Sample preparation for X-ray fluorescence analysis
III. Pressed and loose powder methods

Gakuto Takahashi*

1. Introduction

There are two main sample preparation techniques for measurement of powders with XRF—pressed and loose powder methods—neither requiring any chemical processes. In either case the proper sample preparation and accessories need to be selected to prevent breakage of the pressed powder during measurement. When a thin film for analysis surface (hereafter "sample film") or a binder is used, it is recommended to select the proper sample preparation method to minimize analysis errors of target elements. This note describes key points and considerations for sample preparation by pressed and loose powder methods. In addition, sample preparation technique for the analysis of small quantities of powder sample is introduced.

2. Pressed powder method

Pressed pellets are prepared by pressing loose powders filled in a ring or cup using a set of dies and a press machine. There are two types of dies namely flat disc (Fig. 3) and cylinder types (Fig. 5). The type to be used depends on the characteristic of the powder sample. Ease of pelletization depends on sample characteristics and grain size, and can be improved by sufficient pulverization. Mixing the powder sample with a forming agent (hereafter "binder") is another solution if pelletization is difficult (Fig. 1).

2.1. Rings and cups

Rings and cups used for forming pressed pellets are shown below in Fig. 2. The ring material is either aluminum or PVC, and sizes with 10–43 mm inner diameter (hereafter "ID") are available. Cup material is either aluminum or iron and available IDs are 32–45 mm. Rings are used with the flat type dies, and cups can be used with either type of dies. The cup requires larger quantity of powder than the ring. The larger the analysis area, the higher the sensitivity which results in analysis with higher precision.

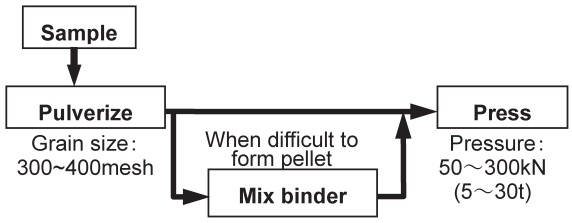


Fig. 1. Process for making pressed pellet

2.2. Type of dies

Selection of die type depends on the characteristics of the sample and is described below.

2.2.1. Flat type dies

A ring placed on a die is filled with the powder sample. Another die is placed on top of the ring and pressure is applied (Fig. 3). Sample quantity is about 3–5 g in case of oxide powders for 30 mm ID rings. Cups can also be used when it is difficult to form pressed pellets or mechanically stronger pellets are required. Advantages of flat type dies are ease of cleaning and different size pellets can be prepared by simply choosing different ring sizes. Material of the ring or cup can also be freely selected depending on available sample quantity and characteristics[(1)]. The material of the die is tool steel. Tungsten carbide (WC) dies can be used for very hard grain samples. Flat type and WC dies are shown in Fig. 4.

2.2.2. Cylinder type dies

The female die (cylinder) is filled with the powder sample and the male die is placed above and pressure is applied to form a pressed pellet (Fig. 5). Dies with various ID (13–45 mm) are available (Fig. 6). It is possible to prepare pressed pellets by placing a cup in the cylinder and filling it with powder sample. In this case, it is necessary to use the proper size cup that fits in the cylinder[(1)]. For organic powders (plants,

Top row: Iron and aluminum cups
Center row: Aluminum rings
Bottom row: PVC rings

Fig. 2. Various rings and cups.

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

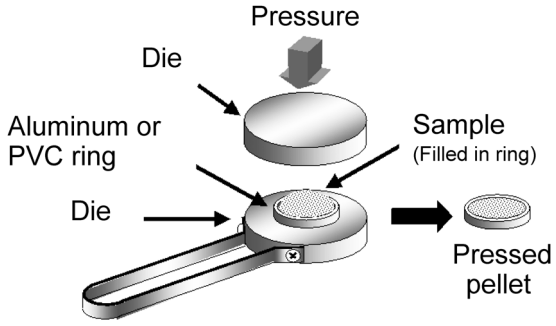
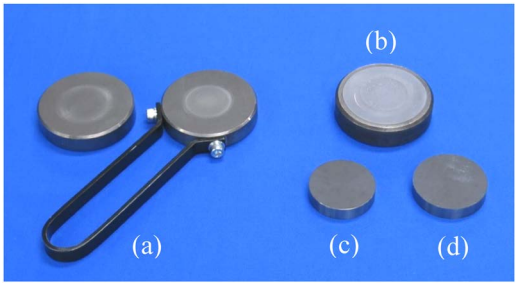


Fig. 3. Sample preparation with flat type dies.



