![EDAX TSL logo — advanced microanalysis solutions]

EDAX Microanalysis Course

Tasks

Version 7.3 –August 2009

TASKS

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Instructions for the TASK section

All spectra used in this TASK part of the EDAX EDS Genesis course are found on the CD given to you.

Some remarks about these tasks:

- Most tasks are split into two levels: basic and advanced. Please complete the advanced task after doing the basic one.

- Before starting, please read the task carefully

- Some tasks needs live X-ray generation, so these need to be done on the XL30 Tungsten (W) scanning electron microscope in the application lab. Most tasks are done using the stand-alone computers with the EDAX Remote software, and the spectra provided with the Task CD.

- Most of the spectra on the CD have been recorded with a SiLi (LN2 cooled) Sapphire detector, some with the Apollo SDD (LN2 free) detector.

TASK 1   **Electron Flight Simulation**

Depth of X-ray generation

On the remote PC in the class room you will find the full version of Electron Flight Simulator (EFS). Your own Task CD contains the Demo version, which has the limitation that it can only analyse C, Cu and Stainless Steel. All other functions are the same.

Start the EFS software, and make yourself familiar with the interface.

Then simulate 3 different bulk materials (C, Cu and Pb) at 3 different voltages. Then complete the following table:

kV	C Depth	C Width	Cu Depth	Cu Width	Pb Depth	Pb Width
5						
15						
30						

Advanced task 1: thin-film analysis

It is not only possible to simulate bulk materials, but also thin layers. This can be a useful tool to determine the optimum analysis conditions before you go to the SEM.

Question: "I want to analyse a sample which has a 0.9 micron coating of Al_2O_3 on top of a W substrate. I need to know the exact film composition. What accelerating voltage should I use so that my X-rays only come from the Al_2O_3 film?".

Use EFS to find an answer.

Advanced task 2: particle analysis

Another option is to simulate particles inside a material. This also can be a useful tool to determine the optimum analysis conditions before you go to the SEM.

Question: "I want to analyse a round MnS particle which has a diameter of 1.2 micron and is embedded in a Fe matrix. I need to know what accelerating voltage should be used so that my X-rays only come from the MnS particle?".

Use EFS to find an answer.

Calibration

An EDS system has different processing times, also called amplification process time (APT) or Time Constants. During this time a pulse is formed (shaped) from an incoming X-ray. Each amplification time can handle a maximum number of counts (throughput). The faster this processing time the higher the throughput can be. A too high throughput (counts per second) will effect the performance of the system, resulting in a high dead time of the detector. During the dead time incoming X-rays are rejected, while others are processed. A reasonable dead time is approximately 30 % (DX4 system) or 40% (Genesis/Phoenix system).
The disadvantage of a fast processing time is the degradation in resolution of the detector (based on the "resolution at Mn Kα" definition), therefore overlapping elements are more difficult to analyse/separate. This is not an issue with Silicon Drift Detectors.

The Genesis microanalysis system can handle much higher countrates (up to a maximum of 150.000 cps. To handle this high countrate the system is equipped with 7 different processing times (102.4–51.2-25.6-12.8-6.4-3.2 and 1.6 μsec.) The resolution will differ from about 128 eV until 190 eV for the Mn Ka line.

For Apollo Silicon Drift detectors (LN2 free, Apollo X, XP and 40), processing times available are 25.6-12.8-6.4-3.2-1.6 and 0.8 μs. Resolution will stay flat going well over 100 kcps. With DPP 3 electronics, even 0.5 μs amp time can be selected.

For analytical work, an amplification time constant around 51.2 μs (12.8 μs for Apollo Silicon Drift) is required. For mapping a fast amplification time constant around 12.8 μsec (3.2 or 1.6 μs for Silicon Drift Apollo 40) should be used to have more input counts.

Instruction.

Perform a calibration of the system, under the two given time constants, for two different count rates (10000 cps and 50000 cps).
Start with Ampl. Time = 12.8 μsec, using 10000 cps.
End with Ampl. Time = 3.2 μsec, using 50000 cps.
Pay attention to the dead time.
Write down the results below.

Results.

	Ampl. Time	kCps	Full scale counts	Resolution	Dead time
1	12.8	10000	20000		
2	3.2	50000	20000		

*All calibration values are stored in the file **calibrat.csv** (located under c:/windows or winnt).*

Energy calibration procedure of the detector

For energy calibration of the detector the X-ray lines of Al Kα (at 1.486 keV) and Cu Kα (at 8.040 keV) are almost always used. A useful calibration specimen in the SEM is a Cu-grid (TEM) or Cu-tape mounted on an Al-stub. In the TEM often a thin Al foil on a copper grid can be used.
Follow the steps below:

- Position specimen at the eucentric position (10 mm WD in the Philips XL30).
- Select 25-30 kV on SEM
- Select a medium magnification (500 - 1000x).
- Adjust the specimen in such a way that the Cu-Ka and Al-Ka X-ray peaks are more or less equal in height.
- Adjust the spot size in such a way that a good count rate is obtained, preferably a count rate that represents a normal working condition for that amplifier time.
- Check the '**Conditions**' of the EDAM box, check if necessary the '**Geometry**'.
- Check also the '**Detector Condition**', eV/Chan = 10 and Amp.Time = 51.2 for normal analytical (quantification) work.
- Select '**Calibration**' under Setup**.**
- Click on **START** (An easy check of whether your system has been calibrated before is that the zero and gain are not equal to zero).
- A calibration is performed automatically.

General remark: make sure that your system is always correctly calibrated.

If one wants to use other element lines to calibrate the EDS spectrum, make sure that the line positions are > 1 keV and the correct peak positions are typed in under reference for peak 1 and 2. In the factory Mn is used (MnKa and MnKb lines)

TASK 3   **PRACTICAL SESSION**

Geometry

Geometry is very important for qualitative and quantitative analysis. In case of correct geometrical parameters the quantification correction model will produce correct results. One of the most important factors is the absorption factor, certainly when light elements are involved. When a rough surface is analysed, the geometrical parameters are not fully correct and errors in quantification may be introduced.

The optimum position of the sample is the eucentric point. When the sample is far out of the eucentric position, hardly any X-rays will enter the detector, resulting in a low count rate. Basically, the specimen is out of the "field of view" of the detector. Retracting the detector to open the solid angle could be a solution.

When the BS Detector is mounted underneath the final lens, the "field of view" (see figure) of the detector is approximately 9 - 12 mm. (using the collimator that is commonly supplied with every SUTW detector).

Performing line scans and mappings at long working distances and low magnification could result in inhomogeneous results due to the "field of view" problem.

Instruction

- Insert a specimen (Al stub) at the eucentric position. At the EDAX Tilburg office the eucentric position of the Philips XL30 is at 10 mm, but if the backscatter detector is installed then it is better to work at 12 mm. Be sure that the specimen is in focus.
- Check the geometry of the instrument.
- Select full frame, 25 kV,
- Adjust the spotsize until the count rate is approximately 2500 cps
- Select a magnification of 50x

- Move the stage to a WD (working distance) of 13 mm, focus on the stub
- Perform a spot measurement on the sample (middle of the screen).
- Note down the count rate (measurement 1) in the result table

- Move the stage to WD 14 mm.
- Repeat the measurement (measurement 2).

- Move the stage to WD 15 mm.
- Repeat the measurement (measurement 3).

- Move the stage to WD 20 mm.
- Repeat the measurement (measurement 4).

- Move the stage to WD 25 mm.
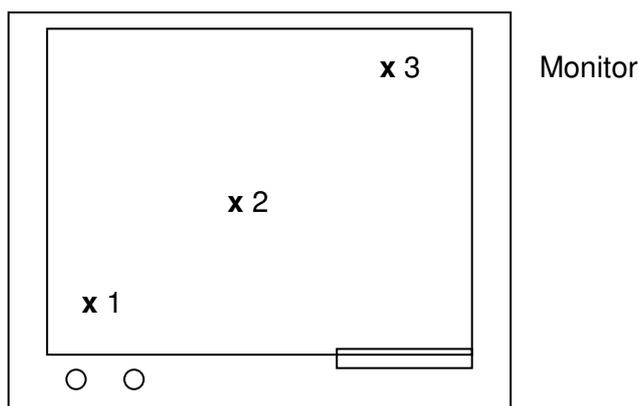- Repeat the measurement (measurement 5).

Results

Microscope type	:				
Working distance	:				
Intersection distance	:				
Azimuth angle	:				
Scale setting	:				
Tilt angle	:				

Start	: WD 12 mm	2500	cps	°	TOA
Measurement 1 : WD 13 mm			cps		TOA
Measurement 2 : WD 14 mm			cps		TOA
Measurement 3 : WD 15 mm			cps		TOA
Measurement 4 : WD 20 mm			cps		TOA
Measurement 5 : WD 25 mm			cps		TOA

Continue geometry

- Go back to 12 mm working distance. Select the spot mode and measure the count rate three times diagonal over the stub (screen), starting at the lower left hand corner (position 1). Note down the countrate.

