QUANTITATIVE X RAY ANALYSIS SYSTEM

USER’S MANUAL AND GUIDE TO X RAY FLUORESCENCE TECHNIQUE

FOREWORD

This guide covers trimmed and re-arranged version 3.6 of the Quantitative X ray Analysis System (QXAS) software package that includes the most frequently used methods of quantitative analysis. QXAS is a comprehensive quantitative analysis package that has been developed by the IAEA through research and technical contracts. Additional development has also been carried out in the IAEA Laboratories in Seibersdorf where QXAS was extensively tested. New in this version of the manual are the descriptions of the Voigt-profile peak fitting, the backscatter fundamental parameters' and emission-transmission methods of chemical composition analysis, an expanded chapter on the X ray fluorescence physics, and completely revised and increased number of practical examples of utilization of the QXAS software package. The analytical data accompanying this manual were collected in the IAEA Seibersdorf Laboratories in the years 2006/2007.

Any queries, comments, or suggestions regarding this guide and the QXAS software package may be directed to:

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EDITORIAL NOTE

CONTENTS

CHAPTER 1. GETTING STARTED

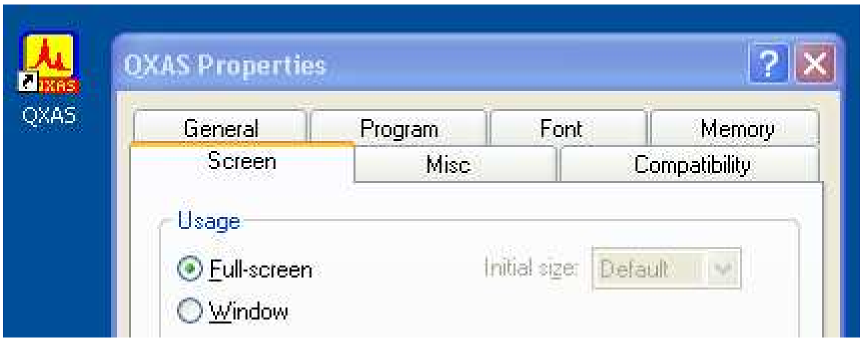
References material: [1], [2], [3], [5], [6], [7], [8], [9], [10], [11], [12], [53]

This Manual has been prepared as a guide, a hand-on reference, for the users of QXAS (**Q**uantitative **X** ray **A**nalysis **S**ystem) 3.6 software package. It should be of help for users with basic experience in X ray fluorescence analysis (XRF). It can also be used by scientists who have not worked before with the QXAS at all. More experienced users should find here answers for many specific questions. Some fundamental features of XRF are discussed as far as the use of QXAS is concerned, some examples are worked out in detail and a guideline for quality assurance (*QA*) matters is given.. All references are made to the version 3.6 of the software package QXAS. The manual and the latest version of QXAS are available on:

http://www.iaea.org/OurWork/ST/NA/NAAL/pci/ins/xrf/pciXRFdown.php

The QXAS software package can be installed under the operating system WINDOWS, but it is actually executed in the command prompt as a DOS program. This fact carries the advantages of the WINDOWS inherent possibility to switch between programs without termination, because of their simultaneous execution. For the purpose of switching from QXAS (DOS environment) to WINDOWS environment and back, one uses the combination of the <ALT> and <TAB> key. By this action active windows are brought in front, one after the other, without termination. Particularly, to toggle between any of the QXAS programs and e.g., the WINDOWS Explorer will facilitate searches for files or enable to edit quickly files. It is not recommended to open QXAS in two command prompt windows simultaneously and run them in parallel. It is also possible to run QXAS software under other operating systems, including 64-bit systems, in a DOS emulator.

It is recommended to run QXAS in full screen mode as default. For this purpose - with the right mouse button - the QXAS icon on the desktop should be selected. From the drop-down menu select “Properties”, then in the option “Screen” enable the “Full screen”.



Usage
● Full-screen
○ Window
Initial size: Default

Fig. 1.1. Setting of the full screen mode for QXAS permanently.

Throughout the guide example spectra and files can be used in order to follow “hands on”. They are found in the “QXASdemo” folder and its sub-directories. When executing the examples it is recommended to set the “QXASdemo” folder as the “set directory”. Usually the “C:\axil\spect” is the “set directory”. The profit of distributing the example files among different folders is to limit their number in a given directory. Another advantage, when *.spe and *.asr files are put into different locations is that previous results (of e.g. example *.asr files, that are provided for demonstration purposes) are not overwritten after attempts of the user to store his or her own results.

1.1. Spectrum fitting (AXIL)

Demonstration files (directory \QXASdemo\Getstart):

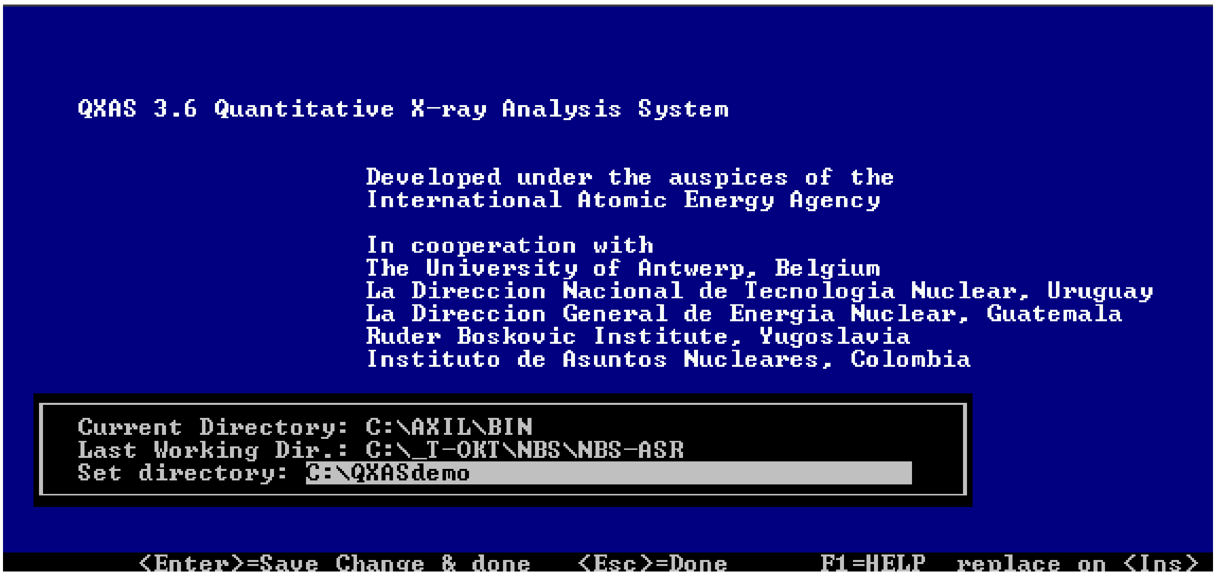
- Spectra: Target1.spe, Pb-pure.spe
- Input files: Target1.inp, Pb.inp

For historical reasons many users will associate the spectrum fitting part of QXAS with the name of AXIL (which stands for **A**nalysis of **X**-ray spectra by **I**terative **L**east-square fitting). The best way to start the QXAS software package is by using the QXAS icon on the WINDOWS desktop.

Fig. 1.2. QXAS icon on the WINDOWS desktop.

The start screen of QXAS allows for setting the default working directory ("Set directory"), a default folder where input data are read from and result files are stored. Still it is possible during programme execution to select other places to load files from, however storing the majority of data is restricted to the working directory (there are few exceptions). The last used "set directory" is proposed as the default for the next run. When the QXAS is run for the first time the "C:\AXIL\SPECT" is proposed as the default "set directory".

1.1.1. *Example: Input model Target1.inp and spectrum Target1.sp, of a demonstration sample*



```
QXAS 3.6 Quantitative X-ray Analysis System

                   Developed under the auspices of the
                   International Atomic Energy Agency

                   In cooperation with
                   The University of Antwerp, Belgium
                   La Direccion Nacional de Tecnologia Nuclear, Uruguay
                   La Direccion General de Energia Nuclear, Guatemala
                   Ruder Boskovic Institute, Yugoslavia
                   Instituto de Asuntos Nucleares, Colombia

  Current Directory: C:\AXIL\BIN
  Last Working Dir.: C:\_I-OKI\NBS\NBS-ASR
  Set directory: C:\QXASdemo

        <Enter>=Save Change & done    <Esc>=Done      F1=HELP  replace on <Ins>
```

Fig. 1.3. Definition of the default working directory for run of QXAS.

After defining the "Set directory" in the start screen the main QXAS screen containing the topmost program navigation menu is displayed. To carry out the example select the option **Spectrum fitting**.

Fig. 1.4. For access to AXIL ***Spectrum fitting*** *must be selected.*

Next, select **AXIL (&Voigt peak profiles option for high energy K-lines)**

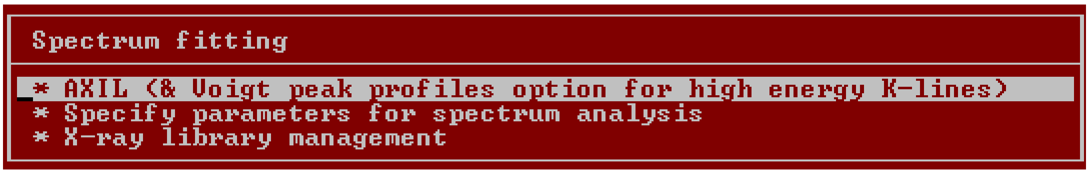
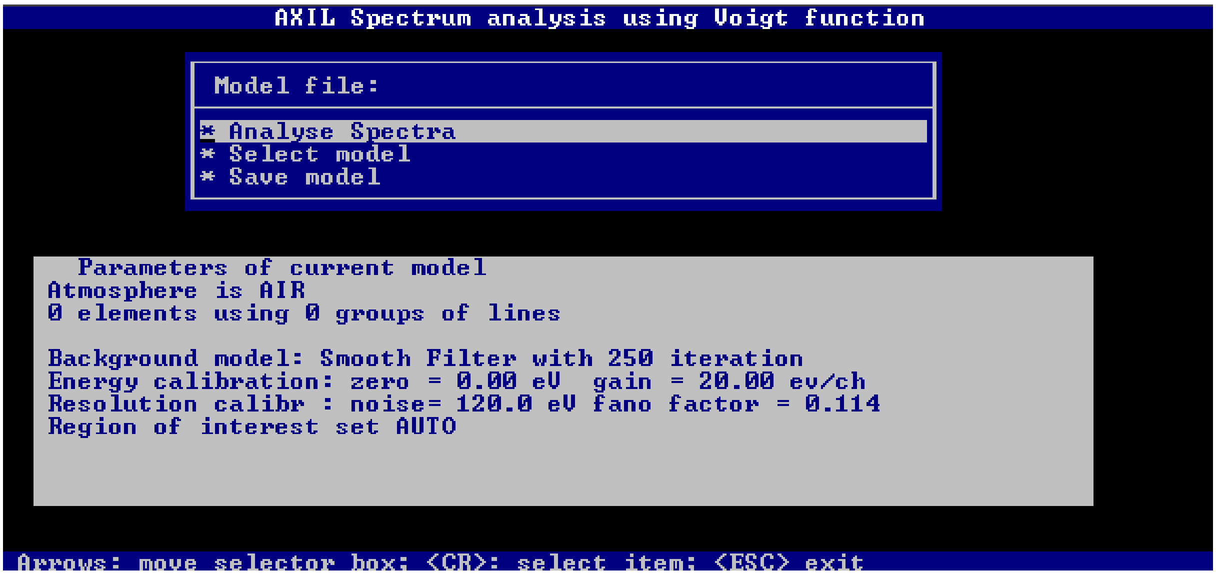


Fig. 1.5. Before loading a spectrum and a specific input model.

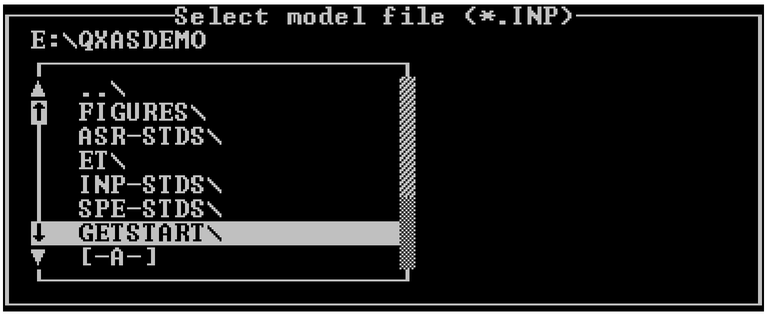
Load the input model (line **Select model**), file Target1.inp, created for the purpose of this demonstration. When no particular model file is loaded, certain parameters like background model, energy calibration coefficients, etc. are set to default values. They require further adjustments.



```
  Parameters of current model
Atmosphere is AIR
0 elements using 0 groups of lines

Background model: Smooth Filter with 250 iteration
Energy calibration: zero = 0.00 eV  gain = 20.00 ev/ch
Resolution calibr : noise= 120.0 eV fano factor = 0.114
Region of interest set AUTO
```

Fig. 1.6. Default input model parameters.

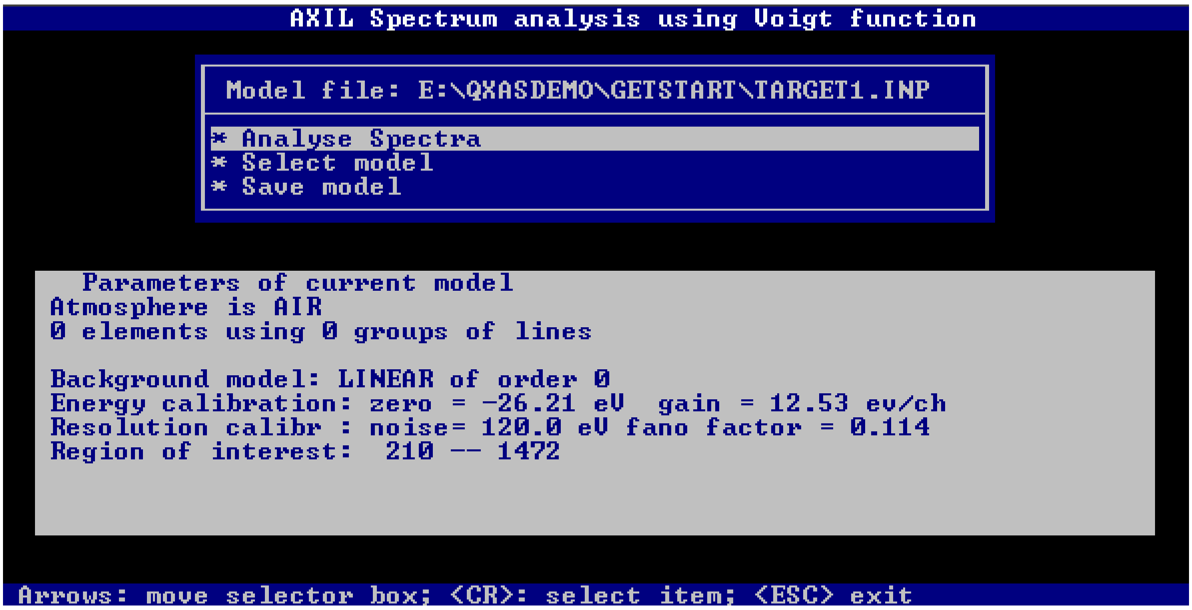
To retrieve the input model use the SCROLL BOX to select the directory \QXASdemo\GetStart and load the Target1.inp file.



```
Select model file (*.INP)
E:\QXASDEMO
  ..\
  FIGURES\
  ASR-STDS\
  ET\
  INP-STDS\
  SPE-STDS\
  GETSTART\
  [-A-]
```

Fig. 1.7. SCROLL BOX for loading the input model file Target1.inp.

The input model file Target1.inp contains the correct energy calibration, an appropriate region of interest (ROI), which brackets all the peaks of interest to be fitted in our example spectrum, the peak positions, and several other pre-defined parameters.



```
AXIL Spectrum analysis using Voigt function

 Model file: E:\QXASDEMO\GETSTART\TARGET1.INP

* Analyse Spectra
* Select model
* Save model

  Parameters of current model
Atmosphere is AIR
0 elements using 0 groups of lines

Background model: LINEAR of order 0
Energy calibration: zero = -26.21 eV  gain = 12.53 ev/ch
Resolution calibr : noise= 120.0 eV fano factor = 0.114
Region of interest:  210 -- 1472

Arrows: move selector box; <CR>: select item; <ESC> exit
```

Fig. 1.8. A brief overview is available for certain parameters contained in the temporary valid input model file (Target1.inp).

Next select **Analyse Spectra** and consecutively use the COMMANDs **LOAD** and **DIR_SEL**

Fig. 1.9. COMMAND LOAD to retrieve an already converted measured spectrum.

Fig. 1.10. Two options are available to load a spectrum: by direct input of the known file name from the correct directory or by browsing through the various directories and files.

to load the file intended for this demonstration, from the directory \QXASdemo\GetStart with the selection of the spectrum Target1.spe from the SCROLL BOX.

```
Select spectrum to fit file (*.spe)
E:\QXASDEMO\GETSTART
  ..\
  TARGET1.SPE
  PB-PURE.SPE
  E-CALIB.SPE
  [-A-]
  [-C-]
  [-D-]
  [-E-]
```

Fig. 1.11. SCROLL BOX for loading the spectrum T1.spe.

Because the input model file Target1.inp was loaded before the spectrum file, the energy calibration is already correctly defined. The sample, which served to collect the spectrum Target1.spe, contains the elements V, Co, Cu, Se, Sr, Mo and elements that are not visible by XRF (H, C, N, O). In order to verify the predictions, select the COMMAND KLM –MARK. It will start by default with the markers at the energies of the iron lines (for iron the Fe K_α, Fe K_β and the rarely visible L-lines are proposed). With arrow keys left/right and up/down (jumps of Z+10) potential peaks can be checked for their presence (qualitative analysis). The lines for the elements to be include can be defined with the COMMANDs

X-LINES, then

ADD and type in: **V CO CU SE SR MO**

And terminate the COMMAND sequence with either **GO** or <enter>. In between each entry of an element a space must be left. Immediately after each entry for an element new markers will be superimposed on the spectrum – for each line of the element. The information gained with the COMMAND **KLM-MARK** can not be transferred other than manually to the COMMAND **X-LINES**. The background can be defined, e.g., with

BACKGRND
LINEAR
PARAM=

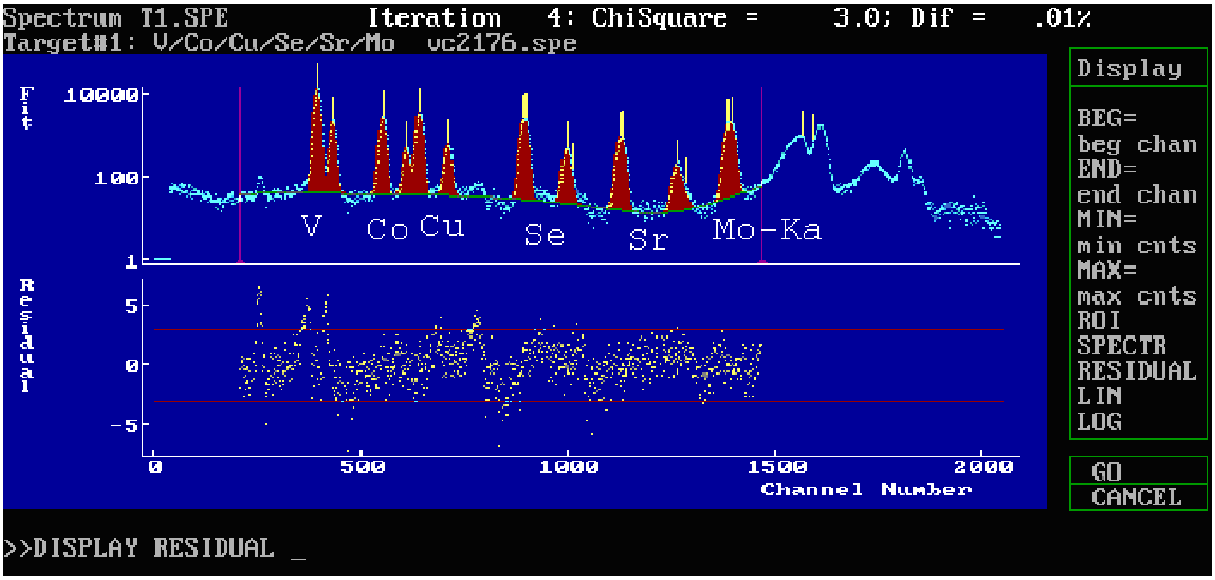
and an input of 5 after (PARAM=). Which means a linear polynomial as function of the channel number (energy) of order 5 is used to approximate the background within the region of interest. Finally the fit of the region of interest, in order to strip the background and resolve peak overlaps, will be initiated with the COMMANDs:

FIT
N_ITER= 10

The adoption of the number 10 is fairly arbitrary. A number of 10 - 20 will usually be sufficient in order to enable the iteration procedure with enough loops. After the AXIL fit some information about the quality of the fit can be gained by first looking at the value of the **ChiSquare= 3.0** (displayed only after the first fit). In the ideal case this number should be 1.0 or close to it (it is defined as reduced Chi square) and is an *overall* information for the region of interest. As next information source inspect the residual with the COMMANDs

DISPLAY
RESIDUAL

This residual offers information about *each spectrum channel* within the ROI. For a well defined fit model all points should be between -3 and +3, indicated by the two red bars. Of course with certain probability random fluctuations of greater magnitude can occur.


```
Spectrum T1.SPE          Iteration    4: ChiSquare =     3.0; Dif =   .01%
Target#1: V/Co/Cu/Se/Sr/Mo   vc2176.spe
```

```
>>DISPLAY RESIDUAL _
```

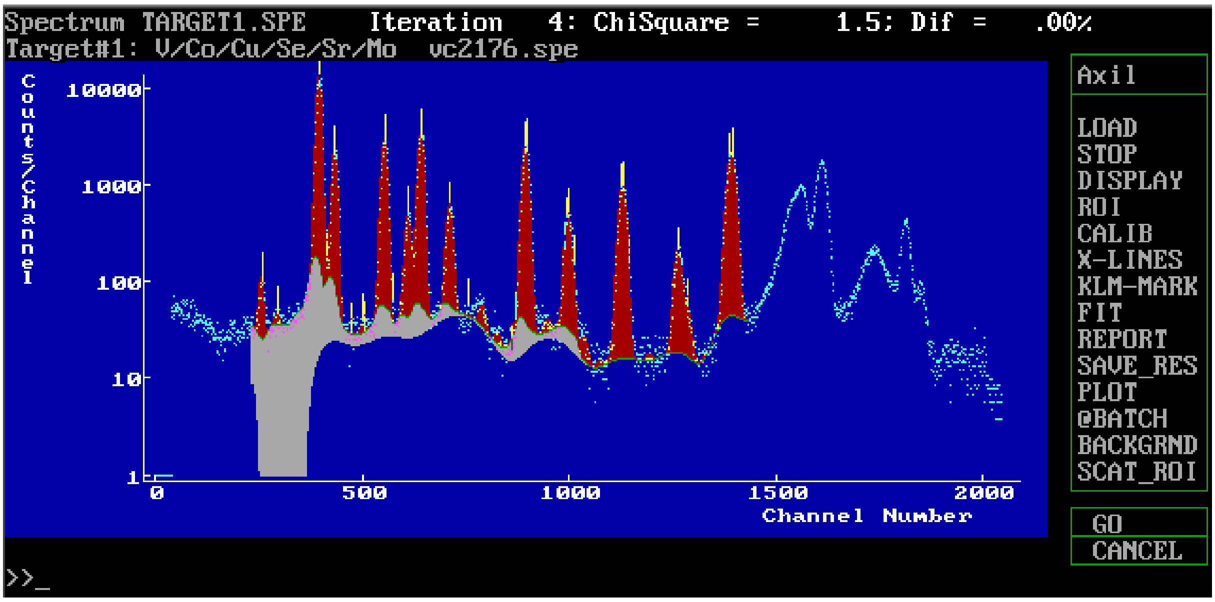
Fig. 1.12. Spectrum Target1.spe displayed after the first AXIL fit run.

The Chi-square value of 3.0 as well as the displayed residual suggest that there is room for improvements: remove the previous entries for the elements with the COMMANDs **XLINES REMOVE ALL** and add instead:

X-LINES ADD: V-KA* V-KB* CO-KA* CO-KB* CU-KA* CU-KB*
X-LINES ADD: SE-KA* SE-KB* SR-KA+ SR-KB+ MO-KA+ SUM

This way of adding X ray lines forces that the K_α and K_β peaks are treated independently, as if they originated from different elements. It means that the ratio between K_α and K_β peaks of a given element is not fixed during the fit. The additional “+” (for Sr K_α, Sr K_β and Mo K_α) includes the escape peaks, the “*” includes not only the escape peaks for an entry, but also experimentally determined “peak shape correction” (deviation from the usually assumed Gaussian profile of the peak). The entry “SUM” includes any possible sum peaks (due to pile-up of the X ray detector pulses). The order of the background polynomial is increased to 20 using the COMMANDs:

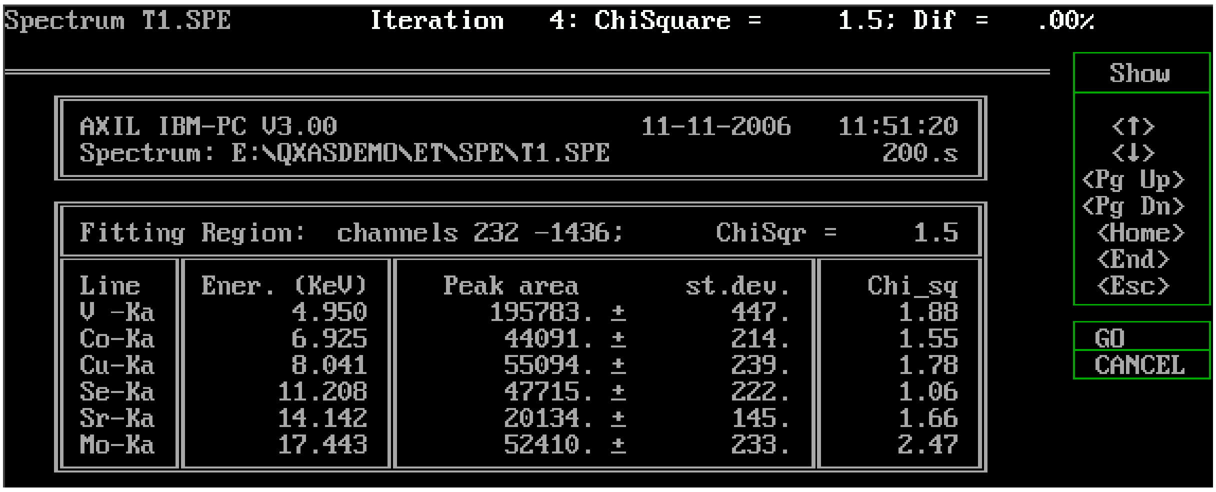
BACKGRND
PARAM= 20



```
Spectrum TARGET1.SPE     Iteration   4: ChiSquare =      1.5; Dif =    .00%
Target#1: V/Co/Cu/Se/Sr/Mo  vc2176.spe
>>_
```

Fig. 1.13. Spectrum Target1.spe displayed after the optimized AXIL fit.

After the re-fit the Chi-square value is reduced to 1.5. The overall magnitude of the residuals is also reduced. Before storing the results one should inspect the numerical values of the calculated peak areas by using COMMANDs **REPORT** (only available after fitting the spectrum) and **GO**.



```
Spectrum T1.SPE          Iteration   4: ChiSquare =      1.5; Dif =    .00%

AXIL IBM-PC V3.00                        11-11-2006    11:51:20
Spectrum: E:\QXASDEMO\ET\SPE\T1.SPE                       200.s

Fitting Region:  channels 232 -1436;        ChiSqr =      1.5

Line     Ener. (KeV)       Peak area          st.dev.      Chi_sq
V -Ka        4.950       195783.  ±           447.         1.88
Co-Ka        6.925        44091.  ±           214.         1.55
Cu-Ka        8.041        55094.  ±           239.         1.78
Se-Ka       11.208        47715.  ±           222.         1.06
Sr-Ka       14.142        20134.  ±           145.         1.66
Mo-Ka       17.443        52410.  ±           233.         2.47
```

Fig. 1.14. AXIL report of the fit results of spectrum T1.spe.

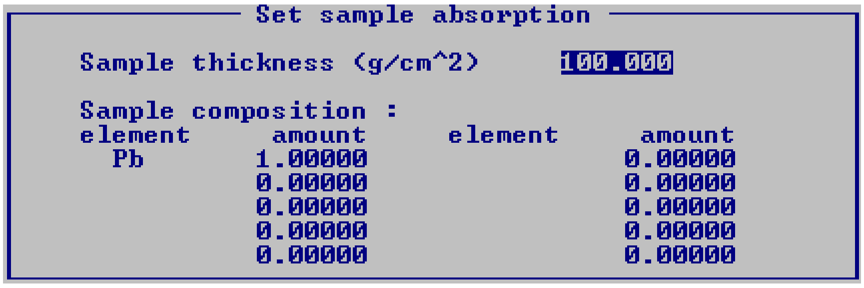
The individual Chi square values should be less than 3.0. For very intense peaks (peak area equal or larger than 10^6 counts) the corresponding Chi square value can be larger than 3. All the net **Peak areas** should be positive and greater than 3 times the standard deviation, otherwise remove the respective peak from the fitting model.

Conclusion: As a basic rule one initiates the first fit with coupled lines and no "*" entry. E.g. start with V+ for vanadium, not with V-KA* V-KB*. The escape peaks should be added for intense peaks already from the beginning. The starting value for the order of the background model for samples (**PARAM=** the parameter for the linear, exponential, orthogonal polynomial background) should be small, say between 0 (exponential 1) and 5.

1.1.2. Example: Input model Pb.inp and spectrum Pb-pure.spe, for a pure lead calibration standard

As an example for a quantification calibration standard pure lead was selected. The input model file Pb.inp does not only, among others, carry information about the energy calibration etc., but also the absorption correction is defined. Under **Specify spectrum analysis parameters** the **Sample absorption** had been defined.

Fig. 1.15. Access to more parameters of an input model file.



```
                    Set sample absorption

    Sample thickness (g/cm^2)      100.000

    Sample composition :
    element      amount      element      amount
      Pb        1.00000                   0.00000
                0.00000                   0.00000
                0.00000                   0.00000
                0.00000                   0.00000
                0.00000                   0.00000
```

Fig. 1.16. Definition of the sample/standard matrix in order to improve the pre-defined line ratios.

The goal of the definition of the sample absorption is to correct the tabulated line ratios for the energy dependent self-absorption. Such correction improves fitting spectra containing intense L-series X ray peaks. To complete the correct definition, select under **Specify experimental parameters** with the COMMAND:

Excitation conditions

and type in for the **Primary excitation energy (keV): 20.6000**, for the

Detector characteristics

Beryllium window (micron): enter 25.000000

and as **Path length (cm): 0.500000**

which are the parameter values specific for the used spectrometer.

```
Specify experimental parameters

* Excitation mode
* Excitation conditions
* Detector characteristics
* Filter absorption
* Funny filter absorption
* Path length
```

Fig. 1.17. Definition of more parameters affecting the pre-defined line ratios.

After loading the input file, load the spectrum Pb-pure.spe. With the **KLM-MARK** COMMAND all possible elements can be checked for their presence in the standard. It is known that the sample consists of lead, but one will find peaks matching the elements Ga, As, Kr, Zr, S.

None of these is present in the calibration standard: The Ga K_α peak is not accompanied by a K_β peak in the spectrum, therefore it is rather one of the so many lead L-lines, namely Pb L_λ. The As K_α peak also would miss its K_β, it is the Pb L_α peak. Identifying the element Kr is a common mistake for beginners, because it is only contained in air in very low quantities, nowhere else and is usually not seen in spectra – it is the Pb L_β peak. The proposed Zr is one of the L_γ-lines of Pb. Sulphur would not match well in terms of energy, for the close-by peak the Pb M-lines are responsible. Unfortunately M-lines are not displayed with the COMMAND **KLM-MARK**.

Recommendation for unknown samples containing lead, identified by approximately equally high Pb L_α and Pb L_β peaks: Due to the problem of line interference one has to check carefully for arsenic (overlap of Pb L_α and As K_α), and for sulphur in the presence of higher quantities of lead (proximity of Pb M and S K peaks).

Add the element lead to the model with the COMMAND

X-LINES ADD: PB-LA PB-LB PB-LG or alternatively **PB-L3 PB-L2 PB-L1**

The usual approach would be to add lead as one element entry with PB only (for minor amounts of this element in a sample). For this spectrum the matrix had been defined, which already improves the fit results, still the three sub-shells of the L radiation are taken into consideration separately.

1.2. Frequent questions raised when working with AXIL

Demonstration files (directory \QXASdemo\Getstart):

- Spectra: E-calib.spe, Ti-Std.spe, Mo-Std.spe, Soil7-1.spe, Cr-Std.spe, KBr.spe, Hf-LStd.spe, PbO2-2.spe, HWC.spe, Instr-bl.spe.
- Input files: E-cal.inp, Ti.inp, Mo.inp, S7-1.inp, Cr.inp, KBr.inp, Hf.inp, PbO2.inp, Samp-bl.inp, Instr-bl.inp

1.2.1. For a new spectrometer - what settings of amplifier and ADC are appropriate?

To lead off with a completely new spectrometer both settings can be at preset values (according to the needs of gamma spectrometry), far away from the needs of XRF, consequently one can maybe observe nothing meaningful in measured spectra, or at the level of QXAS, problems can occur.

The ADC spectrum size should be adjusted to either 1024 or 2048 channels for each spectrum, because AXIL cannot handle spectra with more channels. Otherwise during the spectrum conversion process one either has to have cut parts of the too long spectra or compression must be selected. In many cases both options are undesirable.

With the coarse and fine gain of the amplifier one sets the amplification to 10-20 eV/channel. With such a selection the spectra will be displayed up to the scatter peak region. For the sake of fitting it will be advisable to truncate the sample spectra only after the K_β scatter peak (e.g. at approximately 25 keV for Rh secondary target excitation). For practical purposes, one will do the adjustment acquiring a spectrum of a sample or a single element standard, like a pure metal (Fe, Cu, etc.) in the sample position, while any time the gain settings are changed a new spectrum acquisition is initiated.

1.2.2. What is an energy calibration? How to get an energy calibration for a spectrum measured with my own spectrometer?

There exist spectra, converted from certain multichannel analyzer’s (MCA) spectrum formats that contain already a correct energy calibration intrinsically. Usually this will not be the case. When an appropriate model (*.inp) file can be loaded, which is the case for all example spectra, also no energy calibration step is necessary.

The energy calibration is defined as the correlation between the channel number i of a spectrum obtained from the MCA (with the contents for each channel in counts per channel, usually referred to as intensity) and the energy E_i in (eV) or (keV):

$$E_i = \mathrm{ZERO} + \mathrm{GAIN} \cdot i \tag{1.1}$$

In praxis it means to know the energies corresponding to at least 2 positions (channel numbers) in the spectrum and transfer this knowledge to AXIL. Each chemical element (measurable by XRF) shows characteristic lines seen as peaks in X ray spectrum. Using a simple standard or sample at least two correlation pairs (i, E_i) must be available, where “i” denotes the channel number corresponding to the position of a recognized X ray peak, “E_i” denotes the tabulated energy of that X ray peak. As a rule of thumb well defined K_α and/or L_α peaks should be used to energy calibrate the spectrum. To help the identification of peaks present in the example X ray spectra used through out this guide the spectra files carry self-describing names related to the sample composition.

Note: The *energy calibration* is needed for the proper identification of elements (*qualitative analysis*), whereas the term “*calibration*” (quantification calibration) relates intensities to concentrations (*quantitative analysis*).

For an appropriate energy calibration some conditions should be fulfilled:

- At least two peaks have to be identified in the spectrum. A peak is identified if it is recognized as corresponding to particular X ray line or a group of lines.
- The peaks utilized should have good statistical significance (sufficient number of counts in the peak) so that the maxima (peak position) can be established with good accuracy.

- The selected peaks should be more or less evenly ditributed through out the spectrum. If only two peaks are used one should be located in the lower part of the spectrum and the other in the upper spectrum region. Such selection of peaks ensures the energy calibration accuracy. Consequently it is *not* recommended to use the K_α *and* the K_β peaks of one chemical element as the only two calibration points.

Note: It is possible, but in most of the cases hardly necessary, to use more than two X ray peaks for the energy calibration. The values of the energy calibration parameters are subsequently optimized during the fit

One has to note that after performing the energy calibration procedure the spectrum abscissa is still displayed as **Channel Number**. The validation of the energy calibration can be performed with the **KLM-MARK** COMMAND option as explained in section ***1.2.6***.

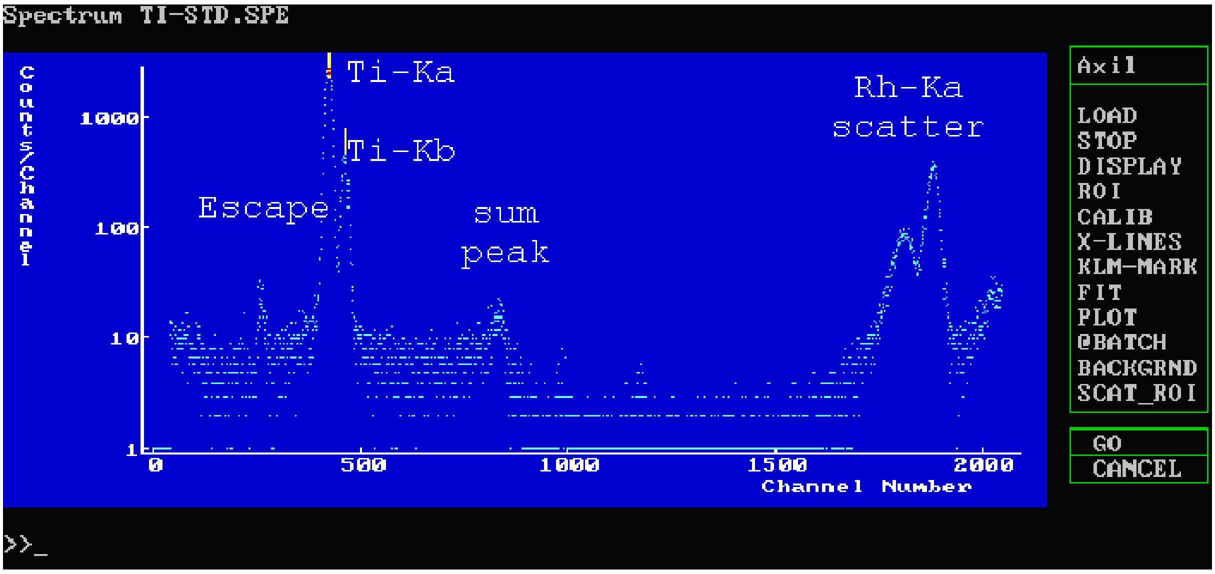
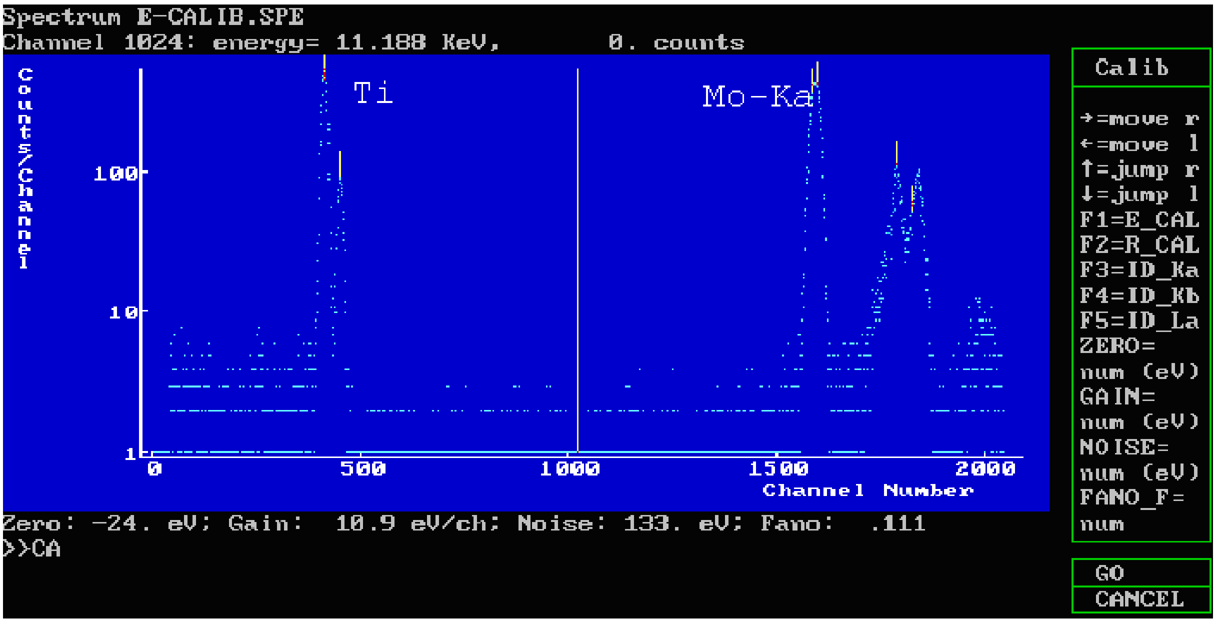


Fig. 1.18. Spectrum of a pure Ti calibration standard, Ti-Std.spe.

1.2.2.1. Example: spectrum E-calib.spe

The spectrum E-calib.spe had been obtained by firstly measuring pure Ti for 60 s live time (similar to Ti-Std.spe). Then the Ti foil was replaced by pure Mo (similar to Mo-Std.spe), the preset measuring time was extended to 63 s and the spectrum acquisition continued for 3 more seconds. The resulting spectrum carries two well defined peaks, Ti K_α and Mo K_α, with their respective maxima at channel number 414 (559 counts) and 1595 (438 counts).



```
Spectrum E-CALIB.SPE
Channel 1024: energy= 11.188 KeV,        0. counts
Zero: -24. eV; Gain:  10.9 eV/ch; Noise: 133. eV; Fano:  .111
>>CA
```

Fig. 1.19. Spectrum obtained by additive acquisition of a pure Ti standard and a pure Mo standard,E-calib.spe .

The energy calibration is performed with the COMMAND **CALIB**. Underneath the spectrum name the actual position of the cursor in terms of channel number, the corresponding provisional energy (not necessarily correct for this spectrum!), and the number of counts accumulated in that channel are displayed. By default the starting point is the centre of a spectrum. The navigation with arrow up and down or mouse clicks into the spectrum will lead to the approximate maximum. The lines of interest have to be carefully examined for their real peak maximum! Once at position 414 press the <F1> key (or select with the mouse the option **F1=E_CAL**), which must be followed by the input “TI” (for the weighted average energy of Ti K_α) or the energy value “4.509”. Very important: after this first energy point the correct key to be used is the <Space bar> but *not* <Enter>, in order to define also the second point for the energy calibration, because <Enter> will be the last command to terminate the energy calibration. The use of <Enter> during the calibration procedure will accomplish the calibration, as a consequence the term ZERO will not be the true intercept as needed for a correct energy calibration, but its value would be 0. The second peak maximum position should be found at channel number 1595, followed by <F1> again. The correct input will be “MO”, or equivalently accepted the corresponding energy value “17.443” (for the weighted average energy of Mo K_α).

As alternative for the Mo K_α peak either Mo K_β (maximum channel 1791) or the coherent (also named: elastic or Rayleigh) scatter peak (either channel 1844 or 1845), originating from the Rh secondary target, could have been used. Not recommended are the incoherent (Compton) peak (around 19.6 keV), which for this spectrum is obscured by the stronger Mo K_β peak, nor the Ti K_β peak (channel 453). The Compton peak has neither a Gaussian peak shape, nor has its maximum a tabulated energy value, because its position is a function of the geometry (scattering angle). In difficult cases, when only one element of a sample is clearly identified, also the K_β peak can be used as second energy calibration point. The obtained preliminary calibration can be used to identify other peaks in the spectrum. The newly gained knowledge is then applied to establish a more precise energy calibration.

1.2.3. In the spectrum E-calib.spe the maximum of Ti K_α is well-defined, in contrast to the ill-defined Mo K_α

A closer inspection of channels 1591-1600 of the above discussed spectrum will reveal the fact that there is no pronounced maximum of the Mo K_α peak (within this region all channels have similar **counts** > 400). The one (better) solution to this problem is to acquire Mo for longer counting times. The more praxis-oriented solution is, not to adopt the channel with the highest **counts** value as peak maximum, but rather the mean channel number, which of course leaves some room for the experience of the user.

1.2.4. With arrow up and down I can jump from one peak to the next (COMMAND CALIB) - is this position correctly used for the energy calibration?

In most cases the cursor will indicate the correct position (calculated by AXIL as a centroid of the peak), in some cases it will not find a peak at all, or it will place the cursor in the proximity of the maximum. In order to identify the last case, it is advisable to check several channels left and right of a proposed peak maximum for a possibly better solution. Unfortunately experience is needed sometimes.

1.2.5. Is it important to find the exact energy calibration for each spectrum to be fitted?

The answer is mixed:

No - because AXIL does not treat the energy calibration as fixed throughout the optimization process (iterations), but varies the values of **ZERO** and **GAIN**. So, to some extend, natural fluctuations (caused by the statistical nature of the number of counts, small amplifier drifts, etc.) are corrected during the fit.

Yes - because the better the energy calibration is described the smaller usually will be the Chi square values (total and individual) and the residual deviations – criteria to judge the goodness of a fit. Sometimes an energy re-calibration will help to overcome serious fitting problems.

1.2.6. How can I check the quality of the energy calibration?

The usual way is to select the COMMAND **KLM_MARK**, which displays in the comment line directly under the AXIL blue spectrum frame the atomic number and the element's chemical symbol. Simultaneously a set of markers corresponding to the X ray lines of that element is shown in spectrum display. If the calibration was established correctly the markers should match the X ray peak positions. One can first check the matching for the peaks used for calibrating the spectrum. In the example spectrum, E-calib.spe, Ti K-peaks, Mo K-peaks and Rh K_α as well as Rh L-peaks should match with the corresponding set of markers. The Rh K_β peaks are out of the range for E-cal.spe. All Rh-lines originate from the Rh secondary target. They are detected after being scattered by the sample. The ill-defined hump around channel 1790 is the Rh K_α Compton peak (incoherently or inelastically scattered radiation).

1.2.7. How to "fill" the spectrum with characteristic lines correctly?

The usual procedure, after establishing a correct energy calibration, will be a careful check with **KLM-MARK**. The default markers will start to propose Fe. The first action will be to "jump" with arrow down to the lowest line in terms of energy. The first element (as inherently defined) that could be identified is sodium (Na).

1.2.7.1. Example: IAEA reference standard spectrum Soil7-1.spe

Before loading the spectrum, Soil7-1.spe, load the input file S7-1.inp. The first element present in the sample is silicon. Then from left to right the elements will be identified. The elements with low atomic number (Na - Cl) will have unresolved K_α and K_β peaks, consequently they have only one peak per element. From Ar on upwards also a K_β peak accompanies the K_α for any proposed element (intensity ratio K_α:K_β is roughly 100:15). From the element Fe upwards (Z >= 26) the L-line markers are displayed, shifted towards lower energies as compared to K-lines markers of the same element. In case of samples highly abundant in e.g. Rb and Sr the L-series peaks of theses elements can be seen in the low energy region. With increasing atomic number the markers pass the region of spectrum containing the scatter peaks, then the K-lines markers move out of the spectrum and only L-lines markers remain. Note the differences in their overall number and proportions as compared to the K-lines. The L_α:L_β peak ratio is roughly 1:1. M-lines and other structures that may be observed in X ray spectra (e.g. satellite lines, diffraction peaks) are left to the interpretation of experienced user. Write down the identified elements/peaks and then feed the information into the fit model with the COMMANDs **X-LINES** option **ADD**.

1.2.8. What background model should be used?

The background should be described by a smoothly changing function which follows the fluctuations in background-only regions. Particularly the edges of the fit ROI should not deviate from the trend of background. Under the peaks, especially the intense ones, the background usually will rise due to the imperfect description of the peaks by Gaussian profile. Recommended are either linear or exponential background models. The exponential background is preferably used if a strong curvature of background is observed or the background level varies significantly in the ROI. Linear background model will usually do better for slowly varying background the magnitude of which is more or less of the same order in the fitted ROI. The orthogonal polynomials overestimate the background and small peaks might be “lost” (their peak area is either underestimated as compared to the recommended models or even negative). The Bremsstrahlung background model was originally meant for charged particle excitation. It makes use of some parameters as defined in the input model. At the time of writing this text, for the current version of QXAS the smooth filter background model did not provide meaningful results.

1.2.9. How to select the ROI (region of interest) properly?

The region of interest (ROI) should be selected such that all peaks of interest are included. Its definition comes *after* the definition of the peaks. Many times the automatic region of interest is appropriate (COMMAND **ROI AUTOMATIC**) – it is already the default. It will start with sufficient room left from the lowest energy peak present in the fit model (previously defined with the COMMAND **X-LINES**) and will stop with sufficient room right of the highest energy peak. There are good reasons to select the ROI manually: Sometimes the low energy part of the spectrum is difficult to describe, so either an exclusion of unneeded lines (e.g. escape peaks), or an extension of the background region to facilitate the fit, may improve the results. In the high-energy part of a spectrum the scatter peaks may sometimes cause a drastic increase in the background counts. An exclusion of the K_β peak of the last (and sometimes pre-last) element, or the exclusion of the L_β and L_γ-lines of elements represented by L-lines can facilitate the fit for the essential peaks. Definitely one should *not* start the ROI at channel zero (the first few channels of a spectrum are usually empty or contain “trash”), nor should one mark the entire spectrum.

1.2.10. What are the minimum requirements in order to initiate a fit of a spectrum?

Under **X-LINES** at least one line has to be defined. Change to another background model than the default smooth filter for the last version of QXAS. When no ROI was selected manually, the automatic ROI will be the default. Select the COMMAND **FIT** then set the number of iterations, e.g. **N_ITER=20** and press <enter>. The fitting should be completed after a few iterations.

1.2.11. What are the criteria to be satisfied with a fit result?

The following criteria are to be checked, in descending order, as listed below.

- Visual inspection by the experienced user.
- Total Chi square (**ChiSquare=**) less than 3.0.
- Residual (COMMANDs **DISPLAY RESIDUAL**) between +/-3. When there is no "trend", it is tolerable that a few points can be ouside of the indicated range.
- Results (COMMANDs **REPORT GO**):
  - Individual Chi square values less than 3.0.
  - For standards: The standard deviation must be greater than the square root of the peak area.
  - For samples: The peak area must be positive and greater than 3 times the standard deviation.
- Full report (COMMANDs **REPORT FULL GO**):
  - For samples: The peak area must be greater than 3 times the background under the peak.

1.2.12. What is the difference between X-LINES ADD: e.g., FE and FE-KA FE-KB? What are the secrets behind "+", "" and "&"?*

The command to include e.g. iron K-series peaks into a fitting model is **X-LINES ADD: FE**. The K-series peaks entered this way have fixed tabulated ratio of K_α:K_β. If, due to the absorption effects, the observed line ratios do not agree with the tabulated ones a better fit is obtained if the ratio is not fixed during the fit. This can be achieved by entering the iron peaks with the COMMANDs **X-LINES ADD: FE-KA FE-KB** (before issuing this new command please eventually remove the iron peaks already entered in the model: COMMANDs **X-LINES REMOVE FE**). If the sample composition is know, as for the standard samples, a good fit can also be obtained using fixed line ratios providing that the sample composition has been defined at earlier stage. For intense peaks the appearance of the escape peaks can be treated with the inclusion of "+" suffix. For Si(Li) detectors the escape peak energy is the parent peak's energy minus 1.74 keV. E.g. an intense iron signal should be defined either by **X-LINES ADD FE+ or FE-KA+ FE-KB+**. The asterisk "*" suffix added to X ray line entry (e.g. FE-KA* FE-KB*) corrects for the deviation of the peak shape from an ideal Gaussian profile. This peak shape correction is counted as background under the peaks, not as part of the parent peak. As a consequence applying this peak shape correction will slightly diminish the net peak area as compared to a fit without this correction added. The peak shape correction includes also correction for the presence of the escape peaks. When the "&" suffix is appended to K-series or L-series peaks they will be fitted with the Voigt peak profile instead of the Gaussian one. It may be of use in the case of high-energy K-series peaks, such as Pb−$K_{\alpha,\ \beta}$. It also improves fitting of high-intensity L-series lines of heavy elements. The suffix "&" can be mixed with the other two.

The three symbols: “+”, “*”, “&” can not stand alone but have to be attached to an element name (e.g. FE+) or a peak (FE-KA+) in the COMMANDs **X-LINES ADD**. Verification with the COMMANDs **X-LINES SHOW**. The lines, included together with any of these symbols, will be accompanied by the respective remark: **Escape peak**, **Peak shape corr**., **Voigt peak**.

1.2.13. What are the peaks in a spectrum that cannot be matched with any KLM-MARK markers?

There is a list of peaks that can sometimes be found in spectra, which are only indirectly or not at all caused by a fluorescing atom of a sample (see example data Figure 1.20: Cr-Std.spe with Cr.inp):

a) Escape peaks: for Si(Li) detector, a parent peak (e.g., Fe K_α, with energy of 6.40 keV) will be accompanied by a small escape peak with an energy of the parent peak minus 1.74 keV (escape peak energy for Fe K_α at: 4.66 keV). The amplitude of an escape peak is usually much less than 1% of the parent. For small parent peaks the escape peaks are “swallowed” by the background. Escape peaks are included in the fit model with “+” or “*”.

b) Sum peaks: the sum peaks are observed at the double energy of the parent peak. For intense lines there is a significant probability that two photons of the same energy are absorbed in the detector crystal within short time interval. They are not collected as two individual signals, but rather as a single *pulse with double energy*. Amplitude of sum peak is a small fraction of the parent peak. All possible sum peaks can be included in the fit model (COMMANDs **X-LINES ADD**) with **SUM** keyword. Their intensity can be influenced, to some extent, with a change of the **Pile-up resolution time** (default value: 2 microseconds) in the FORM **Set detector characteristics**.

c) Scatter peaks: the inclusion of the K-line scatter region in the fit model is discussed in the next paragraph; the utilization of this so gained extra information about samples is given in CHAPTER 7: Utilization of the scatter peaks. For the Rh secondary target excitation also the Rh L-lines are scattered. They easily can be confused with Cl K-lines. In this particular case it is recommended that energy values are added to the fit model with:

X-LINES ADD: 2.7 2.8 2.9

This unusual way to add peaks will suppress Rh L results in *.asr files and therefore also suppress unwanted concentration values in output reports for the element Rh, usually not present in a sample.

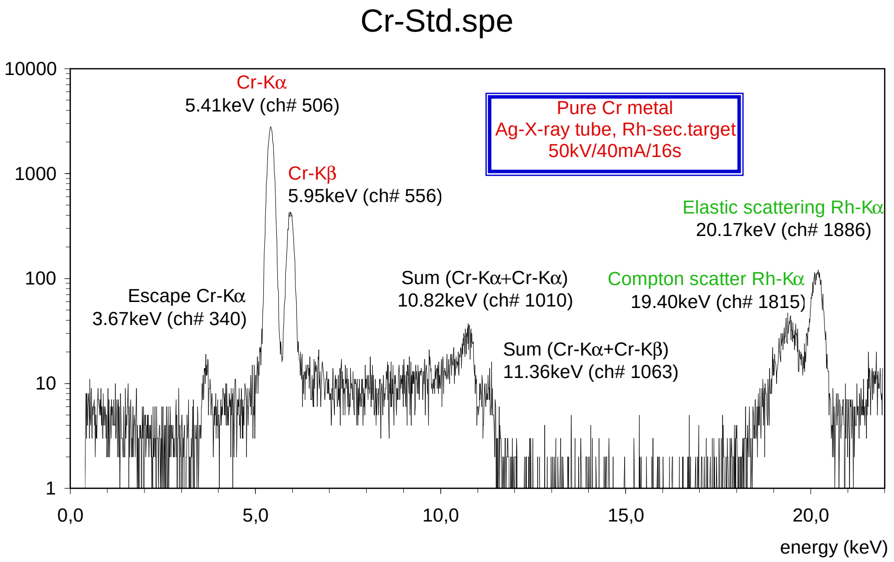
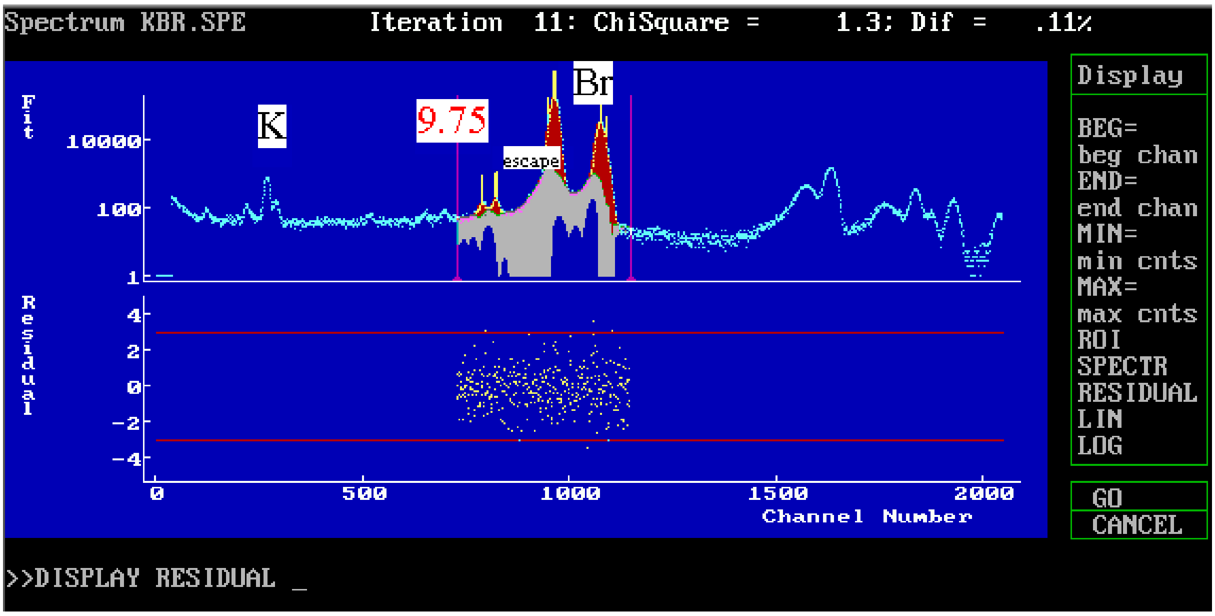


Fig. 1.20. Spectrum plot as obtained by use of the DMP file and further processing with EXCEL (Cr-Std.spe).

d) Diffraction peaks are observed for crystalline samples. In the example shown in Figure 1.21 in the calibration standard spectrum KBr.spe a peak at 9.75 keV was found (input model to be loaded KBr.inp).



```
Spectrum KBR.SPE          Iteration  11: ChiSquare =     1.3; Dif =   .11%
```

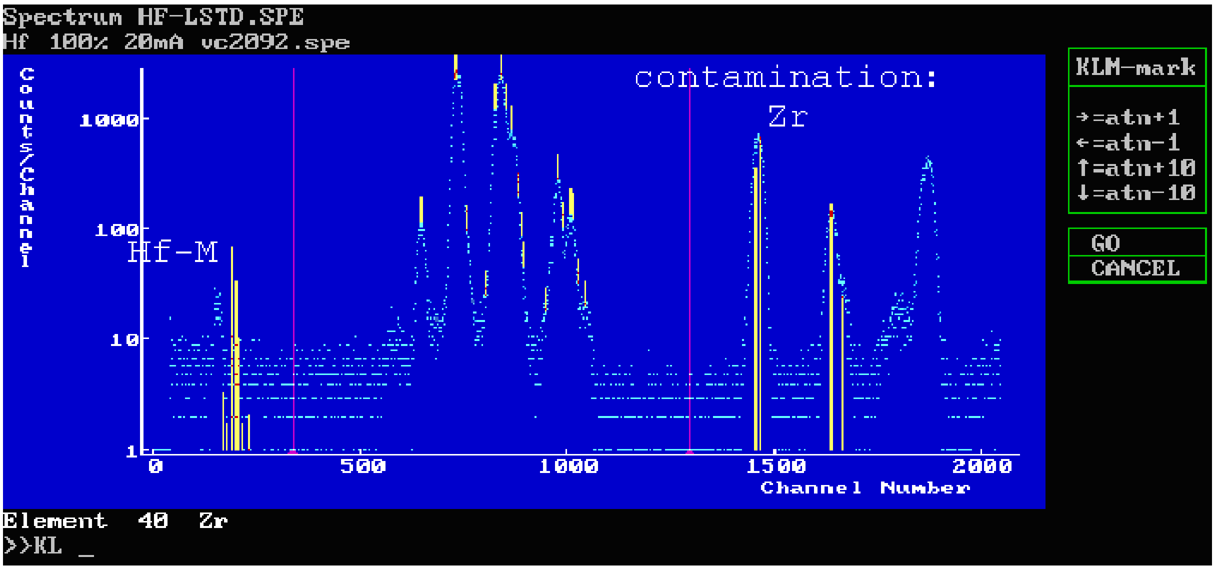
```
>>DISPLAY RESIDUAL _
```

Fig. 1.21. AXIL fit results for the spectrum KBr.spe, which shows a diffraction peak at 9.75 keV.

Other artefacts:

e) Fluorescence lines of other origin than the sample itself: A typical example are the Zr K peaks identified in the hafnium standard (Hf-LStd.spe with Hf.inp). Zirconium is a contamination of the Hf standard (in a strict sense they originate from the sample). Tungsten L-lines can originate from the mill or dye used for the sample preparation of pressed pellets.

Au L lines can originate from the gold contact of a Si(Li) detector. Of importance are elements found in the sample blank and the instrument blank (e.g. Fe, Cu, Zn, Pb…).



```
Spectrum HF-LSTD.SPE
Hf 100% 20mA vc2092.spe
```

```
Element  40  Zr
>>KL _
```

Fig. 1.22. Spectrum of a hafnium standard (Hf-LStd.spe) showing zirconium as contamination.

f) Sometimes M-lines can be identified while L-lines of an element of interest are used for quantification. Typically Pb L is accompanied by M-lines, which have energies in range of 2.3-2.4 keV. This can lead to misinterpretations, because of the proximity to sulphur K. For the example Hf-LStd.spe the Hf M-lines are found around channels 150-160 (1.6-1.7 keV). Unfortunately M-lines will not be displayed as markers when **KLM-MARK** is used for identification.

1.2.14. Ar and/or Kr are identified in a spectrum.

Argon (Ar) is usually identified in spectra collected with spectrometers having no vacuum chamber. This chemical element is present in the ambient air. If the measurements were performed in vacuum an argon signal either points to a misinterpretation or the vacuum chamber is not tight. Krypton (Kr) is present in air at too low concentration to be observed in spectra. It is usually the Pb L_β peak which may be mistakenly identified as Kr K_α by a novice spectrometer operator.

1.2.15. How to define scatter peaks for the fit model?

Scatter peaks can be included in a fit model (e.g.: Rh K_α incoherent and coherent scatter peaks) with the COMMANDs **X-LINES ADD: RH,INC RH-KA,COH**. In order to find a correct position for the relevant marker at the incoherent scatter peak maximum, *before* adding RH,INC, the **Angle of incidence (degrees)** and **Detector take-off angle (degrees)** have to be defined according to the spectrometer sample incidence and take-off angle, respectively. The sum of incident and take-off angle is the scattering angle. For the secondary target measurements the default values of 45^0 for both angles will result in the correct scattering angle of 90^0. For source excitation, or other geometry, the defaults must be adapted. For setting the coherent scatter peak also the line must specified, otherwise both K_α and K_β would be included - with fixed line ratios - which for the scatter peak region fit is not recommended. Setting the incoherent peak as described above, puts only one line marker corresponding to the calculated position of the Compton $K_{\alpha1}$-peak. Another significant feature of the incoherent peak is that it is included with a resolution that is “free”, i.e. independent of the resolution optimization gained from the other peaks. Usually it will be advisable to fit the fluorescence peaks of interest in a first run (with a different background model and within the relevant ROI) then the scatter peaks. As alternative to the fitting of the scatter peaks: the COMMAND **SCAT_ROI** will sum all channel contents within a region of interest (for the experienced user).

Hint: The format of the scatter peak information obtained through the last approach is different, when saved to the *.asr file, than expected by some quantitative METHODs. Editing of the *.asr file might be necessary when unexpected program crashes occur.

1.2.16. What are the criteria for including or excluding a weak peak?

After setting up clearly identifiable peaks one can add to the model other peaks the origin of which is not yet fully confirmed. The relevance and the need of their presence in the final fitting model need further checks. Two criteria are helpful to decide whenever to remove a given peak from the fitting model:

- in the report available after the fit (COMMANDs **REPORT GO**) the respective peak area is followed by the information about its standard deviation (**st.dev.**). For the sake of statistical significance an element with a peak area < 3 times the standard deviation, or a negative area value, should be excluded.
- in the full report (COMMANDs **REPORT FULL GO**) underneath each individual **peak area** the under laying background (**backgr**) for this peak is displayed. When the area of a relevant element peak is < 3 times the square root of this background the element should be excluded.

These criteria are related to the definition of the detection limit and the fact that the peak area must be a positive number. The definition assumes the presence of a peak if the peak area, N is greater than three standard deviations of the background underlaying the peak, BG:

$$N > 3 \cdot \sqrt{BG} \tag{1.2}$$

From AXIL full report the background counts can be read for Co and Ni:

```
                           PEAK   DATA

  # Line          E(KeV)  rel. int.   peak area   st. dev    chi-sq
                  chan#   fwhm (eV)     backgr              tot. abs

 11 Co-K                                 1046. ±       0.
    KA1            6.925    .87927        920. ±       0.       4.5
                 551.543    176.79        510.                9.34E-01
    KB1            7.649    .12073        126. ±       0.       6.8
                 608.976    181.70        516.                9.50E-01

 12 Ni-K                                   81. ±       0.
    KA1            7.478    .58129         43. ±       0.       3.4
                 595.411    180.55        525.                9.47E-01
    KA2            7.461    .29783         22. ±       0.       3.4
                 594.062    180.44        525.                9.47E-01
    KB1            8.265    .12088         10. ±       0.        .8
                 657.841    185.78        478.                9.60E-01
```

For the element cobalt the criterion is fulfilled: $920 > 3*(510)^{1/2}$, for nickel $(43 + 22) < 3*(525)^{1/2}$, therefore Ni peaks should be removed from the fitting model. After the model is modified the fitting should be repeated and the results examined again until no other insignificant peaks are present.

1.2.17. How to remove elements or lines from the list?

To remove all X ray peaks apply COMMANDs **X-LINES REMOVE ALL**. To remove individual peaks or group of peaks replace the keyword **ALL** with the symbol of the peak or a group of peaks, e.g. **FE-KA** or **FE.** Exceptions are the peaks specified directly by using peak energy. They become GR01, GR02, etc. (see **X-LINES SHOW**). To remove particular peak, e.g. GR01 from the list use COMMAND **REMOVE GR01**.

