Sample Preparation Approaches for X-ray Fluorescence Analysis

Shintaro Ichikawa

Meiji University, Kanagawa, Japan

E-mail: sichi@meiji.ac.jp

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Recent research

34 components in 200 mg-rock


**Comparison with a regular specimen**

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Sample-to-flux</th>
<th>Sample</th>
<th>Flux</th>
<th>Number of components</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 mm (Regular)</td>
<td>1:1</td>
<td>2200 mg</td>
<td>2200 mg</td>
<td>42</td>
</tr>
<tr>
<td>12.5 mm (Proposed)</td>
<td>1:1</td>
<td>200 mg</td>
<td>200 mg</td>
<td>34</td>
</tr>
</tbody>
</table>

Pre-heat: 900°C, 120 s
Melt: 1250°C, 120 s
Agitation: 1200°C, 120 s

Comparison with a regular specimen

Na$_2$O, MgO, Al$_2$O$_3$, SiO$_2$, P$_2$O$_5$, K$_2$O, CaO, TiO$_2$, MnO, Fe$_2$O$_3$, V, Cr, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Cs, Ba, La, Pr, Nd, Sm, Gd, Dy, Er, Yb, Hf, W, Pb

**Calibration curves**: synthesis standards

**Validation**: GSJ Geochemical References

GSJ, Geological Survey of Japan

Basalt, andesite $\times$ 2, granodiorite, and rhyolite
Outline

1. Sample preparation
   (1) Analytical depth, (2) Particle size,
   (3) Homogeneity, and (4) Sample thickness

2. Determination
   (1) Calibration standard and (2) Validation

3. Examples of specimen
   (1) Loose powder, (2) Powder pellet, and
   (3) Glass bead for powders and grains
## 1. Sample preparation

### Sample preparations

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pretreatment</th>
<th>Preparation</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mass and plate</strong></td>
<td>Polish</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(for homogenous and flat body)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Recast and polish</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(for heterogenous body)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pulverization</td>
<td>Mold and press: &quot;Powder pellet&quot;</td>
</tr>
<tr>
<td><strong>Solid</strong></td>
<td><strong>Homogenization</strong></td>
<td>Pack into holder: &quot;Loose powder&quot;</td>
</tr>
<tr>
<td></td>
<td>(pulverizing and mixing )</td>
<td>Molde and press: &quot;Powder pellet&quot;</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Borate fusion and vitrification</td>
</tr>
<tr>
<td></td>
<td></td>
<td>: &quot;Glass bead&quot;</td>
</tr>
<tr>
<td></td>
<td>Decomposition and liquefaction</td>
<td></td>
</tr>
<tr>
<td></td>
<td>: Treat &quot;Liquid sample&quot;</td>
<td></td>
</tr>
<tr>
<td><strong>Grain</strong></td>
<td>No pretreatment</td>
<td>Pack into holder: &quot;Loose powder&quot;</td>
</tr>
<tr>
<td></td>
<td>Homogenization</td>
<td></td>
</tr>
<tr>
<td></td>
<td>: Treat &quot;powder and mass&quot;</td>
<td></td>
</tr>
<tr>
<td><strong>Liquid</strong></td>
<td>No pretreatment</td>
<td>Pack into holder</td>
</tr>
<tr>
<td></td>
<td>Concentration</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Put a drop on filter-paper</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Solid-phase extraction</td>
</tr>
</tbody>
</table>

| Powder and mass                          |                                      |                              |
|                                          | such as cramics, rock, and soil       |                              |
| **Liquid**                               | such as tap water and river water     |                              |
1. Sample preparation

Point for preparation

Ideal sample for XRF

1. Flat surface
2. Small particle size
3. Homogeneous composition
4. Abundant (or fixed) thickness

Primary X-ray

Fluorescent X-ray

Penetration depth

Escape depth

Analytical depth
**Lambert-Beer law**

\[ I = I_0 \exp (-\mu_\lambda \cdot \rho \cdot d) \]

