Industrial Minerals - EDXRF for Direct Analysis without Digestion
Today’s Topics

- Introduction
- Basic Instrumentation
- From Lab to Field
  - Limestone
  - Feldspars
  - Cement
- From Field to Lab
  - Type Standardization
  - Limestone
  - Paper Additives
- Comparison of Spectroscopic Techniques
- Benefits of EDXRF
- Q&A
Introduction

Industrial Minerals…
What are we talking about?

Geological materials, widely used as raw materials and additives in a large variety of industrial applications and processes:

- Ceramics
- Glass
- Construction
- Paints
- Chemicals
- Plastics
- Paper
- Electronics
Industrial Minerals

Materials

Typical industrial minerals are:
- Limestone
- Sand
- Kaolin
- Bentonite
- Silica
- Barite
- Gypsum
- Talc

Powerful analytical tools are required to allow close control of the mining process and to establish an accurate quality control.
Industrial Minerals
Analysis of Materials

Today the challenge is to include an analytical procedure in the process that is flexible enough to meet changing quality requirements and to ensure shortest time-to-result.

Analysis adds value and can often determine the suitability of a product for specific applications.

Each application defines the final quality criteria regarding elemental and phase composition, impurities, grain size and other chemical and structural properties.

Examples

- Sand for glass industry (Fe content)
- Kaolin for paper industry (Fe content, mineral composition)
- Kyanite for refractories (mineral composition, Al/Si and Fe)
- Clay as filler for polymers (mineral type and composition)
Advantages of XRF for Industrial Minerals

XRF for the process and quality control of industrial minerals provides:

- qualitative and quantitative analysis
- fast and easy sample preparation
- elements from Be to U in all kind of samples
- even light elements, like B, C, N, O and F
- standardless calibration for all materials
- linear concentration range from ppm to 100%
- highest accuracy and reproducibility up to 0.05% (rel.)
- typical detection limits (LLD): ~ 1 to 10 ppm

The main requirements for industrial mineral testing are easily met by XRF:

- shortest time-to-result
- simple and fast sample preparation
- highest analytical flexibility
Please use your mouse to answer the question to the right of your screen:

What are your current minerals analysis applications? (Check all that apply):

- Limestone
- Dolomite
- Feldspar
- Sand
- Clay
- Phosphate
- Bentonite
- Hard Rock Mining
- Ores
- Other
How does X-ray Fluorescence work?

Bromine atom

Ejected electron

X-ray fluorescence $K_{\alpha}$

X-ray fluorescence $K_{\beta}$

X-ray
Overview

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
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 and homogeneous

Courtesy M. Loubser, PPC
University Western Ontario XRF School

Granite countertop
X-ray Fluorescence Analysis
Energy-dispersive XRF - EDXRF

- Type of detector determines the analytical performance

- Detectors are characterized by:
  - the energy resolution
  - the maximum count rate
# EDXRF Detectors

## Silicon Drift Detector (SDD)

<table>
<thead>
<tr>
<th>Detector</th>
<th>Resolution [eV]</th>
<th>Maximum [kcps]</th>
<th>Cooling</th>
<th>Cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Prop. Counter</td>
<td>1000</td>
<td>&lt; 100</td>
<td>none</td>
<td>low</td>
</tr>
<tr>
<td>PIN Diode</td>
<td>~180</td>
<td>&lt; 10</td>
<td>Peltier</td>
<td>medium</td>
</tr>
<tr>
<td>Si(Li)</td>
<td>~150</td>
<td>&lt; 50</td>
<td>LN₂</td>
<td>high</td>
</tr>
<tr>
<td>Si Drift</td>
<td>~145 -129</td>
<td>100</td>
<td>Peltier</td>
<td>high</td>
</tr>
</tbody>
</table>

- Very good resolution
- Highest count rates
- Fulfill requirements for a wide range of applications
- Low maintenance - low cost
- Fast startup
Example from Limestone.....