(a) Flat type dies [Cat. No. 3399J401]
(b) WC die pellet (Special order item)
(c) WC die pellet [Cat. No. RS2545]
(d) WC die pellet [Cat. No. RS2550]

Fig. 4. Flat tool steel and WC type dies.

pharmaceutical, biological samples, etc.) which have low bulk density, the cylinder type die is suitable because of its larger capacity to hold sample amount compared to flat dies.

2.3. Binder for pressed pellets

Powders which are difficult to be formed into pellets can be pelletized by mixing binder with the sample ideally by pulverization. Without binder, fine powder particles may fall off or scatter from the pellet surface and cause contamination of the spectrometer's sample chamber in vacuum mode. Powders which particles are spherically shaped such as SiO_2 or burned ash are difficult to pelletize[2]. Mixing ratio of sample to binder is typically 10(sample) : 1(binder) or 10 : 2. It is necessary to determine the purity of the binder as it is necessary to select a binder which does not include the elements to be analyzed. Binders typically used are wax types called Spectro Blend®, polystyrene based powders, or boric acid and cellulose powders (Fig. 7). Addition of binder allows pelletization of powders difficult to form, but accurate weighing and complete mixing is essential to minimize analysis errors.

2.4. Press machine

Manual and automatic press machines are available, and both have either 300 kN or 500 kN maximum load (Fig. 8). Both machines are able to be used for pelletization with flat and cylinder type dies.

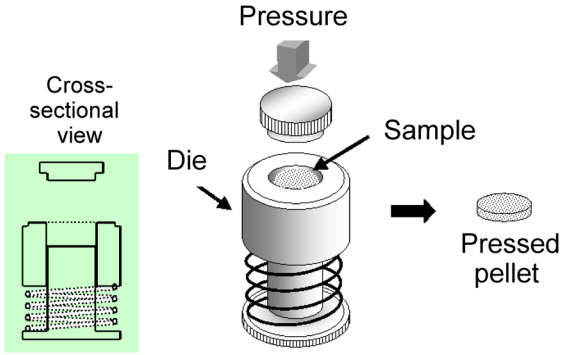


Fig. 5. Sample preparation with cylinder type dies.

(a) RS type dies [Cat. No. RS2013] Pellet dia. 13 mm
(b) SD type dies [Cat. No. 3399J402] Pellet dia. 40 mm

Fig. 6. Cylinder type dies and Trimming die.

Fig. 7. Binder for pelletization (Spectro Blend®).

2.5. Precautions when using press machine

2.5.1. Applied pressure

X-ray intensity changes depending on pelletization pressure. Figure 9 shows the relationship between pressure and X-ray intensity for a cement sample. This graph shows that X-ray intensity increases with applied pressure due to higher sample density. Above a certain pressure the X-ray intensity saturates. Errors due to this effect can be minimized by keeping sample amount and pressure constant for each pellet that is prepared. Sample preparation reproducibility can be further improved by pelletizing the sample with pressure at which X-ray intensity saturates.

When pressure is released after pelletization, the compressed ring and sample can slowly expand over time. This can cause height difference between sample surface and ring resulting in change in X-ray intensity or can even lead to breakage of the pellet [2]. Generally, PVC rings which tend to expand after pressure release are appropriate for samples which also expand. On the

(a) Manual type [Cat. No. 3399K037, 038]

(b) Automatic type [Cat. No. 3399K003, 004]

Fig. 8. Press machines.