Monitor

Results

Measurement 4 : (12 mm WD)	position 1		cps
	position 2		cps
	position 3		cps

Now go to 20 mm WD and repeat the measurement, change the spotsize if the X-ray intensity is too low:

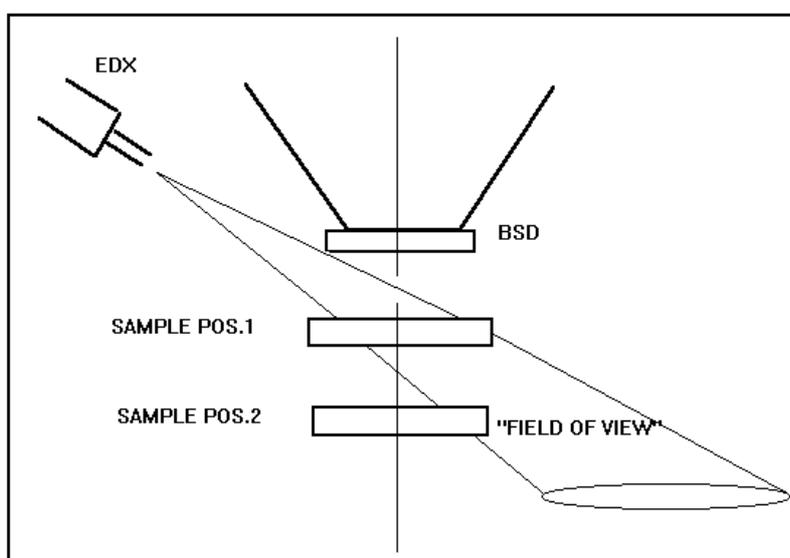|			
Measurement 5 : (20 mm WD)	position 1		cps
	position 2		cps
	position 3		cps

Continue geometry

- Stay at the working distance of 20 mm. A very low countrate will be measured.
- Improve the countrate by retracting the detector (measurement 5). By retracting the detector you open up the field-of-view of the detector, therefore more counts will be detected now.
- Calculate the new take-off angle by changing manually the scale setting at the GEOMETRY menu.

Results

Start	:	20 mm WD	47 mm SS	°	TOA		cps
Measurement 6 :		20 mm WD	SS		TOA		cps

- Put back the detector at its original position (scale setting 47 mm)
- Calculate the TOA again, by changing the scale setting to its original value again.

•
Figure 1. Detector-sample geometry. In case of a long working distance, the "field of view" of the detector is not properly aligned.
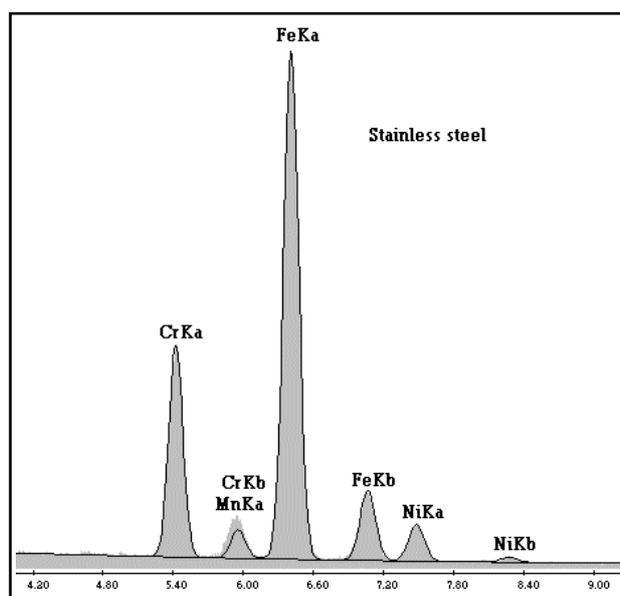
The basis for a good analysis is identifying all possible peaks. Qualitative analysis also requires a calibrated detector otherwise you may draw false conclusions about the presence of particular elements, certainly when overlap with other elements is involved.

One can use the Manual or Auto peak ID mode. In both cases the peak identification is done using a table with all possible elements and all possible lines per element. The correct element is calculated from the nearest possible line transition and displayed in the **Pos Elem** (possible element) box or in case of Auto peak ID, directly displayed near the peak in the spectrum.

When a lot of overlapping lines are present, i.e. L and M-lines of different heavy elements, a method of peak stripping is needed to determine which elements are present. This method is called deconvolution (peak overlap is one of the most important spectral artefacts).

Also before an intensity ratio can be measured EDS peak overlap needs to be considered. In this method the convoluted peak is compared to a standard Gaussian peak for each element of interest. The amount of each pure element spectrum that best accounts for the unknown spectrum, by a special fitting procedure, is the best set of intensity ratios. The method is sensitive to peak shifts, therefore calibration of the system is very important. The figure shows an example of EDS peak overlap. This figure shows the Cr Kβ overlap with Mn Kα. Although the peaks could be resolved by WDS, computer deconvolution methods permit analysis by EDS too.

EDS spectrum of steel showing overlap of the Cr K lines with the Mn K lines.The Mn K line is not deconvoluted to show the difference between the Cr Kβ and Mn Kα

After performing peak deconvolution, the EDX software displays the result graphically to allow inspection of, for example, a missed line. This visualisation is called Halographic Peak Deconvolution, and it provides the means to improve peak identification techniques.

When identifying peaks one has to pay always attention to overlap and spectral artefacts, especially sum and escape peaks.

TASK 4   **PRACTICAL SESSION**
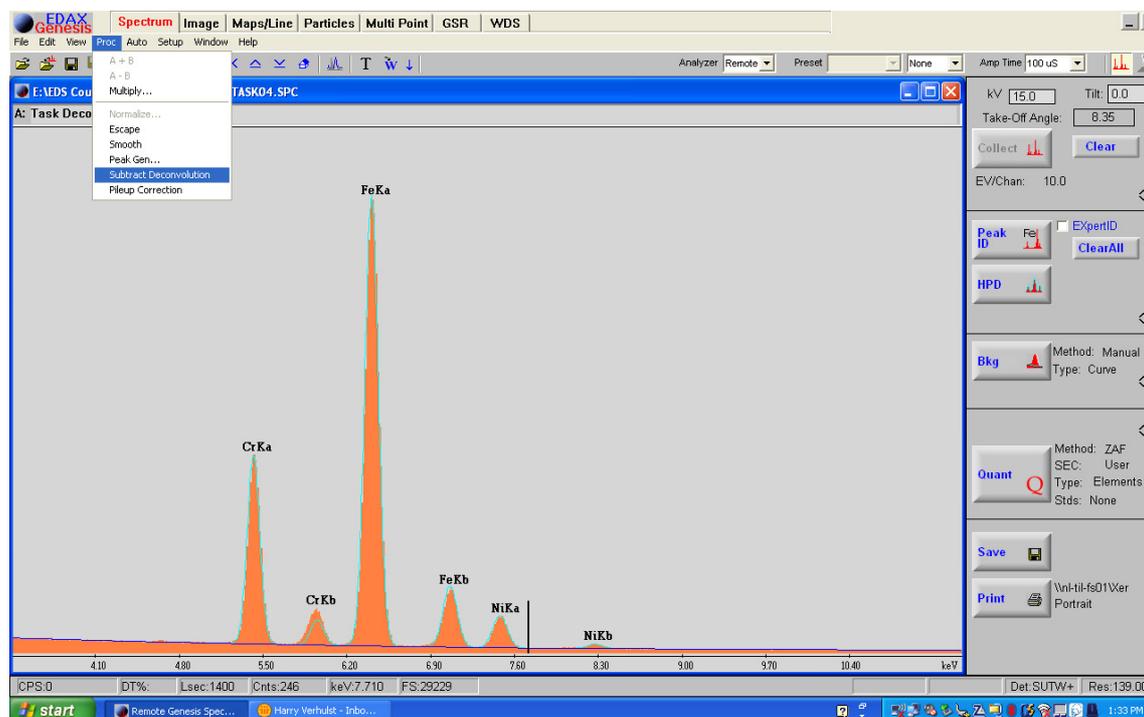
Deconvolution

Deconvolution is a peak stripping method using the halographic model. It can help you to find overlapping elements. This method requires a perfectly calibrated system because you are depending on correct positioning of the peaks. Still, caution must be taken when dealing with overlapping elements. Halographic deconvolution is based on the ratio between the different X-ray lines of an element (see EPIC table).

Instruction

Use spectrum **TASK04.spc** to investigate the overlapping element.

