UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

SUPERXAP MANUAL

by

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INTRODUCTION

SUPERXAP (Super X-ray Analysis Program) is a personal-computer (PC) based program for analysis of energy dispersive spectra generated by an X-ray fluorescence analyzer. Spectra are analyzed on an IBM-compatible computer by the method of least squares fitting of digitally filtered spectra (Schamber et al., 1977). Written in QUICKBASIC 4.5 for interface with a KEVEX 7000 X-ray fluorescence analyzer, the program could be adapted with minor modifications, to accept and analyze data from other instruments. SUPERXAP represents a significant upgrade in power and flexibility over XAP (Quick and Haleby, 1988).

Pull down menus provide 24 subroutines and functions, and allow spectra to be viewed, transferred from the KEVEX to a PC, stored on disc, manipulated, and analyzed. Characteristic X-ray peaks may be identified manually or automatically with color-coded K,L, or M lines. Calibration curves are developed with an interactive routine that creates standard files by least-squares fit of peak intensities to known elemental abundances. Elemental abundances in unknowns may be determined at time of spectral acquisition, or by batch analysis of spectra stored on disc.

SUPERXAP corrects for instrument drift, background, peak overlap, and absorption effects. Instrument drift is corrected by calculating adjustments required to bring two widely spaced reference peaks to their exact theoretical positions. Background removal is accomplished by digitally filtering spectra, which preserves characteristic X-ray peaks while suppressing random noise and low-frequency spectral components such as the continuum background. Peak overlaps are removed by least-squares fitting of filtered, single-element reference spectra, to unknown filtered spectra in regions of interest. Absorption effects are corrected by ratioing peak intensities to that of a Compton-scattered source peak (Giauque et al., 1977). Element concentrations in samples of unknown composition are calculated with first- or second-order regression working curves, previously prepared from standards of known composition. One-sigma standard deviations, based on counting statistics, are reported for each analysis. Computed abundances may be stored in both ASCII (LOTUS 1-2-3 compatible) and DATASAVE (Quick, 1988) formats.

This manual explains menus and options found in SUPERXAP, and more importantly, provides step by step procedures for routine analysis and standardization. An introduction to spectral deconvolution of digitally filtered data is beyond the scope of this manual. For a description of spectral deconvolution using this technique see Quick and Haleby, 1988. The manual is organized as follows: Chapter II describes the minimum hardware operation experience and resources required to run SUPERXAP. Chapter III defines terminology and introduces conventions unique to SUPERXAP. Chapters IV and V present step-by-step procedures to perform routine analysis and standardization. Chapters VI to IX present detailed descriptions of menu options necessary to use advanced functions of SUPERXAP. Appendix 1 contains calibration curves, made using SUPERXAP, for elements run on both the ^{109}Cd and ^{241}Am radioactive sources. Table 1 contains analytical precision and accuracy data for U.S. Geological Survey standards analyzed using SUPERXAP.

The authors thank E.A. du Bray, and G. P. Meeker for their reviews. Also, E.A. du Bray's comments during development of SUPERXAP improved the program.

2.1. USER

This manual presumes:

1) General knowledge of energy dispersive X-ray spectroscopy,
2) Specific knowledge of X-ray fluorescence analyzer operation,
3) Safe handling of radioactive sources,
4) Knowledge of DATASAVE if standardizing for SUPERXAP,
5) Basic understanding of DOS.

2.2. INSTRUMENT/COMPUTER

SUPERXAP requires the following components to collect and analyze spectra.

1) A KEVEX 7000 or equivalent energy dispersive X-ray fluorescence instrument with the BAUD rate set to 4800. The KEVEX 7000 must have a functional "print- spectra key", outputs numerical spectral data via a serial port.
2) An IBM compatible personal computer with DOS 3.0 or higher, a CGA, EGA, or VGA monitor, at least one floppy disc drive, and 640 kb of memory. Standardization can only be performed on systems having EGA or VGA monitors. It is preferable that the computer have a hard disc drive, math co-processor, and a printer.
3) The PC and KEVEX 7000 must be connected with an RS-232 serial cable using the COM1 port on the PC.

2.3. ANALYTICAL STANDARDS

Geologic standard materials needed for SUPERXAP include:

1) Spectroscopic pure elemental references, in powder form, and
2) Sufficient numbers of international standards used in X-ray fluorescence analysis to bracket the range of concentrations of elements expected to be present in unknowns.

2.4. SAMPLE PREPARATION

In order to generate semi-quantitative and quantitative data using SUPERXAP, the following proper sample preparation guidelines should be followed.

1) Samples should be ground to approximately 200 mesh, using equipment known not to contribute contamination for the elements of interest.
2) No less than 2 grams of sample should be loaded into an X-ray fluorescence cup (consisting of a plastic cylinder and two ring caps) enclosed using X-ray mylar film, with a thickness of approximately 6.0 μ.

3.1. DEFINITIONS

The following definitions are provided for terms that are used in SUPERXAP.

ASCII File. A file created by SUPERXAP with a ".ASC" extension that contain analytical results in ASCII format; files are LOTUS 1-2-3 compatible.

A VALUES. Constants relating peak heights to element abundance; required for standardization. **A values** are determined during standardization by least-squares solutions to the following equation.

$$\text{Abundance} = A1 + A2 * \text{peak height} + A3 * (\text{peak height})^2$$

CALIBRATION. Determination of the functional relationship between peak intensity and element abundance.

CODE FILE. A file that defines the number and order of elements in a DATASAVE (Quick, 1988) file or a SUPERXAP reference file. Code files are created and maintained using DATASAVE. SUPERXAP is supplied with a code file named KEVCODES.

DATASAVE. A geochemical database program written in QUICKBASIC for the IBM PC and compatible computers (Quick, 1988).

DATASAVE FILE. File created by SUPERXAP with a ".DSF" extension that contains analytical data in a compressed binary format. Such files may be read by DATASAVE but not spreadsheet programs such as LOTUS 1-2-3.

DECONVOLUTE. The separation of a spectrum into groups of characteristic X-ray peaks. SUPERXAP performs this by least-squares fitting spectra to **reference spectra**. Resulting intensities of characteristic X-ray peaks are related to element abundances.

DIGITAL FILTER. Numerical treatment of spectral data to suppress background and noise.

PC. Personal Computer.

REFERENCE. A sample composed of a single element or oxide and possibly diluted with SiO_2 or Al_2O_3 (to reduce dead-time during spectral acquisition). References are used to obtain peak shapes for **deconvoluting** the more complex spectra of compounds such as rocks. An example of a reference would be Y_2O_3 diluted by SiO_2.

REFERENCE FILE. A DATASAVE file that contains the chemical compositions of **standards**. A reference file is necessary to perform calibration.

REFERENCE SPECTRUM. A spectrum containing a limited number of characteristic X-ray peaks. Such spectra are normally collected from samples consisting of a single element or oxide and contain only characteristic X-ray peaks for one element in addition to the Compton and Rayleigh scatter peaks. These characteristic X-ray peaks are used by SUPERXAP to deconvolute unknown spectra.

REGION OF INTEREST (ROI). That part of a **reference spectrum** (in keV) that contains the characteristic X-ray peaks to be used in spectral deconvolution.

SPEC-PURE REFERENCE. An elemental reference that is essentially free of additional contaminants.

SPECTRUM. Part of the X-ray energy region. In SUPERXAP, spectra must consist of 1024 channels but may cover different energy ranges.

STANDARD. A chemically well-characterized sample used to relate the intensity of X-ray peaks to element abundance. Chemical descriptions of standards are stored in a **reference file** (e.g. KEVEX.REF). An example of a standard would be a well-characterized rock powder such as GSP1 (U.S. Geological Survey standard, Silver Plume Granite).

STANDARD SPECTRUM. A spectrum of a standard.

XAP DATA FILE. DATASAVE file containing measured values of international rock standards made using SUPERXAP.

ZERO AND GAIN. Energy-dispersive spectrometers typically require adjustment to correct for spectral drift. The zero control shifts the spectrum to lower or higher energy and the gain control stretches or contracts the spectrum. SUPERXAP establishes theoretical corrections for zero and gain by analyzing CeO_2 characteristic K and L spectral lines; all subsequent spectra are numerically corrected with these values.

3.2. CONVENTIONS IN THIS MANUAL

1) Names of computer programs and instruments are in capital letters.
2) SUPERXAP menu commands are italicized.
3) KEVEX keyboard commands are in bold capitals.
4) PC keyboard commands are in quotations.

3.3. SUPERXAP PROGRAM CONVENTIONS

1) SUPERXAP automatically assigns DOS extensions to file names. When responding to SUPERXAP questions, **do not include a DOS extension!** Extensions are as follows.

.SPC	Spectrum produced by ^{109}Cd source irradiation
.SPA	Spectrum produced by ^{241}Am irradiation
.SPF	Spectrum produced by ^{55}Fe irradiation
.REF	Reference file
.DSF	Data file in DATASAVE format
.ASC	Data file in ASCII, LOTUS-compatible format
.TMP	Temporary data file

2) All keyboard input must be in upper case. SUPERXAP toggles the "Caps Lock" automatically at start up so that keyboard input is upper case. Do not defeat this by pressing the "Shift" or "Caps Lock" keys.
3) SUPERXAP options are organized into four menus that are "pulled-down" from four headings in a Main Menu at the top of the monitor display.
4) Options are selected from the Main Menu at the top of the screen by pressing "Alt" simultaneously with the first letter of the menu selection.
5) Scroll through options in pull-down menus by moving the ">" adjacent to an option using the "↑ ↓" keys; select options by pressing the "Enter" key. Jump to adjacent pull-down menus by pressing the "← →" keys, or exit to the main menu headings by pressing "Esc".
6) Errors are trapped and reported to the user as BASIC error numbers. These numbers are defined in most BASIC manuals. Following report of the error, press any key to return to the main menu without loss of data.

4.1. INTRODUCTION

This chapter provides a step-by-step procedure for performing routine analyses with SUPERXAP. Detailed descriptions of menu options are in Chapters VI to IX.

4.2. INITIALIZATION

1) Turn on KEVEX. Use the locking toggle switch on the back panel of the instrument. Depending on the type of monitor, turn the KEVEX monitor on by pushing either the switch on the back or the button on the front of the monitor.
2) Turn on the PC and printer.
3) Set the KEVEX range to 0-40 keV. At the KEVEX keyboard, press the **RANGE** key and use the **GREEN** "→ ←" keys to set the energy range from 0-40 keV. Press the **ENTER** key.
4) Collect spectrum for Zero/Gain check. To calibrate the instrument, acquire a spectrum of CeO_2, using the same radioactive source to be used for the analytical run.
   A) At the KEVEX keyboard, press the **ERASE MEM** key, followed by **ENTER**.
   B) Label the CeO_2 spectrum: Press the **LABEL** key then press the **CLEAR** key. Type "CEO_2" (the spectrum name) and press **ENTER**.
   C) Pre-set the count time by pressing the **PRSET** key then press the **CLEAR** key. Type the new count time (100) for the ^{109}Cd source and (300) for the ^{241}Am source, and press **ENTER**.
   D) Put the CeO_2 sample in the KEVEX sample holder and place it atop the detector. Press the **ACQ** key to begin spectrum acquisition.
5) Load SUPERXAP program. SUPERXAP is an executable program and may be run on the PC from DOS by typing "SUPERXAP". Be sure that the program, KLM.DAT and SETUP.EGA are on the default drive and directory. In the Central Mineral Resources KEVEX laboratory (Branch of Central Mineral Resources, U.S. Geological Survey, Denver, CO) SUPERXAP is loaded by an autoexec.bat file and requires no user input. After SUPERXAP is loaded, a logo is displayed on the screen while essential files are being loaded; once files are loaded, the main menu is displayed.
6) **Recall standards.** At the PC, press the "ALT" and "S" keys simultaneously to display the *Setup* menu.
   A) Use the "↑ ↓" keys to select the *recall standards* option and press "Enter".
   B) The query "Standard File?" will be displayed. Answer by typing "DIR" and press "Enter".
   C) The query "Drive & Path?" will be displayed. Type the drive and path identifier (eg. C:\SUPERXAP) for the drive and path that contains the standard file, and press "Enter". Use the "↑ ↓" keys to scroll through the directory and select either the CD.STD or AM.STD standard files for ^{109}Cd or ^{241}Am analysis respectively. Press the "Enter" key.

   A summary of data for the standards will be displayed and a matrix for least-squares calculations is generated. When calculations are complete, a beep sounds, and the prompt, *"Hit any key to continue!"* is displayed.
7) **Store data** (optional). To store analytical data to disk on the PC:
   A) Select the *Store data in file* option from the setup menu.
   B) The computer responds, *"Store Data on disk (Y/N)?"*. Press "Y".
   C) The computer prompts, "File Name?". Type the desired file name using ≤ 8 characters (no extension).
   D) The computer prompts, "Drive & Path". Type the target drive and (if required) path for the file to be stored and press "Enter". (Note: at the end of the run, data may be stored in DATASAVE and or, ASCII formats; with the main menu displayed on the PC screen, and after pressing "Alt" simultaneously with the "Q" key the computer prompts *"Store data in: D Datasave file, A Ascii file,* and *Esc*

Return to DOS". Before terminating the run, type the first letter of the desired data storage format, or press "Esc" to exit to DOS.)

E) The computer reports the number of entries in the selected file, if any (100 maximum). Hit any key to continue.

8) **Zero/Gain check.**
   - A) At the PC, select the *Zero/Gain check* option from the *Setup* menu.
   - B) After the CeO_2 spectra has been acquired (step 4), press the **PRINT**, then the **ENTER** keys at the KEVEX keyboard.
   - C) If the results of calibration are not in the 0 to 10 eV range for both zero and offset, adjust the zero and/or gain manually, collect a new CeO_2 spectrum (step 4) and return to step 8A. See section 6.7 for more details. Refer to the KEVEX 7000 manual if unfamiliar with zero and gain adjustments.

4.3. ANALYSIS

The PC must first be readied to accept and analyze data from the KEVEX 7000. Steps 1-6 performed at the PC keyboard describe this procedure.

1) Press the *"Esc"* key to return to the main menu.
2) Press the "Alt" and "I" keys simultaneously to display the *Input/Output* menu.
3) Select the *On-line analysis* option and press "Enter".
4) The screen displays the question , *"Save spectra automatically (Y/N)?"*. "Y" causes all spectral data to be saved and requires (4.1 Kb of memory for each spectrum). Press "Y" or "N".

A) If "Y" is selected, the screen displays the question, *"Drive & path?"*. Type the target drive and path where spectra are to be stored and press "Enter".

5) The screen displays three radioactive source options. Type "C" for ^{109}Cd, "A" for ^{241}Am, and "F" for ^{55}Fe.
6) The screen displays the message *"READY FOR DATA TRANSFER"*. The PC is now ready to receive and analyze data from the KEVEX 7000.

After executing the following steps at the KEVEX keyboard, spectra may be collected on the KEVEX and sent to the PC.

7) Select the count time:
   - A) Press the **PRSET** key.
   - B) Press the **CLEAR** key.
   - C) Enter the new counting time (100 sec for ^{109}Cd and 300 sec for ^{241}Am radioactive source excitation).
   - D) Press the **ENTER** key.
8) Enter the sample name:
   - A) Press the **LABEL** key.
   - B) Press the **CLEAR** key.
   - C) Enter the new sample name ($\leq$ 8 characters with no spaces, if spectra are to be stored on disk).
   - D) Press the **ENTER** key.
9) Following spectral acquisition press the **PRINT** key followed by the **ENTER** key to send the spectrum to the PC. Once spectral information has been transferred to the PC, SUPERXAP will compute and print data to the display and printer. Note: It is possible to program the KEVEX to automatically output data to the PC once spectral acquisition time has been completed (refer to the KEVEX manual).
10) To analyze additional samples, return to step 8.

4.4. TERMINATE RUN

Terminate an analytical run at the PC keyboard to insure that data is properly stored on disk:

1) Return to the main menu by pressing the "Esc" key.
2) Press the "Alt" and "Q" keys simultaneously to exit SUPERXAP.
3) The program asks "*Terminate run (Y/N)?*". Answer yes by pressing "Y": pressing "N" will return the program to the main menu.
4) The program asks "*Store data in: A ASCII file, D DATASAVE file*, and *Esc Return to DOS*". Press "D" and "A" for DATASAVE and ASCII file format storage respectively. Both or neither formats may be selected. Press "Esc" to exit the program and return to DOS.

