

Sample preparation for X-ray fluorescence analysis

II. Pulverizing methods of powder samples

Atsushi Morikawa*

1. Introduction

In the X-ray Fluorescence analysis (XRF) field, it may fairly be said that sample preparation can be the largest factor that cause analysis error^{(1), (2)}. Especially for the analysis of powder samples, as mentioned in the previous edition [Sample preparation for X-ray Fluorescence Analysis I.], heterogeneity effects such as grain size effect, mineralogical effect and segregation can result in analysis error because of its effect on the X-ray fluorescence intensity. When more precise analysis is required, it is recommended to analyze the sample after pulverization to eliminate the grain size effect and segregation as much as possible. For the fusion bead method which can remove the influences of grain size and mineralogical effects, the pulverization of the sample beforehand may be a key point in successfully preparing a homogeneous fusion bead sample with high reproducibility.

This issue describes the important points for pulverization to make powder samples with particle size less than $50\mu\text{m}$.

2. Pulverizers and vessels

Commonly used pulverization tools are described below.

2.1. Pulverizers

As a pulverizer, vibration type pulverizers such as disk, rod and ball mills, or automatic mortars are used. In this section, commonly used vibration type pulverizer is explained. Figure 1 shows typical pulverizers. Disk mill shown in Fig. 1(a) can pulverize samples of about 100g at a time. Using this disk mill, when small pulverizing vessels are used, three vessels can be

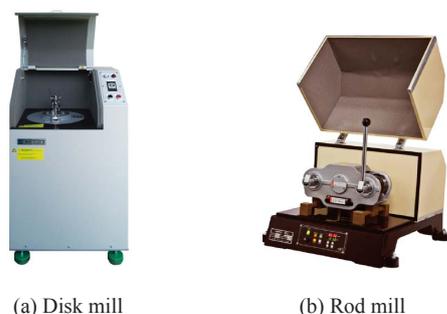


Fig. 1. Sample pulverizers.

mounted at a time, although sample amount which can be pulverized is 10–20g for each. On the other hand, rod mill of the Fig. 1(b) can mount two small vessels at a time.

On the other hand, a small amount of sample (less than several grams) can be pulverized manually with an agate mortar, since the preparation with a pulverizer can be quite difficult.

2.2. Vessels

2.2.1. Materials

Grain size of sample after pulverization varies depending on weight of the vessel and its material. Typical vessel materials are alumina, tungsten carbide, chrome steel, zirconia, etc. For example, since the tungsten carbide is heavy and hard, it has a high grinding capability. Figures 2 show commonly used pulverizing vessels.

Regardless of vessel type, small amounts of the vessel material can be contaminated into the sample. Therefore, it is important to be aware of the elements of interest and its concentrations. Details about the contamination are discussed in section 5.2.

2.2.2. Rods

Available pulverizing rods with different shape are shown in Fig. 3. The cutting rod is used for coarse crushing of fibrous samples such as a plant leaves or resin sample. To obtain highly fine powders, pulverizing balls can be used. The standard round rod can be said to be the most practical rod in terms of pulverization efficiency and ease in cleaning.

However, pulverization capability will decline with long term use due to wearing of the rod. Such a case, X-ray intensity obtained from the sample measurement may change because of insufficient pulverization efficiency.