1.2.18. Why will one need an input model file (.inp) for treating a spectrum with AXIL?*

There are good reasons to create such files, however the AXIL fit itself can be performed without going through an intermediate step of creating an input model file. One motivation for its creation is for repeated fits of similar spectra. Such model file modified as required, can be also used as a base for fitting different types of spectra. The alternations being made can be saved under a different name for further use. Another motivation to create and store input model file for every sample or group of samples comes from quality assurance. In a properly defined and implemented quality assurance system all analytical operations should be documented. It helps tracking back mistakes and formulating appropriate corrective actions. To store a newly created or modified input model file one have to exit the AXIL fitting screen with the COMMAND **STOP** and select **Save model**, then select appropriate action from the list. An input model file will be created. If necessary, other parameters, which can not be changed inside the AXIL window, can be altered by selecting the option **Specify parameters for spectrum analysis** followed by **Specify spectrum analysis parameters** or **Specify experimental parameters,** which make such parameters accessible for editing.

*1.2.19. What are the essentials of a model (input, *.inp) file? How is it created?*

The model input file contains parameters for the energy calibration, definition of the region of the fit, the X ray lines defined with the COMMAND **X-LINES**, the background model, the sample/standard composition, the detector resolution calibration, the allowed variability ranges for the energy and peak resolution calibrations, and several other data. The file should be created / saved immediately after a successful fit is accomplished. For this purpose use the COMMAND **STOP** and select **Save model** action. For creation of a new file use the COMMAND line **In new file**. By selecting the option **In current file** one will update the file associated with the current model. If this step is not performed all the alternations to the current model done in the AXIL session will be lost. Choosing the option **In existing file** allows the operator to select other existing input model file and overwrite it content with the current model settings.

*1.2.20. Will the parameters stored in an *.inp file, influence any of the quantitative METHODs?*

No, the parameters, e.g., the detector specification, the air-path between the sample and the detector, the average excitation energy, etc. are only used for peak ratio correction calculations. They are not used by any of the quantitative METHOD routines.

1.2.21. *What is the FANO factor?*

The response function of a Si(Li) detector is nearly Gaussian due to the fact that Poisson statistics applies (the natural line width is usually neglected, except for the Voigt peak shape model). The FWHM (**F**ull **W**idth at **H**alf **M**aximum) of a Gaussian peak is a function of the characteristic line energy *E* in (eV) and is described by

$$FWHM = \sqrt{\Delta E_{elec}^{2} + 8\ln 2 \cdot \varepsilon \cdot F \cdot E} \tag{1.3}$$

where ΔE_{elec} is the electronic noise contribution (named **NOISE** in AXIL, with a default value of 120 eV). *F* stands for the Fano factor (named **FANO-factor** in AXIL, with a default value of 0.114). The average energy required to produce an electron-hole pair in the detector volume is ε, with a value of 3.76 eV. The usual assumption is that fluorescence lines are governed by Poisson statistics, which describes independent events. An example of Poisson statistics is the decay of a radioactive isotope: each decay is completely independent from all past and future decays. In semiconductor devices, the details of the energy-loss process are such that the individual events of the electron-hole pair production are not strictly independent from each other, therefore a deviation from Poisson behaviour is observed. This deviation is taken into account by the inclusion of the Fano factor. For true Poisson statistics the Fano factor were 1.

1.2.22. *Why does the ASR file information get into the respective SPE file?*

Due to motivation driven by quality assurance every time an *.asr file is created or altered by saving the AXIL fit results (**SAVE_RES**), the results are also appended to the spectrum file. This is sometimes problematic, because, even after an *.asr file is erased and created newly, it can happen that the old fit result information is partly transferred to the newly created *.asr file. Otherwise, this feature is harmless but also not helpful. In the worst case one will erase the block, that represents the fit result, from the *.spe file:

```
$SPEC_ID:
Soil7 2g 40mA  vc2139.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
      1000      1000
$COH_SCAT:
      1
   45   1     20.167    471788.       774.     117.81
$INC_SCAT:
      1
   45   1     19.401    811436.       997.      17.67
$COH_SCAT:
      1
   45   1     20.167    492611.       819.       1.13
$INC_SCAT:
      1
   45   1     19.401    787234.      1013.       8.24
```

1.2.23. *Although a spectrum or file is definitely stored in a directory, its file name will not be displayed in a SCROLL BOX.*

SCROLL BOXes within QXAS can handle only 100 file names of a kind. Although present in a directory, any files exceeding this limit will not be selectable. This is a reason to move files into sub-directories.

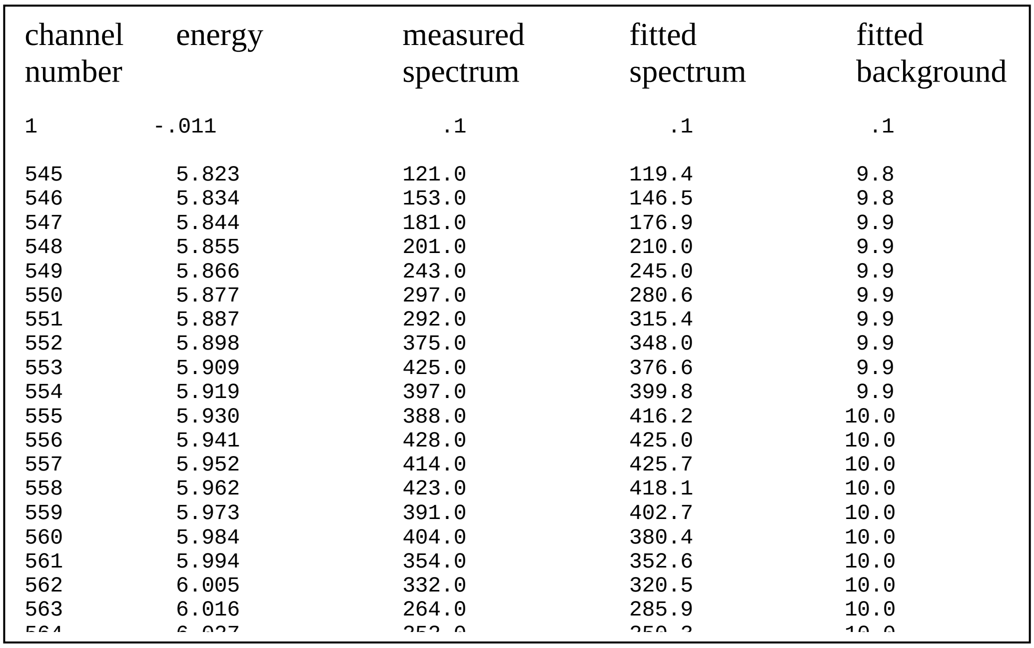
1.2.24. *How can I get spectra into a format that can be used for decent looking printouts?*

It often happens that the **PLOT** and **PRINT** COMMANDS of AXIL do not function as expected. One way to overcome this problem is to use the WINDOWS build-in <Prt Scr> key (often in combination with <Alt> or <Shift>), which will copy the QXAS window to the clipboard memory. When this is not sufficient, screen shots (print screen) will be forced with a combination of commands: First use <Alt> and <Enter>, which runs the DOS screen as reduced size foreground window, then use <Alt> (or <Shift>) and <Prt Scr>, which brings this window contents to the clipboard memory. Finally paste with the usual <Control> “V” into any desktop publishing document, from there print as for any other document. On some combination of PC hardware this method may not work while the AXIL graphical mode is active.

A copy of the AXIL screen may be sufficient in many cases but for reports and publications a higher resolution graphics is usually required. The spectral data can be exported to an ASCII file. Such file can be read in by many data visualization programmes, e.g. to MS EXCEL.

There are two ways to export the spectral data. It is possible to convert the original MCA spectrum file to ASCII format *directly*. In the MENU **Spectrum format conversion** choose the sub-MENU **Select format of source data** and select the MCA format appropriate for your spectrum. In the sub-MENU **Select format of target data** choose ASCII. The resulting file, *.asc, has as many lines as the spectrum has channels, listed in a single column. The major disadvantage of this way of conversion is lack of energy calibration data in the resulting file.

The second method of exporting spectral data becomes available after fitting the spectra. After the fit select COMMAND **REPORT** then **DUMP** and **GO**. An ASCII file *.dmp is created:



```
channel    energy        measured      fitted        fitted
number                   spectrum      spectrum      background

1         -.011              .1            .1            .1

545         5.823        121.0         119.4           9.8
546         5.834        153.0         146.5           9.8
547         5.844        181.0         176.9           9.9
548         5.855        201.0         210.0           9.9
549         5.866        243.0         245.0           9.9
550         5.877        297.0         280.6           9.9
551         5.887        292.0         315.4           9.9
552         5.898        375.0         348.0           9.9
553         5.909        425.0         376.6           9.9
554         5.919        397.0         399.8           9.9
555         5.930        388.0         416.2          10.0
556         5.941        428.0         425.0          10.0
557         5.952        414.0         425.7          10.0
558         5.962        423.0         418.1          10.0
559         5.973        391.0         402.7          10.0
560         5.984        404.0         380.4          10.0
561         5.994        354.0         352.6          10.0
562         6.005        332.0         320.5          10.0
563         6.016        264.0         285.9          10.0
```

The data in the file are arranged in columns. There are five columns and as many lines as the spectrum has channels. The first column contains the channel number. The second column the energy corresponding to that channel, columns 3, 4 and 5 contain the measured spectrum, the fitted spectrum, and the fitted background, respectively. EXCEL can read this file type and one can prepare detailed graph of the spectrum selecting the data from the second and/or the third column. A spectrum graph prepared in EXCEL is shown in Figure 1.20.

As mentioned, direct printing by using the COMMANDs like **PRINT** or **PLOT** may fail. However in many QXAS routines there is also an option available to save the results to a file (depending on the METHOD, as *.ARP, *.PRN, *.RPT file). Such file can be then retrieved by a word processor program for eventual editing and printing.

1.2.25. What is the setup.ax file? What can be done when it gets corrupted and how to recognize it?

The "setup.ax" file is a dynamic file (in editable ASCII format) that accepts certain information from QXAS programs. The current information relevant to the individual programs can be read by the programs and, if necessary, updated. It contains the "menu tree" of some of the installed programs in the package, names of the current data files, information about libraries to be used, etc. The setup file is a block structured file, i.e. it is divided into blocks that are identified by a header name, with "$" as starting character and ":" as last character. The actual position of a block of information within the file is of no importance.

When the "setup.ax" file gets corrupted, which can happen particularly after program crashes, typically the SELECTOR BOX **Axil X-ray Analysis Package** will display one line less than the usual four.

```
Axil X-ray Analysis Package

* Spectrum format conversion
* Spectrum fitting
*
* Utilities
```

Fig. 1.23. Possible consequences from a corrupted setup.ax file.

In such a case delete the faulty "setup.ax", copy the spare "setup.ax" file, which is found in the directory "\axil\backup", and paste it into "\axil" folder. *Do not move* the original backup file with drag and drop, it shoul be stored in the "axil\backup" folder for future use.

1.2.26. Under what measuring conditions the example standards and samples had been collected?

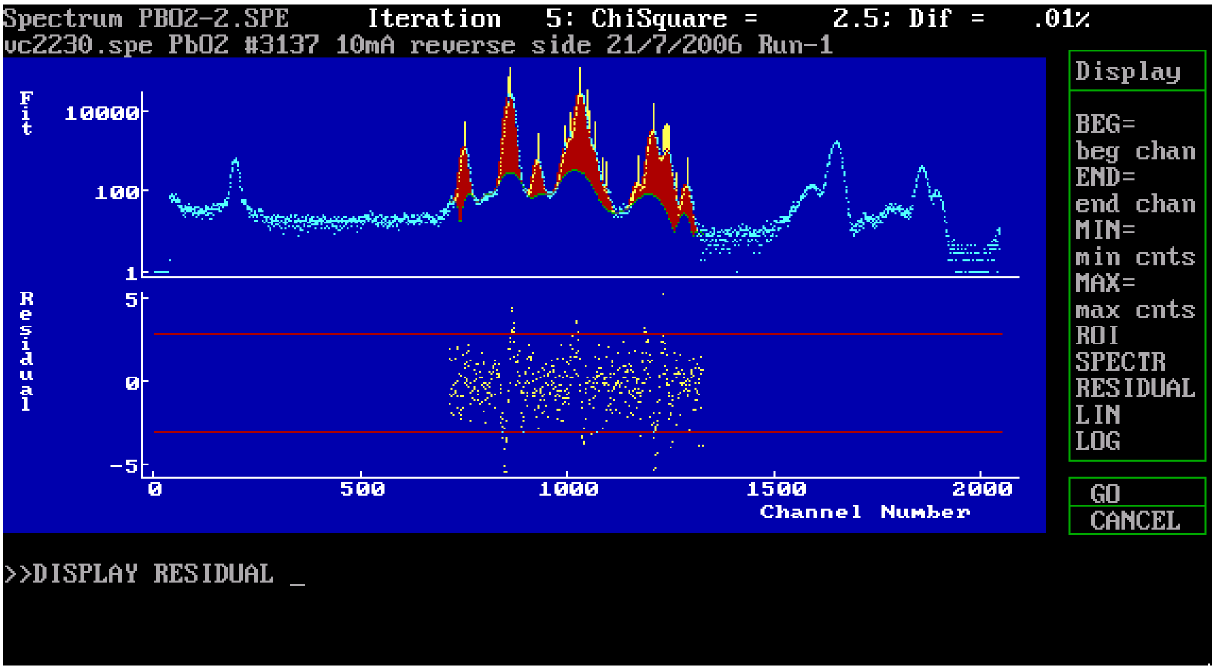
Tube excitation: Ag-anode X ray tube in combination with Rh secondary target was used to excite X ray fluorescence spectra. The tube was operated at 50 kV constant potential. The tube operating potential was kept constant for all the measurements; otherwise the sensitivity calibration would be affected in a non-linear manner. All measurements were under vacuum conditions (pressure in the sample chamber less than 5×10^{-1} mbar). For the calibration standards: in order to minimize pile-up effects (sum peaks) and to keep the peak shape distortions low, the standards' spectra were collected at less than 20 % dead time. To achieve that the tube current was varied between 5 mA and 40 mA. The counting time (live time) varied strongly among the collected spectra. For standards it was selected in such a way to collect around 50 000 counts in the peak of interest. With 50 000 counts a relative standard deviation due to counting statistics of less than 0.5 % can be expected. The other samples were acquired for 1000 s live time and 40 mA tube current, with a few exceptions (when the dead time would have exceeded 40 %, e.g. for alloys). For organic and geological samples the most intense were the scatter peaks. By the acceptance of higher dead times, as compared to the standards, the low intensity fluorescence peaks were measured with relatively good counting statistics.

The Cd-109 annular radioisotope source excitation: for standards the counting time was preset to a value that enabled collecting approximately 10 000 counts in the peak of interest.

The concept to have equal counts for each peak used in method calibration ensures that the same statistical weight is given to each calibration point.

1.2.27. A spectrum can not be fitted properly – what to do?

X ray spectra should be fitted according to the criteria specified in paragraph 1.2.11. When a spectrum like PbO2-2.spe (input file PbO2.inp) can not fulfil a good fit criteria, an explanation for the “failure” should be found.

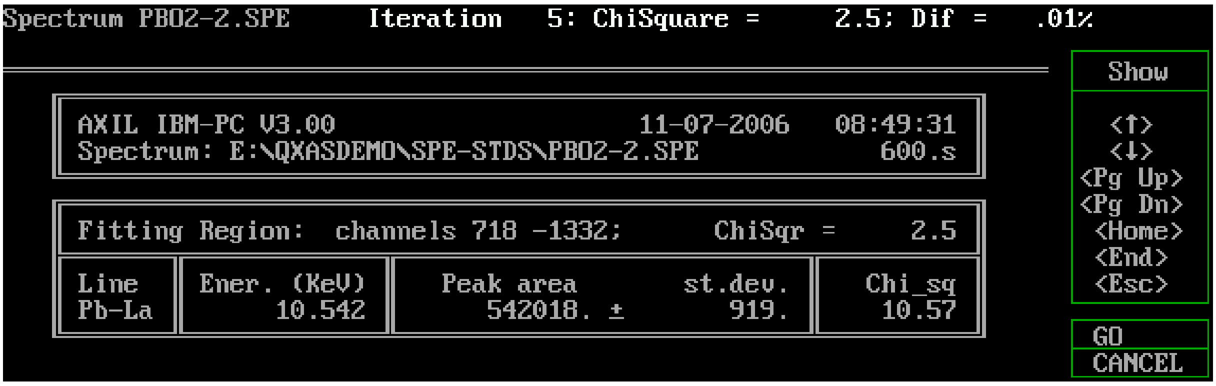


```
Spectrum PBO2-2.SPE      Iteration   5: ChiSquare =     2.5: Dif =    .01%
uc2230.spe PbO2 #3137 10mA reverse side 21/7/2006 Run-1
```

```
>>DISPLAY RESIDUAL _
```

Fig. 1.24. A spectrum of a PbO_2 sample that cannot not be fitted by AXIL according to certain quality criteria.

In the example shown in Fig. 1.24 the lead X ray lines were input by using PB-LA PB-LB PB-LG, the matrix of the standard was defined (PbO_2 plus binder), the background was defined as linear polynomial of order 30. Still the fit results were not satisfactory despite acceptable value of the overall Chi square. The residuals showed misfit around the most intense peaks and the individual Chi square value of the PB-L_α was unacceptably huge. When spectra like this are identified, it usually indicates problems with linearity of the energy calibration or not properly coded fitting procedure.



```
Spectrum PBO2-2.SPE      Iteration    5: ChiSquare =      2.5: Dif =    .01%

AXIL IBM-PC V3.00                      11-07-2006   08:49:31
Spectrum: E:\QXASDEMO\SPE-STDS\PBO2-2.SPE                600.s

Fitting Region:  channels 718 -1332;      ChiSqr =     2.5
Line     Ener. (KeV)    Peak area        st.dev.      Chi_sq
Pb-La       10.542       542018. ±        919.        10.57
```

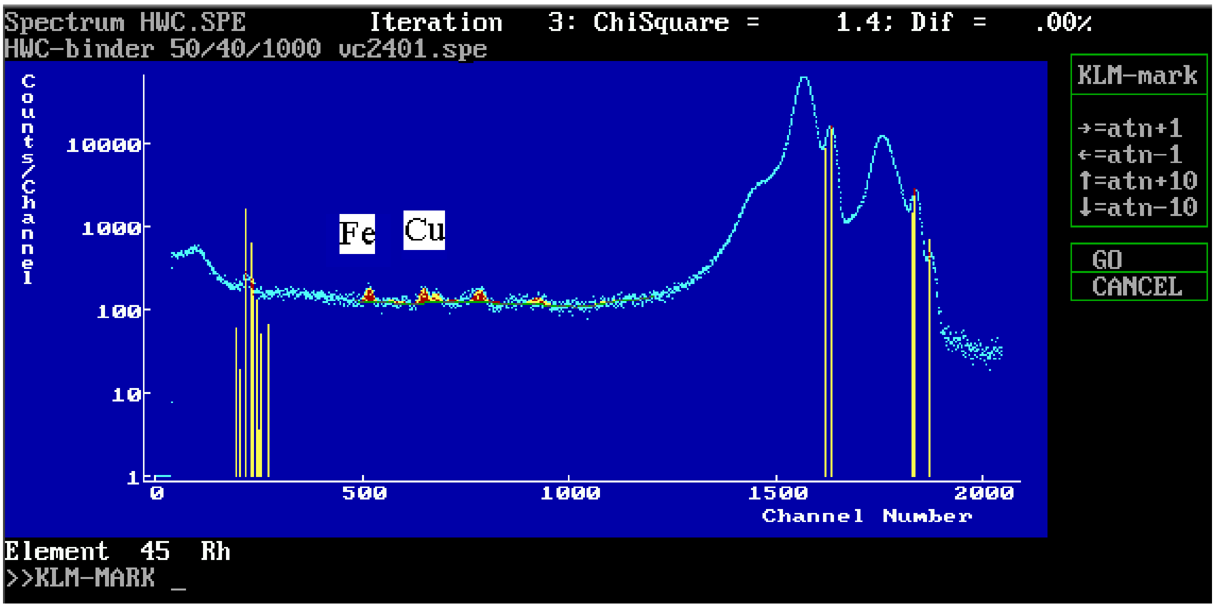
Fig. 1.25. Fit results that do not fulfil certain quality criteria for a PbO_2 *sample.*

The above spectrum should not be incorporated into any “method calibration” due to another reason: it was acquired with the specimen in a wrong position.

1.2.28. How to handle blank problems?

Two kinds of blank spectra can be measured: the sample blank and the instrument blank, both must be taken with the same acquisition time as for the samples and the highest current setting (for tube excitation). The sample blank measurement provide information about the impurities introduced during the sample preparation procedure as well as the contribution coming from the instrument itself modified by the presence of the sample. The sample for the “sample blank” measurement should be of similar shape and kind as the samples to be analyzed, e.g. for “thick” and “intermediate” thickness samples prepared in the form of pellets a blank sample should be also a pellet. It should simulate the sample matrix without presence of any elements exhibiting fluorescence lines, besides the ones originating from impurities. Usually such blank sample is made of pure binder, e.g. cellulose, boric acid, wax or flux if the samples are prepared as fused beads. The impurities (e.g. Fe, Cu, Zn, Pb, W,…) found in blank spectra may originate from different sources. E.g. tungsten may come from the dyes used for pressing. It may also come from grinding in tungsten carbide mill. Eventually, its presence may be due to spattering of X ray tube cathode resulting in contamination with tungsten L-series lines of the excitation spectrum. The peaks of other elements may originate from the instrument chamber itself. Sometimes it is possible to reduce the magnitude of the peaks by coating part of the chamber with pure aluminium or indium foil and/or by adaptation of the sample chamber internal collimators. The so-called “blank subtraction”, i.e. the subtraction of “disturbing” peaks either at the level of the MCA or by editing spectra or *.asr files is generally not recommended. If performed, the blank subtraction should be done carefully as the magnitudes of “blank” peaks may be not constant, e.g. it may vary with the sample matrix. In general the impurity peaks should be eliminated or they magnitude reduced to a degree where it is not significant.

An example blank spectrum (HWC.spe, model file Samp-Bl.inp) is shown in Figure 1.26. The blank sample was a pellet made of pure binder (HWC wax, chemical formula $C_{38}H_{76}N_2O_2$).The element copper was identified, net count rate of 1.3 counts/second, iron (1.3 counts/second) and tungsten L-series lines.

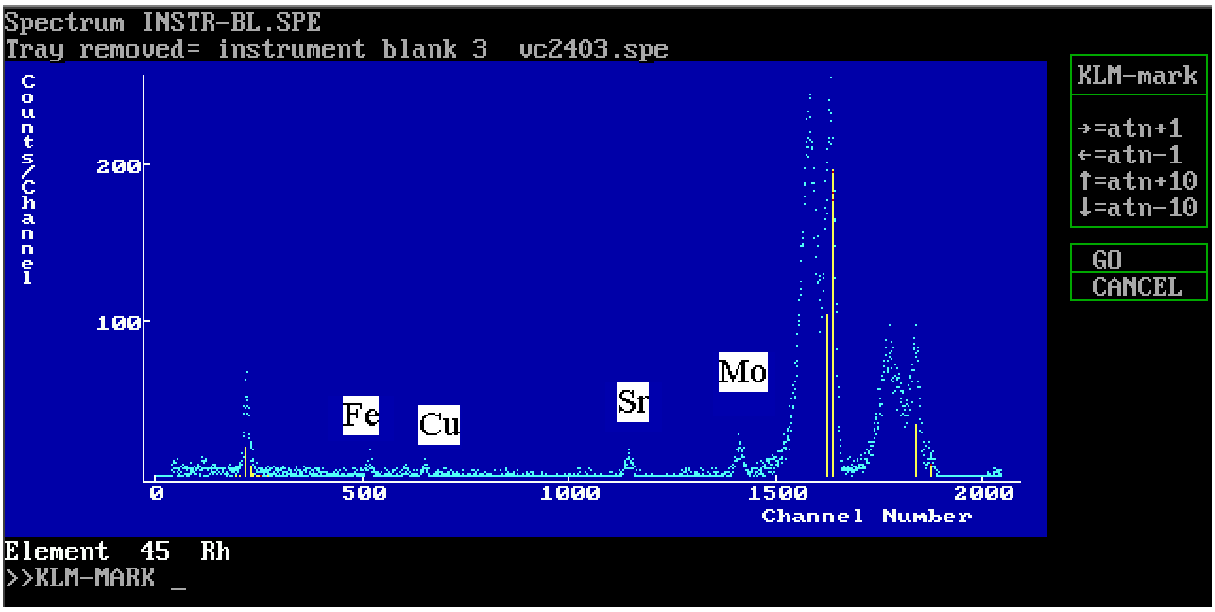


```
Spectrum HWC.SPE          Iteration   3: ChiSquare =     1.4; Dif =   .00%
HWC-binder 50/40/1000 vc2401.spe
```

```
Element  45  Rh
>>KLM-MARK _
```

Fig. 1.26. Sample blank spectrum obtained with a sample pressed from pure binder HWC.

The instrument blank (Instr-Bl.spe, Instr-Bl.inp) is obtained by leaving the sample position empty. Scattering, when a sample is in the measuring position, is mainly caused by the sample itself. When no sample is present, the scattering intensity is low and the exciting radiation can hit parts of the sample chamber otherwise shielded by the sample. Consequently other peaks can be seen above the spectral background. This blank measurement is representative for thin layer samples like air filters. For instrument blank problems a background subtraction might be the only solution in order to get any results - although this will drastically increase the uncertainty in reported concentration values for affected elements. For the used spectrometer Fe with a count rate of 0.1 counts/second, Cu (0.1 counts/second), Sr (0.2 counts/second) and Mo (0.4 counts/second) were identified in the instrument blank.



```
Spectrum INSTR-BL.SPE
Tray removed= instrument blank 3  vc2403.spe
```

```
Element  45  Rh
>>KLM-MARK _
```

Fig. 1.27. Instrument blank obtained from a measurement without any sample in the usual measuring position.

Intermediate thick samples will exhibit an intermediate behaviour, both instrument blank and sample blank must be considered for each element affected.

Conclusion: when blank peaks cannot be eliminated and a precise estimate of the result uncertainty is required, the intensity of a peak in the analyzed sample should exceed tenfold the intensity of that peak observed in the blank. Otherwise the uncertainty of the result for that element should be carefully estimated taking into account the contribution of the blank.

1.3. Batch mode

Demonstration files (files in the sub-directories \Original, \MovePeak and \ZeroCont of directory \QXASdemo\Batch):

- Spectra: Sum-Spec.spe, 01.spe, …, 41.spe
- Input files: SumSpec.inp, CaZnSrPb.inp, MovePeak.inp
- Batch file: FitAll.bat

The **@BATCH** COMMAND is very useful for processing a number of similar spectra (to be treated with the same input model), in an unattended manner. Large groups of spectra are obtained during e.g. scanning measurements (analysis with the use of X ray micro-beam, XANES, etc.) or during bulk analysis of large batches of samples. The number of generated spectra may reach several thousands for a run or batch. It would be very impractical, if not impossible, to process such large number of spectra in the interactive mode. When processing the spectra in batch mode several requirements must be fulfilled:

- All spectra to be processed (already converted to QXAS format) must be located in a single folder.
- It is advisable to generate a single sum spectrum by adding all spectra, channel by channel, in order to identify all possible peaks of chemical elements.

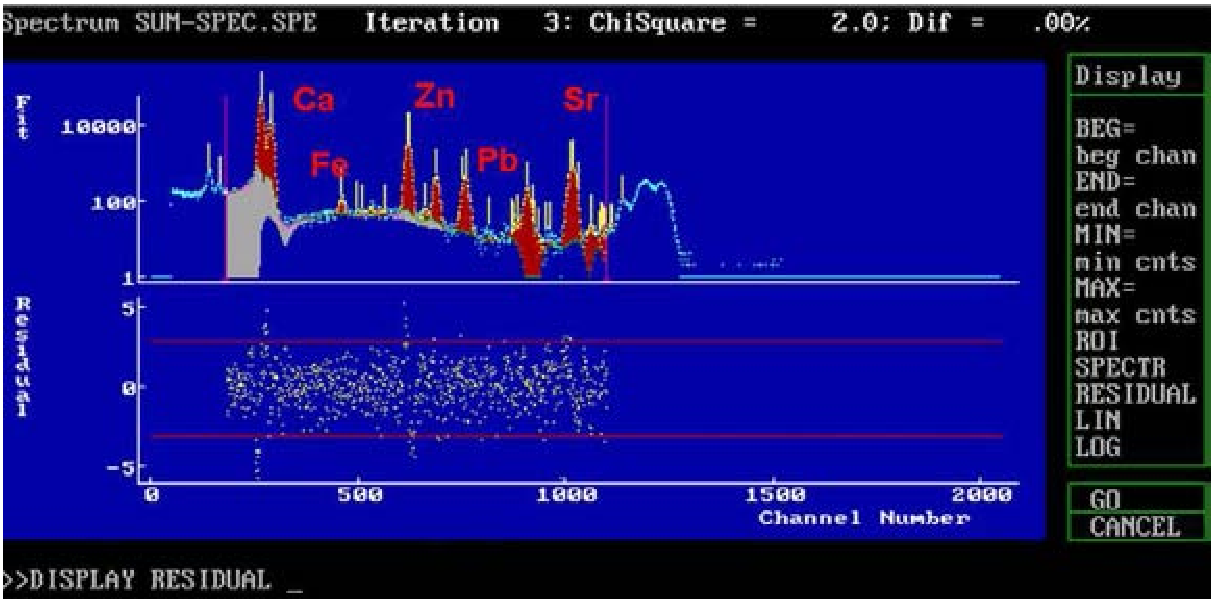
- A suited fit model has to be defined before (with the help of the sum spectrum), in order to finally evaluate all spectra in batch mode.
- An ASCII file must be created (outside QXAS) that carries the minimum information needed for each spectrum to be fitted by AXIL.

After having fulfilled all the previous, the batch fitting routine is initiated with the COMMAND **@BATCH** followed by keying in the file name containing the instructions. Please examine the example batch file FitAll.bat. In contrast to all other kinds of files to be loaded when working with QXAS, when entering the batch command the filename extension (for our batch file, ".bat") must not be omitted.

1.3.1. Example: Forty-one spectra of a µ-XRF scan

All files necessary to carry out batch processing of spectra are contained in the directory \QXASdemo\Batch\Original. This directory must be set as default directory for QXAS data processing. It is done in the QXAS start screen with **Set directory:** \QXASdemo\batch\Original. For this demonstration forty-one spectra from an area scan over a sample (bone cross-section) containing Ca, Zn, Sr and Pb were taken. The sample was excited by monochromatic synchrotron radiation beam, energy of 17.1 keV. Counting time for each spectrum was 1 s. The 41 spectra, sufficient for our demonstration, are only a small subset of all spectra collected during the scan.

In order to establish an input model, describing not only a single spectrum or a limited number of spectra, a sum spectrum (Sum-Spec.spe) was generated by adding channel by channel all the 41 individual spectra. The fit of the sum spectrum (with the model from SumSpec.inp) is shown in Figure 1.28. The elements Ca, Fe, Zn, Sr and Pb were identified. The adequate fitting of this spectrum is only possible with a linear background and highest order of the polynomial (**PARAM=** 30) and inclusion of sum peaks - but this is not really the task of this demonstration.



```
Spectrum SUM-SPEC.SPE   Iteration   3: ChiSquare =    2.0; Dif =   .00%
```

```
>>DISPLAY RESIDUAL _
```

Fig. 1.28. An artificial spectrum (Sum-Spec.spe) obtained by channel-wise summation of forty-one individual spectra.

For the evaluation of the individual spectra also a linear background was selected, but of order 0, to prevent unnecessary background overestimation. The region of interest includes the escape peaks of Ca and stops after the Sr K_α peak. The following peaks were included peaks in the model:

X-LINES ADD: CA-KA* CA-KB* FE ZN-KA* ZN-KB* PB-LA PB-LB PB-LG SR-KA

All the fitting settings were stored in the input model CaZnSrPb.inp. This model should be used for batch fitting the 41 spectra.

The sequence of commands to perform the batch fitting has been stored in the file FitAll.bat. Its structure is shown below:.

```
load spec=01.spe
fit n=10
save

load spec=02.spe
fit n=10
save

          etc.

load spec=40.spe
fit n=10
save

load spec=41.spe
fit n=10
save
```

For each file there are 3 commands executed: (1) to load the spectrum, (2) to perform the fitting, and (3) to store the results of the fit. Before starting the batch fitting a proper input model file should be loaded, in this case CaZnSrPb.inp. Next, with the COMMAND

@BATCH, one enters the full name of the file containing the batch fitting commands, “fitall.bat” (without the apostrophes). The batch mode is invoked, spectrum after spectrum is fitted. After fitting all the 41 spectra the batch mode is finished. The last spectrum, 41.spe, is displayed in interactive mode. The results of fitting of all the spectra are stored in corresponding *.asr files: as 01.asr – 41.asr.

There can be cases when the situation gets more complicated. During a long lasting scan measuring points might be analysed that do not contain the usual composition of elements. Instead, peaks of other elements might appear (imagine the case when the sample holder is hit). If peaks of such elements are not included in the fitting model, it might occur that due to mismatch of the fitting model and the data some of the optimized parameters are improperly evaluated for some of the spectra. The four parameters, namely: **ZERO (eV)**, **GAIN (eV/ch)**, **NOISE (eV)**, and **FANO (unitless parameter)** concern the energy (the first two) and resolution calibration. They can vary within their respective limits **D_ZERO (eV)**, **D_GAIN (eV/ch**), **D_NOISE (eV)**, **D_FANO**. This variability is necessary to compensate for slight drifts in the energy calibration, which may occur due to electronic or temperature related effects. In certain situations, especially when processing a bunch of spectra with poor counting statistics some of the parameters (e.g. GAIN and FANO) should be kept constant. It helps stabilizing the fit and keeps the results within physical limits.

CHAPTER 2. FUNDAMENTALS OF XRF – THEORY

Reference material: [13], [14], [15], [4], [16], [17], [18], [19], [20], [21], [22], [23], [24]

2.1. Fluorescence radiation

Photo-absorption of X rays with energy E_0 is usually associated with an inner-shell ionization of an atom. A photoelectron is hereby emitted from the atom and carries the energy E_0 - E_B. Here E_B is the binding energy (ionization energy) of the electron. The energy of the ionized atom is increased by E_B. Configuration of electrons in the ionized atom is not the optimum one in terms of energy. Therefore, in a very short time of the order of 10^{-15} s ÷ 10^{-17} s, the arrangement of electrons in the electronic shells of the ionized atom starts to change until it achieves a minimum. This process is called relaxation. One of the relaxation paths starts by filling in the vacancy in the ionized shell by another electron of the same atom. Not all electrons can take part in such transition. For a given electron, there is a certain probability that such transition will occur. For the vacancy in the K-shell, the most probable electronic transition to fill in the vacancy is by the electron of the L_{III} shell. Such transition is denoted as $K \leftarrow L_{III}$. To describe this process in terms of energy we have to note that the binding energy of an electron in an atom is expressed by a negative number. In this convention the energy associated with a fully ionized atom (an atom totally stripped out of electrons) is equal to zero. On the opposite end, the energy associated with an atom possessing all of its electrons is equal to a negative number - the smallest energy which can be associated with that atom. Therefore, in terms of energy, removing one electron from an atom, e.g. by photoelectric effect, is equivalent to subtracting a small negative number from the overall (also negative) atom energy:

$$E_1 = -E_G \tag{2.1}$$

$$E_2 = -E_G - \left(-E_K\right) \tag{2.2}$$

$$E_2 > E_1 \tag{2.3}$$

E_1 is the energy of a neutral atom (negative value $-E_G$), E_2 is the energy of the ionized atom lacking one K-shell electron, and the $-E_K$ is the binding energy of the expelled K-shell electron. If the vacancy in K-shell is filled in by an electron from the L_{III}-shell, it creates a new vacancy, this time in the L_{III}-shell. The atom is still ionized, its energy, E_3:

$$E_3 = -E_G - (-E_{L_{III}}) \tag{2.4}$$

The energy $-E_{LIII}$ is the binding energy of an electron in the L_{III} electronic shell. The transition $K \leftarrow L_{III}$ can occur spontaneously because the energy of the ionized atom is reduced in such a process:

$$E_3 < E_2 \tag{2.5}$$

Consequently the atom gives out the energy. There are several ways the energy can be given out. One of the possible paths is by emission of X ray photon, which is essentially called "X-ray fluorescence" (XRF). For $K \leftarrow L_{III}$ transition the emitted X ray line is denoted as $K\alpha_1$ in so called Siegbahn notation or K-L_3 in IUPAC (International Union of Pure and Applied Chemistry) notation. The emitted X ray photon has a characteristic energy, E-$K\alpha_1$:

$$E_{\mathrm{K}\alpha_1} = E_2 - E_3 = E_{\mathrm{K}} - E_{\mathrm{L_{III}}} \tag{2.6}$$

For the vacancy in the K-shell the other most probable transitions include: K ← L_{II}, K ← M_{III}, K ← M_{II}. They are associated with emission of Kα_2, Kβ_1, and Kβ_3 X ray characteristic lines, respectively. New vacancies are created in this process. They are successively filled in by electrons from outer electronic shells, which results in cascade emission of L- and M-series X ray fluorescence lines.

The probability of a photoelectric effect is characterized by so-called cross-section. In atomic scale the cross-section, τ is expressed in barns or in barns per atom:

$$1 \text{ barn} = 10^{-24} \text{ cm}^2 \tag{2.7}$$

In a macroscopic scale more practical unit is in use, the cross-section is called photoelectric mass attenuation coefficient, τ_m. It is expressed in centimetres square per gram of a substance (cm^2/g). It is possible to convert between the atomic cross-section expressed in barns per atom and the photoelectric mass-attenuation coefficient expressed in centimetres square per gram. One can assume an infinitely thin layer of a substance composed of atoms of single chemical element, where each atom K-shell can be ionized by incoming photon with the same cross-section denoted as τ^K [barns/atom]. The assumption about the thickness of the layer is necessary to neglect shadowing or any other interfering effect, which could eventually diminish the cross-section of some atoms in the layer. The total atomic cross-section for the whole layer expressed in barns is equal to:

$$n\tau^K \tag{2.8}$$

where n is the number of atoms in that layer. The photoelectric mass-attenuation coefficient, expressed in cm^2/g is obtained by multiplication of the total atomic cross-section by the factor 10^{-24} and division by the total mass, m, of all the atoms in the layer:

$$\tau_m^K = 10^{-24} \cdot \frac{n\tau^K}{m} \tag{2.9}$$

The number of atoms in the layer can be expressed in terms of the layer mass, m, atomic weight of the element, A, and the Avogadro's constant, N_A:

$$n = N_A \frac{m}{A} \tag{2.10}$$

By combining (2.9) and (2.10):

$$\tau_m^K \left[cm^2 \cdot g^{-1}\right] = 10^{-24} \cdot \frac{N_A}{A} \tau^K \left[barns \cdot atom^{-1}\right] \tag{2.11}$$

The probability of photoelectric effect has contributions from various electronic shells, also called photoelectric absorption edges. The overall mass-attenuation coefficient due to photoelectric effect is a sum of all the individual contributions:

$$\tau_m = \tau_m^K + \tau_m^{L_I} + \tau_m^{L_{II}} + \tau_m^{L_{III}} + \ldots \tag{2.12}$$

The photoelectric mass-attenuation coefficient depends on the energy of the incoming photon:

$$\tau_m = \tau_m(E_0) \tag{2.13}$$

The experimentally obtained values of the total photoelectric mass-attenuation coefficients of elements, tabulated as functions of photon energy can be found in literature. At any given photon energy, the contribution from a given absorption edge can be estimated with the use of the so-called "photoelectric absorption jump" coefficient. The absorption jump coefficient, J, is calculated as a ratio of the photoelectric mass-attenuation coefficient at the energy slightly larger than the energy of the absorption edge, e.g. for the K-edge $E' = E_\mathrm{K} + \delta E$, to its value at the energy just below the edge, $E'' = E_\mathrm{K} - \delta E$ ($\delta E << E_\mathrm{K}$):

$$J_\mathrm{K} = \frac{\tau_m(E')}{\tau_m(E'')} = \frac{\tau_m^\mathrm{K}(E') + \tau_m^{\mathrm{L_I}}(E') + \tau_m^{\mathrm{L_{II}}}(E') + \tau_m^{\mathrm{L_{III}}}(E') + \ldots}{\tau_m^{\mathrm{L_I}}(E'') + \tau_m^{\mathrm{L_{II}}}(E'') + \tau_m^{\mathrm{L_{III}}}(E'') + \ldots} \approx \frac{\tau_m(E')}{\tau_m(E') - \tau_m^\mathrm{K}(E')} \tag{2.14}$$

$$1 - \frac{1}{J_\mathrm{K}} = \frac{\tau_m^K(E')}{\tau_m(E')} \tag{2.15}$$

The value defined in (2.15) tells us what is the fractional contribution of a given photoelectric absorption edge to the overall value of the mass-attenuation coefficient for photon energies only slightly larger than the energy of the edge. It is assumed that the proportion given by formula (2.15) holds also for other photon energies significantly larger than the energy of the photoelectric absorption edge, $E > E_\mathrm{K}$. The contribution of the edge to the photoelectric mass-attenuation coefficient of photons at the energy E can be calculated by using the tabulated overall value of the photoelectric mass-attenuation coefficient at that energy, $\tau_m(E)$ and the absorption jump coefficient of the edge:

$$\tau_m^\mathrm{K}(E) = \tau_m(E)\left(1 - \frac{1}{J_\mathrm{K}}\right) \tag{2.16}$$

The emission of X ray fluorescence photon is not the only process leading to atom relaxation, there are at least few other processes competing with each other. In an assembly of ionized atoms, each atom with a vacancy in a given electronic shell, only a fraction will de-excite with the emission of X ray characteristic photon. This fraction is assigned a number called fluorescence yield of a given shell, e.g. for K-shell it is denoted by ω_K. One of the competing paths of relaxation is a radiationless process called Auger effect. In this process the vacancy, e.g. in K-shell, is filled in by an electron from less tightly bound electronic shells, e.g. $\mathrm{L_{II}}$-shell, the atom energy is reduced but the energy excess, $E_\mathrm{K} - E_\mathrm{LII}$, is not emitted in the form of characteristic photon, instead in a radiationless process it is transferred to another electron (from e.g. $\mathrm{L_{III}}$-shell), binding energy of which is less that $E_\mathrm{K} - E_\mathrm{LII}$. This electron is expelled from the atom. Its kinetic energy equals to $E_\mathrm{K} - E_\mathrm{LII} - E_\mathrm{LIII}$. The fraction of atoms relaxing through the emission of Auger electrons is assigned a number called Auger yield of that shell, e.g. for K-shell it is denoted by a_K. The relation between fluorescence and Auger yields depends on the atomic number Z. For low-Z elements up to and including $Z = 30$:

$$a_\mathrm{K} > \omega_\mathrm{K} \tag{2.17}$$

For the elements with atomic number $Z > 30$ relation (2.13) is reverted, which means that prevailing number of the K-shell ionized atoms relaxes with the emission of X ray characteristic photon.

In case of the non *s*-type atomic subshells (e.g. $\mathrm{L_{II}}$, $\mathrm{L_{III}}$, $\mathrm{M_{II}}$, $\mathrm{M_{III}}$, $\mathrm{M_{IV}}$, $\mathrm{M_V}$, etc.) there is another significant process taking place during atom relaxation, called Coster-Kronig vacancy transition. In this process the number of vacancies in a non *s*-type atomic subshell is increased by radiationless and radiative transfer of vacancies from deeply bounded subshells of that shell. The redistribution of vacancies increases the number of characteristic photons emitted form a given non *s*-type subshell. Without taking into account the Coster-Kronig transitions, the number of X ray characteristics photons emitted due to vacancies created by the photoelectric effect directly in the $\mathrm{L_{III}}$ subshell would be proportional to:

$$\tau_m^{\mathrm{L_{III}}}\omega_{\mathrm{L_{III}}} \tag{2.18}$$

Considering Coster –Kronig vacancy shifts from $\mathrm{L_{II}}$ to $\mathrm{L_{III}}$, from $\mathrm{L_I}$ to $\mathrm{L_{III}}$ (radiationless and radiative) and from $\mathrm{L_I}$ over $\mathrm{L_{II}}$ to $\mathrm{L_{III}}$ this number is increased to:

$$\tau_m^{\mathrm{L_{III}}}\omega_{\mathrm{L_{III}}} + \tau_m^{\mathrm{L_{II}}} f_{2,3}\omega_{\mathrm{L_{III}}} + \tau_m^{\mathrm{L_I}} f_{1,3}\omega_{\mathrm{L_{III}}} + \tau_m^{\mathrm{L_I}} f'_{1,3}\omega_{\mathrm{L_{III}}} + \tau_m^{\mathrm{L_I}} f_{1,2} f_{2,3}\omega_{\mathrm{L_{III}}} \tag{2.19}$$

The $f_{\mathrm{i,k}}$ factors are the Coster-Kronig yields. They define the fraction of vacancies that are shifted from i-th to k-th subshell. Factors $f_{1,2}$, $f_{1,3}$, and $f_{2,3}$ refer to radiationless transitions and $f'_{1,3}$ to the radiative one. For any given subshell the sum of yields (fluorescent yield, Auger yield, Coster-Kronig yields) of all processes leading to its de-excitation (filling in or shifting out the vacancy in that particular subshell) is equal to unity, e.g. for the $\mathrm{L_I}$ subshell:

$$\omega_{\mathrm{L_I}} + a_{\mathrm{L_I}} + f_{1,2} + f_{1,3} + f'_{1,3} = 1 \tag{2.20}$$

and for the $\mathrm{L_{II}}$-, $\mathrm{L_{III}}$-, and K-subshell, respectively:

$$\omega_{\mathrm{L_{II}}} + a_{\mathrm{L_{II}}} + f_{2,3} = 1 \tag{2.21}$$

$$\omega_{\mathrm{L_{III}}} + a_{\mathrm{L_{III}}} = 1 \tag{2.22}$$

$$\omega_{\mathrm{K}} + a_{\mathrm{K}} = 1 \tag{2.23}$$

Formula (2.19) can be written in a different form:

$$\tau_m^{\mathrm{L_{III}}}\omega_{\mathrm{L_{III}}}\left(1 + \frac{\tau_m^{\mathrm{L_{II}}}}{\tau_m^{\mathrm{L_{III}}}} f_{2,3} + \frac{\tau_m^{\mathrm{L_I}}}{\tau_m^{\mathrm{L_{III}}}}\left(f_{1,3} + f'_{1,3} + f_{1,2} f_{2,3}\right)\right) = \tau_m^{\mathrm{L_{III}}}\omega_{\mathrm{L_{III}}} T_{\mathrm{L_{III}}} \tag{2.24}$$

The factor $T_{\mathrm{i}} \geq 1$ is called the hole transfer factor of i-th subshell. It is equal to unity for *s*-type atomic subshells (e.g. K-, $\mathrm{L_I}$-, $\mathrm{M_I}$-subshell). In the case of photoelectric excitation of $\mathrm{L_{II}}$, $\mathrm{L_I}$, and K atomic subshells the probability of atom relaxation through X ray fluorescence process is proportional to:

$$\tau_m^{\mathrm{L_{II}}}\omega_{\mathrm{L_{II}}}\left(1 + \frac{\tau_m^{\mathrm{L_I}}}{\tau_m^{\mathrm{L_{II}}}} f_{1,2}\right) \tag{2.25}$$

$$\tau_m^{\mathrm{L_I}} \omega_{\mathrm{L_I}} \tag{2.26}$$

$$\tau_m^{\mathrm{K}} \omega_{\mathrm{K}} \tag{2.27}$$

, respectively.

Probability of emission of X ray characteristic line, e.g. Kα_1, is given by so-called partial or fractional radiative rate, $p_{\mathrm{K}\alpha1}$. Partial radiative rate is a ratio of the radiative rate of that characteristic X ray line to the total radiative rate for a vacancy in the particular shell. The most intense X ray characteristic lines include Kα_1, Kα_2, Kβ_1, Kβ_3 (K-series), Lα_1, Lα_2, Lβ_1, and Lβ_2 (L-series). For these X ray lines the number of the characteristic photons produced is proportional to:

$$\tau_m^{\mathrm{K}} \omega_{\mathrm{K}}\, p_{\mathrm{K}\alpha 1} \tag{2.28}$$

$$\tau_m^{\mathrm{K}} \omega_{\mathrm{K}}\, p_{\mathrm{K}\alpha 2} \tag{2.29}$$

$$\tau_m^{\mathrm{K}} \omega_{\mathrm{K}}\, p_{\mathrm{K}\beta 1} \tag{2.30}$$

$$\tau_m^{\mathrm{K}} \omega_{\mathrm{K}}\, p_{\mathrm{K}\beta 3} \tag{2.31}$$

$$\tau_m^{\mathrm{L_{III}}} \omega_{\mathrm{L_{III}}} \left(1+\frac{\tau_m^{\mathrm{L_{II}}}}{\tau_m^{\mathrm{L_{III}}}} f_{2,3}+\frac{\tau_m^{\mathrm{L_I}}}{\tau_m^{\mathrm{L_{III}}}}\left(f_{1,3}+f_{1,3}'+f_{1,2}f_{2,3}\right)\right) p_{\mathrm{L}\alpha 1} \tag{2.32}$$

$$\tau_m^{\mathrm{L_{III}}} \omega_{\mathrm{L_{III}}} \left(1+\frac{\tau_m^{\mathrm{L_{II}}}}{\tau_m^{\mathrm{L_{III}}}} f_{2,3}+\frac{\tau_m^{\mathrm{L_I}}}{\tau_m^{\mathrm{L_{III}}}}\left(f_{1,3}+f_{1,3}'+f_{1,2}f_{2,3}\right)\right) p_{\mathrm{L}\alpha 2} \tag{2.33}$$

$$\tau_m^{\mathrm{L_{II}}} \omega_{\mathrm{L_{II}}} \left(1+\frac{\tau_m^{\mathrm{L_I}}}{\tau_m^{\mathrm{L_{II}}}} f_{1,2}\right) p_{\mathrm{L}\beta 1} \tag{2.34}$$

$$\tau_m^{\mathrm{L_{III}}} \omega_{\mathrm{L_{III}}} \left(1+\frac{\tau_m^{\mathrm{L_{II}}}}{\tau_m^{\mathrm{L_{III}}}} f_{2,3}+\frac{\tau_m^{\mathrm{L_I}}}{\tau_m^{\mathrm{L_{III}}}}\left(f_{1,3}+f_{1,3}'+f_{1,2}f_{2,3}\right)\right) p_{\mathrm{L}\beta 2} \tag{2.35}$$

, respectively.

In the absence of interfering effects, when atoms of chemical element x emit characteristic radiation, the intensity of a given characteristic line I_{x} is proportional to the mass fraction of the emitting atoms, c_{x}. This holds for all characteristic lines seen in a XRF spectrum. A set of equations can be defined: $I_x \propto c_x$, $I_1 \propto c_1$, $I_2 \propto c_2$, etc., $I_i \propto c_i$, etc., up to $I_n \propto c_n$. Unfortunately the peaks in the spectrum do not represent all chemical elements present in a sample. In particular the X ray characteristic radiation originating from the sample organic matrix, typically composed of elements like H, C, O, N can not be detected. It is due low fluorescence yields and strong absorption of the energetically low (< 1 keV) characteristic radiation of these elements. The “not detectable” part of the sample is called “dark matrix”. If expressed in per cent the sum of concentrations of all elements present in any sample is 100 %. In terms of mass fractions:

$$c_x + \sum_i^n c_i + c_{dark\ matrix} = 1 \tag{2.36}$$

The direct proportionality between the intensity of X ray fluorescence radiation and the mass fraction of the chemical element holds only for infinitely thin layers of atoms. For samples of finite thickness the intensity is affected by self-absorption (*A*) and the secondary excitation effect (*H*). In general case the intensity is a non-linear function of the mass fractions (or concentrations) of all elements present in the sample:

$$I_x = I_x\left(c_x, c_i, c_{darkmatrix}\right) \tag{2.37}$$

The sample self-absorption is treated as correction factor and is, with a few exceptions, of utmost importance. The secondary excitation (also named enhancement or inter-element effect) can be also treated mathematically, but it is of importance for certain samples only.

2.1.1. Sample self-absorption

The mass-attenuation coefficient of an element, μ_{m} summarizes all possible photon interactions with atoms of that element and it is a function of the incident photon energy, *E*:

$$\mu_m = \mu_m(E) \tag{2.38}$$

For the photon energies below the pair production edge (< 1022 keV) there are tree types of processes leading to photon absorption: photoelectric effect, coherent, and incoherent scattering. The mass-attenuation coefficient is expressed accordingly:

$$\mu_m = \tau_m + \sigma_{coh} + \sigma_{inc} \tag{2.39}$$

Where, σ_{coh} and σ_{inc} are the contributions due to coherent (elastic or Rayleigh) and incoherent (inelastic or Compton) scattering, expressed in (cm^2/g). The attenuation of a parallel beam of photons by a layer of atoms of thickness *t* (cm) and density ρ (g/cm^3) is described by Beer-Lambert law:

$$I = I_0 \cdot \exp(-\mu_m \cdot (\rho \cdot t)) \tag{2.40}$$

where I_0 and *I* are the photon fluxes before and after the absorber, respectively. The product ρt can be expressed in terms of mass, *m* in (g), and area, *F* in (cm^2), of the absorber:

$$\rho t = \frac{m}{F} \tag{2.41}$$

When the beam impinges on the layer surface under an angle of φ (the angle between the beam direction and the surface) the path length is increased:

$$I = I_0 \cdot \exp\left\{\frac{-\mu_m \cdot (\rho \cdot t)}{\sin\varphi}\right\} = I_0 \cdot \exp\left\{\frac{-\mu_m \cdot (m/F)}{\sin\varphi}\right\} \tag{2.42}$$

Note that the mass-attenuation coefficient of a sample that is composed of several elements *i* is calculated as a weighted sum of the individual mass-attenuation coefficients of elements, μ^i_{m}:

$$\mu_m = \sum_i c_i \cdot \mu^i_m \tag{2.43}$$

where c_{i} is the mass fraction of element in the sample. The coherent scattering contribution outweighs the incoherent for lower energies, but for higher energies the incoherent scattering contribution will reach a constant value, outweighing the decreasing coherent contribution, and even become more important than the photo-effect towards the end of the X ray region.

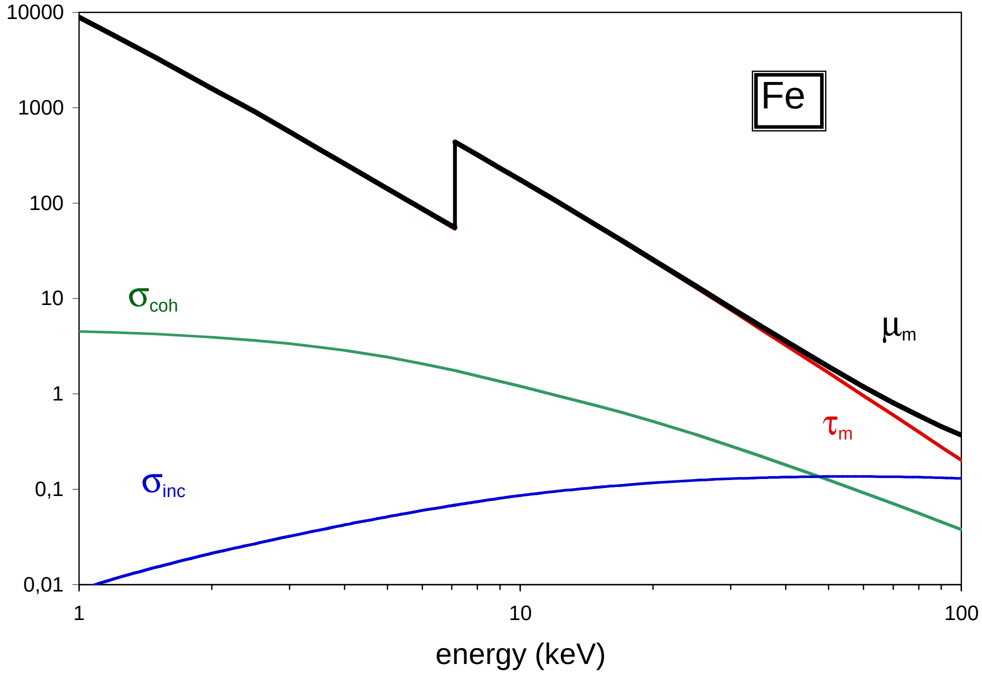


Fig. 2.1. The contributions to the attenuation coefficient are the absorption coefficient (photo effect) and coherent and incoherent scattering coefficients. Iron was selected as absorber, which has its K absorption edge at 7.1 keV.

The self-absorption effects depend on the path length from the sample surface to the location of the atom of interest as well as on the path length from the fluorescing atom through the sample in the direction of the detector. The attenuation of the incoming radiation is characterized by the corresponding path length and the weighted sample mass attenuation coefficient for exciting photon energy, E_0. The attenuation of the characteristic radiation in the direction of the detector is characterised by the corresponding path length and the weighted sample attenuation coefficient for the energy of characteristic radiation (e.g. $E_{\mathrm{K}\alpha}$ or $E_{\mathrm{L}\alpha}$).

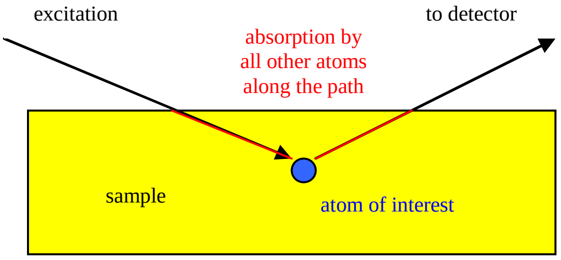


Fig. 2.2. Both the exciting radiation and the fluorescence radiation of an atom (element) of interest suffer from sample self-absorption.

For a monochromatic excitation theory provides a summation (integration) over all possible locations for flat and homogenous samples, with the thickness t as parameter:

$$I_x = c_x \cdot S_x \cdot A_x(t, c_x, c_i, c_{dark\,matrix}) \tag{2.44}$$

where S_x is the sensitivity factor for the element x. The term sensitivity is used in the context of e.g. the **Elemental sensitivities** and **Emission Transmission** METHODs. A is the absorption correction factor which is a function of the concentrations of all elements (c_x, c_i, $c_{\text{dark matrix}}$) present in a sample:

$$A_x(t, c_x, c_i, c_{dark\,matrix}) = \frac{1 - \exp\{-a \cdot \rho \cdot t\}}{a} = \frac{1 - \exp\left\{-a\frac{m}{F}\right\}}{a} \tag{2.45}$$

using the expression a, which depends on the incidence, φ, and take-off, ψ, angles and the weighted mass attenuation coefficients of the sample (constituted of the element x, the other fluorescing elements i, and the dark matrix) for exciting (E_0) and fluorescence (E_x) radiation.

$$a(c_x, c_i, c_{dark\,matrix}) = \frac{\mu_m(E_0)}{\sin\varphi} + \frac{\mu_m(E_x)}{\sin\psi} \tag{2.46}$$

2.1.2. Inter-element effects

Sometimes fluorescent photons have sufficient energy to excite fluorescent radiation of other atoms in the specimen. This effect is called secondary excitation (also called: inter-element or enhancement effect) and can be a major contribution to the observed photons. This effect is strong for elements differing by 2-4 in atomic numbers. Stainless steel (Cr-Fe-Ni) is the usual example for demonstrating secondary excitation (iron excites chromium (Fe -> Cr), nickel excites chromium (Ni -> Cr) and iron (Ni -> Fe). The actual contributions from such effects are often around 5-10 %; in a few cases they are much higher. For calibration standards like KBr and $K_2Cr_2O_7$ this effect prohibits the use of the element potassium for the METHOD **Elemental sensitivities**, analogue for KH_2PO_4 and the element phosphorus.

The intensity of a given characteristic peak of element x excited in a flat, homogenous sample by a polychromatic primary beam of photons (as utilized by the full fundamental parameters METHODs) can be written as:

$$I_x = Gc_x\varepsilon_x f_x \sum_n \left\{ I_n(E_0) f_0 Q_x A_x\left(c_x, c_i, c_{darkmatrix}\right)\left(1 + H_{xi}(c_x, c_i, c_{darkmatrix})\right)\right\} \tag{2.47}$$

G is the geometrical factor (called in QXAS: instrumental constant), ε_x is the detector efficiency (see later) and f_0, f_x correct for absorption of radiation between excitation source-sample and sample-detector (air, protective foils). The summation over n takes into account that the excitation radiation spectrum may not only be composed of a single energy, but also contains a continuum. Q_x is the product of the so-called fundamental parameters, see (2.28 – 2.35) . A is the absorption correction factor and the enhancement correction term H, a rather lengthy expression, taking into account the secondary excitation. It corrects for the increase of intensity of the characteristic peak of element x through secondary excitation by characteristic radiation originating from the same (other X ray lines of that element) and/or other elements:

$$H_{xi} = \frac{1}{2\cdot\tau_m^x(E_0)} \sum_i \left\{ c_i Q_i Y_{xi} \right\} \tag{2.48}$$

The term Y is rather complex, especially for intermediate thick samples. For a “thick” sample (for the thickness classification in terms of XRF see the following paragraph) it can be expressed as:

$$Y_{xi} = \frac{\sin\varphi}{\mu_m(E_0)} \cdot \ln\left[1 + \frac{\mu_m(E_0)}{\mu_m(E_i)\sin\varphi}\right] + \frac{\sin\psi}{\mu_m(E_x)} \cdot \ln\left[1 + \frac{\mu_m(E_x)}{\mu_m(E_i)\sin\psi}\right] \tag{2.49}$$

Note: The METHOD **Full fundamental parameters** uses a different notation for the incident and take-off angles. They are defined in respect to the sample surface normal, opposite to all other METHODs of QXAS where they are defined with respect to the sample surface itself.

2.1.3. *Classification of samples according to their thickness*

In XRF analysis samples are classified according to their thickness or mass loads. For any particular sample the intensity of X ray fluorescence peak given by formula (2.47) depends on the sample thickness t or the sample mass load (m/F). Formula (2.47) can be simplified for two extreme cases: (1) thin samples and (2) thick samples.

For the so-called “thin sample” its mass load is considered infinitely thin:

$$(m/F) << 1 \tag{2.50}$$

If (2.50) holds:

$$\exp\left\{-a\cdot\frac{m}{F}\right\} \approx 1 - a\cdot\frac{m}{F} \tag{2.51}$$

It can be proved that if (2.50) holds the enhancement correction term can also be neglected:

$$H_{xi}(c_x, c_i, c_{darkmatrix}) << 1 \tag{2.52}$$

Taking into account (2.51) and (2.52) the formula for the intensity of characteristic peak emitted by a *thin sample* takes the following form:

$$I_x = \left(G\varepsilon_x f_x \sum_n \{ I_n(E_0) f_0 Q_x \} \right) c_x \frac{m}{F} = S_x c_x \frac{m}{F} \tag{2.53}$$

For a thin sample the intensity of X ray characteristic peak is proportional to the element mass load, $c_x(m/F)$, expressed in g/cm^2. The intensity does not depend on the mass loads of other elements present in the sample. The proportionality constant is the sensitivity factor, S_x, firstly introduced in the formula (2.44). For a given X ray peak and given measuring conditions the sensitivity factor does not depend on the analyzed sample. Its value can be established by measuring thin standard samples with known mass loads of elements. The definition of a "thin sample" given in (2.50) is not very practical or specific. A more specific definition is used in laboratory practice, namely assuming monochromatic excitation and neglecting in (2.47) the enhancement correction term, it has been agreed that for a given X ray peak the sample can be considered a "thin sample" if the error resulting from applying equation (2.53) instead of (2.47) is less than 5%. This definition is equivalent to the following condition:

$$\frac{A_x}{(m/F)} = \frac{1 - \exp\{-a \cdot (m/F)\}}{a \cdot (m/F)} > \frac{1}{1.05} \tag{2.54}$$

Graphical solution of the condition (2.54) is presented in Figure 2.3.

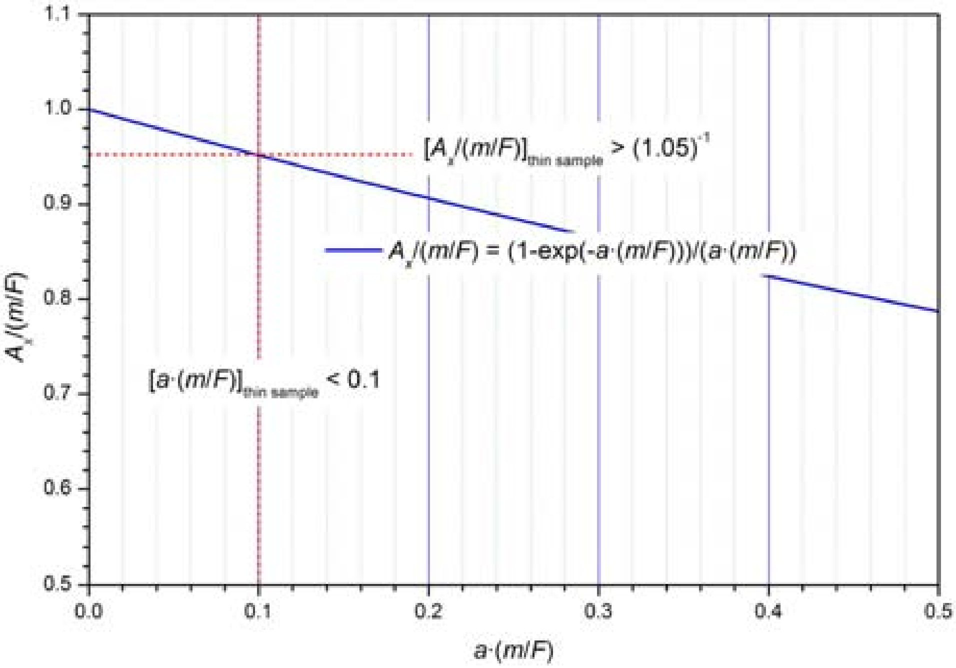


Fig. 2.3. Graphical solution of the condition (2.54) leading to a definition of a thin sample critical mass load.