4.5. POTENTIAL PROBLEMS

1) If chi-squared values are significantly greater than one for several consecutive analysis, this may indicate either:
    A) A *Zero/Gain check* needs to be done, or
    B) An important element in the sample is not included in the standardization.
2) If spectral data do not seem to be transmitted to the PC, the KEVEX BAUD rate may be at the wrong setting. Refer to the KEVEX 7000 manual if the BAUD rate needs to be changed to 4800.
3) Failure to report data on the printer may indicate that the print option in the setup menu has been switched off (see section 6.10).
4) Error number 24 indicates that a printer is not attached or has not been turned on.

5.1. INTRODUCTION

Standardization is time consuming and complicated. Fortunately, it does not need to be repeated except when decay of the radioactive source is sufficient to greatly reduce (by a factor of two or three or more) the dead time, or when the Si(Li) detector has been damaged to the extent that peak widths have changed. As long as Chi-square values are routinely less than 1, restandardization will not significantly improve results and should not be performed.

Standardization involves three main procedures. Following initialization, reference and standard spectra must be acquired. Second, ROI's must be established for each element of interest using the reference spectra. These ROI's form the nucleus of the standard file. Finally, the resulting standard file must be calibrated using standard spectra.

5.2. REQUIREMENTS

Requirements for standardization are as follows:

1) A *Zero/Gain check* must be performed prior to spectra collection (see section 4.2).
2) A suite of powdered element or oxide reference materials must be prepared. If necessary, the powders may be diluted by spectroscopic grade silicon or aluminum powders.
3) A suite of well characterized standards having compositions similar to unknowns to be analyzed, must be prepared.
4) Preparation of a Reference file (see definitions section 3.1) that contains the compositions of the standards.
5) Preparation of a code file which identifies the elements in the reference file.

5.3. INITIALIZATION

1) Turn on KEVEX-7000. Turn on the KEVEX-7000 by using the locking toggle switch on the back panel of the instrument. Depending on the type of monitor, turn the KEVEX-7000 monitor on by pushing either the switch on the back or the button on the front of the monitor.
2) Turn on the PC and printer.
3) Set the KEVEX range to 0-40 keV. At the KEVEX keyboard, press the **RANGE** key and use the **GREEN** "→ ←" keys to set the energy range from 0-40 keV. Press the **ENTER** key.
4) Collect spectrum for Zero/Gain check. To calibrate the instrument, acquire a spectrum of CeO_2, using the radioactive source to be used for the analytical run.
   A) At the KEVEX keyboard, press the **ERASE MEM** key, followed by **ENTER**.
   B) Label the CeO_2 spectrum: Press the **LABEL** key, then press the **CLEAR** key. Type "CEO_2" (the spectrum name) and press **ENTER**.
   C) Pre-set the count time: Press the **PRSET** key then press the **CLEAR** key. Type the new count time (100) for the ^{109}Cd source and (300) for the ^{241}Am source, and press **ENTER**.
   D) Put CeO_2 sample in KEVEX sample holder and place it atop the detector. Press the **ACQ** key to begin spectrum acquisition.
5) If necessary, load the SUPERXAP program. SUPERXAP is an executable program and may be run on the PC from DOS by typing "SUPERXAP". Be sure that program and KLM.DAT and SETUP.EGA are on the default drive and directory. In the Central Mineral

Resources KEVEX laboratory, SUPERXAP is loaded by an autoexec.bat file and requires no user input. After SUPERXAP is loaded, a logo is displayed on the screen while essential files are being loaded; once files are loaded, the main menu is displayed.

5.4. ACQUIRE AND STORE REFERENCE AND STANDARD SPECTRA

1) Perform the following steps at the PC keyboard.
   A) If necessary, press "Esc" to return to the main menu.
   B) Press the "Alt" and "I" keys simultaneously to display the *Input/Output* menu.
   C) Select the *Transfer spectrum* option and press "Enter".
   D) The screen displays three radioactive source options. Type "C" if the source is ^{109}Cd, "A" if it is ^{241}Am, and "F" if it is ^{55}Fe.
   E) The screen displays the message "*READY FOR DATA TRANSFER*". The PC is now ready to receive and analyze data from the KEVEX-7000.
2) Load a reference or rock standard in the sample chamber of the X-ray analyzer.
3) At the KEVEX-7000 keyboard, enter the counting time.
   A) Press the **PRSET** key.
   B) Press the **CLEAR** key.
   C) Enter the new counting time. Collect the spectrum until the counts in the largest characteristic peak are at least 10,000. In some cases high dead times may cause excessively long collection times (see KEVEX-7000 manual for instructions). If this occurs, dilute the reference standard with spectroscopic grade SiO_2 or Al_2O_3 powder to decrease dead time.
   D) Press the **ENTER** key.
4) At the KEVEX-7000 keyboard, enter the sample name.
   A) Press the **LABEL** key.
   B) Press the **CLEAR** key.
   C) Enter the new sample name ($\leq$ 8 characters, with no spaces if spectra are to be stored on disk).
   D) Press the **ENTER** key.
5) Following spectral acquisition press the **PRINT** key followed by the **ENTER** key to send the spectrum to the PC. Once spectral information has been transferred to the PC, SUPERXAP will display the spectrum on the screen.
6) At the PC keyboard, select the *Store spectrum* option of the *Input/Output* menu and press "Enter".
7) The PC screen will display the query, "*Spectrum?*". Type a name $\leq$ 8 characters long.
8) The PC screen will display the query, "*Drive & Path?*". Type in the target drive and directory to store the spectrum on.
9) Return to step 1 until all reference and standard spectra are collected. (Note: In addition to using CeO_2 for *Zero/Gain check*, always collect a CeO_2 reference spectrum and store it to disc, as this will be used in the next step). All references and rock standards need to be run separately using the radioactive source that is to be used for a specific standardization.

5.5. ESTABLISH REGIONS OF INTEREST (ROI's)

Regions of interest (ROI's) are established with the PC after reference and standard spectra have been acquired and stored. The procedure requires that the user is familiar with and can identify characteristic X-ray peaks.

1) **Establish a back-ground (or "1st") ROI.** The "1st" ROI must be a region of the background continuum to be used to correct for absorption effects. Ideally this should be a Compton-scattering peak free of significant peak overlaps. For example, when standardizing with the

^{109}Cd source, the "1st" reference established may be the tallest Compton peak. When standardizing using the ^{241}Am the "1st" reference may be a region of lower energy, between 2.48 and 2.84 keV.

A) Select the *recall spectrum* option from the *Input/Output* menu.
B) The screen will display, "*Use last transferred file (Y/N)?*". Press "N".
C) The screen will display, "*Spectrum?*". Type "DIR" followed by the "Enter" key.
D) The screen will display "*Drive & Path?*". Type the drive and path where the CeO_2 spectrum is located.
E) All spectra in the subdirectory will be displayed.
F) Use the "↑ ↓" keys to select CeO_2 spectrum and press the "Enter" key. The CeO_2 spectrum will be displayed.
G) Choose the *Analyze* menu and select the *Establish reference* option. A cursor will appear on the screen, and can be manipulated with keys detailed at the bottom of the screen.
H) Press the "F1" key to slow cursor motion. If "F2" is pressed, cursor speed is increased.
I) Move the cursor to the upper limit of the ROI with the "→" key. (Reasonable upper limits are 20 channels above the centroid of the Compton peak for ^{109}Cd source radiation, and an energy of 2.84 keV for ^{241}Am source radiation.)
J) Press "U". A beep will sound.
K) Move the cursor to the lower limit of the ROI with the "←" key. (A reasonable lower limit would be 20 channels below the centroid of the Compton peak for ^{109}Cd source radiation, and an energy of 2.48 keV for ^{241}Am source radiation).
L) Press "L". A beep will sound.

Note: "U" and "L" may be pressed multiple times. The recorded limits will be those last indicated. "U" must always be at a higher energy than "L".

M) Press "D" when the ROI is satisfactorily set.
N) The screen will display "Reference 1", the upper and lower limits of the ROI, and the query "*Element/Oxide* query?"
O) Press the "Enter" key. The "1st" ROI is now established. Once established, the "1st" reference cannot be changed without beginning the procedure again.

2) Establish subsequent ROI.

A) Select the *recall spectrum* option from the *Input/Output* menu.
B) The screen will display, "*Use last transferred file (Y/N)?*". Press "N" then the "Enter" key.
C) The screen will display, "*Spectrum?*". Type "DIR" followed by the "Enter" key.
D) The screen will display "*Drive & Path?*". Type the drive and path where the additional reference spectra are located.
E) All spectra in the subdirectory will be displayed.
F) Use the "↑ ↓" keys to select the next reference spectra to create a ROI for and press "Enter". The spectrum will be displayed.
G) Choose the *Analyze* menu and select the *Establish reference* option. A cursor will appear on the screen, and can be manipulated with keys defined at the bottom of the screen.
H) Press the "F1" key to slow cursor motion (the cursor will step in one channel increments). Press the "F2" key to speed cursor movement.
I) Move the cursor to the upper limit of the ROI with the "→" key. A reasonable limit is one peak width above the highest-energy characteristic peak.
J) Press "U". A beep will sound.

K) Move the cursor to the lower limit of the ROI with the "←" key. A reasonable limit is one peak width below the lowest-energy characteristic peak.

L) Press "L". A beep will sound. Note: the ROI should if possible, include all the characteristic peaks for a given element; this depends on spectral peaks present in the reference ie., how pure the reference is, and also if the ROI contains peaks which interfere in the ROI being established.

M) Press "D" when the ROI is satisfactorily set. N) The screen will display the reference number, the upper and lower limits of the ROI, and the query *"Element/Oxide?"*.

O) Type the name of the element (eg.; Sr) and press the "Enter" key. **If the element is expected in trace abundance, preface the element with "*" by pressing the "*" key; this causes the abundance to be reported in ppm (eg., *Sr)**; all other formats will assume output in weight percent.

P) The screen will display the query *"Save standards (Y/N)?"*. If "Y" is selected the program will prompt the user for *"Standard File"* and *"Drive & Path"*. Enter the drive and path where the ROI data is to be stored. Press "N" to return to the current spectrum (the menu options displayed at the bottom of the screen are now functional). Press the "Ctrl" simultaneously while pressing the "E" key to erase a spectrum.

Q) Return to step A until all ROI's to be used in stadardization are established. (A maximum of 20 are allowed.) Although the 1st reference may not be changed once established, subsequent references may be deleted and added again if necessary, for example, to widen the region of interest.

R) After the final ROI, Press "Y" when the *"Save standards (Y/N?)"* query appears; this allows saving of elemental reference ROI to be saved in a preliminary standard file.

5.6. PREPARE TO CALIBRATE STANDARDS

Calibration of standards consists of performing a least-squares solution for each element using the equation,

$$\text{Abundance} = A1 + A2 * \text{peak height} + A3 * (\text{peak height})^2$$

The least-squares analysis requires that standard spectra be acquired with the standard file A values set to:

$$A1 = 0 \quad A2 = 1 \quad A3 = 0.$$

1) **Check that "A values" are appropriately set.**
   - A. Choose the *setup* menu and select the *recall standards* option.
   - B. To answer the query *"Standard File?"* type in the name of the standard file (eg. CD for ^{109}Cd standardization) and press "Enter". Now type the drive and path where the file is to be stored and press "Enter".
   - C. Select the *Setup* menu and choose the *edit standards* option.
   - D. Type "A" to *edit A values*. A summary of A values is displayed. **Note: A1 should be 0.0, A2 should be 1.0, and A3 should be 0.0. If this is not the case, press F1 to reset all A values to 0,1,0.**

2) **Prepare to store batch analysis data** (mandatory).
   - A) Select the *Store data in file* option from the setup menu.
   - B) The computer responds, *"Store Data on disk (Y/N)?"*. Press "Y".
   - C) The computer prompts, *"File Name?"*. Type in a file name (eg. CD for ^{109}Cd standardization) using ≤ 8 characters (no extension). SUPERXAP assigns a .DSF extension to this file.
   - D) The computer prompts, "Drive & Path". Type the target drive and (if required) path for the file to be stored. (Note: at the end of the run, final storage is made in DATASAVE format.)

E) The computer reports the number of entries in the file (100 maximum) and is ready to store batch analysis data. Hit any key to continue.

3) **Toggle the printer off.**
   A) Choose the *Setup* menu
   B) Select the *Printer On/off* option
   C) Press "Enter" until "OFF" is capitalized and "on" is lower case; data generated in the next step will not be printed.

4) **Run batch analysis on standard spectra.** Select *Batch analysis* option from the *Input/Output* menu.
   A. Type the drive and directory where standard spectra are stored. Names of standard spectra will be displayed.
   B. Select the standards for *Batch analysis* by pressing "Enter", after placing the ">>" next to each standard to be used in the calibration procedure, in turn.
   C. After all desired standard spectra have been selected, press the "Esc" key to begin *Batch analysis.*

At the end of the Batch analysis, **store the data as a DATASAVE file. To do this press the "Alt" key followed by the "Q" key while the main menu is displayed. The program prompts, store data in Ascii and or DATASAVE formats. Press "D" to store data as a DATASAVE file.**

5.7. CALIBRATE STANDARDS

Calibrate standards is a subroutine in SUPERXAP that creates standard files by least- squares fitting of peak intensities to known elemental abundances. The standard files are used to calculate elemental abundances in samples with unknown compositions.

1) **Calibrate standards.** Restart the SUPERXAP program and choose the *Setup menu.* Select the *Calibrate standards option.*

2) **Select the sample code file.** A window will open to help select the file. Answer the query "*Code File*?" by either typing "DIR", or the file name (eg. KEVCODES) followed by "Enter". Answer "*Drive and path?*" by typing the drive location and directory of this file.

3) **Select the reference file.** A window will open to help select the file. Answer the query "*Reference file?*" by either typing "DIR" or the file name (eg. KEVEX.REF) followed by "Enter". Answer the query "*Drive and path?*" by typing the drive location and directory of this file.

4) **Select the XAP data file** *(*this is the file created during batch analysis of standards). A window will open to help select the file. Answer the query "*XAP file?*" by typing "DIR" or the name of the file (eg. CD.DSF for the ^{109}Cd standardization) followed by "Enter". Answer the query "*Drive and path?*" by typing the drive location and directory of this file.

(Note: Once the "DIR" is pressed and the query "*Drive and path?*" has been answered for step A above, the "Enter" key may be pressed for subsequent "*file?*" and "*Drive and path?*" query's for steps B and C, since SUPERXAP retains the previous key strokes in memory.

5) **Regression analysis on standard data.** Select the *Regression* option and press "Enter". A window will display the *Calibrate standards Setup Menu* and a list of elements. Select the element for regression analysis by pressing the "↑ ↓" keys to place a highlighted box on the element of interest; Press the "Enter" key. An element may be selected more than once.

6) **Select a regression.** Step through each regression format by using *the "↑↓→←" keys.* Press the "Enter" key, when the desired format has been chosen. For more information see section 6.3.

7) **Input a filter.** SUPERXAP displays the query "*filter?*". User response establishes a filter to eliminate poorly characterized standards. Example: A filter of 10 will eliminate all standards with concentrations for the selected element that are below 10 ppm from the regression. Example: A filter of -10 eliminates all poorly characterized samples from the

regression, regardless of element concentration and all well characterized samples with <10 ppm for the selected element. (Note: To flag poorly characterized standards so that they may be removed from the regression calculation by using a filter, enter poorly determined standard data with a "-" prefix in the KEVEX.REF file). Some experimentation is required but, in general, a filter of -10 or -20 is recommended. Note: an error will result if the filter excludes so many data points that a regression cannot be determined. After entering a filter, the regression is graphically displayed, along with statistical data for the regression, and a list of new menu options. These menu options are described below.

5.8. REGRESSION MENU OPTIONS

The regression menu displays several options. To return to the previous menu: (1) Place the solid ">" adjacent to the *Main Menu* option; (2) Press "Enter". Menu options are as follows.

