

**IMPROVE
STANDARD OPERATING PROCEDURES**

**SOP 301
X-Ray Fluorescence Analysis**

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SOP 301 X-Ray Fluorescence Analysis

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Technical References

J.F. Harrison and R.A. Eldred, “Automatic data acquisition and reduction for elemental analysis of aerosol samples”, in **Advances In X-Ray Analysis, Vol. 17**, Plenum Press, New York, NY., pages 560-583 (1974).

1.0 PURPOSE AND APPLICABILITY

This standard operating procedure describes the Crocker Nuclear Laboratory (CNL) X-Ray Fluorescence (XRF) system and the analyses using this system. The CNL-XRF energy dispersive x-ray fluorescence system is designed to measure the concentrations of elements having atomic weights from Fe to Pb. Lighter elements are detected by used only for quality assurance. XRF elemental analysis is used for aerosol samples on Teflon filters.

SOP 326 describes the standard operating procedure describes the CNL PIXE/PESA system for analysis of elements H and Na-Mn.

2.0 RESPONSIBILITIES

2.1 Spectroscopist

The Spectroscopist shall:

- oversee and maintain records on the X-Ray Fluorescence Analysis System
- perform maintenance and repair of the XRF system as necessary
- perform the analysis runs for XRF
- calibrate and run controls on the XRF system
- resolve any inconsistencies in calibrations, reanalyses, or normal analyses.
- perform periodic back-ups of the acquisition and analysis programs and collected data

2.2 Quality Assurance Manager

The Quality Assurance Manager shall:

- approve the calibrations and reanalyses prior to analysis of normal samples.
- oversee and approve any modifications to the analysis system or software
- check for inconsistencies in calibrations, reanalyses, or normal analyses.

2.3 Computer System Operations Manager

The Computer System Operation Managers shall:

- oversee and maintain records on the data acquisition and analysis programs
- repair or correct any problems with acquisition or analysis programs.

3.0 REQUIRED EQUIPMENT AND MATERIALS

The equipment and materials required for XRF analysis are listed below.

3.1 XRF System

- Molybdenum anode X-Ray tube
- controller and regulated power supply for X-ray tube
- X-ray collimators
- SiLi detector with liquid nitrogen dewar
- Liquid Nitrogen
- Automatic sample changer
- Power supply for sample changer
- XRF laboratory manual override switches for sample changer
- Closed circuit TV camera
- Closed circuit TV Monitor
- XRF Amplifier
- XRF Bias Supply
- XRF system Pre-Amp
- Analog/Digital converter
- CNL/ARB Controller
- Quad Scalar
- Multi-channel Analyzer
- Patch panels (to facilitate wiring)
- Computer room manual override card for sample changer
- MicroVAX

3.2 Calibration Requirements

- Standards tray containing 17 Micromatter™ thin film standards (PbGaAs, CuS, CaF₂, Ti, V, Cr, Fe, Ni, Cu, Zn, GaP, GaAs, Se, CsBr, RbI, SrF₂, Pb) and 2 clean filters (blanks) representative of the filter lot used for IMPROVE aerosol sampling

3.3 Analysis Requirements

- Standards tray (from section 3.2)
- 2 trays of filters analyzed in the previous quarter for reanalysis. Generally SHEN1 and CRLA1 trays are selected.
- “A” module filters, in quarterly site trays, for XRF analysis

4.0 METHODS

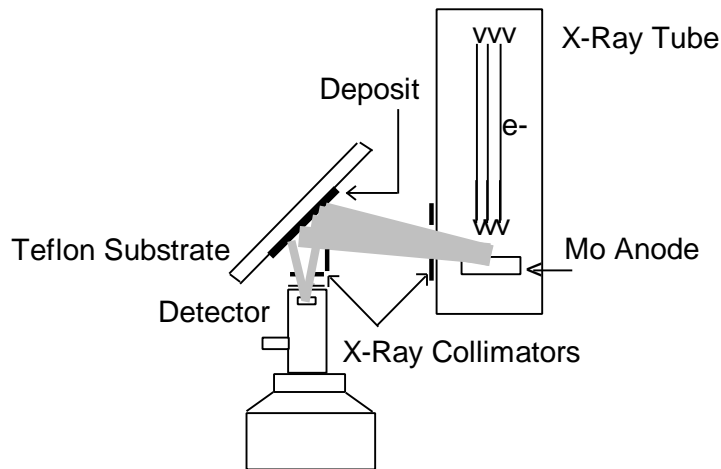
Three analytical methods are used to characterize the elemental composition of the aerosol deposits on the Teflon filters: PESA (H), PIXE (Na - Mn), and XRF (Fe-Pb). This standard operating procedure (SOP) refers to the procedures for performing XRF (X-Ray Fluorescence) analysis of aerosol samples on Teflon filters for elemental composition and concentrations.

- 4.1 Overview of the XRF system
- 4.2 Preparation for XRF analysis—XRF Laboratory
- 4.3 Preparation for XRF analysis—Computer Room
- 4.4 Data Acquisition
- 4.5 Spectral Analysis
- 4.6 Routine Analysis

4.1 Overview of the XRF System

The XRF system uses a General Electric grounded anode diffraction type X-ray tube, with a molybdenum anode. The x-rays produced by the tube are collimated and directed onto an aerosol sample. The sample deposit absorbs the Mo x-ray energy and re-emits the energy as x-rays characteristic to the elements present on the sample. The x-rays are detected by high-resolution SiLi detectors with pulsed optical feedback to provide high count rate capabilities. The data from the detector are processed by standard pulse processing electronics and accumulated in a dual ported analog to digital converter connected to an Ethernet local area network. The data are recorded by a data acquisition program, ACE, and analyzed by a data reduction program, RACE. A diagram of the XRF system is shown in Figure 1.

Figure 1 Setup of XRF Analysis System



IMPROVE network sample analyses by XRF are performed four times a year in analysis run sessions lasting approximately three weeks, with a single break to refill the detectors with liquid nitrogen. Following the break, the system is recalibrated, and tray previously analyzed is reanalyzed to verify no system parameters changed significantly. Each analysis session begins roughly one month after the end of the quarter, pending the return of the filters and completion of gravimetric analysis and level I collection validation.

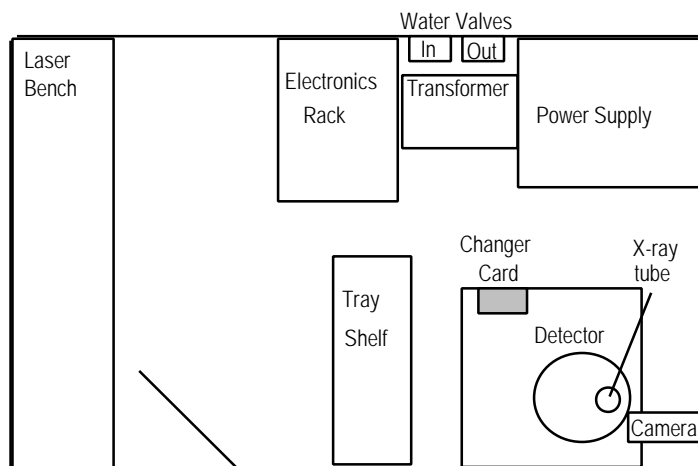
The Acquisition of Composition by Elements program, *ACE*, controls the automatic analysis system and collects the data generated during each analysis, storing it as a data file. *ACE* is run on a MicroVAX terminal and, during analysis, continually displays the status of the XRF system and of the current analysis, including the real time XRF spectrum.

The Rapid Analysis of Composition by Elements program, *RACE*, analyzes the data. *RACE* opens the files created by *ACE* and analyzes the X-ray spectrum. Analysis involves subtracting the background radiation and the ‘blank’ spectrum (the x-rays due to the filter substrate), leaving the spectrum due to the deposits on the filter. *RACE* also locates the peaks in the spectrum, fits each peak with Gaussian curves to calculate its integrated area, identifies the element responsible for each peak, deconvolutes any interfering peaks, and uses a calibration table to determine the concentration in ng/cm² of each element. *RACE* saves this data in a second data file for later reference. The collection and processing of data are controlled by a single terminal running *ACE*, displaying the real time acquisition on X-rays, and displaying the data reduction produced by *RACE*.

4.2 Preparation for XRF Analysis—XRF Laboratory

This section will deal with the procedures that are to be followed in the XRF laboratory for an XRF analysis session. A schematic of the laboratory is shown in Figure 2. Ideally, the setup should be performed at least 24 hours in advance of an analysis run, but it can be done within 4 hours of analysis if absolutely necessary.

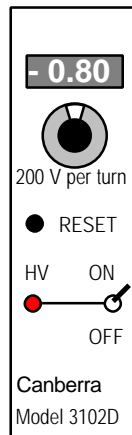
Figure 2 XRF Laboratory Drawing



4.2.1 Filling the Detector.

1. Schedule to fill the detector with liquid nitrogen (LN) at least 4 hours before starting an XRF analysis run. The detector must be filled every 7-10 days and must **NEVER** be allowed to warm up. **NOTE:** Caution must be used when working with LN. Wear gloves and eye protection when using LN. No open toe shoes allowed.
2. Bias down the detector to 0.00 volts and shut off the high voltage (HV) power supply using the dial and the switch on the Canberra Model 3102D module in the electronics rack in the XRF laboratory (see Figures 2 and 3). Verify that the detector is at 0 volts before preparing to fill the detector with liquid nitrogen (LN). (See Section 4.2.6 for instructions on biasing the detector.)
3. To fill the XRF detector with liquid nitrogen
 - a) See Figure 2 for a schematic of the XRF laboratory.
 - b) Wheel in a LN storage tank.
 - c) Connect one end of the Parker 3/8" hose to the LN tank. Thick leather gloves should be worn to protect the skin.
 - d) Open the valve on the LN tank to allow LN to flow through the hose into the dewar.
 - e) Close the valve on the LN tank when a steady stream of LN flows from the exhaust port on the dewar.
 - f) Disconnect the hose, using gloves, and replace the tank.

Figure 3 HV Power Supply



4.2.2 Installing the Detector.

The detector is installed underneath the slide changer in the XRF system. The detector, once installed, is not moved or changed. If the detector has been moved, contact the Spectroscopist for assistance. The Spectroscopist will reinstall and readjust the detector if necessary.

4.2.3 Beam Collimation System

The beam collimation system incorporates two sets of collimators (Figure 1). One set is located on the X-ray tube and the second set is located above the detector head. The collimators are installed and adjusted when a new X-ray tube is installed. They are not adjusted unless a significant change in the system occurs. Generally, the collimators are not changed during the life of the x-ray tube.

Should there be a need to change the collimation system, the Spectroscopist will perform the modifications and adjustments. Following any modification, an x-ray footprint will be taken to satisfy radiation safety requirements and to allow the Spectroscopist to optimize the efficiency of the tube.

4.2.4 XRF Cooling System

The XRF system is cooled by water. The water inlet is through a blue pipe and valve on the wall behind the transformer (labeled "In" in Figure 2). The water passes through a filter, visible below the electronics rack, then runs to the XRF system. The water should be on whenever the XRF tube is receiving power. The outlet valve for the water is through a red tube next to the inlet valve. Both the outlet and inlet valves must be open to provide adequate cooling for the XRF system.