The solution of (2.54) tells us that for a given X ray peak the sample can be considered a "thin sample" if:

$$a\frac{m}{F} < 0.1 \quad \Leftrightarrow \quad \frac{m}{F} < \frac{0.1}{\frac{\mu_m(E_0)}{\sin\varphi} + \frac{\mu_m(E_x)}{\sin\psi}} \tag{2.55}$$

The opposite extreme case is the “thick sample” approximation in which the mass load of the sample is assumed to be infinitely thick:

$$(m/F) >> 1 \tag{2.56}$$

Condition (2.56) implies that:

$$\exp\left\{-a\cdot\frac{m}{F}\right\} \approx 0 \tag{2.57}$$

Taking into account (2.57) the formula (2.47) for the intensity of characteristic peak emitted by a “thick sample” is transformed to:

$$I_x = Gc_x\varepsilon_x f_x \sum_n \left\{ I_n(E_0) f_0 Q_x \frac{1}{\frac{\mu_m(E_0)}{\sin\varphi} + \frac{\mu_m(E_x)}{\sin\psi}} \left(1 + H_{xi}(c_x, c_i, c_{darkmatrix})\right)\right\} \tag{2.58}$$

The enhancement correction term H_{xi} is given in (2.48) and (2.49). It can be noticed that the formula (2.58) does not depend on the sample mass load, (*m*/*F*). It implies that for a “thick sample” the intensity of X ray peak does not increase with increasing sample mass, the sample has reached a saturated thickness. However, the intensity of any X ray peak depends in a non-liner way on concentrations of all elements present in the sample. To arrive at practical definition of a “thick sample” it has been agreed that, assuming monochromatic excitation, for a given X ray peak the sample is considered to be a “thick sample” if the error resulting from applying equation (2.58) instead of (2.47) is less than 1%. It is equivalent to the following condition:

$$a\frac{m}{F} > \ln 101 \quad \Leftrightarrow \quad \frac{m}{F} > \frac{4.615}{\frac{\mu_m(E_0)}{\sin\varphi} + \frac{\mu_m(E_x)}{\sin\psi}} \tag{2.59}$$

The samples with the mass loads greater than that defined in (2.55) and less than that given in (2.59) are called “intermediate thickness samples”. For an intermediate thickness sample the intensity of an X ray peak is a non-linear function of the sample mass load. It also depends in a non-linear way on the concentrations off all elements present in the sample.

There are quantitative analysis methods which deal with only one type of samples, e.g. methods assuming direct proportionality between the X ray peak area and the element mass load work only with thin samples, the **Emission Transmission** METHOD works only with intermediate thickness samples. There are also methods which can handle all kind of sample types, e.g. the fundamental parameter methods. Usually the methods which deal with narrower rage of sample types are more accurate.

2.2. Si(Li) detector

In energy dispersive XRF the acquisition of X ray spectra is performed using detectors that directly measure the energy of photons. The resulting signal is proportional to the energy of the incident photon, the detector is capable of detecting simultaneously photons of different energy.

A lithium-drifted silicon crystal of a Si(Li) detector consists of a p-i-n structure, referring to the p-type contact (dead layer) on the entry side, the intrinsic active volume, and the lithium diffused n-type contact. Typically it is less than 10 mm in diameter and about 3 - 5 mm thick. When a reverse bias (in the range of 500-1000 V) is applied to the device, the drifted region acts as an insulator with an electric field throughout its volume. A photon reaching the active volume generates photo-electrons, as well as Compton and Auger electrons, which lose energy by producing ionization in the form of electron-hole pairs. The free charges are swept away by the applied bias and collected within a time of typically 25-100 ns. Since the average energy to create an electron-hole pair is well defined (3.76 eV at 77^0 Kelvin), the total number of charges is directly proportional to the energy of the incident photon. The frequency of such events is proportional to the photon's intensity.

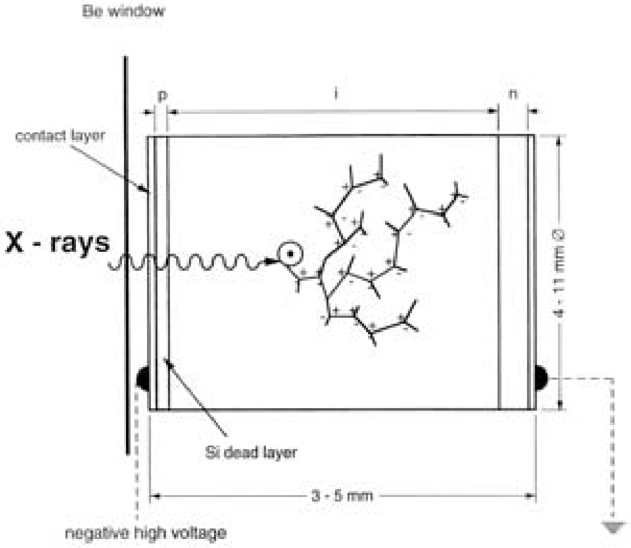


Fig. 2.4. Cross-section of a Si(Li) detector crystal and typical dimensions.

The response function of a Si(Li) detector to monochromatic radiation, e.g. a characteristic line (with characteristic energy E_x), is nearly Gaussian. The natural line width is usually neglected, except for the Voigt peak shape model. The number of counts, N_{ji}, in X ray spectrum channel j in the vicinity of an isolated Gaussian peak with its top positioned at channel i is described by

$$N_{ji} = A\frac{\text{GAIN}}{\sqrt{2\pi}\cdot S(E_i)}\cdot\exp\left\{-\frac{(E_j-E_i)^2}{2\cdot S^2(E_i)}\right\} \tag{2.60}$$

The factor A is the peak area which is equivalent to the total number of counts under the peak. The E_j and E_i are the energies corresponding to channels j and i, respectively. The relation between the channel number and the energy is linear. It is given by the energy calibration equation (1.1). The **GAIN** in (usually given in eV/channel or keV/channel) is one of the two parameters of the energy calibration. The relationship between the peak width S and the previously defined FWHM (equation (1.3)) is:

$$\mathrm{FWHM}(E) = \sqrt{8 \cdot \ln 2} \cdot S(E) \approx 2.355 \cdot S(E) \qquad (2.61)$$

The energy resolution (FWHM) of a semiconductor detector depends on the electronic noise and statistical fluctuations. The electronic noise contribution is determined by the input amplifier stage and the detector leakage current; therefore it is essential to operate the detector at low temperatures (contact to liquid nitrogen or a Peltier element). The statistical spread is affected by the average energy required to produce an electron-hole pair. Usually the FWHM – as one of the measures for the detector quality – is given at the energy of Mn K_α (5.89 keV) and typically ranges between 130 and 180 eV.

The preamplifier stage integrates each detector charge signal (proportional to the energy of the incident photon) to generate a voltage step proportional to the charge. This is then amplified and shaped in a series of integrating and differentiating stages. Owing to the finite pulse-shaping time, in the range of μs, the system will not accept any other incoming signals in the meanwhile ("dead time"), but extend its measuring time instead. The *dead time* is defined as

$$\textit{dead time}(\%) = \frac{RT - LT}{RT} \cdot 100 \qquad (2.62)$$

where *RT* (real time) refers to the time interval that could be measured with a stop watch during the acquisition of a spectrum, *LT* (live time) is the time during which the system is ready to process incoming pulses. Real time is always greater than live time. In the next step the amplitude of the shaped and amplified pulse is digitized, converted to a number in analog-to-digital (ADC) converter. The content of a memory location corresponding (proportional) to that number, called channel, is increased by one. The process is repeated for every valid pulse. As a result a histogram of the puls amplitudes is obtained. It is called a multichannel spectrum. The number of counts in every channel of the spectrum is proportional to a number of photons which deposited in the detector the energy, vide the energy calibration equation (1.1), covered by this channel. In a more advanced approach the output signal of the detector preamplifier is digitized directly with a minimum analog-shaping, the main shaping and pulse filtering in performed in digital domain by a digital signal processing (DSP) circuitry.

For high count-rates there is an increasing probability that two photons of a very intense line are absorbed in the detector crystal within such a short time interval (the sweeping time needed to collect the free charges) that their charges are not collected as two individual signals with a certain energy, but rather as a single one with twice the energy (*sum peak*). All possible combinations of sum events can be included into the AXIL fit model with the "SUM" keyword (COMMANDs **X-LINES ADD: SUM**).

In an ideal detector the charge is collected completely and the response of the system would be a single peak, containing only counts of a certain energy and no other counts elsewhere in the spectrum. In practice some artefacts are observed: incomplete charge collection, resulting in a tail to the low energy side of a principal peak (*low energy tail*), depends on the design of the crystal. The escape of photons (or secondary particles) from the detector surface is most prominent for the case when a hole is created in the K-shell of the silicon and the accompanying emission of its characteristic radiation leaves the crystal. Consequently an *escape peak* at an energy 1.74 keV less than the parent peak energy can be observed. Escape peaks can be included into the AXIL fit model with "+" suffix. In order to include the tailing and the escape peaks simultaneously within AXIL the peak shape correction "*" suffix can be used.

The intrinsic detector efficiency $\varepsilon(E)$ for a Si(Li) detector has a characteristic dependence on the energy and is governed at the low-energy side mainly by the thickness of the beryllium detector entrance window on the cryostat vacuum enclosure, the contact layer and the silicon dead layer (also responsible for the discontinuity at the absorption edge energy of 1.84 keV), and at the high-energy side by the thickness of the crystal itself. Between 5 and 20 keV the efficiency is close to 1 for many conventional Si(Li) detectors. The dependence of the detection efficiency on the energy and other detector parameters is given by the following formula:

$$\varepsilon(E) = \exp - \left[\mu_{Be}(E) \cdot t_{Be} + \mu_{Au}(E) \cdot t_{Au} + \mu_{dl}(E) \cdot t_{dl}\right] \cdot \left\{1 - \exp - \left[\mu_{Si}(E) \cdot t_{Si}\right]\right\} \tag{2.63}$$

where t_{Be}, t_{Au}, t_{dl} and t_{Si} are the area-related masses in (g/cm^2) of the Be window, the gold contact layer, the silicon dead layer, and the detector crystal itself, respectively. Usually these values are specified poorly in the detector data sheet.

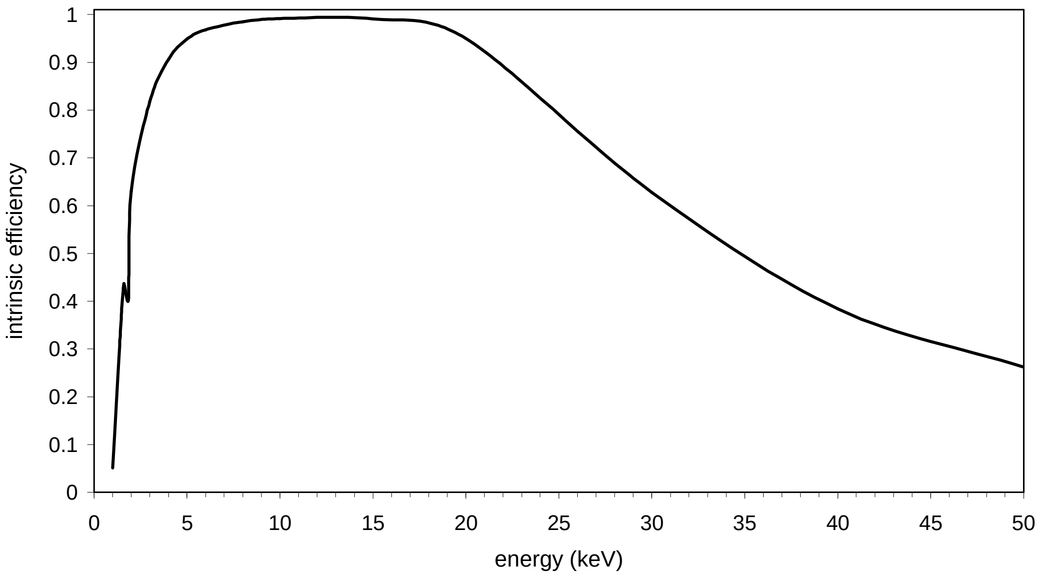


Fig. 2.5. Intrinsic (calculated) efficiency as to be expected for a Si(Li) detector. The discontinuity at 1.8 keV is caused by the Si dead layer.

2.3. Elastic and inelastic Scattering

The spectral background results from a variety of processes: For photon excitation, the main contribution is the incoherently and coherently scattered primary radiation (by sample, sample holder, ambient air, etc.) and therefore depends on the shape of the (usually poorly described) excitation spectrum and on the (later to be determined) sample composition. To the low energy side of a dominant peak the low energy tailing often increases the scatter background significantly. The most straightforward method to obtain the net peak area under a peak of interest consists of interpolating the background under the peak by a suited function, as also done in AXIL. In another frequently used approach the discrete de-convolution of a spectrum with a so-called top-hat filter suppresses the lower frequency component, i.e. the slowly varying background. A severe distortion of the peaks is introduced. But applying this filter to both the unknown spectrum and well defined experimentally obtained reference spectra will result in the net peak areas of interest. A disadvantage of this method is that reference and unknown spectra should be acquired under preferably identical conditions.

The effects of elastic (coherent, Rayleigh) and inelastic (incoherent, Compton) scattering are usually much weaker than photo-absorption. Elastic scattering for a single electron can be deduced from classical electrodynamics, but due to its coherent nature the form factor has to be introduced to account for all electrons of an atom. The differential cross-section, which describes this kind of interaction, depends on the energy of the primary radiation, the atomic number of the scattering atom and the scattering angle – because of its inherent anisotropy. It shows a pronounced maximum for forward scattering. Inelastic scattering is relatively independent of the atomic number of the scattering atom. The observed energy shift $\Delta E = E_0 - E_\vartheta$ of the Compton peak depends on the scattering angle ϑ:

$$E_\vartheta = \frac{E}{1 + \frac{E_0}{511} \cdot (1 - \cos\vartheta)} \tag{2.64}$$

For this expression all energy values used are in (keV). Note, that the scattering angle is the sum of the incidence and take-off angle $\vartheta = \varphi_1 + \varphi_2$. With increasing atomic number scattering effects get weaker and the ratio of coherent to incoherent scattering intensity will change, favouring elastic scattering.

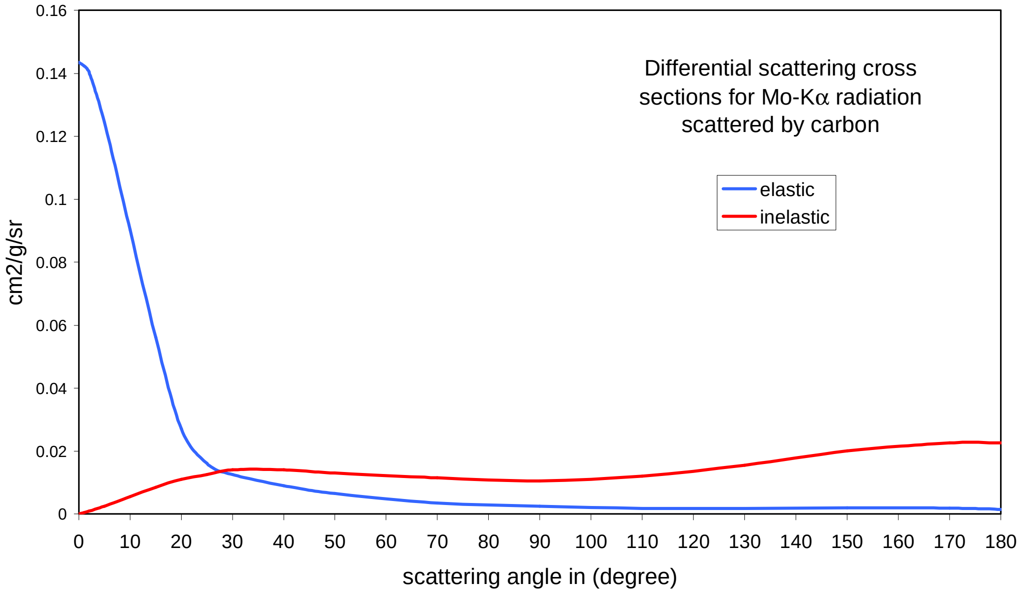


Fig. 2.6. Differential scattering cross sections for a thin scatterer of carbon (Z=6) and an incident energy of 17.4 keV as a function of the scattering angle.

Prior to the computation of an element's concentration for the calculation of the absorption as well as the enhancement correction the concentration of *all* elements in a sample should be known. This vicious circle can be overcome by a suitable iterative procedure. Still there are the elements forming the dark matrix; also their composition needs to be known. The fundamental parameters METHODs use the incoherent/coherent scattering peak ratio for establishing the average atomic number of a sample with dark matrix in order to calculate the absorption correction and, when not defined by an input, also the sample thickness.

The count rates N_{coh}, N_{inc} of these two peaks are respectively given by

$$N_{coh} = G_{coh} \cdot \varepsilon(E) \cdot A_{coh}(E) \cdot I(E) \cdot \sum_i c_i \cdot \frac{d\sigma_{coh,i}}{d\Omega}(E,\vartheta,Z_i) \tag{2.65}$$

and

$$N_{inc} = G_{inc} \cdot \varepsilon(E_{inc}) \cdot A_{inc}(E) \cdot I(E) \cdot \sum_i c_i \cdot \frac{d\sigma_{inc,i}}{d\Omega}(E,\vartheta,Z_i) \tag{2.66}$$

In analogy to the formalism for fluorescence, respectively for elastic and inelastic scattering, is G the instrument constant, ε is the detector efficiency, A is the absorption correction, I is the primary intensity of the line with energy E which is scattered. The summation over i includes all elements with concentration c_{i}. The differential cross section $\frac{d\sigma}{d\Omega}(E,\vartheta,Z_i)$ is a function of the energy E of the line that is scattered and the atomic number Z_i of the scattering atom. Separating the contribution of the high atomic number (fluorescent) elements from the dark matrix elements, the scattering coefficients of the latter can be calculated from

$$S_{coh}^{lowZ} = \sum_{lowZ} c_i \cdot \frac{d\sigma_{coh,i}}{d\Omega} = \frac{N_{coh}}{I(E) \cdot G_{coh} \cdot \varepsilon(E) \cdot A_{coh}(E)} - \sum_{highZ} c_i \cdot \frac{d\sigma_{coh,i}}{d\Omega} \tag{2.67}$$

and

$$S_{inc}^{lowZ} = \sum_{lowZ} c_i \cdot \frac{d\sigma_{inc,i}}{d\Omega} = \frac{N_{inc}}{I(E) \cdot G_{inc} \cdot \varepsilon(E_{inc}) \cdot A_{inc}(E)} - \sum_{highZ} c_i \cdot \frac{d\sigma_{inc,i}}{d\Omega} \tag{2.68}$$

where the concentrations in the summation over the high Z elements are assumed to be known from the fluorescence intensities. All values on the right hand side can be accessed either by measurement or theory. As a result the dark matrix can be represented by two elements, e.g., Z and $Z+2$, where Z is calculated in such a way that

$$\frac{d\sigma_{coh,Z+2}}{d\sigma_{inc,Z+2}} \geq \frac{S_{coh}^{lowZ}}{S_{inc}^{lowZ}} \geq \frac{d\sigma_{coh,Z}}{d\sigma_{inc,Z}} \tag{2.69}$$

and the concentrations of these two representative elements are calculated by solving the system of the two equations in two unknowns c_Z and c_{Z+2} :

$$S_{coh}^{lowZ} = c_Z \cdot \frac{d\sigma_{coh,Z}}{d\Omega} + c_{Z+2} \cdot \frac{d\sigma_{coh,Z+2}}{d\Omega} \tag{2.70}$$

and

$$S_{inc}^{lowZ} = c_Z \cdot \frac{d\sigma_{inc,Z}}{d\Omega} + c_{Z+2} \cdot \frac{d\sigma_{inc,Z+2}}{d\Omega} \tag{2.71}$$

These two concentrations can now be used for the calculations of the absorption correction factors and enhancement effect in order to obtain correct results for concentrations of the fluorescing elements.

CHAPTER 3. CALIBRATION ISSUES

Reference material: [25], [26]

3.1. Calibration standards, instrumental requirements

Demonstration files: the example calibration standards' spectra are stored in the directory \QXASdemo\SPE-Stds, their *.asr files are found in the directory QXASdemo\ASR-Stds. The user can create *.asr files, having tried different parameters than recommended, without danger of overwriting example files. The spectra are accompanied by *.inp files, already optimised to fulfil all AXIL fit criteria. All *.inp files are found in the directory QXASdemo\INP-Stds. A detailed description of all standards related data can be found in the EXCEL standards.xls file.

Due to the fact that input parameters of a previous fit are used as starting values for the next fit the user might encounter slight differences when trying to repeat a fit with the demonstration files, even when using the recommended input files.

All example standards' spectra for Rh secondary target excitation had been collected with the intention to have approximately 50 000 counts in the peaks of relevance for calibration. All spectra had been collected with 50 kV high voltage applied to the Ag X-ray tube, exciting the secondary target. As an example of a non-linear influence measuring parameter the tube voltage value may never be altered, like many other parameters, as the secondary target, vacuum conditions, filters, geometry, etc. – for a specific calibration and consequent unknown samples evaluations with this calibration. The tube current was varied between the generator/X ray tube limits of 5-40 mA (it has in the ideal case linear influence) with the intention to keep the system dead time below 20 % for all standard measurements. These 20 % are far below the problematic range of non-linear response and as another consequence the spectra do not suffer from spectral distortions as observed with spectra of standards collected with higher dead time. The acquisition time (live time, *LT*) was selected to adjust the total counts in the peaks of interest. The rather high number of 50 000 counts for the peaks of relevance results in statistically well-defined signals (relative standard deviation < 0.5 %), whereas the approximate equality gives all standards equal statistical weight. Reference standard materials are usually not well suited as calibration standards, because of their trace elements content, which will introduce high statistical uncertainties.

As a recommendation, if more than one element that could be used for calibration is contained in a standard, two independent spectra should be collected, with measuring times according to the above considerations. All standards' spectra had been fitted with input files as specified in the EXCEL standards.xls file. By use of the correct fit model, among others, for all spectra a standard deviation $SD_n \geq \sqrt{N_n}$, with N_n being the net peak area for the element *n* of interest could be found. In CHAPTER 10: Elements of quality control, a detailed guideline for calibration standard spectra treatment is given.

Note: Information about all relevant details and data files, as needed for calibration of the Rh secondary target spectrometer, can be found in the EXCEL standards.xls file.

3.2. Calibration for the METHOD Elemental Sensitivities

Demonstration files (directory \QXASdemo\ElSens):

- Calibration files: Compound.cal, Metals.cal, AirFilt.cal
- Spectra: AirFilt.spe, Blank-Af.spe, Instr-Bl.spe
- Input files: AirFilt.inp
- AXIL result files: AirFilt.asr, AirF-cor.asr, Blank-Af.asr, Instr-Bl.asr

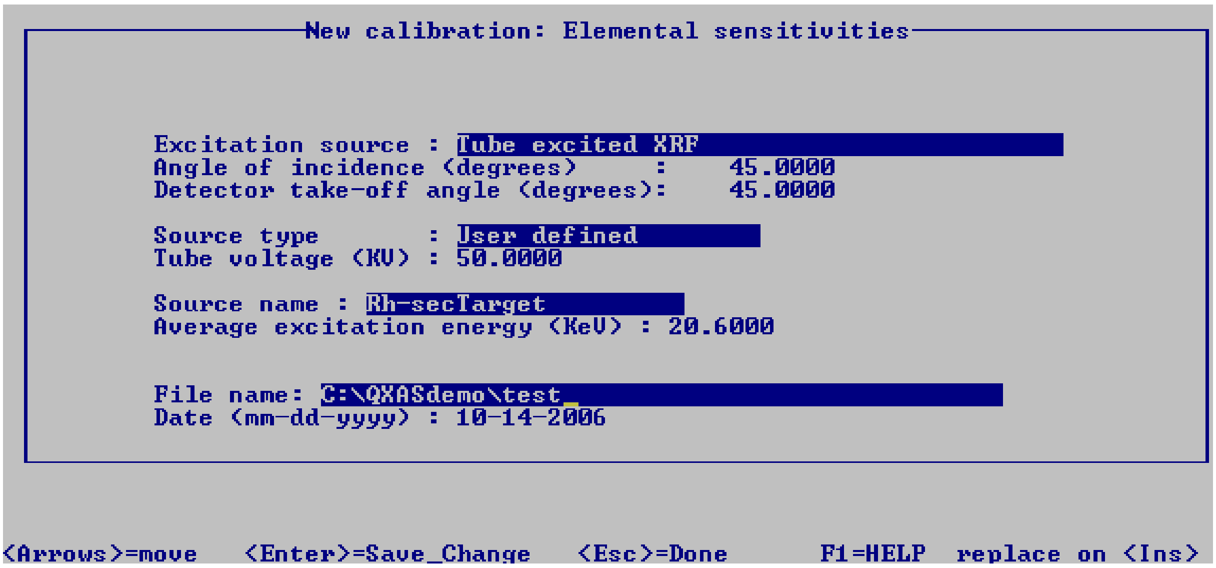
For the calibration of the **Elemental sensitivities** METHOD sensitivities are calculated for characteristic lines from standards, correcting the self-absorption in the standards. It is assumed, that the *excitation radiation* can be *represented by a single X ray line*, the intensity weighted energy (**Average excitation energy)**:

$$E_{average} = p_{K\alpha 1} \cdot E_{K\alpha 1} + p_{K\alpha 2} \cdot E_{K\alpha 2} + p_{K\beta 1} \cdot E_{K\beta 1} + p_{K\beta 2} \cdot E_{K\beta 2} + p_{K\beta 3} \cdot E_{K\beta 3} \tag{3.1}$$

For a Rh secondary target the weighted average of its K_α and K_β lines yields E_{average} = 20.6 keV. For direct X ray tube excitation as primary radiation sometimes so called effective energies are defined. Such a procedure might lead to good results, from the theoretical point of view it is not recommended to apply this METHOD to polychromatic excitation. The calibration for this METHOD is limited to 25 standards in total. Preferably such elements should be covered by standards, which are found in unknown samples. The sensitivity S_n of all elements n is calculated for which a concentration c_n is supplied to the current *.cal file and a peak area N_n can be read in by means of an *.asr file.

$$S_x = \frac{N_x \cdot A}{LT \cdot i \cdot c_x} \tag{3.2}$$

LT is the acquisition time of the respective spectrum, *i* the tube current, and *A* the absorption correction. K_α-lines and L_α-lines are treated independently. If more than one sensitivity is found for a calibration point (one element), the average value will be used. When more than three calibration points (elements) are found for a K_α– or L_α–calibration, non-measured elements can be interpolated (even extrapolated, though not recommended). In the ideal case no interpolations or extrapolations with **Optimize with Least Square Fit** will be necessary. Following the guidelines of CHAPTER 10: Elements of quality control, the use of such treated *.cal file is even prohibited. The report contains all individual results for each standard *.asr file and a summary of the calculated sensitivities. It can be saved as a text file (extension *.arp), which is not necessary for further calculations, because the relevant data is stored in the current calibration file *.cal. This file is used to determine the concentrations of elements in unknown samples, again correcting for the sample self-absorption. The *composition* of the sample's *dark matrix must be known*. Also intermediate thick and thin specimens can be evaluated, their area related mass (aerial density) is need as input. An on-line HELP can be activated throughout the whole METHOD with the <F1> key. The calibration established by this METHOD is also used as input for the **Emission-transmission** METHOD.



```
New calibration: Elemental sensitivities

Excitation source : Tube excited XRF
Angle of incidence (degrees)      :    45.0000
Detector take-off angle (degrees):    45.0000

Source type        : User defined
Tube voltage (KV) : 50.0000

Source name : Rh-secTarget
Average excitation energy (KeV) : 20.6000


File name: C:\QXASdemo\test_
Date (mm-dd-yyyy) : 10-14-2006


<Arrows>=move   <Enter>=Save_Change   <Esc>=Done      F1=HELP  replace on <Ins>
```

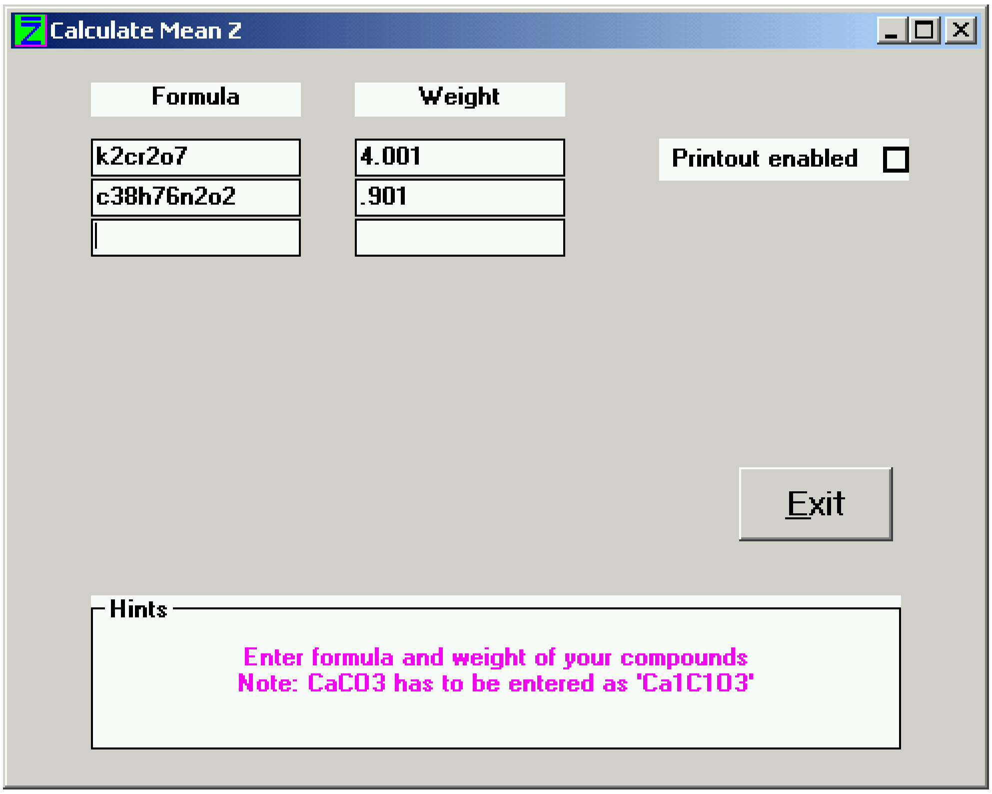
Fig. 3.1. Definition of a calibration file as used by the METHODs Elemental sensitivities and Emission Transmission.

3.2.1. Example: compound.cal

For the calibration compound.cal (using chemical compounds) twenty-four calibration standards' *.asr files were included (**Add standards**): MgSO4, K2CO3, K-KH2PO4, CaCO3, TiO2, V2O5, Cr2-K2O7, MnO2, Fe2O3, CoO, NiO, CuO, ZnO, As2O3, SeO2, Br-KBr, SrCO3, Y2O3, ZrO2, Nb2O5. Ge-Std, Mo-Std and Pb-LStd were included, because no compound standards for these elements were available, S-Std was included to assure the calibration point for sulphur. Pb-Lstd.asr is the only representative of an L-line emitting standard. No effort was made for this calibration to extend the L-lines calibration with more elements, because all samples treated later contain only lead as sole emitter of L-lines.

The standards P-KH2P04, K2-Cr2O7, K-KBr may not be used for this METHOD, because phosphorus is enhanced by potassium (enhancement correction factor: 1.036); potassium is enhanced by chromium (correction factor: 1.41) and potassium by bromine (correction factor: 2.21), respectively. The secondary excitation effect cannot be handled by **Elemental sensitivities**.

As example, how a standard is included as calibration point, the file Cr2-K2O7.asr was chosen. The Cr peak in the spectrum K2Cr2O7.spe of the calibration standard, which consists of 81.63 % K2Cr2O7 and 18.37 % HWC (chemical formula: $C_{38}H_{76}N_2O_2$) as binder, is used to establish the Cr calibration point. The weight percentage of all elements can be calculated with the utility **Calculation of average atomic number** in **Utilities**.



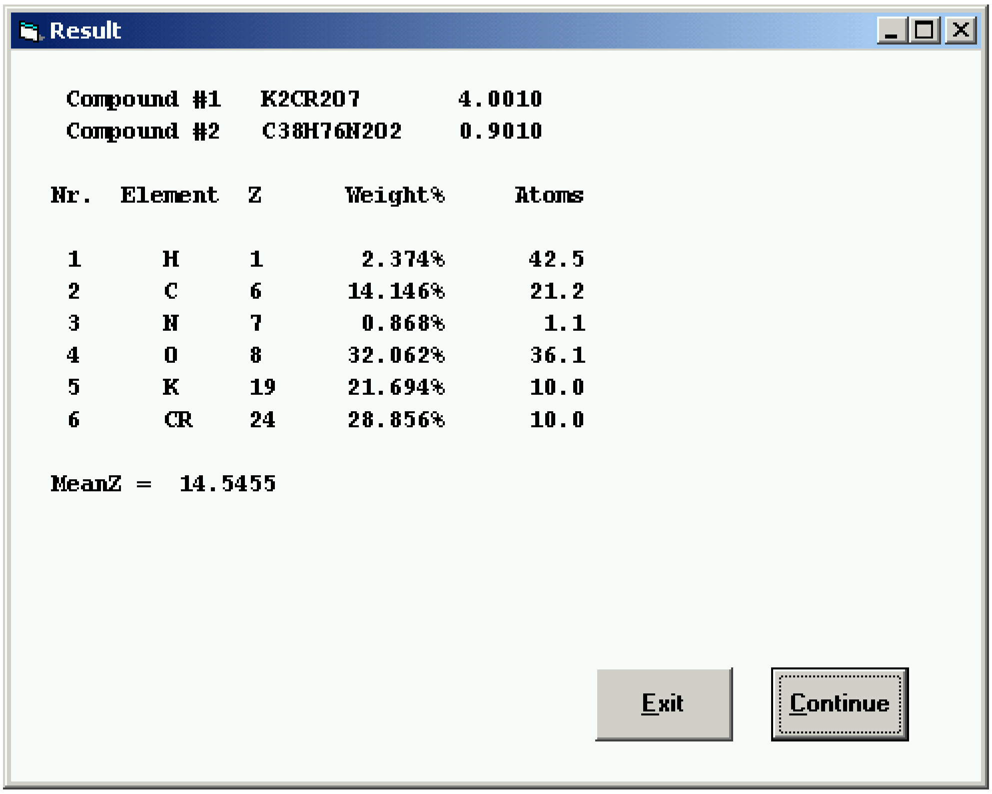
k2cr2o7 4.001

c38h76n2o2 .901

Enter formula and weight of your compounds
Note: CaCO3 has to be entered as 'Ca1C1O3'

Fig. 3.2. Definition of the composition of a calibration standard consisting of 4 g of $K_2Cr_2O_7$ and 0.9 g of HWC as binder, in order to obtain the weight % for each chemical element.

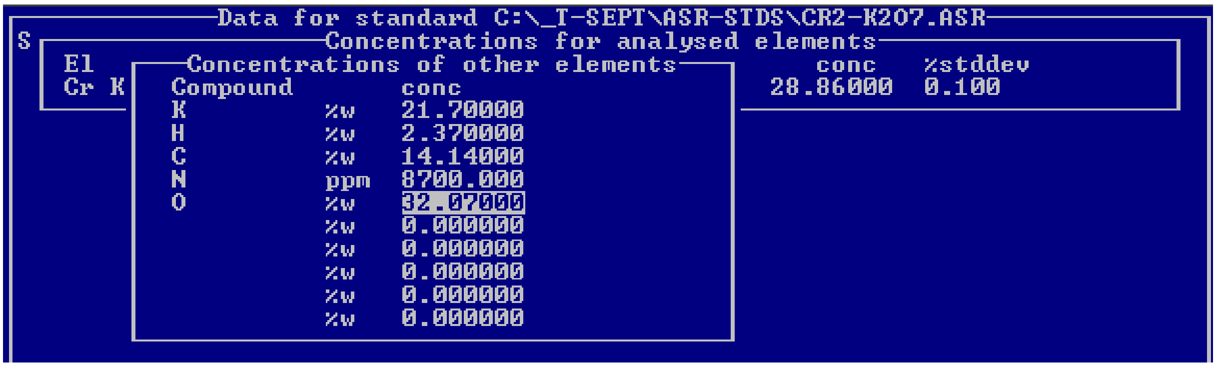
The calculation of concentrations in the mixture of the compound with the binder is initiated with a blank line after the last entry of a compound (and its weight) with <Enter>.



```
 Compound #1   K2CR2O7       4.0010
 Compound #2   C38H76N2O2    0.9010

Nr.  Element  Z      Weight%     Atoms

 1      H     1       2.374%      42.5
 2      C     6      14.146%      21.2
 3      N     7       0.868%       1.1
 4      O     8      32.062%      36.1
 5      K     19     21.694%      10.0
 6      CR    24     28.856%      10.0

MeanZ =  14.5455
```

Fig. 3.3. Weight % results for a calibration standard consisting of 4 g of $K_2Cr_2O_7$ *and 0.9 g of HWC as binder.*

The information gained with this utility cannot be transferred directly to the METHOD **Elemental sensitivities** - taking notes will be necessary. Alternatively, open QXAS in a second window simultaneously and arrange the two windows such that both can be seen. In the one run the METHOD **Elemental sensitivities**, in the other the utility **Calculation of average atomic number**. For the addition of a standard to the calibration knowledge about the tube current, the measurement date (not essential for tube excitation), the live time (usually transferred already from the *.asr file correctly) is needed. The Cr standard is infinitely thick in terms of XRF, so the standard's sample mass was left at the default value 0.00000 (all used example standards are infinitely thick). The concentration values for *all elements* of compound *and* binder must be specified (they are treated as one entity). The most problematic fact in this context is the expected knowledge about the (relative) error in the concentration value of the element used as calibration point (**% stddev**). The default value of 5 % is definitely too high for well-prepared standards. It will overestimate this contribution to the total uncertainty. The second contribution to the total uncertainty comes from the AXIL fit. No effort was made to gain knowledge about the uncertainty in the concentration, but 0.1 % for a standard seems to be reasonable.



```
Data for standard C:\_I-SEPT\ASR-STDS\CR2-K2O7.ASR
S            Concentrations for analysed elements
  El     Concentrations of other elements           conc     %stddev
  Cr K   Compound          conc                   28.86000   0.100
         K          %w    21.70000
         H          %w    2.370000
         C          %w    14.14000
         N          ppm   8700.000
         O          %w    32.07000
                    %w    0.000000
                    %w    0.000000
                    %w    0.000000
                    %w    0.000000
                    %w    0.000000
```

Fig. 3.4. Definition of the composition of the calibration standard $K_2Cr_2O_7$ with added binder.

After the correct inclusion of all standards the calibration will continue with the calculation of the sensitivities for all elements found in the standards (**Perform calibration**). When all elements identified in unknown samples can be covered with a calibration point (standard containing the respective element), this will be the end of the calibration procedure.

For the calibration points sulphur and potassium a plot of the sensitivities as function of concentration with the respective compound as “parameter” reveals some problematic behaviour, see Figure 3.5. Although an unrealistically high relative standard deviation for the concentrations of 5 % was assumed, one can easily see that neither sulphur and the compound $MgSO_4$, nor the compounds KH_2PO_4 and K_2CO_3, respectively, have matching sensitivities. In the ideal case the sensitivities of standards for the same element (calibration point) would have the same values – independent of their compound and the concentration. The sensitivities of potassium in the compounds KBr and K_2CrO_7 are also displayed in this graph, although this METHOD cannot correct the enhancement effect. Therefore they had not been included in the calibration compound.cal.

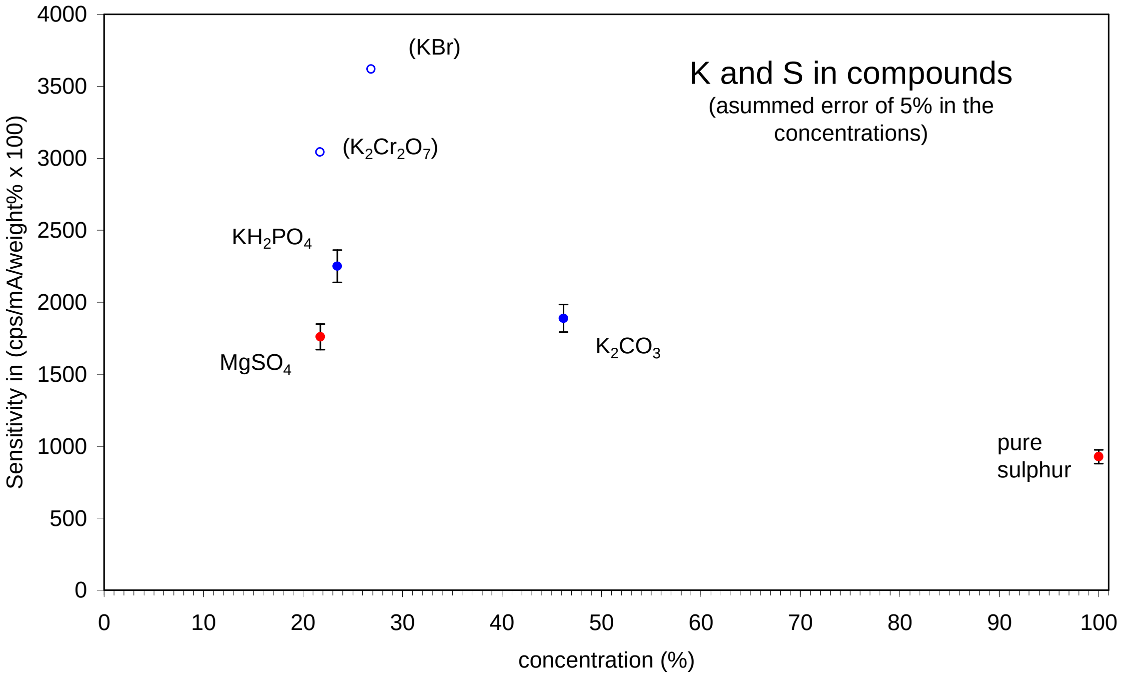
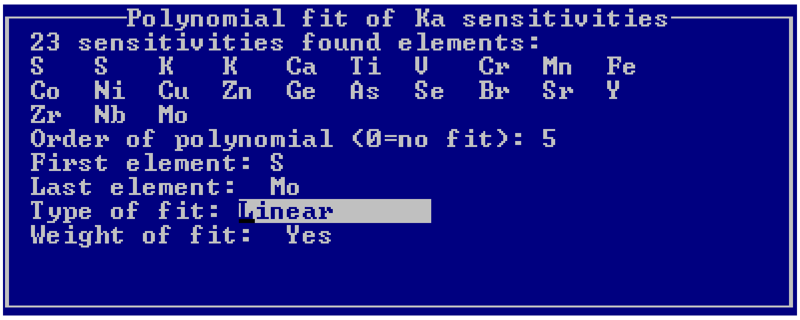


Fig. 3.5. Plot of the sensitivity versus element concentration for selected calibration standards, containing sulphur(red dots) and potassium (blue dots). The compounds KBr and $K_2Cr_2O_7$ are only displayed for comparison, but may not be used for this method, because of the secondary excitation of the elements of interest.

For the case when some elements in unknown sample can not be covered by a calibration point one will proceed: As provided by QXAS, an extension of the element range can be achieved with **Optimize Calibration with Least Square Fit**. The use of this option is very problematic, because otherwise well-defined calibration points can have a systematic bias afterwards. At least, with this procedure an interpolated data point for e.g. the element Rb can be established, as needed later.



```
Polynomial fit of Ka sensitivities
23 sensitivities found elements:
S    S    K    K    Ca   Ti   V    Cr   Mn   Fe
Co   Ni   Cu   Zn   Ge   As   Se   Br   Sr   Y
Zr   Nb   Mo
Order of polynomial (0=no fit): 5
First element: S
Last element:  Mo
Type of fit: Linear
Weight of fit:  Yes
```

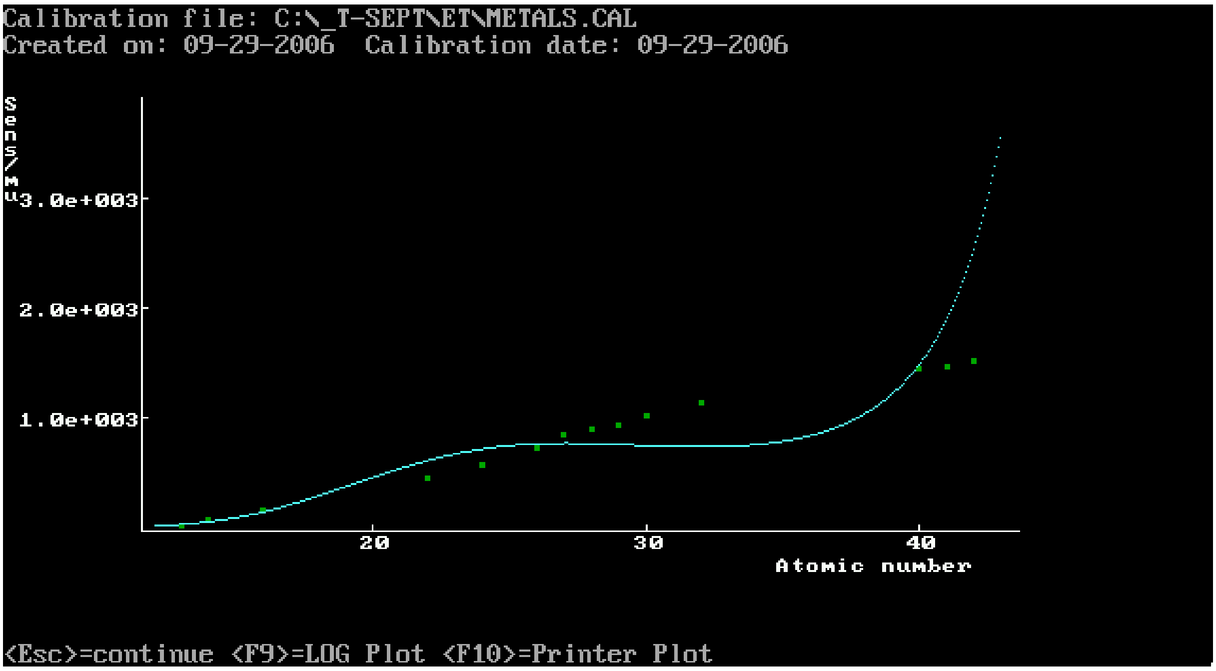
Fig. 3.6. A polynomial interpolation of sensitivities for elements not represented by calibration standards is possible.

For the elements between S and Mo the calibration compound.cal was extended with **Order of polynomial**: 5, as **Type of fit**: Linear and **Weight of fit**: Yes. With this selection a **Mean % Diff of:** 6.2259, as to be found in the later displayed results, was achieved. Any other combination of fit parameters has worse results. The weighted fit option could be used, because all standards were treated properly for their uncertainties in the AXIL fit (standard deviation greater than the square root of the peak area) and realistic uncertainties of the concentration values (relative error: 0.1 %) were entered. In case this can not be assured, **Weight of fit: No**, must be selected. One will usually have to go through this **Polynomial fit of sensitivities** several times, testing all possible combinations of parameters, in order to get knowledge about the optimum. Of major interest are the fit results of neighbouring calibration points of missing elements needed for unknown samples.

```
Calibration file: E:\QXASDEMO\ELSENS\COMPOUND.CAL
Created on: 09-28-2006  Calibration date: 11-08-2006
```

Fig. 3.7. Polynomial representation of sensitivities fitted as a function of the atomic number.

When probing, what kind of polynomial (**Linear** or **Logarithmic**) and what **Order of the polynomial=** (the maximum order is 5) is adequate, and how to deal with the option weighted or not weighted, several possibilities can be excluded - when an obviously bad fit is obtained.

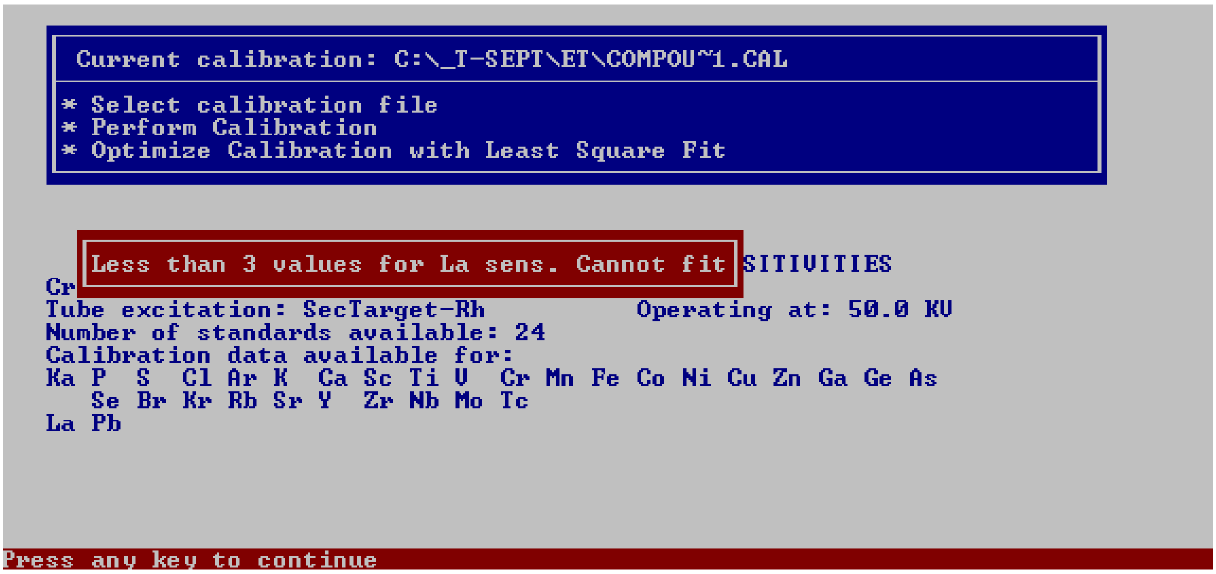


```
Calibration file: C:\_T-SEPT\ET\METALS.CAL
Created on: 09-29-2006  Calibration date: 09-29-2006
```

```
<Esc>=continue <F9>=LOG Plot <F10>=Printer Plot
```

Fig. 3.8. An obviously bad selection of parameters defining the polynomial fit.

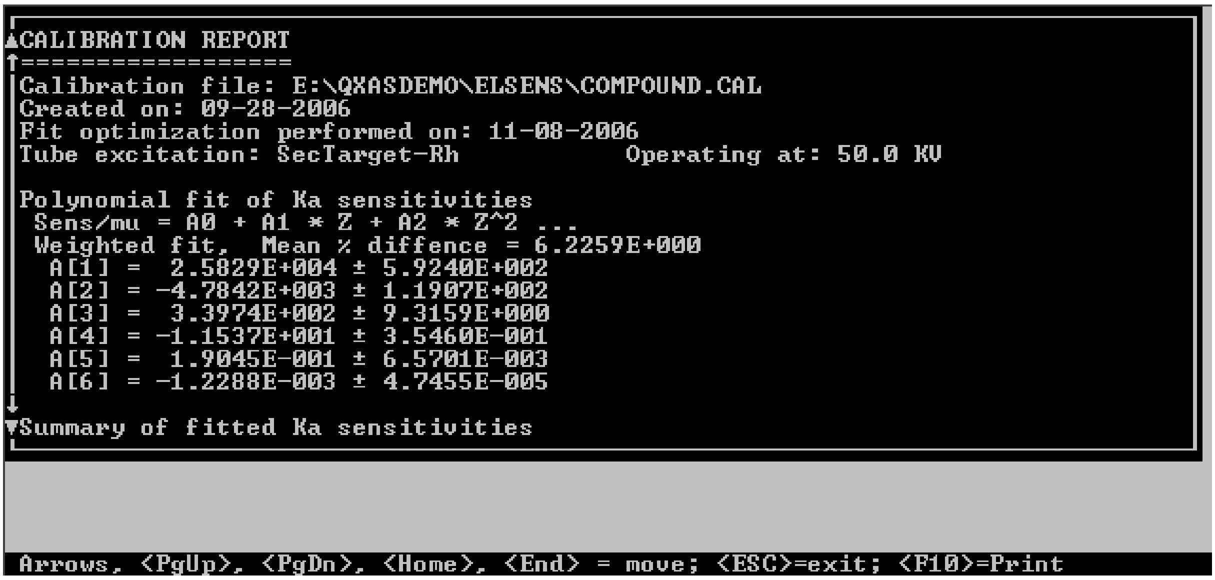
Also a fit for the L-line calibration is attempted by QXAS; but, due to the fact that only Pb-LStd.asr was added as L-line emitting standard, a warning massage will be displayed.



```
Current calibration: C:\_T-SEPT\ET\COMPOU~1.CAL

* Select calibration file
* Perform Calibration
* Optimize Calibration with Least Square Fit


  Less than 3 values for La sens. Cannot fit SITIVITIES
Cr
Tube excitation: SecTarget-Rh          Operating at: 50.0 KV
Number of standards available: 24
Calibration data available for:
Ka P  S  Cl Ar K  Ca Sc Ti V  Cr Mn Fe Co Ni Cu Zn Ga Ge As
   Se Br Kr Rb Sr Y  Zr Nb Mo Tc
La Pb

Press any key to continue
```

Fig. 3.9. Warning message for the case when less than tree calibration standards are available for an attempted polynomial fit. Still it will be possible to quantify sample elements represented by standards. In this particular case only Pb could be quantified, but no other L-line emitting elements.

The ultimate criterion to judge a fit is the **Mean % difference** value found in the report, displayed at the end of a loop. The optimum value of 6.2259 was obtained (**Mean % difference** = 6.2259E+000) for the above named selection; rubidium sensitivity: (7.01 +/- 0.436)*10^4. The compound MnO_2 is problematic, the Mn calibration point will be used, but results for this element are questionable.

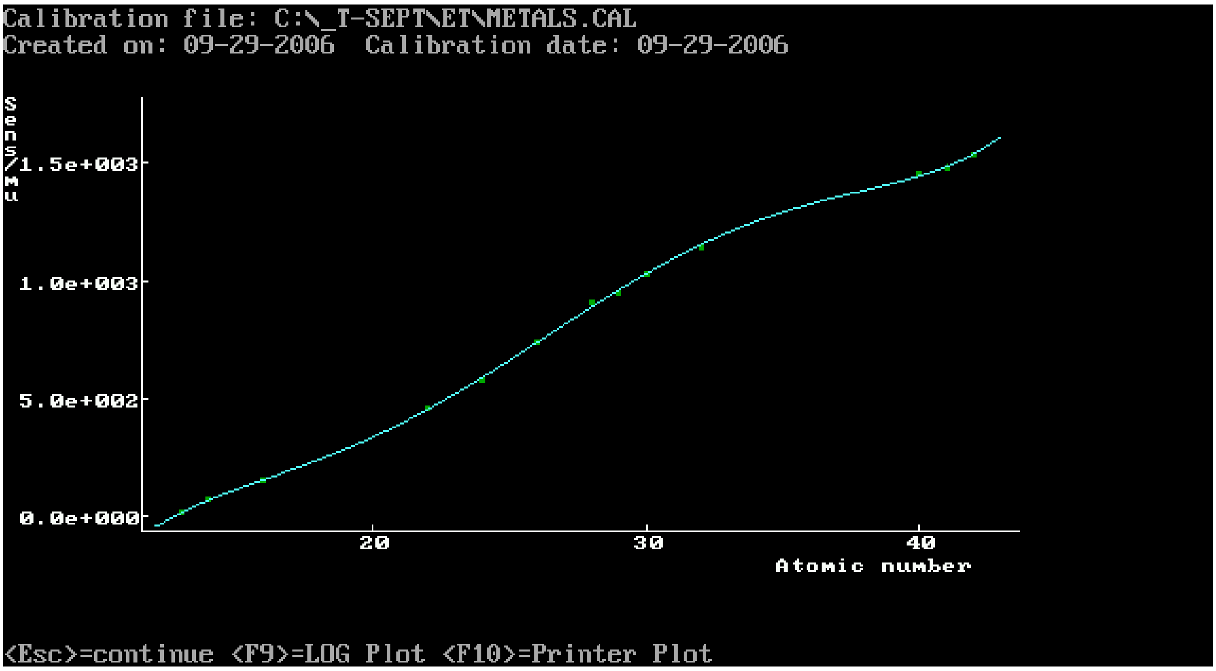


```
CALIBRATION REPORT
==================
Calibration file: E:\QXASDEMO\ELSENS\COMPOUND.CAL
Created on: 09-28-2006
Fit optimization performed on: 11-08-2006
Tube excitation: SecTarget-Rh           Operating at: 50.0 KV

Polynomial fit of Ka sensitivities
 Sens/mu = A0 + A1 * Z + A2 * Z^2 ...
 Weighted fit,  Mean % diffence = 6.2259E+000
  A[1] =  2.5829E+004 ± 5.9240E+002
  A[2] = -4.7842E+003 ± 1.1907E+002
  A[3] =  3.3974E+002 ± 9.3159E+000
  A[4] = -1.1537E+001 ± 3.5460E-001
  A[5] =  1.9045E-001 ± 6.5701E-003
  A[6] = -1.2288E-003 ± 4.7455E-005

Summary of fitted Ka sensitivities

Arrows, <PgUp>, <PgDn>, <Home>, <End> = move; <ESC>=exit; <F10>=Print
```

Fig. 3.10. Report displayed as scroll box, containing the mean % difference between all measured calibration points and fitted sensitivities as criterion to judge the polynomial representation.

3.2.2. Example: metals.cal

For the calibration metals.cal twenty-one *.asr files of pure (metallic) standards had been included (Al-Std, Si-wafer, S-Std, Ti-Std, Cr-Std, Fe-Std, Co-Std, Ni-Std, Cu-Std, Zn-Std, Ge-Std, Zr-Std, Nb-Std, Mo-Std, Cd-LStd, Sn-LStd, Hf-LStd, Ta-LStd, W-LStd, Au-LStd and Pb-LStd). For the elements with K emission lines between Al and Mo (fourteen calibration points) the calibration metals.cal was extended (**Optimize Calibration with Least Square Fit**) with **Order of polynomial**: 5; as **Type of fit**: Linear and **Weight of fit**: Yes. Any other combination of fit parameters has worse results. The weighted fit option could be used, because all standards were treated properly for their uncertainties in the AXIL fit (standard deviation greater than the square root of the peak area) and realistic uncertainties of the concentration values (relative error: 0.1 %) were entered. With this procedure an interpolated data point for e.g. Rb with (7.36 +/- 0.0884)*10^4 could be established.

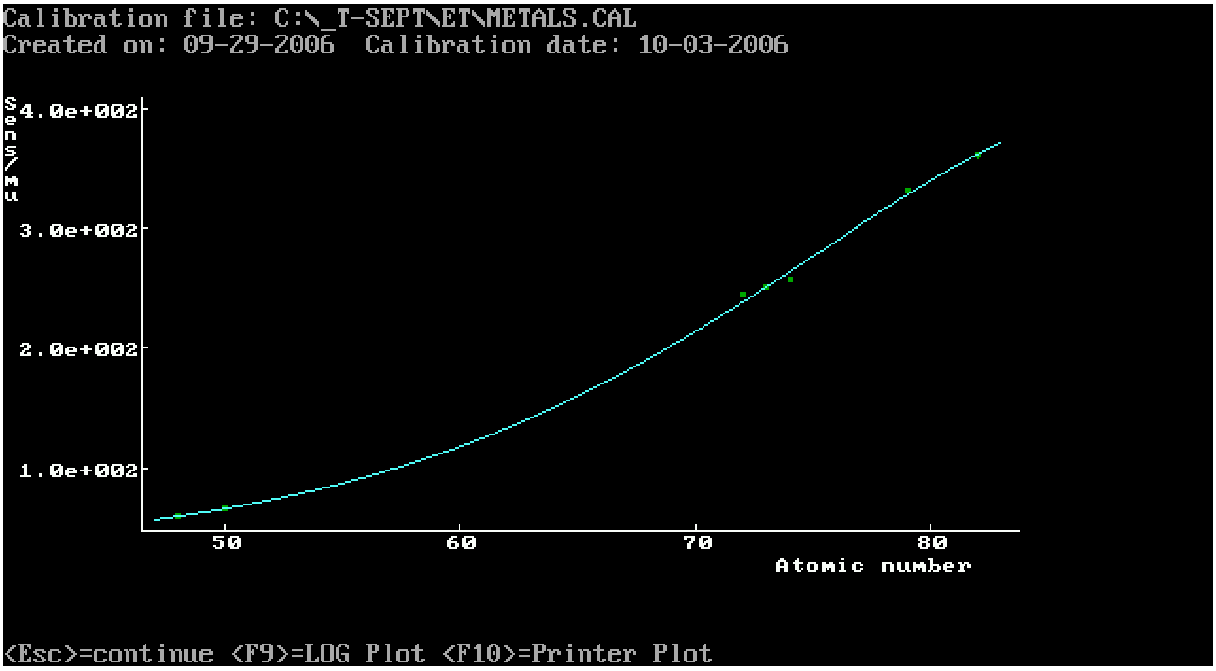


```
Calibration file: C:\_T-SEPT\ET\METALS.CAL
Created on: 09-29-2006  Calibration date: 09-29-2006
```

```
<Esc>=continue <F9>=LOG Plot <F10>=Printer Plot
```

Fig. 3.11. Polynomial representation of sensitivities fitted as a function of the atomic number. All used calibration standards are pure elements and are K-line emitters.

For the L-lines between Cd and Pb (seven calibration points) a logarithmic polynomial of order 3 (weighted option: yes) was found to suffice (scroll down in the SCROLL BOX to find the L-results **Mean % Diff**:, coming after the K-results).



```
Calibration file: C:\_T-SEPT\ET\METALS.CAL
Created on: 09-29-2006  Calibration date: 10-03-2006
```

```
<Esc>=continue <F9>=LOG Plot <F10>=Printer Plot
```

Fig. 3.12. Polynomial representation of sensitivities fitted as a function of the atomic number. All used calibration standards are pure elements and are L-line emitters.

Conclusion: By intuition one could deduce from the comparison of compound.cal with metals.cal that the later calibration is superior. This conclusion in the best case holds true for the better precision. One should rather establish calibrations by inclusion of as many “necessary” calibration points as possible – where the “necessity” of calibration points is imposed by unknown samples. The step **Polynomial fit of sensitivities** is not recommended / prohibited (according to QA requirements). Nevertheless, both calibration files, compound.cal and metals.cal, had been processed with **Polynomial fit of sensitivities** and the relevant calibration data for Rb was noted. The element Rb was selected as example, because the examples for the **ET** METHOD will need such an extension. Both calibrations were re-run with an order of 0 for the polynomial (**Order of polynomial (0 = no fit)**: 0). They were not fitted at all and the original calibration points are not biased. Outside of the QXAS environment, the relevant data for Rb was pasted into the now unfitted calibration files (for further explanations see CHAPTER 4: Editing of data files). Rb results for unknown samples might have a higher uncertainty, but all other elements, represented by measured calibration points, are well defined.

3.2.3. Application: air filter sample

A variety of samples, e.g., organic matter, geological samples, both usually containing dark matrix; or alloys, for which the secondary excitation needs to be corrected, cannot be treated appropriately with this METHOD.

None of these problems applies to air filter samples (aerosols deposited as thin film on a suited support). The major problem with thin samples is the usually low count rate for the peaks of interest. The fit with AXIL will not be problematic, but utmost attention must be paid to the instrument blank and the blank filter material, i.e. the substrate where the aerosols are collected onto. The following elements were identified in the spectrum of AirFilt.spe (standard reference material SRM 2783, batch # 267): Si, Ca, Fe, Ni, Cu, Zn, Sr, Mo and Pb. The scattered Rh L-lines have to be included for the sake of Si, and are preferably described by energy values; the elements had been included with:

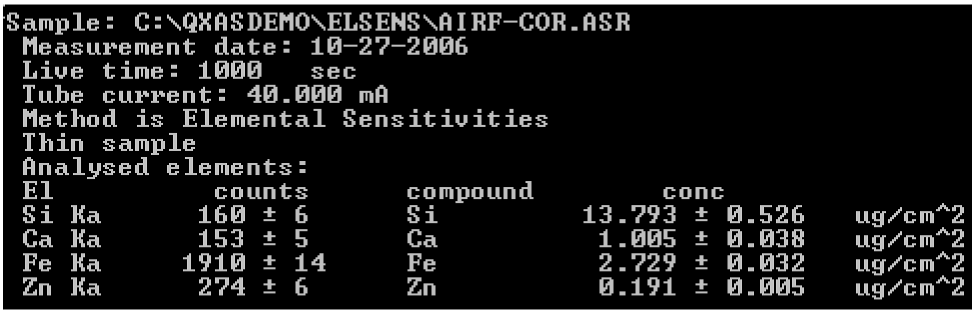
X-LINES ADD: SI CA FE NI CU ZN SR MO-KA PB 2.7 2.8 2.9

The input model AirFilt.inp describes the background as linear of order 8 (because of the strong curvature, caused by Rh K scatter region extending to Mo). Sulphur must not be included, because of a potential interference with the Rh L_l scatter peak. The same input model is used to fit also the blank filter (SRM 2783 blank), spectrum Blank-Af.spe, and the instrument blank, spectrum Instr-Bl.spe, see Figure 1.27. In the instrument blank spectrum the elements Fe, Cu, Sr, and Mo can be identified: A molybdenum foil had been used for shielding purposes, Fe and Cu are of unidentified origin, and Sr, very likely, will originate from a crumb, lost from a previously measured sample. Both blank spectra have a comparable shape, one can assume the sample substrate does not contribute to the blank problems. The comparison of the three *.asr files provides consequences. Have in mind the previously defined rule that peak areas, for results to be used, must exceed 10 times the respective blank values. Si, Ca and Zn peak areas, in comparison with the two blank spectra, can be accepted. Fe will have about 5 % blank contribution. Ni, Cu, Sr and Pb intensities approximately will be half generated by the sample but the other half is caused by the instrument - therefore their results must not be reported. The Mo peak does not originate at all from the sample.

Table 3.1. Net peak area for elements identified in spectra of a standard reference filter material, a blank foil and the instrument blank. Elements in red colour can be used for quantification.

	Si	Ca	Fe	Ni	Cu	Zn	Sr	Mo	Pb
AirFilt.asr	160+/-6	153+/-5	1910+/-14	57+/-3	152+/-4	274+/-6	254+/-5	387+/-8	48+/-2
Instr-Bl.asr	22+/-3	0	112+/-4	37+/-3	94+/-4	15+/-2	200+/-5	381+/-7	18+/-2
Blamk-AF.asr	8+/-11	-34	108+/-12	28+/-8	64+/-10	34+/-8	200+/-15	401+/-24	21+/-6

A calibration file suited for this sample was generated: Airfilt.cal. It carries the calibration points as needed for the four elements of interest, defined by six calibration standards: Si-wafer.asr, CaCO3.asr, Fe-Std.asr, Fe2O3.asr, Zn-Std.asr and ZnO.asr (no extension necessary, all elements of interest are represented by calibration points). Before the AXIL result file AirFilt.asr was used for quantification with Elemental sensitivities, the element entries of the lines containg Ni, Cu, Sr, Mo and Pb peak areas had been erased and the edited file was saved as AirF-cor.asr (for editing of files see CHAPTER 4: Editing of data files). For the use with the above defined calibration file AirFilt.cal this procedure were not necessary, but interested readers might also use other calibration files, which would enable to generate results for elements that should not be reported. The tube current for the measurement was 40 mA; as **Sample type**: thin sample and as concentration units: mass per unit area are applicable.



```
Sample: C:\QXASDEMO\ELSENS\AIRF-COR.ASR
 Measurement date: 10-27-2006
 Live time: 1000   sec
 Tube current: 40.000 mA
 Method is Elemental Sensitivities
 Thin sample
 Analysed elements:
 El           counts       compound         conc
 Si Ka       160 ± 6       Si          13.793 ± 0.526    ug/cm^2
 Ca Ka       153 ± 5       Ca           1.005 ± 0.038    ug/cm^2
 Fe Ka      1910 ± 14      Fe           2.729 ± 0.032    ug/cm^2
 Zn Ka       274 ± 6       Zn           0.191 ± 0.005    ug/cm^2
```

Fig. 3.13. Quantitative results for the reference standard material SRM 2783 (air filter), obtained with the method Elemental sensitivities.

