Welcome
The contenders are:

John Anzelmo
President
Claisse USA
Madison, WI, USA

FUSED BEADS

Alexander Seyfarth
Product Manager
Bruker AXS Inc.
Madison, WI, USA

PRESSED PELLETS
Introduction
XRF is a really great technique

- XRF is the only technique for elemental analysis that allows the direct measurement of a sample without vaporization and prior digestion.
- XRF is generally non-destructive for the sample
  - Handheld or mobile systems offer direct approach
Direct XRF analysis without any contact!

Bruker ARTAX at the MET (NY)
Can we always measure directly?

Direct measurement of the sample is possible, but:

- Size limits applicability
- Physical effects and homogeneity limit application
- Sample needs to be representative

Courtesy M. Loubser PPC
University Western Ontario XRF School

Granite countertop
How do we get a sample?

1. **Sampling**
   - 10^x kg

2. **Pulverizing**
   - 10 - 1000 g

3. **Pelletizing or Fusing**
   - 1 - 10 g

Specimen (analyzed material)
From sample to specimen
Requirements for a prepared XRF Sample

- Representative of the material to be analyzed
- Homogeneous
- Consist of particles small enough so that several particle layers will be measured
- Smooth flat surface without irregularities
- Fit the sample holder being used
  - Completely cover the opening in the sample holder
- Thick enough to be infinitely thick for the X-rays to be measured
The advantage of XRF analysis: easy, fast sample preparation
Please use your mouse to answer the question to the right of your screen:

What sample preparation techniques do you use?

- Pressed Pellets
- Fused Beads
- Metal (polished/surfaced)
- Liquid sample prep
- Loose Powders
- Other
While we wait for the results...

Hands-on seminars for sample preparation:

- ½-day seminar during Denver X-ray Conference (July 27th 2009), Denver, CO, USA
- 3-day seminar during ICDD Sample Prep Workshop (Oct 13th 2009) at Newton Square, PA, USA
- 1-day seminar during 5-day XRF Summer School (May 30th – June 4th 2010) University Western Ontario, London, ON, Canada
Definition of Terms
Accuracy and Precision

**Precision:**
closeness or agreement among replicate results

**Accuracy:**
the nearness of a result to the “true result”
Definition of Terms
Accuracy and Precision

- High Accuracy, High Precision
- High Accuracy, Low Precision
- Low Accuracy, High Precision
- Low Accuracy, Low Precision

Tissue, 1996
In XRF quantification is based on:

\[ C_i = K_i \cdot I_i \cdot M_i \cdot S \]

where
- \( C_i \) = weight fraction of element ‘i’, i.e. \( C_i = C\% / 100 \)
- \( K_i \) = the calibration constant for element ‘i’ (%/kcps)
- \( I_i \) = net peak intensity for analyte element ‘i’ (kcps)
- \( M_i \) = matrix correction term for element ‘i’
- \( S \) = specimen preparation term, equal to \( S_s / S_{Std} \)

\[
\left[ \sum_n (\mu_n C_n) \right] \text{ or } \left[ 1 + \sum_j (\alpha_{ij} C_j) \right]
\]
Definition of Terms

Analyzed layer on the sample surface

- No excitation within upper part of the sample (white)
- Center part of the sample will be excited, but the emitted radiation will be absorbed within the sample (light pink)
- Measured radiation comes from a layer near the sample surface (dark pink)
## Analyzed layer in different matrices

