XRF SAMPLE PREPARATION
XRF SAMPLES

- **Solids**  
  Rod, Sheet, Foil, Glass, Ingots, Bar

- **Small fabricated parts**  
  Rod, Wire, Screws, Pieces

- **Powders**  
  Different grain sizes / Hardness

- **Briquettes**  
  Pressed with Elvacite / Wax etc.

- **Fusion products**  
  Glazes, Ceramics, Fused beads

- **Liquids and solutions**  
  Oils, Aqueous solutions

- **Supported specimens**  
  Thin films, Coatings, Plantings, Filter paper, Scotch tape, Millipore filters
SAMPLE PREPARATION - PRECONDITIONS

• Sample should be fit into the spectrometer

• Garbage in garbage out

• If no preparation;
  ▪ *Big samples (Large sample mode)*
  ▪ *Utilize Liquid sample cups for Liquids, Powders, Slurry, Small pieces*
  ▪ *Utilize filter paper, sand paper, … etc.*
IMPORTANT PHENOMENA
- X-RAY INTERACTION WITH SUBSTANCES

• X-ray penetration / escape depth into / from substances

• Influence of sample surface roughness

• Particle size effect in solid/powder

• Mineralogical effect in most of crystalline materials

• Matrix effect
X-RAY INTERACTION WITH SUBSTANCES

X-RAY PENETRATION / ESCAPE DEPTH

<table>
<thead>
<tr>
<th>Material</th>
<th>Mg-Kα</th>
<th>Cr-Kα</th>
<th>Sn-Kα</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb (Lead)</td>
<td>0.7</td>
<td>4.5</td>
<td>55</td>
</tr>
<tr>
<td>Fe (Iron)</td>
<td>1</td>
<td>35</td>
<td>290</td>
</tr>
<tr>
<td>SiO₂ (Quartz)</td>
<td>8</td>
<td>110</td>
<td>0.9 cm</td>
</tr>
<tr>
<td>Li₂B₄O₇</td>
<td>13</td>
<td>900</td>
<td>4.6 cm</td>
</tr>
<tr>
<td>H₂O</td>
<td>16</td>
<td>1000</td>
<td>5.3 cm</td>
</tr>
</tbody>
</table>

(단위: μm)

- Sample surface is extremely important for light elements
  - Interested in light elements => take care for surface roughness & protection film
  - Interested in heavy elements => take care for sample thickness
The longer the wavelength of the analyte line, the finer the surface finish must be. 30-50 μm finish is adequate for the K lines down to atomic number 13 (Al).
X-RAY INTERACTION WITH SUBSTANCES

HOMOGENEITY : PARTICLE SIZE EFFECT

Layer 1
Layer 2
Layer 3
Layer 4

Surface roughness : Shadow effects

Phase 1
Phase 2 : Preferred orientation
Phase 3 : Segregation
Binder

All phases : Particle statistics ; N(Layer1) <> N(Layer2) etc.
X-RAY INTERACTION WITH SUBSTANCES

MATRIX EFFECT (INTER-ELEMENT EFFECT)

• Secondary fluorescence path indicated with ‘Alpha’
  • Steel  40-50 %
  • Geology < 5 %

Si-Ka Sensitivity change
at  0 % of SiO$_2$:  500 cps/%
at 100 % of SiO$_2$:  1,000 cps/%

\[ C = D + ER(1 + \sum \alpha C) \]
\[ C_i = D_i + E_i R_i \left( 1 + \sum_{j=i}^{n} \alpha_{ij} C_j \right) \]
\[ C_{Ni} = D_{Ni} + E_{Ni} R_{Ni\alpha} \left( 1 + \alpha_{NiNi} C_{Ni} + \alpha_{NiCr} C_{Cr} + \alpha_{NiSi} C_{Si} + \alpha_{NiMn} C_{Mn} + \alpha_{NiV} C_{V} \right) \]
A Na-atom in each phase is subject to different matrix effects.

In order to correct for this effect one has to know the path each photon has traveled through the specimen.

This is impossible.
- Grinding does NOT help.
# Various Effects: Solving Problems

## The Elimination of Various Effects

<table>
<thead>
<tr>
<th></th>
<th>Inhomogeneity solved</th>
<th>Matrix effect solved</th>
<th>Particle size effect solved</th>
<th>Mineralogical effect solved</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spinning the sample</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Mathematical Correction (SW)</td>
<td>No</td>
<td>Yes</td>
<td>No</td>
<td>No</td>
</tr>
<tr>
<td>Grinding (Grain size reduction)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Fusion (solid solution)</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
<td>Yes</td>
</tr>
</tbody>
</table>
TYPICAL XRF SAMPLE PREPARATION

1. Jaw Crush
2. Grinding Mill
3. Fine powder
4. Pressing
5. Various Iron and Steel
6. Resurfacing by Belt Grinder or Grinder/Polisher
7. Powder Pellet
8. Fused Bead
9. Solid Disk

Direct solidification
Remelting
SAMPLE PREPARATION: FUSION MACHINE

- **LeDoser**
  Auto Weighing M/C

- **LeNeo**
  Electric Bead MC (1 pos)

- **M4**
  Gas Burner Bead MC (3 pos)

- **TheOX**
  Electric Bead MC (6 pos)

Powder of Slag, Alloys, Limestone, etc.