- Open file **TASK04.spc**
- Identify the elements
- Go to the **Peak ID** control panel and press **HPD**.
- Automatically a background is made and a deconvolution is done on top of the background.
- Investigate the deconvolution and search for missing elements around the Cr and Fe line (right mouse click will clear the deconvolution)
- Go to the **Proc** menu and select **Subtract deconvolution** (see example).
- Select the **Peak ID** control panel and identify the remaining peak.
- Label the unknown peak
- Select **Edit** and select **Undo**. The original spectrum is re-installed.
- Perform the deconvolution, with the additional element labelled, by selecting **HPD** at the **Peak ID** control panel again

Write down below your results and/or add your prints.

TASK 5   **PRACTICAL SESSION**

Artefact : Peak overlap / deconvolution

Instruction

Use spectrum **TASK05.spc** to investigate the overlap between the different elements. Use the deconvolution to identify the different elements. Identify the elements.

- Identify the first peak and label the peak
- Perform a deconvolution by pressing **HPD** (Peak ID control)
- Investigate the deconvolution and identify the next element
- Repeat until you have identified 3 (main) elements

Write down below your results.

Remark:
Subtracting deconvolution will only work well in case of an overlap of two X-ray lines (see Task 4). In the case of multiple overlapping X-ray lines (like in this Task), the peak fit is difficult to judge. Therefore use the Manual Peak ID by using the cursor.

Results

TASK 5 Advanced   **PRACTICAL SESSION**

Artefact : Peak overlap / deconvolution

Instruction

Use spectra **TASK05_a.spc** and **TASK05_b.spc** (both run at 10 kV) to investigate the overlap between the different elements. Use the deconvolution to identify the different elements. Identify the elements.

- Identify the first peak and label the peak
- Perform a deconvolution by pressing **HPD** (Peak ID control)
- Investigate the deconvolution and identify the next element
- Also use info from spectrum task05_c.spc (same sample as 05_b, but recorded at 30 kV)

Write down below your findings.

Many artefacts may occur. The most important ones are; sum-peaks and escape-peaks. Sum peaks are countrate dependent. Both artefacts can lead to false identification, hence false quantification and false conclusions.

Artefacts: pulse pile-up effects.

At very high count rates under the chosen amplification time (time constants) resulting in a high deadtime percentage, the high possibility exists that two X rays enter the detector exactly at the same time. The pulse pile-up rejecter cannot distinguish these two and they are processed as a single pulse with an energy equal to the sum of the two X-rays. If the X-rays correspond to two elements in the specimen, pulse pile-up results in so-called **sum peaks**. One or both X-rays can also come from the continuum background. Every pile-up event combines two events from lower energies in the normal spectrum, hence all cases of pulse pile-up result in two effects, loss and displacement of pulses. Since pulse pile-up depends on the count rate, it is difficult to devise methods for correction. Pile-up can be avoided to a large extent by keeping the count rate low.

Note: pulse pile effects are not limited to pure elements. For example in cases where large amounts of O and Si are involved, like glasses and minerals, a sum peak might occur around 2.26 keV (0.52 keV O K-line + 1.74 keV Si K-line). Unfortunately this is roughly the position of the S K-line, Mo L-line and the Pb M-line.

To identify sum peaks one can lower the count rate and investigate the shape of the newly formed peak at the same position.
Choose therefore always a deadtime, which will correspond with the chosen amplification time.

Artefacts: escape peak

Some of the X-rays that enter the detector can produce a Si K ionisation, which will result in a Si K X-ray or an Auger electron. In either case, the energy dissipation will result in electron-hole pairs and the total pulse, being [(initial X-ray - Si K) + Si K], is collected. The Si K radiation, with an energy of 1.74 keV, may escape from the front surface of the detector. Consequently, its energy is lost and the pulse is transmitted having an energy equal to **the original energy minus 1.74 keV**. The chances for the escape of a Si-K X-ray are small but finite and strong peaks in a spectrum have associated weak but significant peaks 1.74 keV lower in energy, which are referred to as escape peaks.

Remark: In principle the intensity of the escape peak from a particular element belongs to the main peak. The software has a procedure to automatically subtract the escape peak from the spectrum (after deconvolution) and add the intensity to the element were it belongs to, therefore the intensity of this element will increase.
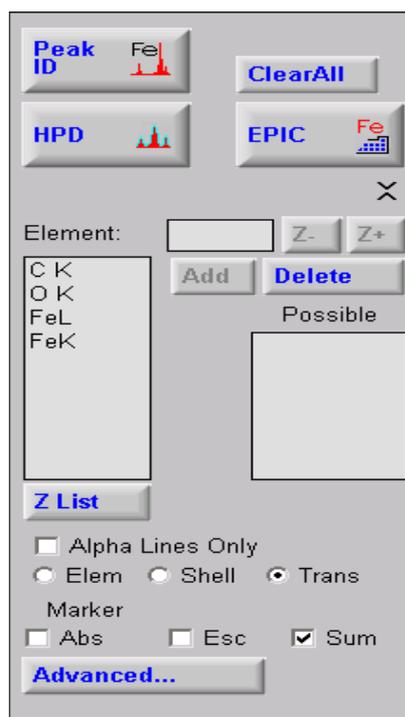
Artefacts : Sum peaks of type A

Instruction

- Generate a spectrum of pure Al (use a specimen stub) at a high deadtime (>60 % DT = high countrate). Use the 51.2 µsec Amplifier Time.
- Put the spectrum in memory B of the EDAX software using View, Compare, Single Overlay and Swap A,B. Make sure that in the compare window the scaling is set to Auto.
- Generate another spectrum, but now at low deadtime (20% DT = low countrate). Compare both spectra with respect to the sum-peak.
- Go to the **Peak Identification** control page.
- Select under the **Marker Options** the **SUM** marker option.
- The position of the sum peak will be displayed as a small coloured marker. Be aware that only the sum peak of the highest peak (so not always the main element) will be visible. Sum peaks from combinations of other elements can **not** be displayed with these markers.
- Look for other differences, like peak shift and peak broadening in the 2 spectra.

You could also use spectrum **TASK06_1.spc** (6.4kcps) and spectrum **TASK06_2.spc** (1.8 kcps) and compare both spectra (under View/Compare/single overlay)

Remark : At low deadtime % the sum peak must decrease in height, compared to another real peak, or even better, completely disappear. If the ratio of the possible sum peak, in relation to the main peak, is equal at high and low deadtime %, than this peak is probably not a sum peak but it represents a real X-ray transition of an element. If the Peak ID list will not show any possible elements, then use the EPIC (Element Peak Identification Chart) or a dedicated X-ray transition table to identify the unknown line.

TASK 6 Advanced   **PRACTICAL SESSION**

Artefacts: Sum peaks of type A +B

A sum-peak is not limited to pure element only. Combination of two major elements is also possible.

Instruction

• Generate a spectrum of a glass or SiO2 (Quartz). Use a normal countrate (dead time 30-35%)
• Look for sum peaks of glass
• Run also a spectrum at high cps or high dt% and compare
• Look again for sum peaks of glass

(You can also use spectrum **TASK06_a.spc**).

Remark: these sum peaks are typical for glasses and minerals.

Write down below your results.

Results

Artefacts: escape peak

Instruction

- Open spectrum **TASK07_1.spc**
- Look for the escape-peak
- Overlay with spectrum **TASK07_2.spc**
- Look at the differences between the two spectra

- Investigate spectrum **TASK07_3.spc** and identify the escape and sum peak (count rate used: 19kcps)

Remark: the escape peak is always positioned at an energy 1.74 keV lower than the element of interest. Changing the count rate will not effect the height of the escape peak therefore identification could be difficult.

Write down below your results.

Results

Peak ID

Peak Identification is one of the most important steps in microanalysis. If the X-ray lines are not correctly identified, correct quantification can not be expected. In case of overlapping elements, look for the higher order X-ray transitions of the possible elements. Especially L and M-lines are difficult to identify in case of severe overlap. This tasks starts with the investigation of elements showing K, L and M-lines. Pay attention to the shape. Use HPD to investigate the fit.