<table>
<thead>
<tr>
<th>Line</th>
<th>Energy</th>
<th>Graphite</th>
<th>Glass</th>
<th>Iron</th>
<th>Lead</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd KA1</td>
<td>23.17 keV</td>
<td>14.46 cm</td>
<td>8.20 mm</td>
<td>0.70 mm</td>
<td>77.30 μm</td>
</tr>
<tr>
<td>Mo KA1</td>
<td>17.48</td>
<td>6.06</td>
<td>3.60</td>
<td>0.31</td>
<td>36.70</td>
</tr>
<tr>
<td>Cu KA1</td>
<td>8.05</td>
<td>5.51 mm</td>
<td>0.38</td>
<td>36.40 μm</td>
<td>20.00</td>
</tr>
<tr>
<td>Ni KA1</td>
<td>7.48</td>
<td>4.39</td>
<td>0.31</td>
<td>29.80</td>
<td>16.60</td>
</tr>
<tr>
<td>Fe KA1</td>
<td>6.40</td>
<td>2.72</td>
<td>0.20</td>
<td>* 164.00</td>
<td>11.10</td>
</tr>
<tr>
<td>Cr KA1</td>
<td>5.41</td>
<td>1.62</td>
<td>0.12</td>
<td>104.00</td>
<td>7.23</td>
</tr>
<tr>
<td>S KA1</td>
<td>2.31</td>
<td>116.00 μm</td>
<td>14.80 μm</td>
<td>10.10</td>
<td>4.83</td>
</tr>
<tr>
<td>Mg KA1</td>
<td>1.25</td>
<td>20.00</td>
<td>7.08</td>
<td>1.92</td>
<td>1.13</td>
</tr>
<tr>
<td>F KA1</td>
<td>0.68</td>
<td>3.70</td>
<td>1.71</td>
<td>0.36</td>
<td>0.26</td>
</tr>
<tr>
<td>N KA1</td>
<td>0.39</td>
<td>0.83</td>
<td>1.11</td>
<td>0.08</td>
<td>0.07</td>
</tr>
<tr>
<td>C KA1</td>
<td>0.28</td>
<td>* 13.60</td>
<td>0.42</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>B KA1</td>
<td>0.18</td>
<td>4.19</td>
<td>0.13</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

- Analyzed layer controlled by:
  - Energy of line being measured
  - Average atomic number of sample (density)

0.01 μm = 10 nm = 100 Å
What do we need to do?

- Sample preparation needs to be **FIT** for purpose.
- We need to provide the requested information
  - as fast
  - as precisely
  - as economically (cost)
  - as easily
  - as repeatably (by different operators)
  - as accurately

as needed.
Grinding
All samples need to be ground...

- Grind the sample to desired/required fineness!

Courtesy RETSCH USA
Grinding
From sample to specimen
Pressed Pellet

- How does it work?
- What do we need to consider?
- Pitfalls?
- Universal?
- Automatic?
- Useful?
Principles
Pressed Pellet Preparation 1
Principles
Pressed Pellet Preparation 2
Pressed Pellet Preparation 3
Issues to consider

- Standards (reference) available from same matrix?
- Desired accuracy?
- Desired precision?
- Cost/sample
- Speed → How fast do you need the result?
- Trace element analysis

Accuracy and precision are limited by sample prep and reference samples
Can we use pressed pellets?

How long do we need to grind?

Do we need an additive to help with the grinding?

Do we need an additive to keep the pellet together?

What pressure do we need to form the pellet?

Can we prepare the standards the same way as the unknowns?

Can we get the precision needed for production?
Sample should be ground to **uniform particle size**