- \( I_0 \): Incident X-ray intensity
- \( I \): Transmitted X-ray intensity
- \( d \): Thickness (cm)
- \( \rho \): Apparent density (g cm\(^{-3}\))
- \( \mu_\lambda \): Mass-absorption coefficient (cm\(^2\) g\(^{-1}\))

**Half-thickness \((t_{1/2})\):**

\[ t_{1/2} = \frac{\ln(I_0/I)}{\mu_\lambda \cdot \rho} = \frac{\ln 2}{\mu_\lambda \cdot \rho} = \frac{0.693}{\mu_\lambda \cdot \rho} \]

* 1. Sample preparation

1. Sample preparation

Example of half-thickness

<table>
<thead>
<tr>
<th>Analytical Line</th>
<th>Energy* / keV</th>
<th>Epoxy resin**</th>
<th>Polyvinyl chloride**</th>
<th>Soil**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr Kα</td>
<td>5.41</td>
<td>0.28</td>
<td>0.036</td>
<td>0.030</td>
</tr>
<tr>
<td>Br Kα</td>
<td>11.92</td>
<td>2.6</td>
<td>0.33</td>
<td>0.28</td>
</tr>
<tr>
<td>Cd Kα</td>
<td>23.17</td>
<td>7.5</td>
<td>1.4</td>
<td>1.2</td>
</tr>
<tr>
<td>Hg Lα</td>
<td>9.98</td>
<td>1.6</td>
<td>0.20</td>
<td>0.17</td>
</tr>
<tr>
<td>Pb Lβ</td>
<td>12.6</td>
<td>2.9</td>
<td>0.38</td>
<td>0.31</td>
</tr>
</tbody>
</table>


**, 1000 μg g⁻¹ of Cr, Br, Hg, and Pb; and 100 μg g⁻¹ of Cd.
Epoxy resin, 1.3 g cm⁻³; PVC, 1.4 g cm⁻³; soil, 2.7 g cm⁻³.
Penetration and escape depth

**Half-thickness** ($t_{1/2}$)

$$t_{1/2} = \frac{\ln(I_0/I)}{\mu_\lambda \cdot \rho} = \frac{\ln 2}{\mu_\lambda \cdot \rho} = \frac{0.693}{\mu_\lambda \cdot \rho}$$

**10%-thickness** ($d_{0.10}$)

$$d_{0.10} = \frac{\ln(I_0/I)}{\mu_\lambda \cdot \rho} = \frac{\ln(1/0.10)}{\mu_\lambda \cdot \rho} = \frac{2.303}{\mu_\lambda \cdot \rho} = t_{1/2} \times 3.3$$

**5%-thickness** ($d_{0.05}$)

$$d_{0.05} = \frac{\ln(I_0/I)}{\mu_\lambda \cdot \rho} = \frac{\ln(1/0.05)}{\mu_\lambda \cdot \rho} = \frac{2.996}{\mu_\lambda \cdot \rho} = t_{1/2} \times 4.3$$

Penetration depth
Escape depth : $t_{1/2} \times 3 \sim 4$
<table>
<thead>
<tr>
<th>Analytical Line</th>
<th>Energy* / keV</th>
<th>Epoxy resin**</th>
<th>Polyvinyl chloride**</th>
<th>Soil**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr Kα</td>
<td>5.41</td>
<td>1.1</td>
<td>0.15</td>
<td>0.12</td>
</tr>
<tr>
<td>Br Kα</td>
<td>11.92</td>
<td>10</td>
<td>1.3</td>
<td>1.1</td>
</tr>
<tr>
<td>Cd Kα</td>
<td>23.17</td>
<td>30</td>
<td>5.7</td>
<td>5.0</td>
</tr>
<tr>
<td>Hg Lα</td>
<td>9.98</td>
<td>6.2</td>
<td>0.80</td>
<td>0.69</td>
</tr>
<tr>
<td>Pb Lβ</td>
<td>12.6</td>
<td>11</td>
<td>1.5</td>
<td>1.2</td>
</tr>
</tbody>
</table>