The reference certificate lists the concentration values in (ng/filter). By use of the average area (9.96 cm^2), as specified there, one can convert the QXAS data in order to compare the results. The standard deviation in the concentration values as provided by QXAS *may not be quoted*. In order to establish the standard deviation, one has to prepare and measure samples repeatedly. From these results the average and the standard deviation must be taken.

Table 3.2. Comparison of results obtained with the method **Elemental sensitivities** with certified values, in (mg), for the reference standard material SRM 2793 (air filter).

	Si	Ca	Fe	Zn
measured	137	10.0	27.2	1.9
Certified value	58.600+/-1.758	13.200+/-1.716	26.500+/-1.590	1.790+/-0.125

Obviously silicon can not be described appropriately (as it is the case some many times for light elements). The other elements' results compare well.

3.3. Calibration for the Full Fundamental Parameters METHOD

Demonstration files (directory \QXASdemo\FP-scatt):

- Instrumental parameter files: Test.fpc, Soil.fpc, OrgaMatr.fpc, NBSalloy.fpc
- AXIL result files: NBS1108.asr (directory \QXASdemo\NBS)
- Binder.reb

Full Fundamental Parameters is the most versatile METHOD for quantification in the QXAS package and is suited even for completely unknown samples. Several modes of excitation with electromagnetic radiation in the range of X-rays can be covered and many parameters can be selected to match the assumptions needed for the calculations with the experiment. The fundamental parameters approach takes into account the spectral distribution of the excitation source, the fundamental parameters, the absorption correction, the inter element effect and the detector efficiency. The sample self-absorption by the dark matrix can be corrected by the use of the scatter peaks. Standards are used to determine the geometry factor (average instrumental constant). In theory the range of elements that can be analyzed by this METHOD is not limited or correlated to any range defined by the elements of the standards. In principle with only one standard the METHOD can be calibrated. As first step in order to run the METHOD correctly the fundamental parameter file *.fpc has to be defined.

Hint: For problems during the final calculations of instrument constants or sample concentrations: When after a short flash the calculation will stop and bring back to the previous COMMAND **Calculations of Geometry constants/Analysis of unknown samp.**, the conventional memory did not suffice. *Terminate QXAS completely* and re-start it; go again to the last COMMAND **Calculations of Geometry constants/Analysis of unknown samp.** (the temporary file fundp.tmp still carries all data) and initiate the calculations again.

*3.3.1. Set-up of the instrumental parameter file *.fpc*

The excitation conditions, geometry, detector characteristics and other influence parameters are to be defined or the pre-defined files (Test.fpc, OrgaMatr.fpc, Soil.fpc) can be inspected with: **Set-up instrumental parameters**.

Fig. 3.14. An instrument parameter file can be defined or modified with the selection of: Set-up instrumental parameters.

3.3.1.1. Example: Test.fpc

With **Select instrument parameter file** the demonstration file Test.fpc, adequately defined for the used setup (Sample changer spectrometer at Seibersorf laboratories), can be loaded (directory: \QXASdemo\FullFP).

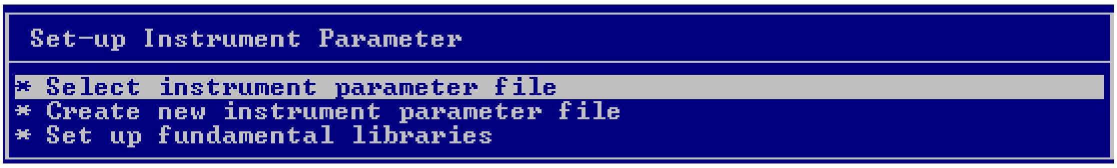
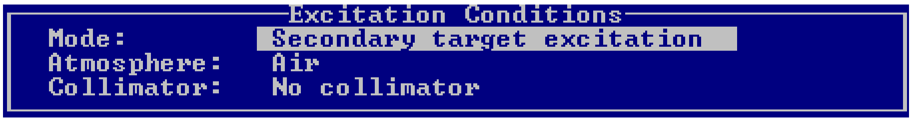


Fig. 3.15. An already existing instrument can be loaded with the selection of: Select instrument parameter file.

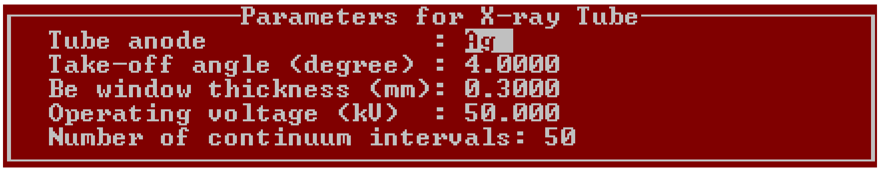
In the FORM **Excitation Conditions**, from all options for **Mode:**, the choice of **Secondary target excitation** will enable to get predefined values for the spectral distribution of the used secondary target. The spectrometer was run with an evacuable sample chamber, but the air gap between the sample chamber exit window and the detector Be entrance window can be incorporated by the definition of **Atmosphere: Air** (instead of the more logic option: **Vacuum**). The term **Collimator** refers to a *SPECTRACE* spectrometer; lucky the owners of such an instrument – for all others there is no relevance for any selection, therefore the calibration continues with the selection of **No collimator**.



```
                     Excitation Conditions
  Mode:           Secondary target excitation
  Atmosphere:     Air
  Collimator:     No collimator
```

Fig. 3.16. Various modes of excitation permit to select a pre-defined secondary target arrangement.

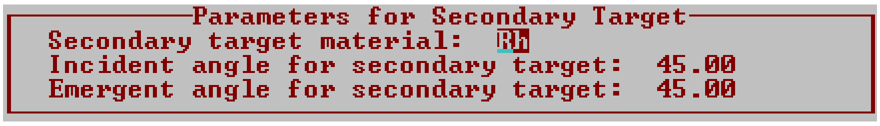
For the excitation of the secondary target a Ag anode X ray tube was used. Because it is a diffraction type of tube the anode take-off angle will be around 4^0; its Be exit window has, according to the description of the manufacturer, a thickness of 300 µm. The tube high voltage was adjusted to 50 kV (for a once established calibration this value never may be changed). Although the scattered continuum originating from the anode will not significantly contribute to the excitation, the **Number of continuum intervals**, taking into account this effect, had been defined as 50. For direct tube excitation one would work with a value of 200 (or slightly less, for the case of computation problems).



```
                Parameters for X-ray Tube
  Tube anode                 : Ag
  Take-off angle (degree)    : 4.0000
  Be window thickness (mm): 0.3000
  Operating voltage (kV)     : 50.000
  Number of continuum intervals: 50
```

Fig. 3.17. The X ray tube used for exciting a secondary target can be specified.

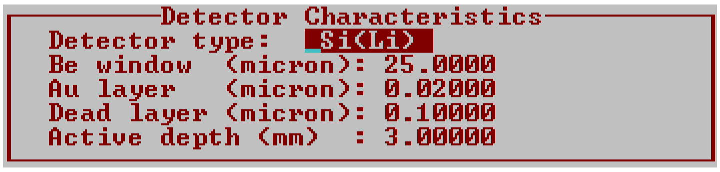
The used secondary target (Rh) is irradiated with an incident angle of 45^0, the direction of the emergent Rh characteristic radiation (K and L lines) is also 45^0, both in respect to the target surface and defined by the collimation system.



```
Parameters for Secondary Target
  Secondary target material:  Rh
  Incident angle for secondary target:  45.00
  Emergent angle for secondary target:  45.00
```

Fig. 3.18. The secondary target is specified by its chemical symbol and incident and take-off angle.

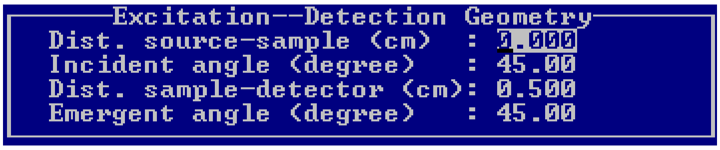
According to the available detector data sheet, the Be entrance window of the used Si(Li) detector has a thickness of 25 µm and a crystal thickness of 3 mm. One should not expect any information about the (Au) contact layer and Si dead layer from the data sheet; usual values are 0.02 – 0.05 µm for the contact layer (let us wish is really made of gold, because it could be other materials, too) and 0.02 – 0.2 µm for the dead layer. These values importantly influence the light element analysis; as they are so poorly known this always serves as explanation for poor results of these elements…



```
Detector Characteristics
  Detector type:    Si(Li)
  Be window   (micron): 25.0000
  Au layer    (micron): 0.02000
  Dead layer (micron): 0.10000
  Active depth (mm)   : 3.00000
```

Fig. 3.19. A Si(Li)-detector is specified in respect to its intrinsic efficiency by its Be entrance window thickness, the thickness of the contact layer, the dead layer thickness and the crystal thickness.

The **Excitation-Detection Geometry** FORM does *not* need data for the distances in agreement with the reality, but rather defines the air path (previous choice **Atmosphere: Air)** between secondary target and sample (the radiation travels only in vacuum, therefore an input of 0 is adequate), and sample and detector (gap between detector and sample chamber of 0.5 cm)**.** The incident and take-off (emergent) angle is defined by the collimation system, with an average value of 45^0 for both.



```
Excitation--Detection Geometry
  Dist. source-sample (cm)   : 0.000
  Incident angle (degree)    : 45.00
  Dist. sample-detector (cm): 0.500
  Emergent angle (degree)    : 45.00
```

Fig. 3.20. The sample geometry is specified by the incident and take-off angle. Both are to be defined in respect to the surface normal. The distances between the excitation source, the sample and the detector entrance window need not reflect the real dimensions but are rather the distances radiation has to travel in air and therefore imposes a specific correction.

No filter between secondary target and sample was used (**Filter between source and sample**). Such a filter is often used for direct tube excitation in order to shape the primary spectral distribution.

The last FORM **Average Instrumental Constant** will display only zero entries for the file Test.fpc, simply because no calibration had been performed. For any attempt to quantify unknown samples at least the line **for fluorescence:** must be defined with the input of a spectrometer relevant number. So far, only the spectrometer was described; by use of e.g. Test.fpc one will be able to use calibration standards' *.asr files to establish individual instrumental constants. By selection and averaging, as outlined later, the average instrument constant can be calculated, which value will be entered in this FORM in another run.

```
Average Instrumental Constant
for fluorecence:            0.0000
for coherent scattering:    0.0000
for incoherent scattering:  0.0000
```

Fig. 3.21. The average instrumental constant values will be zero for the first time the parameters are defined. These values are to be obtained by suited calibration standards and have to be entered later.

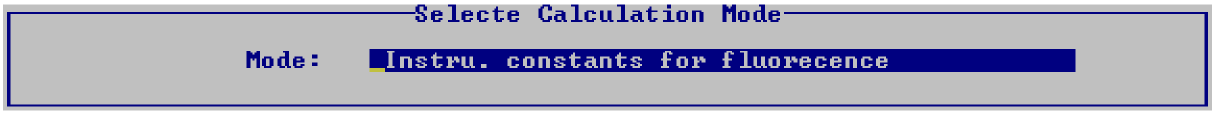
3.3.2. Description of calibration standards for this METHOD

In principle a single standard can be sufficient to calibrate for this METHOD, but with the exception of exotic problems one will try to use as many standards as possible to establish the instrumental constants. In the ideal case all calibration standards will result in the same instrumental constant (different to the concept of e.g. the **Elemental sensitivities** METHOD). With the selection of **Specify standard/sample information** from the SELECTOR BOX **Current Instrument Parameter File:** and **Select samples for quantitative analysis** all standards have to be processed. It is possible, but not necessary, to do this in one run. Not very fortunate, because misleading, the same text (**Select samples for quantitative analysis**) is used for both calibration and the later analysis of unknown samples.

3.3.2.1. Calibration standard example: K-KBr.asr

From the directory \QXASdemo\ASR-Stds the AXIL result file K-KBr.asr was selected to demonstrate the calculation of the potassium instrumental constant, in order to build up finally from all calibration standards the average instrumental constant for fluorescence and how to define also individual instrumental constants.

Within the SELECTOR BOX **Select Calculation Mode** toggle by use of the <space bar> to **Instru. Constants for fluorescence**, otherwise with the default option **Sample concentrations** in the following the attempt will be made to treat the standard as unknown sample, resulting in a crash of the program, because of the so far not established and therefore missing average instrument constant.



```
Selecte Calculation Mode

Mode:    Instru. constants for fluorecence
```

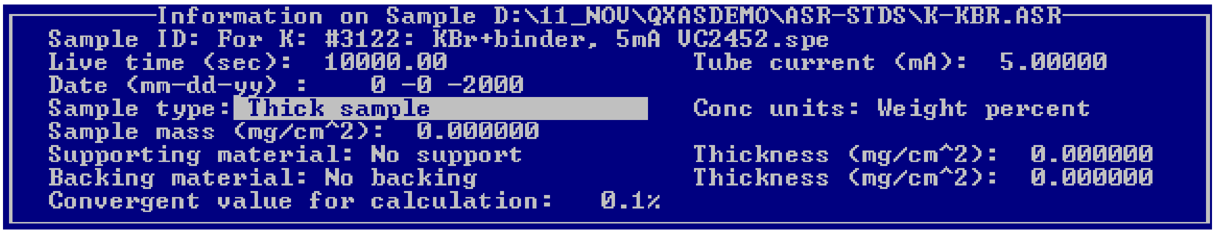
Fig. 3.22. In order to obtain the needed instrumental constants for fluorescence as mode: **Instru. constants for fluorescence** *must be selected.*

The consecutive SELECTOR BOX will offer a choice (**Average and/or Individual**) that should not be taken for a "first round" calibration, but will be needed for the second calibration round. As can not be known a priori, potassium will need to be described by an individual instrumental constant (**Instrument constant type:** Average). For the beginning all calibration standards should only contribute to the average. After all standards' results are available, one will decide to exclude some of them or enable individual element specific instrumental constants. Potassium is already an example for the light elements that will be included individually.

```
Type of Instrument Constant
  Instrument constant type: Average
```

*Fig. 3.23. In a first round for all fluorescence calibration standards instrumental constants should be calculated in way that they will not written as individual constants to the *.fpc file directly. If necessary, this should be done only after careful evaluation of all results.*

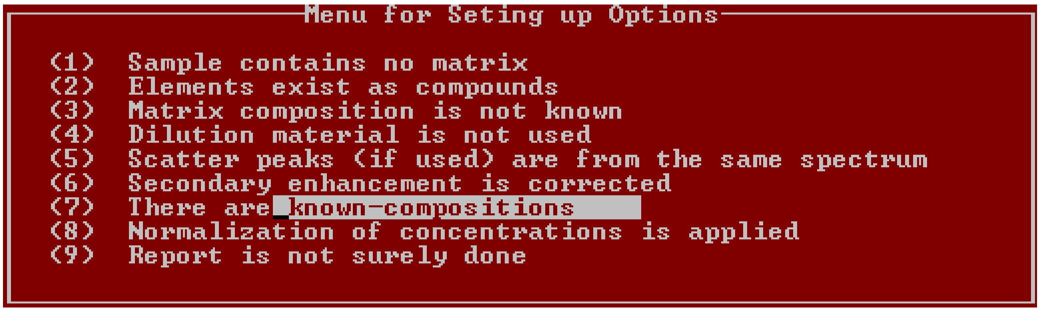
The FORM **Information on sample** should rather be named "information about standard", but bear with us. We profit again from the fact that the spectrum header had been edited such that all relevant information is displayed without search in log books. The acquisition time is read in automatically, but the tube current has to be edited manually, the date as well (of no relevance for tube excitation). As **Sample type:** toggle to **Thick sample** (as for all other calibration standards), otherwise the **Sample mass** needed to be specified. The rest leave untouched.



```
Information on Sample D:\11_NOU\QXASDEMO\ASR-STDS\K-KBR.ASR
  Sample ID: For K: #3122: KBr+binder, 5mA VC2452.spe
  Live time (sec):  10000.00                Tube current (mA):  5.00000
  Date (mm-dd-yy) :    0 -0 -2000
  Sample type: Thick sample                 Conc units: Weight percent
  Sample mass (mg/cm^2):  0.000000
  Supporting material: No support           Thickness (mg/cm^2):  0.000000
  Backing material: No backing              Thickness (mg/cm^2):  0.000000
  Convergent value for calculation:   0.1%
```

Fig. 3.24. Definition of details concerning the potassium calibration standard K-KBr.asr, like the X ray tube current and the sample type.

The consecutive FORM **Menu for Setting up Options** provides several options, which should not be displayed at all ((1), (3), (8)): For a standard it is not permissible to define a (dark) matrix (1), therefore it is irrelevant, if it is known or not (3) and the sum of all concentrations is normalized (8) for standards without exception. For (2) **Elements exist as:** the option **compounds** is rather a nice feature for samples when concentrations are displayed for both the elements and the compounds simultaneously. For samples prepared by use of a binder one would love to be able to use an entry for (4), but any input in order to correct for the dilution factor will crash the program. (5) does not apply to any of the standards used for this calibration; the scatter peak calibration will be discussed in CHAPTER 8: Utilization of the scatter peaks. The default for (6) **Secondary** (excitation), **enhancement** should not be altered, *particularly not* for this calibration standard, because bromine contributes to the potassium signal substantially by secondary excitation. (7) is of utmost importance, because by toggling to **There are known-compositions** all other chemical elements of the compound and the binder can (and must be) defined. Whether one wants to save the final report or not (9) can still be decided when the results are displayed.



```
Menu for Seting up Options

(1)  Sample contains no matrix
(2)  Elements exist as compounds
(3)  Matrix composition is not known
(4)  Dilution material is not used
(5)  Scatter peaks (if used) are from the same spectrum
(6)  Secondary enhancement is corrected
(7)  There are known-compositions
(8)  Normalization of concentrations is applied
(9)  Report is not surely done
```

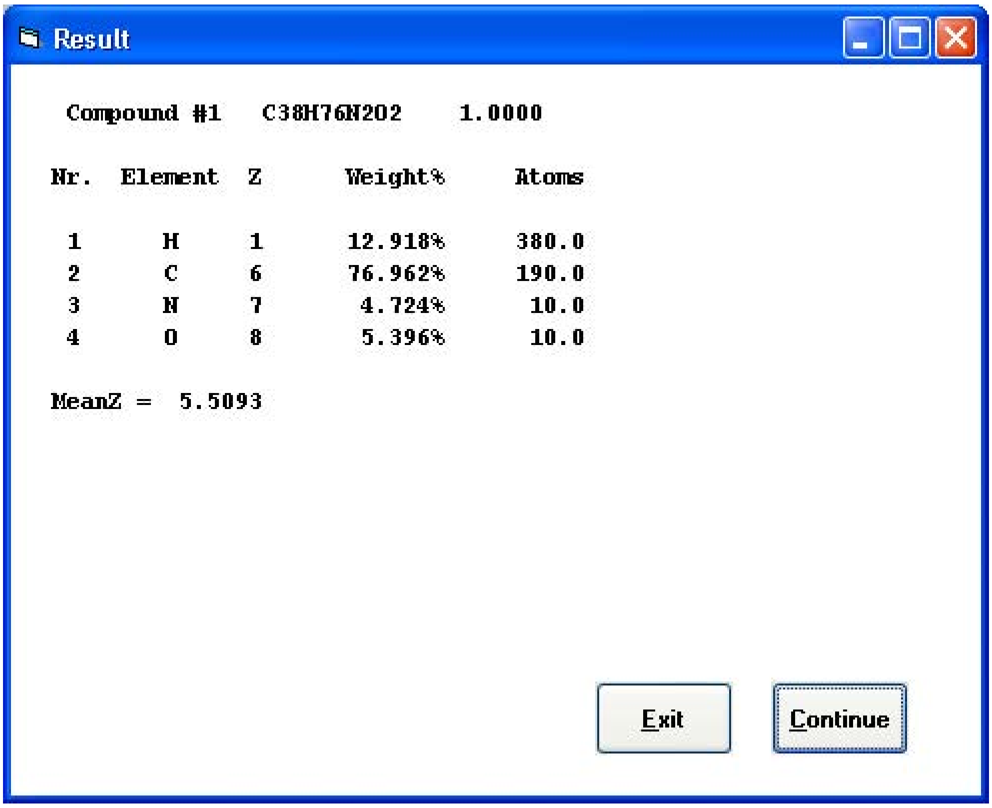
Fig. 3.24. In the form Menu for setting up options the toggle field (7) must be changed to known compositions for standards containing chemical elements in form of a binder.

In the FORM **Analyzed elements of:** as **constituent** the compound must be typed in such that the element under investigation is the leading element. Different results will be obtained for KBr than for BrK! – this has to do with the calculation for secondary excitation correction. As it complicated to define compound standards correctly for this METHOD, for which more than one element should be used for calibration, it is advised to generate different *.asr files for each element used for calibration. This approach is well in accordance with the solution for problems, sometimes encountered, for fitting more than one standard element within one ROI. Do not edit the net peak area. For **composition** the input for the KBr concentration in the mixture of this compound with the binder can be calculated with the use of the EXCEL standards.xls file.

```
Analyzed Elements of: D:\11_NOV\QXASDEMO\ASR-STDS\K-KBR.ASR
Ele.  constituent        counts               composition   %
K  Ka  KBr             54562     ± 247            81.63999
```

Fig. 3.25. Definition of the major compound forming the calibration standard KBr and its concentration. The binder will have to be defined later.

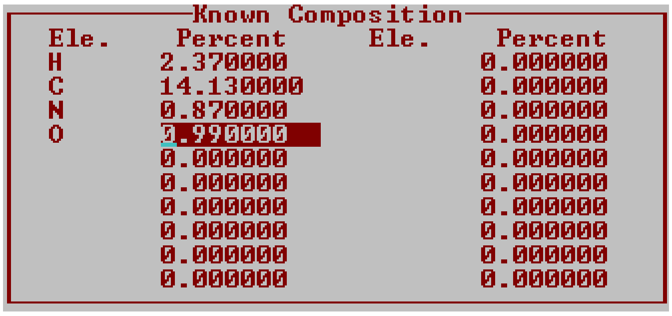
Due to the definition of (7) **There are known-compositions**, one will have to create a file (**Edit a new file**) with extension REB, defining the composition of the used binder, or one can toggle (use the <space bar>) to **Input an old file** and profit from the already pre-defined file Binder.reb. For the eager readers who want to define such a file themselves: One will use the utility **Calculation of average atomic number** and calculate for the used binder HWC ($C_{38}H_{76}N_2O_2$) by input for **Formula** of C38H76N2O2 and any arbitrary **Weight**, the concentration values for 100 % of this binder.



```
 Compound #1   C38H76N2O2    1.0000

Nr.  Element  Z      Weight%     Atoms

 1      H     1      12.918%     380.0
 2      C     6      76.962%     190.0
 3      N     7       4.724%      10.0
 4      O     8       5.396%      10.0

MeanZ =   5.5093
```

Fig. 3.27. Weight % results for the chemical elements contained in the used binder.

The pressed pellet consists of 81.64 % of KBr (4.024 g) and 18.36 % binder (0.905 g), therefore multiply all HWC concentration values with 0.1836; it results in the concentrations to be used as input in order to generate a file like Binder.reb.

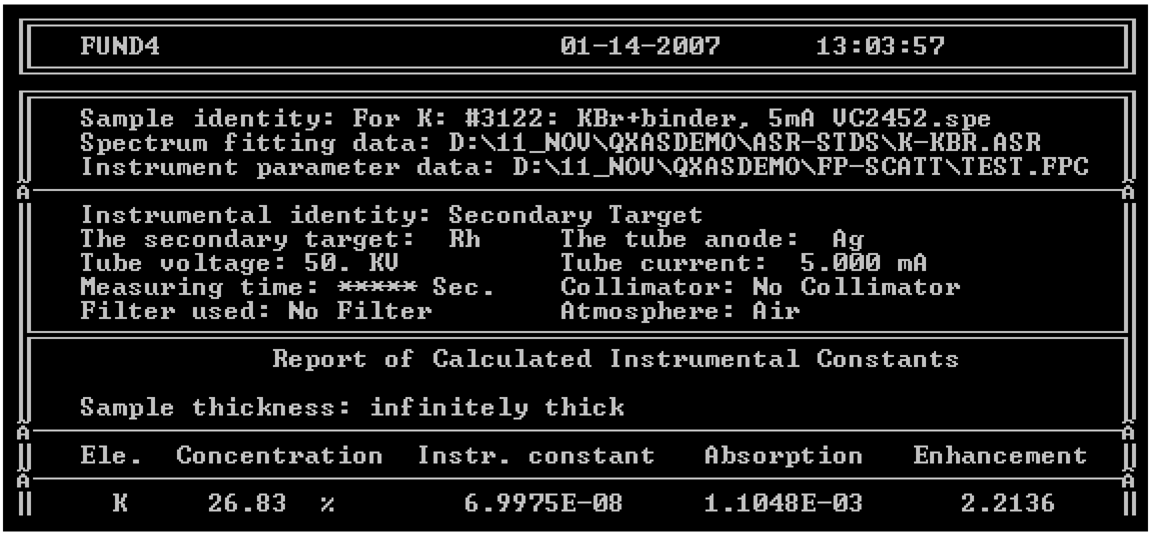


```
-----------Known Composition-----------
 Ele.      Percent      Ele.      Percent
 H         2.370000               0.000000
 C         14.130000              0.000000
 N         0.870000               0.000000
 O         0.990000               0.000000
           0.000000               0.000000
           0.000000               0.000000
           0.000000               0.000000
           0.000000               0.000000
           0.000000               0.000000
           0.000000               0.000000
```

Fig. 3.26 Definition of the binder composition.

This was the last step in order to define K-KBr.asr as a calibration standard for this METHOD. One could have included many more suited *.asr files in one run and define them one after the other. **Calculations of Geometry constants/Analysis of unknown samp.** will initiate the calculation of the element specific geometry (instrumental) constant for potassium.

The instrumental constant for potassium in KBr is obtained as $6.998*10^{-8}$. Note the enhancement correction factor of 2.21, which means the K intensity was corrected with this factor to account for the excitation of potassium by bromine.



```
FUND4                         01-14-2007     13:03:57

Sample identity: For K: #3122: KBr+binder, 5mA VC2452.spe
Spectrum fitting data: D:\11_NOV\QXASDEMO\ASR-STDS\K-KBR.ASR
Instrument parameter data: D:\11_NOV\QXASDEMO\FP-SCATT\TEST.FPC

Instrumental identity: Secondary Target
The secondary target:  Rh      The tube anode:  Ag
Tube voltage: 50. KV           Tube current:  5.000 mA
Measuring time: ***** Sec.     Collimator: No Collimator
Filter used: No Filter         Atmosphere: Air

            Report of Calculated Instrumental Constants

Sample thickness: infinitely thick

Ele.  Concentration  Instr. constant   Absorption   Enhancement

 K     26.83  %         6.9975E-08     1.1048E-03      2.2136
```

Fig. 3.27. Instrumental constant for potassium of the KBr calibration standard.

In this manner all available calibration standards (there is no limit to their number) can be treated. For each of the forty-four *.asr files an instrumental constant for fluorescence can be obtained: Al-Std, Si-wafer, P-KH2PO4 (for phosphorus), K-KH2PO4 (for potassium), S-Std, MgSO4 (for sulphur), K2CO3, K2-Cr2O7 (for potassium), K-KBr (for potassium), CaCO3, Ti-Std, TiO2, V2O5, Cr-Std, Cr2-K2O7 (for chromium), MnO2, Fe-Std, Fe2O3, Co-Std, CoO, Ni-Std, NiO, Cu-Std, CuO, Zn-Std, ZnO, Ge-Std, As2O3, SeO2, Br-KBr (for bromine), SrCO3, Y2O3, Zr-Std, ZrO2, Nb-Std, Nb2O5, Mo-Std, Cd-LStd, Sn-LStd, Hf-LStd, Ta-LStd, W-LStd, Au-LStd and Pb-LStd. For a detailed description see the EXCEL standards.xls file.

Conclusion: In Figure 3.28 all individual values are displayed. Several features can be noticed: Between the elements Ca and Pb the points scatter around an average value, (1.149 +/- 0.0435)$*10^{-7}$, this value is also used as average instrumental constant. One can differentiate between the elements, contained in pure form in the calibration standards, namely elements Ti – Pb, with their sub-group average of (1.165 +/- 0.0215)$*10^{-7}$; and the elements, contained in compounds, which automatically also have binder added, namely elements Ca – Nb, with a sub-group average of (1.133 +/- 0.0543)$*10^{-7}$. There is a systematic difference between the two sub-groups, and not unexpected the standard deviation for elements present in compounds is higher. As a consequence one would obtain slightly different results, by using either only compounds or metals for calibration. From the spread of the points one can conclude, the higher the total number of standards used for calibration the better defined will be the average value and potential troublemakers could be identified and excluded.

For the elements below Ca, namely: Al, Si, P, S and K there is a clear tendency to lower instrument “constant” values with decreasing atomic number. This is an indicator that against all efforts the spectrometer could not be described sufficiently for the low Z elements. For this purpose individual instrument constants can be established for each element where a calibration standard is available. In principle one can do this also for all elements, which can be described by an average constant appropriately. The two demonstration files, Soil.fpc and OrgaMatr.fpc make use of the individual constants for the low Z elements. For the remainder from Ca on the average instrumental constant (established by metals and compounds together) is used. The two instrumental parameter files have individual constants for fluorescence for the low Z elements: Al ($2.70*10^{-8}$), Si ($5.65*10^{-8}$), P ($4.32*10^{-8}$), S ($7.24*10^{-8}$) and K ($8.575*10^{-8}$).

The incorporation of individual instrument constants is preferably achieved by editing of the *.fpc file with a suited text editor (CHAPTER 4: Editing of data files), because for more than one entry per element (e.g. for potassium there are four entries) *only the last* is recognized by the program. Care must be taken that individual constants are incorporated within one run (all relevant *.asr files must be selected from the SELECTOR BOX), because all old entries (for individual instrument constants) of a previous run are overwritten by a new run when **Individual and/or average** is selected for standards (not for samples).

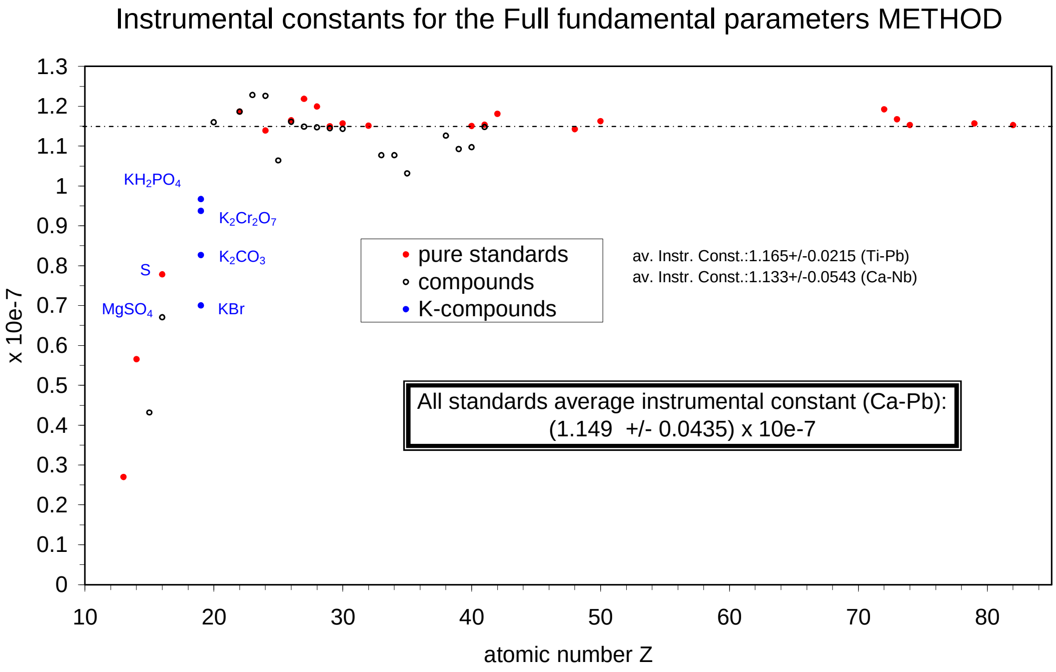


Fig. 3.28. Instrumental constants for all available calibration standards (Rh secondary target spectrometer, 50 kV). Red dots refer to pure element standards, black circles to elements contained in compound. Potassium standards (blue dots) scatter depending on the chemical compound. For pure metals and compound standards different sub-group average values are found, slightly deviating from the total average instrumental constant. For all cases the elements Al, Si, P, S and K were not included into the averaging.

An effort was made to gain further insight for the elements sulphur and potassium. The individual instrument constants are plotted against the concentration of the respective element in the standard; as potential influence parameter also the compound is specified. In contrast to the Elemental sensitivities METHOD potassium in KBr and $K_2Cr_2O_7$ (also phosphorus in KH_2PO_4, which is not included in the graph) can be treated and used for calibration. No clear trend can be found. In the ideal case all individual values would coincide with the total average instrumental constant.

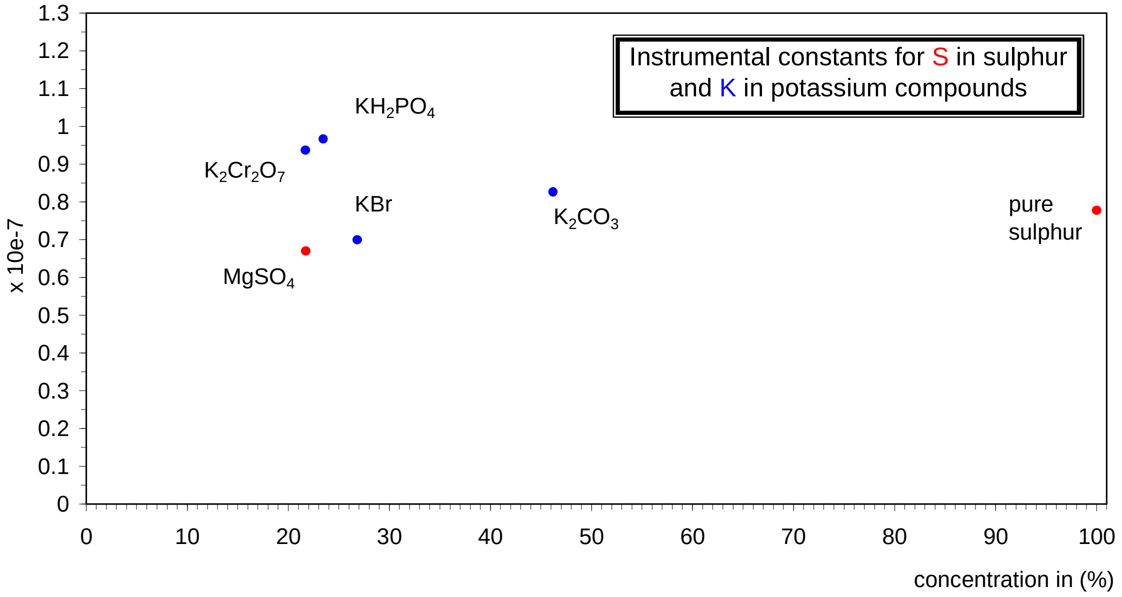


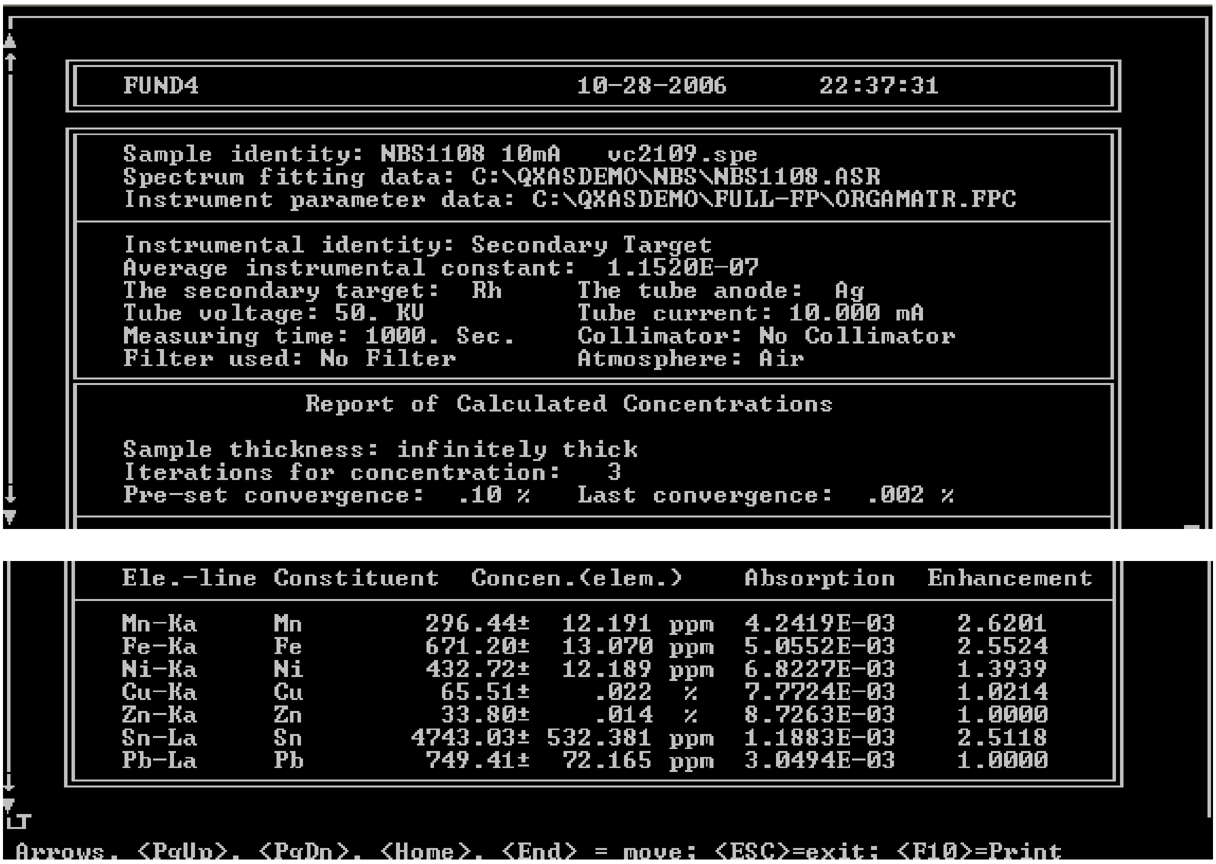
Fig. 3.29. Plot of the average instrumental constants versus element concentration for selected calibration standards, containing sulphur (red dots) and potassium (blue dots).

3.3.3. Application: bronze alloy sample

With the so far achieved calibration (establishment of the average instrumental constant for fluorescence) samples with either well specified matrix or no matrix at all can be treated. The scatter calibration as needed for samples containing a dark matrix will be discussed later (CHAPTER 7: Utilization of the scatter peaks). To test the calibration an alloy reference standard material is well suited. There is no dark matrix contained, but the enhancement effect must be taken into account. For the details of the rather complicated definition of the input model used to fit bronze alloys properly the reader is referred to CHAPTER 6: Use of NBS Alpha coefficients.

3.3.3.1. Use of the average instrumental constant

By use of the predefined instrumental parameter file NBSalloy.fpc and the AXIL fit result file NBS1108.asr (directory: \QXASdemo\NBS) the reference standard material NBS 1108 can serve as example. The equivalent FORMs, as for the calibration for the METHOD already used, have to be passed. For **Select Calculation Mode** this time the default **Sample concentrations** is appropriate. All elements in the sample (Mn, Fe, Ni, Cu, Zn, Sn, Pb) are represented by calibration standards included for the average instrument constant (no low Z elements) the default for the **Type of Instrument Constant: Average** can be used. The FORM **Information on sample** will have to be edited for the tube current value of 10 mA and the **Sample type** must be toggled to **Thick sample** (otherwise one would have to enter the area related mass). The date is of no relevance for tube excitation and all other fields of this FORM can be left unchanged. The next FORM **Menu for setting up options** will need attention. The default of (1) **Sample contains** may not be left at its default, otherwise the presence of a dark matrix will be expected, and together with the data available to the program it will crash. So toggle to **no matrix**. The default of (6) **Secondary enhancement** is not appropriate, it must be changed to **is corrected**. It will be seen from the results, that it is important to correct for the secondary excitation. As rule of thumb, the secondary excitation correction can be selected for every sample, there is no known disadvantage. The default **Normalization of concentrations is applied** (i.e. the sum of all later displayed concentrations will be summed up to 100 %) can be switched off for a first run of samples in order to identify otherwise disguised potential problems. For alloys there is a long lasting dispute whether the normalization is allowed or not. Depending on which party the reader belongs to, the selection should be made. After having gone through all this the final computations are initiated with **Calculations of Geometry constants/Analysis of unknown samp(**le).



```
FUND4                        10-28-2006      22:37:31

Sample identity: NBS1108 10mA    vc2109.spe
Spectrum fitting data: C:\QXASDEMO\NBS\NBS1108.ASR
Instrument parameter data: C:\QXASDEMO\FULL-FP\ORGAMATR.FPC

Instrumental identity: Secondary Target
Average instrumental constant:  1.1520E-07
The secondary target:  Rh      The tube anode:  Ag
Tube voltage: 50. KV           Tube current: 10.000 mA
Measuring time: 1000. Sec.     Collimator: No Collimator
Filter used: No Filter         Atmosphere: Air

              Report of Calculated Concentrations

Sample thickness: infinitely thick
Iterations for concentration:   3
Pre-set convergence:  .10 %    Last convergence:  .002 %

Ele.-line Constituent  Concen.(elem.)     Absorption  Enhancement

Mn-Ka     Mn          296.44±  12.191 ppm  4.2419E-03    2.6201
Fe-Ka     Fe          671.20±  13.070 ppm  5.0552E-03    2.5524
Ni-Ka     Ni          432.72±  12.189 ppm  6.8227E-03    1.3939
Cu-Ka     Cu           65.51±    .022  %   7.7724E-03    1.0214
Zn-Ka     Zn           33.80±    .014  %   8.7263E-03    1.0000
Sn-La     Sn         4743.03± 532.381 ppm  1.1883E-03    2.5118
Pb-La     Pb          749.41±  72.165 ppm  3.0494E-03    1.0000

Arrows, <PgUp>, <PgDn>, <Home>, <End> = move; <ESC>=exit; <F10>=Print
```

Fig. 3.30. Quantitative results obtained with the Full fundamental parameters method for the reference standard material NBS 1108.

In the displayed results, contained in the column **Enhancement**, the correction factor for the respective element can be found. This can be interpreted for e.g. Mn that its concentration would be overestimated by factor of 2.6 when the correction is not applied. Except Zn and Pb (they only enhance the other elements) all elements are influenced by the others in respect to the secondary excitation substantially (Mn, Fe, Sn) or at least not negligible (Ni, Cu).

Table 3.3. Comparison with certified values in (%), for both experimentally obtained results (average and individual instrumental constants); the concentration values are normalized.

	Mn	Fe	Ni	Cu	Zn	Sn	Pb
measured (average instrumental constant)	0.030	0.067	0.043	65.51	33.80	0.47	0.075
measured (individual instrumental constants)	0.032	0.066	0.042	65.66	33.65	0.47	0.075
certified value	0.025 +/- 0.001	0.05 +/- 0.001	0.033 +/- 0.001	64.95 +/- 0.05	34.42 +/- 0.05	0.39 +/- 0.01	0.063 +/- 0.001

3.3.3.2. Definition and use of individual instrumental constants

In case one prefers individual instrumental constants also for elements, otherwise well covered by the average instrumental constant, the individual instrumental constants for the elements Mn, Fe, Ni, Cu, Zn, Sn and Pb must be defined. Use the instrument parameter file NBSalloy.fpc or, to work without predefinitions: test.fpc, but not Soil.fpc or OrgaMatr.fpc, otherwise their individual constants, as needed later, were overwritten. Due to the targeted creation of individual instrumental constants, it is not necessary to have the average instrumental constant defined for this file. As outline in the previous, only one standard can be used per element (for more than on standard per element the relevant *.fpc must be edited manually for incorporating the averaged value entry, as detailed in CHAPTER 4: Editing of data files). The pure element calibration standards' *.asr files: Fe-Std, Ni-Std, Cu-Std, Zn-Std, Sn-Std and Pb-LStd, and MnO2.asr (compound mixed with binder) were selected to contribute. All of them must be processed in one run.

```
Select unknown or standard files (*.ASR)
C:\QXASDEMO\ASR-STDS\TEMP

 ..\
* ZN-STD.ASR
* MNO2.ASR
* FE-STD.ASR
* PB-LSTD.ASR
* SN-LSTD.ASR
* CU-STD.ASR
* NI-STD.ASR
```

*Fig. 3.31. Selection of calibration standards in order to establish individual instrumental constants, that will be written to the *.fpc file.*

With the exception of the FORM **Type of Instrument constant**, where one will toggle from the default to **Individual and/or average**, all steps for establishing the individual instrumental constants are in analogy with Calibration standard example: K-KBr.asr.


Type of Instrument Constant

Instrument constant type: Individual and/or average

*Fig. 3.32. After having selected as Instrument constant type: Individual and/or average, calibration standards will generate individual entries in the *.fpc file. Having created such individual constants, for samples the option Individual and/or average will make use of these constants for elements were they are available.*

The finally obtained individual instrumental constants (**Instr. constant**) for the seven standards are stored automatically into test.fpc; there is no need to save the results.

The only difference in the treatment of the sample file NBS1108.asr, as compared to calculations using the average instrumental constant, is the selection of **Individual and/or average** in the FORM **Type of Instrument constant**. There are no significant differences observed between the results obtained with either average or individual instrumental constants for the standard reference material NBS 1108.

CHAPTER 4. EDITING OF DATA FILES

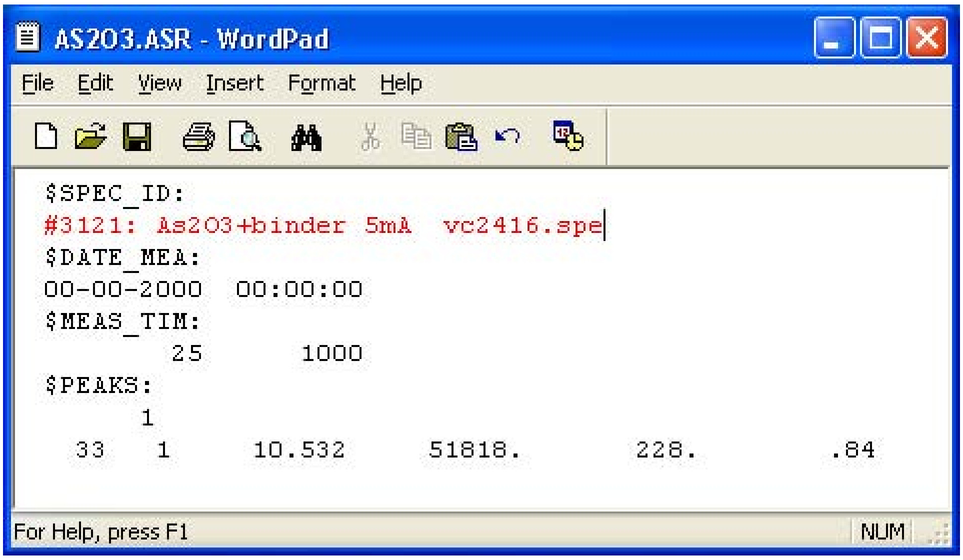
The data files in QXAS are block-structured. Each file is divided in blocks that are identified by a header name with ”$” as the first character and “:” as last. The order of the blocks is random, but within each block the data is well defined. Each program in the package searches, modifies and writes only the blocks known to that program, leaving all other blocks unchanged. The most important block-structured ASCII file is the set-up file setup.ax, in which all the information on the current status of the package is given. This file contains the menu-tree of all the installed programs in the package, the general information for all these programs and the name of the files in use by the package. Some file names are passed from one run to the next so they are will be used as default. Programs can use the same data files without having to know all the details. Modifications to one program have little or no influence on other programs. Examples, when it is necessary or profitable to edit data files, are many.

Note: the rigid syntax of the files has to be maintained at any rate; with only a few exceptions, like the number of space characters (separating number values) or the text of spectrum headers (block $SPEC_ID:).

4.1. Editing of spectrum files (*.spe)

Many times it will be helpful, and by QA requirements it is strongly recommend, to modify the *.spe file header, that should carry information in order to uniquely identify a spectrum when working with AXIL. This information is further passed on to the result file (*.asr) as used for all quantitative METHODs.

Example: in As2O3.spe (directory \QXASdemo\SPE-Sts), the otherwise empty line following the header identifier **$SPEC_ID:**, was edited such that the identification number from the sample preparation log book, a brief description of the standard itself, the tube current and the spectrum name from the spectrometer log book will be displayed, when the file is loaded into AXIL.



```
$SPEC_ID:
#3121: As2O3+binder 5mA  vc2416.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
        25       1000
$PEAKS:
      1
  33   1      10.532      51818.        228.         .84
```

Fig. 4.1. WordPad representation of the file As2O3.asr. Text in red refers to the changes made to the original file.

Example: For spectra acquired with an ORTEC MCA a problem was encountered that is revealed for source excitation, when the so-called decay correction is to be calculated. The date format in the spectrum header is differently defined as expected by QXAS. For the example Cr.spe (directory \QXASdemo\Cd-109\SPE-INP), measured with Cd-109 excitation source, the modification should be:

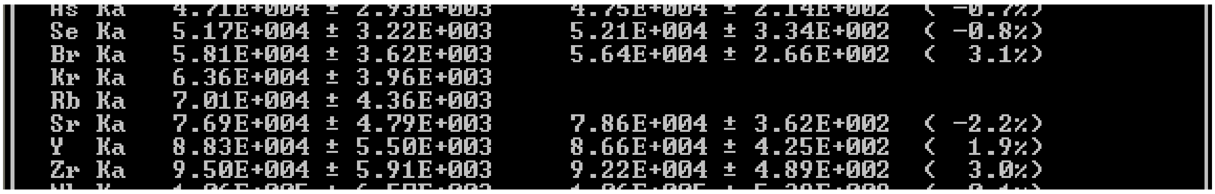
```
$SPEC_ID:
Cr-Std  12/7/06  cd0002.spe
$SPEC_REM:
DET# 1
DETDESC# NAALXRF-GUEST1A MCB 9
AP# Maestro Version 6.01
$DATE_MEA:
07/12/2006 16:33:50

$MEAS_TIM:
100 102
$DATA:
0 2047
       0
       0
       0

       etc.
```

→

```
$SPEC_ID:
Cr-Std  12/7/06  cd0002.spe
$SPEC_REM:
DET# 1
DETDESC# NAALXRF-GUEST1A MCB 9
AP# Maestro Version 6.01
$DATE_MEA:
07-12-2006 16:33:50

$MEAS_TIM:
100 102
$DATA:
0 2047
       0
       0
       0

       etc.
```

4.2. Editing of calibration files (*.cal)

The step **Polynomial fit of sensitivities** is not recommended / prohibited (according to QA requirements). Nevertheless, a calibration file *.cal (directory \QXASdemo\ElSens) can been processed with **Polynomial fit of sensitivities** and the relevant calibration data, for Rb (7.01E+004 +/- 4.36E+003), as an example, must be noted.



```
 As Ka   4.71E+004 ± 2.93E+003     4.75E+004 ± 2.14E+002  ( -0.7%)
 Se Ka   5.17E+004 ± 3.22E+003     5.21E+004 ± 3.34E+002  ( -0.8%)
 Br Ka   5.81E+004 ± 3.62E+003     5.64E+004 ± 2.66E+002  (  3.1%)
 Kr Ka   6.36E+004 ± 3.96E+003
 Rb Ka   7.01E+004 ± 4.36E+003
 Sr Ka   7.69E+004 ± 4.79E+003     7.86E+004 ± 3.62E+002  ( -2.2%)
 Y  Ka   8.83E+004 ± 5.50E+003     8.66E+004 ± 4.25E+002  (  1.9%)
 Zr Ka   9.50E+004 ± 5.91E+003     9.22E+004 ± 4.89E+002  (  3.0%)
```

Fig. 4.2. Interpolation of Rb obtained with Polynomial fit of sensitivities.

Next, the calibration has to be re-run with order 0 for the polynome (**Order of polynomial (0=no fit)**: 0). Consequently the calibration points are not fitted at all and the original calibration points are not biased. Finally, outside of the QXAS environment, the relevant data for Rb is pasted into the now unfitted calibration file and the total number of available sensitivities (**$ CAL_SENS:**) is increased from 22 to 23.

```
$EXP_COND:
0
09-28-2006
0 0
SecTarget-Rh
45.0  45.0  1.4142   1.4142
20.600
50.00  0.00
$STAND:
24

      etc.

$CAL_SENS:
22
16 1 1.346E+003 5.922E+002
19 1 2.120E+003 3.286E+002
20 1 3.805E+003 2.130E+001
22 1 6.640E+003 3.760E+001
23 1 8.617E+003 5.403E+001
24 1 1.164E+004 3.676E+001
25 1 1.217E+004 7.200E+001
26 1 1.749E+004 8.758E+001
27 1 2.061E+004 1.265E+002
28 1 2.599E+004 1.196E+002
29 1 2.946E+004 1.506E+002
30 1 3.561E+004 1.744E+002
32 1 4.414E+004 2.205E+002
33 1 4.745E+004 2.141E+002
34 1 5.211E+004 3.336E+002
35 1 5.554E+004 5.785E+001
38 1 7.864E+004 3.621E+002
39 1 8.661E+004 4.251E+002
40 1 9.217E+004 4.890E+002
41 1 1.055E+005 5.384E+002
42 1 1.152E+005 5.617E+002
82 2 2.874E+004 1.691E+002
```

```
$EXP_COND:
0
09-28-2006
0 0
SecTarget-Rh
45.0  45.0  1.4142   1.4142
20.600
50.00  0.00
$STAND:
24

      etc.

$CAL_SENS:
23
16 1 1.346E+003 5.922E+002
19 1 2.120E+003 3.286E+002
20 1 3.805E+003 2.130E+001
22 1 6.640E+003 3.760E+001
23 1 8.617E+003 5.403E+001
24 1 1.164E+004 3.676E+001
25 1 1.217E+004 7.200E+001
26 1 1.749E+004 8.758E+001
27 1 2.061E+004 1.265E+002
28 1 2.599E+004 1.196E+002
29 1 2.946E+004 1.506E+002
30 1 3.561E+004 1.744E+002
32 1 4.414E+004 2.205E+002
33 1 4.745E+004 2.141E+002
34 1 5.211E+004 3.336E+002
35 1 5.554E+004 5.785E+001
37 1 7.010E+004 4.360E+003
38 1 7.864E+004 3.621E+002
39 1 8.661E+004 4.251E+002
40 1 9.217E+004 4.890E+002
41 1 1.055E+005 5.384E+002
42 1 1.152E+005 5.617E+002
82 2 2.874E+004 1.691E+002
```

Rubidium results for unknown samples might have a higher uncertainty, but all other elements, represented by measured calibration points, are well defined.

4.3. Removing element entries from *.asr files

For the sake of an appropriate fit sometimes elements have to be included but for final results as obtained by quantitative METHODs should be suppressed: Within a defined ROI all peaks must be defined in order to enable an optimized fit. One example to suppress an element from a report is the use of energy values instead of an element symbol (e.g.: **X-LINES ADD 2.7**

2.8 2.9 instead of **RH-L**). Alternatively, all necessary elements are included for the fit, but the *.asr file can be edited. E.g. the air filter spectrum AirFilt.spe was fitted with all elements as identified by peaks, but due to the problem with the blank spectrum several elements' entries were removed from the original AirFilt.asr file (directory \QXASdemo\ElSens) in order to suppress the mistaken use of results for elements that should not be quoted.

```
$SPEC_ID:
Ref Std: SRM2783, #267, 40mA  vc2406.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
      1000      1000
$PEAKS:
      9
  14   1      1.740       160.         6.        .73
  20   1      3.691       153.         5.       1.28
  26   1      6.399      1910.        14.       2.55
  28   1      7.472        57.         3.        .82
  29   1      8.041       152.         4.       2.06
  30   1      8.631       274.         6.       1.27
  38   1     14.142       254.         5.        .63
  42   1     17.443       387.         8.       1.33
  82   2     10.542        48.         2.       1.29
```

Consequently the edited version AirF-cor.asr will only enable to get quantitative results for the elements Si, Ca, Fe and Zn. Edit also the total number of fluorescence net peak areas (**$PEAKS:**): from 9 to 4.

```
$SPEC_ID:
Ref Std: SRM2783, #267, 40mA  vc2406.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
      1000      1000
$PEAKS:
      4
  14   1      1.740       160.         6.        .73
  20   1      3.691       153.         5.       1.28
  26   1      6.399      1910.        14.       2.55
  30   1      8.631       274.         6.       1.27
```

4.4. Individual instrumental constants in instrument parameter files (*.fpc)

Individual instrumental constants are used for the **Full Fundamental Parameters** METHOD at least for low Z elements. The METHOD inherent approach to incorporate these constants will only allow for one standard per element. A way to overcome this shortcoming is to edit instrument parameter files, e.g. Soil.fpc or OrgaMatr.fpc. The instrumental constants for the standards of relevance for this problem are obtained from the *.asr files: Al-Std, Si-wafer, P-KH2PO4 (for phosphorus), K-KH2PO4 (for potassium), S-Std, MgSO4 (for sulphur), K2CO3, K2-Cr2O7 (for potassium) and K-KBr (for potassium). For Al ($2.70*10^{-8}$), Si ($5.65*10^{-8}$) and P ($4.32*10^{-8}$) the constants could also have been generated by the program directly, but for sulphur two standards are available: S-Std ($7.78*10^{-8}$) and MgSO4 ($6.70*10^{-8}$); for potassium even four standards: K-KH2PO4 ($9.67*10^{-8}$), K2CO3 ($8.26*10^{-8}$), K2-Cr2O7 ($9.37*10^{-8}$) and K-KBr ($6.999*10^{-8}$). For sulphur the average constant $7.24*10^{-8}$, for potassium the average constant $8.575*10^{-8}$ will be used. The entries to be incorporated have to follow strictly the syntax rules for the *.fpc files.

```
$INDIV_INSTRU_CONSTS:
13     1     2.70E-08
14     1     5.65E-08
15     1     4.32E-08
16     1     7.24E-08
19     1     8.57E-08
```

+

```
$EXCIT_MODE:
1
$EXCIT_DATA:
47 4.00 3.000e-002
50.00 50
45 45.00 45.00 74
$EXCIT_SPECT:
1.2753E+010 20.216
6.6932E+009 20.074
2.4509E+009 22.724
1.2578E+009 22.699
6.1308E+008 23.173
1.7610E+007 2.916
1.0322E+007 2.892
1.8506E+006 3.364
      etc.
```

⇒

```
$INDIV_INSTRU_CONSTS:
13     1     2.70E-08
14     1     5.65E-08
15     1     4.32E-08
16     1     7.24E-08
19     1     8.57E-08
$EXCIT_MODE:
1
$EXCIT_DATA:
47 4.00 3.000e-002
50.00 50
45 45.00 45.00 74
$EXCIT_SPECT:
1.2753E+010 20.216
6.6932E+009 20.074
2.4509E+009 22.724
1.2578E+009 22.699
6.1308E+008 23.173
1.7610E+007 2.916
1.0322E+007 2.892
1.8506E+006 3.364
      etc.
```

4.5. File format of (*.asr) files as expected by the NBS METHOD

The original AXIL result file of the copper calibration file Cu-Std.asr (directory \QXASdemo\ASR-Stds) as expected by other quantitative METHODs is not adequate for the **NBS alpha coefficients** METHOD.

```
$SPEC_ID:
Cu 100% 5mA vc2099.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
        40      1000
$PEAKS:
      1
  29   1      8.041     50520.       226.       1.67
```

Certain other element entries, as imposed by the elements found in the unknown sample *and* also in the other calibration standards must be represented by rows. Following the syntax of *.asr files, their atomic number, an entry of either 1 or 2 - for either K_α or L_α-peak representation, its characteristic energy, the net peak area, its standard deviation established during the AXIL fit and the individual Chi square value must be contained. Of relevance is the net peak area. As another complication the copper calibration standard had been measured with 5 mA tube current, but the sample with 10 mA. The **NBS** METHOD can neither handle variable tube current nor decay corrections for the case of source excitation, therefore the net peak area is multiplied by a factor of 2, in order to correct to the expectation value at the double current. Edit also the total number of fluorescence net peak areas (**$PEAKS:**): from 1 to 7. Instead of a value of 0.0 for the net peak area for the elements that had to be included for the sake of the program, the (lowest possible) value 0.1 was entered, in order to suppress warning messages. No attention was paid to the standard deviations and Chi squares, none of them is used. All these alterations to the original file had been saved as Cu-NBS.asr (directory \QXASdemo\NBS), now ready for creation of a correct standard description file Cu-NBS.std. In analogy all other *.asr files as needed for the calibration had been edited, with the exception of NBS1108.asr, which represents the reference standard material NBS 1108, and has all seven elements present in the spectrum.

```
$SPEC_ID:
pure Cu 5mA vc2099.spe "Intx2"
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
        40      1000
$PEAKS:
      7
  26   1      6.41          0.1         0.          0.
  28   1      7.47          0.1         0.          0.
  29   1      8.041    101040.          0.          0.
  30   1      8.64          0.1         0.          0.
  82   2     10.54          0.1         0.          0.
  50   2      3.44          0.1         0.          0.
  25   1      5.89          0.1         0.          0.
```

4.6. Source description files (*.sou)

During the use of the METHOD **NBS alpha coefficients** and for the utility **Incident and take-off angles** source description files (*.sou) have to be loaded. Such files have to be created and filled with relevant data. Most important are the entries for the correct incident and take-off angle in respect to the sample surface and the assumed spectral distribution of the primary radiation exciting the sample. As a speciality of this file type instead of energy values for the description of the primary spectrum of, e.g. the secondary target or the radioactive source, corresponding wavelength values in (Angstrom) must be used. The conversion is rather simple:

$$\lambda(Angstrom) = \frac{12.396}{E(keV)} \tag{4.1}$$

Example: For the Rh secondary target with K-energy values of 20.216 keV ($K_{\alpha1}$), 20.074 keV ($K_{\alpha2}$), 22.724 keV ($K_{\beta1}$), 23.173 keV ($K_{\beta2}$) and 22.699 keV ($K_{\beta3}$), which were converted with the above formula, and using the respective relative intensities the file Rh-K.sou was created (directory \QXASdemo\NBS).

```
$IDENT:
Rh secondary target (K-Lines), Ag anode - 50kV
RH
50.
$GEOM:
45.,45.
$CONTINIUM:
2
1.,0.
1.2,0.
$CHARLIN:
5
.61318,53.65
.61752,28.15
.54550,10.32
.54610,5.30
.53493,2.58
```

Example: For the excitation with the Cd-109 source, emitting silver K radiation (treated as K_α and K_β) and a γ-line of 88 keV the source description file Cd-109.sou (directory \QXASdemo\Cd-109) is adequate – but only for the geometry of the used spectrometer. It contains the angles as found by the Monte Carlo approach implemented in the utility **Incident and take-off angles, Geometry constants, *.sen file**.

```
$IDENT:
Cd-109 annular source: incident/take-off angle: 75.0 / 77.0 degrees
Cd 109
0.
$GEOM:
75.0,77.0
$CONTINIUM:
2
1.,0.
1.2,0.
$CHARLIN:
3
.5608,82.770
.4961,17.230
.1408,3.74
```

4.7. Editing of *.asr files to bring the scatter peak information obtained with the COMMAND SCAT_ROI to a format expected by quantitative METHODs.

Three different approaches for obtaining the scatter peak information are proposed (CHAPTER 7), others exist. The use of the AXIL COMMAND **SCAT_ROI** will not fit the scatter peaks, but sum up the channel contents within the ROI. Unfortunately, saving of the so obtained peak areas is not in the format as expected by the quantitative METHODs. When this approach is utilized, it is advisable to edit the so obtained *.asr file. For the example of the spectrum HWC.spe (directory \QXASdemo\FP-scatt\SPE), treated with the input model HWC-3.inp (directory \QXASdemo\FP-scatt\INP), the file HWC-3.asr (directory \QXASdemo\FP-scatt) has to be manipulated in order to obtain the standardized *.asr file.

```
$SPEC_ID:
HWC-binder 50/40/1000 vc2401.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
      1000      1000
$COH_SCAT:
      0
  1615.  1670.    491253.         0.    491253.       701.
$INC_SCAT:
      0
  1250.  1610.   3557881.         0.   3557881.      1886.
```

```
$SPEC_ID:
HWC-binder 50/40/1000 vc2401.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
      1000      1000
$COH_SCAT:
      1
  45   1      20.167     491253.       701.       0.0
$INC_SCAT:
      1
  45   1      19.401    3557881.      1886.       0.0
```

CHAPTER 5. EMISSION TRANSMISSION METHOD

References: [54], [27], [28]

The **EMISSION TRANSMISSION (ET)** METHOD is restricted to *intermediate thick samples* in terms of XRF (in practical terms they have to be less than 1 mm thin). This technique corrects adequately the absorption caused by those elements, which are not recognized by characteristic lines in the spectrum – the *dark matrix*.

A carefully selected irradiator, the so called target (its characteristic lines should not interfere with the ones of the sample), is positioned at the backside of the unknown sample and is excited by the excitation source. In a second measurement the sample is removed and the irradiator is kept at the same position. Finally the unknown sample is excited in a third measurement without the irradiator. As a consequence three *.asr files are needed in order to analyze unknown samples with an unspecified matrix. The intensity ratios of the characteristic lines of the target are used to calculate the energy dependent matrix absorption and, by interpolation, absorption correction factors for selected elements in the sample. The target can either be a pressed pellet, mixed from simple compounds, or a set of pure element standards (metals) can be used instead. The sample element range is defined by the first and the last target element, for which the absorption correction factors are calculated. When the intensity ratio for a target element becomes too high, it is not considered for the absorption calculation; the sample element range will become narrower. As basic assumption of this METHOD the *excitation source must be monoenergetic*. To fulfil this requirement, at least partially, either a secondary target set-up or isotope source excitation has to be used. The **ET** METHOD is applicable with good precision for fluorescing elements in the minor and trace element range.

The calibration for this METHOD is to be established with the METHOD **Elemental sensitivities** previously and is loaded into this METHOD with **Select calibration file**.

Certain measuring parameters must be defined by activating **Change Measuring Parameters**. If applicable, for source excitation, the half-life of the excitation source is defined with an input for **HalfL**. (in days), which will correct for the decay of the excitation source in between the calibration and the measurement of unknown samples. **Incid.A**. and **Emerg.A**. refer to incident and take-off angle in respect to the sample surface and **S.Diam.** is the diameter of the sample (in cm). For tube excitation there is the possibility to measure the unknown sample's spectrum with a different (higher) current, **Cur(S)**, than the target plus sample and target only spectra (**Cur(T)**).

With **Select Files for Analysis**) three SELECTOR BOXes open consecutively, and an *.asr file has to be choose in this order:

- sample *.asr file from first box (**Select Sample file (*.ASR)**)
- target *.asr file from second box (**Select Target file (*.ASR)**)
- sample plus target *.asr file from third box (**Select Sample + Target file (*.ASR)**)

There is no consistency check! An input for the sample mass in (g) is needed.

Define File to Save Analysis Results enables to create an already previously created file for saving the results (*.arp) or to retrieve a new one.

