mm^{-1}. Do not run the program again on the same file once the data are already in Mm^{-1} units.

Select "Calculate Percent Concentrations" from the "Concentration" submenu. Default CON and percent concentration (PER) file names are displayed as shown in Screen 4-15. Correct default names, if necessary, then select "OK." Concentrations in mass percent are calculated and saved in the PER file. The file structure and field definitions for the PER file are the same as the CHM file, except concentrations are in mass percent.



Screen 4-15. Percent concentration calculation dialog.

Select "Calculate Validation Ratios" to create a file containing ratios of key chemical species used for level 2 validation checks. Default CON and validation ratio (VAL) file names are displayed as shown in Screen 4-16. Correct default names, if necessary, then select "OK." Validation ratios are calculated and saved in the VAL file. Structure definitions for the VAL file are given in Table 4-11.



Screen 4-16. Validation ratio calculation dialog.

Conduct Level II validation by examining the ratios in the VAL file and by making scatterplots of selected variables from the CON and VAL files. This is easily by reading the .DBF files directly using Excel. Conduct the tests specified for Level II validation in section 1.7, and any other tests appropriate for the data set. If Level II validation reveals any problems, submit the indicated samples for reanalysis.

4.3.6 Report

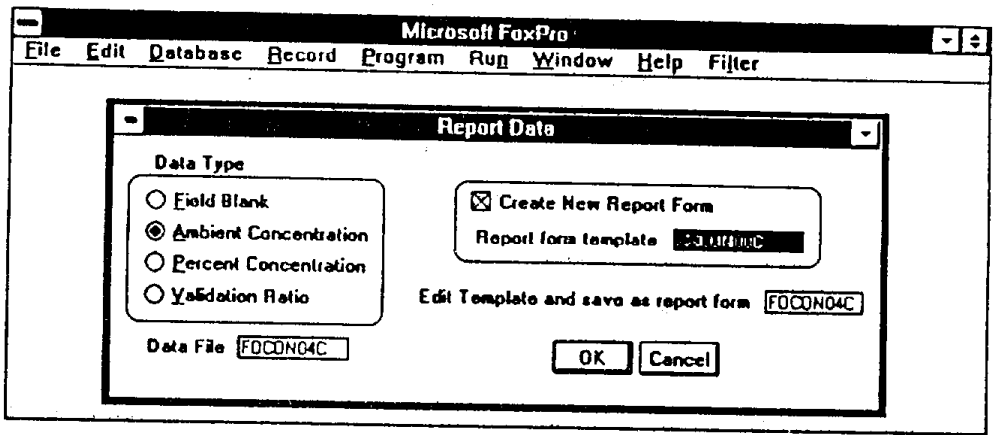
Select "Report" to print hardcopy of concentration data in a standardized output format. Select the data type and edit the default data file name if necessary. Select the

Table 4-11
Database Structure for Default VAL File

Structure for table: XXVAL00X.DBF

Field	Field Name	Type	Width	Description*
1	DATE	Date	8	Sampling site name
2	SITE	Character	10	Sampling start date
3	SIZE	Character	3	Particle size code: 2.5 = $PM_{2.5}$, 10 = PM_{10}, F = $PM_{2.5}$, C = 2.5 - 10 μm, TSP = total suspended particulate
4	TID	Character	10	Teflon filter pack ID
5	QID	Character	10	Quartz filter pack ID
6	STRTHHMM	Character	4	Nominal sample start time, HHMM
7	DURATION	Numeric	5.1	Actual sample duration, hours
8	SPSUMRC	Numeric	8.2	Ratio of sum of species (SPSUMC) to mass (MSGC)
9	SPSUMRU	Numeric	8.2	Uncertainty of ratio of sum of species to mass
10	CLRC	Numeric	8.2	Ratio of Cl^- (CLIC) to Cl (CLXC)
11	CLRU	Numeric	8.2	Uncertainty of ratio of Cl^- to Cl
12	KPRC	Numeric	8.2	Ratio of K^+ (KPAC) to K (KPXC)
13	KPRU	Numeric	8.2	Uncertainty of ratio of K^+ to K
14	SURC	Numeric	8.2	Ratio of SO_4^{2-} (S4IC) to S (SUXC)
15	SURU	Numeric	8.2	Uncertainty of ratio of SO_4^{2-} to S
16	N4CC	Numeric	8.2	NH_4^+ concentration (N4CC), $\mu g/m^3$
17	N4CU	Numeric	8.2	NH_4^+ concentration uncertainty (N4CU), $\mu g/m^3$
18	N4SO4PRDC	Numeric	8.2	Predicted NH_4^+ concentration, $\mu g/m^3$, assuming it exists as $(NH_4)_2SO_4$ + NH_4NO_3
19	N4SO4PRDU	Numeric	8.2	Uncertainty of predicted NH_4^+ concentration, $\mu g/m^3$, assuming it exists as $(NH_4)_2SO_4$ + NH_4NO_3
20	N4HSO4PRDC	Numeric	8.2	Predicted NH_4^+ concentration, $\mu g/m^3$, assuming it exists as NH4HSO4 + NH_4NO_3
21	N4HSO4PRDU	Numeric	8.2	Uncertainty of predicted NH_4^+ concentration, $\mu g/m^3$, assuming it exists as NH4HSO4 + NH_4NO_3
22	N4SO4RATC	Numeric	8.2	Ratio of N4CC to N4SO4PRDC
23	N4SO4RATU	Numeric	8.2	Uncertainty of ratio of N4CC to N4SO4PRDC
24	N4HSO4RATC	Numeric	8.2	Ratio of N4CC to N4HSO4PRDC
25	N4HSO4RATU	Numeric	8.2	Uncertainty of ratio of N4CC to N4HSO4PRDC

"Create New Report Form" checkbox to customize a general report form to a specific project. This option will create a new form based on the default form in the "Report form template" box, and save it with the file name in the "Edit template and save as report form" box. The program starts the report painter to allow you to modify the form. Enter the table number and title, and delete or add data fields and text as needed. The report form files have the extension "FRX" so the root of the data file and report form filenames can be the same. If you do not select the "Create New Report Form" checkbox, the program prints the data using the form in the "Print data using report form" box. Screen 4-17 shows this dialog.



Screen 4-17. Report data dialog.

4.4 Shut-Down

Complete all entries to the DPnns.DOC file. Assemble a printout of this file in a folder together with copies of the CHM file structure, rotometer calibration data sheets, field blank subtract results and other supporting documentation. Label file folder with the project name and batch number and store in project files. After the report has been submitted, select "Project Status Database" from the filter menu and make entries for completed data report in the proper project and batch record. Select "Unload Filter Program" from the Filter menu.