1) Inspect data for each analysis by pressing "Enter" when the ">" is adjacent to the *Inspect data option*. Data for the selected standard include: A) Sample name, B) Accepted and measured concentrations plotted on the "X" and "Y" coordinates respectively, C) Percent deviation of measured concentration from accepted value; this is displayed graphically on the horizontal deviation graph (fig. 5). The solid horizontal line in the middle of the graph represents a value where both measured and accepted values are equal. The two dashed horizontal lines above the solid line represent +10% and +20% or greater deviation of the measured value from the accepted value. The two dashed lines below the solid line show where measured analyses differed from accepted values by -10% and -20% or greater D) And 2 σ standard deviation are displayed on the screen. Select subsequent analyses by pressing the "↑ ↓" keys. An analysis may be omitted from the fit by pressing"-" when the standard is highlighted on the graphic.
2) Rescale display allows the user to look at a specific area of the regression at greater magnification. SUPERXAP provides the query "Maximum value to display?". A value of 20 causes the area between 0 and 20 ppm to be displayed.
3) Attempt new Fit enables a different regression type to be applied to the data for a given element. After selecting *Attempt new Fit*, the regression type menu is displayed. Press the "↑ ↓" keys to scroll through the regression types. Press "Enter" to select the defined regression type. The query *"Filter?"* will be displayed. Type in the desired filter and press "Enter". A new regression will be displayed.
4) Pick new Element allows the user to establish a calibration curve for a new element. After selecting *Pick new Element*, a list of elements will be displayed. Scroll through elements and select the next element for regression and press "Enter". The query *"Filter?"* will be displayed. Type in the desired filter and press "Enter". A new regression will be determined and displayed.
5) *Print Screen* causes the screen image to be output to a printer.
6) *Store Screen* causes the screen image to be stored to disc for later examination. The program provides the query *"Image file?"*. Type the name of the element followed by "Enter". Answer the query *"Drive and path?"* by entering the drive location and directory to which the image is to be stored.
7) Once calibration curves have been established for all elements in the standardization, Select the *Store A values* in a standard file option, and answer the query *"Standard File?"* (eg. CD for ^{109}Cd standardization) and press "Enter". Next, answer the *"Drive and path?"* query by entering the drive location and directory where the standard file is to be stored. Note: This procedure updates A values in the standard file. Make sure to give the standard file a different name than those stored previously if it is desirable to save any of these files, as SUPERXAP writes over those files having the same name.

MENU OPTIONS.

6.1. OVERVIEW

At initialization SUPERXAP displays a logo followed by a list of menus (fig.1). Menus may be selected by simultaneously pressing the *"Alt"* key and the first letter of the menu (example: Alt-S to obtain the *Setup* menu). This will cause a pull-down list of options to be displayed. Having selected one menu, the user can scroll through the menus using the "← →" keys.

The "↑ ↓" keys are used to move a pointer up and down past options in the menu. An option may be selected by pressing the "Enter" key, after the desired option has been pointed to.

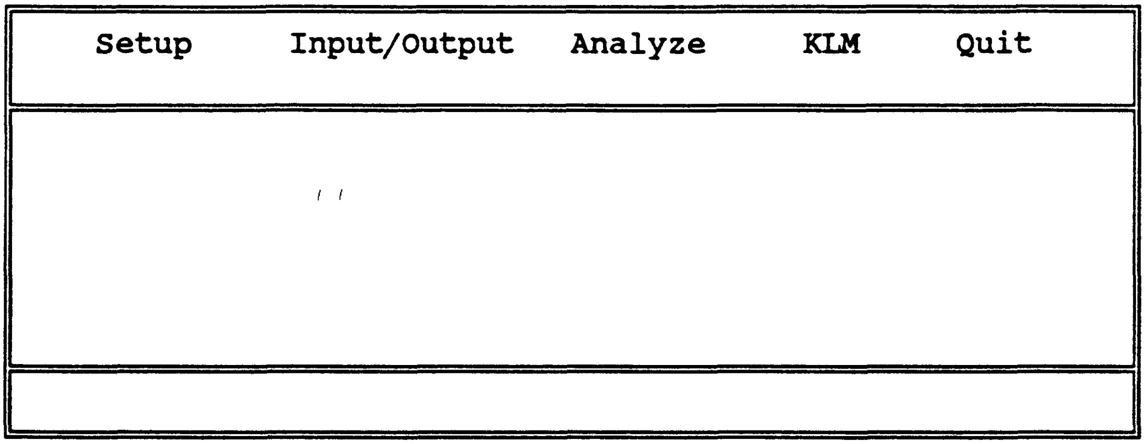


Figure 1. SUPERXAP main menu.

The *Setup* menu (fig. 2) contains ten options. These options are used to prepare SUPERXAP to accept, analyze, output, and store data. Each option is described as follows.

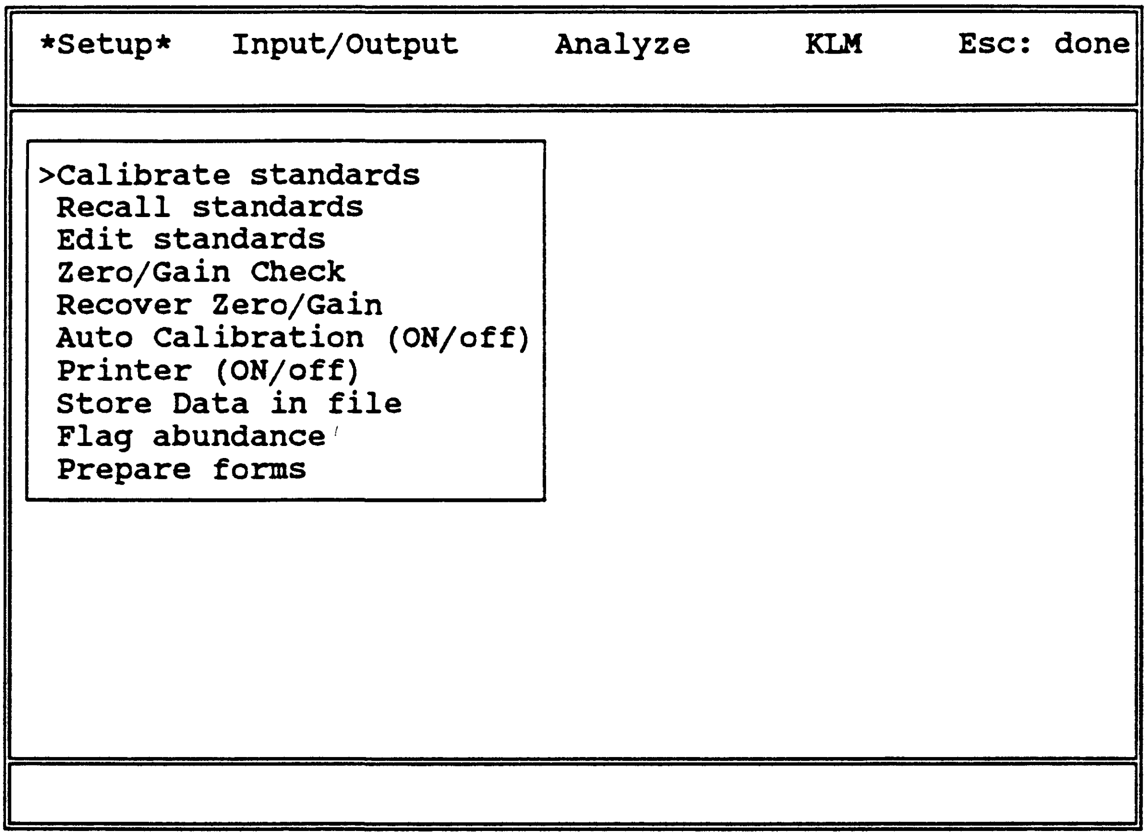


Figure 2. SUPERXAP main menu showing the *Setup* menu options. Asterisks indicate that the *Setup* menu has been selected. ">" points to the current option (Calibrate standards) ready for selection.

6.2. CALIBRATE STANDARDS

Calibrate standards establishes the relations between peak height and concentration in standards.

This option requires
1) A KEVEX.REF file, containing accepted values of standards
2) A Xap Data File, containing measured values of standards, to establish calibration curves.
   Press "Enter" when the ">" is adjacent to the *Calibrate standards* option in the *Setup* menu to display the calibrate-standards menu and the graphical box in which regressions will be plotted (fig. 3).

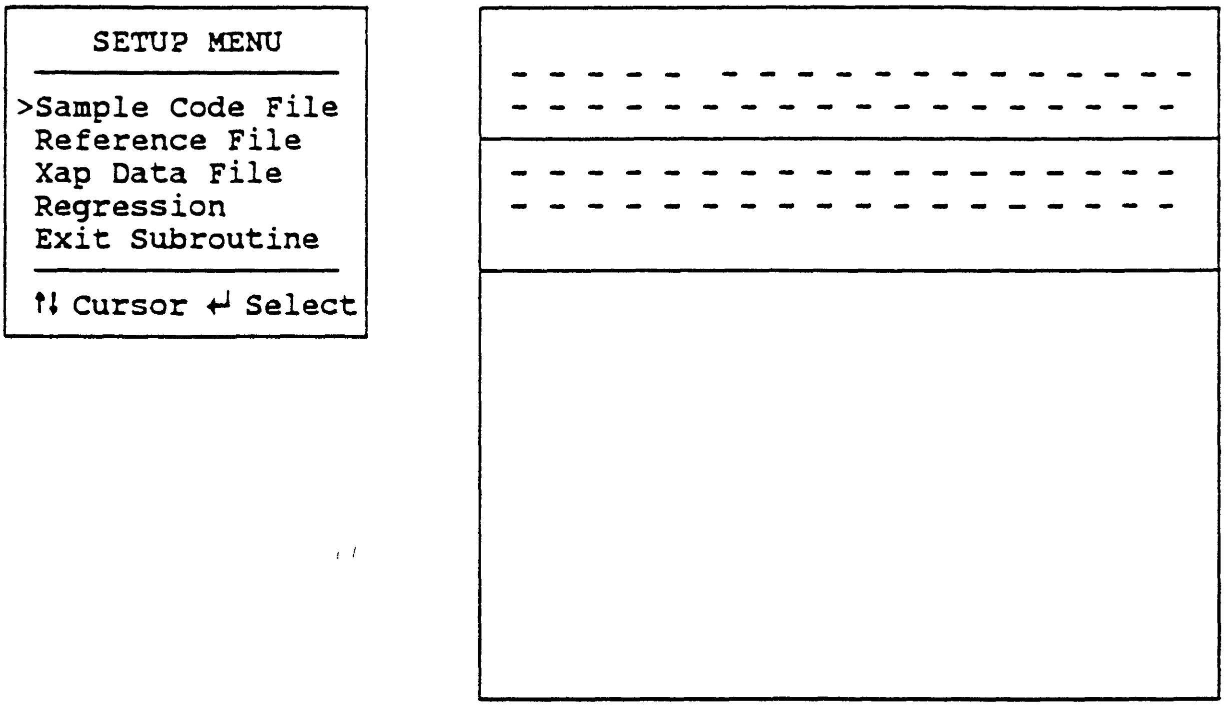


Figure 3. Menu and graph template displayed after selection of the *Calibrate Standards* option.

Use the "↑ ↓" keys to scroll the ">" through this menu and select desired option by pressing "Enter".

Options in this menu are answered in the order they would normally be performed. The *Sample Code File*, *Reference File*, and *Xap Data File* must all be recalled before calibration. Use the following steps to recall each file.

1) Select appropriate option by pointing to it with the ">" and press "Enter".
2) "Type "DIR" followed by "Enter". The prompt *"Drive & Path?"* is displayed.
3) Type the drive and path of the file (e.g. C:\SUPERXAP) and press "Enter". The files used in SUPERXAP will be displayed. Move the ">>" adjacent to the desired files (eg., KEVCODES, KEVEX.REF, CD.DSF) using the "↑ ↓" and press enter.

The *Regression* option is used to prepare calibration curves for each element. After selecting the regression option, a list of the elements included in a specific standardization file is displayed (fig. 4). Move the highlighted box adjacent to an element using the "↑ ↓" keys and press "Enter".

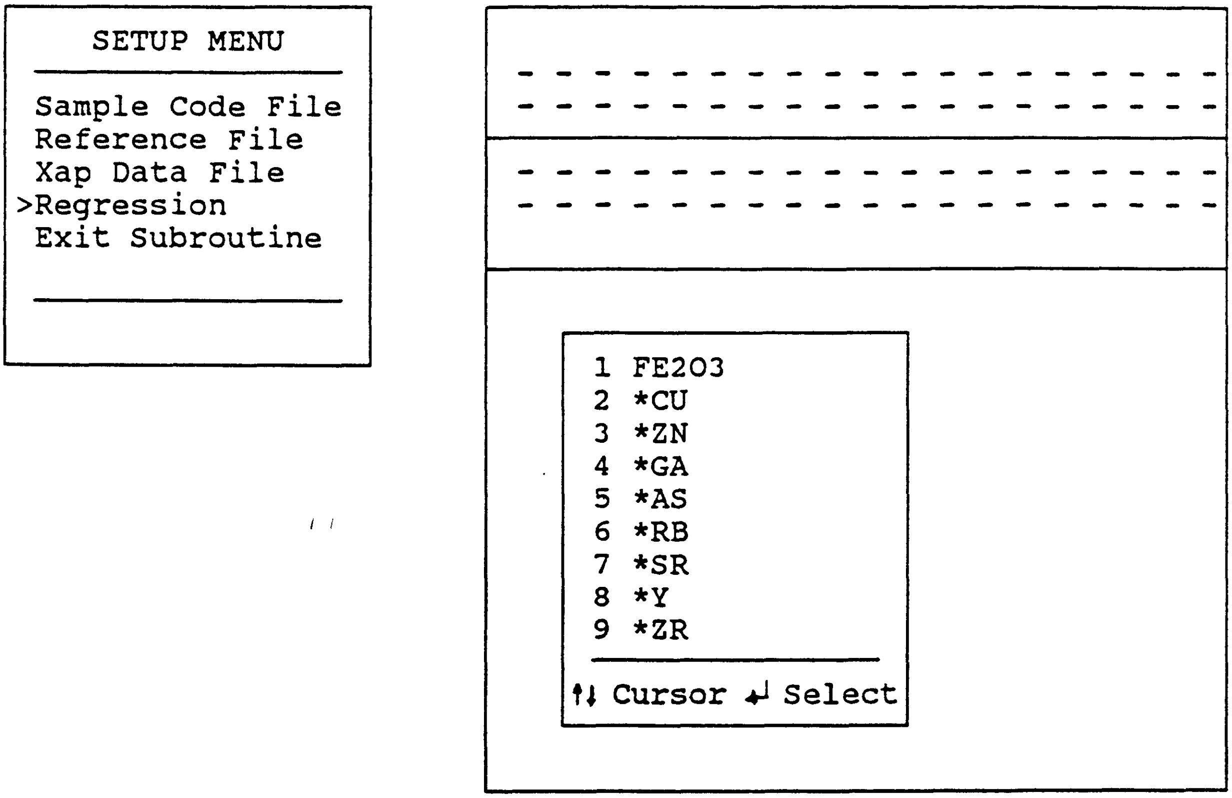
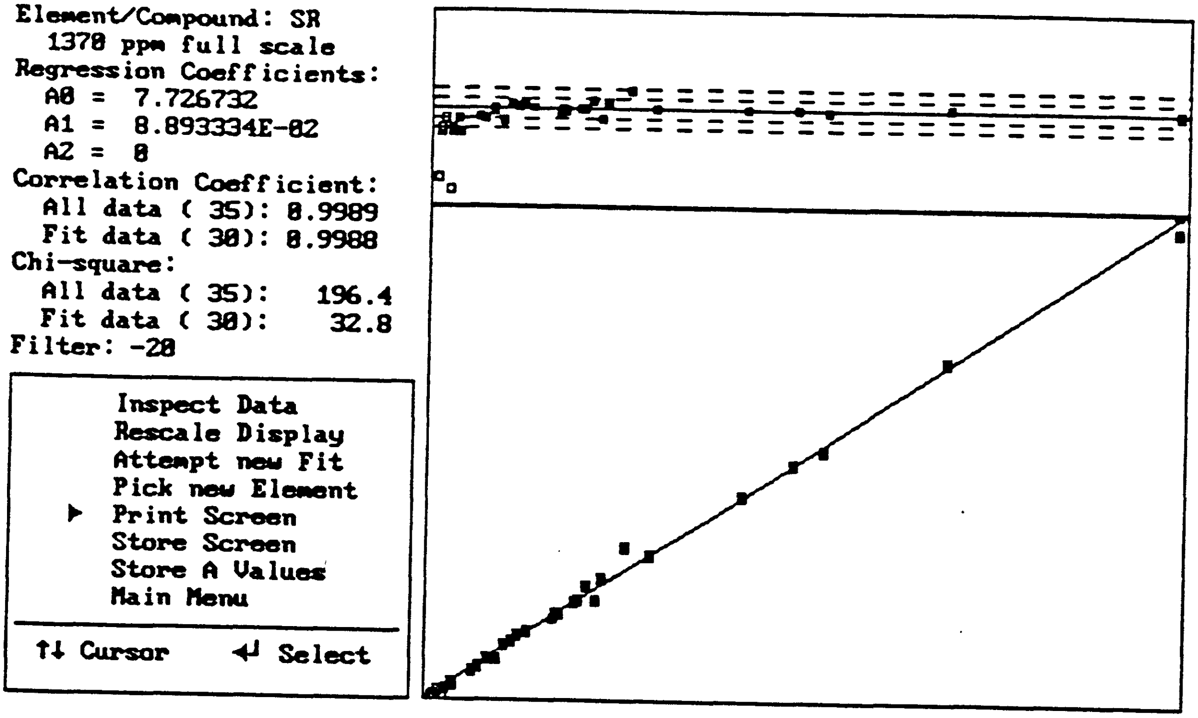


Figure 4. List of elements displayed after the *Sample Code File, Reference File*, and *Xap Data File* were specified, followed by choosing a *Regression* option.