4.2.5 Wiring and Powering Equipment in the XRF Laboratory.

4.2.5.1 Connecting the Detector to Power.

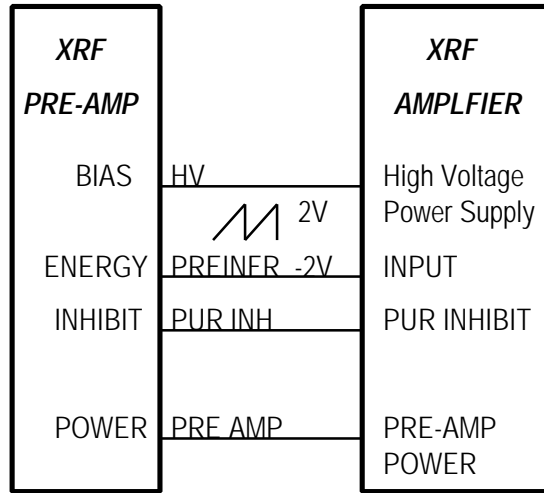
The detector has a regulated power supply, currently a Canberra™ Model 3102D (Figure 3) providing a bias voltage of -800 V. The power supply is located on the electronics rack in the XRF laboratory. Contact the Spectroscopist for assistance if the power supply is not functioning.

4.2.5.2 Pre-Amp to Amp Wiring.

Wiring the detector pre-amp to the signal amplifier involves four input cables, as shown in Figure 4.

- a) bias voltage - HV (black)
- b) preamplifier signal (energy) - black BNC (RG58, 50 Ω) - cable PREINFR
- c) inhibit - red BNC (125 Ω) - cable PUR INH
- d) preamplifier power - gray multi-wire cable - cable PRE AMP

Figure 4 Pre-Amp to Amp Wiring

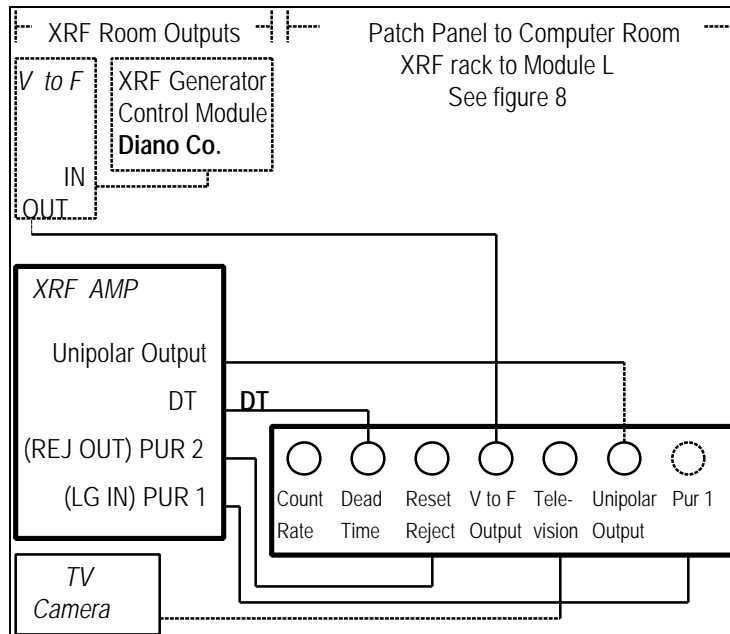


4.2.5.3 Amp Output Wiring.

Use Figure 5 to check the wiring from the XRF electronics. The connections are frequently changed as the computer room is shared them with other users.

- a) Unipolar Output - red BNC - cable # 301
- b) V to F (bipolar output) - red BNC - cable # 302
- c) Dead Time - red BNC - cable # 303
- d) pile-up rejection (PUR 2) - red BNC - cable # 305
- e) linear gate from MCA to amplifier (PUR 1) - black BNC - cable # 304
- f) TV - black BNC

Figure 5 XRF System Amp Output Wiring



4.2.5.4 X-ray Tube Power Supply.

The X-ray tube controller, a Diano Corporation Generator Control, contains a regulated power supply. For XRF analysis, the power supply is generally set to provide the tube with 35 keV power at 23 mA. The power supply is wired directly to the X-ray tube and should never be disconnected. There is no power to the tube except during XRF analysis runs.

- a) At least two hours prior to an analysis run, the power supply must be turned on to allow the tube to warm up and stabilize.
 - i) Verify that the XRF tube cooling water line valves are both in the fully open position. See Figure 2 for location.
 - ii) Turn on the GE transformer using the switch on the side near the electronics rack. See Figure 2 for location.
 - iii) Press the “Line On” button on the front of the tube controller to turn on the power supply. The button will light up when power is being supplied to the tube.
 - iv) Check the power gauge reading on the upper left side of the controller. The power should be at 35KeV. If not, use the knob below the gauge to adjust the power to 35KeV.
 - v) After two hours have passed, press the “X-Ray On” button on the tube controller. Check the amperage reading on the gauge on the upper right side of the controller and on the Data Precision Model 1350 readout module above the tube controller. Note that both gauge displays show $\frac{1}{2}$ the actual amperage. The real amperage is twice the gauge readings. The amperage should be 23 mA for normal analysis (gauge reading 11.5 mA), or, for thin-film standards analysis, 2.6 mA.
 - a) To set the system for 23 mA current, move the lower dial under the amperage gauge on the controller to position 5, a position preset to provide 23 mA.
 - b) To set the controller to 2.6 mA for analysis of standards, move the lower dial under the amperage gauge to position 1, a position preset to provide 2.6mA.
 - c) To adjust the system to a different amperage setting, move the lower dial under the amperage gauge to the ∞ position, then use the upper dial to exactly adjust the amperage.
- b) To turn off the power supply to the X-ray tube, press the “X-Ray Off” button on the front of the X-ray tube controller. The “X-Ray On” button light will turn off, and the power and amperage gauge readings will drop to zero, indicating no x-rays are being produced by the tube. Next, use the dial under the voltage gauge on the tube controller to set the voltage to 0.0 V. Finally, press the “Line Off” button to complete the shut down of the XRF tube.

4.2.5.5 Voltage to Frequency Converter (V to F).

The V to F is wired directly to the X-ray tube controller. It monitors the voltage use by the x-ray tube, processes that value to a frequency measurement, and outputs its signal to the computer room. The voltage use by the tube correlates to the charge exposure of each filter sample while undergoing XRF analysis.

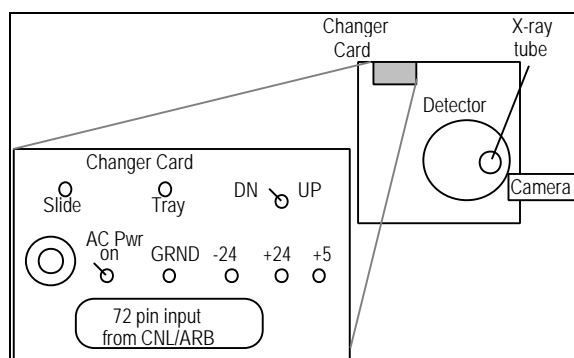
4.2.5.6 Count Rate Meter.

The count rate meter measures the count rate in the detector, and displays this on a visual read out on a vertical meter on the electronics rack in the XRF laboratory. It is used only during set up of the system to verify the system is functioning correctly. The count rate should be 2000 counts per second during normal operation.

4.2.5.7 Slide Changer.

The slide changer is wired directly to power and is mounted onto the XRF system (see Figure 6). It should always function. If not, contact the electrician for assistance. The slide changer is controlled in automatic mode by the data acquisition program ACE, through the CNL/ARB controller to the slide changer. However, there are two manual override methods; the first using the changer card on the XRF system in the XRF laboratory, and the second using manual mode on the CNL/ARB controller in the computer room. The procedures for manual control using the changer card follow.

Figure 6 Changer Card



- To remove a slide from the beam, press the slide button, located on the lower left side of the changer card until the slide has moved out of the beam and back into the storage tray. If you continue to press the button, the slide will cycle between the position in the beam and the position in the storage tray. The slide is in the “Out” position when it is fully in the storage tray, and the lever arm for the slide drive mechanism is horizontal.
- To move the tray, press the tray button in the center of the changer card. Be sure that the slide is in the “out” position or the system will jam.
- To change the direction the tray moves, flip the toggle switch, located on the right side to DN (Down or Forward) or UP (Up or Reverse).
- The tray also moves continuously, so it must be stopped at the correct location or, when the operator attempts to put a slide into the beam, the system will jam. To ensure correct positioning of the tray, verify that the

gap in the drive wheel for the tray is over the LED, so the LED is seen by the LED detector. The drive wheel is inside a protective cowling directly above the changer card on the XRF system.

- e) To insert a slide into the beam, verify the tray is positioned correctly. Next, press the slide button until the slide has moved into of the beam. The slide is in the “In” position if the slide is in the beam, and the lever arm for the slide drive mechanism is horizontal.

4.2.5.8 Remote Monitoring System.

A camera is used to monitor the XRF system. The camera is located near the X-ray tube and is focused on the filter in position for analysis. The camera feed is sent on a coaxial cable to the computer room. See Figures 4 and 5 for connection from the XRF laboratory to the computer room.

In module N of the computer room, there are normally two monitors. Near the monitors there is a toggle switch labeled camera one and XRF. Flip the toggle to XRF to set the monitors to read input from the XRF laboratory camera.

4.2.6 XRF Laboratory Electronics Settings

Set the following switches, pots, etc. as in the Table 1 for the CANBERRA 2024 Amplifier

Table 1 XRF Amplifier Settings

GAIN (typical value)	300 x 0.950	
INPUT POLARITY	+	from Canberra Pre-Amp 2001
SHAPING TIME CONSTANT	8 μ S	GI Amp
BASELINE THRESHOLD	VAR	
BASELINE RESTORER	ASYM	
PILE-UP REJECTION (PUR). MODE	ON UNI	
OUTPUT	UNIPOLAR (rear)	no termination at GAR

4.2.7 Biasing the Detector

1. To bias the detector to -800 volts, turn on the HV switch on the Canberra 3102 D power supply in the electronics rack in the XRF laboratory (see Figures 2 and 3).
2. Use the fine voltage adjustment (pot) on the Canberra 3102 D module to adjust the voltage slowly to coarse=0 and fine=4.00. The final readings on voltage gauge on the module 3102 D should be 0.80 on the analog read out, and 4.00 on the pot.

4.3 Preparation for XRF Analysis—Computer Room

Data acquisition takes place in the computer room of Crocker Nuclear Laboratory (see Figure 7). Cables from the XRF laboratory are routed to the computer room and hooked to conveniently located patch panels. The patch panels are located in the equipment racks,

which also contain the interconnect panels and signal processing electronics. The processed signals are fed into a MicroVAX for storage and initial analysis.