Warning: Such a file *must be* created / selected before the final calculation step – otherwise the program will crash QXAS during the calculations for the *next* sample.

With an applicable calibration file loaded, the measuring parameters correctly defined, three appropriate *.asr files loaded and the mandatory definition of the result file, the absorption correction calculation can be initiated with: **Perform calculation of Concentrations**. A list of proposed target elements together with their net peak areas pops up. The user has to select appropriate elements for the absorption correction calculation, trace elements should be omitted. At least three entries have to be marked. For a too high absorption for a target element, which is more likely for elements with lower atomic number, it will not be used for the calculation. I.e., when the ratio $I^{target}/I^{target+sample} > 20$ (equivalent to $\ln(\ln(I^{target}/I^{target+sample})) > 1.097$. For the other elements a linear regression of the form ln(ln(*a*)) versus ln(*E*) (attenuation coefficient *a*, energy *E*) is displayed. ***Fact*** is the sample self absorption correction factor. (*Both:* log*E* and Lg(*E*) stand for the natural logarithm.) When the regression coefficient (**regress**) is smaller than 0.99, usually one or more elements will be removed from the list. A higher standard deviation (**stdev**) value is usually only an indicator of what can be already seen in the plot: the target element points scatter around the fitted line. The expectation value for the **slope** is around 2.8. Rather cryptic (**Enter Element to start iter.:**), the chemical symbol of an element can be entered for which an edge correction should be considered. The edge correction refers to the sample and makes sense for elements with concentration values expected to be greater than 1 % (such a correction will be applied only after a first run without any edge correction). It applies to the selected element and to all others in the sample with lower atomic number.

5.1. How to compose the target?

In the ideal case one would mix a target according to the sample spectrum of a certain class of samples. For many users this is a bit unrealistic, one will usually try to find a compromise. First of all one has to get a chemical compound containing a fluorescing element with rather low atomic number which is not present in the sample. The lower its characteristic line energy the better; with the constraint that the line is “not completely” absorbed when passing through the sample. Usually potassium and calcium are present in samples, sulphur and chlorine lines will usually suffer already too much from absorption. Potential candidates are Sc, Ti, V or Cr. The concentration of this compound must dominate the target composition. All other target elements should cover uniformly the sample spectrum in terms of energy, preferably with decreasing concentration with increasing atomic number. They should not be present in the sample, at least not dominant, like e.g. Fe in reference standard material Soil 7. In principle the METHOD accounts for these coincidences, the sample contribution is subtracted from the sample plus target spectrum, but a higher uncertainty for such a target element can be related to this fact.

5.1.1. Example: Targets B – F

The approximate composition of five targets (B, C, D, E, F), with respective spectra, TargetB.spe – TargetF.spe (target T1 is identical to TargetB, but different spectra were recorded), is: V = 42 % (V2O5), Co = 7 % (CoO), Cu = 5 % (CuO), Se = 1 % (SeO2), Sr = 0.3 % (SrCO3), Mo = 0.3 % (MoO3), with 5 % binder (HWC, as $C_{38}H_{76}N_2O_2$) added. Target A has a similar composition, with slightly different concentrations, but Sr is missing. All concentration values had been selected to have comparable heights for the target element peaks with a representative sample (intermediate thick Soil 7 pellet) in front. After careful mixing of all components the six pellets were pressed with 10 tons weight.

Table 5.1. Concentration values for elements in synthetic targets B - F and acquistion time and tube current for the accumulative "target".

	Targets B - F (#3114-3118)					
	V (V_2O_5)	Co (CoO)	Cu (CuO)	Se (SeO_2)	Sr ($SrCO_3$)	Mo (MoO_3)
concentration (%)	42.58	7.47	5.31	1.35	0.28	0.32

	pure metals					
	Ti	Cr	Co	Cu	Ge	Mo
live time (s) / tube current (mA)	400 / 40	50 / 40	30 / 10	25 / 5	10 / 5	4 / 5

5.1.2. Example: Accumulative counting of pure targets

As alternative approach to the preparation of a suited compound target, the target and target plus sample measurements can be replaced by pure (metal) targets accumulative counting. For the example spectrum TMetal.spe as first target element the Ti calibration standard was measured for 400 s with 40 mA tube current. The Ti was replaced after the first measurement by Cr, but its spectrum was counted onto the Ti spectrum for extra 50 s with 40 mA. After Cr was replaced by Co, the spectrum was acquired again for 30 s with 10 mA. This was continued in the same manner for Cu (25 s, 5 mA), Ge (10 s, 5 mA) and Mo (4 s, 5 mA). The accumulative spectrum, containing all the lines of the named elements was totally counted for 519 s. The same procedure was repeated, but for the second round (with equal counting times and current settings for all standards) with the sample (Soil 7) in front. The settings for the live time for the individual “target” elements had been selected to have comparable counts in the peaks of the “target” plus sample in front spectrum, the tube current was modified to adjust the dead time.

5.1.3. Example: Sample Soil 7 and target T1

Demonstration files (directory \QXASdemo\ET):

- Calibration file:.Soil7.cal
- Spectra: Soil7-1.spe, T1.spe, S7-1_T1.spe (directory \QXASdemo\ET\SPE)
- Input files: S7-1.inp, T1.inp, S7-1_T1.inp (directory \QXASdemo\ET\INP)
- AXIL result files: Soil7-1.asr, T1.asr, S7-1_T1.asr

The sample was pressed as pellet with 2.5 cm diameter and consists of equal parts of the reference standard material IAEA Soil 7 and binder. As binder HWC (chemical formula: $C_{38}H_{76}N_2O_2$) was used. The total mass of the intermediate thick pellet is 0.1055 g. The sample spectrum Soil7-1.spe was acquired for 1000 s, with a tube current of 40 mA. For the Rh secondary target the incident and take-off angle are 45^0, respectively. The path length in air is 0.5 cm.

In the fit model (S7-1.inp) the matrix of the sample was defined (50 % HWC, 50 % Soil 7). The characteristic lines of the following elements had been included:

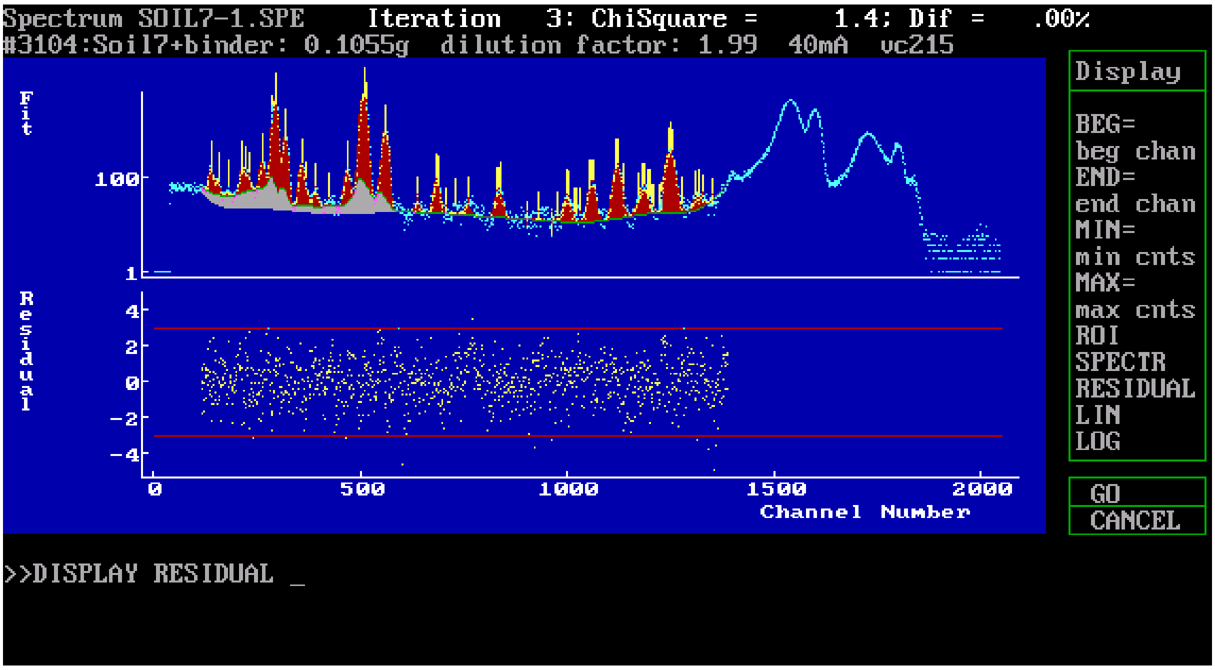
X-LINES ADD: SI K CA-KA* CA-KB* TI MN FE-KA* FE-KB* CU ZN RB SR Y ZR-KA NB-KA PB AS

Note: Description of sample SOIL 7, used to acquire Soil7-1-spe, and the input model details to generate Soil7-1.asr can be found in the EXCEL soil7_description.xls file.

Due to the dominance of Ca and Fe, both element entries were split into K_α and K_β and the escape peaks and peak shape corrections were included. Furthermore for the sake of Si the Rh L scatter region had been defined:

X-LINES ADD: SUM 2.7 2.8 2.9

As will be seen from the later obtained results, silicon needed not to be included, therefore also not the Rh L scatter region, but for the time being one is interested is the behaviour of this METHOD to low Z elements. There are blank problems with the element copper; it resulted in a count rate of 0.1 counts/second – definitely not 10 times higher than the Cu instrument blank value. Not included were elements like: Cr, because the Fe K_β escape peak will potentially mislead its quantification; Ni, because of the proximity to the strong Fe K_β signal; Kr, because the peak at 12.6 keV is rather Pb L_β. The AXIL fit result was saved under Soil7-1.asr.



```
Spectrum SOIL7-1.SPE    Iteration    3: ChiSquare =     1.4; Dif =    .00%
#3104:Soil7+binder: 0.1055g  dilution factor: 1.99  40mA  vc215
```

```
>>DISPLAY RESIDUAL _
```

Fig. 5.1. AXIL fit of Soil7-1.spe.

The spectra of the target (T1.spe) and target plus sample (S7-1_T1.spe) were measured with a tube current of 40 mA. The spectrum for the sample (Soil7-1.spe) was acquired for 1000 s live time, whereas the target and target plus sample spectra were acquired for 200 s, respectively.

Note: Description of the target used in combination with the Soil 7 sample, and the input model details to generate T1.asr and S7-1_T1.asr can be found in the EXCEL target1_description.xls file.

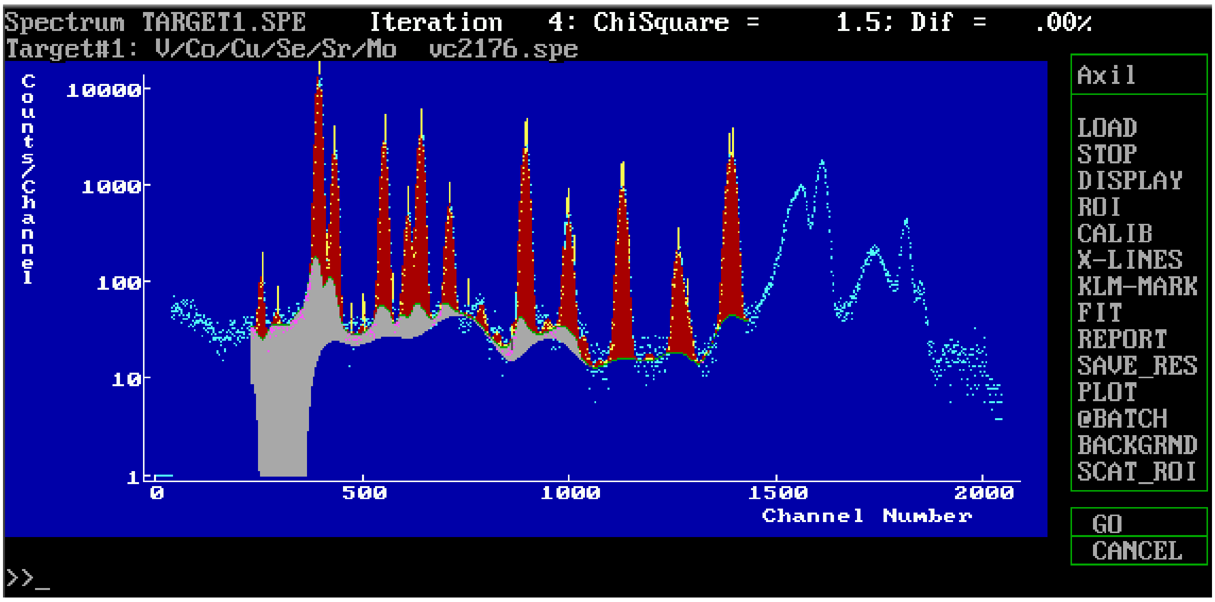
The target was fitted with split K_α and K_β lines and peak shape corrections (input model files T1.inp, S7-1_T1.inp):

X-LINES ADD: V-KA* V-KB* CO-KA* CO-KB* CU-KA* CU-KB* SE-KA* SE-KB* SUM

For Sr and Mo no peak shape correction exists, they were included with:

X-LINES ADD: SR-KA+ SR-KB+ Mo-KA

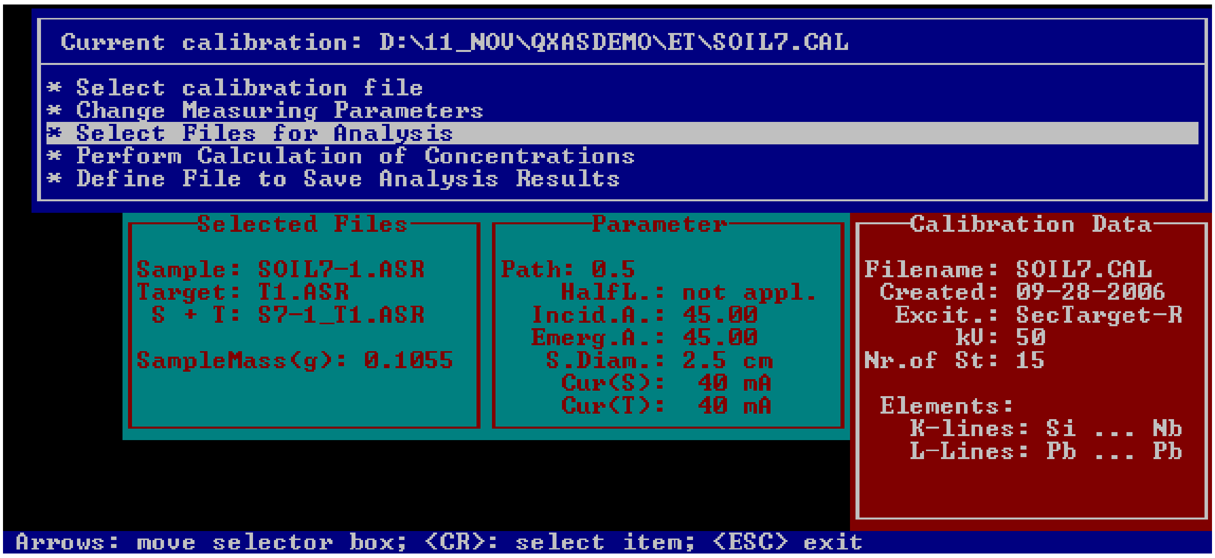
The fit results were saved under T1.asr and S7-1_T1.asr.



```
Spectrum TARGET1.SPE     Iteration   4: ChiSquare =      1.5; Dif =    .00%
Target#1: V/Co/Cu/Se/Sr/Mo   vc2176.spe
>>_
```

Fig. 5.2. . AXIL fit of T1.spe.

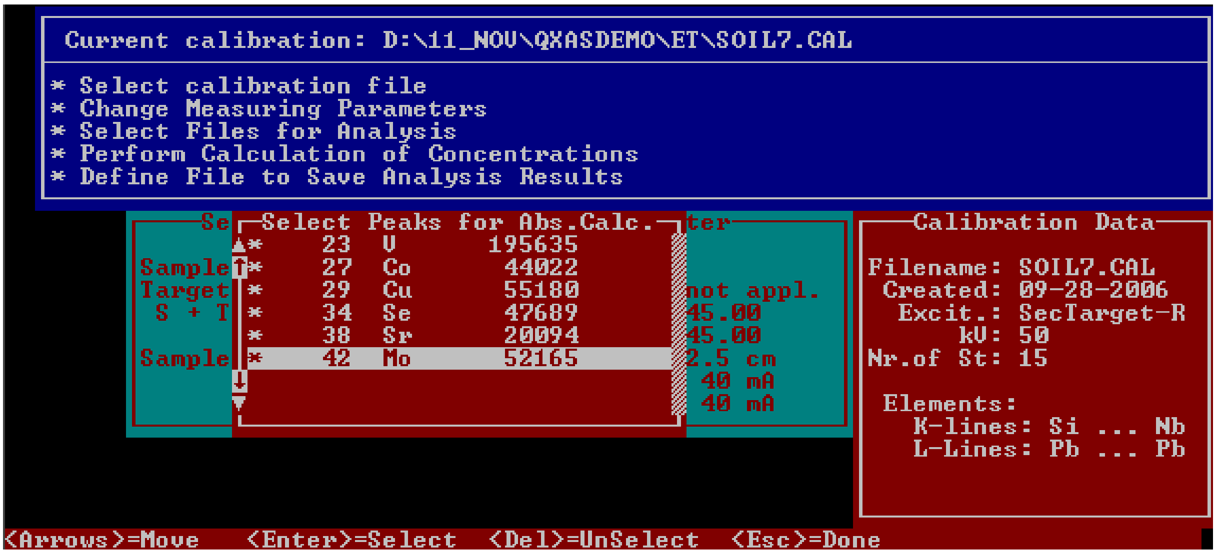
A calibration file Soil7.cal suited for the sample was created with the METHOD **Elemental sensitivities**. Twenty-one calibration standards' *.asr files were included: Si-wafer, K2CO3, K-KH2PO4, CaCO3, Ti-Std, TiO2, MnO2, Fe-Std, Fe2O3, Cu-Std, CuO, Zn-Std, ZnO, As2O3, SrCO3, Y2O3, Zr-Std, ZrO2, Nb-Std, Nb2O5 and Pb-LStd. All elements (except Rb) identified in the demonstration sample can be represented by elements contained in at least one calibration standard. The Rb sensitivity value of (7.15 +/- 0.241)*10^4 had been obtained (**Polynomial fit of sensitivities**) from the optimum fit with a linear polynome of order 4, weighted option. After the polynomial fit the calibration was refitted with order 0 (no fit), in order to use the original calibration points data. Finally the Rb value was pasted into this calibration file.



```
Current calibration: D:\11_NOV\QXASDEMO\ET\SOIL7.CAL

* Select calibration file
* Change Measuring Parameters
* Select Files for Analysis
* Perform Calculation of Concentrations
* Define File to Save Analysis Results

Selected Files
Sample: SOIL7-1.ASR
Target: T1.ASR
 S + T: S7-1_T1.ASR

SampleMass(g): 0.1055

Parameter
Path: 0.5
    HalfL.: not appl.
  Incid.A.: 45.00
  Emerg.A.: 45.00
   S.Diam.: 2.5 cm
    Cur(S):  40 mA
    Cur(T):  40 mA

Calibration Data
Filename: SOIL7.CAL
 Created: 09-28-2006
  Excit.: SecTarget-R
      kV: 50
Nr.of St: 15

 Elements:
   K-lines: Si ... Nb
   L-Lines: Pb ... Pb

Arrows: move selector box; <CR>: select item; <ESC> exit
```

*Fig. 5.3. After the selection of the calibration file and definition of measuring parameters, three relevant *.asr files must be loaded.*

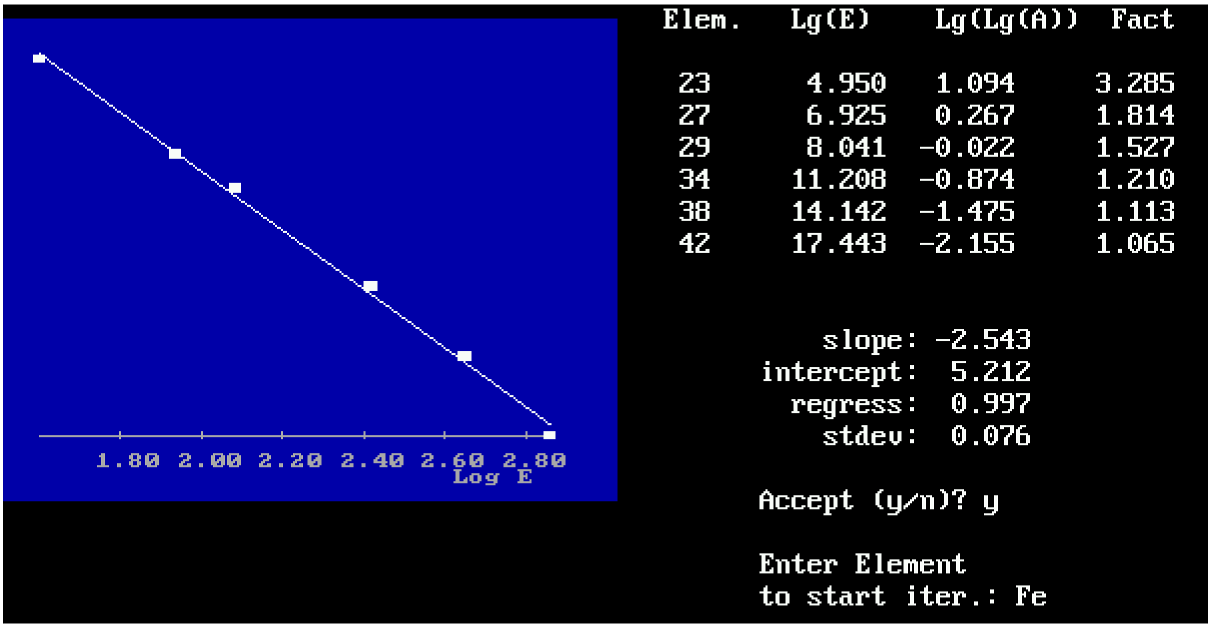
After having selected the correct files and entered the sample mass, all proposed target elements (V, Co, Cu, Se, Sr and Mo) will be selected.



```
Current calibration: D:\11_NOV\QXASDEMO\ET\SOIL7.CAL

* Select calibration file
* Change Measuring Parameters
* Select Files for Analysis
* Perform Calculation of Concentrations
* Define File to Save Analysis Results

Select Peaks for Abs.Calc.
*     23   V       195635
*     27   Co       44022
*     29   Cu       55180
*     34   Se       47689
*     38   Sr       20094
*     42   Mo       52165

Calibration Data
Filename: SOIL7.CAL
 Created: 09-28-2006
  Excit.: SecTarget-R
      kV: 50
Nr.of St: 15

 Elements:
   K-lines: Si ... Nb
   L-Lines: Pb ... Pb

<Arrows>=Move   <Enter>=Select  <Del>=UnSelect  <Esc>=Done
```

Fig. 5.4. Relevant target elements must be selected.

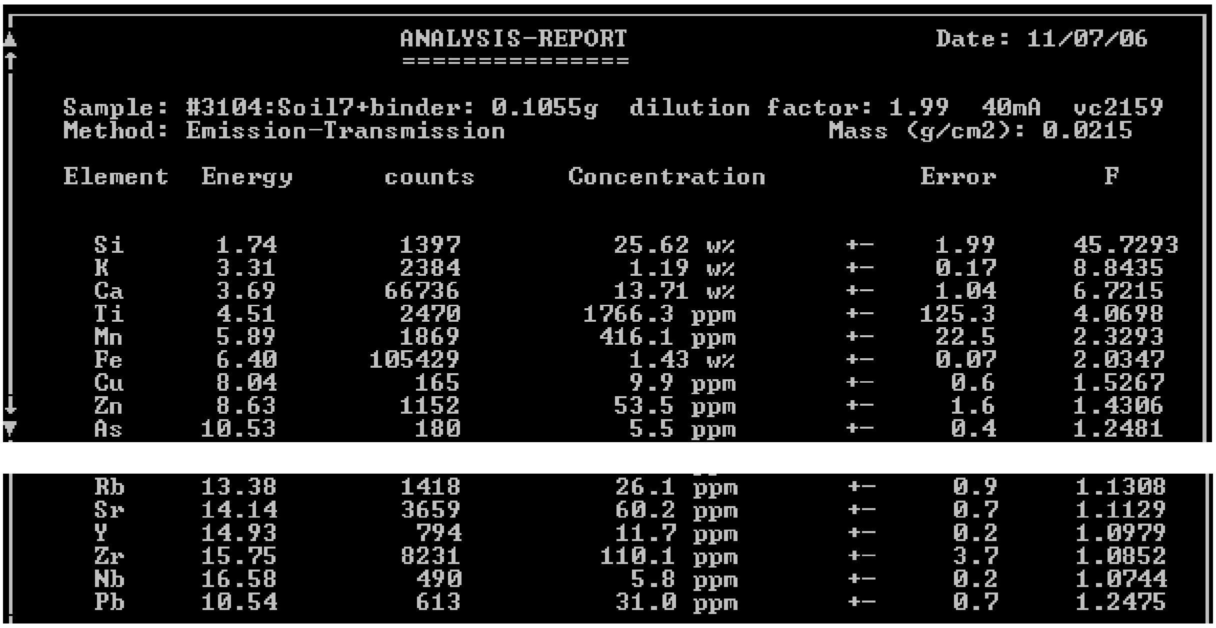
The absorption correction calculation does *not* depend on the selected calibration file. All target elements are accepted, although the parameter for V (Z = 23), **Lg(Lg(A))** = 1.094 is already very close to the threshold limit of 1.097 for rejection. The **slope** (= -2.543) is not close to the expected value of 2.8, the regression coefficient (**regress:** 0.997) and the standard deviation (**stdev:** 0.076) for the fit are good. The edge correction (**Enter element to start iter.:**) was applied from Fe on.



```
Elem.    Lg(E)    Lg(Lg(A))  Fact

 23       4.950    1.094     3.285
 27       6.925    0.267     1.814
 29       8.041   -0.022     1.527
 34      11.208   -0.874     1.210
 38      14.142   -1.475     1.113
 42      17.443   -2.155     1.065


          slope: -2.543
      intercept:  5.212
        regress:  0.997
          stdev:  0.076

      Accept (y/n)? y

      Enter Element
      to start iter.: Fe
```

Fig. 5.5. The absorption correction factors are calculated at the energies of the accepted target elements. Criteria to judge the calculation are the slope, the regression coefficient and the standard deviation. A discontinuity in the absorption behaviour of the sample caused by an element present in higher quantity can be taken into account.

The results for Si, K and Ca have to be ignored, because the METHOD can not calculate an adequate **F** factor for them: The target consists of the fluorescing elements V - Mo, therefore silicon, potassium and calcium are out of range for an appropriate absorption correction.



```
                         ANALYSIS-REPORT                  Date: 11/07/06
                         ===============

  Sample: #3104:Soil7+binder: 0.1055g  dilution factor: 1.99  40mA  vc2159
  Method: Emission-Transmission                     Mass (g/cm2): 0.0215

  Element  Energy      counts      Concentration        Error        F


    Si       1.74        1397          25.62 w%     +-     1.99     45.7293
    K        3.31        2384           1.19 w%     +-     0.17      8.8435
    Ca       3.69       66736          13.71 w%     +-     1.04      6.7215
    Ti       4.51        2470        1766.3 ppm     +-   125.3       4.0698
    Mn       5.89        1869         416.1 ppm     +-    22.5       2.3293
    Fe       6.40      105429           1.43 w%     +-     0.07      2.0347
    Cu       8.04         165           9.9 ppm     +-     0.6       1.5267
    Zn       8.63        1152          53.5 ppm     +-     1.6       1.4306
    As      10.53         180           5.5 ppm     +-     0.4       1.2481

    Rb      13.38        1418          26.1 ppm     +-     0.9       1.1308
    Sr      14.14        3659          60.2 ppm     +-     0.7       1.1129
    Y       14.93         794          11.7 ppm     +-     0.2       1.0979
    Zr      15.75        8231         110.1 ppm     +-     3.7       1.0852
    Nb      16.58         490           5.8 ppm     +-     0.2       1.0744
    Pb      10.54         613          31.0 ppm     +-     0.7       1.2475
```

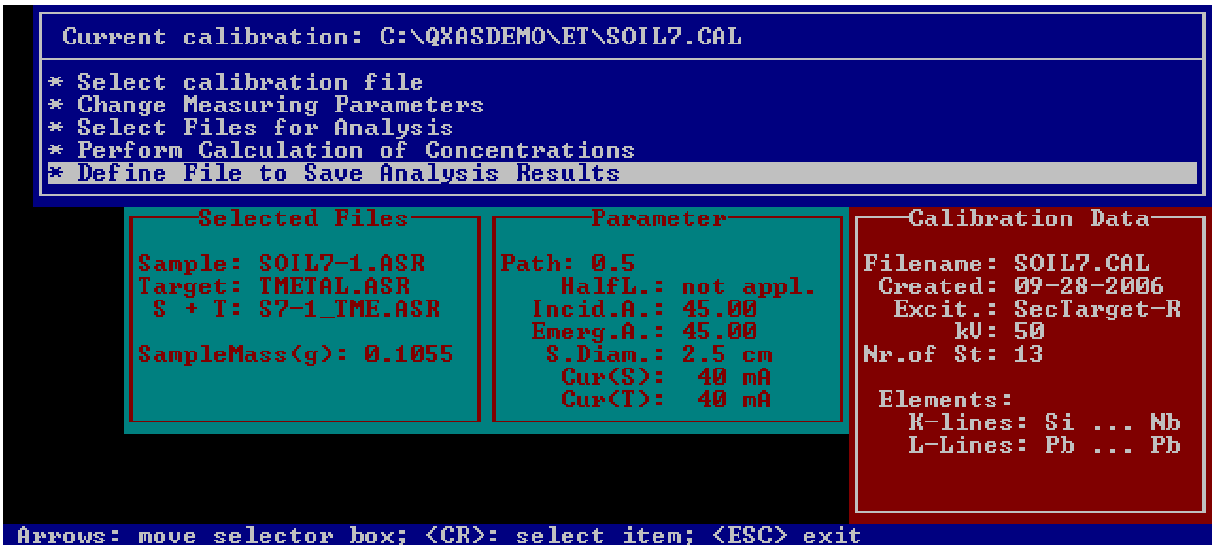
Fig. 5.6. Quantitative results for an intermediate thick pellet of the reference standard material Soil 7 mixed with HWC as binder. A dilution factor of 1.99 applies. Sample elements not within the range spanned by the target elements must be disregarded.

5.1.4. *Example: Sample Soil 7 and target Tmetal*

Demonstration files (directory \QXASdemo\ET):

- Calibration file: Soil7.cal,
- Spectra: Tmetal.spe, S7-1_Tme.spe (directory \QXASdemo\ET\SPE)
- Input files: Tmetal.inp, S7-1_Tme.inp (directory \QXASdemo\INP):
- AXIL result files: Soil7-1.asr, Tmetal.asr, S7-1_Tme.asr

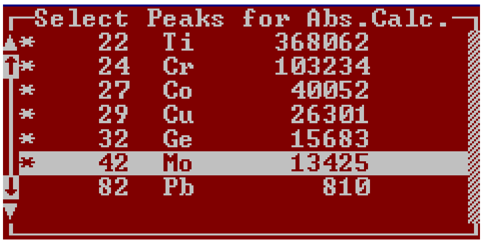
As alternative the accumulative spectra with the artificial accumulative "target" can be used for the establishment of the absorption correction. The spectra of the target (Tmetal.spe) and target plus sample (S7-1_Tme.spe) were measured with varying tube current (5, 10 and 40 mA) depending on the metal standard, acquired for 519 s in total, respectively. A tube current value of 40 mA is assumed to be representative, although not used for all measurements. The target plus sample spectrum, S7-1_Tme.spe, is fitted with the model file: S7-1_Tme.inp. The target spectrum Tmetal.spe (two model files for split ROIs: T-metal.inp and T-metal2.inp) is a typical example where the fit, even with highest order of the linear background, splitting of lines into KA* and KB* (peak shape correction included), and two ROIs will give a bad individual Chi square value for Ti. In principle pure elements' (calibration standards) spectra input models can be well defined, but for the accumulative spectrum no individual treatment is possible. Again Soil7.cal is used for calibration. For the sample representation the previous Soil7-1.asr is used.



```
Current calibration: C:\QXASDEMO\ET\SOIL7.CAL

Sample: SOIL7-1.ASR
Target: TMETAL.ASR
 S + T: S7-1_TME.ASR

SampleMass(g): 0.1055

Path: 0.5
    HalfL.: not appl.
  Incid.A.: 45.00
  Emerg.A.: 45.00
   S.Diam.: 2.5 cm
    Cur(S):  40 mA
    Cur(T):  40 mA

Filename: SOIL7.CAL
 Created: 09-28-2006
  Excit.: SecTarget-R
      kV: 50
Nr.of St: 13

 Elements:
   K-lines: Si ... Nb
   L-Lines: Pb ... Pb
```

*Fig. 5.7. After the selection of the calibration file and definition of measuring parameters, three relevant *.asr files must be loaded.*

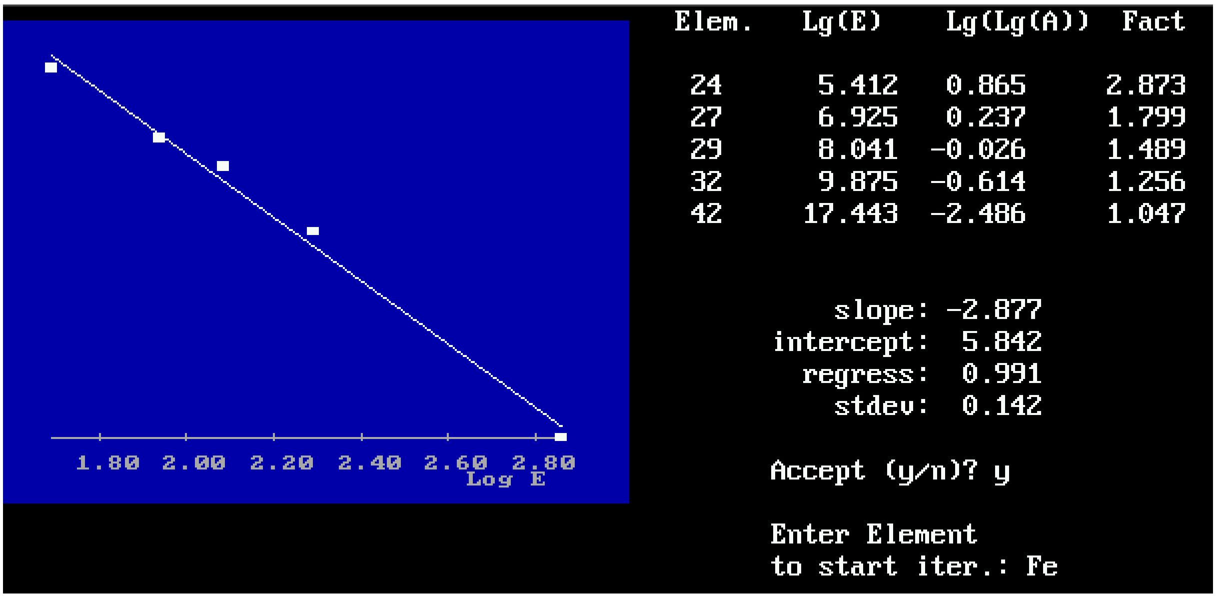
The proposed target element Pb will not be selected, because it had been included for the sake of the spectrum fit with AXIL (lead is a contamination for this measurement).



```
Select Peaks for Abs.Calc.
 *     22  Ti      368062
 *     24  Cr      103234
 *     27  Co       40052
 *     29  Cu       26301
 *     32  Ge       15683
 *     42  Mo       13425
       82  Pb         810
```

Fig. 5.8. Relevant target elements must be selected.

During the absorption correction procedure the target element Ti is rejected, Cr is then the first target element. The iron (and elements with lower atomic number) edge correction (**Enter element to start iter.:**) was applied with the input of Fe.



```
Elem.   Lg(E)    Lg(Lg(A))  Fact

 24      5.412    0.865     2.873
 27      6.925    0.237     1.799
 29      8.041   -0.026     1.489
 32      9.875   -0.614     1.256
 42     17.443   -2.486     1.047


       slope: -2.877
   intercept:  5.842
     regress:  0.991
       stdev:  0.142

   Accept (y/n)? y

   Enter Element
   to start iter.: Fe
```

Fig. 5.9. The absorption correction factors are calculated at the energies of the accepted target elements. Criteria to judge the calculation are the slope, the regression coefficient and the standard deviation. A discontinuity in the absorption behaviour of the sample caused by an element present in higher quantity can be taken into account.

In order to compare the results with the certified values for the two kinds of targets, one has take into account the dilution factor of 1.99. No wonder, the results for Si, K, Ca are out of competition, because non of the two target approaches can handle their absorption correction. Ti (by target T1), Zn, Rb, Y, Nb and Pb results fall within the 95 % confidence interval as given by the certificate. That the titanium result for target Tmetal falls out of the range is due to the rejection of Ti as target element, therefore the working range starts only from sample, element chromium. Mn, Fe, Sr and Zr are overestimated. Rubidium is a positive surprise, because it was only calibrated by interpolation. Arsenic although having the interference with Pb L_α is well specified. The trend for Fe and Sr is due to the blank problem with the two elements; the used standard for Mn (MnO_2) is not well suited for calibration, as already mentioned earlier. Copper was not even taken into account, because of its blank problem. Only slight differences can be found for the two target approaches.

Table 5.2. Certified and measured concentration values for IAEA Soil 7, established by two different target approaches (target T1, target Tmetal). Concentration values within the certified C.I. are coloured red. The respective slope, regression coefficient and standard deviation for the absorption correction calculations are to the bottom lines.

	certified values			
	concentration	95 % C.I.	Target: T1	Target: Tmetal
Si (%)	18	16.9-20.1	50	79
K (%)	1.21%	1.13-1.27	2.37	2.97
Ca (%)	16.3%	15.7-17.4	27.28	33.1
Ti (µg/g)	3000	2600-3700	3515	3959
Mn (µg/g)	631	604-650	828	850
Fe (%)	2.57%	2.52-2.63	2.85	2.85
Zn (µg/g)	104	101-113	106	103
As (µg/g)	13.4	12.5-14.2	10.9	10.5
Rb (µg/g)	51	47-56	52	51
Sr (µg/g)	108	103-114	120	117
Y (µg/g)	21	15-27	23	23
Zr (µg/g)	185	180-201	219	215
Nb (µg/g)	12	7.0-17	11	11
Pb (µg/g)	60	55-71	62	60
		slope:	-2.543	-2.877
		regression c.:	0.997	0.991
		std. deviation:	0.076	0.142

5.1.5. *Example: Lichen 336*

Demonstration files (directory \QXASdemo\ET):

- Calibration file: Lichen.cal,
- AXIL result files samples: Lichen0.asr, Lichen1.asr, Lichen1B, Lichen2.asr, Lichen2B.asr, Lichen3.asr, Lichen4.asr, Lichen5.asr
- AXIL result files targets: TargetF.asr, TargetA.asr, Target1B.asr, TargetB.asr, TargetC.asr, TargetD.asr, TargetE.asr
- AXIL result files target plus sample: Li0_T_F.asr, Li1_T_A.asr, Li1B_T1B.asr, Li2_T_B.asr, Li2B_T1B.asr, Li3_T_C.asr, Li4_T_D.asr, Li5_T_E.asr

Demonstration spectra (directory \QXASdemo\ET\SPE):

- Sample spectra: Lichen0.spe, Lichen1.spe, Lichen1B.spe, Lichen2.spe, Lichen2B.spe, Lichen3.spe, Lichen4.spe, Lichen5.spe
- Target spectra: TargetF.spe, TargetA.spe, Target1B.spe, TargetB.spe, TargetC.spe, TargetD.spe, TargetE.spe

- Target plus sample spectra: Li0_T_F.spe, Li1_T_A.spe, Li1B_T1B.spe, Li2_T_B.spe, Li2B_T1B.spe, Li3_T_C.spe, Li4_T_D.spe, Li5_T_E.spe
- Input files: Lichen.inp, Lichen_T.inp, Lich_T1B.inp, Li4&5_T.inp (directory \QXASdemo\ET\INP)

The reference material IAEA-336, Lichen, had been selected to demonstrate the behaviour of this METHOD with the sample mass as variation parameter. Its overall absorption is much lower as compared to e.g. Soil 7. For Soil 7 the dynamic range in terms of thickness is very limited, simply because intermediate thick pellets in respect to XRF are already very thin when it comes to the realization of pressing pellets - for too thick pellets the METHOD will not work any longer. Of the lichen material eight pellets had been pressed without addition of a binder. The weight of the pellets spans a range from 0.05 - 0.5 g, corresponding to 0.01 - 0.1 g/cm^2 (diameter of the specimens 2.5 cm), the weight for pressing was set to 5 tons. The lightest pellets had been already so thin that they could be used only once. For each sample absorption specification a specific target had been used for the measurement with and without sample in front. Although the mixture for all targets was the same (with exception of target A, which does not contain Sr) slight inhomogeneities can be observed; even front and back side of a target might show slight differences. All measurements were taken with 40 mA tube current. The samples were measured for 1000 s, the targets and target plus sample for 200s, respectively. The air path between sample and detector was 0.5 cm.

A calibration file Lichen.cal was created with the METHOD **Elemental sensitivities**. Eighteen calibration standards’ *.asr files were included: K2CO3, K-KH2PO4, CaCO3, Ti-Std, TiO2, MnO2, Fe-Std, Fe2O3, Cu-Std, CuO, Zn-Std, ZnO, Br-K, SrCO3, Y2O3, Zr-Std, ZrO2 and Pb-LStd. All elements (except Rb) identified in the demonstration sample can be represented by elements contained in at least one calibration standard. The Rb sensitivity value of (6.51 +/- 0.246)*10^4 had been obtained (**Polynomial fit of sensitivities**) from the fit with a linear polynomial of order 5, weighted option. After the polynomial fit the calibration was refitted with order 0 (no fit), in order to use the original calibration points data. Finally the Rb value was pasted into this calibration file.

Note: Description of the samples prepared from the reference standard material IAEA Lichen 336 with different weights and the input model details to generate the *.asr files can be found in the EXCEL lichen_description.xls file.

All lichen spectra had been fitted with the same model file with the inclusion of the elements:

X-LINES ADD: K CA-KA CA-KB TI MN FE-KA+ FE-KB+ ZN BR RB SR Y-KA ZR-KA PB

Chlorine, although of interest, bears the inherent risk of under - or overestimation, due to the proximity to the Rh L scatter region, that only could be described poorly. Molybdenum (only observed for Lichen0.spe) and copper will originate from the sample chamber (blank problems). Copper is included, in order to make the blank problems for this element obvious; Mo for spectrum Lichen0.spe, because this element is contained in the target and it needs to be included for intensity correction. Tungsten lines, as observed, originate from the dye.

X-LINES ADD: CU W SUM

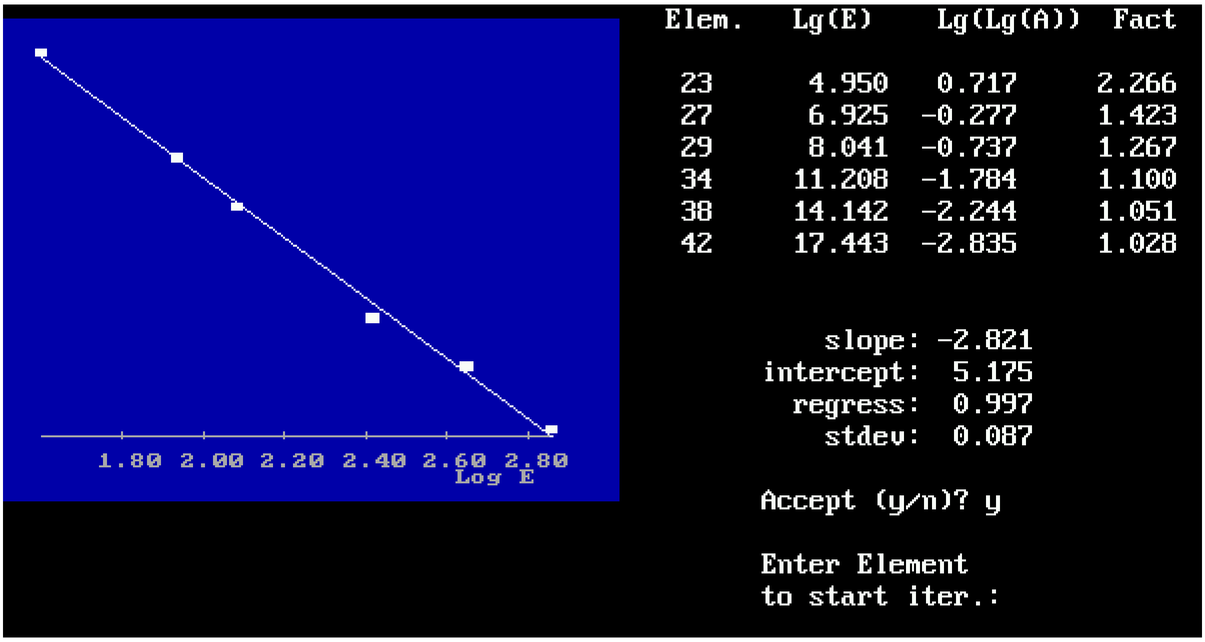
Note: Description of the targets used in combination with the lichen samples, and the input model details to generate the target and target plus sample *.asr files can be found in the EXCEL lichentargets_desc.xls file.

The target spectra were fitted with split K_α and K_β lines and peak shape correction:

X-LINES ADD: V-KA* V-KB* CO-KA* CO-KB* CU-KA* CU-KB* SE-KA* SE-KB*

For Sr and Mo there exists no peak shape correction so they were included with:

X-LINES ADD: SR-KA+ SR-KB+ Mo-KA+ SUM



```
Elem.   Lg(E)    Lg(Lg(A))  Fact

 23      4.950    0.717     2.266
 27      6.925   -0.277     1.423
 29      8.041   -0.737     1.267
 34     11.208   -1.784     1.100
 38     14.142   -2.244     1.051
 42     17.443   -2.835     1.028


        slope: -2.821
    intercept:  5.175
      regress:  0.997
        stdev:  0.087

   Accept (y/n)? y

   Enter Element
   to start iter.:
```

Fig. 5.10. Absorption correction calculation results obtained in connection with the lichen sample spectrum Lichen2B.spe.

The values for the elements (which are certified) agree fairly well for: K, Mn (although the Mn calibration point is questionable), Fe, Zn, Br, Rb, Sr, Pb. But the element potassium must not be included for a report (therefore no average value), because it is out of the range spanned by the targets. This is, because the first target element V is already too high in terms of energy. For the 0.4 and 0.5 g samples (Lichen4.spe and Lichen5.spe) V was rejected from the absorption correction calculation. Consequently one should not make use of the results for the elements below the next target element Co (i.e. Mn, Fe - their entries were not used for the average value calculation). The samples are already too thick. For the lichen pellet with 0.05 g (Lichen0.spe) Mo and Sr of the target elements had been rejected, because their characteristic line intensities where higher for sample plus target than for the target only! Samples can also be too thin for this METHOD. It is evident from the results that copper must be excluded from any report, because of its contamination problem with the used setup.

Note: Comparison of selected concentration values as obtained through the measurements of several samples prepared from IAEA 336, lichen, reference standard material and quantification with the Emission Transmission method with the certificate can be found in the EXCEL lichen_results.xls file. Individual concentration values in blue color are acceptable.

Potassium (not contained within the range spanned by the target elements) and copper (blank problems) values have to be disregarded completely. “Bad” slope, regression and standard deviation values are held in green color. Due to the rejection of target elements during the absorption correction calculation certain concentration values are also disregarded. Disregarded individual values are not used for the establishment of the average value and standard deviation (red color). Most of the results fall within the certified C.I. or are close to it (red color).

Conclusion: There is an optimum sample thickness in respect to the absorption correction. Unfortunately it will be different from sample type to sample type. When a sample matrix shows too high absorption and the pellets can not be pressed thin enough, it will not be possible to apply this METHOD at all, or only to the elements bracketed by target elements accepted for absorption correction.

CHAPTER 6. USE OF NBS ALPHA COEFFICIENTS

References: [29], [30], [31]

The **NBS alpha coefficients** METHOD is restricted to *thick samples* containing only elements of relatively high atomic number Z (metallic or oxides). There is a detectable *fluorescence signal from every constituent* (except oxygen), *samples with dark matrix can not be treated*. The fundamental parameters approach corrects for the *self absorption* and the *enhancement effect*. The program was developed by the **N**ational **B**ureau of **S**tandards (now NIST) (therefore the name for this METHOD: NBS) and the Geological Survey of Canada for wavelength dispersive spectrometers. The algorithm is called COLA (**CO**mprehensive **L**achance **A**lgorithm) in which the influence coefficients are calculated only once, despite the concentration range of unknown analytes to be considered: The *alpha coefficient file neither depends on the concentration values* of the analytes, *nor on intensities*. It was adapted by the IAEA for energy dispersive XRF. Only monochromatic excitation can be defined (quasi - mono energetic excitation). One draw back of the METHOD, *neither varying tube current nor decay corrections* are treated. For tube excitation standards *and* samples must be measured with constant current (alternatively *.asr files have to be edited). In the case of source excitation the decay correction must be calculated by the user and the *.asr files have to be corrected (edited manually).

Samples are classified as:

- Element system
- Oxide system
- Fused disk system

The term *element system* refers to samples where the analytes are present as unbound chemical elements; all of them produce a detectable peak in the spectrum. Examples are stainless steel or brass alloy, where low Z components or impurities can be neglected. For *oxide* sample *systems* the analytes are present as *oxides with known stochiometry*, which is usually the case for minerals and geological materials. In *fused disk system* samples had been diluted with a suitable chemical (flux) and then melted together at high temperatures (1200^0 C), producing a glass bead. The *sample classification* must apply for *all* standards and samples. E.g., a MnO_2 calibration standard cannot be incorporated for an **Element sample (e.g. alloy)** calibration, although maybe needed for the quantification of samples.

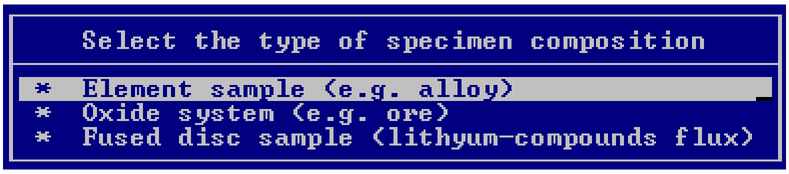


Fig. 6.1. Classification of samples as alloys, oxides or samples prepared by the fusion technique.

In case the above named criteria can be fulfilled and after the proper definition of certain files the METHOD is easy to use and the results compare well with the other more complex fundamental parameters approaches.

The analysis of samples should be performed in four stages:

- Proper AXIL fit and adaptation of *.asr files
- Creation of standard files(*.std)
- Definition the α-coefficients file (*.alp)
- Analysis of unknown samples

Each of the elements of a sample must be represented by an element contained in *at least one* standard (preferably more standards). The standards' *.asr files must be edited such that they become compatible with the *.asr files of the samples and the other standards. Also pure element standards must contain intensity information (at least a negligible small "peak") about the set of the other elements. E.g., as in the later worked-out example, the sample does not contain manganese, but one standard contains this element, then also the other standards' *.asr files must contain an entry with the (otherwise unnecessary) Mn information. The standards' file format expected by the program is obtained through the conversion of the *.asr to *.std file format, with input of the concentration values (**Prepare standard concentration file**). The first step in order to generate the correct alpha coefficients (*.alp) file (**Prepare alpha coefficients file**) is the definition of the element set, as found in one of the *.std files. As each of the standard *.std files must contain the same element list, any of them can be used for the generation of the *.alp file. Then a source description (*.sou) file, describing the excitation source must be loaded (essential are the incidence and take-off angle in respect to the sample surface and discrete wavelength values accompanied by intensity ratios, decribing the excitation source). Finally the previously created *.std files and the appropriate *.alp file have to be recalled in order to evaluate the samples' *.asr files (**Quantitative analysis of unknown samples**). Depending on the number of standards only one or maximum four polynomials, concerning the relationship between concentration and intensity of the calibration standards, are for disposition. All example AXIL result files, the standard description files (*.std), source files (*.sou) and alpha coefficient files are contained in the directory \QXASdemo\NBS.

6.1. Example: Calibration with NBS standards and pure metals, unknown sample synthetic bronze

As set of calibration standards (bronze reference standards: NBS 1103, 1107, 1108, 1115 and pure metals: Fe, Ni, Cu, Zn, Pb, Sn) is used to quantify a synthetic bronze sample. As can be seen in its spectrum, SynBronz.spe, and known from its preparation the elements Cu, Zn, Pb, Sn are present (and should be its only constituents). In order to get an overview about the element specific concentration ranges of the sample and for really unknown samples one will establish an intermediate calibration with pure metals only, according to the sample elements found in the spectrum.

Note: Description of the calibration standards (spectra and input files for the AXIL fit in directory \QXASdemo\NBS\SPE&INP, AXIL result and *.std files in \QXASdemo\NBS) and concentration values as expected from the preparation process of a synthetic bronze sample (SynBronz) can be found in the EXCEL nbs_standards.xls file.

After this intermediate quantification one usually will have to get appropriate standards. For the used NBS 1103, 1107, 1108 and 1115 the concentration ranges spanned by the standards are not ideal, except for Cu: The highest copper concentration (pure metal standard) is 100 %, the lowest is 59.27 % (NBS 1103), therefore the expectation value for the sample (Cu:

87.56 %) is well bracketed. Zn has a much lower, Pb a much higher expectation value, and Sn is only slightly above.

6.2. AXIL fit for NBS bronze alloy standards

The peak evaluation of the pure metallic calibration standards is in analogy to the other METHODs’ calibration standards. Problematic are the reference standards materials (NBS). As example the spectrum fitting of NBS1103.spe is detailed. The spectrum was split into 3 different ROIs with 3 different input models. The careful description of the strong Cu and Zn peaks has too much impact on the Sn L and Pb L_α lines evaluation. With a high value of the background model the entire region could be described, but in this case background oscillations will cause unrealistically differences for the weak peaks, as a function of the value **PARAM=**. For the model file NBS1103.inp the peaks for the Cu - Zn region can be described with

X-LINES ADD: FE NI CU-KA* CU-KB* ZN-KA* ZN-KB* 9.185

Unfortunately Ni and Fe hardly can be split-off, because of the Cu and Zn escape peaks overlaps. Because the Pb L intensity is high, the otherwise small Pb L_l peak, with an energy of 9.185 keV, is taken into account by its energy value. The model file N1103-Sn.inp describes the Sn L-region with

X-LINES ADD: SN-L

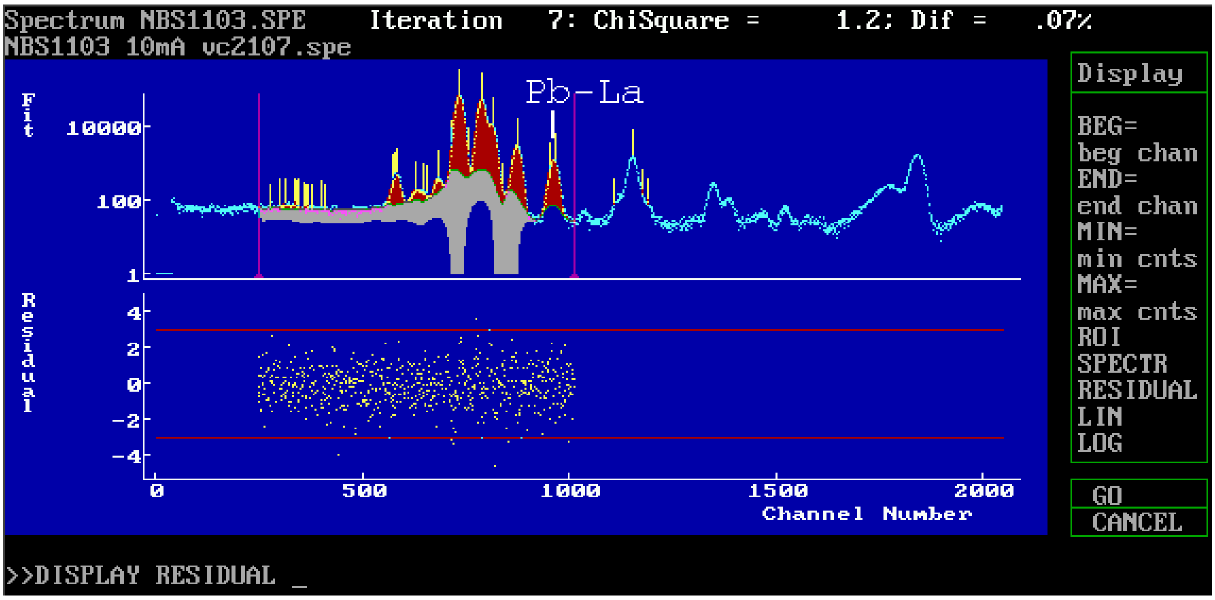
and a linear background of order 1 (**Param=**). The file N1103-Pb.inp describes the narrow region around Pb L_α (**ROI begin**: 910, **end**: 1020), sandwiched by the Zn K_β and Pb L_β peaks.

X-LINES ADD: PB-LA

There is no need to include the other Pb L-lines, nor does one have to care for the other lines originating from the L3-shell transition, defined by PB-LA, which are outside of the ROI.

Note: Description of reference standard NBS 1103 and its spectrum acquisition conditions along with names of the three input files necessary for an adequate AXIL fit, resulting in NBS1103.asr can be found in the EXCEL nbs_srm.xls file.

As can be seen from Figure 6.2, it is possible to fit the entire region for the interesting lines of Sn L, Fe, Ni, Cu, Zn and Pb L_α, but one can recognize the undesirable rise of the background under the Pb L_α peak.



```
Spectrum NBS1103.SPE     Iteration    7: ChiSquare =      1.2; Dif =    .07%
NBS1103 10mA vc2107.spe
```

```
>>DISPLAY RESIDUAL _
```

Fig. 6.2. In principle it is possible to find a fit model to describe the entire ROI of NBS1103.spe, but as can be seen from the background rise under Pb L$_\alpha$, the minor and trace elements might be badly treated.

In analogy to NBS 1103, for the other reference standards: NBS 1107 and NBS 1108 (it also contains Mn) similar models were defined. In the spectrum NBS1115.spe neither Sn nor Pb were identified (consequently only one input model is sufficient). The spectrum of the synthetic bronze sample, Synbronz.spe, was again fitted in 3 parts. In SynBronz.inp Fe and Ni were not included, but the Pb L$_l$-line with its energy of 9.185 keV.

6.3. Creation of Calibration standard files

In order to generate the *.std files the *.asr files have to be modified. Each element to be analyzed in unknown samples or present in any of the standards has to be presented as a row entry in the standards' *.asr files – irrespective, whether the element's peak is present in a spectrum or not. One approach is to use a single *.inp file for the standards and for the samples, containing all possible elements. The more correct solution is to edit the original *.asr files and save them under a different file name. For the alloy example seven element entries need to be found: Mn, Fe, Ni, Cu, Zn, Sn and Pb. E.g., the original Ni-Std.asr file

```
$SPEC_ID:
Ni 100% 10mA vc2073.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
        25       1000
$PEAKS:
      1
  28   1      7.472      53543.       232.       1.74
```

was edited and saved as Ni-NBS.asr:

```
$SPEC_ID:
pure Ni 10mA vc2073.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
        25      1000
$PEAKS:
      7
  25    1       5.89          0.1        0.       0.
  26    1       6.34          0.1        0.       0.
  28    1       7.472     53543.         0.       0.
  29    1       8.04          0.1        0.       0.
  30    1       8.63          0.1        0.       0.
  50    2       3.44          0.1        0.       0.
  82    2      10.54          0.1        0.       0.
```

The lines in red were added / modified. The lowest possible “peak” area accepted is 0.1. According to this, also all NBS reference standards’ files, except NBS1108.asr (which contains all elements in measurable quantities), were modified. E.g. Mn has to be added into all files, because, although for the analysis of the synthetic bronze sample of no interest, NBS 1108 as only standard contains this element.

```
$SPEC_ID:
NBS1103 10mA vc2107.spe
$DATE_MEA:
00-00-2000  00:00:00
$MEAS_TIM:
      1000      1000
$PEAKS:
      7
  25    1       5.89          0.1        0.       0.
  26    1       6.399      6603.        75.      1.18
  28    1       7.472      5056.        74.       .71
  29    1       8.041    1396881.      886.      2.19
  30    1       8.631    1086374.      794.      2.74
  50    2       3.443       339.        12.       .65
  82    2      10.542     26401.        71.      1.12
```

After the delicate task to edit *.asr files the creation of calibration standard *.std files is initiated with the selection of **Prepare standard concentrations file**.

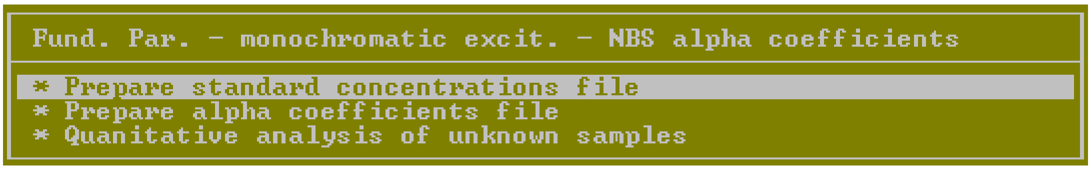
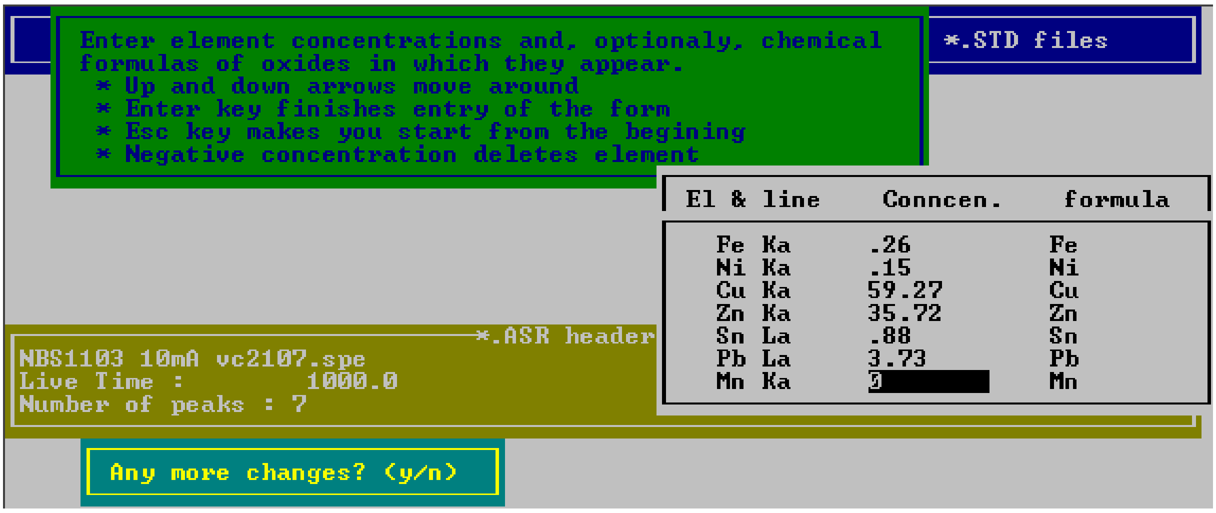


*Fig. 6.3. The *.asr files needed for calibration must be converted to *.std files.*

With the knowledge about the concentration values of the calibration standards at hand the following FORM is easily passed. There is no possibility to add any confidence interval information, therefore the standard deviation values of the edited *.asr files also were ignored previously.



```
Enter element concentrations and, optionaly, chemical
formulas of oxides in which they appear.
 * Up and down arrows move around
 * Enter key finishes entry of the form
 * Esc key makes you start from the begining
 * Negative concentration deletes element
```

```
El & line      Conncen.      formula

  Fe  Ka       .26           Fe
  Ni  Ka       .15           Ni
  Cu  Ka       59.27         Cu
  Zn  Ka       35.72         Zn
  Sn  La       .88           Sn
  Pb  La       3.73          Pb
  Mn  Ka       0             Mn
```

```
*.ASR header
NBS1103 10mA vc2107.spe
Live Time :          1000.0
Number of peaks : 7
```

```
Any more changes? (y/n)
```

Fig. 6.4. The concentration values are attached to the NBS1103.asr file information for the creation of the NBS1103.std file.

Due to the need for consistency elements’ concentration values might be questioned which are not present at all in certain standards. Leave these concentration values at their default 0. When for an element neither a “small peak” in the *.asr file was added (as recommended) nor its concentration value is different from 0, expect a warning message later - which still would not prevent to evaluate samples:

```
Warning : Mn missing or int. & conc. zero !
Press any key to continue
```

```
Reading C:\QXASDEMO\NBS\ZN-NBS.STD and checking consistency...
```

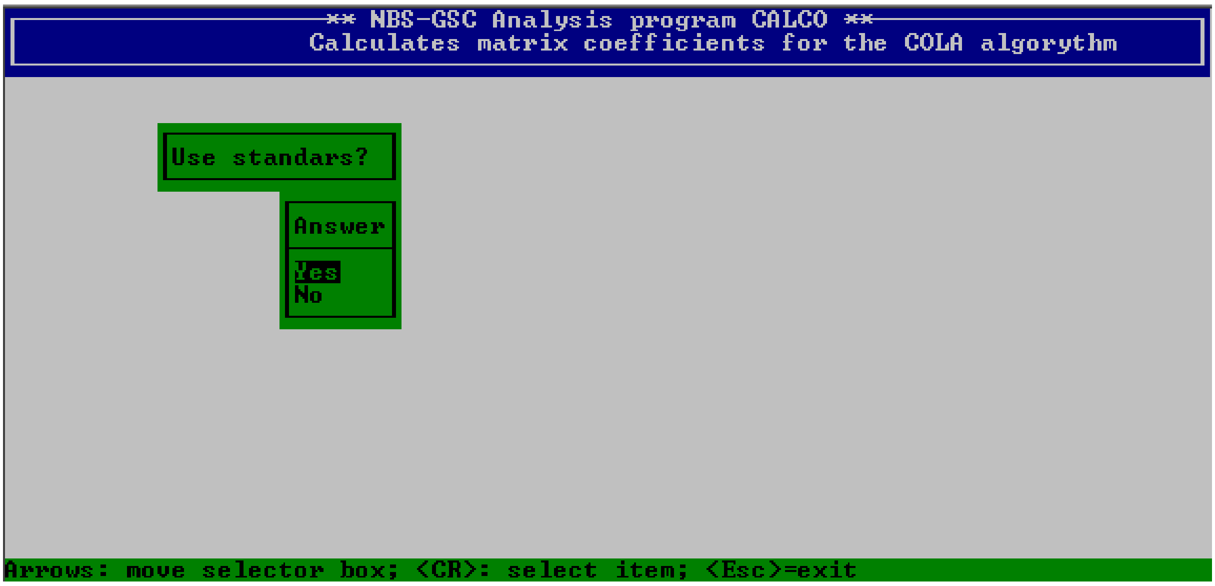
*Fig. 6.5. Warning message displayed when an element entry neither was specified in the *.asr file with a “small” intensity value, nor a concentration value was entered during the generation process of the *.std file.*

For *each* calibration standard, intended to be used later, one has to go through the loop of **Prepare standard concentration file**.