5.0 QUANTIFICATION

The following formulae are used in the calculation of ambient concentrations and precision estimates by the FILTER program:

$$C_i = \frac{M_i - B_i}{V}$$

$$V = F \times t$$

$$B_i = \frac{1}{n}\sum_{j=1}^{n} B_{ij}$$ for $B_i > \sigma_{B_i}$

$$B_i = 0$$ for $B_i <= \sigma_{B_i}$

$$\sigma_{B_i} = STD_{B_i} = \sqrt{\frac{1}{n}\sum_{j=1}^{n}\left(B_{ij} - B_i\right)^2}$$ for $STD_{B_i} > SIG_{B_i}$

$$\sigma_{B_i} = SIG_{B_i} = \sqrt{\frac{1}{n}\sum_{j=1}^{n}\left(\sigma_{B_{ij}}\right)^2}$$ for $STD_{B_i} <= SIG_{B_i}$

$$\sigma_{C_i} = \sqrt{\frac{\sigma_{M_i}{}^2 + \sigma_{B_i}{}^2}{V^2} + \frac{\sigma_V{}^2 \times \left(M_i - B_i\right)^2}{V^4}}$$

$$D_{M_{ijp}} = M_{ijfp} - M_{ijrp}$$ for mass and B_{abs}

$$D_{M_{ijt}} = M_{ijft} - M_{ijrt}$$ for mass and B_{abs}

$$D_{M_{ip}} = \frac{1}{n}\sum_{j=1}^{n} D_{M_{ijp}}$$ for mass and B_{abs}

$$D_{M_{it}} = \frac{1}{n}\sum_{j=1}^{n} D_{M_{ijt}}$$ for mass and B_{abs}

$$\sigma_{M_i} = \sqrt{\frac{1}{n}\sum_{j=1}^{n}\left(D_{M_{ijp}} - D_{M_{ip}}\right)^2 + \frac{1}{n}\sum_{j=1}^{n}\left(D_{M_{ijt}} - D_{M_{it}}\right)^2}$$ for mass and B_{abs}

$$D_{M_i} = \sum_{j=1}^{n}\left[\frac{\left|M_{ijf} - M_{ijr}\right|}{\left(M_{ijf} + M_{ijr}\right)/2}\right]$$ for all other species

$\sigma_{M_i} = M_i \times D_{M_i}$ for all other species

$\sigma_V = 0.05$

where

B_i	= average amount of species i on field blanks
B_{ij}	= the amount of species i found on field blank j
C_i	= the ambient concentration of species i
F	= flow rate throughout sampling period
F_{jf}	= flow rate performance test made before sampling
F_{jr}	= flow rate performance test made after sampling
M_i	= amount of species i on the substrate
M_{ijf}	= amount of species i on sample j from analysis
M_{ijr}	= amount of species i on sample j from replicate analysis
M_{ijfp}	= pre-exposure filter weight or optical density on sample j
M_{ijrp}	= pre exposure filter weight or optical density on sample j from replicate analysis
M_{ijft}	= post-exposure filter weight or optical density on sample j
M_{ijrt}	= post exposure filter weight or optical density on sample j from replicate analysis
t	= sample duration
V	= volume of air sampled
σ_{B_i}	= blank precision for species I
$\sigma_{B_{ij}}$	= blank precision for species I on field blank j
σ_{C_i}	= propagated precision for the concentration of species i
σ_{M_i}	= precision of amount of species i on substrate
σ_V	= precision of sample volume

Gaseous species concentrations are converted from the analyte ion to the gaseous species form by multiplying C_i by the ratio of analyte species formula weight to gaseous species formula weight. Nitrate in nitric acid is determined by subtracting the total particulate nitrate determined by the denuded Nylon filter from the total nitrate determined on the non-denuded Teflon/Nylon sample. The precision of this measurement is determined by adding in quadrature the precisions of these two observables as specified in Bevington (1969). Calculations for other denuder difference measurements such as ammonia are done in an analogous manner.

6.0 QUALITY CONTROL

The major potential source of errors in this procedure is incorrect keying of data into computer files. Data entry routines use default values where appropriate, to minimize the chance for data entry errors. In addition, acceptable data input value ranges are programmed in the data entry routines to catch errors in entry such as misplaced decimal points. All data values entered are verified by comparing printouts of completed data files against original data sheets. All errors found during this verification step are re-entered, and data printouts re-generated and checked again.

7.0 REFERENCES

Bevington, P.R. (1969). *Data Reduction and Error Analysis for the Physical Sciences.* McGraw Hill, New York, NY

1.0 GENERAL DISCUSSION

1.1 Purpose of Procedure

This procedure describes the data processing operations required to produce and validate a data base from meteorological and continuous gaseous analyzer measurements. Operations include the following five steps.

- Combine all meteorological and continuous data into a single FoxPro file.
- Create a validation parameter file with site specific test values.
- Apply validation tests to database; tag data that fail validation tests.
- Plot data and summarize characteristic patterns for each measurement parameter, and relationships between parameters.
- Apply validation flags and comments based on validation test results, tables of measurement parameter characteristics and other site records.

1.2 Measurement Principle

(Not applicable)

1.3 Measurement Interferences and Their Minimization

(Not applicable)

1.4 Ranges and Typical Values of Measurements Obtained by this Procedure

(Not applicable)

1.5 Typical Lower Quantifiable Limits, Precision, and Accuracy

(Not applicable)

1.6 Responsibilities of Personnel

The Data Processing Technician is responsible for assembling and validating the meteorological and gaseous concentration database.

The Project Manager is responsible for reviewing all data processing and validation operations.

The Quality Assurance Officer is responsible for auditing the data processing procedures.

1.7 Definitions

(Not applicable)

1.8 Related Procedures

Related procedures include the following:

- Operation and Maintenance of the Campbell 21X Datalogger (DRI 07)
- Operation and Maintenance of Meteorological Instruments (DRI 01)
- Operation and Maintenance of the Dasibi 1008 AH Ozone Analyzer (DRI 02)
- Operation and Maintenance of the Dasibi 1003 PC Ozone Calibrator (DRI 03)

2.0 APPARATUS, INSTRUMENTATION, REAGENTS, AND FORMS

2.1 Apparatus and Instrumentation

- Computer: An MSDOS based microcomputer with an 80386 or higher processor, math co-processor, 8 Mbytes of RAM, and hard disk.
- Printer: HP LaserJet or Epson dot matrix compatible.
- Operating System Software: MS-DOS, version 6.2 or later, Microsoft Windows, version 3.1 or later (Microsoft Corporation).
- Database software: FoxPro 2.5 for Windows (Microsoft Corporation). FoxPro programs, FINDMISS, FLAGCT, FLAGVALD, and METVAL.
- Plotting software: TSGRAPH is the database editing and plotting program written in Visual Basic (Microsoft Corp.).

2.2 Reagents

(Not applicable)

2.3 Forms

(Not applicable)

3.0 CALIBRATION STANDARDS

(Not applicable)

4.0 PROCEDURES

4.1 General Flow Diagram

Data processing and validation operations described in this procedure are illustrated in the flow diagram shown in Figure 4-1.

4.2 Start-Up

The data processing programs described in this procedure are stored on the Environmental Analysis Facility's main file server, EAFMAIN. Login to EAFMAIN from your workstation and re-direct your local P: drive to EAFMAIN's P-DRIVE. Your workstation must have drive P:\ in its DOS PATH statement. You must have a CONFIG.FPW file in your DOS path that contains the following line.

PATH = P:\FOXPRO25.WIN;P:\PROG.FP2;P:\STRU.FP2

Project related files are also stored on EAFMAIN. Most projects are stored on F-DRIVE with each project having its own subdirectory. Some large projects are stored on drives other than F-DRIVE. The laboratory manager has drive locations for these projects. Redirect one of your local drives (a good choice is F:) to EAFMAIN's F-DRIVE, or to the proper drive if the project is not on F-DRIVE.

Start Windows if it is not already running. Start FoxPro by double-clicking its icon. Change to the correct directory by typing the following in the command window.

<u>set default to <pathname></u>

Substitute the project directory including drive for <pathname>. Note: throughout this procedure, commands to be typed in the command window will be indicated by underlining, as above, and must be followed by pressing the Enter or Return key. Case is not important.