The user interface to the system is through a MicroVAX terminal. A console display terminal, the Micro P90, (M P90), displays real time data acquisition for quality control. Using a MicroVAX terminal running ACE, the operator can oversee data acquisition, and adjust acquisition parameters. With a second terminal running RACE, the operator can review the results of the initial data processing.

Figure 7 Computer Room Schematic

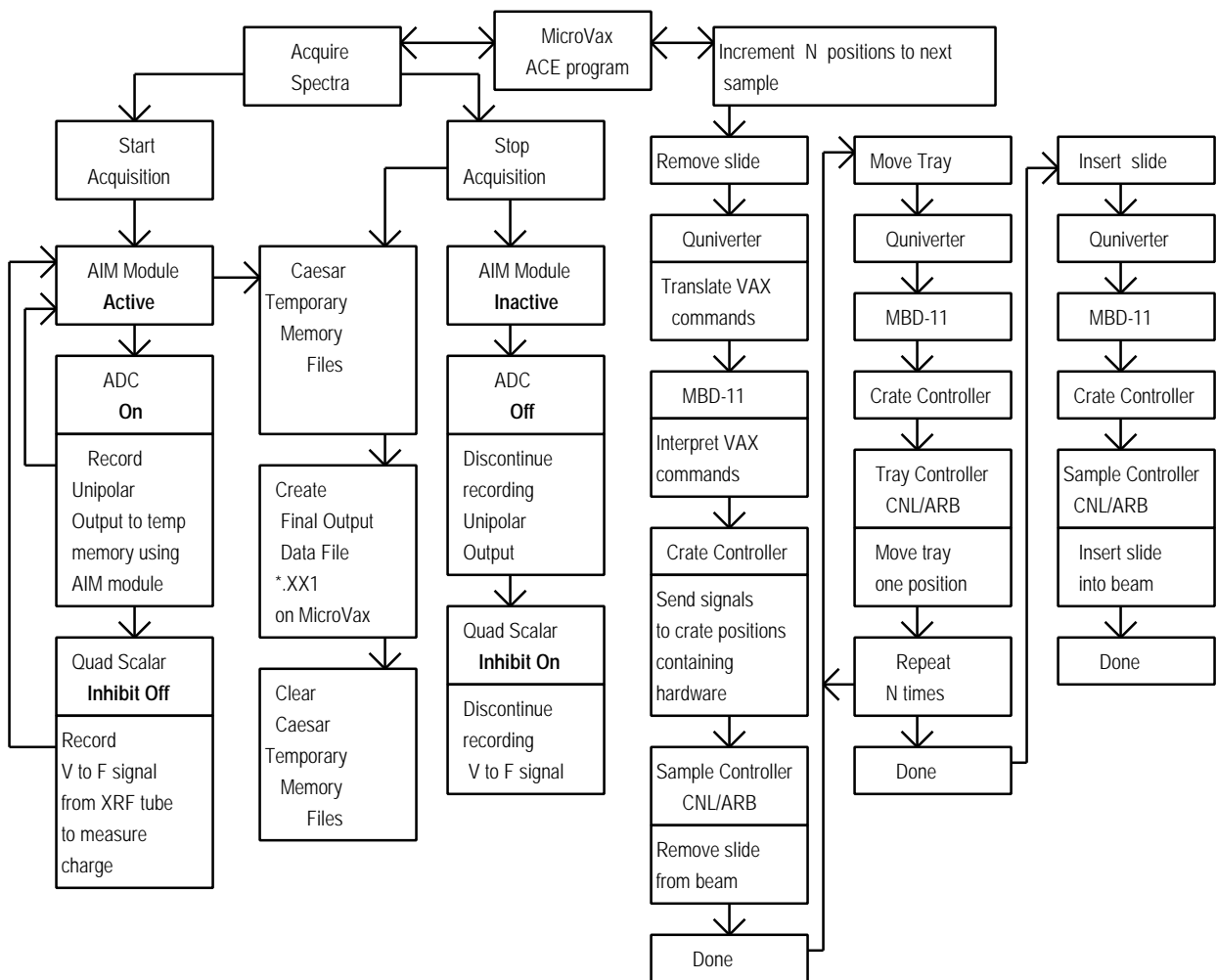


The hardware components for XRF in the computer room are controlled by the ACE program. A schematic of the data acquisition process follows below in Figure 8.

The components shown in Figure 7 are:

1. MicroVAX - Caesar - Runs data acquisition program ACE and data processing program RACE.
2. ADC ND575 - Analog to Digital Converter Nuclear Data-575, the multi-channel analyzer that processes the raw spectrum produced by the XRF system into digital format.
3. AIM - acquisition interface module; connects the ADC to the local Ethernet.
4. Ethernet Transceiver - Ethernet connection to Caesar.
5. Quad Scalar - When inhibit is off, records the cumulative charge to which the sample is exposed. When inhibit is switched on, by ACE, stops counting charge accumulation.
6. MBD 11 - Data connection to Caesar for hardware components in Module N.
7. Quniverter - Interfaces hardware Unibus device with Qbus device for Caesar.
8. Patch panels - Connection panels.

Figure 8 XRF System Control Schematic



4.3.2 ADC Settings

Set the ADC (Nuclear Data-575) to match the values recorded in Table 2.

Table 2 ADC / XRF (ND-575) Settings

CONV. GAIN	512
COIN/ANTI	OFF
ACQ./STRB	ACQ.
SIGNAL	XRF UNI OUT
OUTPUT	ADC 1 of ND-575 Ethernet Acquisition Server 284

4.3.3 Manual Slide Control

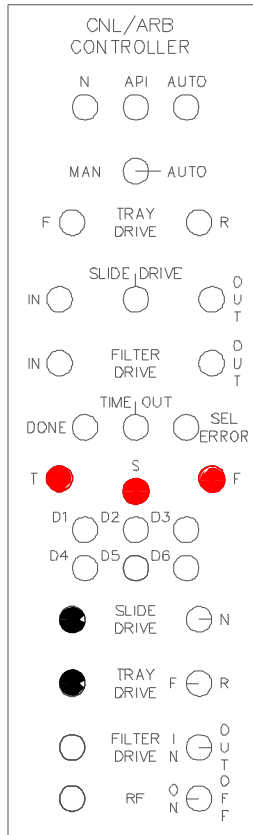
The slide changer can be operated in one of three ways:

1. Computer control using the ACE Program (See section 4.4 Data Acquisition)
2. Manual control using the Slide controller card located in the XRF laboratory (see section 4.2.5.7).
3. Manual control using the CNL/ARB controller located in the computer room, described below.

In the computer room, the manual override controls are located on the CNL/ARB controller module in the electronics rack labeled Module N. A diagram of the CNL/ARB CONTROLLER is displayed in Figure 10. The indicator lights, represented by white circles, are used by the acquisition control program, ACE, to indicate the current status of the slide and tray drives. The meaning of each indicator light is as follows:

- **TRAY DRIVE:**
F indicator lit; tray is moving forward (down) and the tray drive is activated.
R indicator lit; tray is moving reverse (up) and the tray drive is activated.
- **SLIDE DRIVE:**
IN indicator lit, slide is in the X-ray beam.
OUT indicator lit, slide is in the tray.
Center indicator under SLIDE DRIVE lit; the slide is currently moving, or is stuck.
- **FILTER DRIVE:** not used.
- **DONE:** the controller is ready for a new command
- **TIME OUT:** a command was attempted, but did not occur in the allotted time span, and was terminated.
- **SEL ERROR:** inappropriate or conflicting commands were given. No command will be performed.

Figure 10 CNL/ARB Controller



The following procedures describe the operation of the CNL/ARB CONTROLLER under manual control. Refer to Figure 10.

1. Verify that ACE is in MANUAL mode, or is not running. If ACE is in AUTO mode, press the number pad key designated ABO to abort the current run and return to MANUAL mode (the coding for the keys on the number pad is displayed on the ACE screen).
2. Flip the switch on the CNL/ARB CONTROLLER from the AUTO to the MAN position to gain manual control.
3. To remove a slide from the X-ray beam and replace it in the tray:
 - a) If the TV screen and the indicator light for the slide drive show the slide is in the “OUT” position, the slide is in the tray, not in the X-ray beam.
 - b) If the slide appears to be in place on the TV screen, but the indicator light for the slide drive remains in the center position, the slide is stuck somewhere between the tray and the X-ray beam position. To move the slide to the out position, see step c part i.
 - c) If the slide is in the “IN” position, push the black button labeled Slide Drive on the lower section of the controller. The Slide Drive should activate, remove the slide, and light the indicator for the "OUT" position.

- i) If the slide drive light moves to the center indicator, but the slide does not move, or stops moving before reaching the OUT position, push to Slide Drive toggle switch to the "N" position and try step c) again.
 - ii) If the slide drive indicator light remains in the "IN" or center positions, but the slide drive is not moving on the TV monitor, simultaneously press the red button marked "S" and the black Slide Drive button.
 - iii) If this does not remedy the problem, the slide must be moved manually using the slide changer card in the XRF laboratory as described in section 4.2.5.7.

- 4. To move a slide from the tray and place it in the X-ray beam:
 - a) If the TV screen and the indicator light for the slide drive show the slide is "IN", the slide is already in the X-ray beam, not in the tray.
 - b) If the slide drive indicator light moves to the center position and remains on, the slide is stuck somewhere between the tray and the X-ray beam position. To move the slide to the in position, see step c part i.
 - c) If the slide is in the "OUT" position, push the black button labeled Slide Drive on the lower section of the controller. The Slide Drive should activate, move the slide, and light the slide drive indicator for the "IN" position.
 - i) If the center indicator lights and remains lit, push the Slide Drive toggle switch to the "N" position and try step c) again.
 - ii) If the slide drive indicator light continues to read "OUT" or remains in the center position, simultaneously press the red button marked "S" and the black Slide Drive button to override the slide drive.
 - iii) If the slide drive indicator light still indicates "OUT" or is at the center position, the tray drive may not be in position. See step 5 for instructions on moving the tray drive.
 - iv) If the above steps do not remedy the problem, the slide and tray should be moved manually to the correct positions using the slide changer card in the XRF laboratory as described in section 4.2.5.7.

- 5. To move the tray to access another slide:
 - a) Verify that the slide is "OUT" by viewing the monitor screen showing the XRF analysis position, and by checking the tray drive indicator lights on the CNL/ARB controller.
 - b) Toggle the Tray Drive switch on the lower section of the controller to the direction you wish to move the tray (F for forward, R for reverse).
 - c) Press and release the black Tray Drive button on the lower section of the controller. Each time the indicator lights flash, the tray has moved one slide position in the direction indicated in part b). The tray has stopped moving when the DONE indicator light is lit.

- d) Verify that the tray moved by inserting a slide into the beam, following the procedures of step 4. View the slide on the monitor. If it is the same slide as before the operator attempted to move the tray, the slide drive did not function.
 - i) If the drive did not move, return the slide to the tray using the procedures of step 3, then simultaneously push the red button marked "T" and the black Tray Drive button to override the tray motion system..
 - ii) If the tray drive refuses to move after attempting step i.), you must move it manually in the XRF laboratory using the slide changer card as described in section 4.2.5.7.