A regression equation will be displayed on the screen. Scroll through the regression equations using the "↑↓→←" keys. Select one of 4 regression equations by pressing "Enter". The 4 regression choices are as follows.

1) $Y= A_1 * X$: forces A_0 (y-intercept) and A_2 (2nd order term) to 0 in the regression matrix calculation. This is the best alternative for elements in trace abundance without significant interference or problems in background subtraction.
2) $Y= A_0 + (A_1 * X)$: solves for the Y intercept (A_0) and slope factor (A_1) which relates counts per second to parts per million or weight percent. This is the best alternative for cases in which background subtraction is difficult.
3) $Y= (A_1 * X) + (A_2 * X * X)$: sets the Y intercept to 0 and forces a second order fit. This is the best choice for element present in a wide range of abundance from ppm to percents.
4) $Y = A_0 + (A_1 * X) + (A_2 * X * X)$: assumes non zero Y intercept and forces a second order fit.

Choose a regression type and press "Enter". The "*Filter ?*" query will is displayed (filters are described in section 5.6). Press "Enter" and the regression is displayed in addition to the regression menu options (fig. 5). If the filter eliminates too many points to perform the calculation, an error results and the program returns to the first menu of the calibration routine (Solution-- lower the filter to a level, the absolute value of which, will contain enough data to perform the calculation). Return to the calculation by selecting the "*Regression*" option.



```
Element/Compound: SR
  1370 ppm full scale
Regression Coefficients:
  A0 =  7.726732
  A1 =  0.893334E-02
  A2 =  0
Correlation Coefficient:
  All data ( 35): 0.9989
  Fit data ( 30): 0.9988
Chi-square:
  All data ( 35):    196.4
  Fit data ( 30):     32.8
Filter: -20
```

Figure 5. Example of a calibration curve established for Sr.

The following is a list of information contained in the regression display.

1) Element/oxide
2) The scale of the data (in ppm)
3) Calculated regression (A value) coefficients
4) Correlation coefficients for data used in the regression calculation (fit data) and for all available standard data (all data).
5) Chi-square values.
6) The filter value

A menu of options is displayed in the "*Regression* menu" in the lower left corner of the screen. Scroll through the regression menu options using the "↑ ↓" keys and select an option by pressing "Enter". A description of regression menu options follows:

1) *Inspect Data* allows examination of all data included in the regression. The sample name as well as accepted value, measured value, deviation from accepted value, and 2σ standard deviation are displayed. Select an analysis by pressing the "↑ ↓" keys. Omit any analysis from the fit by pressing the "-" key. Press the "Esc" key to return to the regression menu.
2) *Rescale display* enables magnification of a portion of the graph. Answer the query "*Maximum value to display?*" by typing the value in ppm or weight percent that corresponds to the maximum value for the re-scaled graphs, press "*Enter*". The regression graph up to the maximum number entered will be displayed.
3) *Attempt new fit* allows selection of either a new filter and (or) new regression.

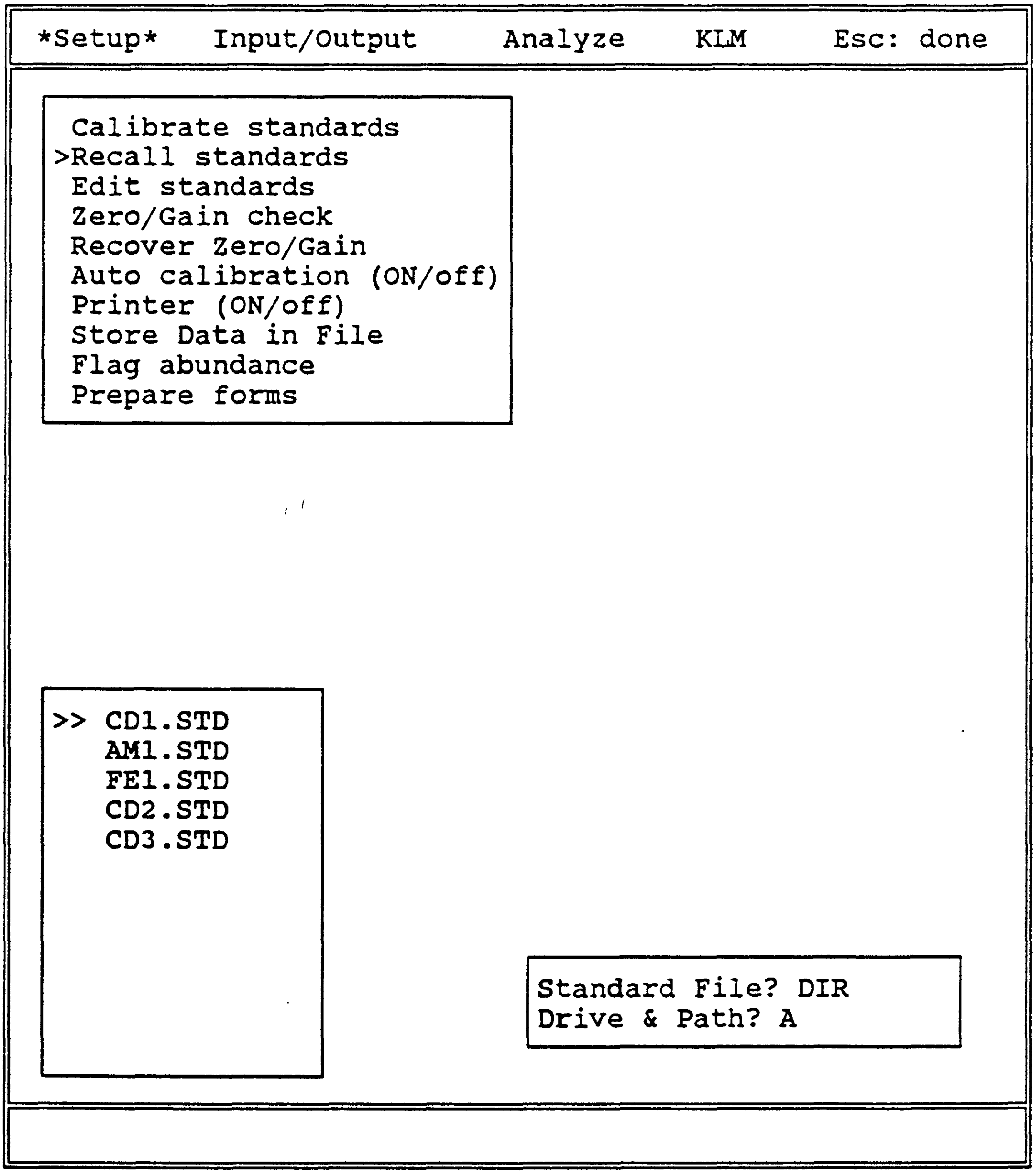
4) *Pick new Element* returns the program to the previous menu so that a new element may be calibrated.
5) *Print Screen* causes the current screen image to be output to a printer.
6) *Store Screen* allows the current screen image to be stored to disc as a DATASAVE image file. Use the following steps to store a regression screen:
   A) Select *Store Screen*; the prompt *"Image File?"* will be displayed.
   B) Type in a file name and press *"Enter"*. The query *"Drive & Path?"* will be displayed.
   C) Type the drive and path where the image file is to be stored. A vertical bar on the right edge of the screen shortens with time, and eventually disappears when image storage is complete.

7) *Store A Values* at any time during the regression procedure.
A) Select this option and answer the query *"Standard File?"* by typing in ≤ 8 characters (no extension) and press "Enter". **A values must be stored before exiting this portion of the program, if this file is to be used as a standard file.**
B) Answer the *"Drive and Path?"* query; type the drive and path to which the calibration data is to be stored.
8) Select the *Main Menu* to return to the *Calibrate standards Setup* menu.

6.3. RECALL STANDARDS

Recall standards enables a previously stored standard file to be recalled from disc. The standard file is required for least squares regression analysis of unknown spectra.
Select *Recall standards* then:

1) Answer the *"Standard File?"* query by typing "DIR" followed by "Enter".
2) Answer the *"Drive & Path?"* query by typing the drive and path that contains the desired standard file; press "Enter" (fig. 6).
3) The standard file is displayed on the screen as is the statement *"Calculating matrix core! Standby Please!"* (fig. 7).
4) When the calculation is complete, the prompt *"Hit any key to continue"* will be displayed. Press any key to return to the *Setup* menu.



```
>> CD1.STD
   AM1.STD
   FE1.STD
   CD2.STD
   CD3.STD
```

```
Standard File? DIR
Drive & Path? A
```

Figure 6. Menu prompts displayed while using the *recall standards* option.

6.4. EDIT STANDARDS

Edit standards allows modification of the existing standard file; this should only be done by those individuals knowledgeable in this procedure. This option may be useful to change the A values, element name, and concentration factor in a standard file, or erase elements completely

To use this option Select *Edit standards* then:

1) Recall the standard file to be edited, as was described previously and press "Enter"
2) Select the *Edit standards* option from the *Setup* menu. The standard file is displayed; a list of edit options is displayed beneath the data (fig.8).

```
    ELE       LROI     UROI     COUNTS/SEC   CONCENTRATION   CONTIUUM

 1  FE203     5840     7560        6354        10000.00        554.41
 2  *CU       7600     9360        3761        10000.00       1421.92
 3  *ZN       7960    10200        3055        10000.00       2209.03
 4  *GA       8760    10880          69        10000.00       4073.95
 5  *AS       9720    12480        4950        10000.00       1094.54
 6  *RB      12600    16200        2040        10000.00       2061.74
 7  *SR      13600    16600         413        10000.00       4026.42
 8  *Y       14240    17600         744        10000.00       3612.55
 9  *ZR      15080    18320         434        10000.00       3104.18
10  *NB      15680    19560         484        10000.00       2958.65
11  *MO      16400    20240         729        10000.00       2603.37
12  *W        6960    12360        2249        10000.00       1810.24
13  *PB       8640    16200        5683        10000.00       1127.10
14  *BI       9000    16280         540        10000.00       1718.24
15  *TH      10680    19480         419        10000.00       2563.18
16  *U       11120    18360         719        10000.00       3383.61

Calculating matrix core!  Standby please!
```

Figure 7. Example of a standard file displayed on a screen, after being recalled from disc.

```
   ELE        LROI      UROI       COUNTS/SEC CONCENTRATION     CONTIUUM

 1 FE203      5840      7560        6354        10000.00          554.41
 2 *CU        7600      9360        3761        10000.00         1421.92
 3 *ZN        7960     10200        3055        10000.00         2209.03
 4 *GA        8760     10880          69        10000.00         4073.95
 5 *AS        9720     12480        4950        10000.00         1094.54
 6 *RB       12600     16200        2040        10000.00         2061.74
 7 *SR       13600     16600         413        10000.00         4026.42
 8 *Y        14240     17600         744        10000.00         3612.55
 9 *ZR       15080     18320         434        10000.00         3104.18
10 *NB       15680     19560         484        10000.00         2958.65
11 *MO       16400     20240         729        10000.00         2603.37
12 *W         6960     12360        2249        10000.00         1810.24
13 *PB        8640     16200        5683        10000.00         1127.10
14 *BI        9000     16280         540        10000.00         1718.24
15 *TH       10680     19480         419        10000.00         2563.18
16 *U        11120     18360         719        10000.00         3383.61

A: Edit A's  L: List  E: Erase  N: Name  C: Concen  S: Store
ESC: Done
```

Figure 8. Example of a standard file that has been recalled and the edit standards option has been chosen.

The standard file data display includes:

1) Element
2) Lower region of interest (LROI) in eV and upper region of interest (UROI) in eV; both of which were defined using the *Establish reference* option)
3) Maximum counts/second for the tallest reference peak
4) A concentration factor, which is the element concentration in the reference material. The concentration of an element in a reference is not always known and, therefore, is arbitrarily set to 10,000 by the program. The option exists, however, to reset this value <u>prior to calibrating standards</u>. (Setting the concentration factor equal to the true element concentration in a reference will cause A1 to approach 1 in most cases).
5) The number of counts in the continuum, as determined after establishing the "1st" reference (described in section 5.4).

To edit the file, type the first letter of the desired option from the list of options located at the bottom of the display.

"L" to output the contents of the standard file to the printer.

"E" to omit an element from the standard file. Answer the query "*Element?*" by typing the element name to be deleted, followed by "Enter".

"N" to either name or re-name an element (answer the query "*Element to rename?*" by typing the new name followed by "Enter". Now type the new element name.

"C" to change a concentration factor (Caution! This should not be done unless you understand the implications). After doing so, the prompt "*Which element?*" will be displayed. Type the element name. **Be sure to include the "*" prefix if it is a trace element.** Type in the new concentration in response to the query "*New concentration?*" and press "Enter".

"S" to store the standard file changes.

"Esc" to return to the main menu. Answer the query *"Standard File?"* by typing the new file name. Answer the prompt *"Drive & Path?"* by typing the drive and path to which the standard file is to be stored. Press "Enter"

"A" to edit A values; A values are displayed (fig. 9.) Answer the query *"Element?"* by typing the element name, followed by "Enter". Enter new A0, A1, and A2 values. Type "F1" to reset all A values to 0,1,0 **(necessary when doing initial satandardization before batch analysis)**. Type "Esc" to escape to the *Edit standards* menu.

```
     ELE              AO              A1              A2
 1   FE203          0.000000        0.055232       -0.000050
 2   *CU         -150.577393       28.561529        0.000000
 3   *ZN           -1.804511       10.048280        0.000000
 4   *GA            5.359668        0.070597        0.000000
 5   *AS           -5.770389       14.170050        0.000000
 6   *RB            0.000000        1.072473        0.000000
 7   *SR            0.000000        0.089458        0.000000
 8   *Y             1.590433        0.170756        0.000000
 9   *ZR            0.000000        0.092384        0.000000
10   *NB            2.930062        0.108149        0.000000
11   *MO          -34.936359        0.227183        0.000000
12   *W             0.000000        1.063151        0.000000
13   *PB            0.000000       10.764870        0.000000
14   *BI            0.000000        0.000165        0.000000
15   *TH            8.757593        0.291646        0.000000
16   *U           -43.951851        0.279036        0.000000

E:   Edit   F1:   Reset all to 0,1,0   Esc:   Done
```

Figure 9. Example of A values in a standard file displayed on a screen.

6.5 ZERO/GAIN CHECK

Zero/Gain check is used to correct spectrometer drift. If the KEVEX zero and or gain requires manual adjustment (ie., the offset and gain after *Zero/Gain check* is > ±10 eV) **refer to KEVEX manual for further instruction.** To adjust zero and gain, proceed as the follows.

A) Adjust the fine gain on the front of the KEVEX-7000 panel using a small screw driver. Turn the gain counter clockwise to lower the gain (causes peaks displayed on the KEVEX monitor to be displaced to lower keV values) and turn the gain clockwise to increase (causes peaks displaced on the KEVEX monitor to be displaced to lower keV values) the gain. Wait approximately two minutes to allow hysteresis effects to stabilize. Re-run a *Zero/Gain check.* Examine the new results and repeat the process if needed.