<table>
<thead>
<tr>
<th>Element</th>
<th>Formula</th>
<th>Atomic Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>Na₂O</td>
<td>1040</td>
</tr>
<tr>
<td>Mg</td>
<td>MgO</td>
<td>1253</td>
</tr>
<tr>
<td>Al</td>
<td>Al₂O₃</td>
<td>1486</td>
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<tr>
<td>Si</td>
<td>SiO₂</td>
<td>1739</td>
</tr>
<tr>
<td>P</td>
<td>P₂O₅</td>
<td>2013</td>
</tr>
<tr>
<td>S</td>
<td></td>
<td>2307</td>
</tr>
<tr>
<td>K</td>
<td>K₂O</td>
<td>3313</td>
</tr>
<tr>
<td>Ca</td>
<td>CaO</td>
<td>3691</td>
</tr>
</tbody>
</table>

Pd is Scatter from Pd tube
We Need Characteristic Signal – Sensitivity!

\[
S = \text{number of detected X-ray photons per concentration and time}
\]

"counts"

\%
ap ppm

s

The sensitivity determines

- the counting statistical error significant for major and minor elements
- the lower limit of detection significant for trace elements
In energy dispersive systems, the detector always sees the whole spectrum.

Older type detectors (SiPin, Si(Li)) could only handle low total count rates!

Typically the maximum count rate of the detector is a bottleneck for an EDXRF systems.

Now we can run above 100,000 cps to 250,000 cps.

The sensitivity is limited by the maximum count rate of the detection system and/or INSTRUMENT power.

Optimization: Primary filters / Primary targets can be used to tune selected energy ranges while attenuating others, thereby making the measurement more “sequential”.
Excitation is the same regardless of handheld or benchtop!

Current of X-ray source defines number of photons interacting with sample. The higher the current, the more signal we are going to detect.

Power is defined by the product of excitation (kV) and current (mA):

e.g. 40 KV X 1.25 mA = 50 Watt (Benchtop)

S2 RANGER at 15kV and 150 µA

100,000 cps total

S1 TRACER at 15 kV and 55 µA

60,000 cps total

DH Limestone

NBS 88 b powder
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)
<table>
<thead>
<tr>
<th>Compound</th>
<th>Line</th>
<th>Concentration [%]</th>
<th>Energy [keV]</th>
<th>Layer Thickness [μm]</th>
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</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>
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<tr>
<td>SiO2</td>
<td>Si KA1</td>
<td>1.130</td>
<td>1.74</td>
<td>13</td>
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<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 a long time to get enough particles!
Sample should be ground to **uniform particle size**

**Ideally**, the particle size should be much smaller than the analyzed layer depth
## Industrial Minerals

### Easy, Fast and Safe Sample Preparation

<table>
<thead>
<tr>
<th>Method</th>
<th>Description</th>
</tr>
</thead>
</table>
| **Loose powder**     | the quick and simple preparation method  
                        The loose powder of the mineral is just poured into a cup and analyzed directly                                                         |
| **(30 sec)**         |                                                                                                                                              |
| **Pressed pellet**   | widely used preparation method for process control  
                        The powder is pressed into pellet for better accuracy and precision                                                                         |
| **(2 min)**          |                                                                                                                                              |
| **Fused bead**       | most accurate and precise preparation method  
                        The material is ignited with Li-Borate flux in a furnace to form a stable glass bead; matrix effects are reduced |
| **(10 min)**         |                                                                                                                                              |
From the Lab to Field
S2 RANGER
Rugged and Tough...
Limestone

Wide range of uses for
- Glass, Ceramics, Porcelain,
- Nutritional Mineral, Fertilizer,
- Building Material,
- Chemicals, Filter Material

- Analytical Task: Characterizing the mined material and quality control of the products
  - Determination of Majors, Minors, Traces in less than 4 ½ minutes
  - Prepared as Pressed Pellets
Limestone: Majors, Minors and Traces