- 6. When you have the correct slide in position, toggle the switch on the controller back to "AUTO" mode and continue normally.

4.4 Data Acquisition (Program ACEX)

4.4.1 Summary

The data acquisition program, ACEX, both acquires the x-ray spectra and controls the XRF analysis system. (ACEX is a variation of ACE, Acquisition of Composition from Elements, designed for the XRF system.) System control involves slide and tray position control, and control of analysis duration and sample identification. ACEX was designed to allow manual and automatic control of analysis parameters, such as slide and tray position or sample duration. Manual control, via keypad switching, allows the operator to instantaneously stop or start analysis, move the slide or tray, or save the collected spectra in a data file. Automatic control is usually provided via an instruction file, called a "trayfile," that indicates which positions have valid samples. In automatic analysis, the operator initially positions the slide and tray, sets the analysis duration, and then enters the appropriate trayfile to control the analysis of all the valid samples in the tray (or trays...trayfiles may contain instructions for analyzing up to ten trays in a sequence).

ACEX automatically writes a file containing the spectrum, the site and sample date for the sample, plus the system parameters of integrated charge, average detector live time, and count rate, following automatic acquisition of a spectrum. (In manual control, the operator can request that ACEX write a similar file.)

During data acquisition, whether in automatic or manual mode, ACEX monitors and displays quality control information such as the accumulated charge and the live time and count rate of the detector. The accumulated charge depends on the number of incident x-rays that pass through the sample. For XRF the number of incident x-rays is proportional to the integrated charge of the tube current, for a given tube current. This relationship changes when the tube current changes. Since all ambient samples are run at a constant tube current, this has negligible effect for these samples. However, a lower tube current is needed to analyze the standards. To correct for this a calibration curve is determined at the time of system calibration that permits an accurate determination of the flux of incident x-rays on the sample from the tube current.

The ACEX program is used to automate the data collection process by controlling the slide changer, collecting spectra, merging spectra and identification information into analysis data files, and clearing the system for further analysis. The ACEX program has several components that must be working in order to successfully acquire data for the XRF system.

Hardware elements of the system include the following:

MicroVAX	- Computer (CAESAR)
AIM	- Acquisition Interface Module
ND575	- Analog to Digital Converter (ADC)
CAMAC CNL/ARB CONTROLLER	- Controller (CTRLR) for slides and trays
CAMAC JORWAY	- Model 84 Quad Scaler (QS)
Video display terminal (VDT)	- Computer (CAESAR)

Software element of the acquisition system are included in the program:

ACEX.EXE

4.4.2 Logging On and Logging Off of ACEX

The ACEX program must be run from a terminal. The program requires that several software components be installed and ready for execution before it can continue. The ACEX program uses Ethernet connections to communicate with the ADC. The LOGIN file ensures logical variables are set for the acquisition system, and checks the status of the ADC channels for data collection. The ACEX program initializes the ND575, sends start/stop/erase commands, and transfers the data. In the following section, commands to be typed into the computer will be italicized, material printed on the computer screen will be in bold face type, and descriptions and instructions will be in normal type. Note that <CR> is the carriage return or enter key. The ACEX program is started by logging on to a terminal.

```
Welcome to CAESAR..... Authorized use only!  
Username:  
Type: ACE <CR>  
Password:  
Type: ACE <CR>
```

Welcome - Crocker Nuclear Laboratory LAN - Caesar

Last interactive login on ...

Last non-interactive login on ...

...

\$XRF <CR>

\$ Do you wish to recreate the MCA displays Y or N> YES

Now the screen is erased and the display created, as shown in Figure 11.

To get out of the ACEX program at any time, press the following keys simultaneously:

<CTRL> <Z >

\$ ACE exiting

4.4.3 ACEX Keypad Commands

The box labeled KEYPAD on the right side of the screen in Figure 11 contains the terminal keyboard number pad mapping scheme. All the number pad keys are redefined by the ACEX program to provide software interrupts to the acquisition program ACEX. When the user strikes a number pad key, the interrupt is queued to the ACEX program and will be serviced when other input or output is completed. It is possible to queue multiple commands, but this should be done with caution.

An expanded view of the keypad box in Figure 11, follows in Figure 12. In Figure 12, the top row in each field is the code shown on the ACEX screen, the second row is the number pad key to which the code has been mapped, and the third row is the function for

which the code is an abbreviation. Pressing a number pad key while the ACEX program is running will activate the command mapped to the key pressed. Some commands will be instantly executed while others will request further information. The requests will appear in the command window below the list of options. Use the regular keyboard to enter requested information. Details and examples will be given later.

Figure 11 ACEX Control Program Screen

Date: 24-Sep-96		XRF		Time: 11:39:46																					
Run No :	Ctrlr Stat:	<table border="1"> <tr> <th colspan="4">KEYPAD</th> </tr> <tr> <td>ENT</td> <td>SLF</td> <td>SLR</td> <td>ABO</td> </tr> <tr> <td>ACQ</td> <td>STP</td> <td>REC</td> <td>CHG</td> </tr> <tr> <td>RNO</td> <td>CNV</td> <td>T&S</td> <td>ERA</td> </tr> <tr> <td>TIM</td> <td>INT</td> <td>SCR</td> <td></td> </tr> </table>				KEYPAD				ENT	SLF	SLR	ABO	ACQ	STP	REC	CHG	RNO	CNV	T&S	ERA	TIM	INT	SCR	
KEYPAD																									
ENT	SLF					SLR	ABO																		
ACQ	STP					REC	CHG																		
RNO	CNV					T&S	ERA																		
TIM	INT					SCR																			
Trayfile:	VAX - MCA :																								
Position:	Acq Start :																								
Profile :	Preset Tim:																								
Sample #:	Elapsed :																								
Cnv Factr:	Min current																								
XRF Reno:																									
Charge :																									
Tray name:																									
Mode: AUTO			Command:																						
Run	Master	Pos	Profile Id	Convf	Table	Charge	Sample desc																		

Figure 12 ACEX Program Keypad Mapping

ENT PF1 Enter Auto	SLF PF2 Slide Forward	SLR PF3 Slide Reverse	ABO PF4 Abort Auto
ACQ 7 Start Acquisition	STP 8 stop	REC 9 Record Date	CHG - Minimum Charge
RNO 4 Renormilization	CNV 5 Conv. Factor	T & S 6 Tray and Slide	ERA + Erase Data
TIM 1 Enter Pre-Set Time	INT 2 Change Intg Scale	SCR 3 Re-draw Screen	ENTER
0		.	

The current definitions for the codes used in the Keypad display are listed in order below:

ENT = Enter automatic mode. This initiates the ACEX program for automated sampling. The ACEX program will request a command file, called a trayfile, containing

information on which slides should be analyzed and which position is the last position in the tray. The trayfiles are described in section 4.4.5. The ACEX program will then automatically run each valid slide in the command file for the duration of time listed on the ACEX program screen as Preset Time.

SLF = Move to the slide located n positions in the forward direction (for use in MANUAL mode). You will be prompted for the number of positions, n, to move the tray. Once n is entered, the current slide will be removed, the tray will increment forward n positions, and the slide in the position at which the tray stops will be moved into the XRF beam.

SLR = Move to the slide located n positions in the reverse direction (for use in MANUAL mode). You will be prompted for the number of positions, n, to move the tray. Once n is entered, the current slide will be removed, the tray will move back n positions, and the slide in the position at which the tray stops will be moved into the XRF beam.

ABO = Abort the automatic mode. ACE will discontinue acquisition, clear the temporary data storage locations, and return to Manual mode.

ACQ = Acquire data (for use in MANUAL mode). Press this button to begin acquisition of data on the current slide. The preset time is not in effect in this mode. You may acquire for as long as you want. The counterpart to this command is STP which stops acquisition.

STP = Stop data acquisition (for use in MANUAL mode). This command allows the user to stop the ND575 from acquiring data.

REC = Record data (for use in MANUAL mode). This allows the user to save the current data for subsequent to analysis by RACE.

SCR = Redraws the screen.

RNO = Enter renormalization factor for the XRF detector. The number entered is renormalization * 1000 and must be in the range of 100 to 2000. If the entered number is out of range it will be rejected, and the user will be prompted to enter a value within range.

CNV = Enter conversion factor (for use in MANUAL mode). This allows the user to enter a conversion factor for analysis being done using ACQ. (In the auto mode the conversion factor is extracted from the trayfile.)

T&S = Enter tray and slide numbers. This function allows the user to enter a tray number and a position to be added to a manually collected output data file. It is used with the ACQ function.

ERA = Erase the spectra in the ND575 and clear the quad scaler (for use in MANUAL mode). This function allows the user to clear all data in the ND575, and zeroes the accumulated charge measurement on the quad scalar.

TIM = Enter the preset time (for use in AUTO mode). This function allows the user to change the preset time for which the samples will be analyzed.

INT = Enter the integrator scale factor (not used during XRF analysis).

4.4.4 ACEX Usage Examples

1. Manual data acquisition.

Move the tray forward 5 positions.

Start the acquisition.

Stop the acquisition at the appropriate elapsed time.

Record the data in the computer.

Erase the data in the Multi-Channel Analyzer.

Move to the next slide to be analyzed and begin the process again.

2. Automatic data acquisition

Set analysis time to 700 seconds

Start automatic data acquisition for SNPA1 in B96 quarter

If necessary to stop acquisition, then

Abort automatic analysis

The keystrokes to perform the analysis above are shown below. Note, the commands in italics are requests for more information by the ACEX program, but the commands in boldface type must be entered by the user.

1. Manual Data Acquisition

SLF (slide forward), *positions forward: 5* <CR>

ACQ (acquire)

STP (stop acquisition)

REC (record data)

ERA (erase data)

SLF (slide forward), *positions forward: 1* <CR>

2. Automated Data Acquisition

ENT (enter AUTO mode), *tray name:SNPA1A1T.B96* <CR>

position: 1 <CR>

TIM (enter preset time), *preset time: 700* <CR>

If necessary to stop acquisition, then use

ABO (abort AUTO mode), *aborting auto mode*

4.4.5 Trayfiles

The automatic mode of ACE is guided by the presence of a trayfile. The trayfile is a computer file which represents the order of samples for analysis, and contains additional information about the samples in the tray. This information is necessary in order to perform a complete analysis of the sample. When ACE is set to begin AUTO mode it checks for the presence of a trayfile. If the trayfile is present under the name given by the operator, the code requests the operator enter the current positioning the tray. Once the position is entered, ACEX uses the trayfile as a guide for which tray positions contain slides for analysis. The data for each particular slide is read in turn as the tray is analyzed. The information that can be provided in the tray file is:

- A. Sample position number. The sample position is a number generated to aid in organizing the trayfile (as a trayfile may be constructed to sequentially run several individual trays).
- B. Sample conversion factor. This field may contain the actual conversion factor (derived below), or one of three default settings; 0, -1, and 1000. The conversion factor relates the filter loading in $\mu\text{g}/\text{cm}^2$ to the aerosol concentration of the sampled air in $\mu\text{g}/\text{m}^3$.
 - Conversion factor = Mask * $\left(\frac{1000}{ET * Flow} \right)$
Mask (mask size) [cm^2],
ET (elapsed time) [minutes],
Flow (Flow rate) [liters/minute ambient]
 - Conversion factor = 0 indicates the position is not to be analyzed; is a skip position command.
 - Conversion factor = -1 indicates the current position is the end of the analysis tray; is a stop automatic acquisition command.
 - Conversion factor = 1000 indicates a normal sample. It is used as a default value during analysis before the conversion factors have been compiled and verified.
- C. Sample identification number. Position of the identified slide in it's slide tray, except for filter blanks. For blanks, the sample identifier is set to 0, no matter what the tray position. Zero as a sample identification number has a special significance in the analysis programs; namely the data is subtracted from subsequent samples as a representation of a blank substrate with no deposit.
- D. Profile number. The profile number is the analysis quarter name converted to decimal code.