Open a new text file and save it with the file name DPMETnn.DOC, where nn is the batch number. The purpose of this file is to document all data processing operations performed on a data set. Keep this file open throughout data processing operations and record all data

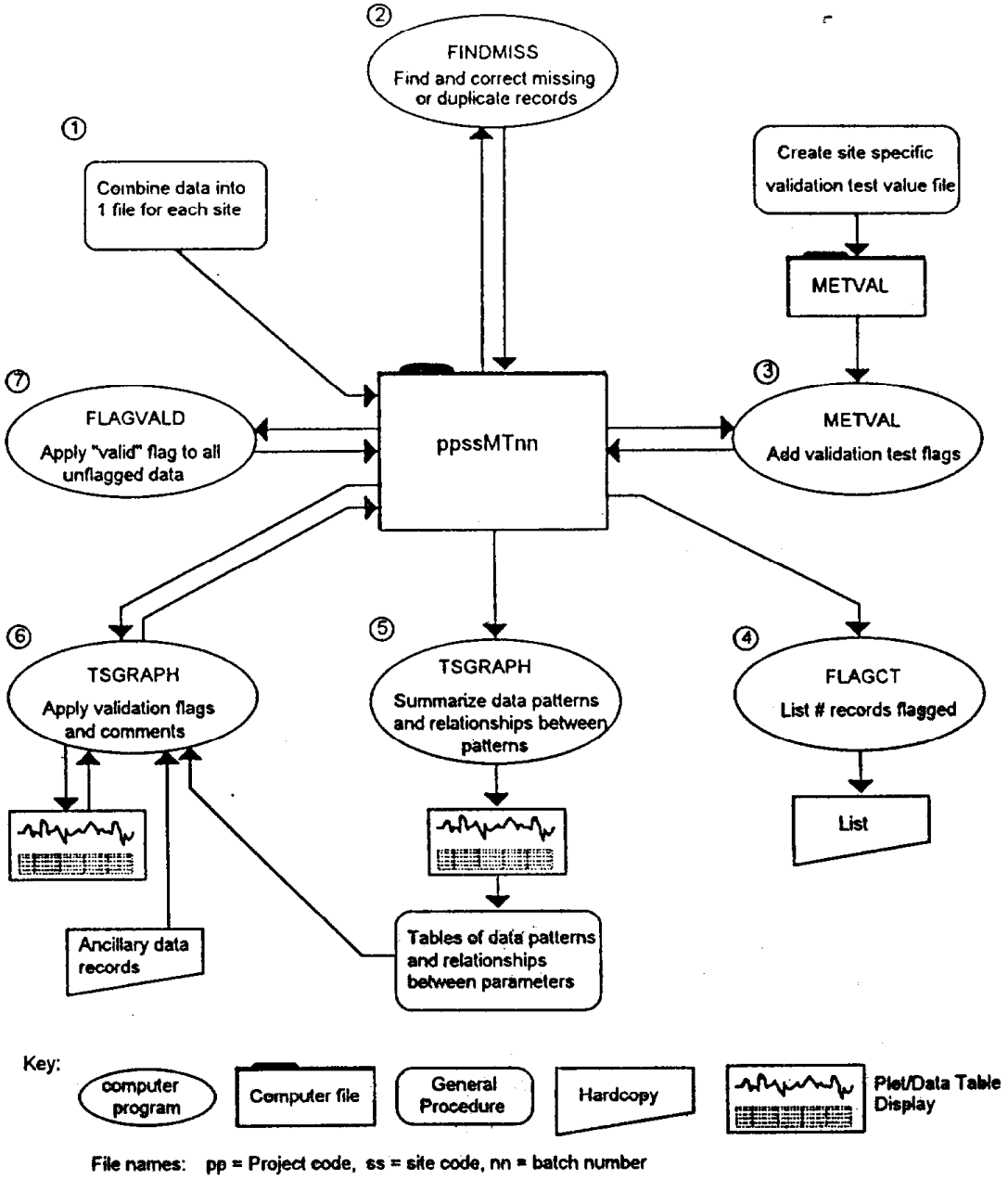


Figure 4-1. Data processing flow diagram.

processing operations performed as they are completed in this file. Record programs run, the input and output file names processed by those programs, parameters used in the programs, etc. The level of detail in the file should be sufficient to allow someone else to duplicate the final database starting from the raw data. It is easy to enter most of the information into the file by cutting and pasting from the command window, and adding explanatory material where necessary.

4.3 Routine Operation

4.3.1 Combine Meteorological/Gaseous Data Files

Meteorological and continuous gaseous analyzer readings are collected and processed at a sampling site by the Campbell datalogger. These data are periodically transmitted to a laboratory computer and saved as both ASCII and FoxPro DBF files as detailed in the Campbell datalogger SOP.

Data to be validated may be saved in more than one DBF file. If so, combine all DBF files created as part of the downloading process into a single file for validation using the FoxPro USE, COPY TO, and APPEND FROM commands. Use the file name convention ppssMTnn, where pp is the two character project code, ss is a two character site code, and nn is a two digit batch number. This file is called the "met" file.

The met file should have a structure similar to the example structure in Table 4-1. By convention, three-character field names are used for the meteorological/continuous measurement parameters, with the first two characters representing the measurement parameter and the third denoting the measurement units. Include a validation flag field, with one column for each measurement parameter, excluding miscellaneous parameters such as shelter temperature, power supply voltage and number of samples in hourly average, etc. Also include an evaluation flag field with one column for each measurement parameter including all of the miscellaneous parameters. The file structure must include SITE, HEC, HR, JDATE, DATE, FDAT, and COMMENTS fields as defined in the example file structure in Table 4-1.

4.3.2 Eliminate Duplicate and Add Missing Records

The program FINDMISS uses fields JDAT and HEC to find missing or extra records, and opens a BROWSE window each time a missing or extra record is encountered. Type the following command in the command window to run the program.

<u>do findmiss</u>

Select the met file from the Open File dialog that appears as shown in Screen 4-1.

Table 4-1
Example Meteorological/Continuous Data File Structure

Structure for table: FOBFMT01.DBF

Field	Field Name	Type	Width	Description
1	SITE	Character	10	Sampling site name
1	ID	Numeric	1	Record type, 1=hourly average
2	YRCC	Numeric	4	Year of sample collection
3	JDAT	Numeric	3	Julian day
4	HEC	Numeric	4	Time in HHMM format at end of hourly average observation, i.e. 0500 is for data collected 0400 through 0500
5	TAC	Numeric	5.1	Ambient temperature, degrees C
6	RHP	Numeric	5.1	Relative humidity, %
7	WSM	Numeric	5.1	Scalar windspeed, m/s
8	WDS	Numeric	3	Scalar wind direction, degrees of angle
9	SGD	Numeric	3	Sigma theta (standard deviation of wind direction), degrees of angle
10	WVM	Numeric	5.1	Vector wind speed, m/s
11	WDV	Numeric	3	Vector wind direction, degrees of angle
12	WHM	Numeric	5.1	Maximum instantaneous windspeed during hour, m/s
13	WLM	Numeric	5.1	Minimum instantaneous windspeed during hour, m/s
14	O3B	Numeric	3	Ozone concentration, ppb
15	LWF	Numeric	5	Fraction of hour that leaf wetness sensor was wet
16	SRW	Numeric	4	Solar radiation, w/m^2
17	TSC	Numeric	5.1	Shelter temperature, degrees C
18	PSV	Numeric	5.1	Datalogger battery voltage
19	MCT	Numeric	4	Number of observations in hourly average (except for ozone)
20	OCT	Numeric	4	Number of observations in hourly average for ozone
21	SNT	Numeric	6.1	Datalogger program ID
22	SITE	Character	2	Site code, BF= Barton Flats
23	HR	Numeric	2	Time in hours at beginning of hourly average observation, i.e. 5 is for data collected 0500 through 0600
24	DATE	Date	8	Sampling date