For good qualitative analysis (and later quantitative analysis) one has to use a proper amplification time (102.4-51.2 µsec for SiLi and 25.6-12.8 µsec for Silicon Drift Detectors (SDD)) to obtain the best peak separation/resolution.
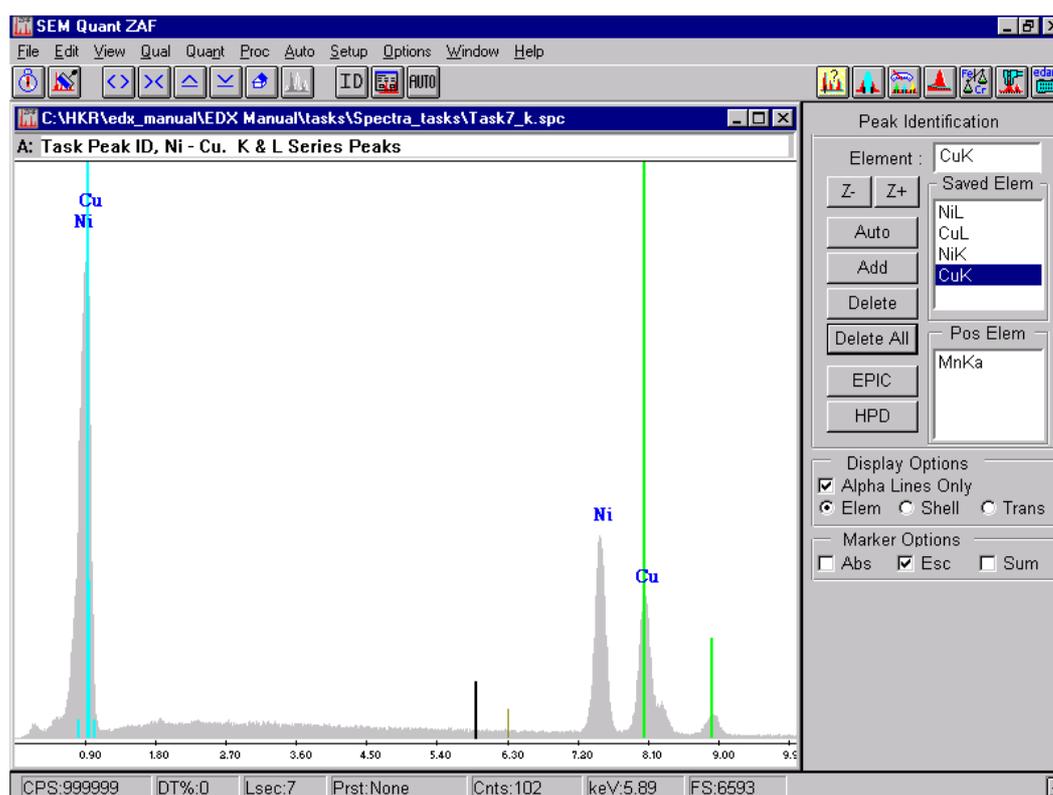
Instruction

- Investigate spectrum **TASK08_K**
- Investigate spectrum **TASK08_L**
- Investigate spectrum **TASK08_M**

- Try to identify all the elements in spectrum **TASK08_1.spc**.
- Pay attention to overlapping elements and sum/escape peaks.

- Repeat by using spectrum **TASK08_2 until TASK08_6.spc**

Write down the results.

Spectrum

TASK 8 Advanced   **PRACTICAL SESSION**

Peak ID

Peak Identification is one of the most important steps in microanalysis. If the X-ray lines are not correctly identified, correct quantification can not be expected. In case of overlapping elements, look for the higher order X-ray transition of the possible elements. Especially L and M-lines are difficult to identify in case of severe overlap. This tasks starts with the investigation of elements showing K, L and M-lines. Pay attention to the shape. Use HPD to investigate the fit.

For good qualitative analysis (and later quantitative analysis) one has to use a proper amplification time (102.4-51.2 µsec) to obtain the best peak resolution.

Instruction

• Try to identify all the elements in the spectra TASK08_a1.spc through TASK08_a3.spc.
• Pay attention to overlapping elements and sum / escape peaks

Write down the results in the spectrum below or print your results.

Spectrum

HOW TO PERFORM AN ANALYSIS?

To analyse an unknown sample could be easier when the following this short guidance:

- Make sure that the system is properly calibrated.
- Choose a proper Amplification time (good resolution = good peak separation in case of qualitative / quantitative analysis)
- Make sure that the microscope is in a good condition (condenser alignment)
- Choose a suitable position on the sample
- Make an image : - SE image will show topography
                            - BSE image will show atomic number contrast
- Focus on the sample (calculation of the TOA)
- Acquire a spectrum
- During spectrum acquisition: label spectrum.
- Perform in the meantime AUTO ID
- Identify all other elements, including trace elements.
- After acquisition: store spectrum to HD
- Quantify spectrum
- For an unknown sample: use 30 – 15 – 5 kV to trace all elements present in the sample.

Remarks:

- Build a library of pure elements (reference spectra), if possible

QUANTITATIVE ANALYSIS

Spectra collected with the EDX system can be analysed to provide weight and atomic percent data. Standards can be used for this analysis or the sample may be analysed without standards (i.e. "standardless").

In principle there are 4 different ways of performing analysis:

1. **Standardless analysis**
2. **Standardless analysis with updated SEC table**
3. **Quantitative analysis with compound standards**
4. **Quantitative analysis with pure elements**

A short description of the different techniques are listed below:

Standardless Analysis

Default a quantitative analysis is performed standardless. The meaning of standardless analysis is to create a flexible and easy to use tool to extract quantitative data from the unknown sample.

Standardless analysis with updated SEC table

Every EDAX detector is unique, but for the most accurate analysis these unique properties have to be taken into account. This can be done with SEC factors. The SEC factors can be calculated by analysing a compound reference standard, and calculate the SEC from the given wt% and the measured intensities.

Quantitative Analysis with Compound Standards

If working under standardless analysis (with or without your own SEC tables) will not give the accuracy you are looking for, the compound method can be used. Using this method the unknown sample will be directly compared (and calculated) from a used standard. This standard is a compound with known concentration for those elements under investigation, and very similar to the unknown sample. Therefore only the elements present in the standard can be analysed.
Under all other circumstances the s/w will automatically switch over to standardless mode. There is no possibility to save the data from the compound standard to hard disk.

Quantitative Analysis with Pure Element Standards

The pure element standards method requires that a series of pure element standards be collected under constant conditions (same geometry, kV, and beam current into a Faraday cup). The constant conditions does not mean that they should have the same dead time or the same absorbed current while on the standards because both parameters will vary with the atomic number and possibly with overvoltage considerations. Probably the dead time should not be more than 30-40% on the sample or standard with the highest dead time. Under pure element standards it is also possible to use compound materials as a standard. One is free in choosing and therefore free in mixing different elements from different standards to a large pure element file. The created standards file can be saved as *.std file.

Background subtraction

Before quantification we have to eliminate the contribution of the background. There are basically two methods; automatic and manual. In both cases a top-hat filter is used to find the background points. Also in both cases it lets the user see and pass judgement on the quality of the model. In the manual mode the user can adjust the background to specific needs.

Instruction

• Open spectrum **Task09.spc**
• Identify the main element and perform a HPD using an automatic background.

Write down the results.

• Under background, transfer all background points (from Automatic background fit) to **Manual** mode (by pushing >> button) and modify the background.
• **ADD** some additional points. Select a point and click **Add**.
• Pay attention to the absorption edge.
• Switch back to the **Peak ID** control page and press **HPD**.

Look at the differences between using auto/manual background.

Results

TASK 9 Advanced   **PRACTICAL SESSION**

Background subtraction/absorption edge

Before quantification we have to subtract the contribution of the background. There are basically two methods; automatic and manual. In both cases a top-hat filter is used to find the background points. Also in both cases it lets the user see and pass judgement on the quality of the model. In the manual mode the user can adjust the background to specific needs.

The absorption edge can also be identified as an artefact. An absorption edge can influence the background modelling, especially in the low Z region. The absorption edge of minerals and glasses will certainly have an effect on the quantitative results. Recognising an absorption edge will require some experience, certainly in a multi element spectrum.

Instruction

- Open spectrum **Task09_a1.spc**
- Identify the main elements and perform a HPD using an automatic background.

Write down the results.

- Switch to the **Manual** mode and modify the background.
- Move the BKGD points to manual mode by pressing the **AUTO>>MANUAL** button, and **ADD** some additional points. Select a point and click **Add**.
- Pay attention to the absorption edges.
- Change the height of the BKGD points using the +/- buttons.
- Switch back to the **Peak ID** control page and press **HPD**.
- Note the differences in quantitative results using auto/manual background (look for the net intensity of the Al and Si peak)

TASK 10   **PRACTICAL SESSION**

Quantification/Background subtraction

Before quantification we have to subtract the contribution of the background.
The best quantitative results will be obtained if the overvoltage is approximately 2 – 5 times higher than the highest X-ray lines under investigation.
When using a standardless quantification method, the s/w will estimate the net intensity for the standard. It uses a complex formula, based on many parameters. However, using this method makes the system very flexible in choosing acceleration voltages. It makes for example practically no difference if an acceleration voltage of 25 or 15 kV is used.

Instruction

- Acquire a spectrum from steel at 25kV and perform a quantification using an automatic background.

Write down the results (use the standardless method).

- Repeat this exercise by using an acceleration voltage of 15kV.

 You can also use spectrum **TASK10_a.spc** (at 25 kV**)** and **TASK10_b** (at 15 kV).

Results

Standardless analysis.

The core function of an EDS system is to do a good and reliable compositional analysis. For this reason the EDX software allows the use of all types of reference standards. But in many cases standardless analysis is the preferred method for its greater speed and ease of use.
In the standardless method the k-ratio is calculated from the measured peak intensity of the elements of interest by using a Pure Element Intensity Factor (these PEIF's are not independent of the kV). The calculated k-ratio is than corrected by ZAF. Standardless analysis always normalises to 100%, or some other value entered by the user. Whether one chooses a standards or standardless technique, a correction is necessary for the effect of other elements present in the unknown material.