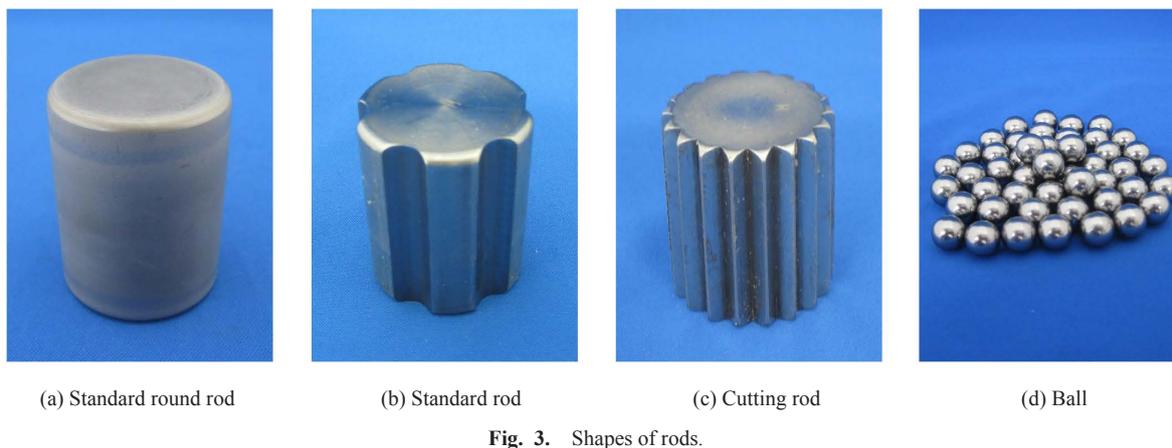
3. Pulverizing methods

3.1. Pulverizing time

Common pulverizing times are several tens of seconds up to 5 min. It is necessary to increase pulverizing time in case of hard samples such like ores. In case of quantitative analyses, it is necessary to keep the pulverizing condition consistent for both standard samples and unknown samples by using the same sample amount and pulverizing time (Refer to section 5.1.).

Grain size after pulverization of less than $50\mu\text{m}$ is

* SBU WDX, X-ray Instrument Division, Rigaku Corporation.



desirable. A general rule of desirable grain size is that the powder does not feel rough or that it can thumb for fit between a fingertip grooves⁽²⁾. If possible, it is recommended to measure the actual sample to find the relationship between X-ray intensity and pulverizing time, and choose the pulverizing time where X-ray intensity saturates⁽¹⁾. Figure 4 shows the relationship between X-ray intensity and pulverizing time for silicon dioxide (SiO₂) reagent pulverized by a tungsten carbide vessel. If speed of sample preparation is more important than analysis precision, pulverizing time can be set at 2 min where change in X-ray intensity of Si-K α is small. On the other hand, if high analysis precision is required and speed is not critical, pulverizing time of 5 min can be chosen.

3.2. Effects of pulverization aid

Some samples can show agglomeration when pulverized, which results in reduced impact force

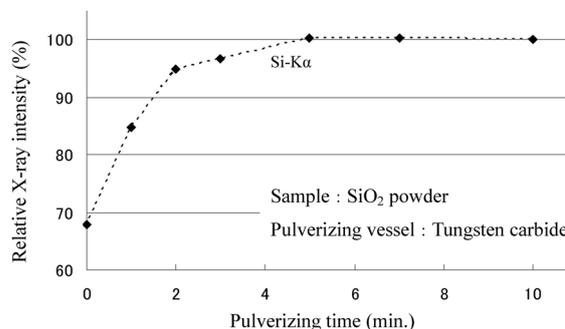


Fig. 4. Relationship between pulverizing time and X-ray intensity.

on the sample by the rod⁽³⁾. To counter this effect, pulverization aids are used which can prevent build up of agglomeration.

There are liquid and solid pulverization aids.

Liquid aid has the advantage that it does not remain in the sample by drying and volatilizing whereas after pulverization. Pulverization with liquid aid is called wet pulverization, without liquid is called dry pulverization. Figures 5 show the inside of the vessel after pulverization with and without *n*-hexane as pulverization aid. As clearly shown in Fig. 5, it is possible to improve pulverization capability and reduce powder adhesion to the vessel wall by using the pulverization aid. Additive amount is roughly 0.6–0.8 mL of *n*-hexane for 1 g of sample, but it is recommended to adjust the amount of aid so that the sample is reasonably wet when collected from the vessel after pulverization.

When using *n*-hexane as pulverization aid, the sample should be dried at 80°C for 30 min prior to forming the powder into a pressed pellet. Since the generated heat due to friction during pulverization turns into vaporized heat when using *n*-hexane, it has also the effect of reducing the likelihood of igniting easily ignitable samples.

On the other hand, when solid pulverization aids such as carbon is used, it is possible to get high pulverization capability by dry pulverization. However, it is important to keep the weight ratio of sample vs. aid constant since solid aids remain in the sample after pulverization.

3.3. Pulverization with binder

When a powder sample is formed into pressed pellet, a binding aid such as boric acid or Spectro Blend® can be mixed with the sample at a certain ratio to improve the forming capability. Mixing of binder with sample can also be performed in the vessel during the pulverization process.