Weighing with fluxes

Oxidizing & Melting

Fused Beads
SAMPLE PREP – OTHERS

Jaw Crusher

Disk Mill

Hydraulic Press

Arc Re-melting Furnace

Belt Grinder

Milling MC

Diamond Cutter

Polishing MC
TYPICAL SAMPLE PREPARATION FOR XRF

• Fusion bead method
  • Bead Machine
  • Sample vs. Flux: type, ratio, Temp

• Pressed powder method
  • Press
  • Mineralogical / Particle size effect
  • Use of binder / Backing

• Liquid / Loose powder method
  • He medium required
  • Liquid : Safety against spillage, corrosion
  • Power, small pieces, odd shapes
SOLID SAMPLE PREPARATION

• Solids
  • Metal & Alloys
  • Grinding
  • Turning
  • Polishing

• Plastics
  • Measurement as such (direct or in liquid cup)
  • Grind using Liquid Nitrogen
  • Press at elevated temperature

• Rocks, Large pieces of metals (Fe-alloys)
  • Reduce size and treat as powder
POWDER SAMPLE PREPARATION

• Powders
  • *Metals & Alloys, Oxides, Sulfides, Carbides, Plastics, Plants, Coal, etc.*

• Metals & Alloys
  • *Pressing at 100 tons Mix with Binder and press at 40 tons*

• Sulfides
  • *Pressing, fusion with pre-oxidation or fusion with pyro-sulfate, grinding and pressing*

• Carbides
  • *Dissolve in acid, evaporate and fusion. Fusion with pre-oxidation (like Fe-alloys)*
POWDER SAMPLE PREPARATION

• Plastics
  • *Hot pressing*
  • *Normal pressing with binders*
  • *Loose granulates in liquid cup*

• Plants
  • *Dry, (Grinding) and pressing*
  • *Ash and measurement of residue :*
    ★ Note: *Volatile substances will disappear*

• Coal
  • *Dry, grinding and pressing*
    ★ Note: *Mind for infinite thickness*
  • *Ash and measurements of residue*
    ★ Note: *Volatile substances will disappear*
POWDER SAMPLE IN LIQUID MODE

- Samples can be poured into liquid cup to analyze
  - Need He flushing system.
  - If no He flushing system is attached, then the “Vulnerable sample mode” can be applicable when “Airlock bypass valve” is attached.
    - Need confirmation from CSE
    - This option prevents breaking of the sample/film while evacuating the vacuum lock chamber by maintaining the same pressure above and below the sample.
• To utilize this method, the user must aware of:
  • The sensitivity for light elements become very low due to energy absorption by film
  • Must aware that the films contain impurities
    ❖ Mylar: Ca, P, Zn, Sb
    ❖ Polypropylene: Al, Ti, Fe, Cu, Si
    ❖ Kapton: Very pure
    ❖ Prolene: Very pure
  • Standards should be measured with same condition (Quantitative mode)
  • Film correction is necessary for Omnan.
  • This mode is only recommended when the other sample preparation methods are not applicable.
    (sample leakage or scatter)
LIQUID SAMPLE PREPARATION

AQUA BASE SAMPLE

- Water (High concentrations)
  - Liquid cup (neutralize if possible)
  - Absorption on filter paper, drying
- Water (Low concentrations)
  - Pre-concentration
  - Ion exchange resin/paper
  - Activated carbon
  - Pre-concentration with Fe addition
- Evaporation and Fusion
- Evaporation and small spot analysis

OIL BASE SAMPLE

- Organic liquids (e.g. S, V. Ni in Oil)
  - Direct measurement in ‘Liquid cup’
  - Internal standard addition
  - Matrix correction
  - Dilution with blank oil
- Wear metals in oil
  - No Particles: Homogenize and measure in ‘Liquid cup’
  - Particles present: Filtrate
    - Measure Filter
    - Measure rest liquid in ‘Liquid cup’
OTHER SPECIAL TECHNIQUES

- Use of liquid cup for non-liquid samples
- Use of filter paper for liquid or suspension
- Use of sand paper or corundum disc
- Use of mounting material (Cold, Hot, Partial)
- Use of press with soft material backing

★Note: In all these cases results will be Semi-Quantitatively
SAMPLE PREPARATION FOR POWDER
ACTUAL TECHNIQUES FOR POWDER SAMPLES