Introduction

The EDX software uses a unique procedure, called the SEC-method, to do standardless analysis, where the intensities of the reference materials are calculated from first principles. More information is given about the background behind the SEC-method.

Theory

For microanalysis the composition of a sample can be calculated from the measured X-ray intensities using:

$$W\% = \frac{k - ratio}{Z \bullet A \bullet F} * 100$$

where:
$$k - ratio = \frac{I^{Meas}}{I^{Std}}$$

Where Z, A and F are the matrix correction parameters, describing the atomic number effect (stopping power and backscatter effect), the absorption effect, and the fluorescence effect. I^{MEAS} and I^{STD} are the measured and standard intensities of the element involved.

Note that EDAX uses ZAF correction factors, which are 1/ZAF factors, as used in some other text books (e.g. Goldstein et al.).

Since for standardless analysis we have no I^{STD} available, EDAX has chosen to use calculated standards, which can be calculated using:

$$I^{Std}_{Calculated} = n \frac{\Omega}{4\pi} \varepsilon_d \omega_j p_{jl} f(\chi) \frac{N^0}{A} R \int_{E_0}^{E_j} \frac{Q_j(E)}{dE / d(\rho s)} dE$$

Where n is the number of electrons entering the sample, $\Omega/4\pi$ is the solid angle, ε_d is the detector efficiency, ω is the X-ray fluorescence yield, p is the relative probability for the transition involved, f(x) is the absorption correction, and the integral represents the cross-section of the ionisation involved.

Since n is unknown, and thus set to unity, the calculated intensity might be in a totally different order of magnitude as the measured intensity. Normalising the weight percentage to 100% solves this problem.

This function has been shown to work very accurately, especially for analyses using K-lines. Compared to scientific literature you might find that some factors have been left out of the calculation, like the Koster-Cronig transitions. As a result this equation is less accurate for the analysis with L- and M-lines.

One disadvantage of this equation is that the detector efficiency, ε_d, can not be predicted with sufficient accuracy for X-ray lines below 1 keV. Small variations in detector parameters (window thickness, Si dead layer, etc.) can cause variations in measured intensity. Therefore EDAX has introduced Standardless Element Coefficient factors, or SEC factors. The first equation on the previous page now becomes:

$$W\% = \frac{k - ratio \bullet SEC}{Z \bullet A \bullet F}$$

SEC factors are relative numbers of course, again due to the normalisation to 100%. So a set of SEC factors will normally contain a value of 1.000 for one element, while the SEC factors for all other elements are scaled relative to it.

Benefits of the SEC method

- SEC factors are independent of the accelerating voltage. As they only correct for variations in detector parameters, the accelerating voltage with which the X-rays were generated is irrelevant. The software does still need to know what the voltage is though.
- SEC factors are matrix independent. So a SEC factor for carbon calculated with SiC can be used for the carbon content in steel, ceramics, polymers, etc.
- SEC factors remain unchanged for a long time. Since detector parameters hardly change, we recommend that you check your SEC factor maybe once a month. But experiences over the last year have shown that even after several months there are only small variations.
- For all elements above Na, a user should never have to change the SEC's. They are all set to 'one' (1) initially, indicating that they are not in use. The SEC's do have to be changed for the lighter elements. This is basically to correct for differences in detector characteristics
- In the software the SEC dialogue box looks exactly like the PEIF box used to look, and is used in the same manner. Users simply change the value of the SEC, and requantify until the quantification result for the element in question is equal to the known result.
- Properly tuned SEC's will offer much better performance than possible with PEIF's. SEC's will also reduce the user choices, and further eliminate corrections (sources of errors) in the quantification routine.

After all these positive comments, we would like to part with a warning: please be realistic in your expectations. Of course every theoretical model has its limits. Do not expect the best quantitative results if you optimized a SEC factor at 30 kV and use them at 4 kV. Or when you optimized your SEC factor for carbon on a 2% carbon steel and now analyze a ceramic with 45% carbon. For such a wide range you might want to have more than one SEC table at hand.

TASK 11 PRACTICAL SESSION

Standardless analysis

Standardless analysis is independent of the acceleration voltage. ZAF correction will take care of this.
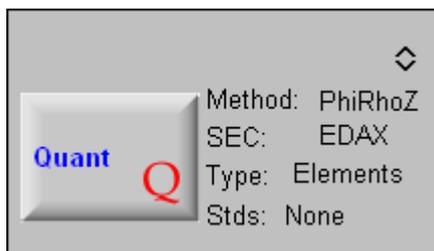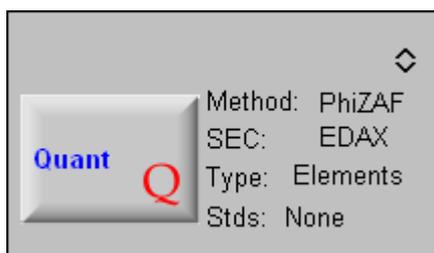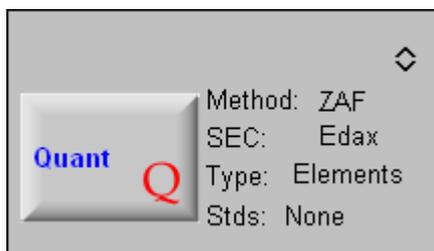
Instruction

- Acquire a spectrum of the Silicon Dioxide (or open spectrum **TASK11.spc**)
  Note : the sample is conductively coated with carbon
- Go to the **Quant** section
- Press **Quant**
- Perform a standardless quantification using the **ZAF** and **Phi-Rho-Z** correction model. Right click on **Method** to change in between both correction models.
- Check the results with the theoretical values.

Theoretical values for Silicon Dioxide::

element   WT%

O   53.25
Si   46.75

Different Quant Methods available (not all are standard software):

TASK 12 PRACTICAL SESSION
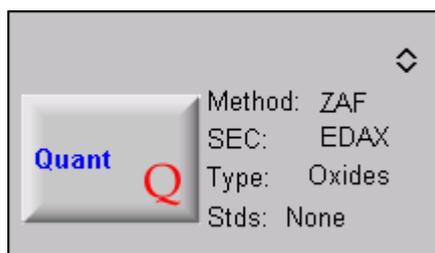
Standardless analysis

In many cases the chemical composition of minerals and glasses will not be calculated as pure elements, mainly because of the problems with the calculation from the element Oxygen. Therefore the results can be calculated based on Oxygen stoichiometry.

Instruction

- Acquire a spectrum of the mineral Plagioclase (or restore spectrum **TASK12.spc**) Note : the sample is carbon coated
- Go to the **Quant** section
- Take Carbon out of the ZAF list
- Press **Quant**
- Perform a standardless quantification using the **ZAF** and **Phi-Rho-Z** correction model. Click on **Method** to change in between both correction models.
- Select under **Type – Oxides**
- Press **Quant** again
- Check the results with the theoretical values.
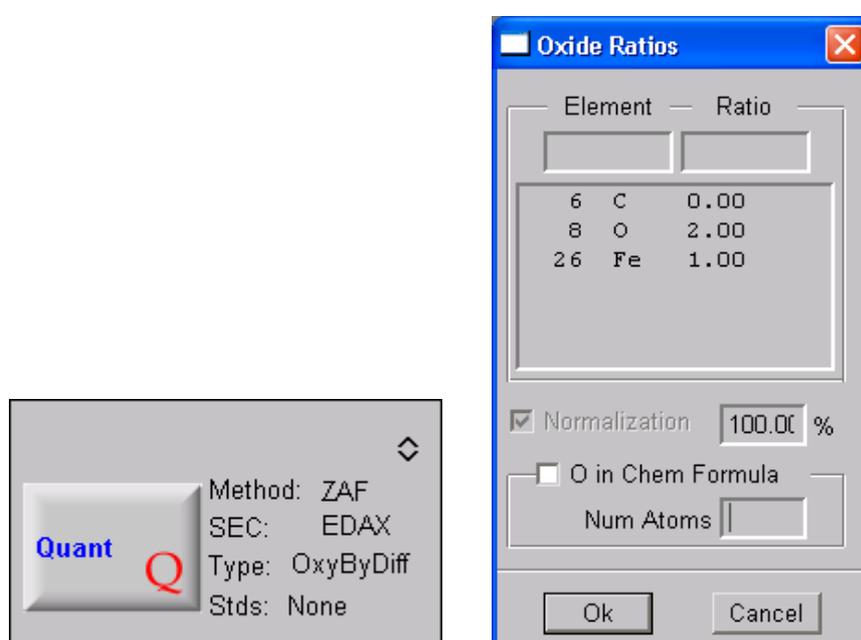
Theoretical values for Plagioclase

Oxide	WT%	
Na2O	4.36	
Al2O3	28.62	
SiO2	54.38	
K2O	0.41	
CaO	11.84	
FeO	0.37	
O		47.27

Additional standardless analysis

- Open spectrum **TASK12_a.spc** (Albite mineral)
- De select Carbon from ZAF list
- Calculate the chemical stoichiometry based on 8 oxygen atoms.
- Select under the Quant page: **Type - Oxy by difference.**
- Expand Quant section, select **Type** and click **O in Chem Formula**
- Choose the correct number of oxygen atoms (in case of Albite 8)
- Open **ZAF List** and deselect the element Oxygen. The system can not perform an oxides quantification with O in the element list.
- Press **Quant**

Results

(Albite : O = 48.76 wt%, Na = 8.60 wt%, Al = 10.34 wt%, Si = 32.30 wt%)

Remark: In the dialogue box above, O in a chemical formula has been chosen and 8 atoms of oxygen are requested in the calculation (the user must know what this number should be, the software can not calculate for it). Then the quant results will be shown as below, with Atomic % column being replaced with the CHEM column.