Major: Calcium Oxide

Minor: Aluminum Oxide

Trace: Manganese Oxide
## Limestone

### CRM Limestone DH 3506 Accuracy

<table>
<thead>
<tr>
<th>Element</th>
<th>Certified Concentration [%]</th>
<th>XRF Concentration [%]</th>
<th>Abs. Deviation [%]</th>
<th>Rel. Deviation [%]</th>
<th>Recovery [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al2O3</td>
<td>1.76</td>
<td>1.73</td>
<td>0.03</td>
<td>1.7</td>
<td>98.3</td>
</tr>
<tr>
<td>SiO2</td>
<td>8.60</td>
<td>8.53</td>
<td>0.07</td>
<td>0.8</td>
<td>99.2</td>
</tr>
<tr>
<td>P2O5</td>
<td>0.066</td>
<td>0.068</td>
<td>0.002</td>
<td>3.0</td>
<td>103.0</td>
</tr>
<tr>
<td>K2O</td>
<td>0.256</td>
<td>0.274</td>
<td>0.018</td>
<td>7.0</td>
<td>107.0</td>
</tr>
<tr>
<td>CaO</td>
<td>46.77</td>
<td>47.0</td>
<td>0.23</td>
<td>0.5</td>
<td>99.5</td>
</tr>
<tr>
<td>TiO2</td>
<td>0.094</td>
<td>0.095</td>
<td>0.001</td>
<td>1.1</td>
<td>101.1</td>
</tr>
<tr>
<td>Mn3O4</td>
<td>0.104</td>
<td>0.107</td>
<td>0.003</td>
<td>2.9</td>
<td>102.9</td>
</tr>
<tr>
<td>Fe2O3</td>
<td>3.40</td>
<td>3.37</td>
<td>0.03</td>
<td>0.9</td>
<td>99.1</td>
</tr>
<tr>
<td>CO2</td>
<td>38.3</td>
<td>FIXED</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
Low Mg Limestone is More Complex... Mg is a Low Yield XRF Element!

1 method with 1 setting:
- 20 KV variable current
- Vacuum!
- Count rate $\geq 120,000$ cps
Calibration Mg with XFlash®

Calibration range

<table>
<thead>
<tr>
<th>Element</th>
<th>Calibration range [wt. %]</th>
<th>Calibration standard deviation 1σ [wt. %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>0.43 - 1.85</td>
<td>0.1032</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.07 - 4.65</td>
<td>0.0914</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.33 - 13.30</td>
<td>0.6778</td>
</tr>
<tr>
<td>CaO</td>
<td>44.15 - 55.19</td>
<td>0.5383</td>
</tr>
<tr>
<td>Mn₃O₄</td>
<td>0.015 - 0.280</td>
<td>0.0048</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.068 - 1.000</td>
<td>0.0206</td>
</tr>
</tbody>
</table>
Repeatability!
Goal <= 0.1 abs for MgO in 100 sec!

<table>
<thead>
<tr>
<th>time</th>
<th>MgO</th>
<th>Al$_2$O$_3$</th>
<th>SiO$_2$</th>
<th>CaO</th>
<th>Mn$_3$O$_4$</th>
<th>Fe$_2$O$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 s</td>
<td>[wt. %]</td>
<td>[wt. %]</td>
<td>[wt. %]</td>
<td>[wt. %]</td>
<td>[wt. %]</td>
<td>[wt. %]</td>
</tr>
<tr>
<td>Rep-1</td>
<td>0.8423</td>
<td>0.4795</td>
<td>1.5988</td>
<td>53.6814</td>
<td>0.0371</td>
<td>0.2547</td>
</tr>
<tr>
<td>Rep-2</td>
<td>0.7691</td>
<td>0.4643</td>
<td>1.5956</td>
<td>53.7039</td>
<td>0.0339</td>
<td>0.2536</td>
</tr>
<tr>
<td>Rep-3</td>
<td>0.8565</td>
<td>0.4690</td>
<td>1.6013</td>
<td>53.6829</td>
<td>0.0379</td>
<td>0.2571</td>
</tr>
<tr>
<td>Rep-4</td>
<td>0.8322</td>
<td>0.4579</td>
<td>1.5827</td>
<td>53.6866</td>
<td>0.0342</td>
<td>0.2491</td>
</tr>
<tr>
<td>Rep-5</td>
<td>0.8419</td>
<td>0.4610</td>
<td>1.6084</td>
<td>53.7157</td>
<td>0.0351</td>
<td>0.2517</td>
</tr>
<tr>
<td>Rep-6</td>
<td>0.9180</td>
<td>0.4777</td>
<td>1.6202</td>
<td>53.7394</td>
<td>0.0349</td>
<td>0.2526</td>
</tr>
<tr>
<td>Rep-7</td>
<td>0.8553</td>
<td>0.4453</td>
<td>1.5973</td>
<td>53.7738</td>
<td>0.0360</td>
<td>0.2613</td>
</tr>
<tr>
<td>Rep-8</td>
<td>0.8533</td>
<td>0.4678</td>
<td>1.6026</td>
<td>53.6778</td>
<td>0.0394</td>
<td>0.2601</td>
</tr>
<tr>
<td>Rep-9</td>
<td>0.7953</td>
<td>0.4646</td>
<td>1.5887</td>
<td>53.7326</td>
<td>0.0345</td>
<td>0.2601</td>
</tr>
<tr>
<td>Rep-10</td>
<td>0.9509</td>
<td>0.4997</td>
<td>1.6049</td>
<td>53.7178</td>
<td>0.0375</td>
<td>0.2592</td>
</tr>
<tr>
<td>Rep-11</td>
<td>1.0649</td>
<td>0.4865</td>
<td>1.6136</td>
<td>53.7308</td>
<td>0.0367</td>
<td>0.2591</td>
</tr>
<tr>
<td>Rep-12</td>
<td>0.9178</td>
<td>0.4689</td>
<td>1.6006</td>
<td>53.7753</td>
<td>0.0367</td>
<td>0.2578</td>
</tr>
<tr>
<td>Rep-13</td>
<td>0.9031</td>
<td>0.4661</td>
<td>1.5924</td>
<td>53.7110</td>
<td>0.0375</td>
<td>0.2570</td>
</tr>
<tr>
<td>Average</td>
<td>0.8770</td>
<td>0.4699</td>
<td>1.6005</td>
<td>53.7176</td>
<td>0.0363</td>
<td>0.2564</td>
</tr>
</tbody>
</table>