B) Once the gain between the K and L lines used for the *Zero/Gain check* are approximately equal, and if the zero, and offset, are not in the 0 to 10 eV range, adjust the zero adjustment screw on the front of the KEVEX panel counter-clockwise or clockwise. A counter-clockwise adjustment causes peaks displayed on the KEVEX to be displaced to lower keV values. A clockwise adjustment causes peaks on the KEVEX monitor be displaced to higher values. Note: **Whenever adjustments to the calibration zero or gain screws on the KEVEX panel are made, document the amount**

of adjustment made in each iteration, as back tracking may be necessary. Also, it is **unlikely that adjustments to the coarse gain will to be required.**

C) Repeat steps A and B until the optimum calibration run conditions have been attained (ie., zero, offset, and gain all below 10 eV). If for any reason SUPERXAP execution is terminated, the calibration must be either recovered, by either selecting the *Recover calibration* option or rerunning a new *Zero/Gain* correction.

6.6. RECOVER ZERO/GAIN

Recover Zero/Gain allows the previous *Zero/Gain check* to be recalled in the event that SUPERXAP execution terminates and additional analysis are to be performed using the previous Zero/Gain check (the Zero/Gain parameter is stored on the default drive and directory). **When SUPERXAP execution terminates, and then is re-initiated,** the Zero/Gain check **will not be recalled unless the** Recover Zero/Gain **option is selected.** Alternatively, **a new** Zero/Gain **check can be performed.** To recover the previous *Zero/Gain*, select *Recover Zero/Gain* from the *Setup* menu and press "Enter"; a beep will sound. The beep indicates that the previous Zero/Gain check has been recovered.

6.7. AUTO CALIBRATION ON/OFF

The *Auto calibration* ON/off function is an option allowing analyses to be performed without a Zero/Gain correction. **It is highly recommended that ALL analyses are performed with the Auto calibration (ON/off) in the ON condition.** This option allows toggling of the *Auto Calibration ON/off*, to the OFF position (ON is the default setting). Press the "Enter" key while the ">" is adjacent to this option. When OFF appears in all capital letters, then the *Auto Calibration on/OFF is in the OFF* setting.

6.8. PRINTER ON/OFF

Printer (ON/off) allows SUPERXAP to analyze data without being output to a printer. If this option is not switched to the OFF position, and SUPERXAP is not interfaced to a printer, error number 24 will be displayed. If this error occurs, press any key to return to the main menu. To switch the printer OFF (ON is the default setting) select this option and press the "Enter" key until the word OFF appears in all capital letters. switch the printer ON by using the same procedure as described above, until the word ON appears in all capital letters.

6.9. STORE DATA IN FILE

Store Data in file allows calculated element abundances to be stored to disc. Refer to section 4.2 for further information.

6.10. FLAG ABUNDANCES

Flag abundance causes abundances (in unknowns) that exceed specified values to be highlighted in the printout. To flag an abundance:

1) Select *Flag abundances*, type "F" to set a flag.
2) Answer the *"Element?"* query by typing the element name for which the flag is to be set, followed by "Enter".

3) Answer the query *"Threshhold?"* by entering the value, above which, printed abundances for the selected element will be highlighted.

6.11. PREPARE FORMS

Prepare forms writes a heading to the printer that indicates that the data acquired was obtained using the energy dispersive technique. The heading is as follows: " ENERGY DISPERSIVE XRF ANALYSIS.

7.1. OVERVIEW

The *Input/Output* menu options are used to transfer, store, and analyze spectra. Also, the user may shell to DOS, and return to SUPERXAP using this menu. The menu consists of seven options (fig. 10).

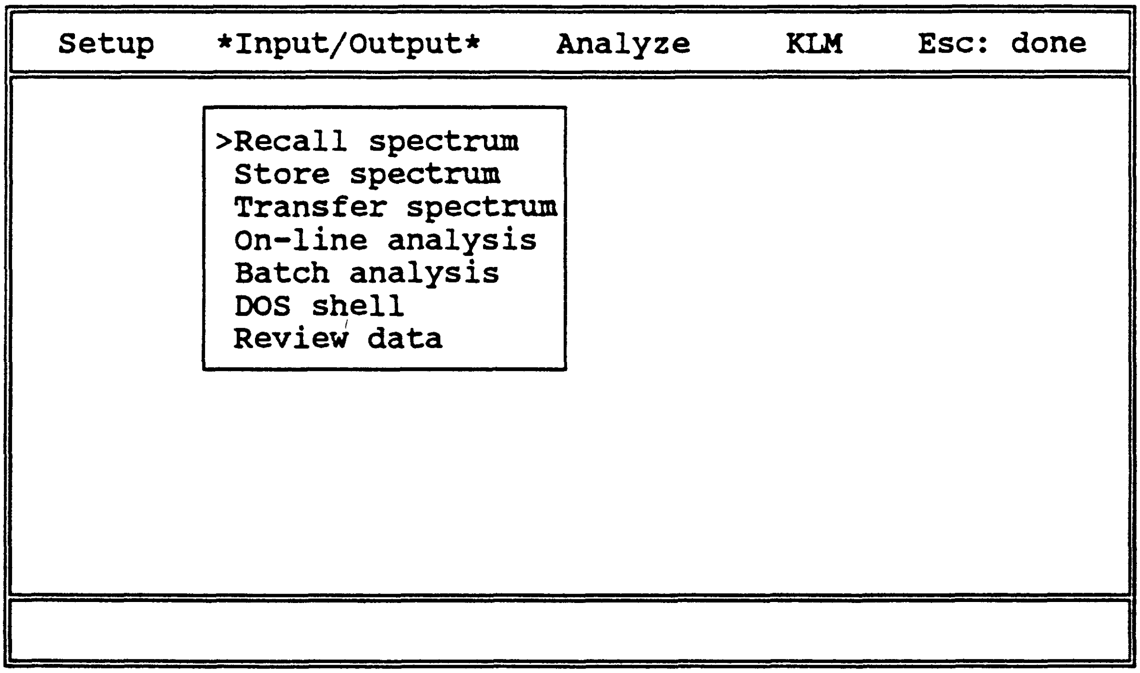
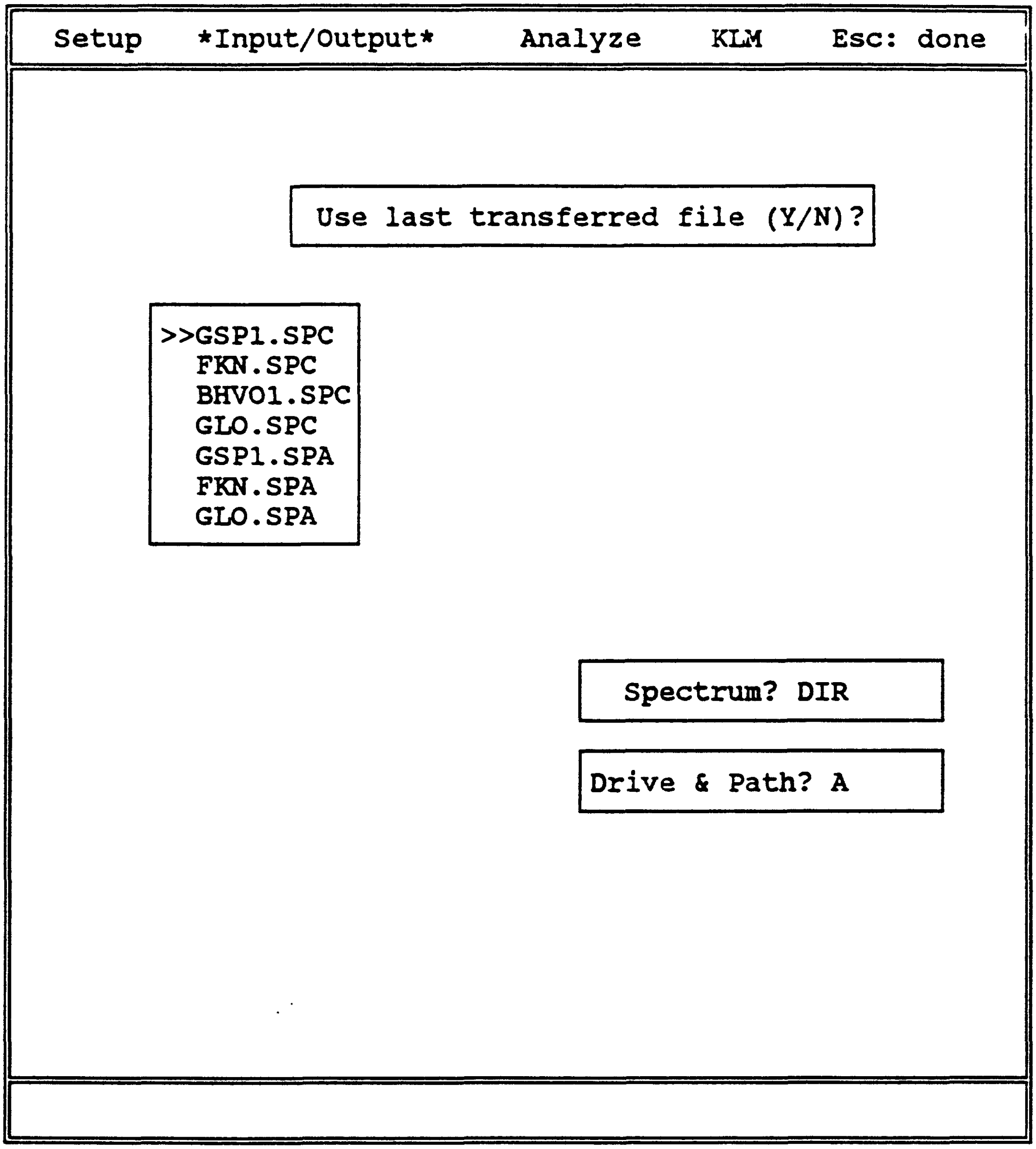


Figure 10. *Input/Output* menu options.

7.2. RECALL SPECTRUM

Recall spectrum allows a stored spectrum (0 to 40 keV) to be recalled from disc and displayed. To recall a spectrum:

1) Select the *Recall spectrum* and press "Enter".
2) Answer the query *"Use last transferred file (Y/N)?"* by typing either "N" or "Enter" if a spectrum stored on disk is to be recalled, or "Y" if the last transferred spectrum from the KEVEX is to be recalled.
3) If "N" is entered, answer the query *"Spectrum?"* by typing the stored spectrum name followed by "Enter". Alternatively type "DIR" and "Enter" followed by the drive and path of stored spectral data (fig. 11).
4) Use the "↑ ↓" keys to scroll through directory contents. Press "Enter" to select a spectrum.



Use last transferred file (Y/N)?

```
>>GSP1.SPC
  FKN.SPC
  BHVO1.SPC
  GLO.SPC
  GSP1.SPA
  FKN.SPA
  GLO.SPA
```

Spectrum? DIR

Drive & Path? A

Figure 11. Main menu showing procedures involving the *Recall spectrum* function.

An example of a screen with a recalled spectrum is displayed (fig. 12).

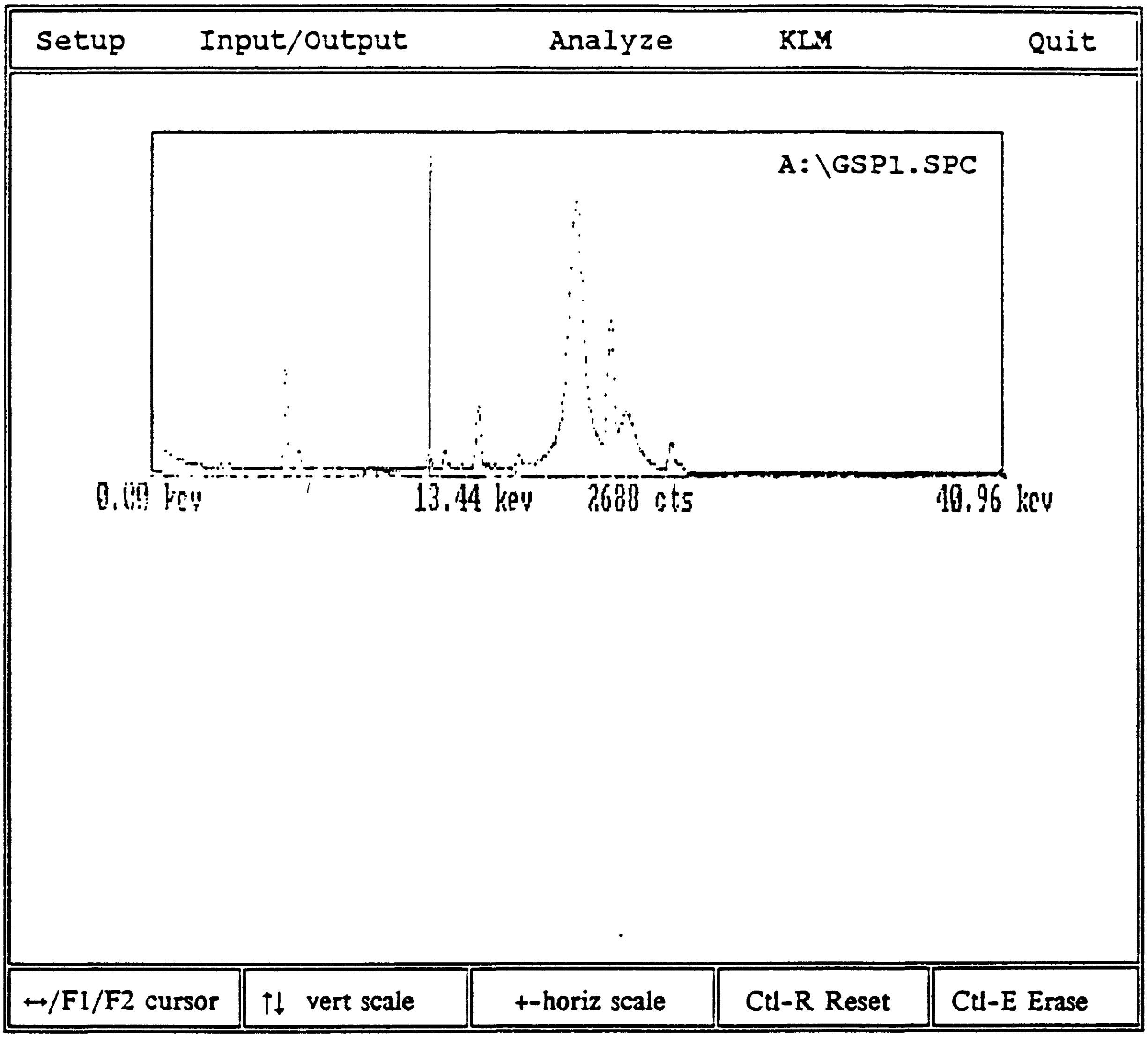


Figure 12. Example of a recalled spectrum.

4) Press the "Esc" key to remove the *Input/Output* menu options from the screen; the recalled spectrum, along with recall spectrum menu options are displayed at the bottom of the screen. A cursor (vertical line) is displayed in the center of the screen; cursor position (in keV) and the number of counts in the channel occupied by the cursor are indicated below the spectrum. Cursor movement and the function of the spectrum manipulation options are described below:

"← →" keys move the cursor left or right, respectively
"F1", or "F2" decrease or increase cursor speed
"↑ ↓" increase or decrease the vertical scale
"+" or "-" expands or contracts the horizontal scale
"Ctrl" simultaneously with "R" resets the display to it's initial settings
"Ctrl" simultaneously with "E" erases the spectrum

To recall and display two spectra simultaneously:

1) **With one spectrum displayed** press the "Alt" and "I" keys simultaneously to select the *Input/Output* menu.

2) Select *Recall spectrum*. After selecting the second spectrum to display, answer the "*Select display!*" prompt.
3) Answer the prompt "*Select display!*" by typing either "1" or "2" and "Enter". "1" displays the spectrum in the upper half of the screen. "2" displays the spectrum in the lower half of the display. Previously displayed spectra will be erased from view as necessary (fig. 13).
4) Press the "Esc" key to remove the *Input/Output* menu and display the spectra manipulation options at the bottom of the screen.