This indicates a chemical formula of $Na_{1.00}Al_{1.10}Si_{2.98}O_8$.

Geologists like to present results in this type of format.

Chemical formula of Albite is $NaAlSi_3O_8$

TASK 13 **PRACTICAL SESSION**

Updating the SEC (Standardless Element Coefficient) table

Because light element detection is important, we want to quantify the light elements as accurate as possible. Using the standardless procedure will not give the correct results. Therefore when light elements are involved in the unknown sample one can update the SEC user table for these elements, using some standards, to make a generic table which will produce more accurate results for these light elements. All other elements will still be measured standardless. Saving the values as a **.SEC** file is possible.
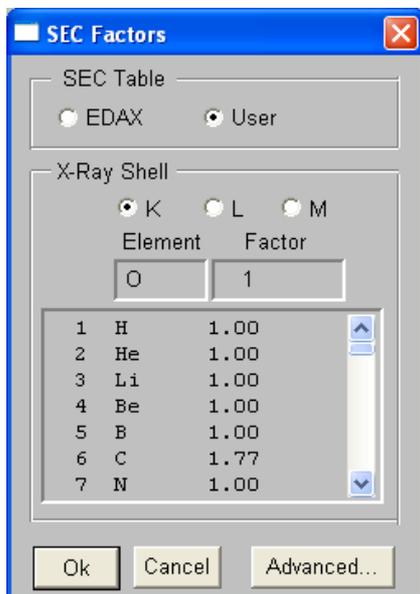
The method on itself is very easy to use . The software, however, does not show you which SEC factors are used to calculate the results. Therefore it is advisable to save a default file and load the file when normal standardless analysis are performed. Then the EDAX and the USER table are identical

Instruction

- Go the **Quant** control page.
- Expand the Quant section and press **SEC** button
- Select **User** and check the table. All values must be 1.00 (K, L and M lines)
     (Remark : it is also possible to VIEW the file. Select **File – View)**
- Go to **File – Save as**, and select the extension **.sec**
- Save the SEC table as **default.sec**

- Acquire a spectrum of SiliconCarbide (or open spectrum **TASK13.spc**)
- If other elements shown in list than Si and C, de-select them in the **ZAF List**
- Go the **Quant section**.
- Select **Stds** and then select **Compound**
- Press **Setup** button
- Type the known chemical composition of SiC
  (Si = 70.05 wt% and C = 29.95 wt%)
- Select **SEC** and update the SEC table (to save values). Press **OK**
- Select under the **Quantify** control page **SEC.**
- Store the SEC table to HD (**File – Save as - .SEC)**
- The EDAX table will produce standardless analysis. The USER table will produce quantitative data using the update SEC table in the background.
- Perform a quantification again

Selecting the USER table will produce more accurate results for, in this example, Si and C. All other results from the remaining elements will still be standardless.

This method is also called the **improved standardless quantification method.**

Updating the SEC table -continued

When light elements are involved in the unknown sample one can update the SEC user table for these elements using some standards, to make a generic table which will produce more accurate results for these light elements. All other elements will still be measured standardless.

Instruction

- Open spectrum **TASK13_a.spc** (mineral Albite, recorded at 10 kV with Apollo 40 SDD detector)
- Do a PeakID
- De-select Carbon from ZAF list
- Do a standardless Quant (using SEC on EDAX)
- Write down the results
- Switch to SEC on User (right mouse button)
- Type in a value of 0.74 for SEC factor Oxygen
- Do another quant
- Compare results with earlier data

SEC factors need to be set-up for elements < 1 keV. They are set-up for B, C, N, O and F, using compound standards.

Selecting the USER table will produce more accurate results for, in this example, Oxygen. All other results from the remaining elements will still be standardless.
This method is also called the **improved standardless quantification method.**

See also additional document on SEC factors.

QUANTITATIVE ANALYSIS

Analysis with standards

There are two ways that standards can be used to enhance quantitative results.

COMPOUND (or multi-element) Standards
PURE ELEMENT Standards

Both methods can be used with normalisation or without normalisation. BCF (Beam Current Factors) can be applied to account for beam current changes if beam current cannot be reset to some precise value. Oxide stoichiometry can also used with standards.

Compound standard

The setup of all these elements is done through the **Standardize – ZAF** dialogue box shown on the next page. If a standard has been measured, i.e., a spectrum has been obtained, then concentrations are entered into the box, and RZAF (Reversed ZAF) is used to calculate pure element intensities. The calculated reverse ZAF intensities are displayed. Selecting the **Use As Compound** tick box, will use the calculated intensities throughout the whole analysis.
Only those elements present in the standard can be measured. In all other cases the s/w will prompt a warning that a mismatch is detected. Automatically the standardless method is selected. The method can be used for elements or oxides.

Pure elements

The result can then be calculated either normalised, or non-normalised.
The same procedure can be repeated when more that one standard has to be used.
After **RZAF** the tick box **Use As Compound** is **NOT** selected, but immediately **OK** is clicked. The pure intensities are displayed and can be saved by selecting the element or elements. Only the highlighted elements are saved (**Save**) in the Pure Intensity Table. It is now possible to combine different elements from different standards. More elements can be put into that file by repeating this process with additional standards. Only select those elements that are added to the already existing standard .

A list of the used pure intensity factors can be displayed by selecting **Quant – Stds – Pure.** Select **Factors**. The used correction model must be equal to the earlier selected one.

This method can improve the accuracy and is therefore mainly used for process control, where differences between the unknown sample and the standard are very small.
Making a .std file out of different standards is a very complex and time-consuming job. It requires a good experience and discipline of the user. Once a set is made one can have the benefit of a very accurate analysis. Quantification now is automatically using the PURE ELEMENT standard.

The file can then be saved to disk by using the SAVE AS and saving it as **.std** file.
A file with only the calculated pure elements from the compound standard is stored.

Quantification by using standards

THE COMPOUND STANDARD

One possibility of using a standard is fully quantitative analysis using compound standards. A dedicated standard set is made out of one compound standard. This method can improve the accuracy, but requires good experience and discipline of the user. This method is mainly used for process control, where the difference between the unknown and the standard is very small.
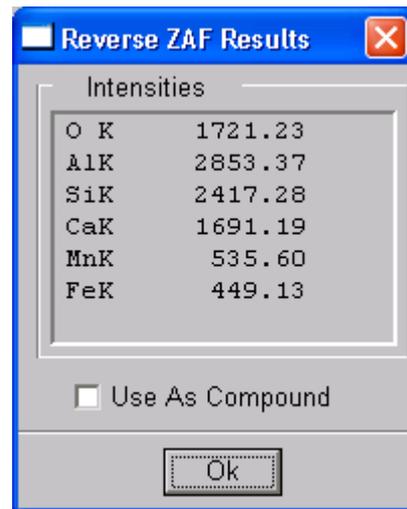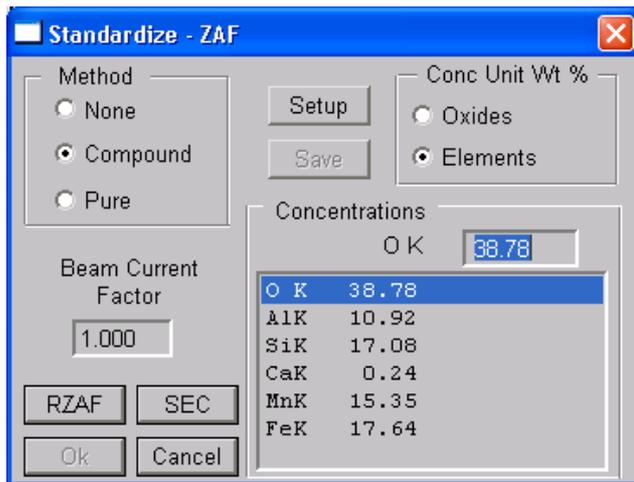
The spectra to be analysed will typically have been collected from a single session in sequence using the same element list, with the same accelerating voltage, and with the same beam current/spot size setting. It is possible to compensate for variations in beam current if a current meter and Faraday cup are available, but this is primarily of value if the user can not be certain that the analysed elements should have a sum which equals 100% (or very near 100%). In this case, an assumption for the garnet standard of 100% for the reported elements (O, Al, Si, Ca, Mn and Fe) is certainly valid.