**Ideally** the particle size should be much smaller than the analyzed layer depth
### Analyzed layer / homogeneity

<table>
<thead>
<tr>
<th>Compound</th>
<th>Line</th>
<th>Concentration [%]</th>
<th>Energy [keV]</th>
<th>Layer Thickness [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₂O₃</td>
<td>Fe   KA1</td>
<td>0.722</td>
<td>6.40</td>
<td>174</td>
</tr>
<tr>
<td>MnO</td>
<td>Mn   KA1</td>
<td>0.016</td>
<td>5.89</td>
<td>139</td>
</tr>
<tr>
<td>TiO₂</td>
<td>Ti   KA1</td>
<td>0.016</td>
<td>4.51</td>
<td>66</td>
</tr>
<tr>
<td>CaO</td>
<td>Ca   KA1</td>
<td>30.12</td>
<td>3.69</td>
<td>104</td>
</tr>
<tr>
<td>K₂O</td>
<td>K    KA1</td>
<td>0.103</td>
<td>3.31</td>
<td>77</td>
</tr>
<tr>
<td>SO₃</td>
<td>S    KA1</td>
<td>0.000</td>
<td>2.31</td>
<td>27</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>P    KA1</td>
<td>0.004</td>
<td>2.01</td>
<td>19</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Si   KA1</td>
<td>1.130</td>
<td>1.74</td>
<td>13</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Al   KA1</td>
<td>0.277</td>
<td>1.49</td>
<td>8</td>
</tr>
<tr>
<td>MgO</td>
<td>Mg   KA1</td>
<td>21.03</td>
<td>1.25</td>
<td>7</td>
</tr>
<tr>
<td>Na₂O</td>
<td>Na   KA1</td>
<td>0.029</td>
<td>1.04</td>
<td>4</td>
</tr>
<tr>
<td>CO₂</td>
<td></td>
<td>46.37</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Thickness of the sample from which 90% of the measured intensity is derived

NBS 88b Dolomite

We need to grind long enough to get enough particles!
Pressed pellet preparation

- Optimize grinding time to ensure that sample fineness is reached
  - Sieve, granulometric determination or “flour feel”
- Parameters to adjust to match reference to samples and analyzed layer!
  - Measure I of characteristic emission line for the element and plot vs. grinding time to assess fineness of material
  - Vary parameters of grinder (impact, time)

Ununknowns need to match standards
John sees some issues here...

- **Issues with grinding** (selection of additive, heat, time)
  - Caking

- **Issues with pressing** (pressure, binder, fineness)
  - Disking
  - Cracking
  - Dusting
  - “Reactions”
Universal pellet preparation method

Advantages

- No caking in vessel
  - Vessel can be cleaned by brush and compressed air
  - Keeps sample homogeneous
  - Minimizes cross contamination (except from vessel)

- Slurry grind
  - Reduces sample size more effectively since larger area of ring and puck is used and avoids caking
  - Keeps sample homogeneous
  - Reduces heat → caking

- Dilutes samples 10% with micro cellulose
  - The finer the particle size, the greater the effect of the diluent

- Stable pellet... No cracking... No dust (when used with Al cup or ring)
Universal pellet preparation method

Recipe

- 5.0X grams sample (100cc vessel) max 20g
- 0.5X grams Cellulose (1 micron Whatman) max 2g
- 5 ml DuPont Vertrel XF™
- 90 sec grind in ring and puck mill (WC 100cc vessel)
  - Depends on matrix and can be 45 to 120 sec (max!)
- 15 sec press at 40,000 lbs (20t) in 40mm die mold (integrated)
- Cellulose backing if needed (based on volume of sample and desired prep (e.g. pressed into cup or “sandwich”))
Caking is Bad...
Boric Acid - 90 sec - after brushing
Cellulose/Vertrel XF – 90 sec – after brushing
Cellulose/Vertrel XF after grinding
Pressed and cleaned
PUNCH!

- UNIVERSAL!
- EASY!
- FAST!
- LOW COST/SAMPLE!
## XRF Analysis (Cement)