INPUT OUTPUT MENU RECALL SPECTRUM

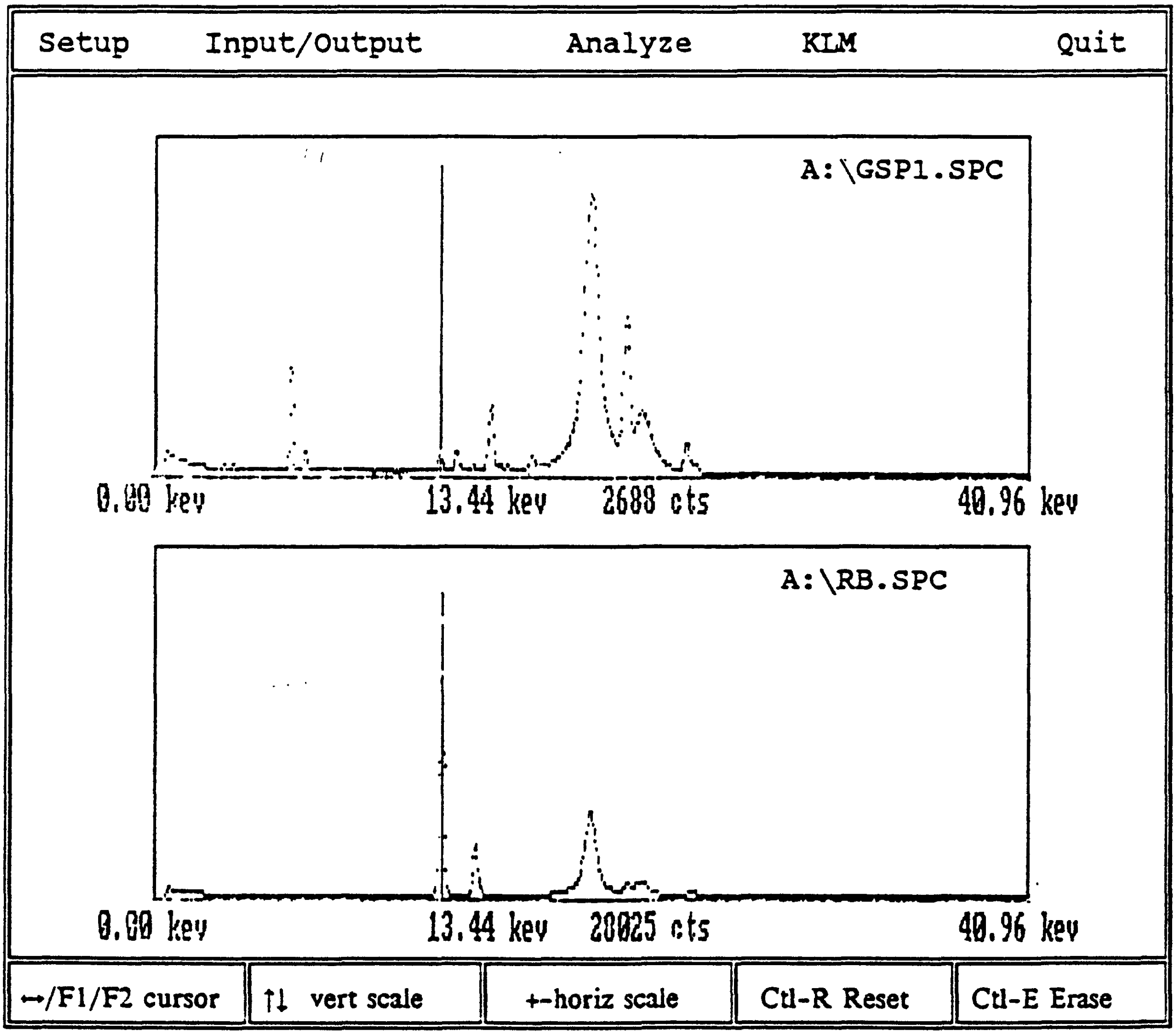


Figure 13. Two spectra displayed simultaneously.

7.3. STORE SPECTRUM

Store spectrum causes any acquired spectrum to be stored for later analysis or spectral manipulation. (Note: *On-line analysis* allows all spectra to be stored automatically as they are transferred to the PC. Refer to section 4.2 to prepare for automatic data storage). To store a spectrum:

1) After spectral data has been transmitted from the KEVEX to the PC, select the *Store spectrum* option
2) Answer the query "*Spectrum?*" by typing the spectrum name ($\leq$8 characters, no extensions) followed by "Enter"
3) Answer the query "*Drive & Path?*" by typing the drive and path where the data is to be stored followed by "Enter"

7.4. ON-LINE ANALYSIS

On-line analysis causes transferred spectra to be immediately and automatically analyzed for element abundances. Use the routine analysis procedure described in section 4.3 to utilize this option.

7.5. BATCH ANALYSIS

Batch analysis allows up to 100 stored spectra to be recalled and analyzed in any sequence. Recall the appropriate standard file (eg. CD for ^{109}Cd analysis) before proceeding. To implement *Batch analysis*:

1) Select the *Batch analysis* option and press "Enter". Enter the drive and path of the stored spectra and press "Enter". A window is displayed showing all data in the directory. Use the "↑ ↓" keys to scroll through the spectra (samples having suffixes of .SPC .SPA or .SPF, acquired using ^{109}Cd, ^{241}Am, and ^{55}Fe excitation respectively) for *Batch analysis.*
2) Select the spectrum for *Batch analysis* by pressing "Enter" when the ">>" is next to the desired spectrum.
3) Continue to scroll and select spectra or press "Esc" to begin *Batch analysis.* See section 4.4 (Terminate run) to store data in either ASCII and or DATASAVE formats.

7.6. DOS SHELL

DOS shell enables a temporary exit from SUPERXAP to DOS. To return from DOS to SUPERXAP, type "EXIT" at the DOS prompt and press "Enter".

7.7. REVIEW DATA

This function allows data from the current analytical run to be reviewed on the monitor. Between transmission of spectral data from the KEVEX to the PC during *On-line analysis*, or after *Batch analysis* the user may select the *Review data* option. A list of analyses for up to 100 samples is be displayed, 5 analyses at a time (fig. 14).

```
          ABUNDANCES IN CURRENT RUN        11-16-1991

ENTRY          1           2          3          4          5
SAMPLE        SY2        GSP1         BR        SDC1        UBN

FE203         6.3         4.1       12.3        6.8        9.0
*CU             0          16         39         16          0
*ZN           271          92        197        113         27
*GA            20          27         15         23         11
*AS           bdl         bdl         10          0         11
*RB           230         252         54        128         13
*SR           267         232       1352        175          5
*Y            126          30         30         37          6
*ZR           258         494        247        286          3
*NB            26          22        104         19        bdl
*MO             0           0          0          0          3
*W            bdl         bdl        bdl        bdl        bdl
*PB           116          63         20         31         17
*BI           bdl           0          0          0          0
*TH           381          94         16        bdl        bdl

Scroll (1/step) Shft Scroll (4/step)  Ctrl  Start/End  Esc  Exit
```

Figure 14. Display of data generated using the *Review data* option.

To review data:

"↑↓→←" keys scroll through analyses slowly.
"Shift" "← →" scrolls fast.
"Ctrl" "← →" moves the display to the start or end of the data set.

8.1. OVERVIEW

The *Analyze* menu contains five options designed for manipulation and analysis of spectra (fig. 15).

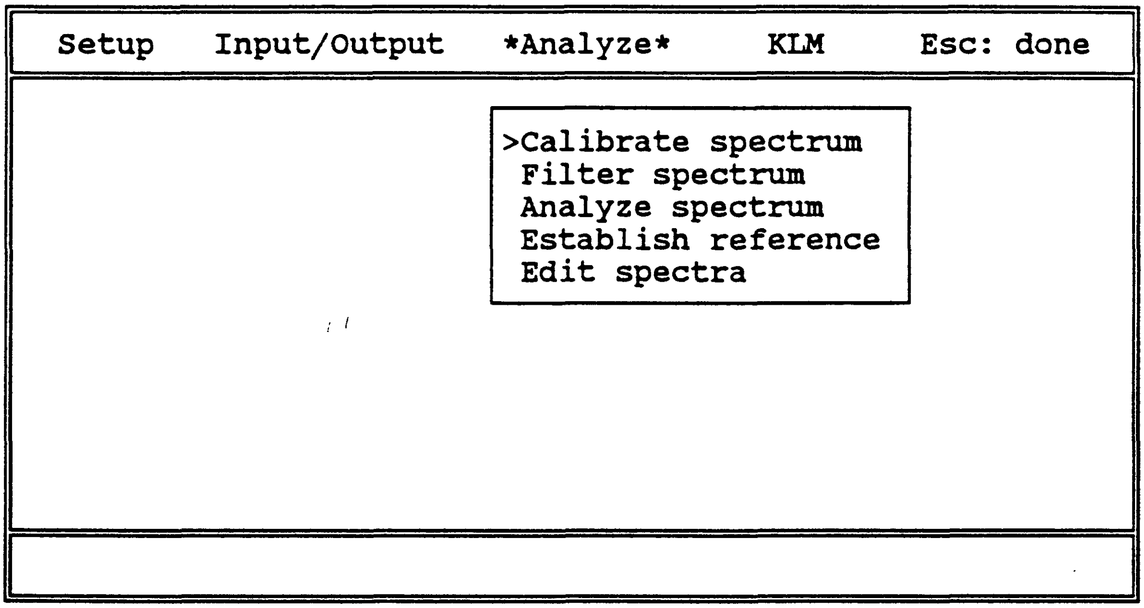


Figure 15. SUPERXAP *Analyze* menu.

8.2. CALIBRATE SPECTRUM

Calibrate spectrum performs the zero/gain correction on the spectrum displayed on the screen. Corrections are performed with zero and gain values at the time of spectrum acquisition; these are always stored with the spectrum.

8.3. FILTER SPECTRUM

Filter spectrum digitally filters a spectrum shown on the screen. The filtered spectrum is displayed in its place (fig. 16).

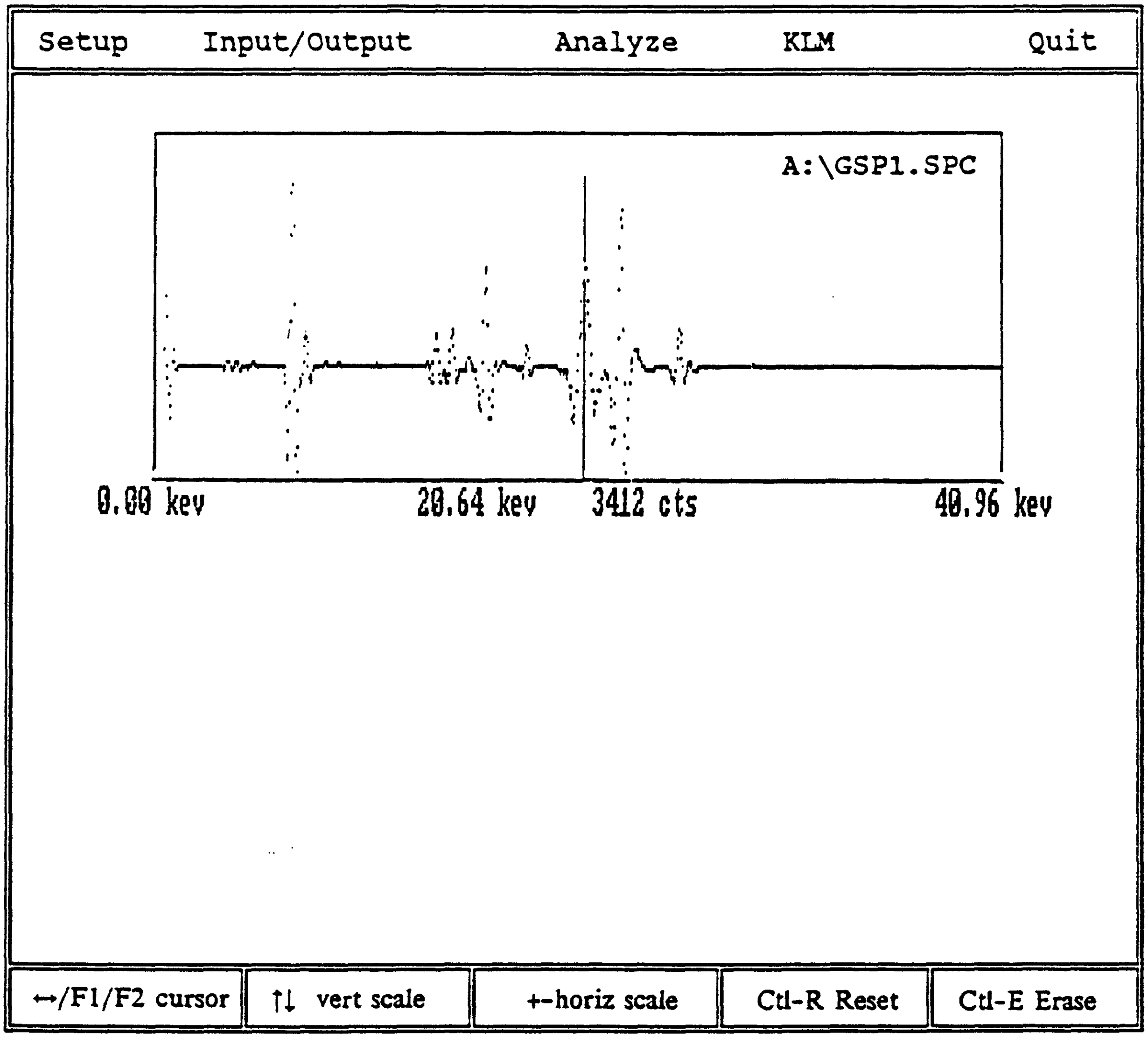


Figure 16. Spectrum after a digital filter has been applied.

8.4. ANALYZE SPECTRUM

Analyze spectrum calculates element abundances for a spectrum displayed on the screen. The calculation requires that an appropriate standard file has been loaded into memory using the *Setup* menu.

8.5. ESTABLISH REFERENCE

Establish reference allows ROIs to be established on references. The ROIs will be added to a standard file and used in least-squares fit of spectra with unknown elemental abundance.

8.6. EDIT SPECTRA

Edit spectra allows addition or subtraction of two spectra displayed on the screen. This may by useful in examining peak overlap effects such as is the case when the peaks of two elements having overlaps occur in the same sample. This feature may also be useful in subtracting an undesirable peak from a reference spectrum. Note: the "↑ ↓" control the vertical axis, and the "+ -" keys control the horizontal axis of the displayed spectra. To *Edit spectra*:

1) Recall two spectra. First recall the spectrum to edit, then the spectrum that is to be added or subtracted (usually an elemental reference).
2) Select the *Analyze* menu.
3) Select the *Edit spectra* option and press the "Enter" key.
4) Answer the statement "*select one: 1) Work on upper spectrum, 2) Work on lower spectrum*" by pressing "1" or "2". "1" causes all modifications to be performed to the upper spectrum and "2" to the lower spectrum.
5) The current addition factor will be displayed as well as the query "*New addition factor?*".
6) Answer this query by typing in the percent of the spectra to be added or subtracted and press "Enter".

Menu options at the bottom of the display are:

"F3" changes the addition factor.
"F9" adds the spectra.
"F10" subtracts the spectra.

Menu options displayed at the top of the screen have the following usage:

"F5" suppresses negative values by setting them to 0.0
"*F6*" saves the edited spectrum
"L" and "U" create a reference by establishing an upper and lower limit for "interpolation" (I)
"*I*" replaces all the spectral data in the region established by "L" and "U" with a straight line. This is useful for stripping out spectral noise or unwanted peaks.
"Esc" exits the *Edit spectra* option. The prompt "Save modified spectrum (Y/N)?" will be displayed. Save spectra by typing "Y" and "Enter". Type the drive and path to which the spectrum is to be stored.

The *KLM* menu (fig. 17) facilitates peak identification.