For the intermediate quantification the files _Cu-NBS.asr, _Zn-NBS.asr, _Sn-NBS.asr and _Pb-NBS.asr were created and edited such that four lines are found for element entries: Cu, Zn, Sn and Pb. These files were used to generate equivalent *.std files.

6.4. Creation of the alpha coefficient file

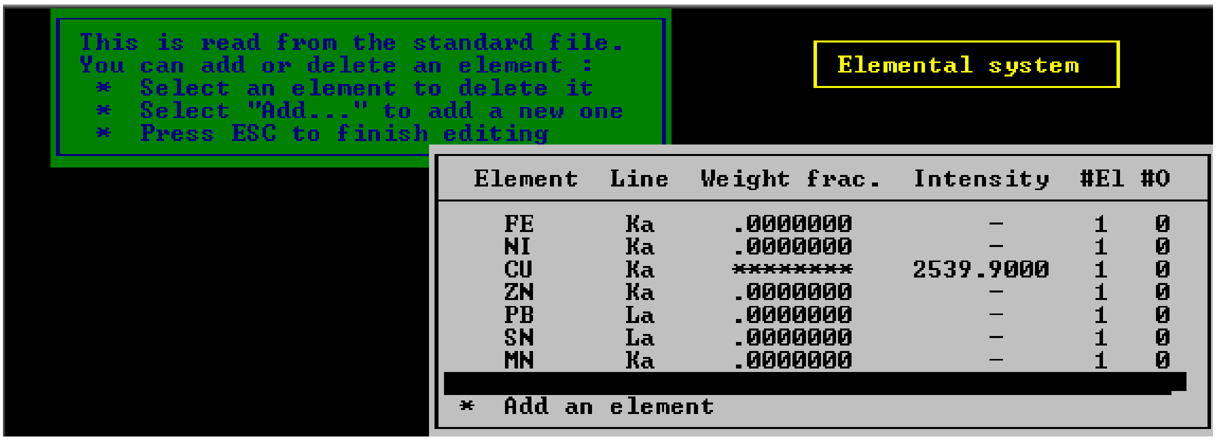
When the standards’ *.asr files had been edited according to the above guideline there is no need to make a fuss about the alpha coefficient file. *Any* single file from the set of the *.std files (NBS1103, NBS1107, NBS1108, NBS1115, Fe-NBS, Ni-NBS, Cu-NBS, Zn-NBS, Sn-NBS, Pb-NBS) is to be loaded. There is no need to go through this procedure for more than once.



```
** NBS-GSC Analysis program CALCO **
Calculates matrix coefficients for the COLA algorythm

Use standars?

Answer
Yes
No

Arrows: move selector box; <CR>: select item; <Esc>=exit
```

*Fig. 6.6. The most convenient way to generate an alpha coefficient file is to load an appropriate *.std file.*

The question **Use standards?** can be answered with **Yes** comfortably. There is no need to care for what so ever displayed **Weight frac.** (normalized concentration) values, even when they are asterisks, nor about **Intensity**. Remember, the α–coefficient file is concentration and intensity independent.



```
This is read from the standard file.
You can add or delete an element :
 *  Select an element to delete it
 *  Select "Add..." to add a new one
 *  Press ESC to finish editing

                                   Elemental system

 Element   Line   Weight frac.   Intensity  #El  #O

   FE       Ka     .0000000          -       1    0
   NI       Ka     .0000000          -       1    0
   CU       Ka     *********     2539.9000   1    0
   ZN       Ka     .0000000          -       1    0
   PB       La     .0000000          -       1    0
   SN       La     .0000000          -       1    0
   MN       Ka     .0000000          -       1    0

 *  Add an element
```

*Fig. 6.7. Once the *.asr file that had been used to generate the loaded *.std file had been defined according to the syntax as expected by the NBS method, the alpha coefficient file will be defined by the correct set of elements.*

With the selection of the source description file, Rh-K.sou, which describes the excitation source (the Rh secondary target) and the sample geometry, the α– coefficient file NBS&pure.alp was created (element set: Mn, Fe, Ni, Cu, Zn, Sn, and Pb). For the preliminary quantification pure-Ele.arp will do (Cu, Zn, Sn and Pb); for its creation any of the *.std files: _Cu-NBS, _Zn-NBS, _Sn-NBS, _Pb-NBS and the source description file Rh-K.sou are to be loaded.

6.5. Quantitative analysis of a synthetic bronze sample

Let us assume, we do not know the composition of the sample, but from the inspection of the spectrum SynBronz.spe it is evident that the elements Cu, Zn, Sn and Pb are to be taken into account.

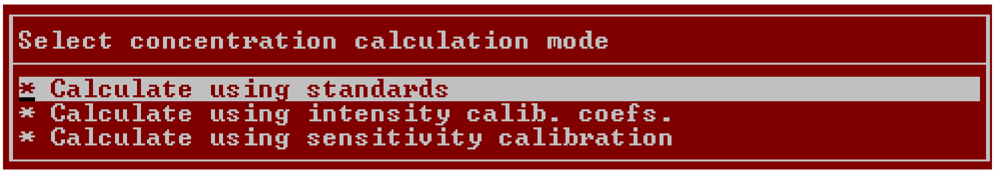


Fig. 6.8. The first stage approach to quantify unknowns is to use calibration standards.

With the preliminary α-coefficient file: pure-Ele.arp, and the preliminary calibration standards: _Cu-NBS.std, _Zn-NBS.std, _Sn-NBS.std and _Pb-NBS.std, intermediate quantitative results can be obtained. From the SELECTOR BOX **Select the function** only the first option should be considered:

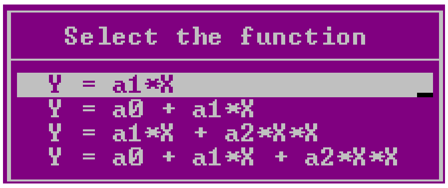
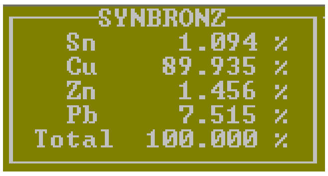


Fig. 6.9. Four polynomials are available to describe the correlation between the relative intensities Y and the normalized concentrations X. This choice is valid for all sample elements.

The functions

$$Y = \sum_{n=0}^{2} a_n * X^n \tag{6.1}$$

with Y being defined as the ratio of the intensity for a calibration standard element to the pure element intensity (= normalized or relative intensity) and X being the normalized concentration (i.e. 100 % => 1). As it is the case with the preliminary calibration, for one point per element (the pure element standards) only a linear relationship makes sense. For the two higher order polynomials program-internal constants will be used to establish the curves (coefficients a_n).

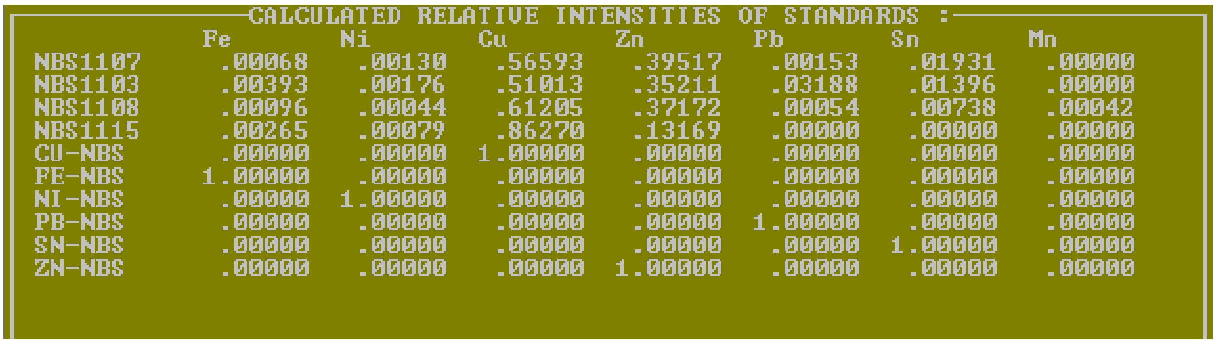


```
SYNBRONZ
  Sn      1.094 %
  Cu     89.935 %
  Zn      1.456 %
  Pb      7.515 %
Total   100.000 %
```

Fig. 6.10. An intermediate calibration with only pure elements as standards leads to preliminary results.

After the preliminary results are obtained, as a consequence one usually will be in desperate need of suited “final” calibration standards - for a more reliable quantification of the unknown sample(s). For the demonstration example the named NBS reference standards were available.

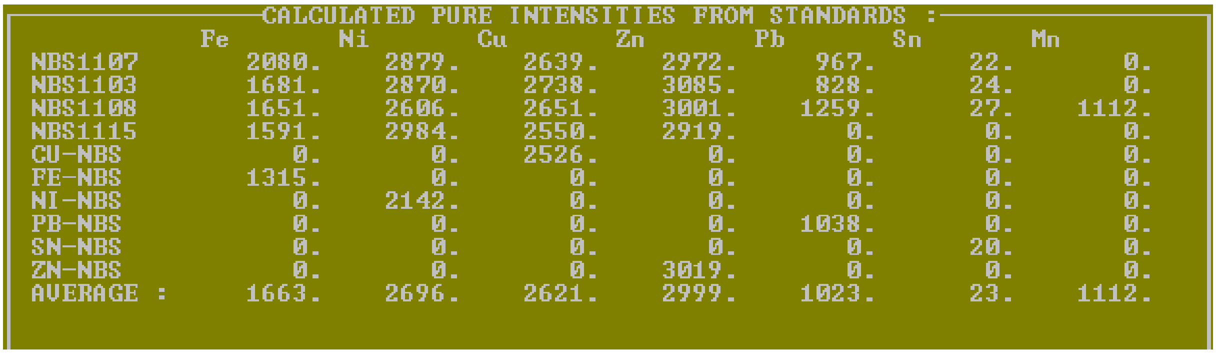
With the set of: NBS1103, NBS1107, NBS1108 and NBS1115 *.std files, the pure element standards' *.std files: Fe-NBS, Ni-NBS, Cu-NBS, Zn-NBS, Sn-NBS and Pb-NBS, and the α-coefficients file NBS&pure.alp the final quantification of the synthetic bronze sample by its AXIL result file, SynBronz.asr, is possible. The sample *.asr file needs not be edited. The SCROLL BOX **CALCULATED RELATIVE INTENSITIES OF STANDARDS** displays the relative intensities (as defined for equation 6.1), which are used for the calculation of the coefficients for the later to be selected kind of polynomial.



```
CALCULATED RELATIVE INTENSITIES OF STANDARDS :
                    Fe        Ni        Cu        Zn        Pb        Sn        Mn
  NBS1107        .00068    .00130    .56593    .39517    .00153    .01931    .00000
  NBS1103        .00393    .00176    .51013    .35211    .03188    .01396    .00000
  NBS1108        .00096    .00044    .61205    .37172    .00054    .00738    .00042
  NBS1115        .00265    .00079    .86270    .13169    .00000    .00000    .00000
  CU-NBS         .00000    .00000   1.00000    .00000    .00000    .00000    .00000
  FE-NBS        1.00000    .00000    .00000    .00000    .00000    .00000    .00000
  NI-NBS         .00000   1.00000    .00000    .00000    .00000    .00000    .00000
  PB-NBS         .00000    .00000    .00000    .00000   1.00000    .00000    .00000
  SN-NBS         .00000    .00000    .00000    .00000    .00000   1.00000    .00000
  ZN-NBS         .00000    .00000    .00000   1.00000    .00000    .00000    .00000
```

Fig. 6.11. Relative intensity values for all calibration standards are displayed in the course of the evaluation of unknowns.

The SCROLL BOX **CALCULATED PURE INTENSITIES FROM STANDARDS** carries valuable information, because a column (for each element) should contain in the ideal case only values slightly deviating from the average (the standard deviation has to be calculated by the user). This is the case for Cu (relative standard deviation: 3 %) and Zn (relative standard deviation: 2 %) - no wonder, because these elements are contained in high quantities in all NBS standards. For Fe and Ni there is a systematic bias to the pure element standards. This can be anticipated, because they are only contained as minor elements in the NBS standards. Fortunately these elements are not found in the sample. For the element Pb (relative standard deviation: 18 %) there is a higher scatter around the average value. Similar for the element Sn (relative standard deviation: 13 %), which unfortunately also shows a systematic bias to the pure element standard. This fact can be explained by the small peaks found in the respective spectra, due to the weak excitation as compared to the other elements. Changes in the fit model can have a drastic impact. Therefore Sn had been isolated with an input model of its own for the AXIL fits of the NBS standards. Mn had only to be included for the sake of NBS 1108, no statement can be made. As a conclusion, for the everyday use of this METHOD: after the analysis of the information gained from this SCROLL BOX one will maybe decide to exclude certain standards.



```
CALCULATED PURE INTENSITIES FROM STANDARDS :
                 Fe        Ni        Cu        Zn        Pb        Sn        Mn
NBS1107           2080.     2879.     2639.     2972.      967.       22.        0.
NBS1103           1681.     2870.     2738.     3085.      828.       24.        0.
NBS1108           1651.     2606.     2651.     3001.     1259.       27.     1112.
NBS1115           1591.     2984.     2550.     2919.        0.        0.        0.
CU-NBS               0.        0.     2526.        0.        0.        0.        0.
FE-NBS            1315.        0.        0.        0.        0.        0.        0.
NI-NBS               0.     2142.        0.        0.        0.        0.        0.
PB-NBS               0.        0.        0.        0.     1038.        0.        0.
SN-NBS               0.        0.        0.        0.        0.       20.        0.
ZN-NBS               0.        0.        0.     3019.        0.        0.        0.
AVERAGE :         1663.     2696.     2621.     2999.     1023.       23.     1112.
```

Fig. 6.12. Pure intensity values for all standards are calculated. In the ideal case the average value is a good representative for all calibration standards. For copper and zinc this holds true. Due to the information gained by this scroll box certain standards may be removed from the list.

The weak part of the program is the almost uncontrollable impact imposed by the selection of the polynomial, as defined in equation 6.1. The number and quality (in terms of the concentration ranges spanned by the elements) of the (for the authors) available standards is not sufficient to make any detailed study in this respect. As a possible criterion in order to take a decision for the order of the polynomial the self-reference results for the standards can be used. I.e., the certified standards used for calibration, treated as samples, must lead to acceptable results.

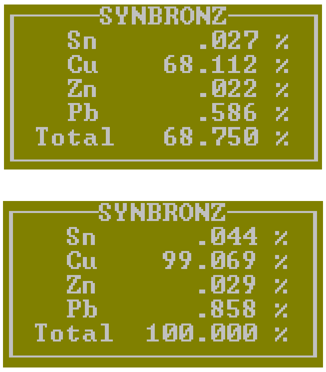
At this stage reference [29] should be quoted. The authors use the nomenclature:

- (1) Straight line for Y = a0 + a1*X
- (2) Quadratic line for Y = a0 + a1*X + a2*X*X
- (3) Straight line constrained to zero intercept for Y = a1*X
- (4) Quadratic line constrained to zero intercept for Y = a1*X + a2*X*X

"… In many cases, calibration curve (4) seems to particularly compensate for inaccuracies in fundamental parameters used in the calculation of theoretical alpha coefficients especially over a wide range of analyte composition, and better results have been observed. However, when the concentrations of the unknowns are out of the range of the standards, it is suggested that the other calibration curves listed above be used for consistency in the results. The extrapolation provided by the quadratic line (2) can sometimes give large errors. When only one multi element standard is available, calibration curve (3) is the only option. At least two multi element standards are required for calibration curve (1) or (4), while three are required for calibration curve (2)." As problematic in this respect was found:

- *All elements* will be described with the *same* calibration curve as selected by the user.
- Sometimes calibration curves can be selected that according to the above recommendations should not be selected. As consequence unrealistic results can be obtained, because for the higher order polynomials (coefficients a_n) program-internal constants will be used to establish the curves.

E.g., for the preliminary calibration all four calibration curves are available. Select any of the quadratic line calibration curves and the preliminary results, either not normalized to 100 % or normalized, can be like this:



```
SYNBRONZ
 Sn        .027 %
 Cu      68.112 %
 Zn        .022 %
 Pb        .586 %
Total    68.750 %
```

```
SYNBRONZ
 Sn        .044 %
 Cu      99.069 %
 Zn        .029 %
 Pb        .858 %
Total   100.000 %
```

Fig. 6.13. a and b: Intentional creation of “bad” results, obtained with the preliminary calibration and a selection of polynomials not adequate for a quantification with only pure element standards.

As there could not be taken a clear decision what calibration function should be used, all four calibration functions were tried. The option **Do you want to normalize conc**(entration)**?** was willingly accepted, under the very likely fulfilled expectation that no other elements constitute the sample.

Table 6.1. Normalized concentration values as obtained by the use of four different calibration functions. The "as expected" values refer to the preparation of the sample.

	Concentration in %			
calibration function	Cu	Zn	Sn	Pb
Y=a1*X	89.702	1.486	1.163	7.650
Y=a0+a1*X	89.649	1.539	1.106	7.706
Y=a1*X+a2*X*X	88.497	1.463	0.943	9.097
Y=a0+a1*X+a2*X*X	88.454	1.497	0.942	9.106
expected values	87.6	1.8	1.4	9.2

Intuitively one would prefer to use different calibration functions for each element. But have in mind that the “as expected” concentration values are not certified. Of course, it is *not* permitted to combine element-wise results from different calibration functions. It also not permitted to construct average values and standard deviations from the four calibration functions. This could be achieved by measurements of several (at least two) individually prepared samples and their evaluation by QXAS.

CHAPTER 7. UTILIZATION OF THE SCATTER PEAKS

References: [26], [27], [32], [33], [34], [35], [28], [36]

7.1. Fitting of scatter peaks, example Rh secondary target excitation

Demonstration files:

- Spectra (directory \QXASdemo\Fp-Scatt\SPE): HWC.spe, Cellulos.spe, Liche336, Cabba359.spe, Soil7-1.spe, LakeSed3.spe, Soil7-2.spe, Instr-Bl.spe
- Spectra (directory \QXASdemo\SPE-Stds): Al-Std, Si-wafer, MgSO4, P-KH2PO4, K-KH2PO4, K2CO3, TiO2, K2Cr2O7, S-Std, Ti-Std, K-KBr, Br-KBr
- Input files for the Rh K scatter region (directory \QXASdemo\FP-Scatt\INP): HWC-1.inp, HWC-3inp, Cell-1.inp, Lic336-1, Cab359-1.inp, S7-1-1.inp, SL3-1.inp, S7-2-1.inp, Ins-Bl-1.inp, Si-1.inp, Al-1.inp, MgSO4-1.inp, P-KH2P-1.inp, K-KH2P-1.inp, K2CO3-1.inp, TiO2-1.inp, K2Cr2O-1.inp, S-Std-1.inp, Ti-Std-1.inp, K-KBr-1.inp, Br-KBr-1.inp
- AXIL result files for the Rh K scatter region (directory \QXASdemo\FP-Scatt): HWC-1.asr, HWC-3.asr, Cellulos.asr, Liche336.asr, Cabba359.asr, Soil7-1.asr, LakeSed3.asr, Soil7-2.asr, Instr-Bl.asr, Si-1.asr, Al-Std-1.asr, MgSO4-1.asr, P-KH2P-1.asr, K-KH2P-1.asr, K2CO3-1.asr, TiO2-1.asr, K2Cr2O-1.asr, S-Std-1.asr, Ti-Std-1.asr, K-KBr-1.asr, Br-KBr-1.asr

Prior to the computation of an element's concentration for the calculation of the absorption as well as the enhancement correction the concentration of *all* elements in a sample should be known. This vicious circle can be overcome by a suitable iterative procedure. Still there are the elements forming the dark matrix; also their composition needs to be known. The fundamental parameters METHODs **Full Fundamental Parameters** and **Fund**amental **Par**ameters **– monochromatic excit**ation **/ scatter peaks** use the incoherent / coherent scatter peak ratio for establishing the average atomic number of the dark matrix of a sample in order to calculate the absorption correction and, when not defined by an input, also the sample thickness. The two scatter peaks of the characteristic K_α lines (e.g. Rh) originating from the excitation source are usually engaged rather than the L-lines or the continuum (spectral background).

To generate useful results representative for the scatter by the sample is an art of its own. Consequently there exist several approaches, how to define the scatter peaks for the AXIL fit model. Three different models are proposed. For all models the background subtraction is tried to be kept to the minimum, because also the background is mainly caused by scattering. As demonstration sample a thick pellet of Soil 7, spectrum Soil7-2.spe, serves.

Model -1: The example spectrum Soil7-2.spe has to be fitted with the model file S7-2-1.inp. A region of interest is selected such that all K scatter peaks (incoherent K_α, coherent K_α, incoherent K_β and coherent K_β) are well contained. A Gaussian function is used to describe the coherent scatter peak (COMMANDs **X-LINES ADD: RH-KA,COH**). The incoherent scatter peak is added to the fit model with **X-LINES ADD: RH,INC**. The incoherent scatter peak maximum energy will be calculated by AXIL according to the angles defined in the input file (default values are 45^0 incident and 45^0 take-off angle, which are acceptable for secondary target excitation, but not for source excitation). The incoherent scatter peak is much broader due to the fact that scattering occurs over a range of angles around the nominal scattering angle (divergence of beams) and the Doppler broadening. On the low energy side of the incoherent scatter peak a tail is formed due to multiple scattering in the sample. This peak profile cannot be accurately described by a single Gaussian function. Instead, a number of Gaussian peaks are used to compose the incoherent scatter peak profile. With a distance in terms of energy of 0.25 keV between each other, energy values are added to the model. The background under the scatter peaks is subtracted in such a way that it fits the neighbouring continuum background (**BACKGRND LINEAR PARAM= 0**). The proposed model has a ROI from the middle of the spectrum to the very end, in order to minimize the subtraction of the background (channels 1024 to 2048). The lines of interest are defined by

X-LINES ADD: RH,INC RH-KA,COH

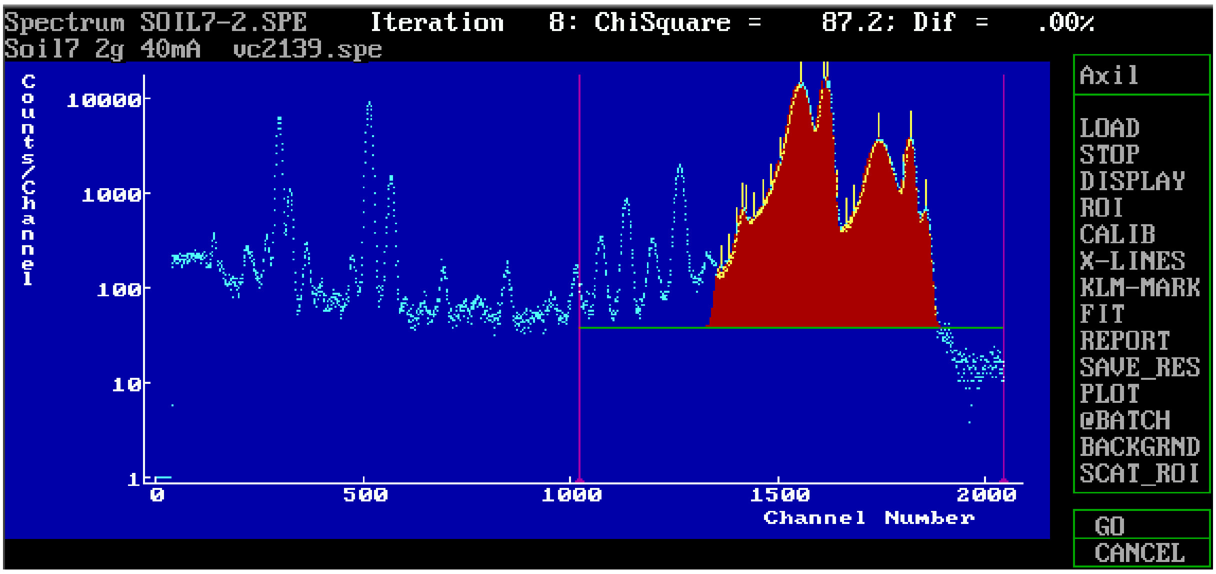
The tailing

X-LINES ADD: 17 17.25 17.5 17.75 18 18.25 18.5 18.75

and the K_β scatter region are described by:

X-LINES ADD: 21.75,INC RH-KB,COH 20.5 20.75 21 22.5

The K_β Compton peak would not be positioned correctly; therefore it was added as an energy value. Sometimes Zr K_β is also added, when the peak is interfering with the ROI. All added lines were included with the goal to stabilize the fit of the incoherent and coherent K_α peaks.



```
Spectrum SOIL7-2.SPE     Iteration    8: ChiSquare =     87.2; Dif =    .00%
Soil7 2g 40mA   vc2139.spe
```

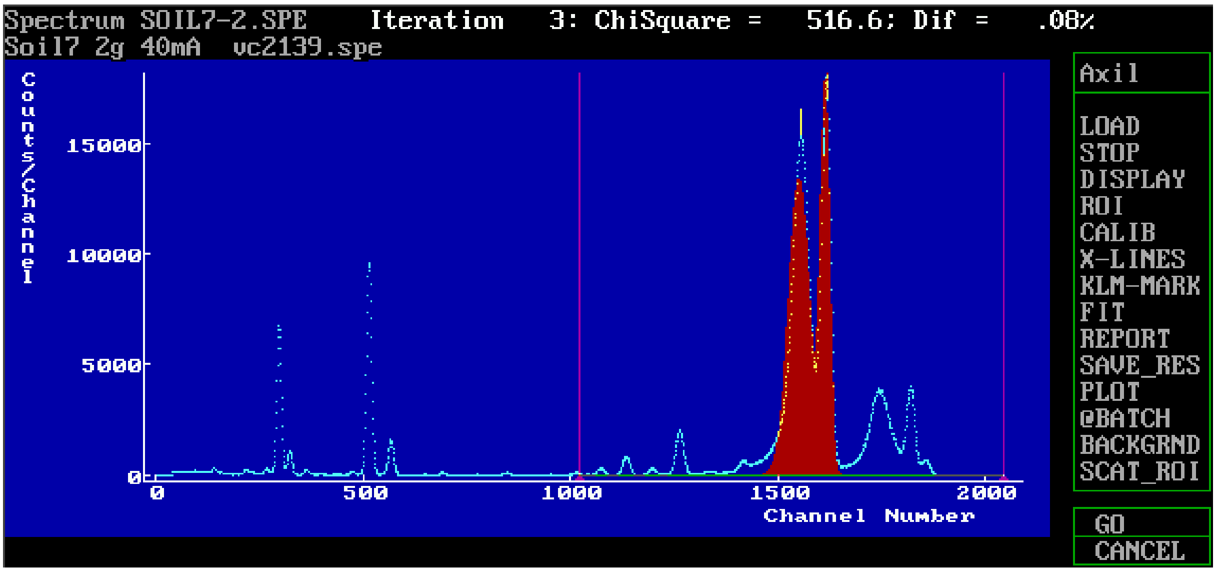
Fig. 7.1. AXIL fit of the Rh K scatter region according to model -1.

Looking at the residual or the Chi square value can be frustrating, but is of no relevance for the results. In the resulting *.asr file only the incoherent and coherent K_α peak information will be stored. All other peak areas can be inspected with **REPORT FULL GO** or even stored as *.out file with **REPORT FULL SAVE**. In order not to overwrite the *.asr file when other scatter peak models are tested the resulting file can be renamed after saving. When problems are observed, like a shift of the energy calibration or unexpected peak broadening during the iterations, locking of input parameters (D_GAIN, D_FANO, etc.) can be useful.

Model -2: In a rather puristic approach with the COMMANDs

X-LINES ADD: RH-KA,COH RH,INC

only the scatter peaks, as needed for the quantification, are fitted - nothing else; background linear, order 0. In the linearly displayed AXIL fitted spectrum Soil7-2.spe one can see that the Compton peak is not well described. This is a reason why one will prefer the rather exotic approach of model -1 or model -3.



```
Spectrum SOIL7-2.SPE     Iteration    3: ChiSquare =    516.6; Dif =    .08%
Soil7 2g 40mA  vc2139.spe
```

Fig. 7.2 AXIL fit of the Rh K_α scatter region according to model -2.

Model -3: The scatter peaks are not fitted at all. Instead, within a region of interest the respective counts per channel are summed up. The background is usually not subtracted at all. This is achieved with the so far not used COMMAND **SCAT_ROI** and consequently **INCOHER** and **COHERENT**, by setting appropriate ROIs for the scatter peaks.

Note: In case one tries the background subtraction (COMMANDs **SCAT_ROI**) for this scatter peak modelling approach, before at least one element peak (free of choice) has to be fitted, otherwise AXIL will crash.

As example the spectrum HWC.spe can be treated with the input model HWC-3.inp. The incoherent Rh K_α region is set within channels 1250 to 1610. The coherent region is set between channels 1650 to 1670. No background subtraction was attempted. The resulting file was renamed to HWC-3.asr. For the further use with the quantitative METHODs the *.asr file must be edited and the scatter peak information brought to “standard” (see CHAPTER 4, Editing of data files).

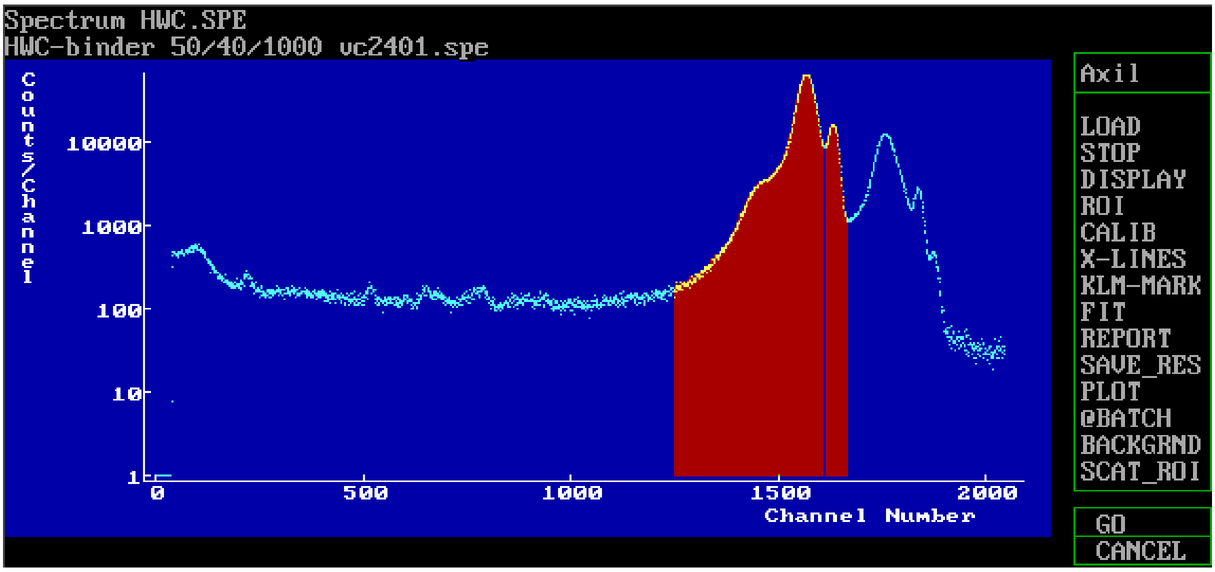


Fig. 7.3. Summation of the channel contents for the Compton and the elastic Rh K_α scatter peaks, model -3.

Conclusion: One can find other approaches to describe the scatter peaks within AXIL, none of the known ones is completely satisfying, because either the background subtraction can not be controlled sufficiently, and/or the deconvolution of elastic and inelastic peaks is not correct. Each of the models will result in different peak areas for the scatter peaks. For what so ever model one has preferences, for scatter calibration standards and the samples the same approach must be used. For the remainder of this book the model -1 will be used.

7.1.1. Classification according to the scatter peak ratio

Depending on the choice for representation of the scatter peaks the samples must be treated accordingly. A classification of samples is possible through the ratio of the incoherent to coherent scatter peak area. For every sample a scatter calibration must be achieved with a scatter calibration standard as similar as possible in the incoherent to coherent peak ratio.

Table 7.1. Incoherent and coherent peak area and their ratio for low Z matrix representatives and several sample spectra for Model -1 scatter peak representation.

Standard/ sample description	*.asr file	*.inp model file for the Rh K scatter region	Peak area Compton Rh $K_{\square}$ scatter	Peak area coherent Rh $K_{\square}$ scatter	Ratio incoherent to coherent peak
$C_{38}H_{76}N_2O_2$	HWC	HWC-1	3077129	475877	6.47
$C_6H_{10}O_5$	Cellulos	Cell-1	2033878	432407	4.70
IAEA 336	Lichen336	Lic336-1	2789663	590248	4.73
IAEA 359	Cabba359	Cab359-1	2925592	820512	3.57
IAEA Soil7 + binder HWC	Soil7-1	S7-1-1	243539	87794	2.77
IAEA SL3	LakeSed3	SL3-1	930573	501443	1.86
IAEA Soil7	Soil7-2	S7-2-1	787234	492611	1.60
Instrument blank	Instr-Bl	Ins-Bl-1	11164	6187	-

One can further reduce the problem by plotting this ratio as a function of the average atomic number of all elements contained in a sample or standard. Soil 7 is the only reference standard material for which the complete composition is known, therefore also standards used for fluorescence calibration are incorporated. All above used spectra (as defined in table 7.1.) and selected spectra *.spe (and *.inp files for the definition of the scatter region): Al-Std (Al-Std-1), Si-wafer (Si-1), MgSO4 (MgSO4-1), P-KH2PO4 (P-KH2-1), K-KH2PO4 (K-KH2P-1), K2CO3 (K2CO3-1), TiO2 (TiO2-1), K2Cr2O7 (K2Cr2O-1), S-Std (S-Std-1), Ti-Std (Ti-Std-1), K-KBr (K-KBr-1) and Br-KBr (Br-KBr-1) were utilized. The scatter peak ratios follow a trend, but some standards like MgSO4, pure aluminium, silicon, etc. are problematic in this respect. The more standards can be used to establish such a plot the better the predictions can be made concerning the correlation between average atomic number and scatter peak ratio of unknowns.

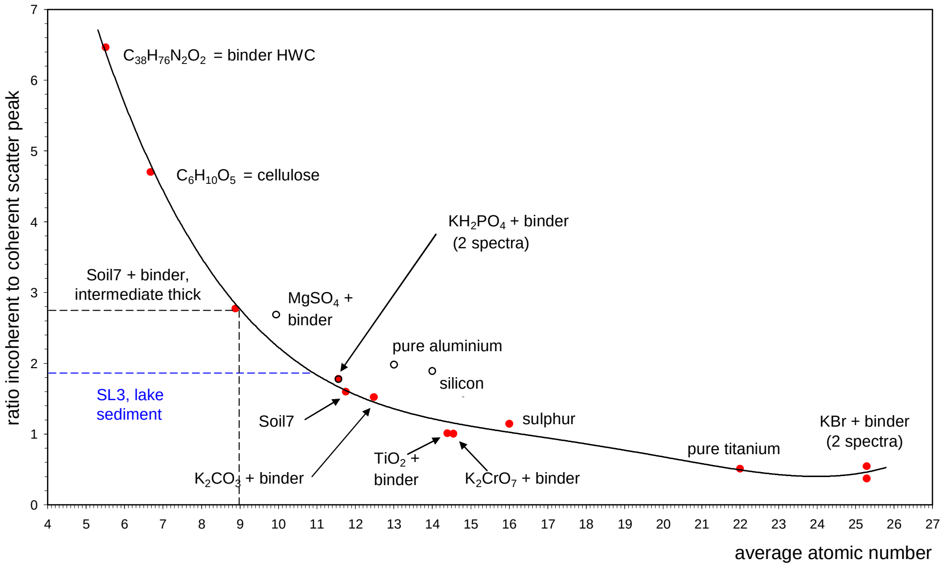


Fig. 7.4. Ratio of incoherent to coherent scatter peak versus average atomic number of the substance used for scattering. Aluminium and silicon do not follow the trend. It can be assumed that the matrix of the sample SL-3 is comparable to Soil-7, as one consequence. From the ratio of the scatter peaks for the intermediate thick pellet of the sample Soil-7 with binder added an average atomic number of 8.88 follows, as another consequence.

When one wants to treat IAEA SL-3, lake sediment, as "unknown" sample, the scatter standard coming closest in respect to the scatter peak ratio is IAEA Soil 7 (ignoring the fluorescence standards spectra K-KH2PO4 and P-KH2PO4).

7.2. Full Fundamental Parameters METHOD

Demonstration files (directory \QXASdemo\FP-Scatt):

- Instrumental parameter files: Soil7.fpc, OrgaMatr.fpc
- Spectra (directory \QXASdemo\Fp-Scatt\SPE): LakeSed3.spe
- Input files (directory \QXASdemo\Fp-Scatt\INP): SL3-A.inp, SL3-B.inp, SL3-1.inp, S7-2-1.inp
- AXIL result files: LakeSed3.asr, OragaMatr.asr, Soil7-2.asr

It is to be mentioned that the METHOD uses only the total scattering cross sections σ_{coh}, σ_{inc} instead of the differential scattering cross sections; in this respect the **BFP** METHOD, soon introduced, is superior.

The fluorescence calibration of this METHOD for e.g. Soil.fpc had been already established (chapter 3.3: Calibration for the Full Fundamental Parameters METHOD). This file carries the average and some individual instrumental constants' information, but for samples with dark matrix the scatter calibration must be established. In principle it is possible to work with a *.fpc file without defined coherent and incoherent instrumental constants, because in such a case a default value of 4π the fluorescence constant will be used. The program will not necessarily fail, but an adequate scatter calibration is usually superior.

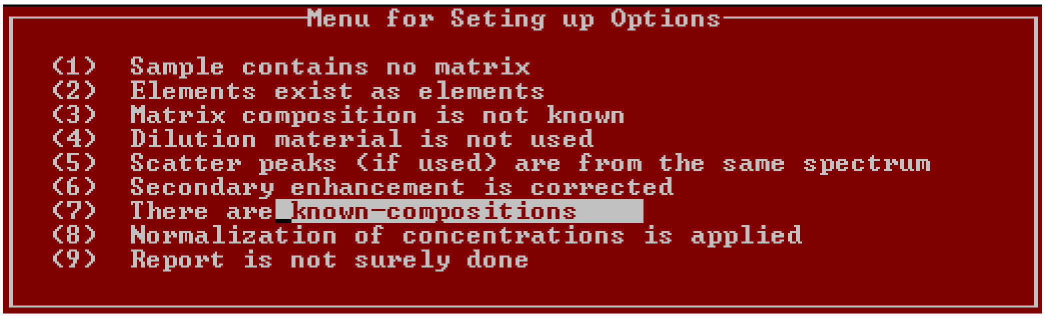
```
        Average Instrumental Constant
  for fluorecence:              1.1490E-7
  for coherent scattering:      0.0000
  for incoherent scattering:    0.0000
```

Fig. 7.5. For the quantification of samples the instrumental constant for fluorescence must have a defined value.

The range of values accepted by the METHOD is unfortunately relatively narrow. Not only the ratio of incoherent to coherent peak, but also their absolute values can sometimes lead to a program crash for samples with dark matrix.

Usually one will employ several standards for fluorescence calibration (representing the elements identified in the unknown sample(s) and one (or more) standard(s) for scatter calibration, being close in its ratio incoherent to coherent scatter peak area to the unknown sample(s). Elements not represented by standards, as well as elements for which no individual fluorescence instrumental constant had been defined, will be calculated by use of the average calibration constant for fluorescence.

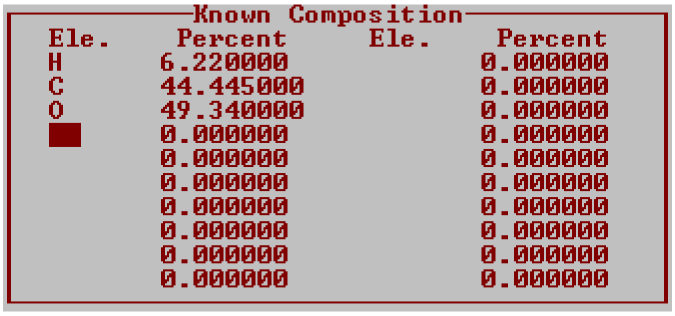
The calculation of scatter constants is selected from the TOGGLE FIELD **Select Calculation mode,** with the selection of **Instru. Constants for fluorescence & scatter**. For the purpose of the scatter calibration it is possible for this METHOD to use *.asr files of standards that do not contain any useful fluorescence peaks but only the scatter peaks information (cellulose, HWC, etc.) or to fit only the scatter region and neglect the fluorescence region (Soil 7, etc.). The *.asr file must contain information of the form: **$COH_SCAT:** and **$INC_SCAT:**. In the later case the matrix composition must be specified, FORM **Menu for setting up options, (7) There are known-compositions**.



```
Menu for Seting up Options

(1)  Sample contains no matrix
(2)  Elements exist as elements
(3)  Matrix composition is not known
(4)  Dilution material is not used
(5)  Scatter peaks (if used) are from the same spectrum
(6)  Secondary enhancement is corrected
(7)  There are known-compositions
(8)  Normalization of concentrations is applied
(9)  Report is not surely done
```

Fig. 7.6. The toggle field (7) there are known compositions will permit to define other elements than fluorescing ones later during the execution of the program.

Consequently one will have to define the matrix. For e.g. cellulose with the chemical formula $C_6H_{10}O_5$ one can calculate with the utility **Calculation of average atomic number** the weight percentage of the elements.



```
                Known Composition
Ele.     Percent       Ele.     Percent
H       6.220000               0.000000
C      44.445000               0.000000
O      49.340000               0.000000
        0.000000               0.000000
        0.000000               0.000000
        0.000000               0.000000
        0.000000               0.000000
        0.000000               0.000000
        0.000000               0.000000
        0.000000               0.000000
```

Fig. 7.7. Definition of the composition of a cellulose pellet.

7.2.1. Example: Establishing the instrumental constants for scattering for Soil7.fpc

For the use of Soil 7 as scatter calibration standard the concentration values of the Soil 7 certificate are needed. The spectrum Soil7-2.spe had been fitted only for the scatter region, according to model -1, with the input model S7-2-1.inp. For the definition of the matrix (selection of **(7) There are known-compositions**) in the FORM **Known compositions** the essential elements' concentration values (> 0.1 %) are represented by : Na (0.24 %), Mg (1.13 %), Al (4.70 %), Si (18.0 %), S (0.12 %), K (1,21 %), Ca (16.3 %), Ti (0.3 %), Fe (2.57 %), the dark matrix is described by H (0.89 %), C (7.18 %) and O (47.36 %), in accordance with reference **[27]**. This information is stored as Soil7.reb file. The specimen was prepared as a "thick" pellet, total weight 2.0 g; the measurement was taken with 40 mA.

Table 7.2. Concentration values for selected elements taken from the certificate for the IAEA reference standard material Soil 7; the values for the elements forming the dark matrix are in accordance with reference [27].

IAEA Soil 7, selected elements		
	concentration (µg/g)	C.I. (95%)
Si	18 %	16.9-20.1
K	1.21 %	1.13-1.27
Ca	16.3 %	15.7-17.4
Ti	3000	2600-3700

IAEA Soil 7, selected elements

		concentration (µg/g)	C.I. (95%)
	V	66	59-73
	Cr	60	49-74
	Mn	631	604-650
	Fe	2.57 %	2.52-2.63
	Co	8.9	8.4-10.1
	Ni	26	21-37
	Cu	11	9.0-13.0
	Zn	104	101-113
	Ga	10	9.0-13
	As	13.4	12.5-14.2
	Br	7	3.0-10
	Rb	51	47-56
	Sr	108	103-114
	Y	21	15-27
	Zr	185	180-201
	Nb	12	7.0-17
	Pb	60	55-71
	Th	8.2	6.5-8.7
	U	2.6	2.2-3.3
low Z	Na	0.24 %	
	Mg	1.13 %	
	Al	4.70 %	
	S	0.12 %	
dark matrix	H	0.89 %	
	C	7.18 %	
	O	47.36 %	

The warning message **No elements analysed in this sample** is - together with the correct definition of the matrix – no problem.

```
No elements analysed in this sample
```

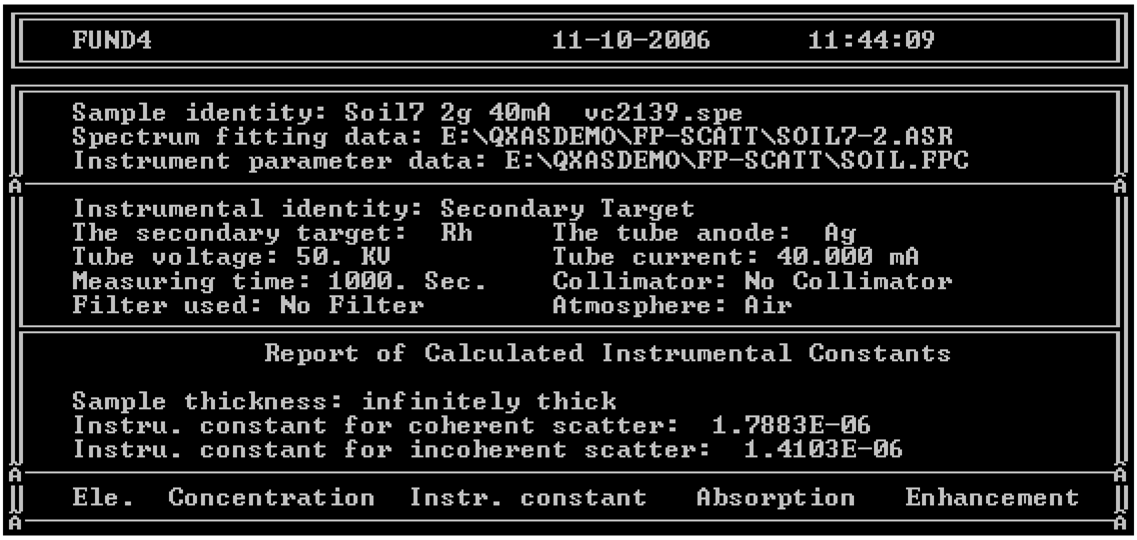
*Fig. 7.8. Warning message, displayed for *.asr files handled with this method not containing any fluorescence peak information.*

When the so far not seen FORM **Information on scatter peaks** appears – in the regular case – it will display the relevant information taken from the *.asr file. It is possible to edit this FORM, but this is not advisable. Only for testing purposes, e.g. when the effect of slight variations in the scatter peak areas should be examined, it is recommended. All other problems should be solved either by changes in the definition of the *.fpc file or different choice for the sample description, etc. In case the values for **Coherent** and **Incoherent scatter peak area:** are displayed as 0.0, the selected *.asr file was not set up for the scatter peaks. For the example of Soil 7 the displayed information matches the values given in table 7.1.

```
Information on Scatter Peaks
Measure time (Sec.):       1000.000
Tube current (mA):         40.00000
Characteristic line: Rh Ka,coh
Coherent scatter peak area:    492611.0    Std: 819.00
Characteristic line: Rh Ka,inc
Incoherent scatter peak area:    787234.0  Std: 1013.0
Atomic difference of Low-Zs:  2
```

Fig. 7.9. The form Information on Scatter peaks can be edited but scarce use of this option should be made.

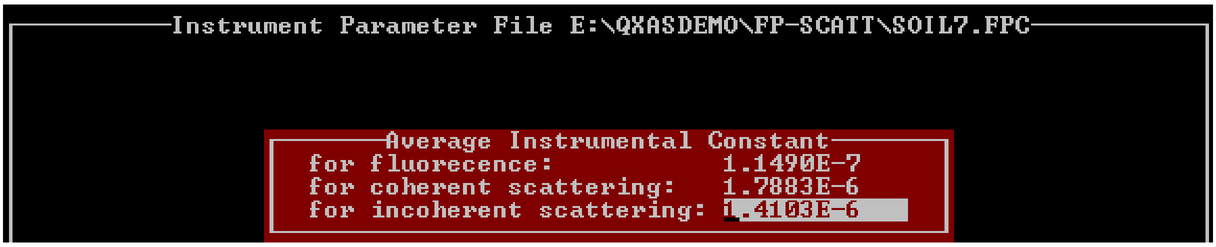
After leaving the last FORM the calculation will be initiated with **Calculation of Geometry constants/Analysis of unknown samp**(le).



```
FUND4                        11-10-2006      11:44:09

Sample identity: Soil7 2g 40mA  vc2139.spe
Spectrum fitting data: E:\QXASDEMO\FP-SCATT\SOIL7-2.ASR
Instrument parameter data: E:\QXASDEMO\FP-SCATT\SOIL.FPC

Instrumental identity: Secondary Target
The secondary target:   Rh      The tube anode:  Ag
Tube voltage: 50. KV            Tube current: 40.000 mA
Measuring time: 1000. Sec.      Collimator: No Collimator
Filter used: No Filter          Atmosphere: Air

            Report of Calculated Instrumental Constants

Sample thickness: infinitely thick
Instru. constant for coherent scatter:  1.7883E-06
Instru. constant for incoherent scatter:  1.4103E-06

Ele.  Concentration  Instr. constant   Absorption   Enhancement
```

Fig. 7.10. After a successful run the instrumental constants for coherent and incoherent scattering can be obtained.

The two instrumental constants for scattering must be manually transferred to the relevant *.fpc file



```
Instrument Parameter File E:\QXASDEMO\FP-SCATT\SOIL7.FPC

            Average Instrumental Constant
    for fluorecence:              1.1490E-7
    for coherent scattering:      1.7883E-6
    for incoherent scattering:    1.4103E-6
```

*Fig. 7.11. Also the instrumental constants for scattering are not transferred automatically to the *.fpc file from the previous program.*

No further changes in the *.fpc file are permissible when the constants are entered, otherwise this would affect the calibration.

7.2.2. Analysis of unknown samples containing dark matrix

As demonstration sample the reference standard material IAEA SL-3, lake sediment, is adequate, because its scatter peak ratio comes closest to the Soil 7. The sample had been prepared as pressed pellet (mass 2.0 g, no binder added), the spectrum LakeSed3.spe had been acquired for 1000 s with a tube current of 40 mA.

Note: Description of reference standard IAEA Lake Sediment SL-3 and its spectrum acquisition conditions along with the names of the three input files necessary for an adequate AXIL fit, resulting in LakeSed3.asr can be found in the EXCEL sl3_dm.xls file.

The spectrum had been fitted in three parts, with input models SL3-A.inp, for the lower energy part of the spectrum for the element peaks included with

X-LINES ADD: SI K CA-KA+ CA-KB+ TI MN FE-KA+ FE-KB+ 2.7 2.8 2.9

The higher energy part of the spectrum, fitted with the input model SL3-B.inp:

X-LINES ADD: ZN BR RB SR+ Y ZR-KA+ NB-KA PB

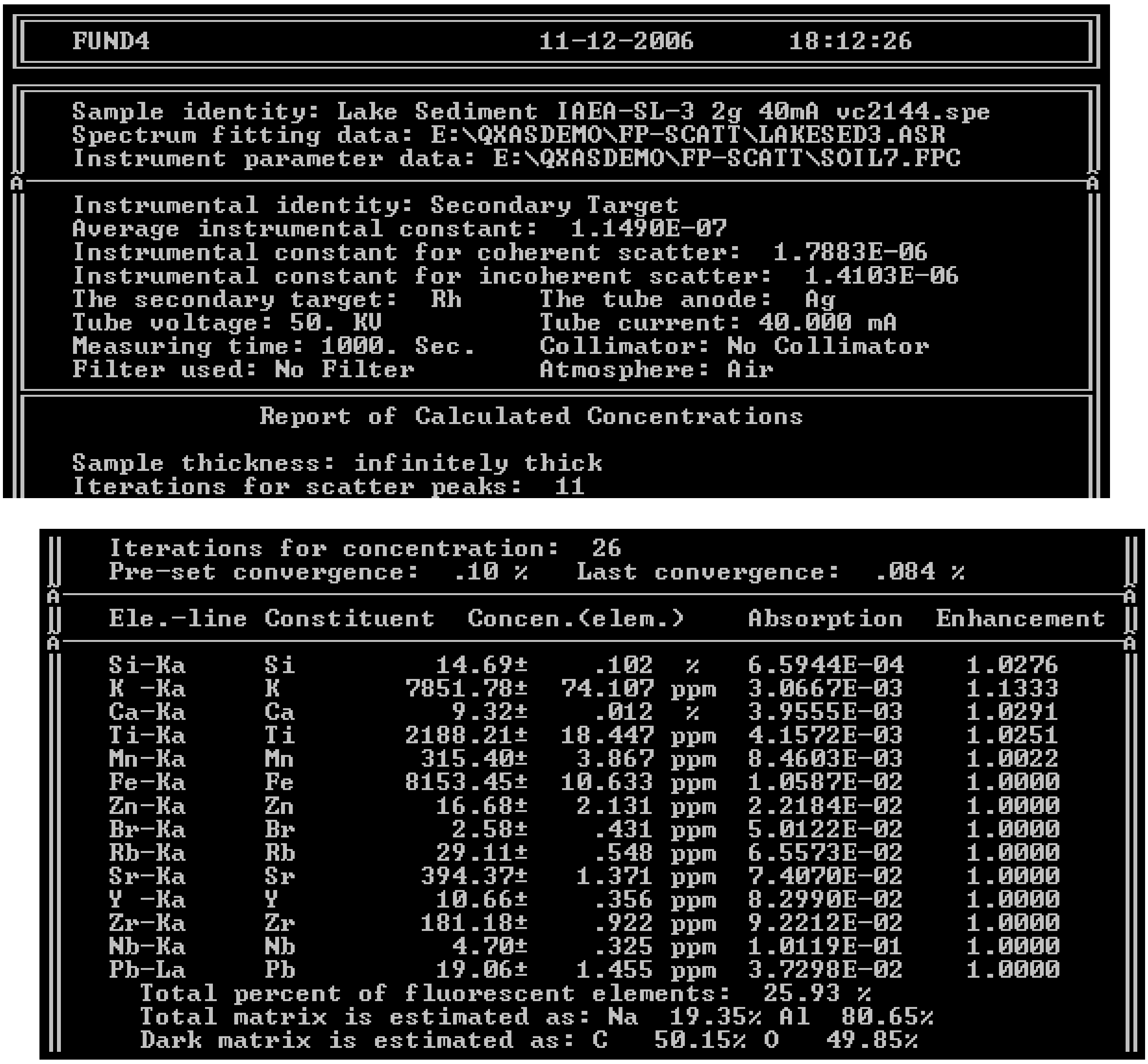
had been split off, because some of the individual Chi square values were too high with a single ROI for the fluorescence peaks. Finally is the Rh K scatter region (SL3-1.inp) approximated with the previously introduced model -1 defined by:

X-LINES ADD: RH,INC RH-KA,COH RH-KB,COH 21.75,INC 17 17.25 17.5 17.75 18 18.25 18.5 18.75 20.5 20.75 21 22.5 ZR-KB

The scatter region has to be split off, because the background is described for the first spectrum part as linear polynomial, of order 10; for the second part also as linear, of order 15. Any such high parameter would subtract the background from the scatter peaks in an uncontrollable manner. The first saved result was expanded with the second coming result with the COMMANDs **SAVE_RES** and **ADD**. For the scatter peaks it is advantageous to use **UPDATE** instead of **ADD**, when the spectrum had been fitted before for the scatter peak region. Otherwise a second block with scatter peak information will be stored – only the first block will be used by AXIL. In doubt, inspect the final file, LakeSed3.asr.

The definition of the sample is achieved with **Specify standard /sample information** and selection of the default **Sample concentration** for **Select calculation mode**. The **Type of Instrument Constant** is to be selected as **Individual and / or average**, which will correct for the lighter elements the systematic deviation from the average instrumental fluorescence constant. The sample thickness one usually will leave for unknowns at the default **intermediate thick**, but not specify the actual value, because the program will calculate the thickness itself. For true intermediate thick samples, as used also for the **ET** METHOD, the thickness is better specified explicitly by the known value. In the FORM **Menu for setting up options** the only alteration should be, to switch to **Secondary enhancement corrected**, because only for ancient PCs one had to think of the speed for the computation. Otherwise select this option automatically for samples. The final iterations are initiated with **Calculation of Geometry constants / Analysis of unknown samples**.

Hint for problems during the final calculations of instrument constants or sample concentrations: When after a short flash the calculation will stop and bring back to the previous COMMAND **Calculations of Geometry constants/Analysis of unknown samp.**, the *conventional memory* did not suffice. *Terminate QXAS completely* and re-start it; go again to the last COMMAND **Calculations of Geometry constants/Analysis of unknown samp.** (the temporary file fundp.tmp still carries all data) and initiate the calculations again.



```
FUND4                         11-12-2006      18:12:26

Sample identity: Lake Sediment IAEA-SL-3 2g 40mA vc2144.spe
Spectrum fitting data: E:\QXASDEMO\FP-SCATT\LAKESED3.ASR
Instrument parameter data: E:\QXASDEMO\FP-SCATT\SOIL7.FPC

Instrumental identity: Secondary Target
Average instrumental constant:  1.1490E-07
Instrumental constant for coherent scatter:  1.7883E-06
Instrumental constant for incoherent scatter:  1.4103E-06
The secondary target:  Rh      The tube anode:  Ag
Tube voltage: 50. KV           Tube current: 40.000 mA
Measuring time: 1000. Sec.     Collimator: No Collimator
Filter used: No Filter         Atmosphere: Air

            Report of Calculated Concentrations

Sample thickness: infinitely thick
Iterations for scatter peaks:  11
```

```
Iterations for concentration:  26
Pre-set convergence:  .10 %   Last convergence:  .084 %

Ele.-line Constituent  Concen.(elem.)    Absorption  Enhancement

Si-Ka     Si          14.69±    .102  %  6.5944E-04    1.0276
K -Ka     K         7851.78±  74.107 ppm 3.0667E-03    1.1333
Ca-Ka     Ca           9.32±    .012  %  3.9555E-03    1.0291
Ti-Ka     Ti        2188.21±  18.447 ppm 4.1572E-03    1.0251
Mn-Ka     Mn         315.40±   3.867 ppm 8.4603E-03    1.0022
Fe-Ka     Fe        8153.45±  10.633 ppm 1.0587E-02    1.0000
Zn-Ka     Zn          16.68±   2.131 ppm 2.2184E-02    1.0000
Br-Ka     Br           2.58±    .431 ppm 5.0122E-02    1.0000
Rb-Ka     Rb          29.11±    .548 ppm 6.5573E-02    1.0000
Sr-Ka     Sr         394.37±   1.371 ppm 7.4070E-02    1.0000
Y -Ka     Y           10.66±    .356 ppm 8.2990E-02    1.0000
Zr-Ka     Zr         181.18±    .922 ppm 9.2212E-02    1.0000
Nb-Ka     Nb           4.70±    .325 ppm 1.0119E-01    1.0000
Pb-La     Pb          19.06±   1.455 ppm 3.7298E-02    1.0000
  Total percent of fluorescent elements:  25.93 %
  Total matrix is estimated as: Na  19.35% Al  80.65%
  Dark matrix is estimated as: C   50.15% O   49.85%
```

Fig. 7.12. Quantitative results for the reference standard SL-3 obtained with the Full Fundamental Parameters method.

Table 7.3. Selected element concentration values for IAEA SL-3 standard reference material, established with Full fundamental parameters and Backscatter fundamental parameters METHOD, in comparison with the certified values.

	K (μg/g)	Ca (%)	Ti (μg/g)	Br (μg/g)	Rb (μg/g)	Sr (μg/g)
Full fundamental parameters METHOD	7852	9.32	2188	2.6	29.1	394
Backscatter FP METHOD	9537	12.06	2815	3.7	39.8	522
Certified values	8740	11.11	2610	5.6	38.8	0.47
C.I. (95 %)	7910-9570	10.72-11.5	2300-2920	4.8-6.4	36.9-40.7	0.45-0.49

The comparison of the two sets of results as obtained by the **Full fundamental parameters** and the **Backscatter fundamental parameters** METHOD exhibits for both a problem with the element strontium for this sample. Bromine is underestimated by both by approximately a factor of two, but its low intensity only demonstrates that working close to the detection limit is generally problematic – another fit model could have resulted in e.g. an overestimation. For potassium, calcium and titanium there is no other statement than the **Full FP** METHOD tends to the lower confidence interval limit and **Backscatter fundamental parameters** to the upper limit. Rubidium is better described by **Backscatter fundamental parameters**.

7.2.3. Artificial scattering calibration standards

As can be seen from Figure 7.4, it might be difficult to impossible to find a suited scattering calibration standard. E.g. the intermediate thick pellet of Soil−7, prepared with binder, has no near neighbours (except $MgSO_4$). The composition of this sample is well known, it consists of half binder (HWC), half standard reference material; with the elements' content (above 0.1 %) of: H (1.9 %), C (48.7 %), N (1.4 %), O (25.3 %), Mg (0.6 %), Al (2.3 %), Si (9.1 %), K (0.6 %), Ca (8.1 %), Ti (0.15 %), and Fe (1.3 %). The resulting average atomic number is 8.88.

It is possible to construct artificial scattering standards. An instrumental parameter file OrgaMatr.fpc, identical with Soil.fpc, with the exception of the instrumental constants for scattering, was created. In order to obtain the scatter calibration the scatter peak information from the sample AXIL result file, Soil7-1.asr, was copied and a pasted into a new file, OrgaMatr.asr, containing this scatter peak information (and supplementary information as needed to fulfil the *.asr file syntax). This OrgaMatr.fpc file was loaded by the METHOD **Full fundamental parameters** and the scatter calibration standard, OragMatr.asr, was evaluated: In the TOGGLE FIELD **Select Calculation mode, Instru. Constants for fluorescence & scatter** was selected. With an input for the tube current of 40 mA, the sample type left at the default as intermediate thick, use was made of the known aerial density (area related mass) of 21.5 mg/cm^2. There are no fluorescence peaks found in this file, therefore the matrix composition must be specified: FORM **Menu for setting up options**, **(7) There are known-compositions**. Let us assume the matrix composition were unknown, then one had to utilize the graph of Figure 7.4: The scatter peak ratio for the intermediate thick Soil 7 pellet is 2.77, from this an average atomic number of 8.95 can be deduced. Consequently an artificial sample composition must be constructed, that will result in an average number close to this value. As representatives the elements nitrogen (its atomic number represents the major constituents of the binder) and as sample "contribution" calcium (or silicon) are proposed. Their stochiometry was varied until the average atomic number was found. The first "compound": $N_{14}Ca_1$ is equivalent to N (85.59 %) and Ca (14.41 %). It results in the instrumental constants for coherent scattering: $1.8328*10^{-6}$ and incoherent scattering: $1.6765*10^{-6}$. The second "compound": N_5Si_1 is equivalent to N (71.375 %) and Si (28.625 %). It results in the instrumental constants for coherent scattering: $2.0813*10^{-6}$ and incoherent scattering: $1.6494*10^{-6}$. Other compositions are possible, with the constraints of the given average atomic number and a "realistic" description of the sample composition.

7.3. METHOD: Fundamental Parameters-monochromatic excitation/scatter peaks

Demonstration files (directory \QXASdemo\FP-Scatt):

- Calibration file: Soil.clb

- AXIL result files for calibration (directory \QXASdemo\ASR-Stds)): Soil7-2.asr, Instr-Bl.asr, Si-wafer.asr, K2CO3.asr, K-KH2PO4.asr, K2-Cr2O7.asr, K-KBr.asr, CaCO3.asr, Ti-Std.asr, TiO.asr, MnO2.asr, Fe-Std.asr, Fe2O3.asr, Zn-Std.asr, ZnO.asr, Br-KBr.asr, SrCO3.asr, Y2O3.asr, Zr-Std.asr, ZrO2.asr, Nb-Std.asr, Nb2O5.asr, Pb-LStd.asr
- AXIL result files sample: Instr-Bl.asr, LakeSed3.asr

Fundamental Parameters for **monochromatic excit**ation by use of the **scatter peaks** (also named **Backscatter Fundamental Parameter**, **BFP**) is a very versatile METHOD for quantification and is suited for completely unknown samples (thickness and dark matrix are calculated). Source and X-ray tube excitation can be covered. The fundamental parameters approach calculates calibration constants from standards' *.asr files and takes several theoretical values into account: The fundamental parameters, various absorption corrections, the enhancement effect, and the detector efficiency. The sample self-absorption by the dark matrix is corrected by the use of the scatter peaks. As important feature of the program are the *differential scattering cross sections* used for the calculations. The range of elements that can be analyzed by this METHOD is not limited or correlated to any range defined by the elements of the standards, but when elements of standards represent unknown sample elements the individual calibration constant is used. One constraint of the METHOD is the fact that *only monochromatic excitation* can be handled. Even for more than one line of a source or secondary target the intensity weighted average energy must be calculated, $E_{average} = p_{K\alpha1} \cdot E_{K\alpha1} + p_{K\alpha2} \cdot E_{K\alpha2} + p_{K\beta1} \cdot E_{K\beta1} + p_{K\beta2} \cdot E_{K\beta2} + p_{K\beta3} \cdot E_{K\beta3}$. For a Rh secondary target the weighted average of its K_α and K_β lines yields E_{average} = 20.6 keV. For direct X ray tube (continuous) excitation as primary radiation sometimes so called effective energies are defined. Such a procedure might lead to good results, from the theoretical point of view it is not recommended to apply this METHOD to polychromatic excitation.

A handicap of the program is the missing <ESCape> command throughout the various lines that have to be entered with appropriate information. Any single mistake in the input will force the user to terminate the program with <BREAK> (some computers <Ctrl> plus <BREAK>, <Fn> plus <BREAK>. No re-runs, to add or remove standards from the calibration procedure, are possible. In such cases the calibration has to be re-done.