**Precision versus Accuracy**

<table>
<thead>
<tr>
<th>compound</th>
<th>CaO (%)</th>
<th>SiO₂ (%)</th>
<th>Fe₂O₃ (%)</th>
<th>MgO (%)</th>
<th>Na₂O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>typical <strong>concentration</strong> (%)</td>
<td>45</td>
<td>20</td>
<td>2</td>
<td>1</td>
<td>0.2</td>
</tr>
<tr>
<td>typical <strong>intensity</strong> (kCounts in 40 s)</td>
<td>6000</td>
<td>4000</td>
<td>2000</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>counting <strong>statistics</strong> (% abs.)</td>
<td>0.018</td>
<td>0.01</td>
<td>0.0015</td>
<td>0.006</td>
<td>0.003</td>
</tr>
<tr>
<td>counting statistics &amp; instrument <strong>precision</strong> (% abs.)</td>
<td>0.03</td>
<td>0.02</td>
<td>0.004</td>
<td>0.01</td>
<td>0.005</td>
</tr>
<tr>
<td>multiple sample <strong>preparation</strong> (% abs.)</td>
<td>0.2</td>
<td>0.1</td>
<td>0.02</td>
<td>0.05</td>
<td>0.02</td>
</tr>
<tr>
<td>typical <strong>accuracy</strong> (% abs.)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.05</td>
<td>0.05</td>
<td>0.03</td>
</tr>
</tbody>
</table>

*prepared as pressed powders*
XRF Analysis (Slag)
Precision: 10 samples from “same”

<table>
<thead>
<tr>
<th></th>
<th>SiO₂ (%)</th>
<th>Al₂O₃ (%)</th>
<th>Cr₂O₃ (%)</th>
<th>CaO (%)</th>
<th>MgO (%)</th>
<th>MnO (%)</th>
<th>TiO₂ (%)</th>
<th>P₂O₅ (%)</th>
<th>S (%)</th>
<th>FeO (%)</th>
<th>B₃ Ratio (%)</th>
<th>V-Ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average</td>
<td>9.78</td>
<td>6.76</td>
<td>1.04</td>
<td>31.01</td>
<td>6.76</td>
<td>4.94</td>
<td>0.5</td>
<td>0.47</td>
<td>0.12</td>
<td>34.18</td>
<td>1.8</td>
<td>3.2</td>
</tr>
<tr>
<td>Std.Dev.</td>
<td>0.05</td>
<td>0.04</td>
<td>0.00</td>
<td>0.08</td>
<td>0.11</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.09</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

S2 RANGER SLAGANALYZER (EAF SLAG) 15 minutes from sampling to result!
PUNCH!

- Best counting statistics due to high signal!
  - FAST measurement
  - IDEAL for process control

- Good precision!
  - IDEAL for process control
Tricky Samples
Salt

<table>
<thead>
<tr>
<th>Analyte</th>
<th>Range of Conc. [%]</th>
<th>Accuracy [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>0.46 - 4.1</td>
<td>0.05</td>
</tr>
<tr>
<td>Mg</td>
<td>1.5 - 3.6</td>
<td>0.04</td>
</tr>
<tr>
<td>P</td>
<td>3.7 - 6.6</td>
<td>0.05</td>
</tr>
<tr>
<td>S</td>
<td>1.8 - 10</td>
<td>0.07</td>
</tr>
<tr>
<td>K</td>
<td>10 - 23</td>
<td>0.2</td>
</tr>
<tr>
<td>Ca</td>
<td>10 - 17</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Bruker Lab Report  XRF-40
Mineral Salts by WDXRF (1kW) 2000
# Tricky Samples

## Car Catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Date</th>
<th>Rh (PPM)</th>
<th>Pd (PPM)</th>
<th>Pt (PPM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NM24D</td>
<td>7/16/2002 17:04</td>
<td>232</td>
<td>1048</td>
<td>380</td>
</tr>
<tr>
<td>NM24C</td>
<td>7/16/2002 16:31</td>
<td>222</td>
<td>1004</td>
<td>356</td>
</tr>
<tr>
<td>NM24B</td>
<td>7/16/2002 15:58</td>
<td>225</td>
<td>1043</td>
<td>372</td>
</tr>
<tr>
<td>NM24</td>
<td>7/16/2002 15:25</td>
<td>233</td>
<td>1029</td>
<td>371</td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>228</strong></td>
<td><strong>1031</strong></td>
<td><strong>369.75</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Stdev</strong></td>
<td></td>
<td></td>
<td><strong>5.4</strong></td>
<td><strong>19.7</strong></td>
</tr>
<tr>
<td><strong>rel Stdev</strong></td>
<td></td>
<td></td>
<td><strong>2.35</strong></td>
<td><strong>1.91</strong></td>
</tr>
</tbody>
</table>