Analysis Quarter	ASCII code	Decimal Code
A: March - May	A	65
B: June - August	B	66
C: September -November	C	67
D: December - February	D	68

- E. Sample Description. IMPROVE network samples use this field for filter mask size; the area, in cm^2 , of the aerosol deposit on a filter. However, it can be used for ASCII text.

Filter Mask	Mask Area (cm^2)
MO	3.51
M1	2.2
M2	1.1

- F. Matrix correction table name. XRF data correction table correcting for the 'shadowing effect' of particles on filters. Correction tables were derived in the 1970's through experimentation with a variety of substrates and deposits to derive values for expected filter and loading types.
- G. Profile description. Location for putting in the study name, source, etc. of the associated filter.
- H. Unused Fields. Each 0 represents an unused field. The unused fields, in order, are sample mass, error in mass, laser value (for B_{abs}), laser error, beta gauge value, and error in the beta gauge value. These fields are no longer included in the IMPROVE trayfiles.
- I. Site name. The site name is a five character code representing a site. The first four characters are an abbreviation of the site name. The fifth character is a number.
- J. Filter type. The filter type is A1 or D1. A1 indicates a Teflon filter with a sample deposit consisting of particles $\text{PM}_{2.5}$ particles. D1 indicates a Teflon filter with a sample deposit consisting of PM_{10} particles.
- K. Sample date. The sample date is the date upon which the filter deposit was collected.
- L. Start time. The start time is when the collection of the filter deposit began, using a 24 hour clock.
- M. Elapsed time. The elapsed time is the duration of the sample collection period.
- N. Flow rate. The flow rate for air through the filter during sampling is recorded in liters per minute of ambient air.

O. Filter status. The filter status, generally NM or normal, indicates whether a filter represents a valid sample. The conversion constant controls whether the filter will be automatically analyzed. The status merely provides a visual check of scheduled analyses.

For the IMPROVE network, the Spectroscopist generally creates the trayfiles. Trayfiles are named according to the sampling site, filter type, and analysis quarter. The file names can contain from 1 to 9 characters, with a three character extension. The IMPROVE network files generally contain 8 digits with a three digit extension. The file SNPA1A1T.B96, for example, is for the Snoqualamie Pass site, for module A Teflon filters that were collected during the B96 quarter.

The minimum trayfile must include the first two items (A,B) in the above list. Items left out of the trayfile will be defaulted or incremented automatically by the program. Trayfiles are ended by inserting line containing a position number and -1 as the conversion factor. An example of a minimum trayfile is:

A	B	I	N
1	12345	54321	23.2
20	-1		

The above trayfile represents a physical tray with 19 samples. All samples will be analyzed with the same conversion factor, 12345. The sample position and sample identifier are the same and each will be incremented automatically until 19. There is no sample description so all samples will be described automatically with the word SAMPLE and the identifier number. There is no matrix correction table name so RACE will not perform matrix correction effects. There is no profile description so the profile will be described automatically with the profile number. There is no mass, laser or beta values so they will be zeroed in the data. The filter type, start time, elapsed time, sample date, and filter status are not recorded. However, the site name is listed as 54321, and the flow rate is shown as 23.2 liters per minute.

If the user wants control of some more of the analysis a better example of a trayfile might be:

```
1 12345 0 'BLANK' 'SFU2' 'GRAND CANYON FOR 1ST QUARTER 1988' 54321
2 12345 1 'FIRST DAY' 'SFU2' 54321
20 -1
```

In this example, the first row (filter position) contains A,B,C,E,F,G,I. The sample identifier, C, for position 1 is zero, indicating the filter is a blank. The second filter position, the first real sample, contains A,B,C,E,F, and I. For this trayfile, the blank and first real sample will have sample descriptions; the information in single quotes will be appended to the output data. However, the analyses for the samples in positions three through nineteen will be identified with the same trailer as position 2. This is because the trayfile will not end until it sees a -1 as a sample identifier. So, ACEX will continue

incrementing through the tray, analyzing one position at a time, using the last trailer as a template for the current analysis trailer.

For the IMPROVE network analyses, the trayfiles generally appear as shown below in Table 3. The columns are labeled to reflect the list derived earlier of data that can be incorporated into a trayfile.

Table 3 Sample IMPROVE Trayfile

A	B	C	D	E	F	G	H	I	J	K	L	M	N	O
1	9994	1	66	'M0'	'FINE'	''	0 0 0 0 0 0	'SAGO1'	'A1'	'06/01/96'	0000	24.00	24.5	'NM'
2	10035	2	66	'M0'	'FINE'	''	0 0 0 0 0 0	'SAGO1'	'A1'	'06/05/96'	0000	24.00	24.6	'NM'
3	9872	3	66	'M0'	'FINE'	''	0 0 0 0 0 0	'SAGO1'	'A1'	'06/08/96'	0000	24.00	24.2	'NM'
4	9954	4	66	'M0'	'FINE'	''	0 0 0 0 0 0	'SAGO1'	'A1'	'06/12/96'	0000	24.00	24.4	'NM'
5	9954	5	66	'M0'	'FINE'	''	0 0 0 0 0 0	'SAGO1'	'A1'	'06/15/96'	0000	24.00	24.4	'NM'
6	9627	6	66	'M0'	'FINE'	''	0 0 0 0 0 0	'SAGO1'	'A1'	'06/19/96'	0000	24.00	23.6	'NM'

4.5 Spectral Analysis (Program RACE)

4.5.1 Summary

The x-ray spectra produced during XRF are analyzed by the program RACE. Prior to analysis of filter samples, the following must be provided:

1. System blank. X-ray spectral analysis requires a system blank to estimate the incremental addition to the spectrum due to the presence of the filter substrate. The system blank is derived by analyzing several clean filters, 'blanks', at the beginning of an analytical session. The cleanest filter is selected to become the system blank. The spectrum from the system blank is smoothed and stored on disk for subtraction from the spectra of subsequent analyses.
2. XRF system calibration. In order to identify the peaks it is necessary to provide an energy calibration between the energy of the x-ray line and the spectral channel. This is done at the beginning of the analytical session using the thin film standards, and the reanalysis filters. The standards are analyzed, the peak locations are noted, and the MCA channel and x-ray energy of each elemental peaks is entered into a calibration table. The x-ray energies for each element are looked up in standard x-ray tables. Four elements are generally used. For an in depth description of the process, see TI 301A.
3. Cross section table. To calculation the elemental concentrations on filters using XRF requires knowledge of the relationship between the area under a peak and the elemental concentration. This information is contained in a cross section table, which gives the line identification (e.g. Fe $K\alpha$), the line energy, the product of cross section and detector efficiency, and the atomic weight of the element. The cross section-efficiency numbers for this table are determined during system calibration, by analyzing a series of 30 single element, double element, and multi-element thin film standard foils from a commercial vendor. In order to determine the cross sections for elements not included in the standards, and to verify that a given standard is correct, the cross sections are plotted against the atomic number. The resulting smooth curve allows the calculation of cross sections for non-measured species, and reduces the uncertainty for a given line to much less than the 5% quoted for a given foil. This system calibration is performed whenever the system is reconfigured, including following detector replacement. It is also performed if the calibration checks made every quarter at the beginning of each analytical session indicates that the system has changed. The system calibrations for derivation of cross section tables are conducted by the Spectroscopist under the direct supervision of the Quality Assurance Manager. See TI 301A for more information.

The steps followed by RACE in performing elemental analysis are:

1. Remove most of the spectral background by subtracting the system blank. This removes the portion of the spectrum due only to the presence of the filter substrate. To achieve the best fit, the system blank is floated by a multiplicative factor until a preset number of

channels are exceeded. The operator can adjust the factor by changing the number of channels required.

2. Remove any remaining background spectrum by subtracting a smooth function calculated as the lesser of the counts in a channel and the average counts per channel over a specified width. To change this fit, the operator can adjust the width and the number of iterations of the process.
3. Use a peak search routine to identify the peaks and valleys by comparing the shape of the spectrum near a given channel to what would be expected if there were a peak at that channel.
4. Fit each peak to one or more Gaussians. Using the centroid of the peak and the energy calibration, determine the energy of the peak. Identify the line using a "cross section table." With the area of the Gaussian, the "cross section" from the table, and the beam charge and detector live time for this analysis, calculate the concentration in ng/cm² of the element on the filter. For peaks close to two lines, calculate the concentration for each line as if it were the only line.
5. Determine the uncertainty of the concentration from the uncertainty in the Gaussian area. For a well-shaped peak this is the standard Poisson value based on the number of counts in the peak and background. For poorly shaped peaks the uncertainty can be somewhat larger. The uncertainty is expressed as ng/cm².
6. Calculate the minimum detectable limits for all elements in the cross section table. Use 3.29 times the square root of the background counts under the region that would have been occupied by a peak of normal width. Minimum detectable limits are expressed in ng/cm².
7. Resolve the interferences between the various lines, using preset criteria. The most common interference is when the β line of one element overlies the α of the next element. The concentration for the α line of the next element can be determined by subtracting the contribution of the lighter element using its α value. The interference between Pb L α and As K α is resolved using the β lines of both.

The RACE program for data processing requires a VAX/VMS micro-station, a graphics terminal, and a printer. RACE must be installed and active before it can analyze data. ACEX and RACE are often run simultaneously during analysis to allow the operator to view the initial analysis of the collected spectra for quality control.

4.5.2 Logging onto RACE

In the following section, commands to be typed into the computer will be italicized, material printed on the computer screen will be in bold face type, and descriptions and instructions will be in normal type. The RACE program is started by logging on to the MicroVAX console

<CR>

Welcome to CAESAR VAX/VMS V5.4-2.....Authorized use only!

Username:

ACE <CR>

Password:

ACE <CR>)

Welcome - Crocker Nuclear Laboratory LAN - Caesar - VAX/VMS V5.4-2

Last interactive login on ...

Last non-interactive login on ...

...

\$CD RACE\$COM <CR>

Moves the user to the RACE directory, *asg.com.race*, which contains all the data, default parameters, and pointers for each analysis run.

asg.com.race->@STANDSET <CR>

This will set the defaults for RACE to the current (or last) settings used in the XRF analysis run. Defaults include data storage locations for input and output files, and system calibrations. To reprocess an archived analysis run instead of the current analysis run, follow the procedures in section A, below.