(a) Wet pulverization (with *n*-hexane) (b) Dry pulverization (without aid)

Fig. 5. Inside of vessels after pulverization.

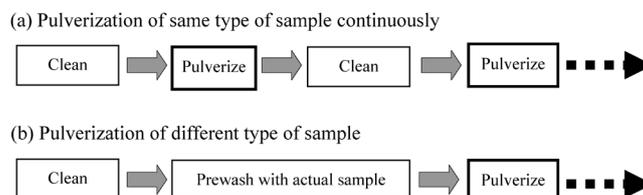


Fig. 6. Example of pulverization procedures.

4. Pulverization procedures

When pulverizing samples, it is also necessary to pay attention to the possible contamination from the previously pulverized sample.

When same type of samples are pulverized in sequence, clean the vessel with an air blower or vacuum cleaner, then pulverize the next sample. Cleaning the vessel with water followed by drying decreases contamination from the previous sample. To pulverize different type of samples in sequence, pulverize a small amount of the new sample before pulverizing the new sample to “pre-wash” the vessel with the actual sample. Figure 6 is an example of pulverization procedures.

5. Other important considerations

5.1. Influence of pulverization on analysis results

Quantification error of powder samples such as minerals is mostly due to grain size effect. However, as mentioned already, the heterogeneity effect such as grain size effect can be reduced by pulverization. Grain size effect has a larger influence on light than heavy elements. Moreover, it is recommended that the grain size for a set of samples is the same. If pulverization condition differs, the analysis result can be different even for the same sample. This is because the X-ray intensity can vary depending on grain size distribution after pulverization. Figures 7 show calibration curves for Al₂O₃ in clay with different grain sizes. It can be seen that the analysis with finer grain size sample gives better accuracy, and confirms that pulverization reduces quantitative error.

5.2. Contamination of sample

There are two sources of sample contaminations, namely from the pulverization vessel material and the remained sample from the previous pulverization.

5.2.1. Contamination from pulverization vessel

During pulverization, the vessel and rod are worn down and small amount of its material enters the sample. For example, several 100 ppm–several 1000 ppm of tungsten may be mixed into the sample when hard materials such as silicate rock, are pulverized in the tungsten vessel for a long time. Therefore, in case of trace element analysis, use of the vessel containing the analyte element should be avoided. Table 1 shows the material of common vessels which are the elements that can be mixed into the sample when pulverized.

Furthermore, it is necessary to consider overlap on the analyte spectrum from the vessel material. For example, trace analysis of mercury (Hg), selenium (Se), and arsenic (As) which are important elements for environmental monitoring analysis become difficult if tungsten (W) is mixed into the sample⁽⁴⁾. Tungsten carbide vessel is therefore not an appropriate choice since Hg-L α line is overlapped by W-L β_2 (Refer to Fig. 8.). Although the overlap correction of W-L β_2 is performed, it is preferred to choose Hg-L β_1 as the analysis line which does not have any overlap, or choose a different pulverization vessel such as zirconia. Compared to wavelength dispersive instruments, contamination from the vessel can be especially problematic for energy dispersive instruments. The poorer resolution results in many overlaps from the tungsten contamination.

5.2.2. Contamination from the previously pulverized sample

Contamination can occur from the previously pulverized sample if the vessel is not sufficiently cleaned. Refer to section 4 “Pulverization procedure” for details.

5.3. Drying of sample

Powder samples can easily absorb the moisture contained in the air. Sample after pulverization increases moisture absorption capability since the surface area to volume ratio of the particles is increased due to smaller grain size. Care should be taken especially for

hygroscopic materials. Absorption of moisture by the sample not only decreases X-ray intensity for light element range but also may lead to preventing the inside of the instrument not properly being evacuated for measurement. Considering these points, it is therefore recommended to dry the sample at 105–115°C for about two hours after pulverization and store it in a desiccator.

5.4. Samples having possibility of ignition

Ferroalloys or powders composed mostly of rare earth elements can potentially ignite due to increase of surface area by pulverization. Spontaneous ignition can occur even at ambient temperatures by reacting with oxygen in the air. Use of liquid nitrogen as a pulverization aid can be effective in such cases⁽⁵⁾. Liquid nitrogen itself is an effective pulverization aid, and also eliminates the possibility of ignition due to its low temperature and causing an absence of oxygen. Furthermore, if a gas replacement type vessel as shown in Fig. 9 is used, pressure build-up due to liquid nitrogen evaporation can be prevented by slowly leaking gas out of the valve. In addition, wearing for example leather gloves is essential when liquid nitrogen is used since the vessel itself becomes extremely-low in temperature.