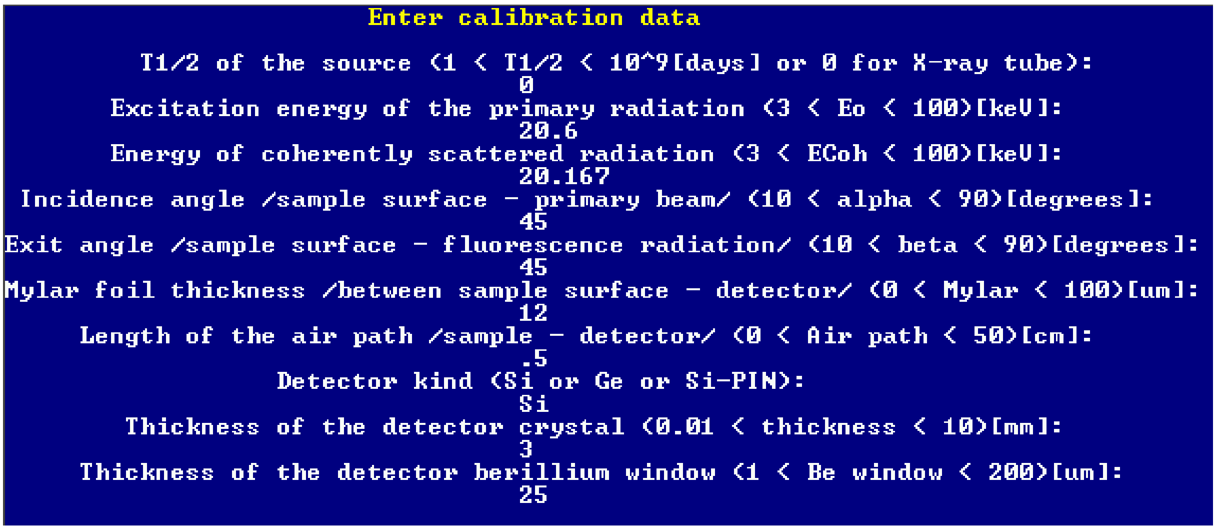
7.3.1. Calibration

Generally it is recommended to start QXAS with the directory information of the directory where *all* calibration standards are contained in (also the blank file and scatter calibration standards should be found in this directory; for the demonstration: \QXASdemo\ASR-Stds). As minimum one spectrum *.asr file together with the complete knowledge about its composition will serve for the calibration. The more the standards cover the element range of unknown samples the better, because individual calibration constants will be used. Usually one will employ several standards for fluorescence calibration (representing the elements identified in the unknown sample(s) and one (or more) standard(s) for scatter calibration, being close in its ratio of incoherent to coherent scatter peak area to the unknown sample(s). Elements not represented by standards will be calculated by use of the average calibration constant for fluorescence. For the purpose of the scatter calibration it is possible for this METHOD - and highly advisable - to use *.asr files of standards that do not contain any useful fluorescence peaks but only the scatter peaks information (cellulose, HWC, etc.) or to fit only the scatter region and neglect the fluorescence region (Soil 7, etc.). Otherwise insignificant peaks can contribute to the fluorescence calibration. The *.asr file must contain information of the form: **$COH_SCAT:** and **$INC_SCAT:**. At least one so-called **blank sample** file must exist. Usually this will be a spectrum acquired without any standard / sample in the usual position of the sample holder (instrument blank) and it should represent the scatter contribution from the spectrometer and the ambient air. If necessary, blank problems for certain elements can be treated here, but the basic idea is the determination the scatter blank. As result of a calibration run a *.clb file will be created, only then unknowns can be analyzed.

7.3.1.1. Example: Creation of Soil.clb

For demonstration a calibration file had been created, containing twenty-one calibration standards' *.asr files for the establishment of the fluorescence calibration constant: Si-wafer, K2CO3, K-KH2PO4 (potassium), K2-Cr2O7 (potassium), K-KBr (potassium), CaCO3, Ti-Std, TiO, MnO2, Fe-Std, Fe2O3, Zn-Std, ZnO, Br-KBr (bromine), SrCO3, Y2O3, Zr-Std, ZrO2, Nb-Std, Nb2O5 and Pb-LStd. One standard for the scatter constants (pellet of IAEA Soil 7), only evaluated for the scatter peaks, Soil7-2.asr. The first FORM of this METHOD (**Select:**) will lead to the calibration (**1.Perform calibration**) by typing "1". Any other character will not be accepted (and "2" brings to the later to be passed quantification of unknown samples). The FORM **Enter calibration data** (and all other FORMS of this program) will have to be filled in correctly, e.g. numbers must be entered that are between certain limits (any < signs will rather mean that the actual limits are included into the range and are also applicable). When capital/small letters are expected, as usually specified one line above the expected input, the operator will have to obey, otherwise the program will respond with an error message and the input will have to be repeated correctly.

For tube excitation the first line of the FORM will have to be passed with "0". The **excitation energy** (input: 20.6 keV) can be different from the coherent scatter peak energy, because the weighted average for K-excitation is higher than the coherent scatter peak energy (**Energy of the coherently scattered radiation**) of the K_α line, $E_{el\text{-}scat} = E_{K\alpha}$ (input: 20.167 keV). **Incident** and **Exit angle** (input for both: 45^0) refer to the sample surface – beam geometry (lines 4, 5) A **Mylar foil** between detector and sample can be used to protect the detector window and/or represent the exit window of an (evacuable) sample chamber, the unit of the **thickness (um)** is µm (input: 12). The next line, **Length of the air path**, takes into account the absorption of the characteristic radiation by air on the way from the sample to the detector (input: 0.5). Three different **detector**s, predefined so that dead layer and gold layer are taken into account, are for selection. The Si-PIN detector description is the same as for the Si(Li) detector – (no Au layer is used for the first one). Type exactly **Si**, **Ge**, or **Si-PIN** (input: Si). The **thickness of the detector crystal** (input: 3) is important for the higher energy intrinsic efficiency, whereas the **beryllium window** thickness, in µm, is of influence to the lower energetic radiation (input: 25).



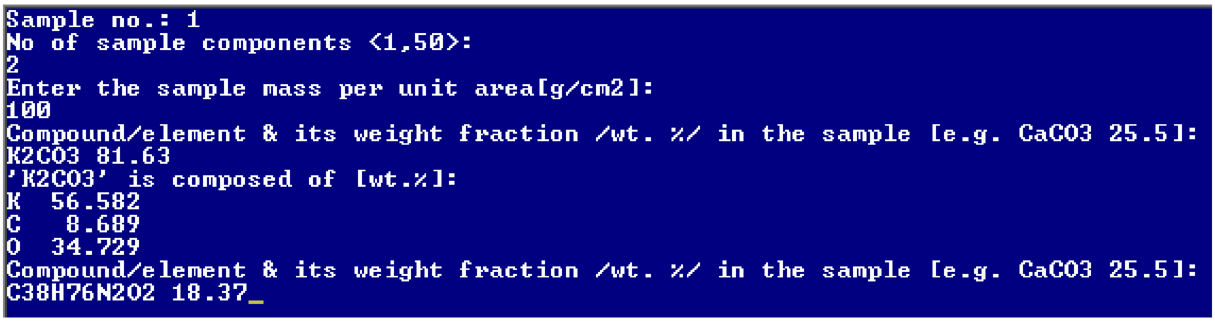
```
                         Enter calibration data

          T1/2 of the source (1 < T1/2 < 10^9[days] or 0 for X-ray tube):
                                   0
        Excitation energy of the primary radiation (3 < Eo < 100)[keV]:
                                   20.6
        Energy of coherently scattered radiation (3 < ECoh < 100)[keV]:
                                   20.167
 Incidence angle /sample surface - primary beam/ (10 < alpha < 90)[degrees]:
                                   45
Exit angle /sample surface - fluorescence radiation/ (10 < beta < 90)[degrees]:
                                   45
Mylar foil thickness /between sample surface - detector/ (0 < Mylar < 100)[um]:
                                   12
     Length of the air path /sample - detector/ (0 < Air path < 50)[cm]:
                                   .5
                    Detector kind (Si or Ge or Si-PIN):
                                   Si
         Thickness of the detector crystal (0.01 < thickness < 10)[mm]:
                                   3
     Thickness of the detector berillium window (1 < Be window < 200)[um]:
                                   25
```

Fig. 7.13. In the form Enter calibration data the excitation source, the geometry, the detector and the air path must be specified.

After the successful completion of the FORM the so-called **blank sample file name** (input of an *.asr file name, but the extension .ASR must be omitted) has to be entered – Instr-Bl. It contains the fit results of the scatter peaks originating from scattering of the excitation radiation by the empty sample holder (instrument blank) and, if applicable, the ambient air. **Enter the x-ray tube current** refers to this blank measurement. The question **Save results in the file report** will enable to save the individual calibration results to a report (file name *.rpt, which later also can be used to store final results of sample analysis) in readable ASCII format, but the further calculations are not affected by this decision. The actual calibration file will have the extension *.clb and is created at the end of the calibration procedure.

7.3.1.2. Example: pellet of K_2CO_3 plus HWC as binder, K2CO3.asr, as fluorescence calibration standard.

The next FORMs refer to the first standard (**No of sample components <1,50>**) and expresses the need of the program for an input of the total number of chemical compounds constituting the first standard; the input must be an integer between 1 and 50. For the K_2CO_3 calibration standard, pressed as pellet with added binder, the input will be 2. The area related mass (aerial density) of the first standard must be entered after the line **Enter the sample mass per unit area** (for thick standards any high number will do, e.g. 100). In the next line for the K_2CO_3 part of the calibration standard, with a concentration of 81.63 %, input K2CO3 81.63. Consecutively enter C38H76N2O2 18.37 for the binder. The number of times a line, with the need of an input for an element / compound and its concentration, will show up, corresponds to the previously entered integer (**No of sample components <1,50>**).



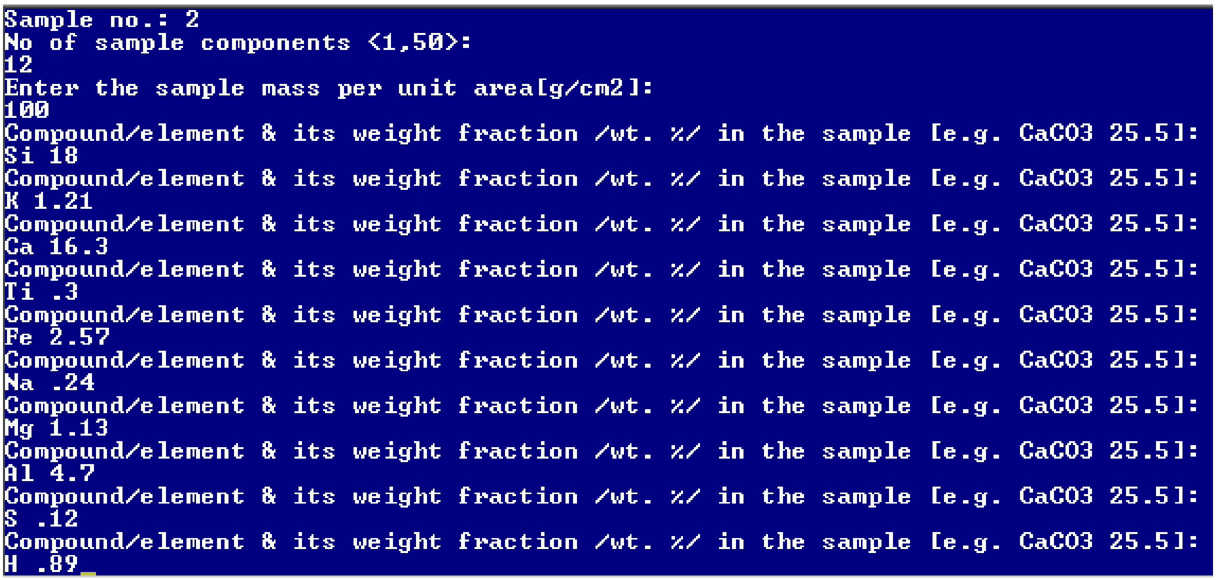
```
Sample no.: 1
No of sample components <1,50>:
2
Enter the sample mass per unit area[g/cm2]:
100
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
K2CO3 81.63
'K2CO3' is composed of [wt.%]:
K  56.582
C   8.689
O  34.729
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
C38H76N2O2 18.37_
```

Fig. 7.14. The calibration standard K_2CO_3 must be described concerning the compound of interest and the binder used for pelletizing.

The next FORM (**Enter sample filename**) will need the *.asr file name for the calibration standard, matching the defined elements / compounds as specified above (input: K2CO3). There is no immediate check for consistency! The consecutive FORM refers to the tube current as used for the measurement of this standard (input: 40). The question **Scatter peak intensity from other ASR-file?** will be asked for fluorescence calibration standard files, because no scatter information is found in the respective *.asr files; answer must be: “n”, otherwise a further spectrum bust be loaded. After the successful completion of the first standard the question **Next sample? (Y/N)** will permit the definition one standard after the other – input “y”, in the same way as for the first standard.

7.3.1.3. Example: pellet of IAEA Soil 7, Soil7-2.asr, as scatter calibration standard

The input needed to describe the scatter standard is for **No of sample components <1,50>**: 12. From the certificate the essential elements’ concentration values (> 0.1 %) are represented by : Na (0.24 %), Mg (1.13 %), Al (4.70 %), Si (18.0 %), S (0.12 %), K (1,21 %), Ca (16.3 %), Ti (0.3 %), Fe (2.57 %), the dark matrix is described by H (0.89 %), C (7.18 %) and O (47.36 %) in accordance with reference **[27]**. Tube current input: 40; file name input: Soil7-2. The successful termination of the calibration is achieved with “n”.

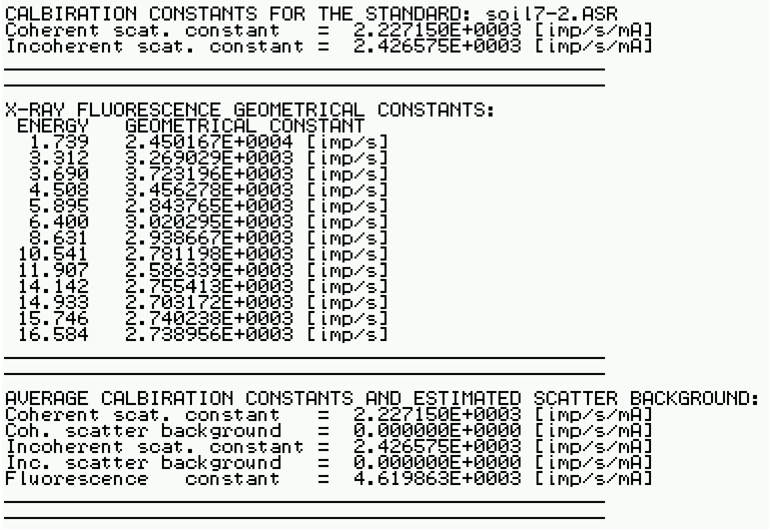


```
Sample no.: 2
No of sample components <1,50>:
12
Enter the sample mass per unit area[g/cm2]:
100
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
Si 18
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
K 1.21
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
Ca 16.3
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
Ti .3
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
Fe 2.57
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
Na .24
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
Mg 1.13
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
Al 4.7
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
S .12
Compound/element & its weight fraction /wt. %/ in the sample [e.g. CaCO3 25.5]:
H .89_
```

Fig. 7.15. For the description of the composition the reference standard Soil 7 used for scatter calibration twelve chemical elements are considered to contribute significantly.

The last-but-one SCROLL BOX for the calibration procedure summarizes the **AVERAGE CALIBRATION CONSTANTS** for the coherent and incoherent scatter peaks and for fluorescence.

Finally all relevant data will be stored (FORM **Enter the name for the calibration file**). A meaningful name, but no extension (it is by default *.clb) is needed. It is advisable to match it with the report file name (*.rpt), in case this option to create and save a report had been selected previously. The report (Soil.rpt) contains a wealth of information: Among others, the spectrometer specification as entered previously, data for all standards and the calculated individual and average calibration constants.



```
CALBIRATION CONSTANTS FOR THE STANDARD: soil7-2.ASR
Coherent scat. constant   =  2.227150E+0003 [imp/s/mA]
Incoherent scat. constant =  2.426575E+0003 [imp/s/mA]

X-RAY FLUORESCENCE GEOMETRICAL CONSTANTS:
 ENERGY   GEOMETRICAL CONSTANT
  1.739   2.450167E+0004 [imp/s]
  3.312   3.269029E+0003 [imp/s]
  3.690   3.723196E+0003 [imp/s]
  4.508   3.456278E+0003 [imp/s]
  5.895   2.843765E+0003 [imp/s]
  6.400   3.020295E+0003 [imp/s]
  8.631   2.938667E+0003 [imp/s]
 10.541   2.781198E+0003 [imp/s]
 11.907   2.586339E+0003 [imp/s]
 14.142   2.755413E+0003 [imp/s]
 14.933   2.703172E+0003 [imp/s]
 15.746   2.740238E+0003 [imp/s]
 16.584   2.738956E+0003 [imp/s]

AVERAGE CALBIRATION CONSTANTS AND ESTIMATED SCATTER BACKGROUND:
Coherent scat. constant   =  2.227150E+0003 [imp/s/mA]
Coh. scatter background   =  0.000000E+0000 [imp/s/mA]
Incoherent scat. constant =  2.426575E+0003 [imp/s/mA]
Inc. scatter background   =  0.000000E+0000 [imp/s/mA]
Fluorescence   constant   =  4.619863E+0003 [imp/s/mA]
```

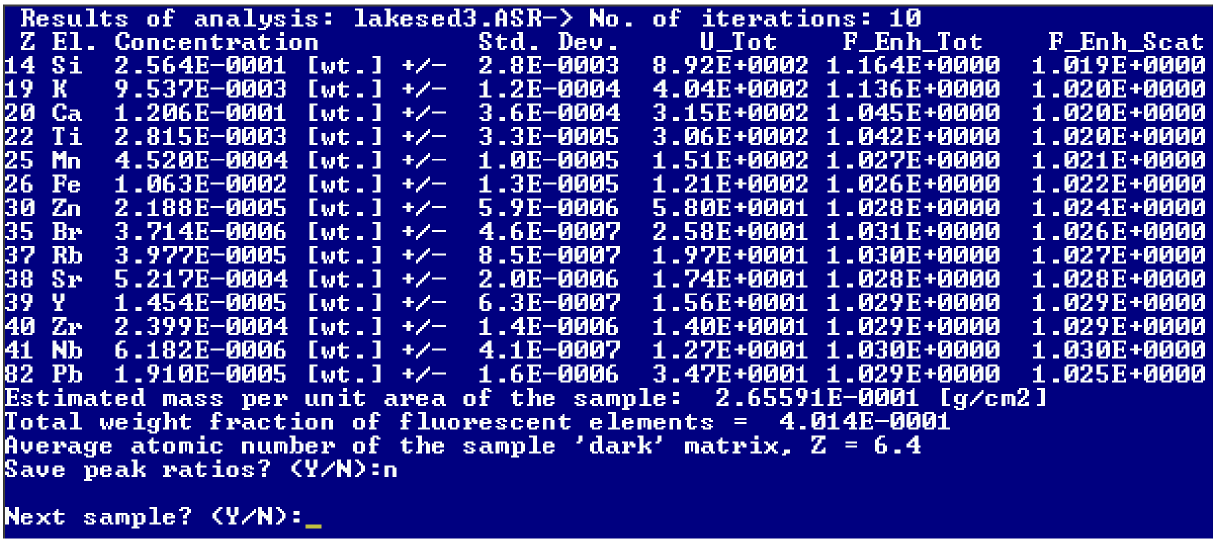
Fig. 7.16. The calibration report is available as ASCII file.

7.3.2. Analysis of unknown sample

It is possible to work with sample *.asr files without scatter peak information, contrary to the calibration procedure where at least one file must contain relevant scatter peak information. This makes sense for samples without dark matrix. Usually the unknown samples *.asr files should contain the fitted scatter ROIs. However, when no scatter peak information is found, all concentration values will be normalized to 1 (e.g. for alloys this will be a good option).

Warning: The program will crash for elements included into the *.asr files with absorption edges above the excitation energy. If this has to be done for fitting purposes, the *.asr file has to be edited manually to remove such elements. Although in the simplified secondary target excitation approach it were impossible to excite, e.g., Zr with a Mo secondary target, in reality it is possible, because the secondary target scatters also continuum radiation from the x-ray tube.

The first screen of this METHOD (**Select:**) will lead to the analysis of unknown samples (**2. Analyze unknown sample(s)**) by typing “2”. Any other character will not be accepted (and “1” opens the calibration procedure). The relevant calibration file (*.clb) and the blank file (*.asr) names (usually the same blank as already used for this calibration procedure), both without extension, are to be entered. Independent of the selection for a report file name previously used, the results can be saved in a file with the extension *.rpt. It is possible to create a new report file, or use the same report file as for the calibration measurements. The calculation will start after the unknown sample *.asr file name was entered. For a correct calculation run the number of iterations will briefly be displayed, ending with a screen named: **Results of analysis**: . With the calibration Soil.clb it is possible to evaluate the IAEA reference standard SL-3, AXIL result file LakeSed3.asr, because the calibration standards were selected in order to represent the sample elements (except Rb) and the scatter peak ratio compares well for Soil 7 and the sample.



```
 Results of analysis: lakesed3.ASR-> No. of iterations: 10
 Z El. Concentration           Std. Dev.     U_Tot    F_Enh_Tot    F_Enh_Scat
14 Si  2.564E-0001 [wt.] +/-  2.8E-0003  8.92E+0002 1.164E+0000  1.019E+0000
19 K   9.537E-0003 [wt.] +/-  1.2E-0004  4.04E+0002 1.136E+0000  1.020E+0000
20 Ca  1.206E-0001 [wt.] +/-  3.6E-0004  3.15E+0002 1.045E+0000  1.020E+0000
22 Ti  2.815E-0003 [wt.] +/-  3.3E-0005  3.06E+0002 1.042E+0000  1.020E+0000
25 Mn  4.520E-0004 [wt.] +/-  1.0E-0005  1.51E+0002 1.027E+0000  1.021E+0000
26 Fe  1.063E-0002 [wt.] +/-  1.3E-0005  1.21E+0002 1.026E+0000  1.022E+0000
30 Zn  2.188E-0005 [wt.] +/-  5.9E-0006  5.80E+0001 1.028E+0000  1.024E+0000
35 Br  3.714E-0006 [wt.] +/-  4.6E-0007  2.58E+0001 1.031E+0000  1.026E+0000
37 Rb  3.977E-0005 [wt.] +/-  8.5E-0007  1.97E+0001 1.030E+0000  1.027E+0000
38 Sr  5.217E-0004 [wt.] +/-  2.0E-0006  1.74E+0001 1.028E+0000  1.028E+0000
39 Y   1.454E-0005 [wt.] +/-  6.3E-0007  1.56E+0001 1.029E+0000  1.029E+0000
40 Zr  2.399E-0004 [wt.] +/-  1.4E-0006  1.40E+0001 1.029E+0000  1.029E+0000
41 Nb  6.182E-0006 [wt.] +/-  4.1E-0007  1.27E+0001 1.030E+0000  1.030E+0000
82 Pb  1.910E-0005 [wt.] +/-  1.6E-0006  3.47E+0001 1.029E+0000  1.025E+0000
Estimated mass per unit area of the sample:  2.65591E-0001 [g/cm2]
Total weight fraction of fluorescent elements =  4.014E-0001
Average atomic number of the sample 'dark' matrix, Z = 6.4
Save peak ratios? (Y/N):n

Next sample? (Y/N):_
```

Fig. 7.17. Quantitative results (for the reference standard IAEA SL-3) are displayed with normalized concentration values, where 1.0E-0 corresponds to 100 %.

The concentration values are given as weight fraction: **2.564E-0001** corresponds to 25.64 % for e.g. Si. In case the AXIL fit had not been carefully examined, in order to eliminate elements with too low peak areas, all results have to be checked so that the standard deviation (**Std. Dev.**) does not exceed the corresponding concentration value, which would mean the respective result is below the detection limit. **U_Tot** stands for the total absorption correction for the line of interest, **F_Enh_Tot** for the inter-element plus enhancement by scattering correction and **F_Enh_Scat** for the enhancement by scattering. For the two last two columns values close to 1 will correspond to small correction (less important enhancement by other elements, or scattering).

For the experienced user: The line **Save peak ratios? (Y/N):** aims to the fact that improvements in the AXIL fit will have a (positive) effect on the quantification. When the question is answered with "**y**", files with the extension .RAT will be created which can be used for the model file (*.inp) of AXIL (manual input by copy and paste only). This will affect the intra-line peak ratios of K- and L-lines for a given element (different sample self-absorption for different energies). With these improved fit results the quantification is to be repeated.

For samples measured under the same conditions and adequately represented by the fluorescence and scatter calibration the calculation can be started for another sample (**Next sample? (Y/N)**: with "**y**".

CHAPTER 8. SOURCE EXCITATION

References: [37], [38], [39], [40]

Note for users of ORTEC MCAs and software: The MCA spectra can be saved in ASCII format and *.spe files are already generated at the level of storing the spectra after the measurement – the spectrum conversion with QXAS is not necessary. Unfortunately there is a problem with the format of the date (also other MCAs' spectra formats might be affected), which only is of relevance for source excitation, because of the calculations for the decay correction. For repair of *.spe files see CHAPTER 4: Editing of data files. When the date format is left unchanged the **ET** METHOD will crash.

8.1. Establishment of numeric values for incidence and take-off angle

Demonstration files (directory \QXASdemo\Cd-109):

- Spectra for the preliminary calibration (directory \QXASdemo\Cd-109\SPE-INP): Ti.spe, Cr.spe, Fe.spe, Co.spe, Ni.spe, Cu.spe, Zn.spe, Ge.spe, Zr.spe, Nb.spe, Mo.spe
- Input files (directory \QXASdemo\Cd-109\SPE-INP): Ti.inp, Cr.inp, Fe.inp, Co.inp, Ni.inp, Cu.inp, Zn.inp, Ge.inp, Zr.inp, Nb.inp, Mo.inp
- AXIL result files (directory \QXASdemo\Cd-109\ASR-Std): Ti.asr, Cr.asr, Fe.asr, Co.asr, Ni.asr, Cu.asr, Zn.asr, Ge.asr, Zr.asr, Nb.asr, Mo.asr
- Source file: Cd-test.sou
- Calibration file: Cd_52_90.cal
- Spectra: Cabbage.spe, Lichen.spe, SL3.spe, Soil7.spe, SL7-thin.spe
- Input file: Cabbage.inp, Lichen.inp, SL3.inp, Soil7.inp, SL7-thin.inp

The major problem with source excited XRF is the ill definition of the incident and take-off angle in respect to the sample surface. The wide spread of angles of X rays, the divergence, complicates the quantification. In the ideal case one would treat this problem with the Monte-Carlo method or with an additional integration over the solid angles. None of it is performed by any of the QXAS METHODs. Rather average (effective) angles will have to be defined. For this purpose use the utility: **Incident and take-off angles, Geometry constants, *.sen file**. This utility is rather user unfriendly, will need a lot of input, but this is the only way to calculate these angles – by QXAS. Unfortunately during the establishment of values for the angles a calibration file will have to be loaded. Such a *.cal file must be generated *before* with the METHOD Elemental sensitivities. All what was mentioned to be essential for this METHOD has to be applied with slight modifications for a source excitation system.

8.1.1. Calibration standards

All example standards' spectra for Cd-109 source excitation had been collected with the intention to have approximately 10 000 counts in the peaks of relevance for calibration. The measuring time (live time, LT) was selected to adjust the total counts in the peaks of interest. The number of 10 000 counts for the lines of relevance should result in statistically well defined peaks (relative standard deviation 1 %).

A Cd-109 source emits silver radiation (Ag K_α, Ag K_β) and a γ-line at 88 keV.

Note: Description of the calibration standards available for Cd 109 source excitation can be found in the EXCEL cd109_standards.xls file.

8.1.2. Preliminary calibration with the METHOD Elemental Sensitivities

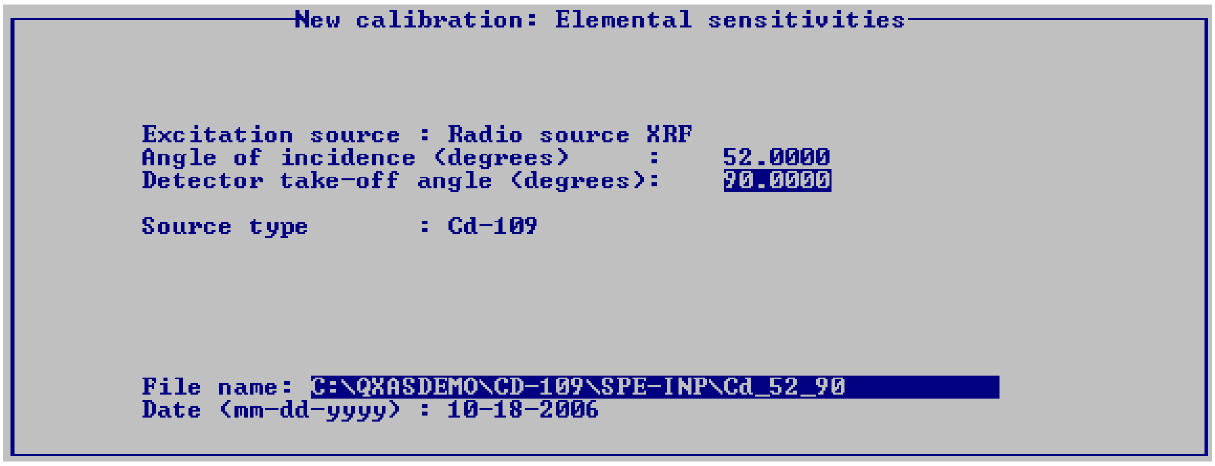
For the calibration of the **Elemental sensitivities** METHOD sensitivities are calculated for characteristic lines from standards, correcting the self-absorption in the standards. It is assumed, that the *excitation radiation* can be *represented by a single X-ray line* with specified energy (intensity weighted energy). The sensitivity S_n of all elements n is calculated for which a concentration c_n is supplied to the current *.cal file and a peak area N_n can be read in by means of an *.asr file.

$$S_n = \frac{N_n \cdot A}{LT \cdot c_n} \cdot T \tag{8.1}$$

LT is the acquisition time of the respective spectrum, and A the absorption correction. K_α-lines and L_α-lines are treated independently. The decay correction T is defined as

$$T = \exp\left(\frac{\ln 2}{T_{1/2}} \cdot t \right) \tag{8.2}$$

where $T_{1/2}$ is the half life of the used isotope, t is the time interval between measurement and calibration – both in matching units of time. The report will contain individual results for each standard *.asr file and a summary of the calculated sensitivities.



```
New calibration: Elemental sensitivities

Excitation source : Radio source XRF
Angle of incidence (degrees)     :    52.0000
Detector take-off angle (degrees):    90.0000

Source type        : Cd-109

File name: C:\QXASDEMO\CD-109\SPE-INP\Cd_52_90
Date (mm-dd-yyyy) : 10-18-2006
```

Fig. 8.1. Definition of the preliminary calibration file Cd_52_90.

8.1.2.1. Example: Preliminary calibration file Cd_52_90.cal

As almost first input for the establishment of the preliminary calibration file an input for the **Angle of incidence (degrees)** is needed, defined by the primary radiation and the sample surface the take-off angle between sample surface and detector axis (**Detector take-off angle (degrees)**). One has to breath deeply, but then one can relax – any angle, not too far away from reality of course, will do (these angles are needed for the absorption correction calculation of the standards). By a first guess for the take-off angle a value of 90^0 had been chosen – parallel to the detector axis direction. For the incidence angle the basis angle of a cone, defined by the central ring of the annular source as basis and as peak the centre of the sample front surface, is good enough. From the naturalistic sketch in Figure 8.5 an angle of 52^0 can be depicted. The two angles, 52^0 for the incidence and 90^0 for the take-off angle, had been chosen, firstly they can be justified by simple arguments, and secondly in order to demonstrate, even though the take-off angle value is relatively far away from the later to be calculated value, that the choice is not too critical.

In the preliminary calibration file, Cd_52_90.cal, eleven *.asr files of pure (metallic) standards had been included (Ti, Cr, Fe, Co, Ni, Cu, Zn, Ge, Zr, Nb and Mo). No effort was made for this calibration to establish also a L-lines calibration, because it serves only as a "slave" for the calculation of incident and take-off angles. For the addition of a standard to the calibration knowledge about the measurement date (essential for source excitation) and the live time (usually transferred already from the *.asr file correctly) are needed. The standards can be treated as infinitely thick in terms of XRF, so the standard's sample mass is left at the default value 0.00000. The (relative) error in the concentration value of the standards (**%stddev** - with a default value of 5 %), it is of no relevance for this intermediate calculation, was set to 0.1 %. After the correct inclusion of all standards the calibration for all elements found in the standards was finalised with **Perform calibration**. The option **Optimize Calibration with Least Square Fit** was not used, only the raw data is needed.

8.1.3. Definition of the excitation source and geometry for the Monte Carlo simulation

To be aware, as pre-requisites for the calculations are needed: Two properly defined files, namely a *.cal file (Cd_52_90.cal) and a *.sou file (Cd-test.sou), a wealth of information about the geometry of the system, and the detector characteristics (to be taken from the detector data sheet, hopefully supplied by the manufacturer). The detector characteristics are not critical, when medium to high energy lines are used for calibration.

Select from the SELECTOR BOX **Excitation selection** the item ***Annular source excitation**, next select from **Source selection** the item ***NEN source**. The used Cd-109 source is of unknown provenience; but the two other options were not brought to working, despite the fact that there are only slight differences between the three).

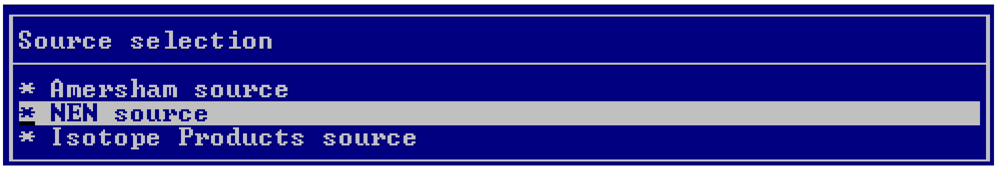


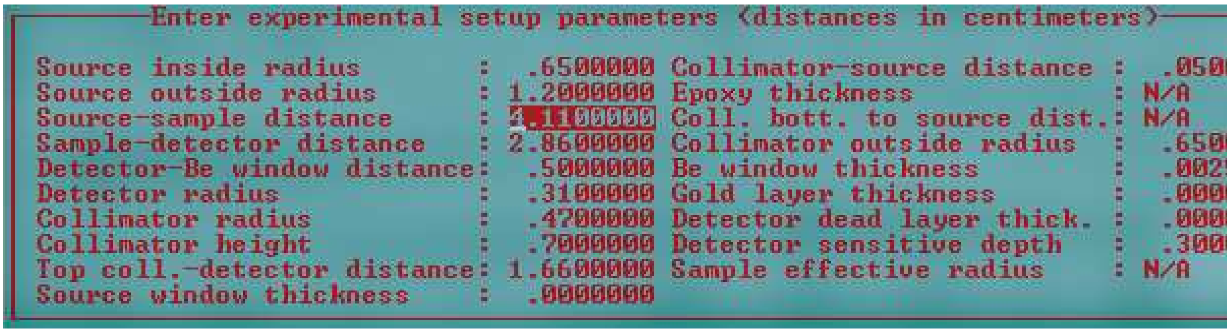
Fig. 8.2. From three brands of sources the NEN source is selected.

From the SELECTOR BOX **Isotope selection** choose the item ***Cd-109 source**, from **Spectral lines selection** the item ***K-alpha lines** (the calculations by use of L-alpha line emitters is possible too, but the calibration file Cd_52_90.cal was only defined in terms of K-lines standards, because there are more standards available for the first selection), from **Data input selection** the item **Enter data from keyboard**. This is now deep enough down in QXAS!

```
Data input selection

* Enter data from keyboard
* Enter data from old file
```

Fig. 8.3. The manual input of certain dimensions describing the source – sample – detector geometry will be activated.

A FORM **Enter experimental setup parameters (distances in centimetres)** has to be filled in with relevant data, describing the geometry of the spectrometer. For lazy users a pre-defined FORM, of course only applicable in its details for the used spectrometer, can be loaded with **Enter data from old file** and the sensitivity file Cd-angle.sen.



```
Enter experimental setup parameters (distances in centimeters)

Source inside radius         :  .6500000 Collimator-source distance :  .050
Source outside radius        : 1.2000000 Epoxy thickness            : N/A
Source-sample distance       : 4.1100000 Coll. bott. to source dist.: N/A
Sample-detector distance     : 2.8600000 Collimator outside radius  :  .650
Detector-Be window distance  :  .5000000 Be window thickness        :  .002
Detector radius              :  .3100000 Gold layer thickness       :  .000
Collimator radius            :  .4700000 Detector dead layer thick. :  .000
Collimator height            :  .7000000 Detector sensitive depth   :  .300
Top coll.-detector distance  : 1.6600000 Sample effective radius    : N/A
Source window thickness      :  .0000000
```

Fig. 8.4. Several dimensions in (cm, describing the geometry of the spectrometer must be known.

From the sketch, in scale with the real situation, see Figure 8.5, all relevant dimensions in (mm) can be taken. The used letters (from A to L, and X) can serve together with Figure 8.5 and its explanations to correlate the (brief) descriptions of the above FORM with measures to be taken from reality.

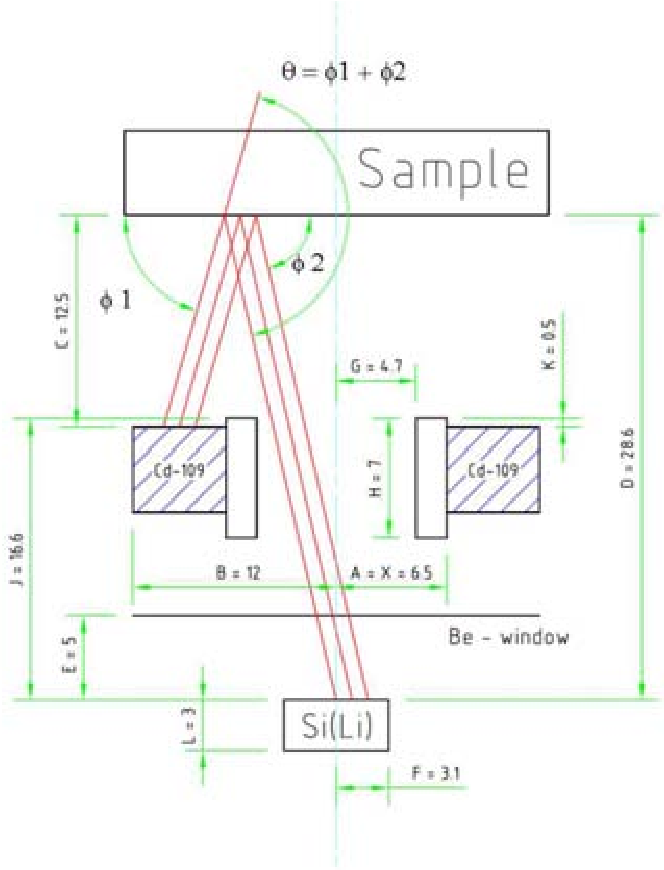


Fig. 8.5. Sketch depicting the relevant dimensions in (mm) the used Cd 109 source excitation system.

Note: Description of the geometry parameters as expected as input in the form **Enter experimental setup parameters**.

All measures had been taken with sliding callipers. Figure 8.5 with dimensions in (mm) refers to the used letters and stated dimensions of Figure 8.4 and relates them to data input as expected by QXAS.

Warning: It is easy to destroy a Be-window of a detector. Utmost care must be taken not to touch it. Also the front surface of the sealed excitation source must not be scratched.

Hazard: Sources as used for XRF will have activities around 1 GBq (10-100 mCi), when they are new. Minimize the duration of exposure when taking any measures. Never touch a radioactive source with hand, use forceps. Respect the $1/r^2$ – law, which means in words: the greater the distance to a source the less dose rate received.

After the FORM had been filled in with relevant data (or had been loaded, utilizing the file Cd-angle.sen), a source file has to be loaded, Cd-test.sou. The relevant data to be contained therein are the spectral lines (Ag K_α, Ag K_β and a γ-line at 88 keV) with their respective wavelengths in Angstrom and their relative intensities, describing a Cd-109 source. Usually for a *.sou file also the geometry were of relevance (defined with the two numbers in the line after **$GEOM:**). As the two numbers correspond to exactly the incidence and take-off angle, being under investigation, the two values were set to zero.

```
$IDENT:
Cd-109 annular source: incident/take-off angle: unknown
Cd 109
0.
$GEOM:
0,0
$CONTINIUM:
2
1.,0.
1.2,0.
$CHARLIN:
3
.5608,82.770
.4961,17.230
.1408,3.74
```

One will pass through the SELECTOR BOX **Current calibration** by loading the previously generated preliminary calibration file, Cd_52_90.cal, without caring about the stupid ITEM **Define sample current**.

```
Current calibration: C:\QXASDEMO\CD-109\CD_52_90.CAL
* Select calibration file
* Define Sample Current
```

Fig. 8.6. The file Cd_52_90.cal is used for the Monte Carlo calculation.

Finally, exhausted one arrives at a FORM **Enter number of Monte-Carlo iterations**. This number will influence the time need for the execution of the Monte-Carlo simulation. For the sake of precision, with nowadays computer processors, the highest possible number of 999999 should be typed in.

```
Enter number of monte-carlo iterations
999999_
Sample radius is :   1.033855
```

Fig. 8.7. The Monte Carlo calculation is initiated with the input for the number of events.

Having everything defined properly, the calculation run will start and a flashing screen will show the progress.

```
Working.....
67% COMPLETE_
```

Fig. 8.8. During the calculation the screen will flash and display the progress in%.

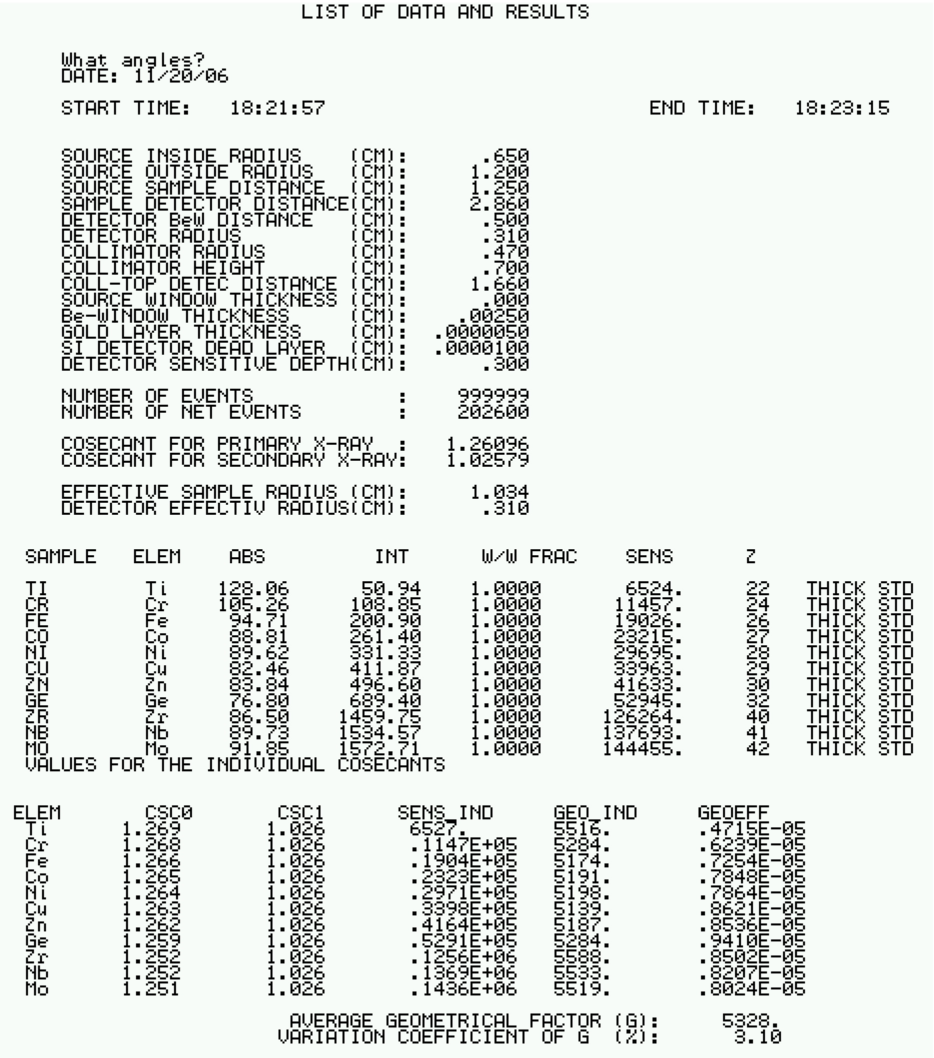
The SCROLL BOX **LIST OF DATA AND RESULTS**, will provide the desired angles. A bit cryptic they can be reached by scrolling down and will read as:

COSECANT FOR PRIMARY X-RAY : 1.26096

COSECANT FOR SECONDARY X-RAY : 1.02579

8.1.4. Results for the incidence and take-off angle and verification

The *cosecans* of an angle is defined as *1/sin* of the angle. Therefore we obtain as average (effective) angle of incidence 52.5^0 and for the take-off angle 77.1^0, both of them in respect to the sample surface. How can one know, after all this lengthy procedure, that the results are meaningful? There is not a complete proof, but some kind of verification is possible. For consistency of the calibration, typed in values for the geometry and detector, etc. the result file (to be saved as *.sen and also found as *temporary* file temp.dat when the COMMAND **<F10>=Print** is used, after the evaluation run until the next run) will provide a wealth of parameters, like the **AVERAGE GEOMETRICAL FACTOR** and its **VARIATION COEFFICIENT**, which can be compared with the individual values, like the relative efficiencies, etc.



```
                          LIST OF DATA AND RESULTS

     What angles?
     DATE: 11/20/06

     START TIME:   18:21:57                             END TIME:   18:23:15

     SOURCE INSIDE RADIUS    (CM):       .650
     SOURCE OUTSIDE RADIUS   (CM):      1.200
     SOURCE SAMPLE DISTANCE  (CM):      1.250
     SAMPLE DETECTOR DISTANCE(CM):      2.860
     DETECTOR BeW DISTANCE   (CM):       .500
     DETECTOR RADIUS         (CM):       .310
     COLLIMATOR RADIUS       (CM):       .470
     COLLIMATOR HEIGHT       (CM):       .700
     COLL-TOP DETEC DISTANCE (CM):      1.660
     SOURCE WINDOW THICKNESS (CM):       .000
     Be-WINDOW THICKNESS     (CM):     .00250
     GOLD LAYER THICKNESS    (CM):   .0000050
     SI DETECTOR DEAD LAYER  (CM):   .0000100
     DETECTOR SENSITIVE DEPTH(CM):       .300

     NUMBER OF EVENTS            :     999999
     NUMBER OF NET EVENTS        :     202600

     COSECANT FOR PRIMARY X-RAY  :    1.26096
     COSECANT FOR SECONDARY X-RAY:    1.02579

     EFFECTIVE SAMPLE RADIUS (CM):      1.034
     DETECTOR EFFECTIV RADIUS(CM):       .310

  SAMPLE   ELEM    ABS         INT      W/W FRAC    SENS      Z

  TI        Ti    128.06      50.94    1.0000      6524.     22    THICK STD
  CR        Cr    105.26     108.85    1.0000     11457.     24    THICK STD
  FE        Fe     94.71     200.90    1.0000     19026.     26    THICK STD
  CO        Co     88.81     261.40    1.0000     23215.     27    THICK STD
  NI        Ni     89.62     331.33    1.0000     29695.     28    THICK STD
  CU        Cu     82.46     411.87    1.0000     33963.     29    THICK STD
  ZN        Zn     83.84     496.60    1.0000     41633.     30    THICK STD
  GE        Ge     76.80     689.40    1.0000     52945.     32    THICK STD
  ZR        Zr     86.50    1459.75    1.0000    126264.     40    THICK STD
  NB        Nb     89.73    1534.57    1.0000    137693.     41    THICK STD
  MO        Mo     91.85    1572.71    1.0000    144455.     42    THICK STD
  VALUES FOR THE INDIVIDUAL COSECANTS

 ELEM       CSC0        CSC1       SENS_IND     GEO_IND     GEOEFF
  Ti      1.269       1.026       6527.        5516.       .4715E-05
  Cr      1.268       1.026        .1147E+05   5284.       .6239E-05
  Fe      1.266       1.026        .1904E+05   5174.       .7254E-05
  Co      1.265       1.026        .2323E+05   5191.       .7848E-05
  Ni      1.264       1.026        .2971E+05   5198.       .7864E-05
  Cu      1.263       1.026        .3398E+05   5139.       .8621E-05
  Zn      1.262       1.026        .4164E+05   5187.       .8536E-05
  Ge      1.259       1.026        .5291E+05   5284.       .9410E-05
  Zr      1.252       1.026        .1256E+06   5588.       .8502E-05
  Nb      1.252       1.026        .1369E+06   5533.       .8207E-05
  Mo      1.251       1.026        .1436E+06   5519.       .8024E-05

                        AVERAGE GEOMETRICAL FACTOR (G):      5328.
                       VARIATION COEFFICIENT OF G  (%):       3.10
```

Fig. 8.9. The temporary file temp.dat contains a wealth of information, among others individual and average geometrical factor.

The average geometrical factor has a value of 5328 with a so called variation coefficient of 3.1 %.

In the spectra of various samples (thick samples: Cabbage.spe, Lichen.spe, SL3-spe, Soil7.spe, etc., intermediate thick sample: SL7-thin.spe) the Compton peak of Ag K_α is found at a constant energy position, namely at 20.45 +/- 0.02 keV. By transformation of the Compton formula (formula 2.18) one can deduce the scattering angle from the position of the Compton peak maximum in the spectra:

$$\cos\vartheta = 1 + 511 \cdot \left(\frac{1}{E_0} - \frac{1}{E_\vartheta} \right) \qquad (8.3)$$

All energies are in (keV). With $E_0 = 22.10$ keV (weighted average energy of Ag $K\alpha_1$ and Ag $K\alpha_2$) and $E_\delta = 20.45$ keV the scattering angle for this particular geometry is 150.0^0. The sum of the calculated effective incidence and take-off angles (129.6^0) is not close to this experimentally determined scattering angle. A slight deviation could be explained by (*a*) the inaccuracies introduced by taking all necessary measures with sliding callipers and (*b*) the fact that also the maximum of the Ag K_α Compton peak in the spectra exhibits slight variations, depending on sample type and thickness – but these deviations are much less than the observed difference between the sum of the calculated angles and the observed scattering angle.

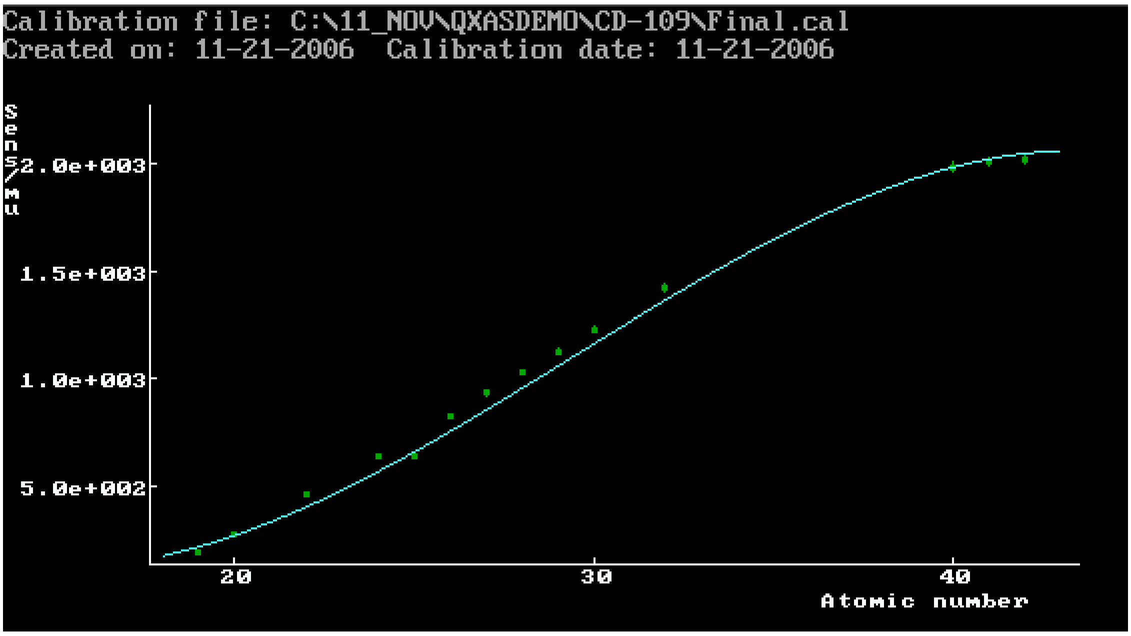
8.2. Calibration

Demonstration files (directory \QXASdemo\FP-Scatt):

- Spectra for the calibration (directory \QXASdemo\Cd-109\SPE-INP): Ti.spe, Cr.spe, Fe.spe, Co.spe, Ni.spe, Cu.spe, Zn.spe, Ge.spe, Zr.spe, Nb.spe, Mo.spe, Hf.spe, Ta.spe, W.spe, Au.spe, Pb.spe, KH2PO4.spe, CaCO3.spe, K2Cr2O7.spe, MnO2.spe
- Input files (directory \QXASdemo\Cd-109\SPE-INP): Ti.inp, Cr.inp, Fe.inp, Co.inp, Ni.inp, Cu.inp, Zn.inp, Ge.inp, Zr.inp, Nb.inp, Mo.inp, Hf.inp, Ta.inp, W.inp, Au.inp, Pb.inp, KH2PO4.inp, K2-Cr2O7.inp, CaCO3.inp, Cr2-K2O7.inp, MnO2.inp
- AXIL result files (directory \QXASdemo\Cd-109\ASR-Std): Ti.asr, Cr.asr, Fe.asr, Co.asr, Ni.asr, Cu.asr, Zn.asr, Ge.asr, Zr.asr, Nb.asr, Mo.asr, Hf.asr, Ta.asr, W.asr, Au.asr, Pb.asr, KH2PO4.asr, K2-Cr2O7.asr, CaCO3.asr, Cr2-K2O7.asr, MnO2.asr
- Source file: Cd-109.sou
- Calibration file: Final.cal
- Instrumental parameter file: Cd-109.fpc

8.2.1. Elemental sensitivities

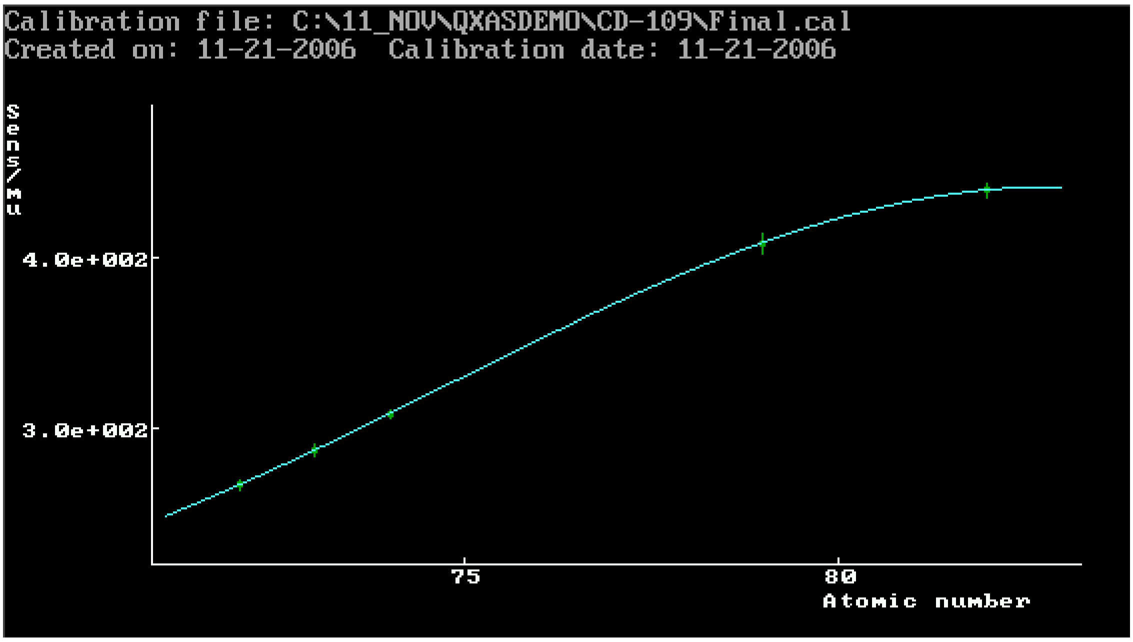
Fifteen standards (*.asr files) for K_α-calibration are available for the METHOD **Elemental sensitivities**: KH2PO4 (for potassium), CaCO3, Ti, Cr, Cr2-K2O7 (for chromium), MnO2, Fe, Co, Ni, Cu, Zn, Ge, Zr Nb and Mo. K2-Cr2O7 may not be used, because of the enhancement effect (Chromium excites potassium). Final.cal is the result of this calibration; values for the angle of incidence of 52.5^0 and take-off 77.1^0 were used. The Mn calibration point is problematic; this behaviour was already observed for the secondary target excitation.



Calibration file: C:\11_NOV\QXASDEMO\CD-109\Final.cal
Created on: 11-21-2006 Calibration date: 11-21-2006

Fig. 8.10. Calibration for K-line emitters for Cd-109 excitation with the method Elemental sensitivities.

Five standards are available for L_α-calibration (Hf, Ta, W, Au and Pb).



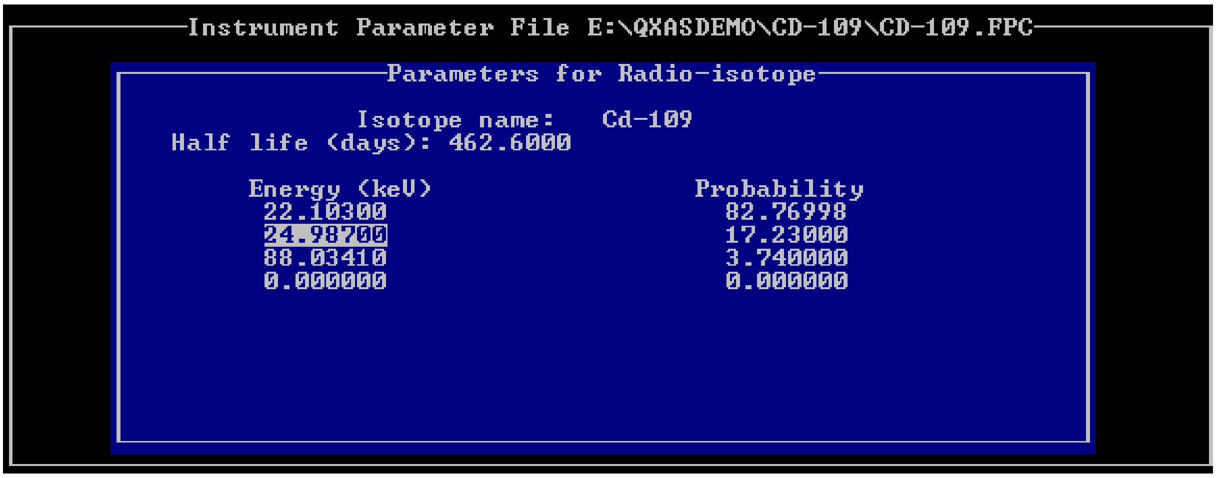
Calibration file: C:\11_NOV\QXASDEMO\CD-109\Final.cal
Created on: 11-21-2006 Calibration date: 11-21-2006

Fig. 8.11. Calibration for L-line emitters for Cd-109 excitation with the method Elemental sensitivities.

8.2.2. Full fundamental parameters

With the **Full fundamental parameters** METHOD a calibration established by all available standards can be performed. The program is full of “surprises” for the source excitation with Cd-109. The source type is selected with **Radioisotope excitation** from the FORM **Excitation conditions** in the line **Mode**. In the consecutive FORM **Parameters for Radio-**

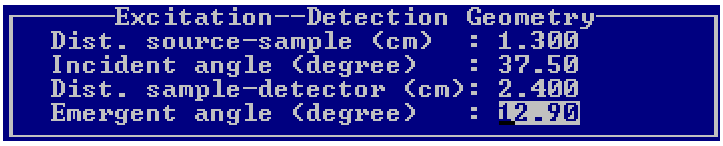
isotope the energy of the emitted Ag K_β line is defined wrongly: the energy of 26.10000 (Cd K_β) must be edited to the correct value of 24.9870. For each editing run of the *.fpc file it will adopt the wrong default, each time the user has to enter the correct value.



```
Instrument Parameter File E:\QXASDEMO\CD-109\CD-109.FPC
Parameters for Radio-isotope

            Isotope name:   Cd-109
    Half life (days): 462.6000

         Energy (keV)                 Probability
          22.10300                     82.76998
          24.98700                     17.23000
          88.03410                     3.740000
          0.000000                     0.000000
```

Fig. 8.12. Correction to the wrong energy value for the pre-defined Cd-109 excitation source as used by the Full fundamental parameters method.

The radiation travels between source, sample and the detector beryllium window through air, therefore the FORM **Excitation-Detection Geometry** will expect an average path length for the two distances (**Dist. Source-sample**, **Dist. Sample-detector**). The first of the two path lengths is approximated with 1.3 cm, the distance between sample and detector entrance window with 2.4 cm.



```
Excitation--Detection Geometry
Dist. source-sample (cm)   : 1.300
Incident angle (degree)    : 37.50
Dist. sample-detector (cm): 2.400
Emergent angle (degree)    : 12.90
```

Fig. 8.13. Definition of incidence and take-off angle (in respect to the sample surface normal) and the air-path.

Hint: An important fact to treat correctly the **FP** METHOD, is the use of the angles defined between *sample surface normal* and incoming and outgoing radiation. Therefore the expected input will be 90 - 52.5 = 37.5 degrees for the **Incident angle** and 90 - 77.1 = 12.9 degrees as **Emergent angle**. For the secondary target spectrometer and other Cartesian geometry set-ups the differentiation between the angles (90 - 45 = 45) for **Full fundamental parameters** and the other METHODs is only academic, for source excitation systems it is important.

The file Cd-109.fpc was created with the use of twenty-one standards *.asr files: KH2PO4 (for potassium), K2-Cr2O7 (for potassium), CaCO3, Ti, Cr, Cr2-K2O7 (for chromium), MnO2, Fe, Co, Ni, Cu, Zn, Ge, Zr, Nb, Mo and L-line standards: Hf, Ta, W, Au and Pb (all files from directory \QXASdemo\Cd-109). For the establishment of the average instrumental constant for fluorescence (38.38 +/- 0.849) the two potassium standards (in analogy to the secondary target excitation), the one for Mn (this compound is problematic as was already found out) and the L line standards (the intra element effect: K lines of an element excite also its L–lines, which is not considered by the **FP** METHOD) were not included.

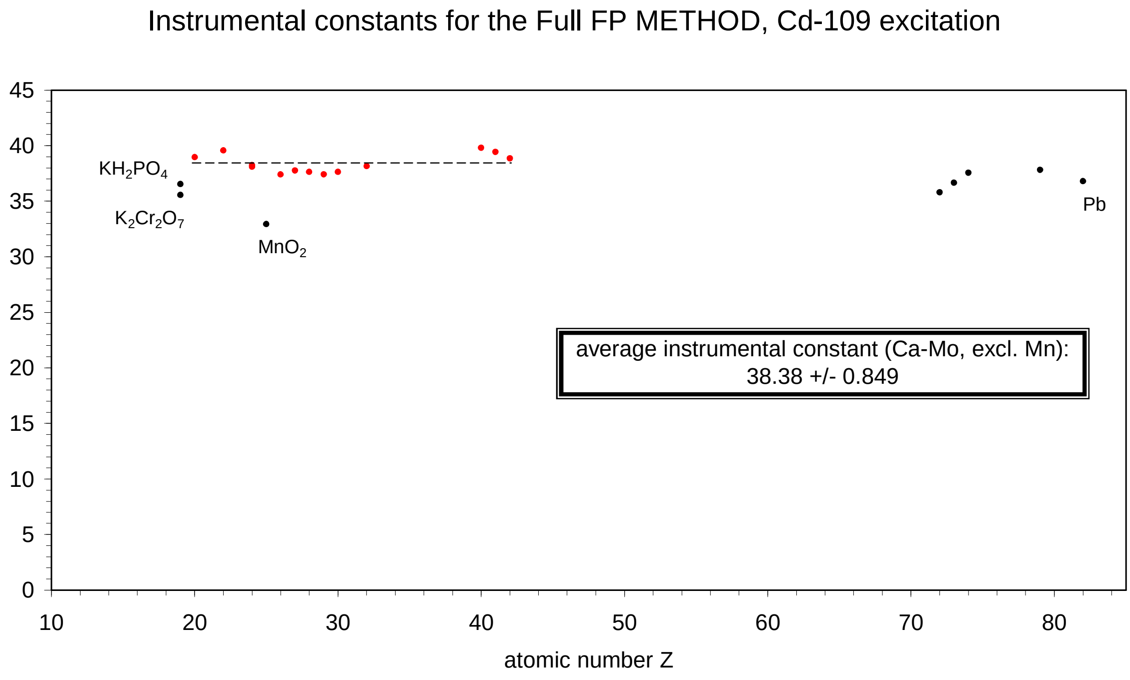


Fig. 8.14. Instrumental constants for all available calibration standards (Cd-109 source excitation). Red dots refer to standards used to establish the average instrumental constant for fluorescence. The elements K, Mn and the L-line emitting standards were not included into the averaging.

For potassium an individual instrumental constant of 36.05 was defined, which is the average value from standards KH2PO4.asr and K2-Cr2O7.asr. For Pb a value of 36.81 was defined.

CHAPTER 9. TOTAL REFLECTION X RAY FLUORESCENCE - TXRF

References: [41], [42], [43], [44], [45], [46], [47], [48], [49]

9.1. Fundamentals

For standard **T**otal **R**eflection **X** ray **F**luorescence (TXRF) spectrometry a small droplet of a liquid sample (volume 1 - 100 μl) is deposited in the centre of the plane-polished surface of a suited substrate (usually a disk shaped quartz reflector, with a diameter of 30mm). Whenever possible the liquid matrix is removed by evaporation through heating or pumping. Due to the geometrical arrangement the primary radiation of an X ray tube will impinge on the surface of the substrate under a rather shallow angle (in the range of 1.6 mrad, equivalent to 0.1^0) and will be totally reflected on this surface. This physical phenomenon can be explained by the refraction index slightly smaller than 1 for X rays. It can be shown that only a small amount of the primary photons can penetrate into the reflector. On the other hand is the small sample excited by the primary radiation (irregularly shaped, therefore no total reflection effect) and the interesting fluorescence radiation is collected very efficiently by the detector that is positioned much closer to the sample (~ 5 mm) than in conventional energy dispersive XRF. As a result superior detection limits can be achieved. A special equipment is needed and practically only samples in liquid form that must be spiked with an internal standard element can be analyzed. Users of a TXRF equipment quantify their samples by the addition of a suited internal standard. From the intensity ratios (element of interest / internal standard element) and the known concentration of the internal standard the sample element concentration values are determined.

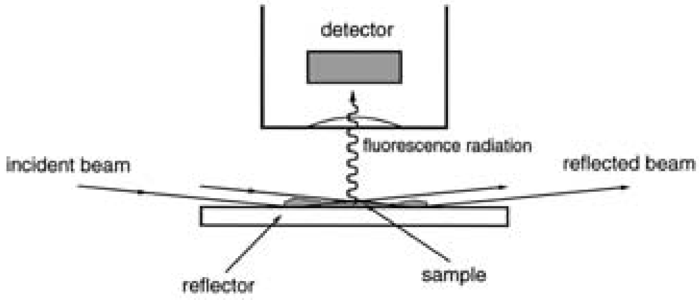


Fig. 9.1. Total reflection XRF geometry where a small sample (residue of a liquid sample) rests on top of a suited reflector.

The angle of incidence in respect to the reflector surface and the angle of the reflected beam are identical. There exists also a refracted beam that penetrates into the sample, but due to the low value of the transmission coefficient the resulting scattering by the reflector and the silicon fluorescence radiation are well under control. Scattering will predominantly be caused by the residual, therefore usually higher sample volumes will be counter-productive for background reduction.

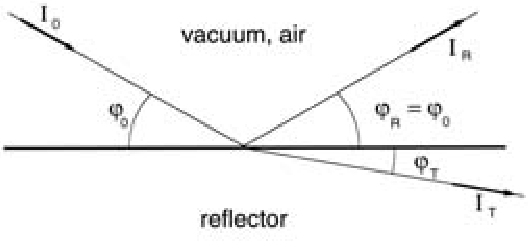


Fig. 9.2. Incident, reflected and transmitted beam with respective intensities I_0, I_R and I_T.