A. To reprocess an archived analysis run, type, at the *asg.com.race* prompt,

asg.com.race->DIR <CR>

This will display all the command files for setting the defaults for RACE. The files, other than *STANDSET.COM* will be named *RACEqtr.COM*, where *qtr* is the quarter the analyzed data was collected in. Examples of *qtr* are *A96* for March through May of 1996, *B96* for June through August of 1996, *C96* for September through November for 1996, and *D96* for December of 1996 through February of 1997. The user will enter the command file for the quarter to be emulated. For *A96* analysis, as an example, the user would enter the following:

asg.com.race->@RACEA96 <CR>

The user may start the RACE program at any prompt. Here, as an example, RACE is started in the *asg.race* directory.

asg.race->VAXRACE

This will start the interactive RACE program on the terminal or console being used.

**WARNING: NO CALIBRATION TABLE
RACE Exiting**

asg.src.race->

If the warning above appears, there is no calibration table for RACE in the default directory. RACE will not function until a calibration table is installed in the appropriate directory (specified by the default program...usually STANDSET during analysis).

Archived quarters should have calibration tables; if a calibration table is missing for an archived quarter, contact the quality assurance manager for assistance.

If the current analysis does not have a calibration table, contact the quality assurance manager or the Spectroscopist for assistance.

If RACE is installed, and the input files are present, the following will appear on the screen:

First Run to Analyze (^Z to Exit):

Pressing the <CTRL> and <Z> keys simultaneously, or pressing the <ESC> key twice will exit the RACE program and return the user to the asg.src.race cursor.

To continue in RACE, the number of the first run to be analyzed, for example 23142, must be entered. Then,

1. RACE will look for the ACEX output file labeled 23142.XX1 where XX1 is the file extension indicating the file contains XRF data.
2. When RACE finds the file 23142, it will look at the file extension for that run file. If the extension is for XRF, (XX1), RACE will input the XRF analysis default settings.

NOTE: For a given filter, the PIXE1, PIXE2 and PESA files will have the same run numbers, but XRF files will have a different run number. No XRF file in an analysis quarter can have the same run number as any PIXE or PESA file in that quarter or RACE will not execute properly.

3. Assuming the file extension was for XRF, RACE will begin analysis of the input file using the standard defaults for display and output, as listed in section 4.5.3.
4. With the standard settings (default), RACE will display, for each run analyzed, the spectral peaks found, the concentrations (in ng/m^3) and error (in ng/m^3) for each species found, and the correction factor. A sample output is shown in Figure 13.
5. Following the reporting of the peaks found and elemental concentrations, RACE will list the calibration and matrix table factors used to derive the output data. These data, seen at the bottom of Figure 13, are described in section 4.5.4.

Figure 13 XRF RACE Analysis Sample Output

```

UC DAVIS  XRF-1 ANALYSIS  RUN 13156 XX1  FILE 66  ITEM 12  27-SEP-96
                                PORE1A1 07/10/96

FILPRO=PORE1A1B.96X
CONCENTRATIONS OBTAINED BY DIVIDING AREAL DENSITIES BY 14.727 M**3/CM**2
MATRIX CORRECTIONS USING TABLE FINE
UNCERTAINTIES ARE STATISTICAL PLUS A 5% OVERALL UNCERTAINTY, ADDED QUADRATICALLY
ELEMENT          NANOGRAMS PER M**3      CORRECTION
1      S      K      496.03  ±  27.07      1.024
2      K      K      22.23   ±  1.64      1.031
3      CA     KA      20.87   ±  1.23      1.027
           KB      23.59   ±  2.55      1.027
4      TI     KA      0.68    ±  0.11      1.020
5      V      KA      1.72    ±  0.16      1.006
6      MN     JA      0.26    ±  0.04      1.005
7      FE     KA      3.33    ±  0.20      1.013
           KB      3.29    ±  0.33      1.013
8      NI     KA      0.42    ±  0.04      1.004
9      ZN     KA      0.36    ±  0.03      1.003
           KB      0.49    ±  0.11      1.003
10     PB     L       0.32    ±  0.03      1.003
           LB      0.41    ±  0.13      1.003
11     SE     KA      0.20    ±  0.02      1.000
           KB      1.16    ±  0.36      1.000
12     BR     KA      1.18    ±  0.07      1.002
           KB      1.33    ±  0.15      1.002
13     SA     KA      0.36    ±  0.03      1.000
  
```

```

Parameters from 27-SEP-96 run 13156
AX= 0.8979242 E+00 , BX= 0.3767027 E-01
KOVER NTHICK JITER WIDTH
1      100    17      7
  
```

4.5.3 Setting RACE Analysis Parameters

Once RACE has imported the default settings, RACE will begin sequential analysis of the data in each analysis run file. The default analysis parameters, shown in the Analysis Parameter Input screen in Figure 14, will be applied to each run to be analyzed. To change the analysis parameters, press the PF4 key. NOTE: Before pressing the PF4 key to access the parameter input screen, always make sure the program is either analyzing, printing a list of elements, or printing a spectrum on the screen. Never press PF4 when the program is asking a question as this will cause RACE to abruptly discontinue the output file, and exit. After pressing the PF4 key, the screen is erased and a new image appears, as shown in Figure 14.

Figure 14 RACE Analysis Parameter Input Screen

Analysis Parameter Input				(1792)
(1)	CHECK BLANK <u>F</u> LOAT	OFF	(2)	CHECK <u>B</u> ACKGROUND FIT OFF
(3)	CHECK THE PEAK <u>W</u> IDTH	OFF	(4)	BEGIN <u>N</u> EW SEQUENCE OFF
(5)	SQUARE ROOT <u>T</u> PLOT DATA	OFF	(6)	WRITE <u>A</u> LL FULL OUTPUT OFF
(7)	WRITE <u>R</u> EDUCED OUTPUT	OFF	(8)	ENTER NEW <u>C</u> ALIBRATION OFF
(9)	NO AUTO <u>O</u> RECALIBRATION	ON	(10)	NO PREF FOR <u>P</u> B OVER AS ON
(11)	NO GRAPHICS <u>D</u> ISPLAY	ON	(12)	<u>M</u> INIMUM DISPLAY OUTPUT OFF

* Enter the switch letter to be toggled : → Xit Parameter Input Screen
 (PF4 to exit VAXRACE)

The screen in Figure 14 represents a switchboard. Each option can be either On or OFF. The default setting has all the switches off except for O, P and D (switches 9, 10, and 11) To toggle a switch, press the highlighted letter for the desired operation. To toggle switch 10, for example, press P. Each option influences the final data output; definitions for the options follow.

Toggle	Toggle Switch Label	Switch Activity
F	Check Blank Float:	Enables you to change the blank subtraction.
B	Check Background Fit:	Enables you to change background fit
W	Check Peak Width:	Enables you to change accepted peak width
N	Begin new sequence:	Enables you to start analysis from another run
T	Square Root Plot Data:	Plot data as square root plots
A	Write all full output:	Informs computer to print all data on samples
R	Write reduced output:	Informs printer to print reduced data
C	Enter new calibration:	Enables input of energy calibration data
O	No Auto re-calibration:	Will not re-calibrate automatically
P	No pref. for Pb over As:	Computer will treat both equally when found
D	No graphics display:	No spectral plots to screen
M	Minimum display output	Does not output data or plots to screen
X	Exit back to RACE:	Get back to RACE exactly where left off

Enter the switch letter to be toggled:..... Self explanatory

If a file is analyzed by RACE with the wrong parameters set, the file can be reanalyzed. However, RACE will append the earlier output file with the new information, rather than writing over the old file. To avoid creating large, confusing output files, the parameters are generally set before the first analysis is run. Since RACE works rapidly, if the operator entered a valid run number as the first run to analyze, RACE would nearly have

completed analysis before the operator could press the PF4 key to change the parameters. Thus, the first file would have to be reanalyzed following the setting of the parameters. To avoid reanalyzing the first file, the operator enters a dummy run number, 99999. While RACE is searching for the non-existent input file for the dummy run number, there is time to press the PF4 key and change the parameters, including the start new sequence parameter. A sample RACE analysis start-up including changing the parameters follows.

asg.src.race->RUN VAXRACE

First Run to Analyze (^Z to Exit):99999

Waiting for run 99999 (Hit PF4 for parameters) <PF4>

Analysis Parameter Input				(1792)
(1)	CHECK BLANK <u>F</u> LOAT	OFF	(2)	CHECK <u>B</u> ACKGROUND FIT OFF
(3)	CHECK THE PEAK <u>W</u> IDTH	OFF	(4)	BEGIN <u>N</u> EW SEQUENCE OFF
(5)	SQUARE ROOT <u>P</u> LOT DATA	OFF	(6)	WRITE <u>A</u> LL FULL OUTPUT OFF
(7)	WRITE <u>R</u> EDUCED OUTPUT	OFF	(8)	ENTER NEW <u>C</u> ALIBRATION OFF
(9)	NO AUTO <u>R</u> ECALIBRATION	ON	(10)	NO PREF FOR <u>P</u> B OVER AS ON
(11)	NO GRAPHICS <u>D</u> ISPLAY	ON	(12)	<u>M</u> INIMUM DISPLAY OUTPUT OFF

*** Enter the switch letter to be toggled :Exit Parameter Input Screen**

.....(PF4 to exit VAXRACE)

When a key representing one of the switches is pressed, the switch status will toggle. For example, pressing D, R, and N will instruct RACE to, in future analyses, display the graphics (spectra), write a shortened version of the output data to the line printer, and to not automatically analyze more than one run. To return to RACE, the operator will press X to exit the input screen. If the first valid analysis is for run 34336, the operator will now enter that run number.

First Run to Analyze (^Z to Exit):34336

The operator should now immediately press the PF4 key (the - key on the number pad), to return to the parameter input screen and turn off the begin new sequence switch by pressing the N key. Finally, exit back to RACE by pressing X to exit the analysis parameter input screen.

If the begin new sequence key is not turned off, after completing the analysis for each run, RACE will request that the operator enter the next run number to be analyzed.

4.5.4 RACE Calibration and Matrix Tables

The parameters displayed at the bottom of Figure 13 are the factors necessary to process spectral data using the RACE program. AX and BX refer to the slope and intercept of the best fit to the calibration equation for the XRF detector relating the MCA channels to the x-ray energies. The calibration is derived in two steps, the coarse fit from the standards tray analysis, and the fine tuning from filter sample reanalysis. KOVER has a value of 1 and represents the percentage that the blank will be allowed to ride over the sample data. NTHICK has a value of 100 and represents the sample substrate thickness. JITER is a correction factor for broad spectrum background radiation from the loading on the filter. Here it involves a smoothing function using 17 iterations. WIDTH has a value of 9 and refers to the minimum width in MCA channels at half a suspected peak's height that it must have before RACE classifies it as a valid elemental species peak. The procedures to derive these factors are as follows.