**, 1000 μg g⁻¹ of Cr, Br, Hg, and Pb; and 100 μg g⁻¹ of Cd. Epoxy resin, 1.3 g cm⁻³; PVC, 1.4 g cm⁻³; soil, 2.7 g cm⁻³.
Particle size effect (1)

X-ray depth = Half-thickness × 3~4

\[ t_{1/2} = \frac{\ln 2}{\mu_\lambda \cdot \rho} = \frac{0.693}{\mu_\lambda \cdot \rho} \]

- \( t_{1/2} \): Half thickness (cm)
- \( \mu_\lambda \): Mass-absorption coefficient of X-ray with certain wavelength (\( \lambda \)) to sample (cm\(^2\) g\(^{-1}\))
- \( \rho \): Sample density (g cm\(^{-3}\))

1. Sample preparation
1. Sample preparation

**Particle size effect (2)**

**X-ray depth** = Half-thickness $\times 3 \sim 4$

$$t_{1/2} = \frac{\ln 2}{\mu_\lambda \cdot \rho} = \frac{0.693}{\mu_\lambda \cdot \rho}$$

- $t_{1/2}$: Half thickness (cm)
- $\mu_\lambda$: Mass-absorption coefficient of X-ray with certain wavelength ($\lambda$) to sample (cm$^2$ g$^{-1}$)
- $\rho$: Sample density (g cm$^{-3}$)

---

**Sample**

**Primary X-ray**

**Fluorescent X-ray**
## Analytical depth – Igneous rock

<table>
<thead>
<tr>
<th>Analytical Line</th>
<th>Energy* / keV</th>
<th>Depth** / μm</th>
<th>Analytical Line</th>
<th>Energy* / keV</th>
<th>Depth** / μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na Kα</td>
<td>1.04</td>
<td>3.0</td>
<td>Fe Kα</td>
<td>6.4</td>
<td>84</td>
</tr>
<tr>
<td>Mg Kα</td>
<td>1.25</td>
<td>5.0</td>
<td>Ni Kα</td>
<td>7.48</td>
<td>160</td>
</tr>
<tr>
<td>Al Kα</td>
<td>1.49</td>
<td>7.5</td>
<td>Cu Kα</td>
<td>8.05</td>
<td>190</td>
</tr>
<tr>
<td>Si Kα</td>
<td>1.74</td>
<td>9.2</td>
<td>Zn Kα</td>
<td>8.64</td>
<td>230</td>
</tr>
<tr>
<td>P Kα</td>
<td>2.01</td>
<td>6.7</td>
<td>Rb Kα</td>
<td>13.4</td>
<td>800</td>
</tr>
<tr>
<td>K Kα</td>
<td>3.31</td>
<td>27</td>
<td>Sr Kα</td>
<td>14.2</td>
<td>840</td>
</tr>
<tr>
<td>Ca Kα</td>
<td>3.69</td>
<td>35</td>
<td>Y Kα</td>
<td>15</td>
<td>1100</td>
</tr>
<tr>
<td>Ti Kα</td>
<td>4.51</td>
<td>53</td>
<td>Zr Kα</td>
<td>15.8</td>
<td>1200</td>
</tr>
<tr>
<td>V Kα</td>
<td>4.95</td>
<td>110</td>
<td>Nb Kα</td>
<td>16.6</td>
<td>1400</td>
</tr>
<tr>
<td>Cr Kα</td>
<td>5.41</td>
<td>130</td>
<td>Ba Lα</td>
<td>4.47</td>
<td>51</td>
</tr>
<tr>
<td>Mn Kα</td>
<td>5.9</td>
<td>69</td>
<td>Pb Lβ</td>
<td>12.6</td>
<td>660</td>
</tr>
</tbody>
</table>


Density: 2.7 g cm⁻³, Elemental composition: rock references issued by Geological Survey of Japan.
1. Sample preparation

**Analytical depth** - Igneous rock

- **Penetration**
  - X-ray
  - Na $K\alpha$: 1.04 keV
  - Fe $K\alpha$: 6.40 keV
  - Flatness, grains, homogeneity: $≤ 3 \, \mu m$