- **Powder as it is** (loose powder)
  1. Put into liquid sample cell (tapping and press by hand)
  2. Filtrate with filter paper or adhere on double sided tape

- **Powder needs to be pressed?**
  1. Press without Binder
     - Direct press - *no binder is easy & simple, but most probably no good*
     - Use of plastic ring
     - Use of H3BO3 backing
  2. Press with Binder – *precise weighing and homogenization is necessary*
     - Direct press
     - Use of Aluminum cup
     - Use of backing of H3BO3
SAMPLeS WITHOUT PRESSING

- The most easy and simple method for powder, liquid, slurry and piece of samples.
- Analysis result can be good or bad. Need to test before applying this method except liquid samples.
One of easier way to press the powder without binder.
Moderate strength.
Difficult to store for long period.
PRESS WITHOUT BINDER – USE OF BORIC ACID BACKING

- Need a special tool
- Most of powder samples can be pressed without binder with fairly good strength
PRESS WITHOUT BINDER – USE OF BORIC ACID BACKING
PRESS WITH BINDER – USE OF ALUMINUM CUP

Sample + Binder

Boric acid or Sample + Binder
PRESS WITH BINDER – USE OF BORIC ACID BACKING
USE OF LIQUID BINDER

Drop 1~2 ml of liquid binder into sample

Add acetone into the sample for homogenization

Grind until sample completely dried

• Best powder pressing
• Good for long storage
• Minimum dilution
• Take a bit long prep. time
SPECIAL BINDER FOR FATTY POWDER (MILK POWDER) - PANBLEND-1

- Patented formulation developed for the pressed pellets from fatty samples.
- Effectively immobilizes the fat and other fluids, allowing very fatty samples (up to 40% fat) to be pressed at higher pressures.
- PANblend-1 also acts as a grinding aid, facilitating the homogenization of the sample during mixing and avoiding clumping.
- 4.5 g of infant formula with 0.5 g of PANblend-1
- Press applying 100 kN of force for 30 s.

<table>
<thead>
<tr>
<th></th>
<th>Ca</th>
<th>Cl</th>
<th>Cu</th>
<th>Fe</th>
<th>K</th>
<th>Mg</th>
<th>Na</th>
<th>P</th>
<th>S</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure sample, pressed as is @ 30 kN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average of 10 samples (mg/kg)</td>
<td>3974</td>
<td>4196</td>
<td>3.3</td>
<td>37.4</td>
<td>5208</td>
<td>402</td>
<td>1762</td>
<td>2384</td>
<td>1310</td>
<td>41.0</td>
</tr>
<tr>
<td>SD (mg/kg)</td>
<td>125.03</td>
<td>124.57</td>
<td>0.43</td>
<td>3.35</td>
<td>132.50</td>
<td>16.67</td>
<td>75.90</td>
<td>71.68</td>
<td>40.32</td>
<td>2.72</td>
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<tr>
<td>Relative SD (%)</td>
<td>2.80</td>
<td>2.93</td>
<td>13.09</td>
<td>8.97</td>
<td>2.32</td>
<td>4.15</td>
<td>4.32</td>
<td>3.01</td>
<td>2.87</td>
<td>5.84</td>
</tr>
</tbody>
</table>

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<th>P</th>
<th>S</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample+PANblend-1, homogenized, pressed @ 100 kN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Average of 10 samples (mg/kg)</td>
<td>3892</td>
<td>4159</td>
<td>3.1</td>
<td>38.7</td>
<td>5235</td>
<td>404</td>
<td>1816</td>
<td>2333</td>
<td>1340</td>
<td>40.0</td>
</tr>
<tr>
<td>SD (mg/kg)</td>
<td>13.32</td>
<td>19.34</td>
<td>0.34</td>
<td>2.44</td>
<td>31.28</td>
<td>15.65</td>
<td>75.34</td>
<td>32.41</td>
<td>15.28</td>
<td>1.57</td>
</tr>
<tr>
<td>Relative SD (%)</td>
<td>0.34</td>
<td>0.46</td>
<td>10.85</td>
<td>6.30</td>
<td>0.60</td>
<td>3.88</td>
<td>4.15</td>
<td>1.39</td>
<td>1.14</td>
<td>3.92</td>
</tr>
</tbody>
</table>

Improvement factor 8.2 6.3 1.2 1.4 3.9 1.1 1.0 2.2 2.5 1.5
TIPS FOR WEIGHING

• If binder is used for the press, then need weighing twice, for a sample and binder

• Guide for weighing
  • Put sample without fine control of the amount of sample, just read the recorded weight.  
    - This will reduce the effort for weighing,  
    - and will help to maintain the precision of weighing
  • Calculate binder amount as per the predefined ratio of sample to binder ratio.  
    Weigh the calculated amount of binder with fine control
THANK YOU FOR YOUR ATTENTION

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