1. To derive the rough calibration for the XRF system:
 - a) Reset the XRF tube current to 2.6 mA. Analysis of standards requires a lower current. See section 4.2.5.4 for instructions.
 - b) Set the analysis time to 180 seconds per sample using the ACEX key pad (see section 4.4.3).
 - c) Analyze the XRF standards tray containing 17 Micromatter™ thin film standards (Pb, GaAs, CuS, CaF₂, Ti, V, Cr, Fe, Ni, Cu, Zn, GaP, GaAs, Se, CsBr, RbI, SrF₂, Pb) and 2 clean filters (blanks) representative of the filter lot used for IMPROVE aerosol sampling.
 - d) RACE will derive elemental concentrations from the spectral data.
 - i) RACE uses a detector specific cross section table for analysis. A cross section table must be derived for each detector in each system. The derivation and purpose of the table are described in the article "Automatic data acquisition and reduction for elemental analysis of aerosol samples" by J.F.Harrison and R.A.Eldred, published in *Advances In X-Ray Analysis*, Vol 17, Plenum Press, New York, NY.
 - ii) RACE uses a peak search routine to identify the peaks and valleys by comparing the shape of the spectrum near a given channel to what would be expected if there were a peak at that channel.
 - iii) RACE fits each peak in the spectra to one or more Gaussians. Using the centroid of the peak and energy calibration, the energy of the peak is determined. The line is identified using a "cross section table." Using the area of the Gaussian, the "cross section" from the table, the beam charge and detector live time for this analysis, the concentration in ng/cm² is calculated. If the peak is close to two lines, calculations are made for each line as if it were the only line.
 - iv) RACE calculates the uncertainty of the concentration from the uncertainty in the Gaussian area. For a well-shaped peak, this is the standard Poisson value based on the number of counts in the peak

and background. For poorly shaped peaks, the uncertainty can be somewhat larger. This is expressed as ng/cm².

- v) RACE calculates the minimum detectable limits for all elements in the cross section table as 3.29 times the square root of the background counts under the region that would have been occupied by a peak of normal width. This is expressed as ng/cm².
- vi) RACE resolves interferences between the various lines, using preset criteria. The most common is when the β line of one element overlies the α of the next element. The concentration for the α line of the next element can be determined by subtracting the contribution of the lighter element using its α value. The interference between Pb L α and As K α is resolved using the β lines of both.
- e) RACE will report estimated elemental concentrations of the certified species for each standard thin film sample. Record and compare these values with the certified concentrations. Each should be within 10%, or the system is malfunctioning. Use the Standards sheets in the XRF run book containing the certified concentrations to record the measured values and calculate differences.
- f) Press the PF4 key, then press the “A” key to set the input parameters on RACE to produce full output for the Pb, CuS, and Fe standards (see section 4.5.3 for instructions). Exit back to RACE by pressing the “X” key.
- g) Collect the full output sheets from the printer, then use the PF4 key to enter the RACE Input Parameters screen. Press the “A” key to deselect the print full output option, then select the “C” key to enter a new calibration and exit back to RACE by pressing “X”. The full output sheets will resemble the sheet for the CuS standard shown in Figure 15.
- h) RACE will complete the current analysis, then ask

Do you want to enter a 1,2,3, or 4 point calibration?

Enter the number four to specify entry of a four point calibration.

4 <CR>

- i) RACE will place a blinking cursor on the screen and wait for the operator to enter the calibration data. Four rows of data, two fields in each row, with the fields separated by a space must be entered. To determine what data to enter, the operator will review the full output sheets for the Pb, CuS, and Fe standards (see Figure 15 for an example of a full output sheet for the CuS standard).
 - i) The largest concentrations (in the NANOGRAMS PER CM**2 column) refer to the largest peaks. The largest peak (or peaks, in the case of CuS) should correspond to the elemental species by which each standard is labeled.

- ii) Locate the peaks having the highest concentration on each full output form for the standards being used for the calibration (Pb, Cu, S, Fe).
 - iii) For the peaks located in step ii, highlight the channel. This value will be entered into the first field of a row during calibration value entry.
 - iv) For the peaks located in step ii, look up the x-ray energies (energy, in KeV of the Pb L α , Cu k α , S k α , and Fe k α lines). Each value will be entered into the second field of the calibration row containing the corresponding channel data for the peak.
 - v) The first field of data entered for the calibration will contain the data channel for an element peak. The second field will contain the predicted energy, in KeV, of the same peak. Separate the fields with a single space, and press return after entering each row to proceed to the next entry.
 - vi) When all four rows have been entered, RACE will process the data to determine the slope and intercept of the calibration line defined by the points. The slope and intercept, respectively, will be saved by RACE as the AX and BX values in the analysis parameter file.
- j) This completes the rough calibration of the XRF system through RACE.
2. Analyze the filter blanks to determine the portion of the x-ray spectra from samples due solely to the filter media. The blanks are located in the last five positions of the standards tray.
- a) Reset the XRF tube current to 23 mA for normal analysis.
 - b) Use the ACEX keypad to reset the TIM (time) to 900 seconds.
 - c) Use the ACEX keypad to enter a false trayfile name (for Sept 13, 1996, a false trayfile name would be 961309.dat, the date in reverse), and filter position # '0'. This trayfile does not exist. The filter position of zero tells ACEX that this is a blank filter analysis.
 - d) Begin analysis of the blank filter (unused Teflon filter from the same filter lot as those being analyzed). Review the spectral output from the analysis. There should be no significant x-ray peaks other than from argon and the Molybdenum x-ray tube. If significant peaks exist, discontinue analysis of this filter as it may be contaminated.
 - e) Repeat steps c and d until at least two good blanks are found.
 - f) Choose the cleanest blank filter, the filter having the fewest significant spectral peaks, as the blank for the analysis run.
 - g) Record the analysis run number of the selected blank filter on the standards sheet.

3. Perform the fine calibration of the XRF system.
 - a) Reanalyze two trays of filters from IMPROVE sites analyzed during the previous IMPROVE analysis session. The two reanalysis trays generally selected are SHEN1 and CRLA1, representing a moderately heavily loaded site and a lightly loaded site.
 - b) Use the ACEX keypad to reset the TIM (time) to the analysis duration used on the first tray during the previous quarter analysis.
 - c) Adjust the blank float to remove most of the x-rays from the filter substrate by subtracting a system blank (a blank filter spectra).
 - i) On RACE, press the PF4 key to access the Analysis Parameter Input screen. Press the “F” key to check the blank float, the “D” key to turn on the graphics display, the “N” key to begin a new sequence, and the “X” key to exit back to RACE.
 - ii) Begin RACE by entering the run number of the selected filter blank from part 2.
 - iii) When RACE has analyzed the filter blank, press the PF4 key to access the Analysis Parameter Input screen. Press the “N” key to begin a new sequence, and the “X” key to exit back to RACE.
 - iv) Enter the first run number for the reanalysis tray. RACE will recreate the spectra, then superimpose the blank filter spectra. To achieve the best fit, the blank filter spectra is floated by a multiplicative factor until a preset percentage of channels is exceeded. The operator can adjust the factor by changing the percentage of channels exceeded. The default percentage is 1%.
 - v) RACE will display:
BLANK SUBTRACTION: DISPLAY OF RAW DATA AND FLOATED BLANK
 (use SHIFT-VIEW to toggle between screens.)

BLANK * 0.800 BASED ON 1% OF CHANNELS BETWEEN 4 AND 9 KeV ABOVE DATA

ENTER NEW PERCENTAGE (<CR> TO KEEP, -1 FOR BLANK AT 100%)
 - vi) Review the superimposed spectra. The goal is to set the blank so that when it is subtracted from the filter sample spectra, the resulting spectra does not contain any peaks due to the filter itself, or the air between the x-ray tube and the detector. The blank float should be set to barely eliminate the argon peak (large peak on the left side of the spectrum), to avoid eliminating valid spectral peaks.
 - a) If too much spectra is being lost, reduce the percentage by entering a lower number. The program will repeat parts iv) and v).
 - b) If not enough spectra is being subtracted, increase the percentage by entering a higher number. The program will repeat parts iv) and v).
 - c) If the spectra looks good, press <CR> and the program will continue.

vii) RACE will display:

ABSORPTION CORRECTION FOR THE THICKNESS OF SUBSTRATE, (left side of spectrum)

Nominal Values are	Mylar	75
	Teflon	100
	Nuclepore	170

ENTER THICKNESS FACTOR, CURRENT = 100
(<CR> TO KEEP CURRENT VALUE)

- i) IMPROVE filters are Teflon, so press <CR> to continue. RACE will draw the spectra resulting from the subtraction of the blank from the filter sample analysis.
 - ii) Press the PF4 key to access the Analysis Parameter Input screen. Press the “F” key to turn off the blank float check, and the “X” key to exit back to RACE.
- b) Adjust the background fit to remove most of the background due to scattering of x-rays off the filter and deposit.
- i) On RACE, press the PF4 key to access the Analysis Parameter Input screen. Press the “B” key to check the background fit, and the “X” key to exit back to RACE.
 - ii) RACE will create a spectra, automatically perform the blank subtract, then display the following on the screen:

FITTED BACKGROUND: DISPLAY OF DATA - BLANK AND FITTED BACKGROUND

(Use SHIFT-VIEW to toggle between screens)

SAMPLE CONSIDERED TO HAVE LIGHT LOADING

ENTER ITERATIONS FOR FIT, CURRENT = 17

(<CR> to keep current value)

- iii) Review the spectra. The goal is to remove the remaining background by subtracting a smooth function calculated as the lesser of the counts in the channel and an average counts per channel over a specified width. To change this fit, the operator can adjust the width and the number of iterations of the process. The bases of the peaks in the resulting spectra should barely reach the zero counts level. The background subtract cannot be too large, or the peaks in the resulting spectra will appear smaller, causing RACE to underestimate the elemental concentrations. If the background subtract is too small, the peaks in the resulting spectra will appear higher, causing RACE to overestimate the elemental concentrations.
 - a) If too much spectra is being lost, increase the number of iterations used to calculate the background subtract. The program will repeat part ii).
 - b) If not enough spectra is being subtracted, decrease the number of iterations. The program will repeat part ii).

- c) If the spectra looks good, press <CR> to continue. RACE will calculate elemental concentrations from the peak locations, areas, the cross section and calibration tables, and the matrix corrections.
 - iv) On RACE, press the PF4 key to access the Analysis Parameter Input screen. Press the “B” key to turn off the check of the background fit, and the “X” key to exit back to RACE.
- c) Press the PF4 key to access the Analysis Parameter Input screen. Press the “A” key to print all full output, the “N” key to begin a new sequence, and the “X” key to exit back to RACE.
- d) Get full output for five analyses, then press the PF4 key to access the Analysis Parameter Input screen. Press “A” to stop printing full outputs, press the “N” key to begin a new sequence (pause the program), and press “X” to return to normal analysis.
- e) Review the full output, highlighting the data for the S, Fe K α , Zn K α , and Se K α , peaks.
 - i) Check the difference between the Predicted and Found Energy for each of the peaks in part f. For a good calibration, this difference should be less than 0.004. Note: the difference is printed below the Predicted Energy.
 - ii) If the differences from part i.) are greater than 0.004, from the five full outputs, select the peak having the greatest reported concentration (NANOGRAMS PER M³) for each of the species of interest (S, Fe, Zn, and Se).
 - iii) Use the channel and predicted energies for the peaks selected in step ii.) to enter a new calibration, using the procedure described in part 1, step a.), subsection vi).
- f) Repeat steps d) through h), except analyze a different set of five reanalysis filters. Preferably, analyze two or three filters from each reanalysis tray. The differences between predicted and found energy should be less than 0.004. If not, enter a new calibration equation and repeat steps d) through h) again.
- g) When an acceptable calibration equation has been derived, analyze both reanalysis trays through RACE. Report to the Quality Assurance Specialist when both trays are completed. The QA Specialist will plot the reanalysis data against the original analysis data for both reanalysis trays. If the correlations are stable, the Quality Assurance Specialist will release the XRF system for use. These procedures are covered in depth in the Quality Assurance SOP.