- **Absorption**
  - $\uparrow 3 \, \mu m$
  - $\downarrow 84 \, \mu m$

**Excitation**

**Rock** (ideal)
1. Sample preparation

Analytical depth – Igneous rock

Excitation

Penetration

X-ray

Na Kα
1.04 keV

Absorption

Fe Kα
6.40 keV

Flatness, grains, homogeneity

≤ 3 μm
1. Sample preparation

**Homogenization**

**Heterogeneous sample**

: Pulverization and mixture

**Example**

Granodiorite (sampled at Taba-River, Yamanashi, Japan)

- Default
- Coarse grains
- Sieving < 500 μm
- Ball milling 10 min (ca. 25 μm) Modal diam.
- Ball milling 60 min (ca. 10 μm) Modal diam.
1. Sample preparation

**Preparation for solid sample**

**Heterogeneous sample**

- Pulverization and mixture
  - Agate pestle and mortar
  - Ball mill (Fritsch, P-6)

**Drying**

**Specimens for powder**

- (1) Loose powder
- (2) Powder pellet
- (3) Glass bead
1. Sample preparation

Measurement of particle size

Measurement of particle size distribution

Sieving

No particle feel < 10~15 μm

Good particle size

“≤ Analytical depth ” or “constant (e.g. 10–15 μm)”
1. Sample preparation

Example 1. Preparation of rock


- **Preparation of rock**
  - Sample: 0.400 g
  - Flux: 4.000 g

**Sample preparation**

- **Rock**
- **Ultrasonic cleansing**
- **Smashing**
- **Pulverizing with alumina mortar and pestle**
- **Sieving** < 500 μm

- **Glass bead** (35 mm diam.)
- **High-frequency induction heating**
- **Drying at 600°C for 1 h**
- **Ball milling for 60 min**

- **Pre-heat**: 800°C, 120 s
- **Melt**: 1200°C, 120 s
- **Agitation**: 1200°C, 120 s

- **Sample**: 100 g
Example 2. Preparation of fly ash

Fly ash of municipal solid waste

Ball milling for 80 min

Sample: 10 g

Drying at 110±5°C for 18 h

Sample: 1.1 g

ABS ring
Inner diam.: 18 mm
Height: 7 mm

Sample thickness

Analytical depth $\gg$ particle (sample) size

Sample thickness (amount): Fixed or Abundant

*Rice grains and plastic disc composed of C, H, and O*

Example: $\text{Cd K}\alpha$ (23.17 keV)

Large analytical depth
1. Sample preparation

Analytical depth – Plastic

![Graph showing Cd Kα intensity vs. sample amount for polyester discs labeled JSAC0611 to JSAC0615.]

JSAC0611–6015, Polyester disc CRMs for XRF of hazardous metal.

1. Sample preparation

Analytical depth – Rice

Rice grains*

\[ \text{Cd Kα Intensity / kcps} \]

- ●, brown rice grain
- ○, white rice grain containing 10 mg kg\(^{-1}\)

Thickness / g cm\(^{-2}\)

Conclusion – points of preparation

For reliable XRF determination

- Estimate of “Analytical depth”!!
- Preparation of “specimen” such as loose powder, powder pellet, and glass bead.

Small depth
- (1) Homogenization
- (2) Particle size < the depth
- (3) Flat surface
- (4) Abundant thickness

Large depth
>> grain or sample size
- Fixed thickness and sample amount
  (or abundant thickness and the amount)

1. Sample preparation
Determination methods

Fundamental parameter
Calculation by software with XRF spectrometer, using experimental and theoretical intensities

- Simple and convenient
- Dependence on program
- Total of measured analytes = 100%

Calibration curve
Calculation from regression line based on measurement data

\[ I = aC + b \]

- Use of measurement data
- Analysis of only targets
- Complication by drawing the curves
2. Determination

Calibration standard

**Reference materials**
- National Institute of Standards and Technology (NIST)
- International Atomic Energy Agency (IAEA)