**Pd KA1-HR-Min**
Tricky Samples
PetCoke – EDXRF: 210 sec!

<table>
<thead>
<tr>
<th>Element</th>
<th>Range</th>
<th>RSD</th>
<th>LLD(100s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>1.5-6.8 %</td>
<td>0.036</td>
<td>18 ppm</td>
</tr>
<tr>
<td>Ni</td>
<td>100-390 ppm</td>
<td>9 ppm</td>
<td>0.5 ppm</td>
</tr>
<tr>
<td>V</td>
<td>80-2000 ppm</td>
<td>26 ppm</td>
<td>0.5 ppm</td>
</tr>
</tbody>
</table>

Application precision (preparation n=10)
S +/- 0.07 %
V +/- 35 ppm
Ni +/- 5 ppm
Tricky Samples
Low F in Cement

LLD: 40 ppm/100s
LOQ: 120 ppm
(S4 PIONEER) 2006
PUNCH!

- Low dilution... best for traces!
- No loss of volatile elements
- Works on coals, catalysts, salts...
- Precious metals or crucible toxins can be prepared
Automate Your Preparation
Integrated Mill and Press

Material in

Tablet out
Automation: Unattended Analysis
Drop and Go!

Courtesy KRUPP POLYSIUS
PUNCH!

- Easy, compact automation!

- Completely unattended operation
  - Belt driven

- Rugged and proven
Pressed pellets work great!

When to use the pressed pellet preparation?

- Reference material is available with same matrix and mineralogy
  - Secondary reference materials from same location (quarry)
  - “Acceptable” bias from non-mineralogical references
- Reference (standards) and sample can be ground fine enough to be “homogeneous” for the analyzed layer
- Fineness of standards can be matched to unknowns
- Speed is of importance (>5 minutes)
- Low cost/sample
- Ease of use / ease of training (operator skill)
- Potential automation capabilities (unattended preparation)
- Tricky samples
- Trace elements are of interest
The Other Way?

- What if there are no matrix-matched standards available or none at all?
- What if there are no mineralogical matched samples?
- Bad sample homogeneity in pellets
- Higher accuracy needed
- Larger “calibration ranges” needed for materials and flexibility
- Traceable analysis to International Reference Materials
- “Defendable” analysis

Fusion solves all of these problems!
Benefits of Borate Fusion Method of Sample Preparation for XRF Analysis

Corporation Scientifique Claisse - 2009

www.claisse.com
Definition of Terms
Accuracy and Precision

**Precision:**
closeness or agreement among replicate results

**Accuracy:**
the nearness of a result to the “true result”
Accuracy vs. Precision

Fusion

XRF with Pressed Pellet

Fusion

XRF with Fused Bead
Basics of XRF Spectrometry

- XRF is a comparative technique
  - The signal intensity generated by an element of the specimen must be compared with that in a standard of known composition in order to determine the concentration of the element
- The signal of an element is proportional to its concentration in the specimen
- Interference, absorption and enhancement, grain size and mineralogy change the measured signal intensity of the element
Since the highest accuracy in XRF is achieved by comparing unknowns with standards, the standards and unknowns must be as similar as possible in mineralogy, particle size, particle homogeneity and matrix characteristics.
In XRF quantification is based on:

\[ C_i = K_i \cdot I_i \cdot M_i \cdot S \]

where:
- \( C_i \) = weight fraction of element ‘i’, i.e. \( C_i = \) \( C\% / 100 \)
- \( K_i \) = the calibration constant for element ‘i’ (\%/kcps)
- \( I_i \) = net peak intensity for analyte element ‘i’ (kcps)
- \( M_i \) = matrix correction term for element ‘i’
- \( S \) = specimen preparation term, equal to \( S_s / S_{Std} \)
Definitions: Quantification

When does $S = 1$?