Table 4-1 (continued)
Example Meteorological/Continuous Data File Structure

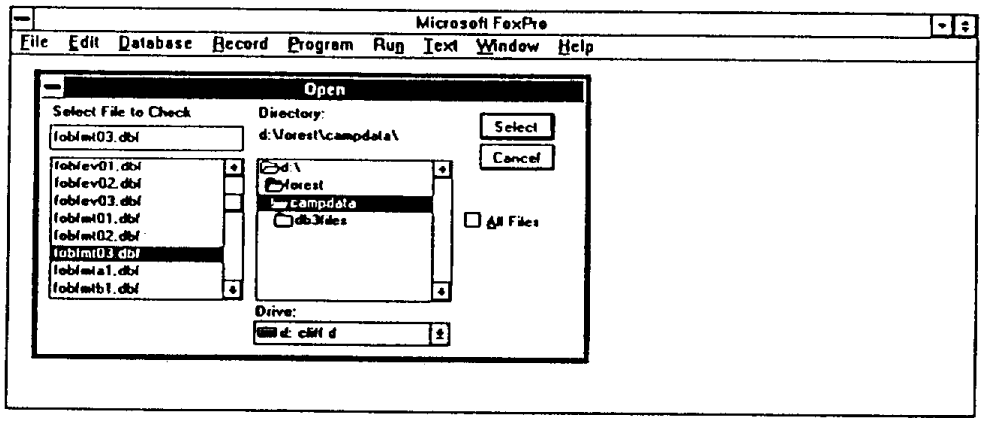
Field	Field Name	Type	Width	Description
25	VALFLAGS	Character	12	Data validation flags. Each column contains the flag for a single parameter, as follows:

Column	Field
1	TAC
2	RHP
3	WSM
4	WDS
5	SGD
6	WVM
7	WDV
8	WHM
9	WLM
10	O3B
11	LWF
12	SRW

Field	Field Name	Type	Width	Description
26	TESTFLAGS	Character	17	Data evaluation flags. Each column contains the flag for a single parameter, as follows:

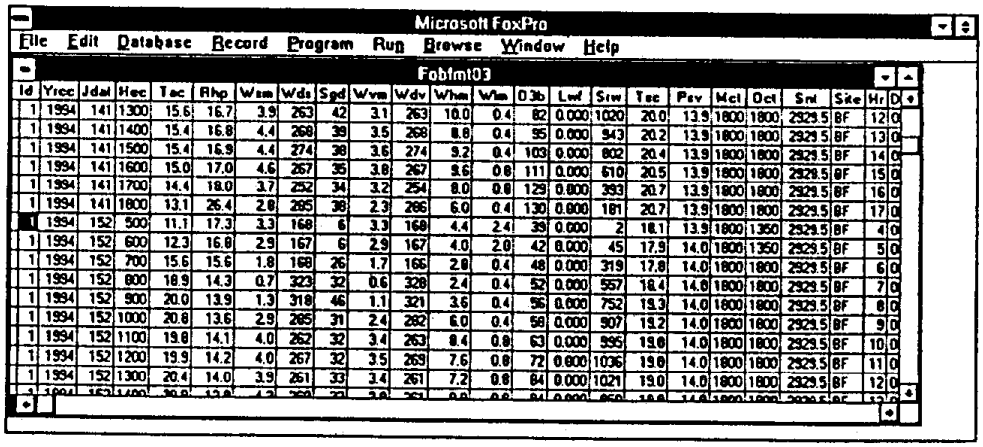
Column	Field
1	TAC
2	RHP
3	WSM
4	WDS
5	SGD
6	WVM
7	WDV
8	WHM
9	WLM
10	O3B
11	LWF
12	SRW
13	TSC
14	PSV
15	MCT
16	OCT
17	SNT

Field	Field Name	Type	Width	Description
27	FDAT	Numeric	7.3	Fractional Julian day, i.e. Julian day + HR/24
28	COMMENTS	Memo	10	Data validation notes



Screen 4-1. Open File dialog in FINDMISS program.

If the program finds data records that do not follow in one hour increments, it opens a BROWSE window with the of sequence record highlighted as shown in Screen 4-2. Note the SITE, DATE and HR of missing or extra records and close the BROWSE window by pressing Esc or double-clicking the close box to allow the program to continue. The program searches through the rest of the file, opening a BROWSE window each time it locates missing or extra records.



Id	Yrcc	Jdat	Hec	Tac	Rhp	Wsm	Wds	Sgd	Wvm	Wdv	Whm	Wlm	O3b	Lwf	Srw	Tsc	Pcv	Mct	Oct	Srd	Site	Hr	D
1	1994	141	1300	15.6	16.7	3.9	263	42	3.1	263	10.0	0.4	82	0.000	1020	20.0	13.9	1800	1800	2929.5	BF	12	0
1	1994	141	1400	15.4	16.8	4.4	268	39	3.5	268	8.8	0.4	95	0.000	943	20.2	13.9	1800	1800	2929.5	BF	13	0
1	1994	141	1500	15.4	16.9	4.4	274	38	3.6	274	9.2	0.4	103	0.000	802	20.4	13.9	1800	1800	2929.5	BF	14	0
1	1994	141	1600	15.0	17.0	4.6	267	35	3.8	267	9.6	0.8	111	0.000	610	20.5	13.9	1800	1800	2929.5	BF	15	0
1	1994	141	1700	14.4	18.0	3.7	252	34	3.2	254	8.0	0.8	129	0.000	393	20.7	13.9	1800	1800	2929.5	BF	16	0
1	1994	141	1800	13.1	26.4	2.8	285	38	2.3	286	6.0	0.4	130	0.000	181	20.7	13.9	1800	1800	2929.5	BF	17	0
1	1994	152	500	11.1	17.3	3.3	168	6	3.3	168	4.4	2.4	39	0.000	2	18.1	13.9	1800	1350	2929.5	BF	4	0
1	1994	152	600	12.3	16.8	2.9	167	6	2.9	167	4.0	2.0	42	0.000	45	17.9	14.0	1800	1350	2929.5	BF	5	0
1	1994	152	700	15.6	15.6	1.8	168	26	1.7	166	2.8	0.4	48	0.000	319	17.8	14.0	1800	1800	2929.5	BF	6	0
1	1994	152	800	18.9	14.3	0.7	323	32	0.6	328	2.4	0.4	52	0.000	557	18.4	14.0	1800	1800	2929.5	BF	7	0
1	1994	152	900	20.0	13.9	1.3	318	46	1.1	321	3.6	0.4	56	0.000	752	18.3	14.0	1800	1800	2929.5	BF	8	0
1	1994	152	1000	20.8	13.6	2.9	265	31	2.4	262	6.0	0.4	58	0.000	907	18.2	14.0	1800	1800	2929.5	BF	9	0
1	1994	152	1100	19.8	14.1	4.0	262	32	3.4	263	8.4	0.8	63	0.000	995	19.0	14.0	1800	1800	2929.5	BF	10	0
1	1994	152	1200	19.9	14.2	4.0	267	32	3.5	269	7.6	0.8	72	0.000	1036	19.0	14.0	1800	1800	2929.5	BF	11	0
1	1994	152	1300	20.4	14.0	3.9	261	33	3.4	261	7.2	0.8	84	0.000	1021	19.0	14.0	1800	1800	2929.5	BF	12	0

Screen 4-2. BROWSE window with out of sequence record in FINDMISS.