**Synthesis standards**
- Mixture of high purity reagent
- Matrix added solution containing analytes

- Commercial products:
  - Convenient
  - Limited composition
  - Bias of plots

- Selectable composition
- Complicated preparation
2. Determination

Validation

Reference materials similar to “sample”

Available

Analysis of reference materials

Geochemical references (GSJ)

Polyester disc CRMs (JSAC)

Unavailable

Cross check using other method such as AAS and ICP-AES

AAS Zeenit 600s (Analytik Jena AG)
Example of reference materials

National Institute of Standards and Technology (NIST)

278 Obsidian Rock
688 Basalt Rock
1633c Trace Elements in Coal Fly Ash
1646a Estuarine Sediment
2587 Trace Elements in Soil
2689 Coal Fly Ash and more

List (https://www-s.nist.gov/srmors/pricerpt.cfm)
3. Examples of specimen

Loose powder specimen

- Support
- Holder

**Tapping !!**

Polymer film (polypropylene)

Analytical surface

- Very simple preparation
- Large sample amount (several grams)
- Low reproducibility
- Low homogeneous powder

**Determination**: × or △ light elements
- ○ heavy elements
3. Examples of specimen

Hazardous metals in soil


8 g of soil (< 12.5 μm modal diam.)

Polyethylene cup

Polypropylene film (6-μm-thick)

Spike test of Cr, As, Se, Cd, and Pd added to soils

<table>
<thead>
<tr>
<th>Added /mg kg⁻¹</th>
<th>Powder pellet</th>
<th>Loose powder</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pumiceous soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>986</td>
<td>1066</td>
</tr>
<tr>
<td>As</td>
<td>493</td>
<td>500</td>
</tr>
<tr>
<td>Se</td>
<td>1972</td>
<td>1923</td>
</tr>
<tr>
<td>Cd</td>
<td>986</td>
<td>988</td>
</tr>
<tr>
<td>Pb</td>
<td>1479</td>
<td>1502</td>
</tr>
<tr>
<td><strong>Gravel soil</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr</td>
<td>491</td>
<td>485</td>
</tr>
<tr>
<td>As</td>
<td>982</td>
<td>969</td>
</tr>
<tr>
<td>Se</td>
<td>982</td>
<td>954</td>
</tr>
<tr>
<td>Cd</td>
<td>1473</td>
<td>1490</td>
</tr>
<tr>
<td>Pd</td>
<td>1964</td>
<td>1970</td>
</tr>
</tbody>
</table>
3. Examples of specimen

**Rare metals in printed-board ash**


**Determination:** Co, Ni, Pd, Ag, and Au

**Ash** *(ca. 2.9 μm modal diam.)*

**Acrylic plate**

**Polypropylene film** *(6-μm-thick)*

**Mesh for powder-support**

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**Graphs:**

- **Co**
  - $r = 0.992$
  - $a = 1.03$
  - $b = -5.89$

- **Ni**
  - $r = 0.991$
  - $a = 1.07$
  - $b = 112$

- **Pd**
  - $r = 0.988$
  - $a = 1.04$
  - $b = -1.38$

- **Ag**
  - $r = 0.994$
  - $a = 1.08$
  - $b = 10.7$
3. Examples of specimen

Cadmium in brown rice grain


- Rice grains: 7 g constantly
- Analytical depth of CdKα: 65 mm
- Polypropylene film (6-μm-thick)
- Polyethylene cup: 23 mm thickness

![Diagram showing calibration curve of CdKα with points representing brown and white rice grains, and notes on correction by RhKα-Compton scattering]

Calibration curve of CdKα

- ●, brown rice grain
- ○, white rice grain

Correction by RhKα-Compton scattering

Brown rice ≈ White rice

Intensity ratio

Concentration/mg kg⁻¹
3. Examples of specimen

Loose powder for 100 mg-sample


Sample: 100 mg-powder of ancient pottery
Flat surface and no film: measurement of light elements
Chamber: He-flow
Determination: 10 major and 12 minor elements
3. Examples of specimen

**Powder pellet specimen**

- Improved reproducibility by “press”
- Low homogeneous powder (particle size and constituent)

*Determination*: ▲ light elements ○ heavy elements
3. Examples of specimen

18 elements in fly ash


1.1 g of fly ash of municipal solid waste (ca. 12 μm modal diam.)