| Abs. Std. Dev. | 0.0729 | 0.0131 | 0.0096 | 0.0312 | 0.0016 | 0.0036 |
| Rel. Std. Dev. | 8.31   | 2.78   | 0.60   | 0.06   | 4.39   | 1.41   |
Light elements such as Na and Mg have very low characteristic emission line energies (1 keV and 1.2 keV) in addition to a low fluorescence yield. They are easily absorbed by Air, reduced by measurements in Helium and even under Vacuum show low sensitivity.

- Factors include
  - Ambient mode (Helium, vacuum)
  - Coupling
  - Transmission Windows (snout as well as the “detector window”)

Analysis of low concentrations or the analysis of FUSED (diluted with 1:5 to 1:10 with a flux) samples is difficult with the standard system as well as impossible with the handheld unit.

Using a NEW XFlash® detector changes the sensitivity!
S2 RANGER
XFlash® LE Silicon Drift Detector

- XFlash LE
  - 4th generation Silicon Drift Detector (SDD)
  - 10 mm² active area
- Unique light element performance
  - High transmission window
- Unique energy resolution
  - 129 eV FWHM
  - @ Mn Kα
  - @ 100 000 cps
- Unmatched count rates
  - up to 300 000 cps input count rate
  - up to 100 000 cps output count rate without resolution degradation
- Peltier cooled
S2 RANGER
XFlash® LE

- More than 8 times sensitivity for Na (compared to standard SDD)

- More than 4 times sensitivity for Mg (compared to standard SDD)

- Higher intensities in the ranges
  - less than 3.0 keV (Pd LB)
  - higher than 12.6 keV (Pb LB)

- Lower background in the energy range up to 12.6 keV
Analytical requirements:
Alkali feldspars are a common raw material for ceramics and porcelain

Quality control (composition of major elements) and impurities (trace elements):
Na2O – 10 %
Al2O3 – 18 %
SiO2 – 70%
and trace elements:
Fe2O3 – 0.5 %
TiO2 – 0.05%
S2 RANGER with XFlash® LE
Feldspars

- Best separation of light elements: Clear identification from Na – P
- High sensitivity
- Preparation of pressed pellets... GRAIN SIZE based bias
- Analysis in vacuum
S2 RANGER with XFlash® LE
Feldspars

Linear range from 2.4 – 10.4 %
Calibration standard deviation < 0.05%
Detection Limit: 200 ppm
## S2 RANGER with XFlash® LE