The TASK14_1.spc has been implemented as the standard to analyse the remaining 5 spectra which have been collected from different spots on the same standard.

.

Instruction

- Open spectrum **TASK14_1.spc**
- Expand the **Quant** section (select ZAF model, type Elements)
- Select **Stds** and then **Compound**
- Click on **Setup** and select **Elements** (If Oxides are selected one can not have the element O labelled in the peak ID list)
- Type in the true concentration per element of the Garnet mineral under **Concentration.** Press each time return to switch to the next element.
- Click on **RZAF.**
- Select under the **Reverse ZAF Results** the **Use As Compound.**
- Click two time **OK** and press **Quantify**
- Note that the result must be equal to the original composition of the Garnet (as typed in)

Garnet			
Oxide	WT%	Element	WT%
		O	38.78
Al2O3	21.20	Al	10.92
SiO2	34.96	Si	17.08
CaO	0.44	Ca	0.24
MnO	18.75	Mn	15.35
FeO	24.66	Fe	17.64

- Restore spectrum **TASK14_2.spc / TASK14_6.spc**
- Select **all** current conditions
- Select **Multiple** (above Quant button)
- Quantify the 5 "unknown" spectra, running the Garnet standard in the background.

- Select from the main icon bar, **Auto** and **Process spectra**
- Select the 5 files and **ADD** to the **Spectra to Process** box.
- Choose a correct output file name
- Perform an automatic recalculation using **Standardless** and **Compound** quantification by selecting **Process**
- Automatically a .csv file (MS Excel compatible) will stored.
- Note the differences in the results.

Results are given in task14-quant-outcome.xls file.

Quantification by using standards
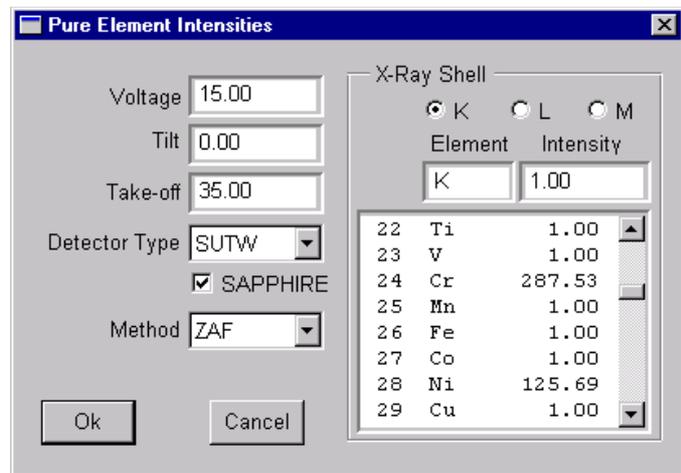
PURE ELEMENTS

One other possibility of using a standard is fully quantitative analysis using pure element standards. If no pure elements are available one can use a compound standard and extract one or more elements from this standard in order to create a pure element table. This method can improve the accuracy, but requires good experience and discipline of the user. This method is mainly used for process control, where the difference between the unknown and the standard is very small.

In the exercise we will use three pure element spectra (Al, Ni and Cr) to create out own standard file.

Instruction

- Open spectrum **TASK15_4.spc**
- De-select Carbon from the ZAF list
- **Quantify** the spectrum using the standardless method.
- Write down the results

- Open spectrum **TASK15_1.spc**
- Open the **Quant** section (select ZAF model, type ELEMENTS)
- Select **Stds** and then under **Methods, Pure**
- Click on **Setup**
- The pure element net intensity is calculated for the corresponding element.
- Click **Save**
- Click **OK**
- Repeat for spectrum **TASK15_2.spc** and **TASK15_3.spc**
- Expand the quant section and look under **Quantify – Factors**
- Open spectrum **TASK15_4.spc** until **TASK15_6.spc**
- Perform a quantification
- Compare with standardless quant results from above

- If screen appears as below, change kV value under **Factors** (expanded Quant section)

When running this quantification routine with standards, one can display the results non-normalized (i.e. not summed to 100%). This is available under the expanded Quant section and then under Type.

The more close to 100% total (in practice between 95-105 wt%), the more accurate the standard quant was. If deviating a lot from 100%, this could be o.a.:

- Pure element intensities not determined correctly
- Element (s) missed
- Analyis conditions not constant (e.g changing beam current, kV)
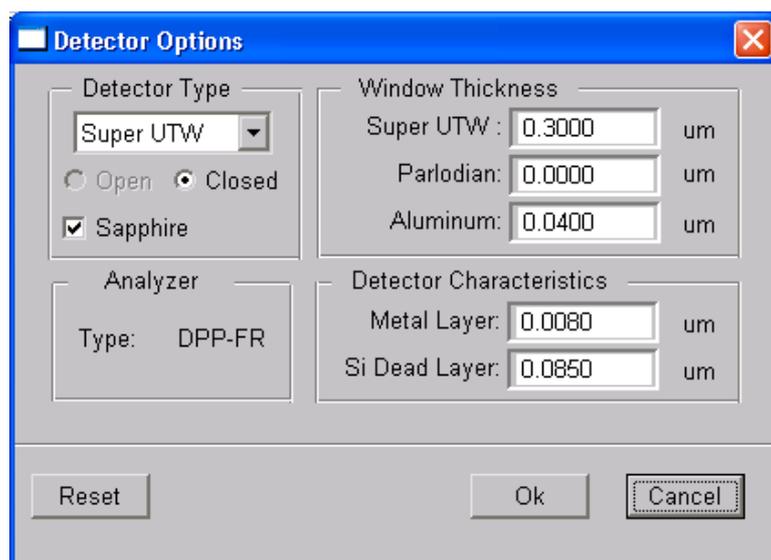- Standards used not best choice or not pure enough

QUALITATIVE ANALYSIS
Detector Non-linearity

Below 1 keV the non-linearity of the detector electronics plays an important role. All recent detectors are from the Sapphire type. This detector is equipped with very good electronics, however a small peak shift can occur and the extreme low end region of the energy scale.

Under the EDAM parameter control page – detector options, the detector parameters can be made visible (see figure below).

Detectors built before June 1996 are **non** Sapphire types.

Detector Type : When changed to **non-Sapphire** an EDAX Error message will be prompted :

The detector type does not match the current energy table. Be sure to RESET the energy table in EPIC Table before Quantifying.

The reset is done under the **Identify** control page by pressing the **EPIC** button. A DXEnrg - SET 2 will open. Press **Reset** and close the program.

When restoring an old spectrum under these conditions (sapphire settings) the same EDAX Error message will be prompted. For correct quantification Reset the EPIC table again under normal (non-sapphire) conditions (See figure under TASK 5).
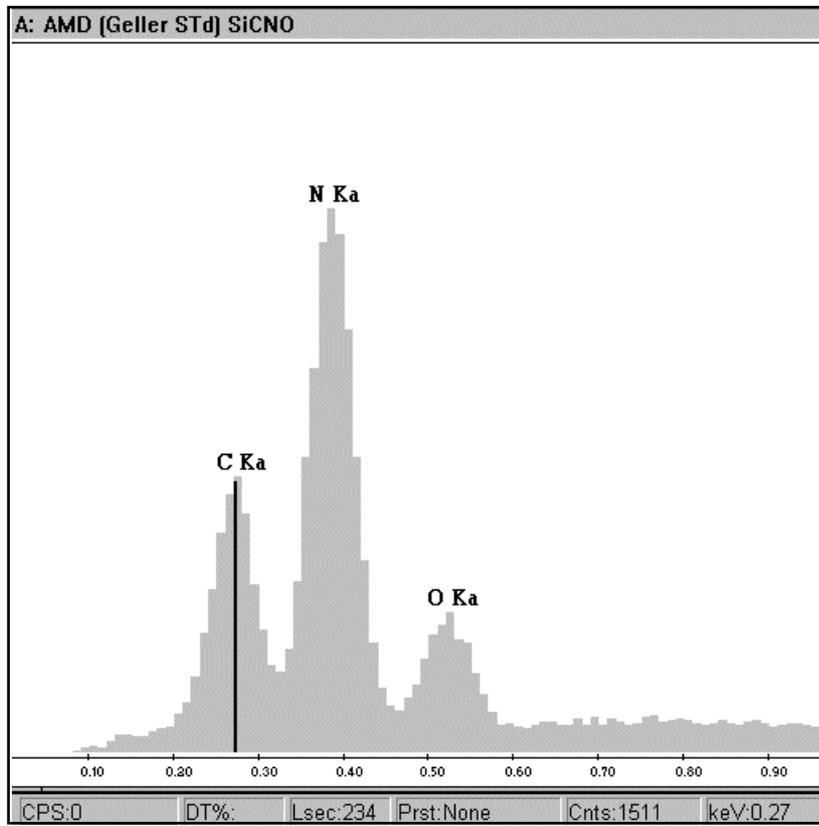
Remark : in both cases the used DXEnrg SET is number 2. In the background it will select an other file (EDAX Peak Set 3 for Sapphire and EDAX Peak Set 2 for LEAP detectors).

