Become a Microprobe Power User
Part 2: Qualitative & Quantitative Analysis

Mike Spilde
Spring IOM Seminar
February 5, 2008
Qualitative Analysis

• Why use qualitative scans?
  – Elemental ID (especially trace element ID)
  – Locating Background Positions
  – Identifying peak overlaps

• Setup a Qualitative Scan
ID of Trace Elements: Qualitative Jarosite Scan

Neither the As nor the P will be detected using the EDS
Question: Is sulfur present?

Parasitic overlap between Pb Mα & S Kα is resolved in WDS Qualitative Scan.
Determination of Background Positions

Question: Will the 2nd order Fe lines interfere with the background positions for K?

Hint: right-click here to “tear off” Spectral Display menu

Select “Zooming” to zoom in around K & Fe peaks in Channel 2. Then select “Quant. Background”
Upper K background at the default 5 mm offset is too close to 2nd order FeKα. Click on right background line and drag to the right. Then “Exec” to write to file.
Low background at 5 mm on diopside standard produces 600 cts (10 sec count) background differential. Background measured on enstatite sample yields 200 cts less. Sample has higher counts relative to standard. Result? High totals on sample.
Stored Qualitative Scans

Qual_Database: everyone has a copy

WDS_Scans: Change Working Directory to /export/home/spilde
Change Working Directory to get to WDS_Scans

Select **File** and click on “Change Working Directory”

Select `/export/home/spilde` (be sure Qualitative Analysis is closed before switching)

Be sure to return to your working directory when finished
How to Setup a Qualitative Scan

Set # of spectra, Channel #, and Crystal

Set for range (e.g. length of spectrometer) or click on **Elem** to set specific elements.
QUANTATIVE ANALYSIS

The reason most of us use the probe

DON'T MOVE OR I'LL FILL YOU FULL OF 98% LEAD, 1% ANTIMONY, 0.75% SILVER, 200 PPM NICKEL, WITH TRACE AMOUNTS OF COBALT, AND OTHER COMPONENTS BELOW THEIR RESPECTIVE DETECTION LIMITS!!

WAIT A MINUTE! ARE THOSE VALUES CERTIFIED??

ANALYTICAL CHEMISTS IN THE WILD WEST
Quantitative Analysis

• **Setup**
  – Setup Quantitative Analysis file first
  – Then setup Standard Analysis file, if necessary

• **Calibrate**
  – Verify that peak position is appropriate
  – Verify that background counts are reasonable
  – Verify that Std Variance is low

• **Check analysis file**
  – Check the places where you can get tripped up
Quantitative Analysis Setup

Work sequentially through the Measurement setup menu

- Select Correction Method
- Enter Element Conditions
- Enter EOS Conditions
- After calibration, set Standard Conditions
- If necessary, set Additional Functions
- **Save with Conditions Store**
- Then set Stage Conditions
Quantitative Analysis Setup
Correction Method

Set Material type according to what you are analyzing:

- Select **Oxide** for most silicate analysis conditions
- Select **Metal** for oxygen analysis, metals, sulfides, etc.
- Use **ZAF** for most conditions
- **PRZ** tends to give better results for light element analysis
Quantitative Analysis Setup

Element Selection

Click buttons to select

To delete, click or drag across elements to select, then Clear
Quantitative Analysis Setup

Element Setup

Element Conditions

“Global” conditions file

“Global” file is available to Quant and Standard Analysis, Map, Line, etc.
You can have multiple setups on the same spectrometer for different conditions

Conditions specific to this file
Quantitative Analysis Setup

Element Setup

After element entry, click on the Peak overlap button.

Always check the “Peak Overlap” window. Red highlighted entries are critical.
Quantitative Analysis Setup

“Differential” vs. “Integral” mode

<table>
<thead>
<tr>
<th>Order</th>
<th>Diff</th>
<th>Element</th>
<th>Peak overlap</th>
<th>Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si Ka</td>
<td>back</td>
<td>83.103</td>
<td>Mn Kβ1,3</td>
<td>(4)</td>
</tr>
<tr>
<td>Al Ka</td>
<td>peak</td>
<td>90.842</td>
<td>Cr Kα1,3</td>
<td>(4)</td>
</tr>
<tr>
<td>P Ka</td>
<td>back</td>
<td>192.384</td>
<td>Ni Kα1,3</td>
<td>(4)</td>
</tr>
<tr>
<td>Mg Ka</td>
<td>back</td>
<td>111.849</td>
<td>K Kβ5</td>
<td>(3)</td>
</tr>
<tr>
<td>P Ka</td>
<td>peak</td>
<td>197.384</td>
<td>Ca Kα5</td>
<td>(2)</td>
</tr>
<tr>
<td>P Ka</td>
<td>back</td>
<td>202.884</td>
<td>Mn Kα2</td>
<td>(3)</td>
</tr>
<tr>
<td>Si Ka</td>
<td>back</td>
<td>83.103</td>
<td>Mn Kβ5</td>
<td>(4)</td>
</tr>
<tr>
<td>Si Ka</td>
<td>back</td>
<td>71.603</td>
<td>Ni Kα1</td>
<td>(4)</td>
</tr>
<tr>
<td>P Ka</td>
<td>peak</td>
<td>197.384</td>
<td>Ca Kβ1,3</td>
<td>(2)</td>
</tr>
<tr>
<td>Si Ka</td>
<td>back</td>
<td>71.603</td>
<td>Ni Kα1,2</td>
<td>(4)</td>
</tr>
<tr>
<td>Al Ka</td>
<td>peak</td>
<td>90.842</td>
<td>Mn Kα1</td>
<td>(4)</td>
</tr>
<tr>
<td>Al Ka</td>
<td>peak</td>
<td>90.842</td>
<td>Cr Kβ5</td>
<td>(4)</td>
</tr>
</tbody>
</table>

Higher order Ca peaks interfere with P peak.