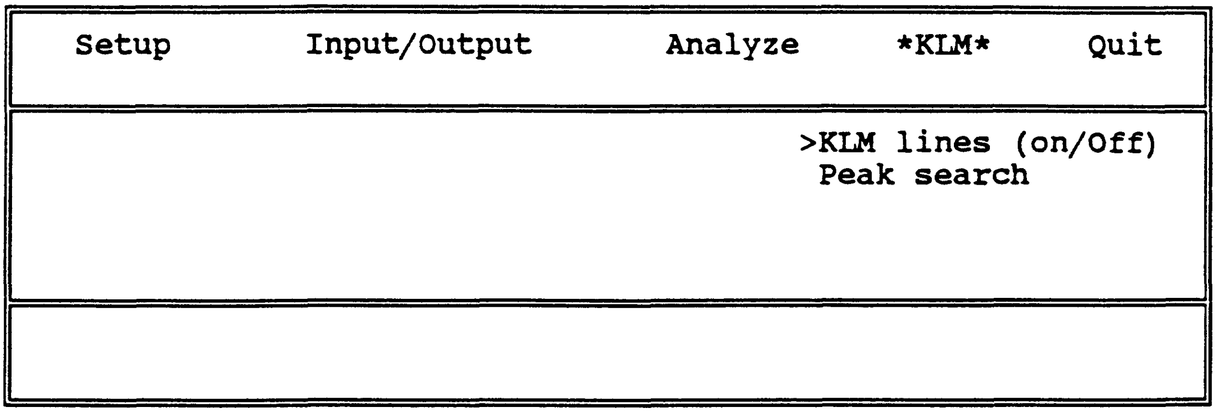


Figure 17. *KLM* menu.

9.1. KLM LINES ON/OFF

KLM lines (ON/off) enables display of the K, L, and M spectral energy lines whenever a spectrum is on the screen.

1) Toggle the "*KLM lines (on/Off)*" to the on position by pressing the "Enter" key, so that the "ON" appears as capital letters
2) Press the "Esc" key to exit the menu. When a spectrum is displayed, *KLM lines* are selected by typing the symbol of the element or with the "< >" keys.

PEAK SEARCH 9.2

Peak search facilitates identification of unknown peaks:

1) With a sectrum displayed, place the cursor on the peak maximum of the unknown peak.
2) Select the *KLM* menu and choose the *Peak search* option.
3) Press the "Enter" key (K,L, and M lines will scroll across the screen and stop at the cursor location displaying the element whose K,L, and M lines match those of the unknown peak). The peak position in keV and the number of total counts in the energy channel occupied by the cursor is also displayed.
4) Press the "Esc" key to terminate a search; press any other key to continue searching for the element whose K,L, and M lines best match those of the unknown peak.

REFERENCES

Giauque, R.D., Garret, R.G., and Goda, L.Y., 1977, Energy-dispersive X-ray fluorescence spectrometry for determination of twenty-six trace and two major elements in geochemical specimens: Analytical Chemistry, v. 49, p. 52-67.

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Quick, J.E., 1988, DATASAVE manual: U.S. Geological Survey Open-File Report 88-213, 11 sections.

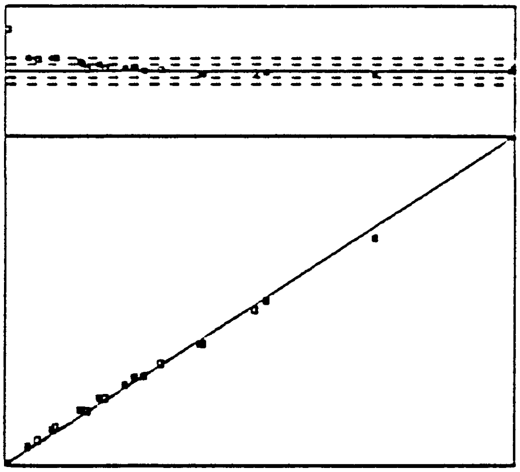
Quick. J.E. and Haleby, A.M., 1988, Xap, a program for deconvolution and analysis of complex X-ray spectra: U.S. Geological Survey Technical Record TR-08-3, Saudi Arabia Ministry of Petroleum and Mineral Resources, 33 p.

Schamber, F.H., Wodke, N.F., and McCarthy, J.J., 1977, Least squares fit with digital filter: The method and its applications to EDS spectra, <u>in</u> Proceedings of the Twelfth Annual Conference of the Microbeam Analysis Society, Boston.

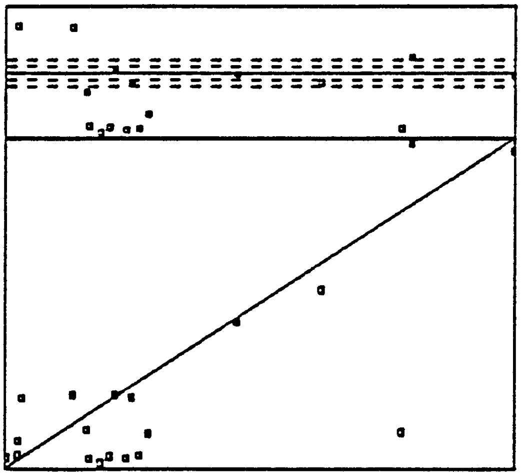
APPENDIX 1. CALIBRATION RESULTS

Appendix 1 contains sample regression results for standardizations developed using the ^{241}Am and ^{109}Cd radioactive sources are shown. The "1st" reference established for the background continuum for ^{109}Cd was 20 channels on either side of the Compton peak centered on the tallest Compton peak. A region of the background continuum from 2.48 to 2.84 keV was used when standardizing the ^{241}Am source.

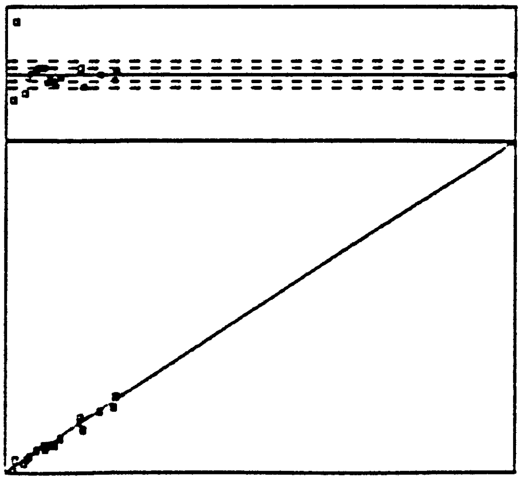
```
Element/Compound: FE203
   26 ppm full scale
Regression Coefficients:
  A0 =  0
  A1 =  4.975451E-02
  A2 = -2.401418E-05
Correlation Coefficient:
  All data ( 24): 0.8259
  Fit data ( 11): 0.9991
Chi-square:
  All data ( 24):     17.7
  Fit data ( 11):      0.4
Filter:   0
```



```
Element/Compound: CU
   142 ppm full scale
Regression Coefficients:
  A0 = -102.7002
  A1 =  22.59005
  A2 =  0
Correlation Coefficient:
  All data ( 20): 0.7906
  Fit data ( 11): 0.9278
Chi-square:
  All data ( 20):  1662.9
  Fit data ( 11):   265.1
Filter:   5
```

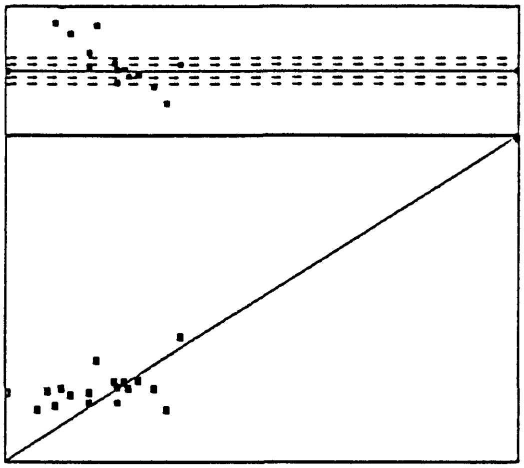


```
Element/Compound: ZN
  1300 ppm full scale
Regression Coefficients:
  A0 =  0
  A1 =  10.00129
  A2 =  0
Correlation Coefficient:
  All data ( 22): 0.9986
  Fit data ( 17): 0.9989
Chi-square:
  All data ( 22):     43.1
  Fit data ( 17):     23.5
Filter:  20
```

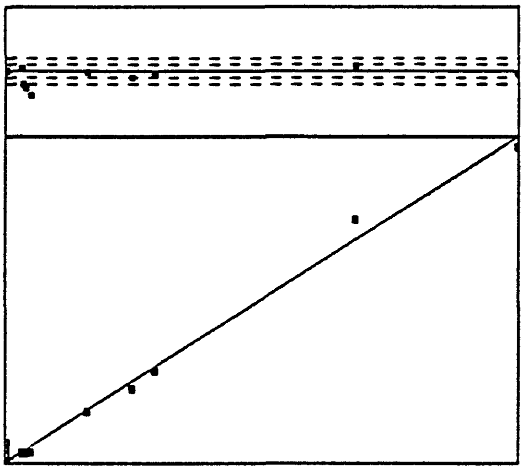


Appendix 1 continued.

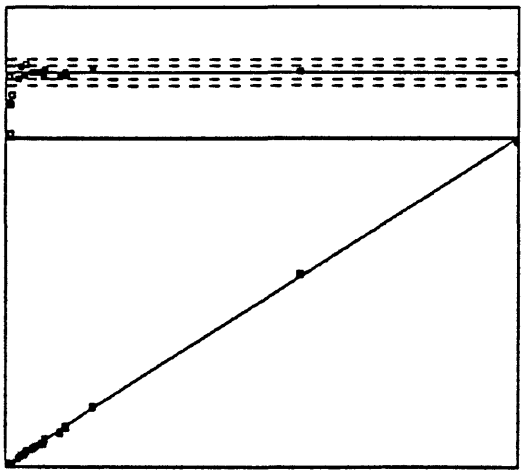
```
Element/Compound: CA
    96 ppm full scale
Regression Coefficients:
  A0 =  0
  A1 =  0.845536E-02
  A2 =  0
Correlation Coefficient:
  All data ( 19): 0.9168
  Fit data ( 18): 0.9341
Chi-square:
  All data ( 19):    70.3
  Fit data ( 18):    50.3
Filter:  -0
```



```
Element/Compound: AS
   441 ppm full scale
Regression Coefficients:
  A0 =  0
  A1 =  13.82843
  A2 =  0
Correlation Coefficient:
  All data ( 13): 0.9953
  Fit data (  9): 0.9970
Chi-square:
  All data ( 13):    62.5
  Fit data (  9):    10.9
Filter:  -0
```

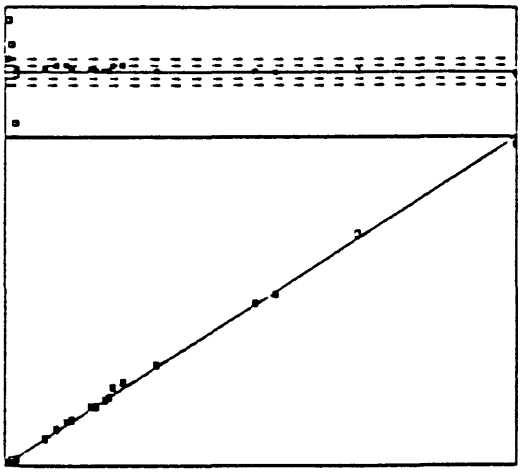


```
Element/Compound: RB
  2222 ppm full scale
Regression Coefficients:
  A0 = -2.096181
  A1 =  1.000484
  A2 =  0
Correlation Coefficient:
  All data ( 22): 0.9998
  Fit data ( 16): 0.9998
Chi-square:
  All data ( 22):   227.2
  Fit data ( 16):     4.9
Filter:  20
```

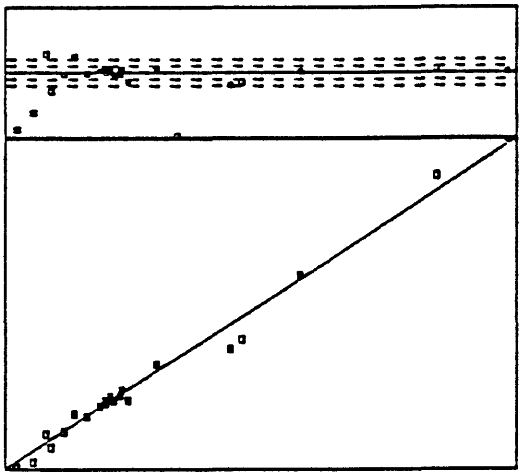


Appendix 1 continued.

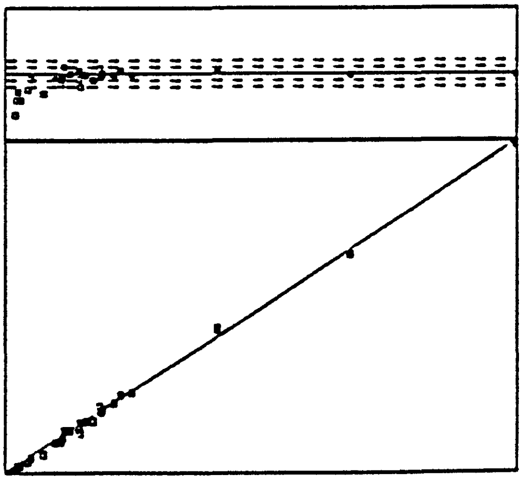
```
Element/Compound: SR
  1340 ppm full scale
Regression Coefficients:
  A0 =  0
  A1 =  9.891842E-02
  A2 =  0
Correlation Coefficient:
  All data ( 23): 0.9993
  Fit data ( 16): 0.9995
Chi-square:
  All data ( 23):    91.4
  Fit data ( 16):    11.0
Filter:  20
```



```
Element/Compound: Y
   120 ppm full scale
Regression Coefficients:
  A0 =  1.009431
  A1 =  .1696979
  A2 =  0
Correlation Coefficient:
  All data ( 22): 0.9572
  Fit data ( 13): 0.9929
Chi-square:
  All data ( 22):  1760.3
  Fit data ( 13):     4.2
Filter:  20
```

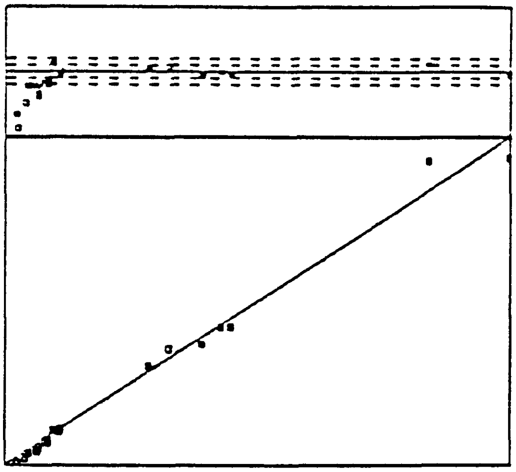


```
Element/Compound: ZR
  1224 ppm full scale
Regression Coefficients:
  A0 =  17.90513
  A1 =  .0895822
  A2 =  0
Correlation Coefficient:
  All data ( 27): 0.9983
  Fit data ( 17): 0.9998
Chi-square:
  All data ( 27):    85.0
  Fit data ( 17):    21.2
Filter:  20
```

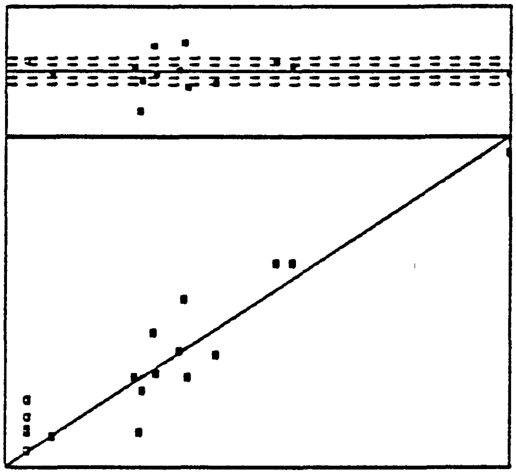


Appendix I continued.