Non-linearity

At energy values smaller than about 1 keV the spectrum is not linear i.e. peaks appear at incorrect energies, due to electronic effects. This non-linearity only affects ultra thin window or windowless detectors, since for Be window systems the Be cuts off the non-linear region. The non-linearity is countered by adjusting the peak energies in the table (EPIC table) used by the software.

Element	Theor. position	Table position
B K	0.183	0.172
C K	0.277	0.266
N K	0.392	0.381

Energy set for the Sapphire series

Example of a light element spectrum generated with a sapphire detector.
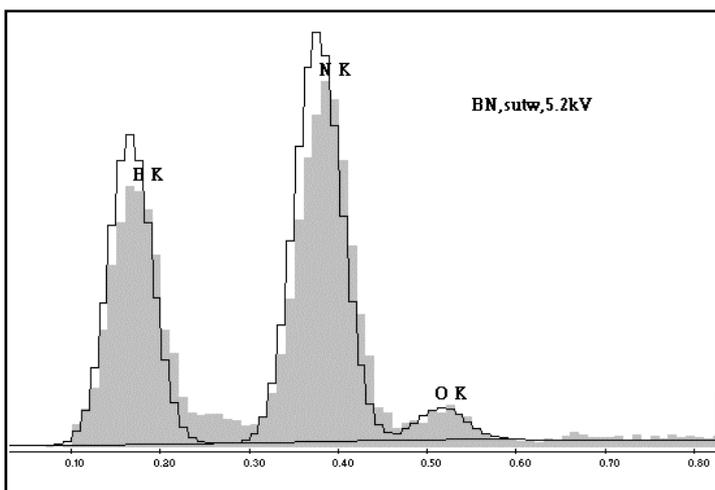
Light element detection

For the detection of light elements a few special preparations need to be done. Below the energy of 1 keV, the detector is no longer linear. Therefore the theoretical position for the ultra light elements like B, C and N, can be shifted. This shift needs to be corrected for each ultra light element. However for modern detectors (sapphire series) the non-linearity is very small, therefore in many cases it is not needed to update your EPIC table. This adjustment is needed for accurate quant results.
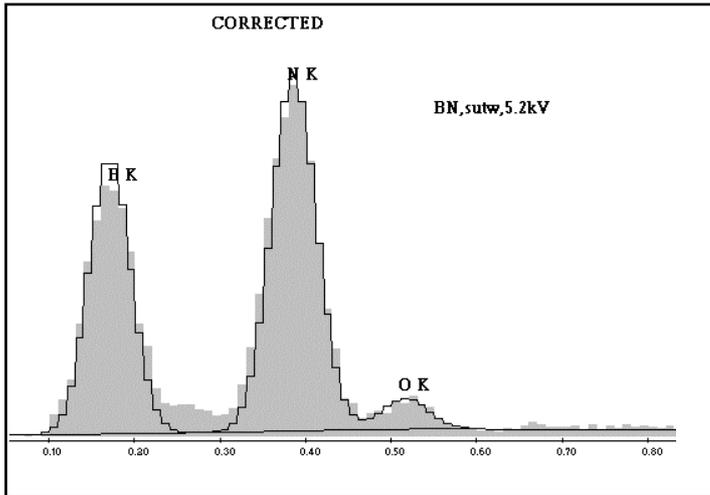
Instruction

• Acquire a spectrum from BN at 5-10kV (or use spectrum **TASK16.spc**).
• Perform a deconvolution to judge the peak fit. If no perfect peak fit is shown, calculate the centroid of the peak.
• Open the **EPIC** table (Peak ID control panel) and change the stored peak position for the current one. Identification and quantification of these elements is now correct (see also figures).
• Note down your results and make a print of the spectra.

Remark : this is slightly different for every other EDS detector

Results

Light element detection without correcting for non-linearity. Note the bad fitting of the deconvolution.

CORRECTED

N K

BN,sutw,5.2kV

B K

O K

0.10   0.20   0.30   0.40   0.50   0.60   0.70   0.80

Deconvolution after corrections are made. Note: to make the new correction active, click inside the spectrum and/or identify the peak again.

EPIC table

Open the Energy Table by selecting the button **Energy Table**

The boron K line is changed into the correct one to perform a better deconvolution.

Results of the EDAX tasks:

Task 1:

Element	Carbon		Copper		Lead	
kV	Depth	Width	Depth	Width	Depth	Width
5	0.46	0.44	0.14	0.16	0.15	0.20
15	3.2	3.1	0.85	0.95	0.86	0.90
30	12	15	2.9	3.2	2.6	2.9

All values in µm

Advanced task 1:   about 12 kV
Advanced task 2:   10 kV (especially width is important)

Task 2:   Resolution should be around 132 eV for 51.2 µs amp time
                (for 10mm2 SiLi detector)

Task 4:   Element missed by only using PeakID is Mn (Kα line).

Task 5:   Ag, Rh, Pd (+ B, C)

Task 5a: Hg, S (Cinnabar)
Task 5b: Pb, S (Galena)
Task 5c: Galena at 30 kV, showing confirmation for Pb (Pb L-lines
                present!)

Task 6:   Sum peak of Al at 2.98 keV.

Task 6a: Sum peak around 2.3 keV (0.525 keV (O Kα) + 1.739 (Si
                Kα). Might be mis-identified as S Kα!

Task 7:   Escape peak of Mn Kα at 4.15 keV (5.893-1.74 keV).

Task 7-3:   Escape peak of TiKa at 2.77 keV and sum peak at 9.020 keV

Task 8-1:   C, O, Fe, Al, Si, Mn (FeL might be mis-identified as FKa)

Task 8-2:   C, O, Fe, Si, S, Cr, Mn, Ni, escape peak of Fe

Task 8-3:   C, O, Co, Fe, S, As, Ni

Task 8-4:   C, O, Si, Pb, Na, Al, K, sum peak of Si + O

Task 8-5:   C, O, Ce, P, Si, Cd (?), Ag, Pr, Co, La, Nd, S (?)

Task 8-6:   C, O, Fe, Ni, Cr, Co, Mn, Mo, Si, W

Task 8-a1:   C, O, Cr, Co, Ni, Al (?), Si (?), W, Ti, Mo, escape peak Cr

Task 8-a2:   C, Ti, O, Cr, Ni, Al, Ta, W, Nb, Mo, Co

Task 8-a3:   C, O, Na, Mg, Al, Si, P, Pb, Cl, K, Ca, Ba, Ti, V, Cr, Mn, Fe,
              Co, Ni, Cu, Zn, Ge, As, Bi, Rb, Sr, Zr

Task 9:   C, O, Fe, Al, Si, Mn

Task 9a-1:   O, Na, Al, Pb, Si, K

Task 10:   Quant results steel at 15kV (in wt%):
              Si=0.85/Mo=2.59/Cr=18.62/Mn=1.70/Fe=63.74/Ni=11.81/
              Cu=0.69

              Quant results at 25kV (in wt%):
              Si=0.76/Mo=2.58/Cr=18.68/Mn=1.79/Fe=63.64/Ni=11.59/
              Cu=0.40

Task 11:   46.74 wt % O and 53.26 wt % Si

Task 12:   4.63% Na2O, 28.99 wt% Al2O3, 54.06 wt% SiO2, 0.42 wt%
              K2O, 11.34 wt% CaO and 0.57 wt% FeO.

Task 13:   SEC factor for Carbon=1.77

Task 13a: Quant results Albite (in wt%):

              No SEC factor used: O=41.6/Na=9.4/Al=12.3/Si=36.7

              SEC factor used: O=47.8/Na=8.5/Al=11.1/Si=32.6

              Composition given: O=48.8/Na=8.6/Al=10.3/Si=32.0

              SEC factor used for Oxygen=0.74

Task 14:   See file: task14-quant-outcome.xls

Task 15:   Standardless Quant gives Al=3.24 wt%, Cr=36.95 wt% and Ni=59.80 wt%.

Pure intensities: Al=1246.4, Cr=287.5 and Ni=125.7

Quant with standards (non normalized) gives Al=3.02 wt%, Cr=37.81 wt% and Ni=58.04 wt% (total of 98.85 wt%).

Composition should be: Al=3 wt%, Cr=38.5 wt% and Ni=58.5 wt%.