When can we eliminate the sample preparation term?
- Standards and samples are MATRIX MATCHED
- Standards and samples are “grain” SIZE MATCHED
  - Analyzed layer same for standards and samples

When standards and samples are prepared the “SAME” way
- ONLY then can the relationship be expressed as

\[ C_i = K_i \cdot I_i \cdot M_i \]

If the specimen is poorly prepared, NO amount of correction can improve the quality of the analytical result.
Basics of XRF Spectrometry

- There is no substitute for good sample preparation
- If the sample specimen is poorly prepared,
  
  NO AMOUNT OF CORRECTION can improve the analytical result
- If $S \neq 1$, your results are not accurate
- Time and resources should be devoted to sample preparation to benefit fully from an XRF spectrometer
Pressed Powder Method of XRF Sample Preparation

**Advantages**
- Speed
- Inexpensive
- Easy to learn/execute
- Highest count rate (precision)
- Lowest limit of detection

**Disadvantages**
- Particle size effects
- Surface roughness
- Homogeneity effects
- Matrix matching problems
- Mineralogical effect (accuracy problems)
Problems with Pressed Pellet and Powder Techniques

- Matrix Problems
- Surface Roughness
- Particle Size Effects
- Low Homogeneity
- Mineralogical Effects

Low Analytical Accuracy
Particle Size Effect
Pressed Powders for XRF

Pressed pellets

A closer look
Grinding of different mineralogical phases and compositions produces particles of different sizes and shapes.

The particular shape and size of a particle influence its reaction to an applied pressure.

The surface flatness is also affected by the particle size and shape distribution.

A pressed pellet is not a homogenous specimen.
Particle Size Effect
Pressed Powders for XRF

- The analyzed layer thickness is affected by the particle size and shape distribution (density)
- The particle’s size, shape and the effect on flatness cannot be predicted and will vary with the type of matrix

- Since the signal only comes from a few atomic layers, it is not always representative of the whole specimen
### Particle Size Effect
**Pressed Powders for XRF**

Comparison of analyses of two aliquots of the same sample milled to different particle sizes

<table>
<thead>
<tr>
<th></th>
<th>&lt; 75 µm</th>
<th>&gt; 75 µm</th>
<th>Fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>36.9</td>
<td>31.8</td>
<td>36.29</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.44</td>
<td>0.31</td>
<td>0.47</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>9.40</td>
<td>10.61</td>
<td>10.33</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.07</td>
<td>0.07</td>
<td>0.08</td>
</tr>
<tr>
<td>MnO</td>
<td>0.29</td>
<td>0.24</td>
<td>0.34</td>
</tr>
<tr>
<td>MgO</td>
<td>12.3</td>
<td>10.5</td>
<td>13.73</td>
</tr>
<tr>
<td>CaO</td>
<td>34.3</td>
<td>41.3</td>
<td>35.28</td>
</tr>
<tr>
<td>Na₂O</td>
<td>n/d</td>
<td>n/d</td>
<td>0.23</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.01</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.002</td>
<td>0.008</td>
<td>0.02</td>
</tr>
<tr>
<td>Cr₂O₃</td>
<td>4.28</td>
<td>2.93</td>
<td>3.83</td>
</tr>
<tr>
<td>V₂O₅</td>
<td>0.05</td>
<td>0.05</td>
<td>0.01</td>
</tr>
<tr>
<td>SO₃</td>
<td>0.07</td>
<td>0.10</td>
<td>0.08</td>
</tr>
</tbody>
</table>

Courtesy M. Loubser PPC
University Western Ontario XRF School
PUNCH!