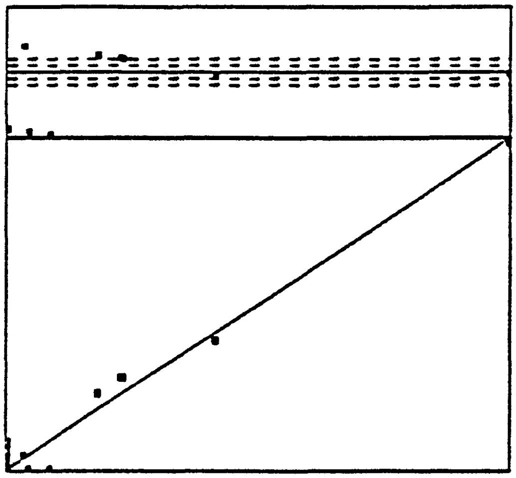
```
Element/Compound: NB
   200 ppm full scale
Regression Coefficients:
  A0 =  5.946146
  A1 =  .1052843
  A2 =  0
Correlation Coefficient:
  All data ( 23): 0.9948
  Fit data (  8): 0.9986
Chi-square:
  All data ( 23):     72.8
  Fit data (  8):      5.6
Filter:  20
```



```
Element/Compound: PB
    89 ppm full scale
Regression Coefficients:
  A0 =  3.463886
  A1 =  7.971535
  A2 =  0
Correlation Coefficient:
  All data ( 18): 0.9357
  Fit data ( 13): 0.9386
Chi-square:
  All data ( 18):     63.8
  Fit data ( 13):     36.8
Filter:  -0
```

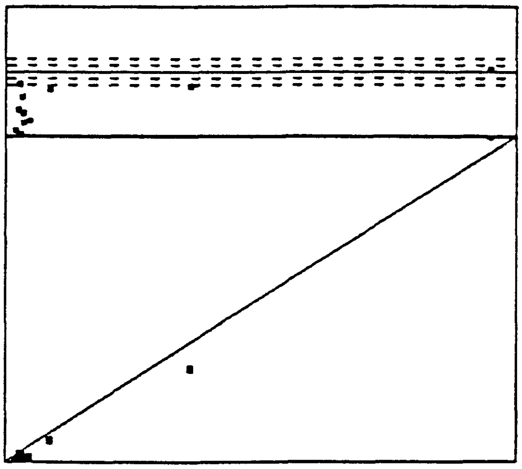


```
Element/Compound: TH
   384 ppm full scale
Regression Coefficients:
  A0 =  .3514539
  A1 =  .3887189
  A2 =  0
Correlation Coefficient:
  All data ( 26): 0.9882
  Fit data (  8): 0.9888
Chi-square:
  All data ( 26):  1045.1
  Fit data (  8):   886.9
Filter:  -0
```



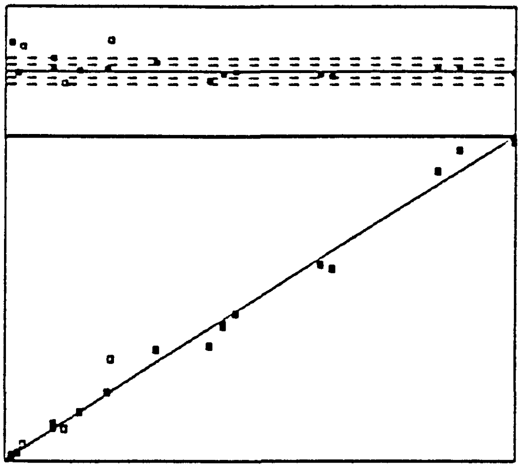
Appendix I continued.

```
Element/Compound: U
   284 ppm full scale
Regression Coefficients:
  A0 = -28.00991
  A1 =  .2585465
  A2 =  0
Correlation Coefficient:
  All data ( 15): 0.9845
  Fit data ( 15): 0.9845
Chi-square:
  All data ( 15):   630.2
  Fit data ( 15):   630.2
Filter:  -0
```

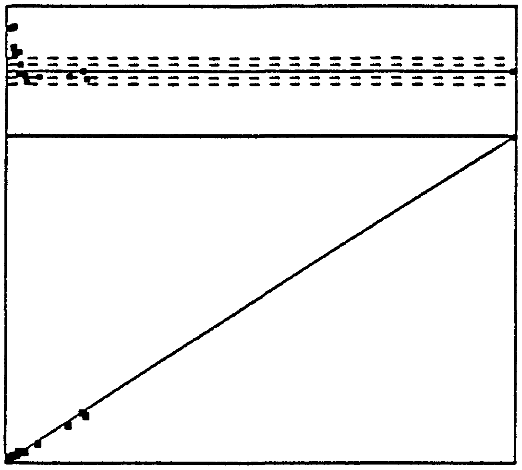


Appendix 1 continued.

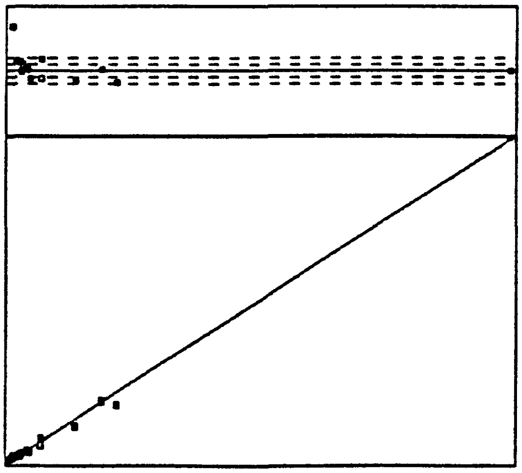
```
Element/Compound: BA
  1396 ppm full scale
Regression Coefficients:
  A0 =  0
  A1 =  3.783992
  AZ =  0
Correlation Coefficient:
  All data ( 19): 0.9926
  Fit data ( 16): 0.9950
Chi-square:
  All data ( 19):   101.5
  Fit data ( 16):    44.0
Filter:  20
```



```
Element/Compound: LA
  1340 ppm full scale
Regression Coefficients:
  A0 = -16.69887
  A1 =  .1064288
  AZ =  0
Correlation Coefficient:
  All data ( 16): 0.9994
  Fit data ( 14): 0.9994
Chi-square:
  All data ( 16):    67.9
  Fit data ( 14):    38.5
Filter:  20
```

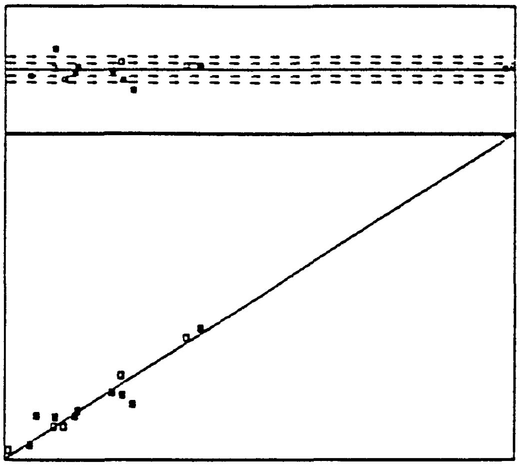


```
Element/Compound: CE
  2230 ppm full scale
Regression Coefficients:
  A0 = -22.25563
  A1 =  3.65671
  AZ =  0
Correlation Coefficient:
  All data ( 17): 0.9985
  Fit data ( 14): 0.9986
Chi-square:
  All data ( 17):    86.7
  Fit data ( 14):    66.8
Filter:  20
```



Appendix 1 continued.

```
Element/Compound: ND
   637 ppm full scale
Regression Coefficients:
  A0 = -6.918044
  A1 =  .3982825
  A2 =  0
Correlation Coefficient:
  All data ( 16): 0.9988
  Fit data ( 10): 0.9881
Chi-square:
  All data ( 16):     33.5
  Fit data ( 10):     19.4
Filter:  20
```



APPENDIX 2. ANALYTICAL PRECISION AND ACCURACY

Appendix 2 contains KEVEX-7000 data acquired using SUPERXAP on a suite of U.S. Geological rock standards (Unpublished data, D.A. Sawyer, U.S. Geological Survey). Multiple analyses were done on these standards over a ten day period. Statistical analysis on this data shows an indication for the analytical precision and accuracy of analyses obtained using SUPERXAP.

	FeTO3%	Rb ppm	Sr ppm	Zr ppm	Nb ppm	Y ppm	Ba ppm	La ppm	Ce ppm	Nd ppm	Th ppm	Pb ppm	Zn ppm	Cu ppm	Sn ppm	Ga ppm
GH																
Recommended Value	1.34	390	10	150	85	75	20	25	60	29	87	45	35	14	9	23
Average Value	1.26	372	7	137	83	85	24	22	66	20	74	50	68	17	9	20
Precision	0.01	7	3	3	3	4	3	6	5	6	6	6	8	13	5	8
Precision (%)	0.9	1.9	38.3	2.5	3.4	4.5	12.5	29.1	7.6	31.0	7.6	12.3	11.3	79.6	52.6	39.9
CS Precision (%)	1.5	1.7	128.2	2.3	6.4	5.7	24.5	26.5	9.1	19.0	26.0	29.4	28.6	16.4	17.5	132.1
Accuracy (%)	94.2	95.3		91.4	97.4	112.7	119.5	86.0	110.0		84.5	111.6	80.2	120.0	96.7	85.2
RGM-1																
Recommended Value	1.86	149	108	219	8.9	25	807	24	47	19	15.1	24	32	11.6	4.1	15
Average Value	1.75	155	101	223	10	26	891	19	46	17		30	43		3	16
Precision	0.02	3	4	5	2	4	15	5	3	44		9	9		3	10
Precision (%)	0.9	1.7	3.9	2.2	16.0	15.2	1.6	25.3	6.8	53.3		29.5	21.5		115.3	61.9
CS Precision (%)	1.2	4.2	4.8	1.8	85.1	20.7	1.0	40.3	14.2	20.2		54.7	49.4		25.0	143.2
Accuracy (%)	94.2	104.2	93.2	101.9	109.0	102.4	110.5	79.2	97.9	91.6		126.3	133.8		73.2	105.3
GSP-1																
Recommended Value	4.29	254	234	530	27.9	26	1310	184	399	196	106	55	104	33	6.6	23
Average Value	4.11	248	233	498	25	28	1296	173	390	188	97	50	98	32	7	24
Precision	0.04	5	5	7	2	2	23	13	13	11	12	7	12	16	3	11
Precision (%)	1.0	2.0	2.0	1.4	7.8	8.4	1.8	7.3	3.4	5.6	12.5	14.6	12.1	52.3	35.3	44.6
CS Precision (%)	0.0	3.8	3.0	1.1	31.3	25.7	0.8	6.6	1.9	3.3	25.1	41.8	24.7	18.8	18.3	299.0
Accuracy (%)	95.7	97.7	99.4	93.9	87.3	107.3	98.9	94.2	97.7	96.1	91.2	90.9	94.5	95.5	107.6	104.3
QLO-1																
Recommended Value	4.35	74	336	185	10.3	24	1370	27	54.5	26	4.5	20.4	61	29	2.3	17
Average Value	4.26	80	327	183	13	26	1446	19	53	19		31	60	23	1.8	18
Precision	0.04	3	8	4	2	3	21	7	5	5		10	14	18	2	10
Precision (%)	0.8	4.3	2.4	2.2	13.8	10.4	1.5	38.5	9.7	27.5		31.6	22.9	77.5	123.3	54.2
CS Precision (%)	0.6	4.0	3.9	1.5	58.2	23.2	0.9	23.4	8.1	11.7		48.2	37.0	19.6	21.6	221.1
Accuracy (%)	98.0	108.5	97.2	98.7	126.2	106.7	105.6		96.3	71.5			97.3	80.0	78.3	105.3
STM-1																
Recommended Value	5.22	118	700	1210	268	46	560	150	259	79	31	17.7	235	4.6	6.3	36
Average Value	5.40	112	727	1281	250	51	600	148	257	70			240		5	37
Precision	0.05	4	15	9	6	5	17	8	11	7			18		3	9
Precision (%)	0.9	3.6	2.1	0.7	2.5	10.7	2.9	5.4	4.4	10.0			7.7		63.7	23.9
CS Precision (%)	0.7	11.1	1.4	0.6	3.5	19.7	1.4	6.6	2.7	7.4			10.4		19.9	44.0
Accuracy (%)	103.4	95.3	103.9	105.9	93.1	111.1	107.1	98.4	99.0	88.1			102.2		76.5	102.8
AGV-1																
Recommended Value	6.76	67	662	227	15	20	1226	38	67	33	7	36	88	60	4.2	20
Average Value	6.33	71	654	220	16	21	1194	35	67	32		46	96	59	5	18
Precision	0.31	3	9	6	2	4	28	9	9	6		3	15	25	4	2
Precision (%)	0.2	3.6	1.3	2.7	10.6	17.2	2.4	24.5	13.3	19.6		17.5	16.1	42.5	69.2	13.5
CS Precision (%)	0.6	12.3	1.1	2.1	46.5	33.1	0.7	25.2	9.3	14.3		45.7	26.6	16.6	29.0	35.3
Accuracy (%)	101.0	104.3	98.8	96.9	108.0	103.5	97.4	92.4	99.3	97.3		126.4	108.3	98.2	121.4	99.5

Appendix 2 continued.

	FeTO3%	Rb ppm	Sr ppm	Zr ppm	Nb ppm	Y ppm	Ba ppm	La ppm	Ce ppm	Nd ppm	Th ppm	Pb ppm	Zn ppm	Cu ppm	Sn ppm	Ga ppm
W-2																
Recommended Value	10.74	20	194	94	7.9	24	132	11.4	24	14	2.2	9.3	77	103		20
Average Value	10.33	30	192	87	8	22	175		28			13	75	117	1.9	14
Precision	0.06	3	9	4	2	3	14		4			7	17	31	2	9
Precision (%)	0.5	10.4	4.6	4.3	21.0	14.5	7.9		15.4			54.1	22.3	26.3	121.1	60.7
CS Precision (%)	0.5	23.0	2.3	4.3	164.2	26.4	4.4		27.1				37.3	14.2	30.8	
Accuracy (%)	100.3		98.9	92.0	97.5	90.0	96.2		117.3				96.3	113.3		70.5
BHVO-1																
Recommended Value	12.23	11	403	179	19	28	139	15.3	39	25.2	1.08	2.6	105	136	2.1	21
Average Value	12.15	17	398	155	21	29	122	9	41	20	1		107	122	2	18
Precision	0.06	4	12	5	1	2	9	5	5	6	3		17	25	2	10
Precision (%)	0.5	20.5	2.9	3.0	5.6	8.6	7.5	57.3	11.6	31.2	300.0		16.2	20.6	107.3	54.1
CS Precision (%)	0.5	54.9	1.3	3.0	38.2	23.6	4.6	67.7	13.7	17.2			28.6	15.5	19.5	
Accuracy (%)	99.3		98.7	92.1	109.5	103.6	88.0		106.2	78.6	92.6		101.9	89.4	104.3	83.3
BIR-1																
Recommended Value	11.26	1	108	22	2	16	7.7	0.9	2.5	2.5	0.39	3.2	71	126	0.7	16
Average Value	11.18		108	16		14	11						64	125		15
Precision	0.11		5	2		3	4						24	20		11
Precision (%)	0.9		4.3	13.4		21.2	40.0						38.0	15.7		68.7
CS Precision (%)	0.5		4.4	26.1		40.5	67.9						53.7	14.9		186.4
Accuracy (%)	99.2		99.9	71.4		87.5							90.6	99.2		96.3
BR																
Recommended Value	12.38	47	1320	250	98	30	1050	82	151	65	11	8	160	72	2.5	19
Average Value	12.48	46	1369	254	107	34	1027	77	137	54			160	85		17
Precision	0.07	5	9	6	4	3	25	13	10	13			25	31		11
Precision (%)	0.6	11.5	0.7	2.4	4.2	9.3	2.4	17.2	7.1	23.5			15.3	36.5		62.2
CS Precision (%)	0.5	30.3	0.3	2.6	8.0	29.5	0.3	13.3	5.3	10.5			21.0	19.7		
Accuracy (%)	96.3	97.7	103.7	101.8	109.2	112.0	97.3	94.3	90.5	83.4			99.8	117.5		89.5

Recommended values are the published concentrations for the standards from Govindaraju (1989).
Average values are the means of 10 analytical determinations on the standard using SUPERXAP, analyzed over a 10 day period in December 1990 by S.A. Fournier, U.S. Geological Survey, Denver, Colorado.
Precision as defined here, is the observed standard deviation (in ppm) of the analyses used in the average calculation.
Precision (%) as defined here, is the observed standard deviation of the 10 analytical determinations, divided by the average value measured for the element.
CS precision, or counting statistic precision (%) is the one-sigma theoretical precision calculated by the SUPERXAP program and reported as % s.d.
Accuracy as defined here, is the average value measured for an element divided by the recommended value (%) and published by the International Working Group on "standards of minerals, ores, and rocks" Govindaraju (1989).

If accuracy or relative precision are 100% off, data are deleted. If accuracy is more than 30% off recommended value, this is considered an inaccurate determination. SUPERXAP data for Sb, Mo, W, U, Cd, Bi, and As are considered inaccurate and (or) imprecise in the compositional range of these rock standards.