<table>
<thead>
<tr>
<th>Element</th>
<th>Present / mass%</th>
<th>Certified / mass%</th>
<th>Present / μg g⁻¹</th>
<th>Certified / μg g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na₂O</td>
<td>0.22 (5.0)</td>
<td>0.39</td>
<td>Cr 274 (3.0)</td>
<td>198</td>
</tr>
<tr>
<td>MgO</td>
<td>0.64 (1.0)</td>
<td>0.94</td>
<td>Ni 154 (2.0)</td>
<td>121</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>29.4 (0.8)</td>
<td>29.5</td>
<td>Cu 118 (2.0)</td>
<td>113</td>
</tr>
<tr>
<td>SiO₂</td>
<td>44.9 (0.4)</td>
<td>45.1</td>
<td>Zn 206 (0.7)</td>
<td>210</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.29 (0.7)</td>
<td>0.45</td>
<td>Pb 68.7 (2.0)</td>
<td>68.2</td>
</tr>
<tr>
<td>SO₄</td>
<td>0.42 (1.3)</td>
<td>0.62</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
</tr>
<tr>
<td>K₂O</td>
<td>2.5 (0.5)</td>
<td>3.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>2.8 (0.3)</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiO₂</td>
<td>2.1 (2.0)</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO</td>
<td>0.018 (4.0)</td>
<td>0.017</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>16.9 (0.2)</td>
<td>15.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Br</td>
<td>N. D.</td>
<td>0.00026</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Total: 99.8 99.9

(), relative standard deviation, n = 5.
3. Examples of specimen

Glass bead specimen

- Homogeneous glass body by fusion process
- Decrease of matrix effect by dilution with flux
- High durability and preservation
- Complicated preparation
3. Examples of specimen

**Precautions for glass bead**

(1) Volatile-elements can’t be analyzed because of high-temperature process.

(2) Melt of reduction materials (organic, sulfide, and metal) seriously damage Pt crucible.

(3) Poor pulverization of sample and short mixing of sample and flux remain powders and bubbles in the specimen.

(4) In cooling process, some shock on melt produce the devitrified and broken specimen.

The white parts are Pt removed from the crucible.
Major components in pottery


3. Examples of specimen

**Determiniation of ancient potteries**

<table>
<thead>
<tr>
<th></th>
<th>Hodogaya-pottery (in Jomon period)</th>
<th>Daikata-pottery (in Yayoi period)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na$_2$O</td>
<td>0.978 (0.6)</td>
<td>0.798 (1.0)</td>
</tr>
<tr>
<td>MgO</td>
<td>1.19 (1.2)</td>
<td>0.674 (0.8)</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>21.9 (0.4)</td>
<td>18.7 (0.1)</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>57.3 (0.4)</td>
<td>67.5 (0.1)</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.080 (0.7)</td>
<td>1.33 (0.1)</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.850 (0.3)</td>
<td>0.981 (0.6)</td>
</tr>
<tr>
<td>CaO</td>
<td>1.37 (0.5)</td>
<td>1.37 (0.1)</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>1.27 (0.4)</td>
<td>0.994 (0.2)</td>
</tr>
<tr>
<td>MnO</td>
<td>0.100 (0.2)</td>
<td>0.014 (1.4)</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>13.3 (0.4)</td>
<td>7.30 (0.1)</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>98.4</td>
<td>99.7</td>
</tr>
</tbody>
</table>