- Removes particle size effect
- Removes roughness effect
Mineralogical Effect on Fe Intensities Using Pressed Pellets

Typical Fe line intensities for Fe when present in same concentration, in same size particles, but as different minerals in a sample.
Pressed Powder Technique
Mineralogical Effect on Raw Mix

Figure 2. SiO₂ analysis before fusion
Eliminate the Mineralogical Effect
From the Crystal Structure to...
Eliminate the Mineralogical Effect
To a Glassy Matrix
Fusion for XRF
Accuracy of Fusion - Comparison of Pressed Pellets to Fused Beads

SiO₂ in Raw Mix
1) Before Fusion  2) After Fusion  3) After Fusion and Corrections

Figure 2. SiO₂ analysis before fusion
Figure 3. Uncorrected SiO₂ analysis after fusion
Figure 4. Corrected SiO₂ analysis after fusion
PUNCH!

- Removes mineralogical effect for highest accuracy by XRF
- Allows for application of matrix corrections where previously not applicable
- Allows selection of unmatched matrix standards
- Allows creation of synthetic standards
What is Fusion?

Oxide + Flux → 1050 °C → XRF

{ AA, ICP }
Weigh into crucible borate flux

Add sample ground to minus 200 mesh

Add iodide or bromide non-wetting agent

Rotate crucible on incline

Heat at 1000°C while agitating
Fusion Steps

- Casting
- Free cooling
- Forced cooling
- Bead retrieval

XRF

AA & ICP

Acid
Fusion Bead Examples

- Soils
- Clays/Geological
- Catalysts
- Glass
- Ores
## Fusion Precision

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>CaO burners</th>
<th>SiO&lt;sub&gt;2&lt;/sub&gt; burners</th>
<th>SO&lt;sub&gt;3&lt;/sub&gt; burners</th>
<th>K&lt;sub&gt;2&lt;/sub&gt;O burners</th>
<th>Na&lt;sub&gt;2&lt;/sub&gt;O burners</th>
</tr>
</thead>
<tbody>
<tr>
<td>FUSION</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>1</td>
<td>65.14</td>
<td>65.19</td>
<td>64.99</td>
<td>21.37</td>
<td>21.42</td>
</tr>
<tr>
<td>2</td>
<td>65.28</td>
<td>65.32</td>
<td>65.13</td>
<td>21.42</td>
<td>21.53</td>
</tr>
<tr>
<td>3</td>
<td>65.32</td>
<td>65.14</td>
<td>65.16</td>
<td>21.43</td>
<td>21.48</td>
</tr>
<tr>
<td>4</td>
<td>65.14</td>
<td>64.98</td>
<td>64.88</td>
<td>21.51</td>
<td>21.29</td>
</tr>
<tr>
<td>Burner average (%)</td>
<td>65.22</td>
<td>65.16</td>
<td>65.04</td>
<td>21.43</td>
<td>21.43</td>
</tr>
<tr>
<td>Standard deviation</td>
<td><strong>0.14</strong></td>
<td><strong>0.08</strong></td>
<td><strong>0.01</strong></td>
<td><strong>0.003</strong></td>
<td><strong>0.004</strong></td>
</tr>
<tr>
<td>95% confidence interval</td>
<td>0.09</td>
<td>0.05</td>
<td>0.01</td>
<td>0.002</td>
<td>0.003</td>
</tr>
</tbody>
</table>

**Gaussian Distribution**

- CaO: 65.05, 65.14, 65.23, 21.37, 21.42, 21.47, 2.49, 2.50, 2.51, 0.427, 0.429, 0.431, 0.079
- SiO₂: 65.14, 65.16, 65.23, 21.42, 21.47, 2.50, 0.429
- SO₃: 65.05, 65.14, 65.23, 21.37, 21.47, 2.49, 0.427
- K₂O: 65.05, 65.14, 65.23, 21.37, 2.49, 0.427
- Na₂O: 65.05, 65.14, 65.23, 21.37, 2.49, 0.427
Alex sees some issues here...

- What about the volatiles in the sample?
  - For example: S, Cl, F, Br?