If the program finds missing data, check to make sure that data was not collected for those periods. If data is available, rebuild the met file, then run FINDMISS again. If

data is not available, BROWSE the met file, select the record immediately before the first missing data point, click on the command window, and type

INSERT

in the command window. Add records so that there are no missing measurement intervals. Enter appropriate values for SITE, DATE, HR, etc. so that data records occur in one hour intervals and enter -99 (the missing data value) for the measurement parameters. Repeat for each missing data section.

If there are extra records, delete them by selecting the extra record and clicking the "deleted" box at the leftmost side of the BROWSE window. The box will turn black, indicating the record is marked for deletion. After marking all duplicate records, type

PACK

in the command window to eliminate records marked for deletion.

4.3.3 Create Validation Parameter File

Create a validation parameter file (METVAL.DBF) with values for applying tests for minimum value, maximum value and rate of change for each measurement sensor. Rate of change tests include a maximum rate of change over one hour and a minimum rate of change over a specified number of hours. Include one record in this file for each observable (all fields except those like site, date, hour, flags and comments) in the meteorological/continuous data file. The METVAL.DBF file structure is defined in Table 4-2.

Appropriate values for these tests are site specific, as they depend on local meteorological and pollutant conditions. The MIN, MAX and JUMP test values should be selected to flag results that are 1) physically impossible, i.e. wind direction > 360, or 2) so unusual as to suggest a possible sensor malfunction, i.e. temperature > 40 degrees C. The STATIC and STATICNUM values should be selected to identify results that 1) suggest a sensor is physically stuck in one position, i.e. wind direction changes less than 5 degrees over a 6 hour period, or 2) suggest that a sensor or instrument may not be operating over its full range, i.e. relative humidity changes less than 5% over a day. An example file is shown in Table 4-3. The objective of these tests is to identify records with data that is either unreasonable or unusual enough to warrant further investigation. If an appropriate value for any test is unknown, make a reasonable estimate.

Table 4-2
METVAL Data File Structure

Structure for table: METVAL.DBF

Field	Field Name	Type	Width	Description
1	FIELD	Character	10	Name of field in meteorological data file of continuous data measurement parameter.
2	MIN	Numeric	6.1	Lower limit test value. Data lower than this value are flagged.
3	MAX	Numeric	6.1	Upper limit test value. Data higher than this value are flagged.
4	JUMP	Numeric	6.1	Jump test value. Data are flagged if difference between previous record and current record is greater than jump test value.
5	STATIC	Numeric	6.1	Static test value. Data are flagged if the maximum difference between this record and the last STATICNUM - 1 records is less than the static test value.
6	STATICNUM	Numeric	2	Number of records included in static test.

Table 4-3
Example METVAL.DBF File

Record#	FIELD	MIN	MAX	JUMP	STATIC	STATICNUM
1	TAC	-10.0	30.0	6.0	0.2	8
2	RHP	10.0	100.0	30.0	0.2	12
3	WSM	0.0	10.0	3.0	0.3	12
4	WDS	0.0	360.0	360.0	5.0	12
5	SGD	5.0	90.0	60.0	1.0	12
6	WVM	0.0	10.0	4.0	0.3	12
7	WDV	0.0	360.0	360.0	5.0	12
8	WHM	0.5	25.0	12.0	0.0	0
9	WLM	0.0	3.0	3.0	0.0	0
10	O3B	5.0	200.0	60.0	2.0	16
11	LWF	0.0	1.0	1.0	0.0	0
12	SRW	0.0	1100.0	500.0	4.0	16
13	TSC	-10.0	35.0	5.0	0.0	0
14	PSV	13.0	14.5	1.5	0.0	0
15	MCT	1800.0	1800.0	1800.0	0.0	0
16	OCT	1200.0	1800.0	1800.0	0.0	0
17	SNT	0.0	4000.0	0.1	0.0	0

4.3.4 Perform Validation Tests

Validation tests include 1) missing data, 2) minimum, maximum and rate of change tests as defined in file METVAL.DBF, and 3) site specific tests. Site specific tests must be including in the testing procedure by inserting the appropriate code in FoxPro program file METVAL.PRG before running the program. Site specific tests may include tests such as scalar windspeed < vector windspeed, and leaf wetness > 0 while relative humidity < 50%. The METVAL program evaluates data with respect to the criteria listed above.

Data which fail the testing criteria are tagged by placing a flag in the evaluation flag field (TESTFLAGS). Data evaluation flags are defined in Table 4-4. Flags a, b, c, d and m are the same for all projects; flags that are site or project specific should be assigned other letters. Flags f and g in Table 4-4 are examples of site specific flags. Since only one flag can be applied to any one measurement value, flags are ordered according to importance by a "hierarchy number." If more than one flag applies to a sample, the flag with the lowest hierarchy number is assigned. Tests with the highest hierarchy number appear first in the METVAL program. If you include site specific tests, place program code in the position in the program that matches its hierarchy number.

Apply flags by typing

<u>do metval</u>

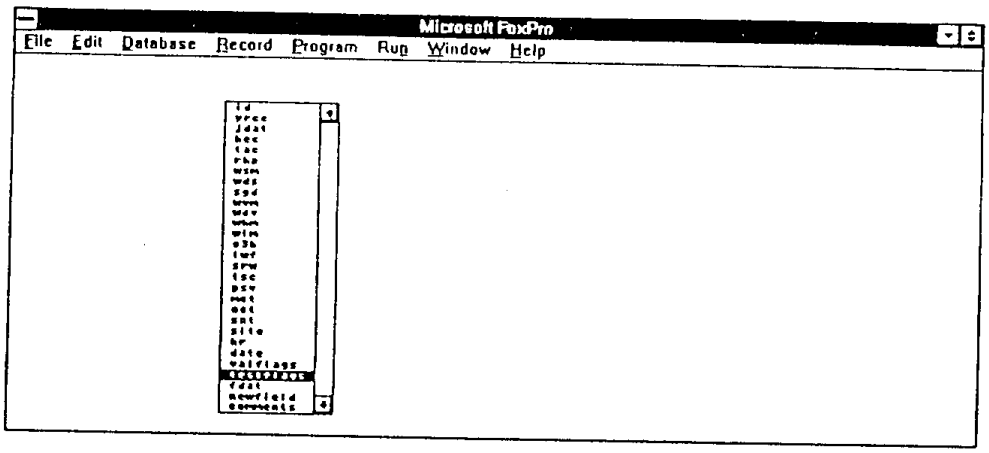
in the command window. Select your meteorological data file from an Open File dialog and enter the name of the evaluation flag field from the popup list as shown in Screen 4-3. The program initializes the data evaluation flag field to all periods (.....), then applies the flags listed in Table 4-4. The periods allows one to easily identify which column a flag appears in, and thus to relate the flag to a measurement parameter. The program displays each field name and the current validation test as it proceeds field by field with the validation tests.