5.5. Samples difficult to pulverize

When layered sheet like objects such as mica are contained in the sample, it has a tendency to remain unpulverized or only coarsely ground, while the rest of the sample is finely pulverized (mica effect). When such

Table 1. Materials of vessels and possible elements mixed into samples.

Material of vessel	Impurity mixed into sample
Alumina	Al
Tungsten carbide	W, Co, C
Special steel	Cr, Fe
Chrome steel	Cr, Fe
Zirconia	Zr, Hf

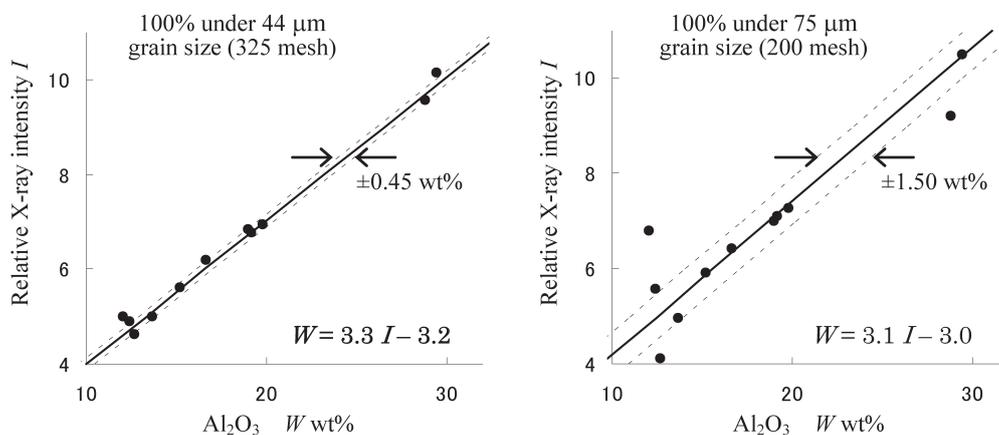


Fig. 7. Grain size effect (Calibration of Al_2O_3 in clay).

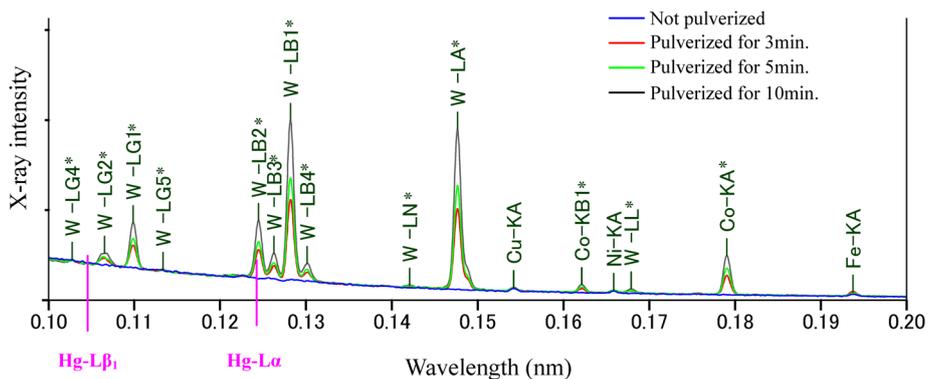


Fig. 8. Influence of contamination from pulverization vessel.
 Instrument: Wavelength Dispersive XRF spectrometer ZSX PrimusII
 Sample: SiO₂ powder, Pulverization vessel: Tungsten carbide
 Peaks with * mark are due to pulverization vessel contamination.



Fig. 9. Specialized gas replacement vessel.

inconsistently pulverized are formed into pressed pellets, the X-ray intensities can vary greatly. In such cases, fusion bead method is preferred preparation technique ⁽¹⁾.

6. Summary

This issue describes appropriate pulverization procedures to obtain analysis results with improved accuracy for powder samples. In practice, the accuracy and precision required by the application are needed to be weighed against the time and effort that can be allotted to sample preparation. The actual sample preparation method is chosen by balancing these considerations.

References

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