**Feldspars**

<table>
<thead>
<tr>
<th>Repetitions</th>
<th>Na2O (%)</th>
<th>MgO (%)</th>
<th>Al2O3 (%)</th>
<th>SiO2 (%)</th>
<th>P2O5 (%)</th>
<th>K2O (%)</th>
<th>CaO (%)</th>
<th>TiO2 (%)</th>
<th>Fe2O3 (%)</th>
<th>Ba (ppm)</th>
<th>Sr (ppm)</th>
<th>Zr (ppm)</th>
<th>Rb (ppm)</th>
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<tbody>
<tr>
<td>1</td>
<td>8.82</td>
<td>0.20</td>
<td>18.36</td>
<td>69.40</td>
<td>0.23</td>
<td>1.52</td>
<td>0.83</td>
<td>0.31</td>
<td>0.29</td>
<td>86</td>
<td>103</td>
<td>74</td>
<td>54</td>
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<td>0.19</td>
<td>18.35</td>
<td>69.42</td>
<td>0.23</td>
<td>1.49</td>
<td>0.80</td>
<td>0.31</td>
<td>0.29</td>
<td>80</td>
<td>100</td>
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<td>53</td>
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<tr>
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<td>1.51</td>
<td>0.85</td>
<td>0.31</td>
<td>0.29</td>
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<td>54</td>
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<td>69.36</td>
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<td>0.84</td>
<td>0.32</td>
<td>0.29</td>
<td>93</td>
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<td>69.37</td>
<td>0.24</td>
<td>1.55</td>
<td>0.83</td>
<td>0.32</td>
<td>0.29</td>
<td>74</td>
<td>103</td>
<td>74</td>
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<td>6</td>
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<td>0.19</td>
<td>18.35</td>
<td>69.37</td>
<td>0.23</td>
<td>1.52</td>
<td>0.83</td>
<td>0.32</td>
<td>0.29</td>
<td>90</td>
<td>102</td>
<td>73</td>
<td>55</td>
</tr>
<tr>
<td>7</td>
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<td>0.18</td>
<td>18.37</td>
<td>69.45</td>
<td>0.22</td>
<td>1.50</td>
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<td>69.44</td>
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<td>0.29</td>
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**Mean Values**

<table>
<thead>
<tr>
<th>Repetitions</th>
<th>Na2O (%)</th>
<th>MgO (%)</th>
<th>Al2O3 (%)</th>
<th>SiO2 (%)</th>
<th>P2O5 (%)</th>
<th>K2O (%)</th>
<th>CaO (%)</th>
<th>TiO2 (%)</th>
<th>Fe2O3 (%)</th>
<th>Ba (ppm)</th>
<th>Sr (ppm)</th>
<th>Zr (ppm)</th>
<th>Rb (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean Values</td>
<td>8.86</td>
<td>0.20</td>
<td>18.35</td>
<td>69.39</td>
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<td>0.29</td>
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**Abs. Std Dev.**

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<th>MgO (%)</th>
<th>Al2O3 (%)</th>
<th>SiO2 (%)</th>
<th>P2O5 (%)</th>
<th>K2O (%)</th>
<th>CaO (%)</th>
<th>TiO2 (%)</th>
<th>Fe2O3 (%)</th>
<th>Ba (ppm)</th>
<th>Sr (ppm)</th>
<th>Zr (ppm)</th>
<th>Rb (ppm)</th>
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<tbody>
<tr>
<td>Abs. Std Dev.</td>
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**Rel. Std. Dev.**

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<th>Al2O3 (%)</th>
<th>SiO2 (%)</th>
<th>P2O5 (%)</th>
<th>K2O (%)</th>
<th>CaO (%)</th>
<th>TiO2 (%)</th>
<th>Fe2O3 (%)</th>
<th>Ba (ppm)</th>
<th>Sr (ppm)</th>
<th>Zr (ppm)</th>
<th>Rb (ppm)</th>
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</thead>
<tbody>
<tr>
<td>Rel. Std. Dev.</td>
<td>0.23%</td>
<td>4.15%</td>
<td>0.11%</td>
<td>0.05%</td>
<td>2.35%</td>
<td>1.09%</td>
<td>1.75%</td>
<td>0.92%</td>
<td>0.40%</td>
<td>12.12%</td>
<td>0.99%</td>
<td>3.70%</td>
<td>1.26%</td>
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</tbody>
</table>
S2 RANGER with XFlash® LE
Feldspars

Results:
Na₂O:  8.86 +/- 0.23 %
MgO:  0.20 +/- 0.008 %
Al₂O₃: 18.35 +/- 0.02 %
SiO₂:  69.39 +/- 0.038 %
P₂O₅:  0.23 +/- 0.005 %
K₂O:  1.52 +/- 0.017 %
CaO:  0.83 +/- 0.014 %
Fe₂O₃: 2.37 +/- 0.02 %

Accurate control of the composition and impurities of mined Feldspars with the S2 RANGER with XFlash LE.
S2 RANGER with XFlash® LE
Spectrum: Cement as Fused Bead

- High sensitivity thanks to direct excitation and vacuum mode
- High resolution: clear separation of Sodium and Magnesium
- High dynamic range
S2 RANGER with XFlash LE
Cement – Calibration of Na in Fused Beads
S2 RANGER with XFlash® LE
Stability – Cement – 77 Days

<table>
<thead>
<tr>
<th>#</th>
<th>Datum</th>
<th>Na2O (%)</th>
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<th>Al2O3 (%)</th>
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So We Can Drive On-site (2003)
Or We Can Use a Mobile Lab... for European Customer Trials
Something Smaller...
Easily Portable!