\( (), \) relative standard deviation, \( n = 5 \).
3. Examples of specimen

42 components in felsic rocks


<table>
<thead>
<tr>
<th>Sample-to-flux ratio</th>
<th>Components (total 42)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:10 (Sample: 0.4 g)</td>
<td>14 components</td>
</tr>
<tr>
<td></td>
<td>Major (mass%): Na₂O, MgO, Al₂O₃, SiO₂, P₂O₅, K₂O, CaO, TiO₂, Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>Minor (μg g⁻¹): Rb, Sr, Y, Zr</td>
</tr>
<tr>
<td>1:2 (Sample: 1.5 g)</td>
<td>14 components (μg g⁻¹)</td>
</tr>
<tr>
<td></td>
<td>V, Cr, Co, Ni, Cu, Zn, Ga, As, Nb, Ba, W, Pb, Th, U</td>
</tr>
<tr>
<td>1:1 (Sample: 2.2 g)</td>
<td>14 components (μg g⁻¹)</td>
</tr>
<tr>
<td></td>
<td>Sc, Sn, Cs, La, Ce, Pr, Nd, Sm, Gd, Dy, Er, Yb, Hf, Ta</td>
</tr>
</tbody>
</table>

**Calibration curves**: synthesis standards

**Validation**: GSJ Geochemical References

GSJ, Geological Survey of Japan

**Application**: granite, rhyolite, and obsidian
3. Examples of specimen

**1:300 glass bead for 11 mg-sample**


**Reduction of sample amount**

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Sample-to-flux</th>
<th>Sample</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 mm</td>
<td>1:10</td>
<td>400 mg</td>
<td>4000 mg</td>
</tr>
<tr>
<td></td>
<td>(Regular)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35 mm</td>
<td>1:300</td>
<td>11 mg</td>
<td>3289 mg</td>
</tr>
<tr>
<td></td>
<td>(Proposed)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Calibration curves:** synthesis standards

**Determination:** 10 major oxides

(Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe)

**Validation:** GSJ Geochemical References

**Application:** rock and pottery
3. Examples of specimen

12.5 mm glass bead for 11 mg-sample


### Reduction of sample and flux

<table>
<thead>
<tr>
<th>Diameter</th>
<th>Sample-to-flux</th>
<th>Sample</th>
<th>Flux</th>
</tr>
</thead>
<tbody>
<tr>
<td>35 mm (Regular)</td>
<td>1:10</td>
<td>400 mg</td>
<td>4000 mg</td>
</tr>
<tr>
<td>12.5 mm (Proposed)</td>
<td>1:36</td>
<td>11 mg</td>
<td>396 mg</td>
</tr>
</tbody>
</table>

**Pre-heat:** 900°C, 60 s  
**Melt:** 1250°C, 60 s  
**Agitation:** 1200°C, 120 s

**Calibration curves:** Synthesis standards

**Determination:** 10 major oxides  
(Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe)

**Validation:** GSJ Geochemical References

**Application:** rock and pottery
3. Examples of specimen

Micro-glass-bead for 1.1 mg-sample


![Diagram of sample preparation process]

- **Mixed powder**
  - Sample: 1.1 mg
  - Flux: 11 mg

- **10 μl drop**: 1.84 mass% LiCl solution (releasing agent)

- **Pre-heat**: 800°C, 60 s
- **Melt**: 1000°C, 60 s

**Determination**: 10 major oxides (Na, Mg, Al, Si, P, K, Ca, Ti, Mn and Fe)

- **About 3.5 mm diameter**
- **About 0.8 mm thickness**
3. Examples of specimen

Conclusion – specimen

The specimen should be selected based on “sample characteristics”, “analytical components”, and “reliability for purposes”.

- Glass bead
- Powder pellet
- Loose powder

Simple and convenient

Heterogeneous sample

No-preparation

Reliability
Conclusion

For reliable XRF determination

(1) Estimate of “Analytical depth”
   for consideration of Homogeneity, particle size, surface, and thickness

(2) Preparation of specimen for powder
   Simplicity: no-preparation > loose powder > powder pellet > glass bead
   Reliability: glass bead > powder pellet > loose powder > no-preparation

(3) Validation of the method
   by analysis of reference materials or cross check using another method