- What about ores, such as sulfide ores or sulfide minerals?
Sulfide ores as well...

Sulfides
(Ores & concentrates)

Glass disk
Really!

25 minutes
Fluorides (CaF$_2$, AlF$_3$) → Glass disk

It can be fused too...
Automated Fusion Machine
Claisse “M4” Fluxer
Claisse “rFusion”
Modular Automation

TheAnt Weighing & Flux Dispenser

Robot

TheBee Fluxer

Storage

Mixer
What if there are no matrix matched standards available or none at all –
This is the case most of the time

What if there are no mineralogical matched samples –
You won’t even know when this happens

“Defendable analysis” –
NOW you know the samples and standards weren’t matrix matched!

Bad sample homogeneity in pellets –
Happens often in spite of lengthy grinding

Higher accuracy needed –
This is why you bought and paid so much money for an XRF spectrometer in the first place

Larger “calibration ranges” needed for materials and flexibility –
This happens when your process goes out of control

Traceable analysis to International Reference Materials –
Is the norm in today’s ISO/ROHS/WEEE driven world. see “defendable analysis”
PUNCH – PUNCH – PUNCH! (1)

- Eliminates particle size effects
- Eliminates mineralogical effects
- Eliminates roughness effects
- Provides excellent homogeneity and flatness
- Creates perfectly matrix matched standards and unknowns
- Allows for matrix corrections where previously not possible
- Provides highest accuracy
- Provides defendable analysis (without worry)
PUNCH – PUNCH – PUNCH! (2)

- Provides high precision
- Provides universal calibration capability
- Allows for use of matrix-unmatched standards
- Allows for creation of synthetic standards
- Allows for traceable analysis to International Reference Materials
- Easy to use – unattended operation
- Automation ready
Final Round!

THE FINAL FACE-OFF

FUSED VS PRESS

FUSED

PRESSED
## Comparison – Pressed Powder vs Fused Beads

<table>
<thead>
<tr>
<th></th>
<th>Pressed Powder</th>
<th>Fused Beads</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Desirable size of powder (microns)</strong></td>
<td>5 - 30 (difficult)</td>
<td>100 - 200 (easy)</td>
</tr>
<tr>
<td><strong>Obtaining standards</strong></td>
<td>Difficult</td>
<td>Easy (Synthetic)</td>
</tr>
<tr>
<td><strong>Affected by particle size</strong></td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td><strong>Affected by mineralogy</strong></td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td><strong>Time for one sample (min)</strong></td>
<td>5</td>
<td>15</td>
</tr>
<tr>
<td><strong>Time for three samples (min)</strong></td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td><strong>Accuracy</strong></td>
<td>0.10 – 10% rel</td>
<td>0.10 to 1% rel</td>
</tr>
</tbody>
</table>
You Decide The Winner!

Please use your mouse to answer the question to the right of your screen:

Who is the champion?
- Pressed Pellets
- Fused Beads
- Tie!
And The Winner Is...
Any Questions?

Please type any questions you may have in the Q&A panel and then click Send.
Thank you for attending!

Please take a moment to complete the brief survey on your screen. Your feedback is very important to us.

Copies of this presentation and related resource materials will be emailed to you.
Where to learn more...

- Denver X-ray Conference Workshop - ½ day

- Bruker Training Central (www.brukersupport.com) - XRF Sample Preparation Online Course – two 1-hour sessions

- Seminars
  - ICDD XRF Sample Preparation Seminar - 3 days
  - University of Western Ontario Summer XRF School - Sample Prep day as part of 1-week course on fundamentals on XRF
Visit us at:

Denver X-ray Conference (DXC)
July 27-30, Colorado Springs, CO

Gulf Coast Conference (GCC)
October 13-14, Galveston, TX

Geological Society of America (GSA)
October 18-21, Portland, OR

Material Science & Technology (MS&T)
October 29-31, Pittsburgh, PA

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