XFlash®
Technology
Limestone and Sandstone Analysis
Non-destructive and On-site

Thomas Oliver Pryce
PhD in Cambodia

UWO hands-on course
Field use of HHXRF
Portable and Handheld XRF
Standard and Custom Applications

Grade Control, Prospection
- Factory or TYPE STANDARD tuned calibration used for “generic” overview of majors and minors
- Tuned for mineralogical and “inhomogeneity”

Customized Calibrations
- Putting the benchtop applications in your hands
- Using the same software, SPECTRA EDX from the S2 RANGER, you can develop a FP or empirical calibration for desired materials

Cluster Analysis
- Known from the “IR” world as Chemometrics
- Instead of looking at concentrations we look at entire spectra or regions
- “Determining degrees of similarity”
- Example: “Sourcing limestone blocks (Cambodia), Sourcing sandstone in buildings of the Western Ontario University Campus” (Seminar topic 2010)
Handheld XRF Mineral Analysis
Limestone

- In house analysis of Limestone “deposits” and stone done by S2 RANGER on pressed pellets and fusion beads

- Using the quarry samples as standards prepared as pressed pellets (certified as fusion beads vs. NIST and CRM’s) the S1 TRACER unit was calibrated (with same software). The S1 TRACER was operated with PDA in the quarry!

![Graphs showing CaCO3 and Fe2O3 results](image)
From Field to Lab: Use of Portable XRF for Geological Investigation

**Overview:**

- Portable XRF makes geological investigations very easy
- XFlash SDD makes analysis of light elements possible in the field
- Sample preparation determines the level of accuracy and precision of the measurement
- 5-10% of the samples should be analyzed in the laboratory for confirmation
- Brief summary of CaCO₃ application
Typical Field-Portable XRF

Instrument Characteristics:

• Weight < 2 kg
• Measurement times 30-60 sec
• Detection limits on the order of ~10 ppm
• GPS compatible for mapping of results
XFlash SDD for Light Elements

XFlash SDD:

- Provides light element detection e.g. Mg, Al, Si, Ca
- No vacuum or He purge required
- Gives more complete analysis of geological samples
Portable XRF for Field Prospecting

- Use global FP calibration
- Provides good analysis of general levels and extent of ore body
- 5-10% of Samples are sent to laboratory
- GPS Coordinates allow easy mapping
Portable XRF for Mine Control

- Use site-specific calibration
- Use Empirical Calibration based on Standards
- Use Type Standardization based on analyzed samples
- Provides good analysis which optimizes the excavation and removal of ore
- Provides instantaneous assay information
Type Standardization

- Linear relationship between Measured and actual
- Differences caused by differences between calibration assumptions and real sample
- Calculate slope and offset

\[ y = 1.0326x + 0.4829 \]

\[ R^2 = 0.9999 \]
Type Standardization

- Type standardization feature enables user to adjust factory calibrations by setting element-specific slope and offset coefficients with the PDA software.

- This feature is specifically designed for mining applications to enable easy on-site calibration optimization based on known standards.

- In many cases, type standardization can replace customer-specific calibration.

- Multiple coefficient sets can be saved for each calibration, which in practice makes it possible to create “sub-calibrations” for different sample types.
Sample Preparation

- Sample Preparation Determines the Accuracy achieved

In-situ direct measurement

- Direct measurement of the soil/rock face
- Gives good qualitative to semi-quantitative assay
- Gives sufficient information to define the boundaries of a deposit
Sample Preparation

Sample preparation determines the accuracy achieved

In-situ with minor sample preparation

- Removal of sample
- Remove debris
- Crush larger rocks
- Dry sample
- Sample in XRF cup

- Provides semi-quantitative to quantitative analysis

- Desktop stand kit includes sample holder and safety shield to protect from scattering X-ray radiation, AC adapter and PDA remote cable.
Sample Preparation

Sample preparation determines the accuracy achieved

In Laboratory:

- Ground to uniform particle size
- Completely dry sample
- Prepared press pellet or fused bead
- Provides quantitative analysis
- Best assay with lowest detection limits
Limestone Mining

- Limestone, calcium carbonate (CaCO$_3$), is one of the most versatile minerals found in the earth's crust. Physical properties and low processing cost makes it the most widely used filler material.