Due to the special geometry not only the primary beam will excite the sample, but also parts of this beam that impinge onto the reflector in front of the sample. This results in double excitation.

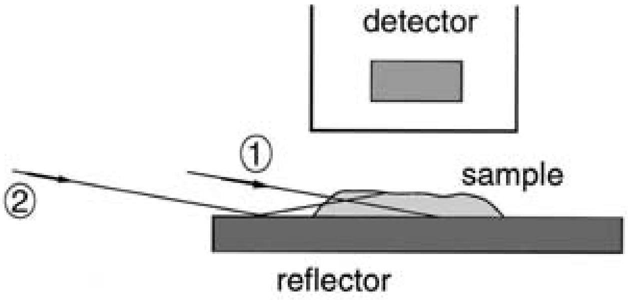


Fig. 9.3. Double excitation of the sample by primary (1) and reflected beam (2).

For standard TXRF a calibration standard will be a solution, consisting of several elements with properly chosen concentration values (in order to cover the elements as well as their concentration range as expected in the sample) and an extra element the internal standard. It must not interfere with the spectral lines of the calibration standard nor must it be contained in the samples. The concentrations of such a set of elements will vary from one standard to the other, whereas the concentration of the internal standard element usually will be kept fixed for all of them and is preferably close to the amount added to the unknown samples.

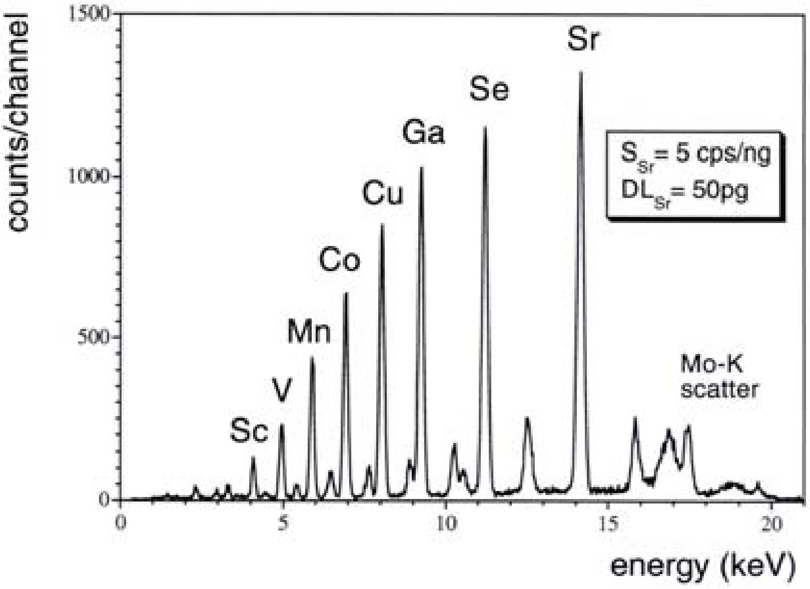


Fig. 9.4. A typical spectrum of a calibration standard for TXRF analysis. All specified elements are present with equal amounts.

It should be mentioned that not only residues of liquid samples can be investigated by this technique, but also the reflecting surface itself for contaminations. A practical application is the search for traces on and in the plane and polished surface of silicon wafers as manufactured for the semiconductor industry. By the controlled change of the incidence angle for total reflection a fluorescence signal originating from a residue can be distinguished from a thin layer and from homogenously distributed atoms embedded in the bulk material. Shallow implantations in bulk material can also be investigated for their depth profile.

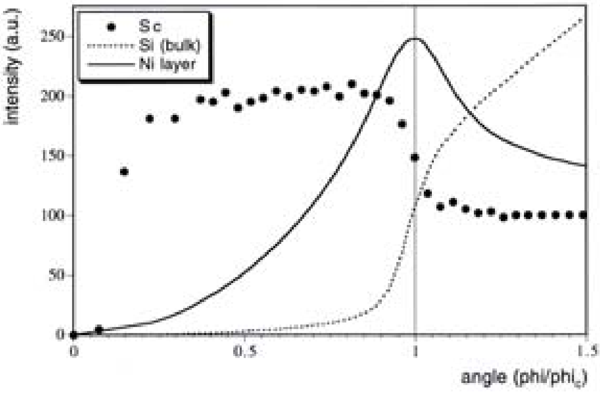


Fig. 9.5. It is possible by variation of the incidence angle to differentiate between a residue's fluorescence signal of e.g. Sc on the surface and a bulk signal, like Si (the substrate), which is important e.g. during the search for contaminations. A thin layer (Ni) on top of a reflector also shows a distinct angular behaviour.

TXRF is a very sensitive technique for trace element determination, therefore contaminations can be a major issue. Strict cleaning procedures for the sample reflectors must be followed and all chemicals used must be of spectroscopy grade. Furthermore it is not sufficient to examine the instrument and sample blank once in while. *Before each deposition* of a standard or sample onto a reflector, the clean reflector must undergo a blank measurement.

In the following the concentration units of ppm (parts per million) and ppb (parts per billion) will be used. They are defined for liquids as µg/ml and ng/ml, respectively.

9.2. Calibration

Demonstration files (directory \QXASdemo\TXRF):

- AXIL result files: 20ppb.asr, 40ppb.asr, 60ppb.asr, 80ppb.asr, 100ppb.asr, 120ppb.asr, 140ppb.asr, 160ppb.asr, 180ppb.asr, 200ppb.asr
- Calibration file: Extra2.cal
- Input file: TXRF.inp
- Spectra (directory \QXASdemo\TXRF\SPE):
- 20ppb.spe, 40ppb.spe, 60ppb.spe, 80ppb.spe, 100ppb.spe, 120ppb.spe, 140ppb.spe, 160ppb.spe, 180ppb.spe, 200ppb.spe

Ten calibration solutions containing the elements manganese, copper and strontium with concentrations ranging from 20 ppb to 200 ppb, in steps of 20 ppb and yttrium as internal standard element, with fixed concentration of 500 ppb for all standards, had been prepared. The concentration ranges were selected in order to find the finally obtained results for unknown samples within the spanned calibration range. As this cannot be known before, usually one would prepare only one calibration solution and try to get preliminary results for the unknown sample. The combination of the elements (Mn, Cu, Sr) had been selected with the intention to avoid peak overlaps that would introduce through the peak de-convolution an additional source of uncertainty. The element Y had been chosen as internal standard, because the inspection of the spectrum of the later used sample does not contain this element. In case a sample of interest contains elements with overlapping peaks, other sets of calibration standard solutions, covering the other elements, needed to be prepared.

Single element mother solutions of Mn, Cu, Sr and Y with 1000 ppm concentration as used for AAS or ICP were firstly diluted to 10 ppm solutions in order to use pipette volumes for the final calibration standards high enough to avoid unnecessary big relative errors as found for volumes of less than 10µl. Plastic vials with a volume of 10 ml served as containers. In order to obtain 10 ml as final volume with a concentration of 10 ppm, from a 1000 ppm mother solution 100 µl (0.1 ml) were pipetted into the vial and 9.9 ml of tri-distilled water were added. All volumetric manipulations were cross-checked with a balance.

$$10\,ppm = 1000\,ppm \cdot \frac{0.1ml}{(9.9 + 0.1)ml} \tag{9.1}$$

As example for the preparation of the final calibration standard solutions the 100 ppb standard can serve: For 10 ml final volume 100 µl, from each of the 10 ppm single element solutions of Mn, Cu and Sr, were pipetted into a new vial. Yttrium was added with a volume of 500 µl. Tri-distilled water was added to the mixture with a volume of 9.2 ml. For any of the three elements Mn, Cu, Sr the concentration is

$$100\,ppb = 10\,ppm \cdot \frac{0.1ml}{(9.2 + 0.1 + 0.1 + 0.1 + 0.5)ml} \tag{9.2}$$

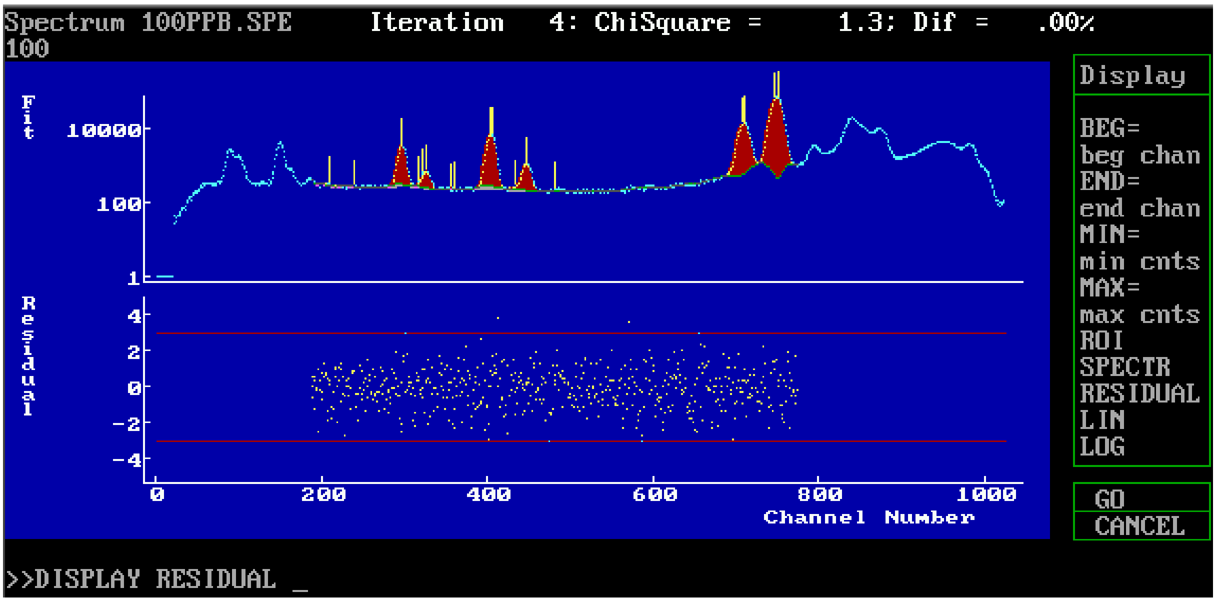
For the internal standard Y the concentration is 500 ppb. Onto the reflectors 20 µl of the mixed calibration solutions had been pipetted and dried on a hotplate inside a clean bench until complete removal of the water matrix before the respective measurements.

For the AXIL fit an input model TXRF.inp was used for all calibration standards’ spectra with the inclusion of:

X-LINES ADD: MN-KA* MN-KB* CU-KA* CU-KB* SR-KA Y-KA

The splitting of lines for manganese and copper was necessary for the sake of fitting of the spectra of the higher concentration standards. Further included were elements, occasionally showing up as contaminants, with

X-LINES ADD: FE ZN SUM

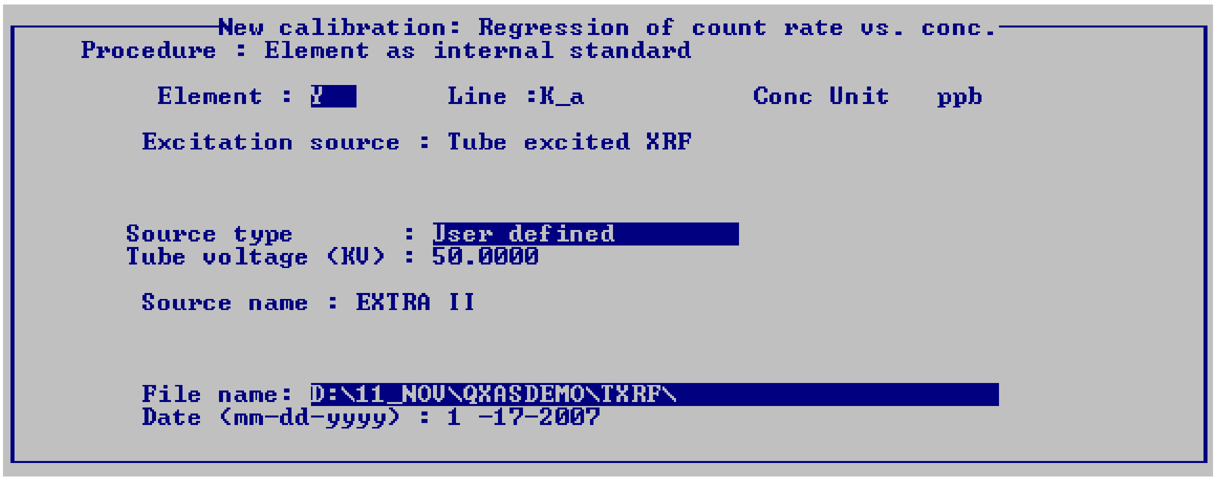


```
Spectrum 100PPB.SPE      Iteration   4: ChiSquare =      1.3; Dif =    .00%
100
```

```
>>DISPLAY RESIDUAL _
```

Fig. 9.6. Spectrum of the calibration standard containing 100 ppb of Mn, Cu, Sr and Y as internal standard element with 500 ppb.

A calibration file Extra2.cal was created (FORM **New calibration: Regression of count rate vs. conc.**). As **Procedure:** for TXRF always **Element as internal standard** will be selected (default), the other options can be applicable for thin film samples analysis, measured in standard XRF geometry. Essential are the definitions for the internal standard element, its fluorescence peak used (**Line:**), which normally will be K_{α}, and the concentration units (if the <%> character is needed, it must be typed twice <%%>). The instrument used for the measurements taken was an ATOMIKA Extra 2 spectrometer, equipped with a Mo X ray tube and for excitation beam shaping a so-called cut-off reflector. A tube voltage of 50 kV was applied for all the measurements. In the pre-last line the file name has to entered under which the calibration will be stored.



```
                 New calibration: Regression of count rate vs. conc.
     Procedure : Element as internal standard

          Element : Y         Line :K_a          Conc Unit   ppb

         Excitation source : Tube excited XRF


        Source type       : User defined
        Tube voltage (KV) : 50.0000

         Source name : EXTRA II


         File name: D:\11_NOV\QXASDEMO\TXRF\
         Date (mm-dd-yyyy) : 1 -17-2007
```

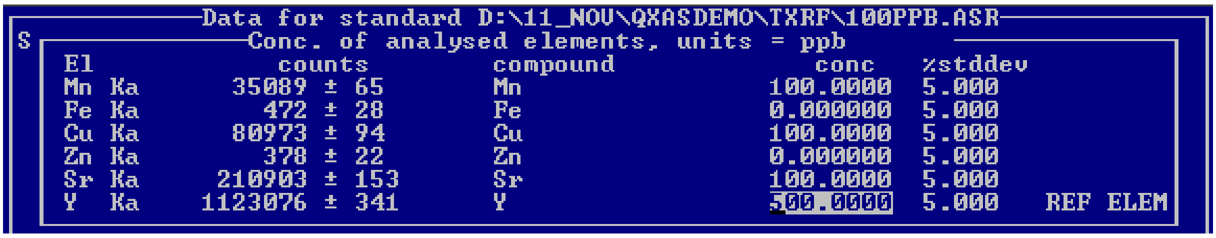
Fig. 9.7. Definition of the calibration file TXRF.cal.

With **Add Standards** the ten calibration standards were included in the calibration file. The acquisition time was set to 1000 s and a tube current of 38 mA was used throughout all the calibration measurements. Usually the tube current setting is used to fulfill certain dead time criteria imposed by the spectrometer. As for none of the data collections the maximum permissible dead time limit was passed, the maximum current permissible for this machine could be utilized throughout.

```
             Data for standard D:\11_NOV\QXASDEMO\TXRF\100PPB.ASR
Sample ID: 100
  Live Time (sec):   1000.000              Tube Current (mA):  38.0000
  Date (mm-dd-yyyy):   12-10-2006
```

*Fig. 9.8. Usually the acquisition time and the date are read from the respective *.asr file used for calibration.*

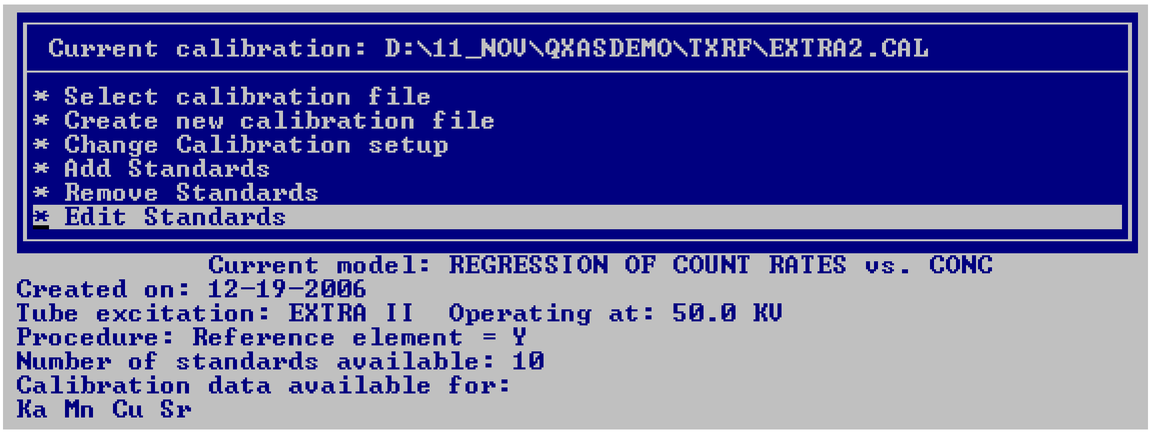
The concentration values have to be entered in the second FORM named **Data for standard** for the elements Mn, Cu, Sr and the internal standard Y. Iron and zinc values, included only for the sake of the fit, will be left at their defaults 0.0.



```
             Data for standard D:\11_NOV\QXASDEMO\TXRF\100PPB.ASR
S               Conc. of analysed elements, units = ppb
   El           counts          compound              conc     %stddev
   Mn  Ka     35089 ± 65        Mn                100.0000   5.000
   Fe  Ka       472 ± 28        Fe                0.000000   5.000
   Cu  Ka     80973 ± 94        Cu                100.0000   5.000
   Zn  Ka       378 ± 22        Zn                0.000000   5.000
   Sr  Ka    210903 ± 153       Sr                100.0000   5.000
   Y   Ka   1123076 ± 341       Y                 500.0000   5.000    REF ELEM
```

Fig. 9.9. The concentration values as known from the standard's preparation must be entered. Elements only included for the sake of the AXIL fit will be left with their concentration at the default 0.0.

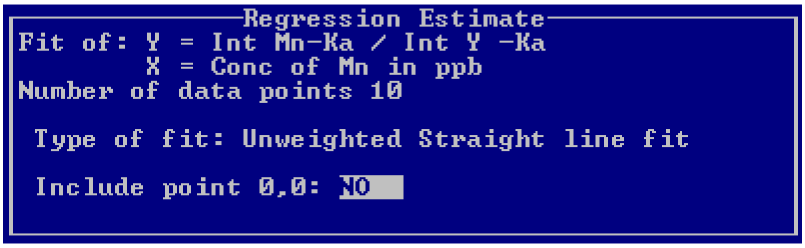
After the successful inclusion of all standards, editing of any of them still is possible.



```
 Current calibration: D:\11_NOV\QXASDEMO\TXRF\EXTRA2.CAL

* Select calibration file
* Create new calibration file
* Change Calibration setup
* Add Standards
* Remove Standards
* Edit Standards
            Current model: REGRESSION OF COUNT RATES vs. CONC
Created on: 12-19-2006
Tube excitation: EXTRA II  Operating at: 50.0 KV
Procedure: Reference element = Y
Number of standards available: 10
Calibration data available for:
Ka Mn Cu Sr
```

Fig. 9.10. The calibration file Extra2.cal contains calibration data for three elements originating from ten standards.

The calibration is achieved with **Perform calibration**. For one element after the other a regression calibration will be performed. Due to the fact that the uncertainty of calibration solutions was not even attempted to be known, for the demonstration the **Type of fit** should be specified as **Unweighted Straight line fit**. It is possible (but not recommended) to include the point with zero concentration, which would correspond to a sample reflector blank measurement - forced to zero intensity.



```
              Regression Estimate
Fit of: Y = Int Mn-Ka / Int Y -Ka
        X = Conc of Mn in ppb
Number of data points 10

 Type of fit: Unweighted Straight line fit

 Include point 0,0: NO
```

Fig. 9.11.For the regression applied to the data points representing the calibration element Mn the origin (zero concentration, and zero intensity) should not be forced in.

For the element Mn (comparable also for Cu and Sr) a fairly good linear correlation between the concentration and the intensity ratio (Mn K_{α} to Y K_{α}) is observed.

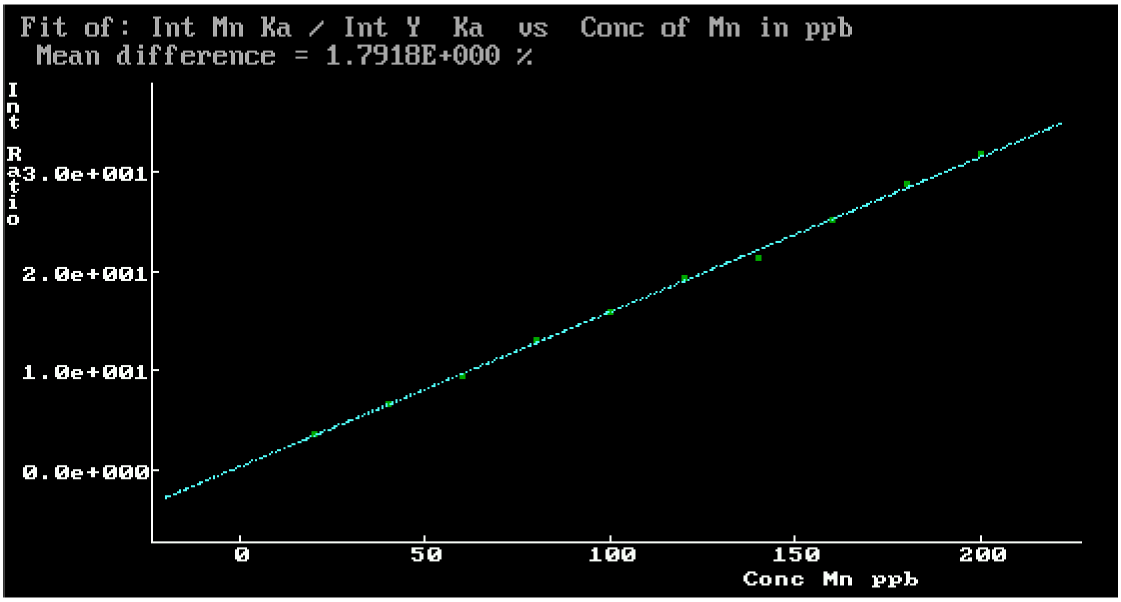


Fig. 9.12. Regression line for the element Mn.

After having passed this routine as many times as calibration elements are found, in this case after Mn for Cu and Sr, a report will be displayed.

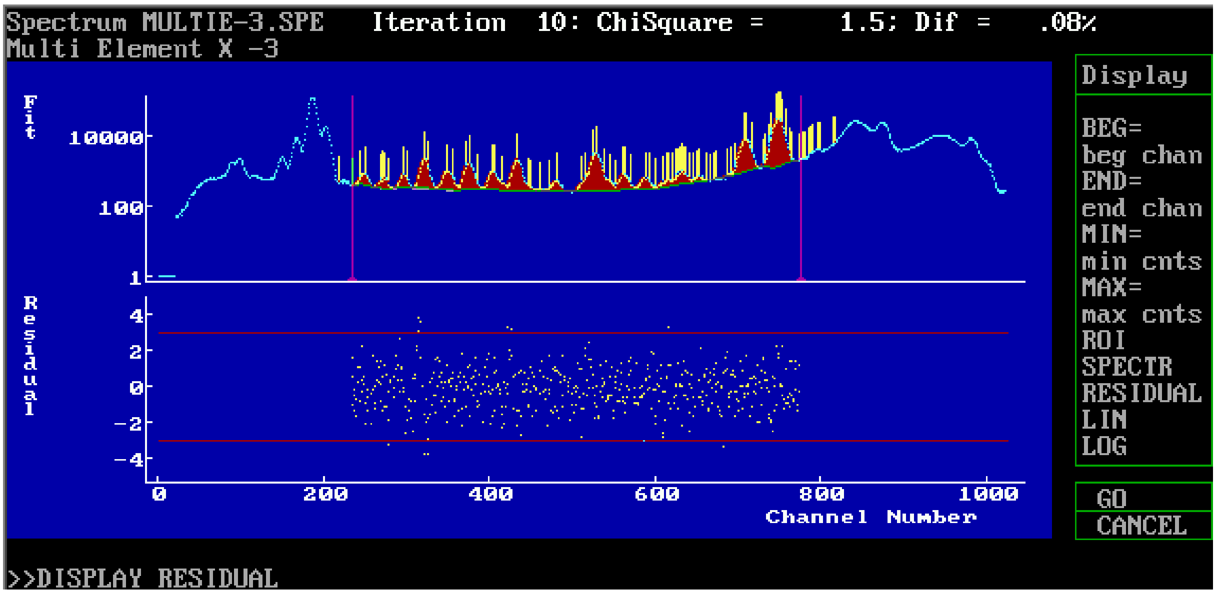
The option **Extend calibration for not measured elements** will permit to interpolate and extrapolate the calibration, incorporating elements not even represented by a single calibration standard. It is recommended to make as little use as absolutely necessary of this possibility. The same arguments apply as already given for the calibration of METHOD **Elemental sensitivities**. For reliable quantitative results each element contained in a sample should be represented by several calibration standards.

9.3. Quantitative analysis of a water sample for the elements Mn, Cu and Sr

Demonstration files (directory \QXASdemo\TXRF):

- Spectrum: MultiE-3.spe
- AXIL result file: MultiE-3.asr
- Input file: MultiE.inp

To an aqueous sample, taken from a mixture of standards (multi element solution X) yttrium had been added. The content of Y in this samples is 385 ppb. Onto a reflector 30 µl of the yttrium spiked sample was pipetted and treated like the standards concerning the matrix removal. The tube current could be again set to the maximum of 38 mA, the spectrum was acquired for 1000 s.


```
Spectrum MULTIE-3.SPE   Iteration  10: ChiSquare =    1.5; Dif =   .08%
Multi Element X -3
```

```
>>DISPLAY RESIDUAL
```

Fig. 9.13. AXIL fit of the spectrum MultiE-3.spe measured in TXRF geometry.

The calibration included only the elements Mn, Cu and Sr; quantification is only possible for them. For the sake of the AXIL fit other elements had to be included.

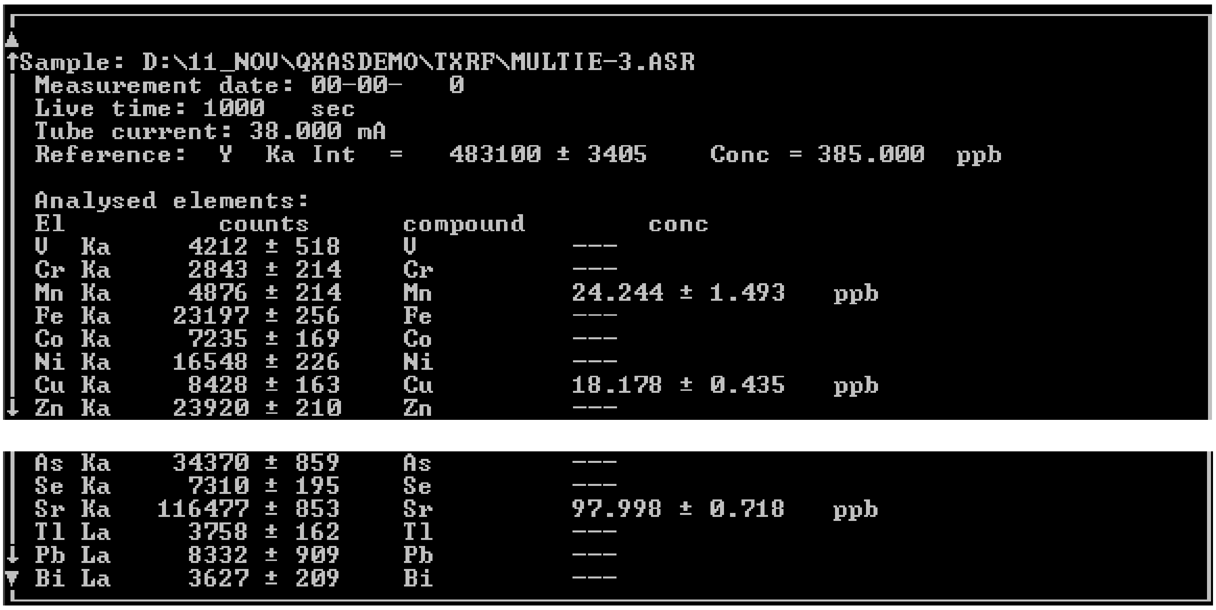

```
Sample: D:\11_NOV\QXASDEMO\TXRF\MULTIE-3.ASR
 Measurement date: 00-00-   0
 Live time: 1000    sec
 Tube current: 38.000 mA
 Reference:  Y  Ka Int  =   483100 ± 3405    Conc  = 385.000  ppb

 Analysed elements:
 El          counts        compound         conc
 V   Ka     4212 ± 518     V          ---
 Cr  Ka     2843 ± 214     Cr         ---
 Mn  Ka     4876 ± 214     Mn         24.244 ± 1.493   ppb
 Fe  Ka    23197 ± 256     Fe         ---
 Co  Ka     7235 ± 169     Co         ---
 Ni  Ka    16548 ± 226     Ni         ---
 Cu  Ka     8428 ± 163     Cu         18.178 ± 0.435   ppb
 Zn  Ka    23920 ± 210     Zn         ---

 As  Ka    34370 ± 859     As         ---
 Se  Ka     7310 ± 195     Se         ---
 Sr  Ka   116477 ± 853     Sr         97.998 ± 0.718   ppb
 Tl  La     3758 ± 162     Tl         ---
 Pb  La     8332 ± 909     Pb         ---
 Bi  La     3627 ± 209     Bi         ---
```

Fig. 9.14. Quantitative results obtained for an aqueous sample measured with TXRF.

In a strict sense the copper results are out of the calibration range, calibration standards for this element (e.g. with 5 and 10 ppb) should be prepared and included into the calibration. Due to the addition of the internal standard solution a dilution factor of 1.02 applies. I.e., the reported results must be multiplied with this factor.

CHAPTER 10. ELEMENTS OF QUALITY CONTROL

References: [27], [50], [25], [51], [52]

For good laboratory praxis keeping a “log-book” is essential. Better are two log-books, one documenting the sample preparation (date of preparation, unique sample preparation number, calibration standard / sample description, weight for pressing, fluxing procedure, etc.). The other documenting the spectrum acquisition (date of measurement, spectrum file name, sample preparation number – as “shake-hand” between the two log-books, acquisition time (live time, *LT*), dead time (*DT*), tube current - when applicable). Any essential changes (replacement of protective foils, changes in geometry, other high voltage setting, etc.) and problems (instabilities, repair of equipment, etc.) must noted.

For an established calibration during the measurements there have to be kept constant: geometry; anode material, kind of secondary target, high voltage (for tube excitation); vacuum conditions (if applicable); thickness and kind of protective foils. The sample position must be reproducible and the irradiated area must be in the centre and smaller than the sample area itself. For tube excitation the detector must be electrically insulated from the rest of the spectrometer, because grounding problems will result in unexpected spectrum behaviour.

Reference Standard materials are to be avoided as calibration standards (exception **NBS** METHOD), because of their trace elements content, which will introduce high statistical uncertainties.

10.1. Parameters under control

Certain parameters have to be carefully examined in order to establish a working range (e.g. the influence of the applied tube current on the peak area behaviour); some have to be under permanent regular surveillance (e.g. sample blank and instrument blank); others have to be checked but can vary within certain constraints, because they have negligible influence on the results, like the resolution of the detector (FWHM) and the stability of the energy calibration. The experienced user will simply have “an eye” on the later category.

10.1.1. Linearity as a function of the tube current

The tube current for secondary target and direct X ray tube excitation spectrometers will have linear influence on the spectrum emitted by the sample. Any increase or decrease of the tube current will increase or decrease the fluorescence and scatter intensities strictly linear proportional, of course with statistical deviations. Given that all circuitry of the electronic chain from the preamplifier output to the MCA is correct, the detector side of the spectrometer might not react accordingly, because the signal processing is count rate dependent. Between the two extremes of a very low count rate and the saturation of the detection system a non-linear behaviour can exist: the measured intensity will not follow the increase of the tube current with the same rate. A dead time dependency can be specified. In order to avoid dead time dependent misinterpretations, one has to establish a series of measurements with the tube current as parameter. In the praxis a calibration standard (producing already a high count rate for the lowest current value) will be measured repeatedly with increasing tube current as parameter, from the lowest to the highest setting. In this manner the iron calibration standard peak area was recorded between 5 and 50 mA, in 5 mA steps.

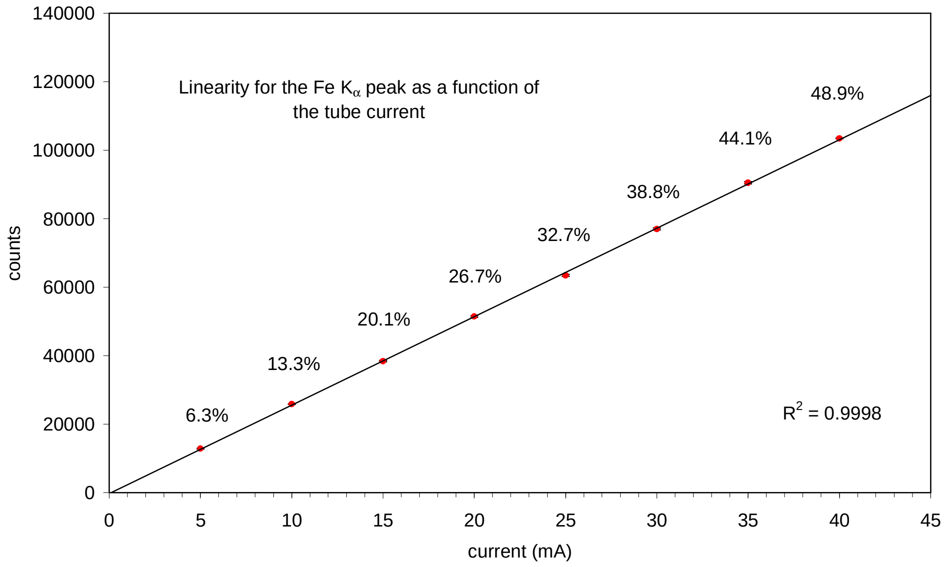


Fig. 10.1. Check of the linearity of the Fe K_α peak as a function of the tube current up to a dead time level of 48.9%.

Two facts in this respect are to be considered: Small peaks can behave differently than the intense peaks, causing the dead time. Sometimes an energy dependence can be observed, but not all peaks of a spectrum ranging from the lowest to highest energy must have the same behaviour. For the used system the iron K_α net peak area followed the tube settings up to the maximum, equivalent to almost 50 % dead time. When a non-linear response is observed for a spectrometer all measurements must be taken within the linearity approximation range. For source excitation such an easy going approach does not exist, although by insertion of absorbers with varying thickness a comparative concept can be followed. For such a study the transmission factors for the absorbers must be precisely defined.

10.1.2. Detector resolution as function of time

In principle the resolution of a detector has no influence on the quantification, due to the principle of constant peak area: both, a detector with poor resolution and lower peak height, as well as a good detector with a slimmer resolution and a more elevated peak maximum will result, under otherwise identical conditions, in the same peak area. Still the FWHM is a major criterion for the quality of a detector. The better the resolution the better overlapping peaks can be apportioned. The detection limits, proportional to the square root of the background under a peak, get lower. A value for the FWHM close to specification of the detector should be reached. The manufacturer had specified his detector under certain conditions, usually at a low count rate for a Mn K_α peak (originating from an Fe-55 source). A ground loop to e.g. the high voltage generator of the X ray tube, a higher count rate than specified, detector aging and a non-perfect energy calibration can lead to an increased FWHM value result. Of importance in this context is a rather constant value over the time.

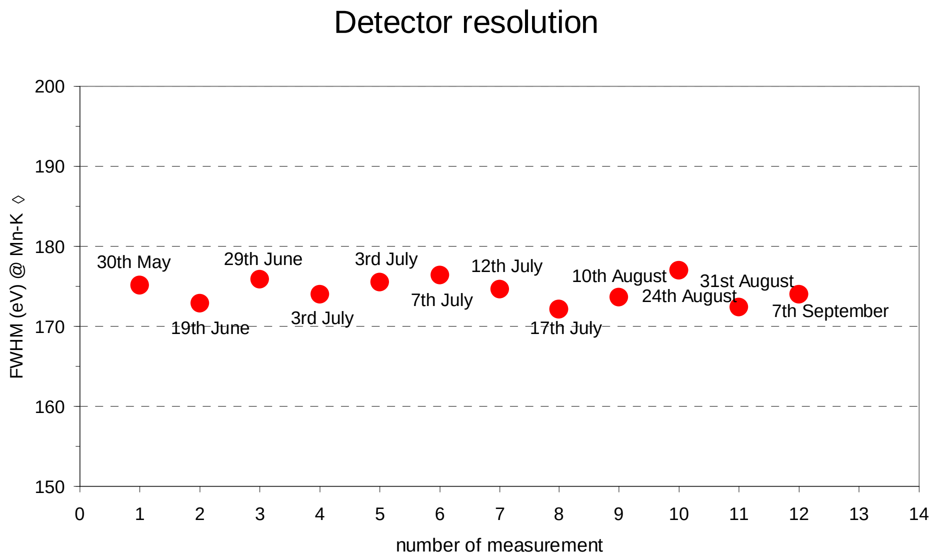
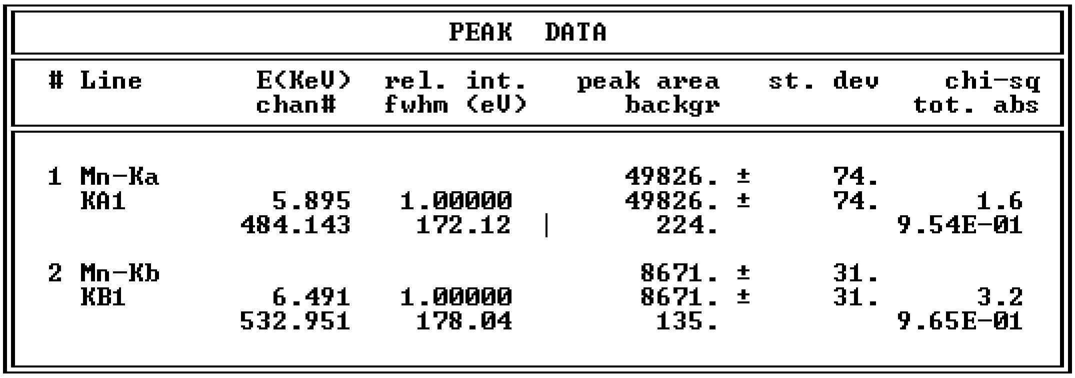


Fig. 10.2. The FWHM of Mn K_{α} *controlled on a regular basis over a period of three months.*

For the detector as part the secondary target spectrometer over a period of three months the FWHM of Mn K_{α} for the MnO_2 calibration standard was recorded repeatedly. An average of 174.37 +/- 1.61 eV was determined by use of the AXIL COMMAND: **REPORT FULL GO**.



```
                          PEAK   DATA

 # Line          E(KeV)  rel. int.    peak area   st. dev       chi-sq
                 chan#   fwhm (eV)       backgr                tot. abs

 1 Mn-Ka                                49826. ±      74.
   KA1            5.895   1.00000       49826. ±      74.          1.6
                484.143    172.12  |      224.                9.54E-01

 2 Mn-Kb                                 8671. ±      31.
   KB1            6.491   1.00000        8671. ±      31.          3.2
                532.951    178.04         135.                9.65E-01
```

Fig. 10.3. Full report for an AXIL fit of a Mn standard used for the control of the FWHM.

10.1.3. Stability of the energy calibration

For the Rh secondary target spectrometer a drift of the energy calibration was observed. This behaviour is unpractical, because each spectrum, as can be seen by a closer inspection of the provided demonstration *inp files needs an energy calibration for its own. In case also a deterioration of the resolution had been found, the combination of the two effects can be an indicator for some severe detector problem. For the isolated problem either the amplifier or the MCA card is responsible, but otherwise it is harmless, because intensities must be constant, independent of the gain. In order to control the situation a Zr foil had been measured repeatedly. The channel number of the maximum of the Zr K_{α} peak, determined during the AXIL fit as the median of the Gaussian (and accessible by the COMMAND: **REPORT FULL GO**), was plotted against the time since the first evaluation in days. Sometimes measurements were taken within one day, like at day zero (3 measurements) and after four days (2 measurements). This should demonstrate that the drift appears only during longer periods of time. Short term drifts would affect individual spectra and could not be accepted. At day thirty-five the amplifier gain was changed willingly, with a measurement before and after. The instability continued in the course of time.

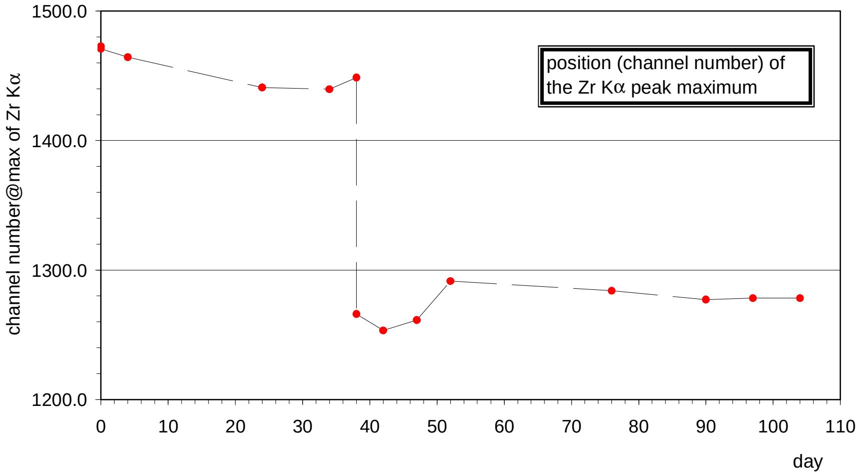


Fig. 10.4. Drift of the energy calibration controlled by the peak maximum position of Zr K_{α}.

The observed energy drift represents a parameter that is "out of control", but has no direct impact on quantitative results.

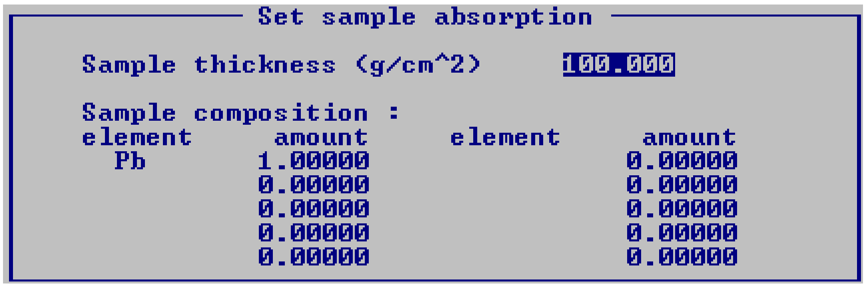
10.2. How to fit standards' spectra according to QA

10.2.1. Before the fit with AXIL

) Optional: Copy the converted spectra (.spe) into a directory - with a directory name with less than 8 characters (for the examples as used in this book the directory name \SPE-stds had been found adequate).

*) Edit, if not already done at an earlier stage, the *.spe files so that the header **($SPEC_ID:**) will contain the sample preparation number, taken from the sample preparation log-book. Include also the spectrum file name from the spectrometer log-book, in case the name was changed, like for the example standards. Helpful (but not mandatory) will be some information about the standard itself.

) Optional: Create a model file (.inp) *already before the fit* with AXIL, in order to define the matrix (**Sample absorption**), **Excitation conditions**, **Detector characteristics**, **Path length**, etc. This information for most of the standards will be of no relevance, except if line ratios that are kept fixed during the fit are affected. Examples are the inclusion of escape peaks and L-line ratios within one group.



```
Set sample absorption

Sample thickness (g/cm^2)      100.000

Sample composition :
element        amount       element        amount
  Pb          1.00000                     0.00000
              0.00000                     0.00000
              0.00000                     0.00000
              0.00000                     0.00000
              0.00000                     0.00000
```

Fig. 10.5. Definition of the sample/standard matrix in order to improve the pre-defined line ratios.

10.2.2. Spectrum fit with AXIL

*) Energy calibration: Usually best with the K_α (L_α) peak of the major constituent of the standard and the coherent K_α scatter peak (where not visible: use the K_β (L_β) peak of the element of which the first peak already was used for energy calibration, instead).

Example for CaCO3.spe: with the COMMAND **CALIB** the Ca K_α peak maximum was found at **channel number 340** and was identified with <F1> CA <Space bar>. **channel number 1846** was identified with <F1> RH <Enter> as the Rh K_α elastic scatter peak.

*) Add only the peaks (COMMAND **X-LINES ADD**) that will result in the information needed (K_α or L_α). Add also all visible lines within the ROI (which will be defined in the next step). E.g., most of the times the K_β (or L_β and L_γ) peak, although not carrier of relevant information, will overlap with the K_α (L_α) peak.

Hint: The automatic region of interest can be displayed only *after* a fit, with the COMMAND:

DISPLAY ROI GO

Split the elements into K_α and K_β for K lines and L3, L2, L1 for L-lines (also instead: LA, LB, LG). Usually it will not be necessary to include escape peaks, scatter peaks or contamination elements (e.g., there is no need to include the Sr contamination into the fit model for CaCO3.spe).

Examples: For Fe-Std.spe and Fe2O3.spe define the elements with:

X-LINES ADD: FE-KA FE-KB

For Pb-LStd.spe:

X-LINES ADD: PB-L3 PB-L2 PB-L1

As an example for exceptions: Rh L scatter peaks (which are included by their approximate energies) for e.g. CaCO3.spe:

X-LINES ADD: CA-KA CA-KB 2.7 2.8 2.9

Avoid stand-alone peaks, because the four calibration parameters (two for the energy calibration, two for the resolution) will have too much freedom during the fit. As example, although elements with higher atomic number could be fitted by their K_α peak only, one still works with K_α and K_β. As alternative approach, for e.g., S-Std.spe, where the two K-lines are not resolved, the fitting of these four parameters was restricted with:

D_FANO: 0.00000

*) Use the automatic region of interest (**ROI AUTO**).

Exceptions are low Z standards. In order to enable a better defined background shape, for e.g., S-Std.spe use the COMMAND **ROI** with:

Begin channel: 80

End channel: 350

*) As background model, COMMAND **BACKGR**, select either **LINEAR** or **EXPON** (free of choice) and begin with the lowest value (**PARAM=**), which is 0 or 1, respectively. Not recommended are the **BREMS**strahlung background model, meant for charged particle excitation; the **FILTER** background did not work at all with the version of QXAS available, although in principle it was an alternative to the above named background models for former versions; **ORTPOL** has one more parameter (**R=** with default 1.5) to be optimised (usually between: 0.5, 0.75, 1.0, 1.25, 1.5, 1.75, 2.0, …) It showed a strange behaviour for some example spectra (overestimation of background with the consequence of negative intensities for small peaks - which could be identified positively with other background models).

*) Initiate the first fit with a sufficiently high number of iterations (sufficient means, that the number of iterations executed in a fit run will be found less than the starting value, **FIT N_ITER=**, entered by the user).

The following criteria are to be checked, in descending order:

- Total Chi square (**ChiSquare=**) less than 3.0.
- Residual (COMMANDs **DISPLAY RESIDUAL**) between +/- 3. When there is no “trend”, it is tolerable that a few points can be ouside of the indicated range. The residual should “please the eye”, therefore it is a “soft” criterion, because the experience of the user will be of influence.
- Results (COMMANDs **REPORT GO**):
  - Individual Chi square values less than 3.0
  - The standard deviation (**st.dev.**) must be greater than the square root of the peak area (this criterion only can be checked by use of a calculator). Not necessarily the peak area will change much due to this criterion for a refit with changed parameter(s).

Each of the criteria must be fulfilled, otherwise one or more of the parameters of the input model have to be varied: The order of the background (**PARAM=**) must be increased (usually the first choice), a different background model has to be chosen, lines could have to be added, the ROI could have to be set manually, the self-absorption, etc. must be defined. Each of such changes will necessitate a re-fit and re-inspection of all the above named criteria. The last two criteria must be fulfilled at any rate for lines of elements which the standard is composed of.

*) After all the criteria were fulfilled the results have to be saved as *.asr files (**SAVE_RES**).

*) For QA requirements, although not necessary to proceed with any of the quantitative METHODs, it is mandatory also to save the input model. This is not executed automatically, nor is there any reminder to this action. After *each* successful fit of a calibration standard spectrum the fit program AXIL has to be terminated with the **STOP**, in order to save also the *.inp file (**Save model**). With any further <Escape>, after the **STOP**, any changes to the model are lost, even when an *.inp file had been created before loading the spectrum.

*) All *.asr files are stored with the same name as the *.spe file into the same directory. It is advisable to move the *.asr files in a different directory.

10.3. Recommendations for the fit of sample spectra

Remembering the complicated definitions of the input models for the demonstration sample spectra of the previous chapters, particularly for alloys or the inclusion of scatter peaks for dark matrix representation, it is evident that no rigid rules can be formulated. But it is possible to give some advices.

*) The first step for the AXIL fit always must be the *energy calibration*. By loading an input model with established energy calibration (e.g. of a calibration standard) one must already be able to identify elements. For the demonstration spectra this does not apply, because the gain was changed in between calibration and measurement of unknowns. Next remove all previous element entries with the COMMAND **X-LINES REMOVE ALL**, set the **ROI** to **AUTO**.

10.3.1. Example: intermediate thick pellet pressed from 50 % Soil 7 and 50 % HWC as binder, Soil7-1.spe

*) *Fine tuning of the energy calibration*: For this spectrum channel number 295 as the maximum position of the highest “low energy” peak was used. By the coarse energy calibration this element must be identified as calcium. In the “high energy” end usually the elastic scatter peak will be used as second calibration point; channel number 1602 is the Rh scatter peak maximum position.

*) Identify all possible elements with **KLM MARK**. For a really unknown sample there is neither the need to “find” all of them already in the beginning nor will any “over-interpretation” of realistic elements do any harm - as long as the below named criteria are used. Usually one will agree upon the elements Si, K, Ca, Ti, Mn, Fe, Zn, Rb, Sr, Y, Zr and Pb. Chlorine is not a good choice, because, may it be present or not, the Rh L scatter region will prevent good results due to its proximity to Cl K.

*) *Adding of the identified peaks* to the fit model with the COMMANDs **X-LINES ADD**. The intensive peaks, in this spectrum: calcium and iron, also need an input for their escape peaks. Possible sum peaks are to be included:

X-LINES ADD: SI K CA+ TI MN FE+ ZN RB SR Y PB SUM

Do not split the elements into e.g. KA and KB for the first fit run of a sample.

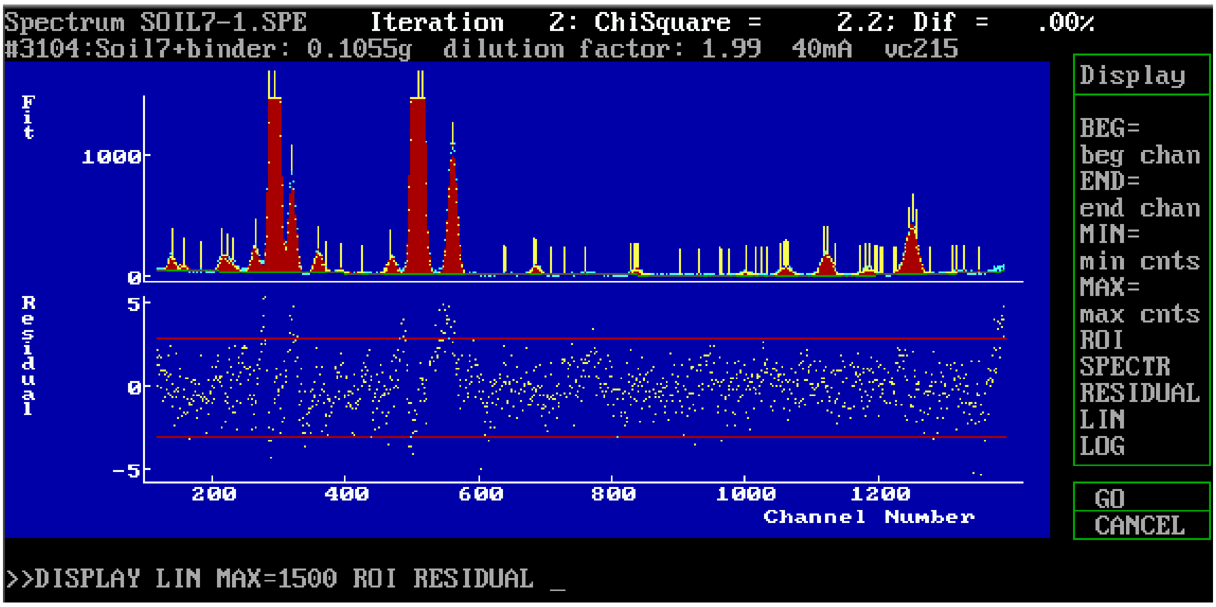
Silicon is separated from the other elements by the Rh L scatter peaks therefore the energy values 2.7 2.8 2.9 will have to be included. Arsenic is always problematic in the presence of lead, therefore it will be included and carefully checked by its standard deviation and background counts. Niobium might be present, therefore it will be included. The elements zirconium and niobium will be included with the K_α-peaks only, because Zr K_β and Nb K_β

carry no relevant information but suffer already from the high background caused by Rh K scatter. For the used spectrometer copper is known as a problematic element in respect to the blank spectra. The obtained peak area must be compared to the blank results, as well as for the elements iron and strontium.

X-LINES ADD: 2.7 2.8 2.9 AS ZR-KA NB-KA CU

*) The region of interest for fitting must include all elements of interest. For this “simple” spectrum even the automatic ROI will do for all fluorescence peaks of interest. In cases when a complicated fit situation is identified, the spectrum has to be fitted in parts. Examples are alloy spectra or the scatter peak fit for the sake of the dark matrix representation as needed by the fundamental parameters METHODs. When another region is fitted, after the first region had been fitted and saved, the attempt will result in a warning message: **ASR exists: …** The usual continuation of the saving will be to type in “A” for combining the results.

*) The *background model must be simple for a first run,* i.e. the parameter describing the model must be low (0-5). The linear background model is usually the first choice. The exponential background will be better suited for steep increases of the underlying background. Select for the example spectrum e.g. **BACKGR LINEAR** and **PARAM=** 5, because the background within the region of interest does not change drastically.



```
Spectrum SOIL7-1.SPE     Iteration   2: ChiSquare =     2.2; Dif =    .00%
#3104:Soil7+binder: 0.1055g  dilution factor: 1.99  40mA  vc215
```

```
>>DISPLAY LIN MAX=1500 ROI RESIDUAL _
```

Fig. 10.6. AXIL fit results obtained by a rather simple definition of input parameters, adequate for a “first round”.

*) The first three *criteria* as already used *to evaluate the fit results* of the standards apply also for samples:

- total Chi square > 3,
- residual within +/- 3,
- individual Chi square values > 3.

After the first round the total Chi square is found with a value of below 3, but the residual as well as the fitted spectrum itself show a problem at Ca and Fe, and the report provides bad individual Chi square values for the two elements. Therefore remove Ca and Fe and add instead:

X-LINES ADD CA-KA* CA-KB* FE-KA FE-KB*

Alternative to this approach one can define the matrix of the sample, but for unknown samples this is unrealistic, because the composition is known only after the quantification step. For severe problems with fluorescence peaks either the peak shape correction "*", an increase of the background parameter, a slightly better defined energy calibration, or the splitting of the ROI into sub-regions (should be the last choice) can improve the situation. The background parameter value also is to be increased, because the edges of the fitted ROI are not well described as can be seen from the residual; change with the COMMAND **BACKGR PARAM=** to a value of e.g. 10.

The refit with the named improvements, splitting of Ca and Fe, inclusion of the peak shape correction and an increase of the background parameter, will result in the fulfilment of the three criteria for this spectrum.

Two more criteria must be checked - for small peaks.

*) The last criterion, as used for the standards, does not apply for samples. Instead use for small peaks the two criteria:

- A negative peak area or a peak area less than three times the standard deviation should result in the exclusion of the element.
- The peak area must exceed three times the square root of the background, otherwise exclude the element

Applying these two criteria, arsenic and niobium "survived".

*) *Blank problems*: Copper was out of doubt identified, but its count rate is only 0.2 counts/second, which is far less than 10 times the blank value. Fe and Sr peak areas might lead to systematically elevated results, but are well above the threshhold.

*) After having saved the fit results it is *mandatory to save also the fit model*.

10.4. Elemental Sensitivities METHOD

Under the aspect of QA the METHOD **Elemental Sensitivities** must not be applied, when there is an input needed for the dark matrix of any sample (**Compound by difference:**), except when it can be specified very precisely (e.g. the dark matrix was specified by another METHOD), element by element.

Chemical elements of calibration standards, which are excited by the inter element effect must not be included into the calibration (e.g., not potassium of KBr, not phosphorus of KH_2PO_4, not potassium of $K_2Cr_2O_7$).

The calibration for this METHOD is limited to 25 standards in total. All elements which are found in unknown samples must be represented by standards. For the case when some elements in unknown sample can not be covered by a calibration point one will proceed with **Optimize Calibration with Least Square Fit**. The use of this option is very problematic, because otherwise well-defined calibration points can have a systematic bias afterwards. With this procedure interpolated “missing” data points can be established. After having noted the desired sensitivities, the calibration has to be re-run with order 0 for the polynomial (**Order of polynomial (0=no fit)**: 0). The calibration points are not fitted at all and the original calibration points are not biased. Outside of the QXAS environment, the relevant data is pasted into the calibration file. The interpolated elements are worse defined than the surrounding elements, but the rest of the elements do not suffer from a systematic error.

10.5. Emission Transmission METHOD

The calibration established by the **Elemental Sensitivities** METHOD is used as input for the **ET** METHOD, so the same arguments concerning the calibration also apply in this case. For the **ET** METHOD the dark matrix is well treated, but the range of reported elements must be restricted to the range that is spanned by the elements with useful lines of the target. In case some of them are rejected during the calculation of the *F* factors, i.e. the sample is either too thin or too thick, reported elements of such samples must fall within this range. As criteria for the quality of the absorption correction:

- Sample element range (equivalent to the energy range of characteristic lines), spanned by the first and the last element of the accepted target elements.
- Sufficient target elements (for acceptance by the absorption correction calculation routine the minimum is 3) to uniformly define the named range.
- Slope (expected value around 2.8).
- Regression coefficient (**regress**) better than 0.99.
- Standard deviation (**stdev**) low.

Example A: The reference standard IAEA-Soil 7 was analyzed by this METHOD with the use of a target, composed of V, Co, Cu, Se, Sr, Mo. Consequently the results for elements named in the analysis report for Si, K, Ca must be disregarded (the results for the element Ti can still be used, because of its proximity to the established value of the target element vanadium).

Example B: The reference standard IAEA-336, Lichen was studied with the total weight of the intermediate thick pellets as parameter. For the lightest sample with the weight of 0.0497 g the target lines of Sr and Mo were rejected, consequently the element range for this sample is narrowed to the characteristic energies between 4.5-12 keV, excluding elements like K, Rb and Sr from the analysis report. For the thickest samples, with 0.4039 g and 0.5007 g, the target element V was rejected, so the characteristic energies of the sample must range within 6.9-17.5 keV, excluding K, Mn and Fe from the analysis report. The following samples should be rejected, because: The slope for Lichen0.asr is -4.675 (as to be compared to the expected value of -2.8). The regression coefficients for Lichen0.asr, Lichen1.asr and Lichen1B.asr are 0.976, 0.958, 0.966, respectively (recommended: better than 0.99). The standard deviations for Lichen0.asr, Lichen1.asr, Lichen1B.asr are 0.306, 0.320, 0.279, respectively (which is a factor of roughly 3 - 5 higher than for the other samples).

When working with several targets, like for the comparison of the lichen reference standard samples one must respect that inhomogeneities may be found, even when the mother mixture was thoroughly homogenized and the pellets were prepared identical.

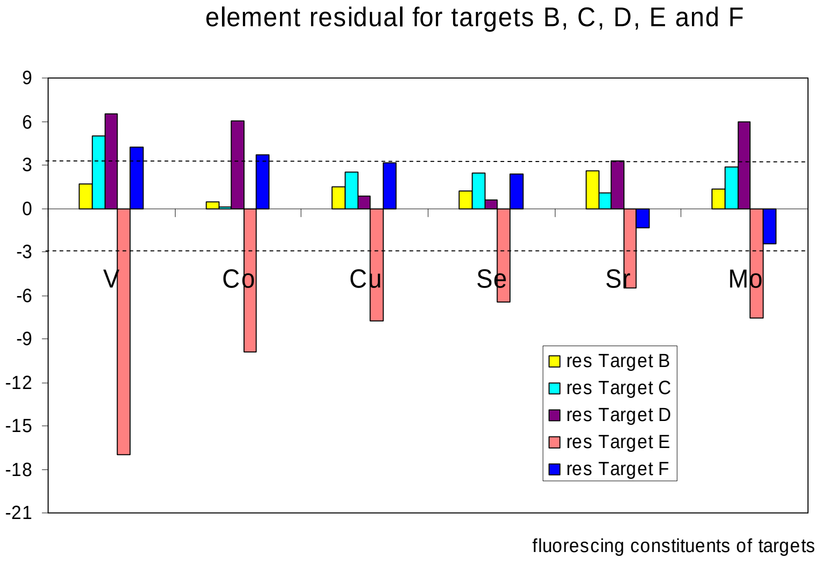


Fig. 10.7. Residual for the fluorescing elements contained in five targets used for the ET method. In the ideal case all results were found within the range +/- 3. For target E a systematic deviation is observed. For other targets inhomogeneities for selected elements can be identified.

For the five targets (B - F) the residual was constructed from the *.asr file results (peak area) for the respective elements by calculation of the element average and individuals' subtraction, divided by the standard deviation. The fluctuations should not exceed +/- 3. From this comparison one can learn that the targets should be numbered (even front and back side may behave differently) and care must be taken that the same target is used for the target and target plus sample measurements.

10.6. Calibration according to QA norms

For *each* element under consideration (in principle for each element found in an unknown sample) an adequate number of very well defined standards, with a *range of concentration values bracketing the sample concentration*, must be prepared.

Let us assume a linear calibration function can be defined for each element, although it were possible to define the following equations also for a non-linear function. A linear calibration function for the element x established with N standards with concentrations c_n^{St-x} ,where n is the running index for the various concentration values, can be written as:

$$I_n^{St-x} = b \cdot c_n^{St-x} + a \qquad (10.1)$$

In order to work with a linear calibration function the corrected intensity I^{corr} has to be calculated, which is built up from the net peak area $N^{\mathrm{St\text{-}x}}$ of standard element *St-x*, and is corrected in terms of self-absorption *A*, enhancement effect *E*, tube current *i* (alternative: decay correction *T*) and live time *t*

$$I_n^{St-x} = I_n^{corr} = \frac{N_n^{St-x}}{i \cdot t} \cdot \left(\frac{1}{A} \cdot \frac{1}{E} \right)_{St-x} \qquad (10.2)$$

The slope *b* (measure of sensitivity) is defined as

$$b = \frac{\sum \left[(c_n^{St} - \overline{c^{St}}) \cdot (I_n^{corr} - \overline{I^{corr}}) \right]}{\sum (I_n^{corr} - \overline{I^{corr}})^2} \tag{10.3}$$

Using the mean of the measured intensities

$$\overline{I^{corr}} = \frac{1}{N} \cdot \sum I^{corr} \tag{10.4}$$

and the mean of the standard concentrations

$$\overline{c^{St}} = \frac{1}{N} \cdot \sum c_n^{St} \tag{10.5}$$

the axis intercept *a* can be written as

$$a = \overline{c^{St}} - b \cdot \overline{I^{corr}} \tag{10.6}$$

Usually for QXAS applications the calibration for each element of interest, as described above, is substituted by one or only few calibration measurements of either pure standards with 100 % concentration (metals), or simple compounds (of highest possible concentration) pressed as pellets, with the following qualities:

- Metal standards are usually homogenous and have a good surface quality (smoothness) but also must be flat, resulting in a good precession. Compounds are easier available, but have to fulfil certain criteria, like stability, homogeneity (particularly when a binder must be used) and should not be hygroscopic (otherwise they cannot be stored and, when needed, re-used).
- The purity must be close too 100 %, otherwise the impurity concentrations should be well specified.
- The self-absorption (enhancement), which must be calculated in order to obtain the corrected intensities, is more accurately described for simple standards.
- For some compounds the enhancement effect must be taken into consideration, for which some METHODs cannot be used.
- When a compound is used which forms a crystalline structure, diffraction peaks complicate the peak fitting.

The corrected intensity for the sample element *x* (net peak area N_x):

$$I_x^{corr} = \frac{N_x}{i \cdot t} \cdot \left(\frac{1}{A} \cdot \frac{1}{H} \right)_{sample} \tag{10.7}$$

is unfortunately, through its corrections *A* and *H*, a function $f(c_x, c_i, c_{dark\ matrix})$, i.e. of the concentrations of the other fluorescing elements, the dark matrix and the element itself. Therefore in strict terms *XRF falls into the category of an analytical process that can not be calibrated*.

The results (*M* repetition measurements) are reported as c_x and confidence intervals CI_x in the form of $c_x \pm CI_x$. The concentration c_x is calculated according to the formalism of CHAPTER 2 (Fundamentals of XRF – Theory) and the confidence interval CI_x is given by:

$$CI_x = \frac{s \cdot t_V}{\sqrt{M}} \tag{10.8}$$

The standard deviation *s* has to be taken from a *precision control chart*. t_V is a t-table value for a certain significance level (usually 95 %) as a function of the degrees of freedom.

XRF with *thin* samples, the ***ET** METHOD* (absorption correction is established independent from the sample measurement) and *TXRF* are *analytical processes that can be calibrated*, the unknown concentration can be calculated with the pre-mentioned calibration, according to:

$$c_x = \frac{\overline{I_x^{corr}} - a}{b} \tag{10.9}$$

$$\overline{I_x^{corr}} = \frac{1}{M} \cdot \sum I_x^{corr} \tag{10.10}$$

Also the confidence interval CI_x can be established from the calibration data:

$$CI_x = s_c \cdot t_V \cdot \sqrt{\frac{1}{N} + \frac{1}{M} + \frac{(\overline{I_x^{corr}} - \overline{I^{corr-cal}})^2}{b^2 \cdot Q_{xx}}} \tag{10.11}$$

The process standard deviation s_c is defined as

$$s_c = \frac{1}{b} \cdot \sqrt{\frac{\sum (I_n^{corr} - I_n^{corr-cal})^2}{N-2}} \tag{10.12}$$

with

$$I_n^{corr-cal} = b \cdot c_n^{St} + a \tag{10.13}$$

and

$$Q_{xx} = \sum \left(c_n^{St}\right)^2 - \frac{1}{N} \cdot \left(\sum c_n^{St}\right)^2 \tag{10.14}$$

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