2. Run the actual IMPROVE samples. Each tray contains all samples for a given season from a single site. Initialize the analysis of the samples in the tray by entering the identification code of the tray file in the acquisition program. Note that a tray file may contain instructions for analysis of one to ten sample trays. Verify the correct tray file is being used. Initialize the spectral analysis program by entering the run number of the analysis. Check the following features in the XRF spectral analysis of the sample. If any problems are detected, consult with the QA Manager, the PIXE/PESA Manager, or a senior scientist.
 - a) Is the background completely removed by the two background steps? That is, do the valleys between the peaks in the final spectrum go to zero. If not, determine if the problem is an inappropriate blank. Verify on the output log that the run number of the blank is correct. Do not revise the fitting parameters without consulting with the QA Manager or Spectroscopist.
 - b) Monitor the live time of the detector. If the live time drops below 90%, or if the integrated charge begins to decrease, contact the Spectroscopist for assistance.
3. Rerun the reanalysis trays and filter blanks every 1000 analyses.
4. Before ending the XRF analysis run, wait until the QA Manager is able to validate the results for all of the reanalysis trays. If problems in the analysis are determined, select the trays and samples involved and reanalyze them.

Figure 15 Full Output of CuS Standard

UC DAVIS XRF-1 ANALYSIS 13001 OUTPUT: FILE 1, ITEM 2 CROSS SECTION TABLE XRFOCT95 * 1.000 18-SEP-96															
LIVE TIME = 171.0 / 180.0 = 0.95 CHARGE = 173 NC, CURRENT = 1 NA ADC RATE = 917 COUNTS/SEC DCON = 1.000M**3/CM**3															
PEAK WIDTH = 7 CHANNELS BLANK RUN 13017 * 0.51 NTHICK = 100 ITERS = 17 KOVER = 1 ENERGY = 0.8979 + 0.0377 * CHAN ()															
MATRIX CORRECTIONS ARE NOT INCLUDED UNCERTAINTIES IN CONCENTRATIONS ARE STATISTICAL PLUS 5%, ADDED QUADRATICALLY															
PROFILE 1															
VAXRace															
PEAK	ELEMENT	NANOGRAMS PER CM**2	ENERGY (KEV) PRED	CHANNEL FOUND	COUNTS	LINEAR BACKGROUND SUM	LOC	CUTA	WIDTH	CHISO	MULT	LOOP			
1	S K	20689.70 ± 2017.75	2.307 -0.019	2.288 ± 0.007	36.9 ± 0.2	361. ± 30.	462.	21.	37	26 46	6.47 ± 0.57	0.6	1	5	
2		0.000 ± 0.00	0.000 0.000	2.935 ± 0.006	54.1 ± 0.1	561. ± 38.	648.	178.	54	57 66	6.25 ± 0.40	0.7	1	5	
3	CA KA	1428.03 ± 165.31	3.690 -0.018	3.672 ± 0.011	73.6 ± 0.3	290. ± 30.	312.	30.	73	67 81	7.15 ± 0.82	0.1	1	5	
4	FE KA	178.61 ± 24.65	6.400 -0.093	6.307 ± 0.012	143.6 ± 0.3	211. ± 27.	214.	203.	143	134 152	6.83 ± 0.84	0.7	1	5	
5	CU KA	50206.23 ± 2521.38	8.041 0.001	8.042 ± 0.000	189.7 ± 0.0	101911. ± 479.	104055.	1013.	190	176 199	5.85 ± 0.02	0.4	1	3	
6	CU KB	52055.13 ± 2686.85	8.907 0.001	8.908 ± 0.001	212.6 ± 0.0	14281. ± 183.	14719.	732.	213	200 227	6.06 ± 0.07	0.5	1	4	
7		0.00 ± 0.00	0.000 0.000	16.924 ± 0.006	425.4 ± 0.2	9564. ± 516	9592.	4826.	426	412 434	12.37 ± 0.79	0.7	1	8	
8		0.00 ± 0.00	0.000 0.000	17.481 ± 0.004	440.2 ± 0.1	4043. ± 154	3900.	3461.	441	435 452	8.46 ± 0.36	1.3	1	6	
9		0.00 ± 0.00	0.000 0.000	18.955 ± 0.007	479.3 ± 0.2	4494. ± 295.	5606.	4053.	479	465 491	11.47 ± 0.91	0.6	1	8	
10		0.00 ± 0.00	0.000 0.000	19.664 ± 0.006	498.2 ± 0.2	1920 ± 102.	2035.	638.	498	492 508	8.69 ± 0.56	1.2	1	6	
MINIMUM DETECTION LIMITS															
	S	CL	K	CA	TI	V	CR	MN	FE	NI	CU	ZN	GA	HG	AS
	384.42	389.56	105.48	46.78	30.44	22.75	19.76	17.99	22.66	24.41	25.32	19.83	11.00	5.24	0.00
	PB	SE	BR	RB	SR	Y	ZR								
	0.86	1.80	3.89	5.25	6.23	8.41									
UC DAVIS XRF-1 ANALYSIS RUN 13001 XX1 FILE 1 ITEM 2 03-OCT-96															
PROFILE 1															
CONCENTRATIONS OBTAINED BY DIVIDING AREAL DENSITIES BY 1.000 M**3/CM**2															
NO MATRIX CORRECTIONS APPLIED															
UNCERTAINTIES ARE STATISTICAL PLUS A 5% OVERALL UNCERTAINTY, ADDED QUADRATICALLY															
ELEMENT	NANOGRAMS PER CM**2		CORRECTION												
1	S K	20689.70 ± 2017.75	1.000												
2	CA KA	1428.03 ± 165.31	1.000												
3	FE KA	178.61 ± 24.65	1.000												
4	CU KA	50206.23 ± 2521.38	1.000												
5	KB	52055.13 ± 2686.85	1.000												
MINIMUM DETECTABLE LIMITS OF ELEMENTS WITH MATRIX CORRECTIONS															
1	S	384.42	7	CR	19.76	13	GA	11.00	19	RB	3.89				
2	CL	389.56	8	MN	17.99	14	HG	5.24	20	SR	5.25				
3	K	105.48	9	FE	22.66	15	AS	0.00	21	Y	6.23				
4	CA	46.78	10	NI	24.41	16	PB	0.00	22	ZR	8.41				
5	TI	30.44	11	CU	25.32	17	SE	0.86	23	0.00					
6	V	22.75	12	ZN	19.83	18	BR	1.80	24	0.00					

4.6 Routine Analysis

The standard analysis procedures for XRF are listed below.

4.6.1 RENO Calculation and System Calibration

4.6.2 Blank Filter Analysis

4.6.3 Reanalysis Trays

4.6.4 Filter Sample Analysis

4.6.5 Data Storage

4.6.1 RENO Calculation and System Calibration

At the beginning and end of every analytical session, the calibration is checked with a series of 20-30 thin film standard foils. Following analysis, the measured elemental concentrations from the thin film standards are compared to the concentrations quoted by the manufacturer for each elemental thin film standard. If the ratios of measured to quoted values show that the shape of the calibration curve has significantly changed, the analysis cannot proceed until the problem is rectified. A mean ratio is less than 0.90 or greater than 1.10, indicates the calibration curve has deviated significantly. This mean ratio, called a RENO or renormalization factor, is applied to all concentrations measured during the analytical session. This corrects the measured values to a standard to allow direct comparison of data from different analysis quarters. The RENO is normally between 0.98 and 1.02.

4.6.2 Blank Filter Analysis

Once the standards have indicated the system functioning correctly, a set of unexposed Teflon filters, blanks, are analyzed. The cleanest blank is selected and defined to be the system blank for the XRF spectra. The system blank spectrum is subtracted from all subsequent filter sample analyses to remove the x-ray spectrum due to the clean filter substrate.

4.6.3 Reanalysis Trays

After the calibration check and the inclusion of a system blank, two trays of filters that were analyzed during the previous analysis quarter, approximately 52 filters, are reanalyzed. The concentrations of key elements from the re-analyses, generally, S, Ca, K, Mn, V, Fe, Zn, Cu, Se, Pb, and Br, are plotted against those from the initial analysis. If the slope on any plot is less than 0.90 or greater than 1.10, a problem with the system exists and the analysis cannot proceed until it is rectified.

These two reanalysis trays are analyzed at the start and end of the run, and following every thousand analyses during the run. They are also analyzed just prior to and following any analysis break. Each analysis run has at least one break, around the fifteenth day of analysis, to refill the detector with liquid nitrogen. Since refilling the detector requires that the detector be biased down, the reanalysis trays are run just prior to and immediately following the procedure to ensure the system has remained stable.

The XRF system used by the Air Quality Group is designed to see elements such as Se with higher accuracy and lower minimum detectable limits. As a check of the XRF system, the reanalysis trays are generally from the sites SHEN1 and CRLA1. CRLA1 filters have low Se concentrations, so the reanalysis is a useful check of the minimum detectable limit for Se. SHEN1

filters have moderate Se concentrations which are compared to historical values to verify the mean minimum detectable limit is reasonable, as was the measured concentration and ratio of times that Se was historically found. This analysis is performed by the Quality Assurance Manager prior to releasing the system for normal filter analysis use.

4.6.4 Filter Sample Analysis

Once the standards and reanalyses trays have been run and the systems are validated by the Quality Assurance Manager, the analysis of normal filters begins. XRF analysis is conducted automatically using trayfiles containing instructions for subsequent analysis of up to ten site trays of filters. The Spectroscopist shall review the system parameters and the results of the XRF analysis several times each day to ensure that no problems have occurred. Checking the system parameters and analysis results includes checking the tube integrated charge and the detector count rate, checking the analysis filter position, and verifying that a reasonable number of elements are being identified. Also, the Spectroscopist checks for reasonable agreement between the α and β lines of the same element, and monitors Fe and Se concentrations to ensure these elements were found and the minimum detectable limits were reasonable. If any parameter is incorrect, or any result is suspicious, the problem is corrected and all potentially affected samples are reanalyzed.

4.6.5 Data Storage

The data are backed up on magnetic tape every night to ensure that in case of a system failure, no more than a single day of data will be lost. Also, at the end of each quarterly analysis session, all the data collected during the XRF analysis run are backed up on a permanent storage medium and archived.