- The principal element in the calcium carbonate ore is calcium (Ca). The ore normally contains other elements that affect whiteness, hardness and specific gravity.
Handheld XRF Mineral Analysis
Limestone Mining

- Handheld XRF can be used to measure calcium carbonate composition directly from rock or from quarry. This information can be used to effectively control mining and excavation process.

- Bruker S1 TRACER can effectively measure calcium content and all other critical elements from limestone, such as Ca, Mg, Al, Si, K, Ti, Fe, Mn.
Paper Additives
- Paper additives such as CaCO3 are critical to the paper making process. Besides cellulose and lignin, paper contains up to 50% inorganic fillers and pigments, which are used to modify properties of paper.
- CaCO3 is used as a filler for making bright, opaque paper at minimum cost.

Paper Ash content
- The ash content is one of the most important paper properties. It is basically the residue on ignition from a paper. Ash content number indicates quantity of inorganic substances, such as Ca.
- Direct XRF measurement of paper provides composition of inorganic materials (Mg, Al, Si, Ti, Ca etc.) and an estimate of ash content in fraction of time that normal ash content test takes.
Handheld XRF Mineral Analysis
Paper Additives

Field Measurement XRF Advantage

- XFlash SDD allows the accurate measurement of CaCO$_3$
- Completely non-destructive testing - The same exact sample can be sent to the laboratory for confirmatory analysis.
- Fast analysis time, from a few seconds to one minute, depending on precision requirements.
- At site measurements allow instant decisions for excavation
- Same analyzer can be used to test also bulk raw materials and additives.
- Handheld XRF measurement can be made directly on the paper roll without any preparation.
Please use your mouse to answer the question to the right of your screen:

What analytical methods do you use for your industrial minerals? (Check all that apply):

- AAS
- ICP-OES
- ICP-MS
- Titration
- EDXRF
- WDXRF
- Field Portable EDXRF
- Gravimetric Analysis
- None
How XRF Solves Day-to-Day Industrial Challenges

The instrumentation for an analytical task must meet many different criteria:

- Time to result
- Instrument setup and calibration
- Cost of ownership
- Easy, fast sample preparation
- Safe investment for future applications
- Fit for purpose
- Experience and skill of laboratory employees
- Analytical performance
Elemental Analysis Using Electromagnetic Radiation: Light

- Absorption of light (infrared/visible/ultraviolet)
  - AAS - Atomic Absorption Spectrometry

- Emission of light (infrared/visible/ultraviolet)
  - OES - Optical Emission Spectrometry
    - OES-Spark: metals
    - ICP-OES: dissolved/liquid samples

- Transitions of electrons between outer shells of the atom
- Energy of photons = energy of chemical binding
- Usable spectra only for “free” atoms or ions
- Sample has to be evaporated
Elemental Analysis Using Electromagnetic Radiation: X-rays

- Emission of characteristic X-rays
  - XRF - X-ray Fluorescence Analysis

- Transitions of electrons between inner shells of the atom
- Energy of photons > energy of chemical binding
- Energy of characteristic X-rays independent of chemical binding
- Solid and liquid samples can be measured directly
- Non-destructive (for the sample)
Comparison of Spectroscopic Techniques

<table>
<thead>
<tr>
<th>Technique</th>
<th>Precision</th>
<th>Range</th>
<th>Sample Preparation</th>
<th>Materials</th>
<th>Cost</th>
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<td>5 to 15 min.</td>
<td>Inorganics</td>
<td>$35K to $200K</td>
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<td>AAS</td>
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<td>PPB to PPM</td>
<td>Need solutions – hrs to days</td>
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<td>ICP</td>
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<td>OES-Spark</td>
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<td>PPM to 5%</td>
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<td>Only metals</td>
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<td>NIR &amp; FTIR</td>
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<td>Organics</td>
<td>$35K to $100K</td>
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Poll Results
What Method to Use?

- The method used needs to be fit for purpose
- Select according to requirements for:
  - Accuracy
  - Precision
  - Cost of analysis
  - Speed of analysis
  - Regulatory purpose
  - Operator compatibility
  - Flexibility
  - Infrastructure needs
  - Cost of ownership
Environmentally Clean and Safe Method

- XRF doesn’t require the use of HF and other strong acids
- XRF doesn’t require microwave digestion - acids under high pressure and temperature
- No hazardous chemicals, no hazardous waste
Better Precision

- XRF is more precise than ICP because dilution factors are much lower.
  - ~500X for ICP
  - ~1.2X for XRF

- Lower dilution factors and better analytical precision allow product manufacturers to tighten the specification limits on metals added to products.