Table 4-4
Example Data Evaluation Flags

FOREST Meteorological and Ozone Data Evaluation Flags

Flag	Description	Field Name[a]	Hierarchy[b]
a	Data value < lower limit test value	MIN	3
b	Data value > upper limit test value	MAX	2
c	Difference between data value and prior reading > jump limit test value	JUMP	4
d	Maximum difference between data value and n[c] prior readings < static limit test value	STATIC, STATICNUM	5
f	Scalar windspeed < vector windspeed		6
g	Leaf wetness > 0 while relative humidity < 50%		7
m	Missing data value		1

[a] Field name of test value in file METVAL.DBF
[b] If more than one flag applies, the flag with the lowest hierarchy number is assigned
[c] Integer n specified by field STATICNUM



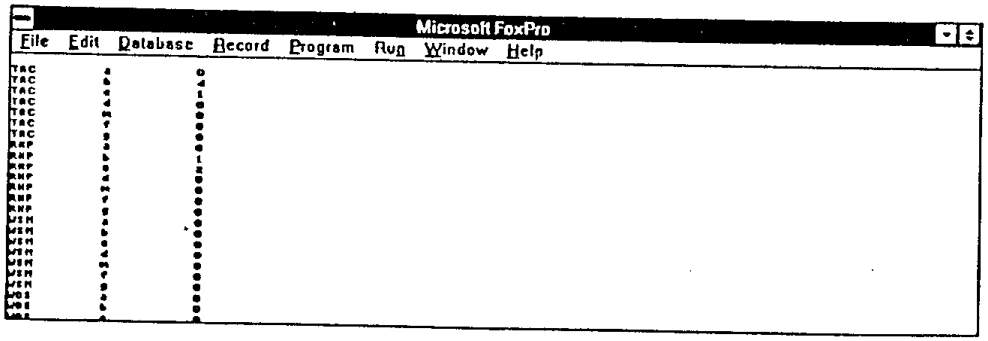
Screen 4-3. Evaluation flag selection from popup list in METVAL.

4.3.5 List Number of Records Flagged

Print out the number of records flagged by measurement parameter and by flag. If you have site specific flags defined, first modify FLAGCT to count site specific flags. Then type

do flagct

in the command window and select your met file in the Open File dialog and the evaluation flag field in the field popup list as before. The program lists the number of occurrences of each flag to the screen as shown in Screen 4-4. The same data is printed also. The first column is the field name, the second is the flag, and the third is the number of records flagged.



Screen 4-4. List of number of records flagged produced by FLAGCT.

If one of the validation test values you entered in the METVAL.DBF file is too stringent, the number of records flagged for that test will be large (5 - 10% of the total number of records). Conversely, if few or no records are flagged, the test value may be too lenient. However, test values should not be adjusted strictly on the basis of the number of records flagged. Records flagged with data evaluation flags are flagged simply for further investigation, and do not by themselves indicate suspect data. The overriding considerations are 1) what values are physically possible, and 2) what values are reasonable or usual at a given site. The number of records flagged provides information with respect to what is reasonable at a given site. You may adjust one or more of the test values and repeat steps 4.3.3, 4.3.4 and 4.3.5. When flagging is completed, make a hardcopy of the METVAL.DBF file by typing the following commands in the command window.

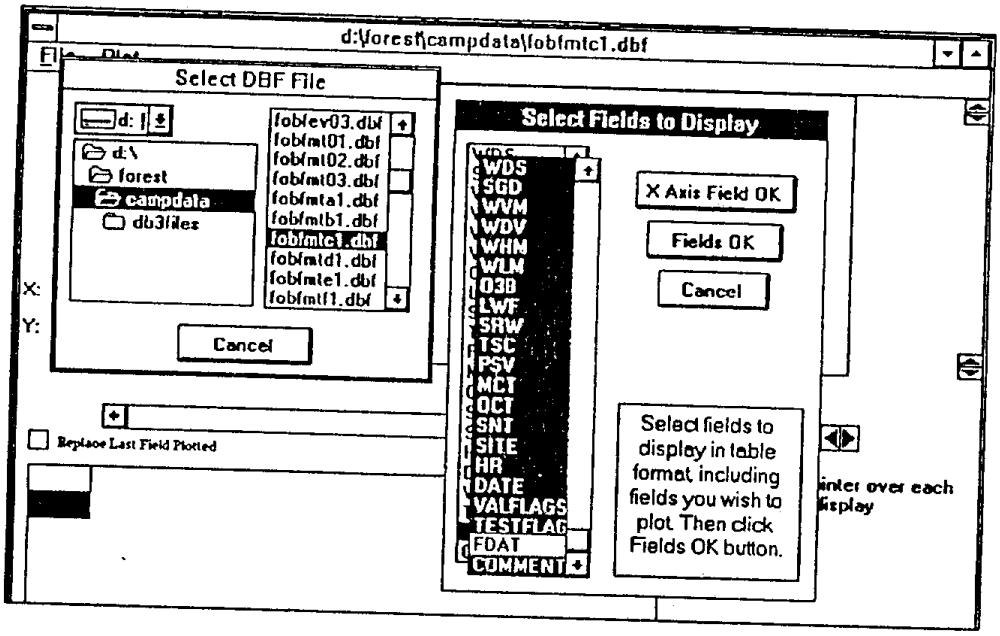
```
use metval
list to print
eject
```

4.3.6 Summarize Data Patterns and Relationships between Parameters

A key part of validating meteorological and continuous gas analyzer data is identification and investigation of data that do not fit normal patterns. Run the TSGRAPH (Time Series Graph) program to plot data from the met file and summarize 1) the patterns associated with each measurement parameter, and 2) the relationships between parameters.

- If the met file has more than 2000 records, divide it into subfiles of 2000 records or less as the TSGRAPH program cannot process larger files.
- Collect all ancillary records related to the meteorological/continuous data measurements including telephone call records, e-mail, site audit dates, field data sheets for meteorological and continuous gas analyzer site checks, and rain gage strip charts.
- Start the Time Series Plot program from Windows by double clicking its icon.
- Select data drive, path and met file. If the met file has more than 2000 records, select the first subfile.
- Select FDAT as the X axis field and click the "X Axis Field OK" button.
- Select all of the fields included in METVAL.DBF plus the HR and DATE fields, the validation and evaluation flag fields, and the COMMENTS field as fields to

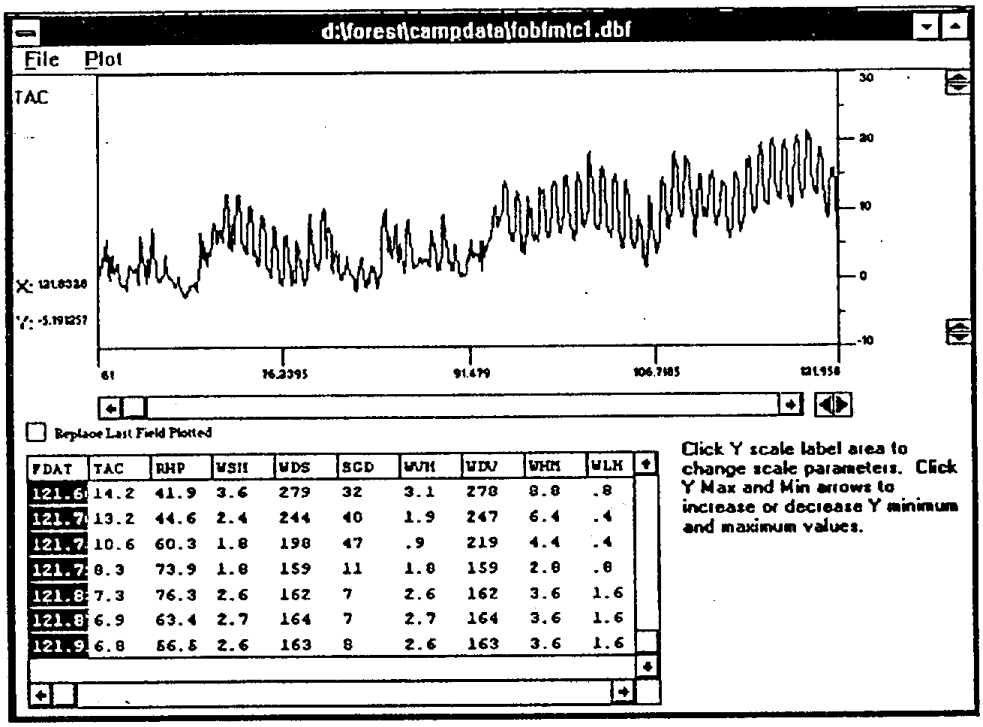
display. Select multiple fields by clicking on the first field to select and dragging, or by clicking on the first field, then holding Shift and clicking on the last field in a continuous range, or by holding Ctrl and clicking to add individual fields. Selection of drive, file and fields is illustrated in Screen 4-5. Click the "Fields OK" button. The program loads the file into memory; this may take several minutes, depending on the size of the file and the number of fields selected.