Diff mode w/ 4 volt window.

Int mode

Diff mode filters out interference.
Quantitative Analysis Setup

Calculated elements setup

Hydrated mineral setup
Ex: jarosite $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$

Carbonate mineral setup

CO₂ is calculated by atomic ratio to the 3 anions of oxygen.
Quantitative Analysis Setup

EOS (Electron Optics) setup

For constant beam current, click check box and then enter value in Auto window

Expand beam for unstable minerals

Make sure beam scan is off!!!

Beam stabilizer is set here if desired (CL or CL & Tilt)
Quantitative Analysis Setup
Additional Function setup

For overnight runs involving 100’s of analyses, run peak search every 100 or so analyses.

For fairly constant compositions, background measurements are not needed at every point.

Set overlap correction for V-Ti, Cr-Mn, Mo-S, etc.

Software measures the contribution to Mo from S and corrects for the overlap.
Quantitative Analysis Setup

Stage Conditions

- Focus on point and hit **Read & Apply** to record point
- Use down arrow to move to new point
- Small star indicates current position
- Use **Move** button to move to recorded position
- Larger red X indicates where saved point is set (where stage will move to)
Quantitative Analysis Setup

Stage Conditions: Line Traverse

Select **Line Set** to set line traverse

Move to starting point and select **Read**

Move to ending point and select **Read**

Set points in between start and stop by number of points or distance between points
Quantitative Analysis

• **Setup**
  – Setup Quantitative Analysis file first
  – **Then setup Standard Analysis file, if necessary**

• **Calibrate**
  – Verify that peak position is appropriate
  – Verify that background counts are reasonable
  – Verify that Std Variance is low

• **Check analysis file**
  – Check the places where you can get tripped up
Make **absolutely sure** that you are entering the right values:

If Standard Type is set for oxide, enter oxide values in composition window. If Type is set for metal, enter elemental values in composition window, including oxygen.
Make sure that your calibration setup is correct:
- Calibrate each element on the same spectrometer and crystal as the analysis file.
- The PHA conditions must be the same for calibration and analysis.

Other conditions may vary between standard and analysis setup files:
- Counting times can be different.
- Background positions can be different.
Quantitative Analysis

• Setup
  – Setup Quantitative Analysis file first
  – Then setup Standard Analysis file, if necessary

• Calibrate
  – Verify that peak position is appropriate
  – Verify that background counts are reasonable
  – Verify that Std Variance is low

• Check analysis file
  – Check the places where you can get tripped up
Use Peak Search Monitor (Analysis menu) to inspect peak positions during calibration
  • Open the Peak Search Monitor ONLY before you start calibration
  • If the resulting peak is not on the peak centroid, redo the search
Look at your calibration (possibly save for later reference)

- Check accumulated values. Are there significant deviations?
- Check Standard Variance (S.V.). Ideally 0.5% or less.
- Check backgrounds. If one is significantly higher (2X), double check your background positions for interfering peaks, such as Kβ.
- Compare with previous calibration. Did peak position or count rate change?

### Standard Intensity of WDS

<table>
<thead>
<tr>
<th>Curr.(A)</th>
<th>2.031E-08</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Elem.</strong></td>
<td>Cryst. CH</td>
</tr>
<tr>
<td>Ni</td>
<td>LIFH</td>
</tr>
<tr>
<td>Previous</td>
<td>114.803</td>
</tr>
</tbody>
</table>

All Measurement over
Standard Analysis
After Calibration

If S.V. is too high, select **Check Data** to remove bad data

- **Click Acm button**
- Then click on standard accumulations
- Unselect values that deviate significantly from the average, then **Save**
Quantitative Analysis

• Setup
  – Setup Quantitative Analysis file first
  – Then setup Standard Analysis file, if necessary

• Calibrate
  – Verify that peak position is appropriate
  – Verify that background counts are reasonable
  – Verify that Std Variance is low

• **Check analysis file**
  – **Watch the places where you can get tripped up**
After Calibration

Places where you are going to get tripped up

Open **Standard Condition** window and make sure that the correct standards are selected. If not, open the Standard Data for that element and select the right standard.

If the standard that you just calibrated does not appear in the list, make sure **STD Group “All”** is selected. If you still cannot see the standard that you calibrated, you have probably calibrated the element on the wrong spectrometer or at the wrong conditions (20 kV when you meant to use 15 kV).
After Calibration

Places where you are going to get tripped up

If peak has not updated, open global element window for that element and click **OK**

Open **Element Conditions** window and verify that all Peak Positions have been updated.

Old peak position

New peak position