- Manufacturers can therefore produce materials closer to the low end of specification and save money.

- This operational principle is difficult with ICP because precision errors are much larger.

- Manufacturers using ICP for metals analysis produce materials towards the high end of specification, just to be on the safe side.
Shorter Analysis Time

- Analysis time, including sample preparation:
  - XRF - typically less than 20 minutes
  - ICP - at least 2 hours, 6 times longer!
- ICP technicians hold samples to be measured in a batch for convenience. This increases turnaround time. With XRF, there is no need to batch samples for measurement.
- ICP daily warm-up can take up to 2 hours to stabilize for analysis.
- Clean-up of sample preparation equipment is much faster for XRF.
Effective quality and process control requires the shortest time-to-result possible. This is the time needed from sampling to the final quantitative result. Any advantage results in:

- Higher sample throughput
- Stable industrial processes due to immediate feedback
- Constant high product quality
Low Analysis Cost

- Cost of consumables for XRF is one tenth that of ICP.
- ICP uses 1 to 2 liquid Ar dewars a week.
- EDXRF doesn’t use gas at all, only in case of liquid analysis a small amount of Helium purge is needed.
- ICP requires that new standards be purchased at least once a year. XRF standards are purchased once; there is no need to purchase new standards annually.
A True Comparison of the Real Cost of Ownership

The investment for the analytical instrument is only one part of the total cost of ownership. Expenses for laboratory equipment and consumables add to that cost. For example:

- Use of expensive accessories (AAS: graphite tubes)
- Consumption of noble gases (ICP: Argon)
- Need for hazardous chemicals (compliance with high-level safety regulations)
- Complicated sample preparation equipment (training and time)
Lab Standardization

- XRF calibrations are easily transferred from one instrument to another, ensuring consistent results from one plant to another within a company.
- ICP lab standardization is far more difficult due to the number of steps in sample preparation and larger precision errors.
  - ICP doesn’t work well in real world situations.
  - With ICP, metals analysis results rarely match up from site to site within the same company.
Shorter Learning Curve

- Once an XRF method is set up, a technician can be trained to prepare and analyze samples in less than 2 hours.
- With ICP, method setup and technician training take weeks to months.
- The shorter learning curve with XRF allows technicians to fill in quickly when emergencies arise or demand is high.
- Cross training is much easier with XRF, as there is less “art” to sample preparation and instrument operation.
XRF minimizes instrument setup and calibration time. A simple one-time calibration based on your own standards is sufficient. After calibration, a stable drift correction sample is measured. Modern XRF instrumentation, like the S2 RANGER, provide ready-made solutions and powerful tools for standardless analysis (EQUA ALL).
Standardless Analysis

- XRF standardless analysis can be used for quick composition measurement of non-routine samples. With ICP, standards need to be purchased and method development may take weeks.

- When developing new products, metal concentrations may vary considerably or be constantly changing. Analysis with ICP therefore requires constantly changing standards and methods.

- XRF standardless analysis can also be used for quick evaluation of non-routine samples from process upsets.
Analytical Performance: Advantage XRF

XRF provides:
- qualitative and quantitative analysis
- fast and easy sample preparation
- elements from Be to U in all kind of samples
- even light elements like B, C, N, O and F (WDXRF)
- standardless calibration for all materials
- linear concentration range from ppm to 100%
- highest accuracy and reproducibility up to 0.05% (rel.)
- typical detection limits (LLD): ~ 1 to 10 ppm

Is there any analytical method better than XRF for fulfilling the demands for fast and flexible multielement analysis?

Since XRF can analyze solid samples directly, it is the only analytical method to leave the lab to field!
If the application is defined and the requirements are clear, there is no problem identifying the right solution. Analytical methods like ICP, AAS, and titration are often limited: sample amount, interfering matrix elements, insufficient digestion, difficult to relocate... There are so many reasons why an application cannot be done.

Not so with XRF. Bruker AXS offers a wide range of XRF instruments to meet all your elemental analysis needs.

- **S1 TURBO** - Handheld XRF for material verification
- **S1 TRACER** - Handheld XRF for classification
- **S2 RANGER** - Cost-effective benchtop EDXRF analysis
- **S8 TIGER** - Superior WDXRF performance
- **S8 LION** – Simultaneous Multichannel WDXRF
Any Questions?

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