Screen 4-5. Selection of drive, path, file and fields in program TSGRAPH.

- The display has a plot area at the top half of the screen, the data in table form in the lower left portion of the screen, and an instruction area in the lower right as shown in Screen 4-6. Move the mouse cursor over each area of the screen to display brief instructions for controlling that part of the display. Scroll bars on the data table allow you to view all records for all fields selected. Increase or decrease the display width of any field by clicking and dragging the vertical bar between field names on the top row of the data table. Click a field name to plot it or to remove it from the plot. Click the "Replace Last Field Plotted" box to plot only one field at a time. Hold Shift and click a field name to toggle between the field name and column numbers (useful for validation flag fields). Double click any data cell to edit its contents. Change the X or Y axis scales by selecting from the Plot menu, by putting the cursor over the X or Y scale area and clicking, or by clicking the arrows and scroll bars next to the plot area. Position the cursor over any point on the plot to display its X and Y values, and to scroll the data table to the

corresponding position. Hold the mouse button to freeze the X and Y values and data table while moving the cursor off the plot area.



FDAT	TAC	RHP	WSH	WDS	SGD	WVH	WDV	WHM	WLH
121.6	14.2	41.9	3.6	279	32	3.1	278	8.8	.8
121.7	13.2	44.6	2.4	244	40	1.9	247	6.4	.4
121.7	10.6	60.3	1.8	198	47	.9	219	4.4	.4
121.7	8.3	73.9	1.8	159	11	1.8	159	2.8	.8
121.8	7.3	76.3	2.6	162	7	2.6	162	3.6	1.6
121.8	6.9	63.4	2.7	164	7	2.7	164	3.6	1.6
121.9	6.8	56.5	2.6	163	8	2.6	163	3.6	1.6

Screen 4-6. Example TSGRAPH screen showing plot and data table.

- Plot each measurement parameter in turn. Expand the x-axis scale if necessary to see fine details. Summarize the data for each parameter in terms of normal mimima and maxima, rate of change, and patterns that repeat over time. There may be more than one characteristic pattern as weather systems move past a site. Individual patterns combine to create the "normal" pattern. Make a table of normal data patterns like the example in Table 4-5.

- Plot two or more fields together in various combinations to explore the relationships between parameters. Look for strong positive or negative correlation between parameters. Two or more fields may be plotted together if their data values (Y scales) are similar or by using the 2nd Y axis scale setting. Summarize the significant data relationships and make a table describing those relationships like the example in Table 4-6.

Table 4-5
Example of Meteorological/Continuous Data Patterns

Meteorological and Ozone Measurement Data Patterns for Barton Flats, California

Parameter	Pattern Description
Temperature	Displays a strong diurnal pattern, with higher daytime and lower nighttime temperatures. In addition, there is a pattern of gradual increases and decreases over a time scale of one to two weeks as weather patterns change. Finally, there is a seasonal pattern of decreasing temperatures in the fall, lower temperatures in the winter, increasing temperatures during spring, and higher temperatures during summer.
Relative humidity	Shows its most dominant pattern as a rapid change from relative humidity < 40% to values near 100%, and then back to low values as moist air moves past the sampling site. These weather system related patterns typically last from several days to a week. There is also a week diurnal pattern of higher nighttime values associated with nighttime cooling.
Windspeed	Has a rapidly changing component, with large deviations occurring on the order of hours. Maximum values are usually < 10 m/s; minimum values are in the 0.5 to 2 m/s range. It sometimes also has a weak diurnal component, with speeds lower during the night than the day. In addition, there is also a pattern of lower windspeeds just before sunrise, and just after sunset. Windspeeds increase and diurnal patterns cease as unstable air moves past the sampling station.
Wind direction	Exhibits a strong diurnal component during stable weather conditions associated with upslope/downslope flows. Large changes in wind direction can occur from hour to hour. Daytime winds are generally from the NW while nighttime winds are from the SSE. Weather systems are usually associated with westerly winds.
Sigma theta	Shows a strong diurnal component also, with lower values during night than day. Unstable air masses result in large sigma theta values.
Maximum windspeed	Can change rapidly, with nearly full scale changes occurring from hour to hour. Maximum windspeeds increase during unstable air conditions, and can reach 15 to 20 m/s. There is often a small increase during midday.
Minimum windspeed	Is often near zero and rarely above 2 m/s.
Ozone	Has a strong diurnal pattern, with maximum occurring in the afternoon. It shows a strong seasonal variation also, with higher concentrations during summer months.

Table 4-5 (continued)
Example of Meteorological/Continuous Data Patterns

Meteorological and Ozone Measurement Data Patterns for Barton Flats, California

Parameter	Pattern Description
Leaf wetness	Appears as a series of spikes, with long or short periods of leaf wetness values of zero interrupted by values up to one for a period of from one to several hours. The sensor is checked every week on Tuesday. Flag these events as instrument checks.
Solar radiation	Typically has a very regular diurnal pattern. The daily maxima changes seasonally as time of daylight changes, with summer time maxima over 1000 w/m^2 and winter time maxima near 600 w/m^2. Periods of cloud cover decrease the solar radiation. Accumulation of snow on the sensor attenuates the signal as well.

Table 4-6
Example of Meteorological/Continuous Data Relationships

Meteorological and Ozone Data Relationships for Barton Flats, California

Parameter 1	Parameter 2	Relationship
Temperature	Relative humidity	Inverse relationship of low to moderate correlation exists except during periods of unstable air mass movement past sampling site. Correlation also decreases during the colder winter months.
Temperature	Ozone	Strong positive correlation exists except during winter months. Ozone maxima are delayed past temperature maxima 2 - 3 hours.
Temperature	Wind direction	Deviation from strong diurnal temperature pattern occurs when weather system moves past site, generally causing deviation from upslope/downslope diurnal wind direction as well
Temperature	Sigma theta	Deviation from strong diurnal temperature pattern usually occurs when weather system moves past site, generally causing deviation from normal sigma theta pattern of higher values during daytime as well.
Temperature	Solar radiation	Correlation between the difference between daytime and nighttime temperature and solar radiation usually very strong.
Relative humidity	Wind direction	Deviation from normal diurnal relative humidity pattern occurs when weather system moves past site, generally causing deviation from upslope/downslope diurnal wind direction as well
Relative humidity	Leaf wetness	Periods of high relative humidity are often associated with leaf wetness values above 0. Leaf wetness plots often appear as short duration spikes even during prolonged periods of high relative humidity.
Relative humidity	Solar radiation	Periods of high relative humidity are often associated with attenuated solar radiation signals due to cloud cover.
Windspeed	Wind direction	During stable air conditions, a sharp drop in windspeed of just 1 or 2 hours duration occurs just after sunrise and after sunset and is associated with a shift in wind direction, as the flow changes from downslope to upslope in the morning and back again in the evening.

Table 4-6 (continued)
Example of Meteorological/Continuous Data Relationships

Meteorological and Ozone Data Relationships for Barton Flats, California

Parameter 1	Parameter 2	Relationship
Windspeed	Maximum windspeed	A weak correlation exists between hourly average windspeeds above 2 m/s and maximum windspeed.
Wind direction	Sigma theta	Nighttime wind direction is generally from SSE and is associated with low sigma theta values. Daytime wind direction is generally from NW and is associated with higher sigma theta values. This relationship ceases as weather systems move past the sampling site.
Scalar wind direction	Vector wind direction	These parameters rarely differ by more than 10 degrees for more than a few hours. Where differences do occur, they are usually associated with high sigma theta values and scalar wind direction tends to show more rapid changes.
Wind direction	Maximum wind speed	Easterly winds are often associated with higher maximum wind speeds.
Wind direction	Solar radiation	During stable air conditions, NW winds occur during daylight and SSE winds occur during nighttime.
Sigma theta	Solar radiation	During stable air conditions, sigma theta is higher during daylight hours.
Ozone	Solar radiation	Ozone is strongly correlated with solar radiation above 500 w/m2. Ozone peaks several hours after solar radiation peaks.

4.3.7 Apply Validation Flags and Comments

- Plot each field again, using the full time scale range to scan the data for inconsistencies with patterns and relationships established in Section 4.3.6. Note any areas that potentially have problems so that you may examine them in further detail in the next step. Start with one parameter and advance through the entire file before going to the next parameter. You may examine data for two parameters that are very similar such as vector and scalar wind speed at the same time, however.

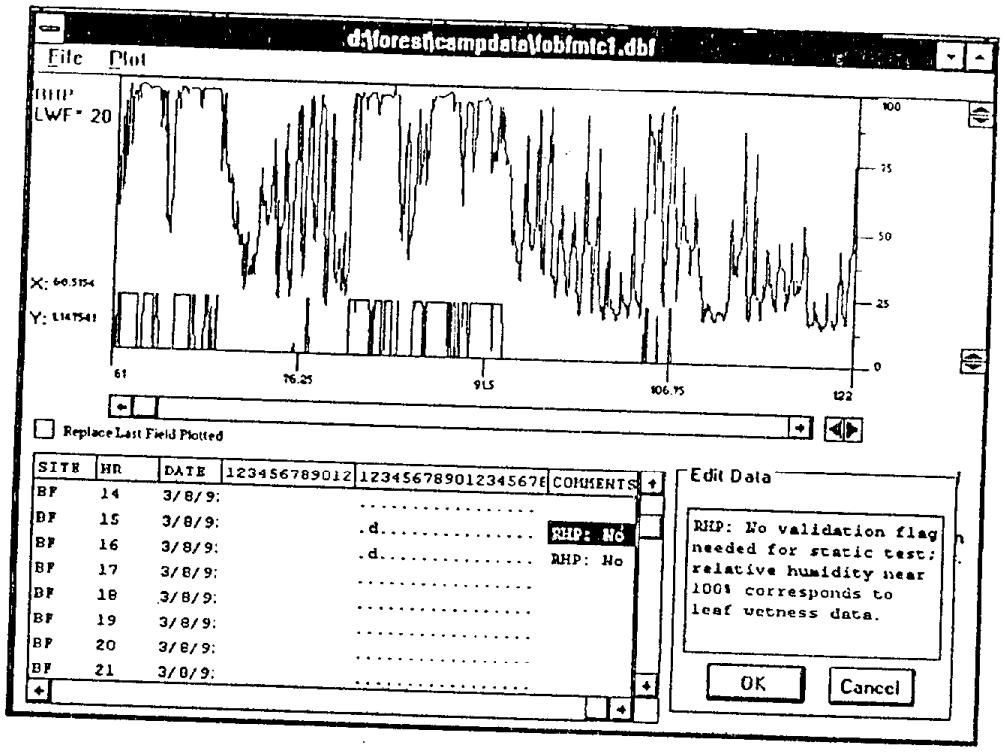
- For each parameter, plot the data on a shorter time scale. Time scales of one or two weeks generally works best. Scan the plots for deviations from normal patterns or relationships and at the same time scan the data table for data evaluation flags, and examine ancillary records for any applicable data or comments. Apply data validation flags as warranted based on all these data sources. The column numbers of validation flags and evaluation flags are the same as the record number of the field from your METVAL.DBF hardcopy. Make sure you apply validation flags in the correct column, and that you do not change column spacing of existing flags when editing. Data validation flags are defined in Table 4-7. If more than one flag is applicable, apply the flag with the lowest hierarchy number. Do not enter flag '0' (Valid data). Valid data flags will be applied to parameters with no other flags by a program after all validation checks are complete.

- Always enter an explanation in the COMMENTS field for any flags you apply. Likewise, always enter an explanation in the COMMENTS field for any data evaluation flag that does not require a validation flag. Specify the field to which a comment applies when entering comments by typing the field name followed by a colon and the comment. Screen 4-7 shows an example of validation comment entry. Note that the validation and evaluation test flag field names have been toggled to column numbers to facilitate matching flag with field. Note that some flags require changing the data value to missing (-99) as shown in Table 4-7. Record the original value in the comments field in these cases. No other data values should be changed unless a calibration adjustment is applied. Those changes must be fully documented in the comments field.

Table 4-7
Meteorological/Continuous Data Validation Flags

Flag	Description	Change Data to Missing Value[a]	Hierarchy[b]
0	Valid data	no	12
1	Estimated value	no	9
2	Calibration or instrument check	yes	1
3	Instrument failure	yes	3
4	Off-scale reading	yes	2
5	Interpolated	no	8
6	Below detection limit	no	7
7	Suspect	no	6
8	Invalid	yes	5
9	Missing	yes	4
a	45 <= averaging period <= 60 minutes	no	11
b	Averaging period < 45 minutes	no	10

[a] Missing data value is -99.
[b] If more than one flag applies, the flag with the lowest hierarchy number is assigned



Screen 4-7. Example TSGRAPH screen showing COMMENTS field editing.

- Complete the data scanning and flagging procedure for all measurement parameters, then exit the TSGRAPH program by selecting "Close" from the File menu.

- If the original met file was divided into subfiles, repeat this section for each file. After all files have been processed, select "Exit" from the File menu to quit the TSGRAPH program. Switch back to FoxPro and combine all subfiles back into a single met file.

- Run the FoxPro program FLAGVALD to enter the valid data flag (0) for all unflagged data by typing do flagvald from the command window. Select the met file name from the Open File dialog, and the validation flag field (not the evaluation flag field) name from the field selection popup.

4.4 Shut-Down

Type close data from the command window in FoxPro to close all data files. Complete all entries to the DPMETnn.DOC file. Assemble a printout of this file in a folder together with copies of the met file structure, the METVAL file printout, data pattern and data relationship tables. Label file folder with the project name and batch number and store in project files.

5.0 QUANTIFICATION

(not applicable)

6.0 QUALITY CONTROL/ASSURANCE

The major potential source of error in this procedure is missing data points that should be invalidated or flagged. Use of graphical plotting routines, together with examination of all related documents and records minimizes this possibility.

7.0 REFERENCES

(not applicable)