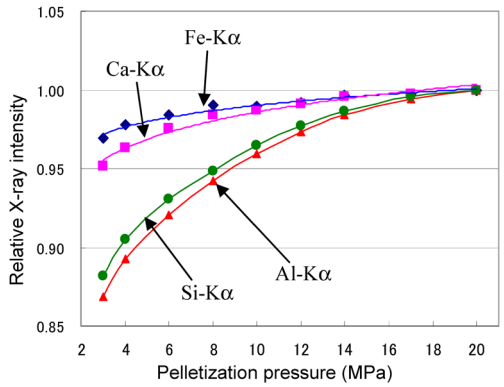


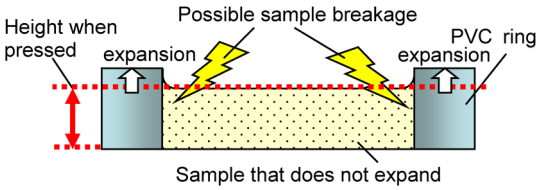
Fig. 9. Relation between pressure applied and X-ray intensity (sample: cement).

other hand, aluminum rings which do not expand are chosen for samples that do not expand after pressure release.

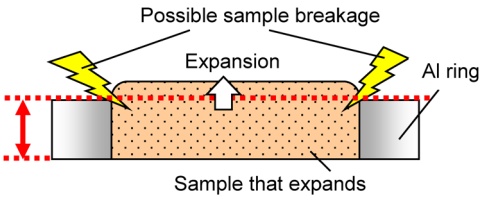
If the target pressure is reached too quickly, sample can crack or be flaky due to expansion of the air trapped in the sample when pressure is released. It is therefore recommended to release pressure several times before target pressure is reached to let air escape from the sample and avoid sample breakage [(2)].

2.5.2. Contamination from die surface

When pelletizing samples, there is a possibility that contamination occurs due to previously pelletized sample remains on the die surface. Therefore, it is recommended to clean the die surface every time before pelletization and to prepare samples starting with lower concentrations[(2)]. Powder sticking to die can be prevented by placing a film in between. Use of the film is effective not only to minimize contamination but also for samples such as iron or titanium oxides which cannot be easily pelletized since significant amount of powder sticks to the die surface as shown in Fig. 11. Sample films such as polypropylene or polyester can be used as film for pelletization. If a sample needs to be repelletized due to breakage, contamination due to ring or cup material may occur.



(a) Pelletized sample with PVC for powder that does not expand after pressure release



(b) Pelletized sample with Al ring for powder that expands after pressure release

Fig. 10. Examples of height difference between sample and ring after pressure release.

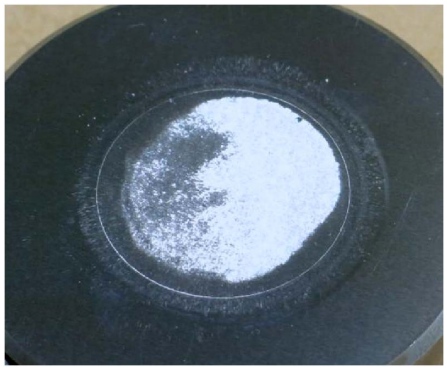


Fig. 11. Titanium oxide powder stuck to die after pelletization

2.6. Special pressed powder methods

2.6.1. Double pellet and embedded methods

Double pellet or embedded methods can be used when sample quantity is too small for pelletization. A previously pressed cellulose or boric acid powder is covered with the small amount of powder sample and pelletized again to form a double pellet. For even smaller sample quantities, place the sample in the center of a previously formed cellulose or boric acid based pellet and reapply pressure to form the embedded pellet. (Figs. 12, 13)[(3)]. Since the sample comes in contact with a different material, this method is not suitable when the sample needs to be completely recovered without contamination and reused. The amount of sample used for these methods should be constant to avoid error caused by thickness differences in calibration method.

2.6.2. Disc for grass sample preparation

Grass samples can be pressed onto polypropylene discs with an adhesive surface. When this is used in combination with cylinder type dies, small quantity of dried grass sample or powder can be measured in

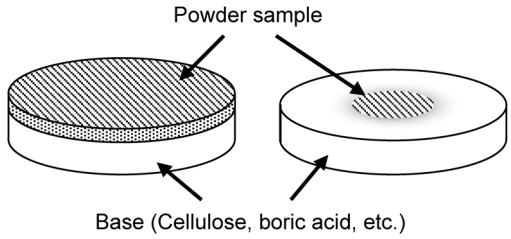
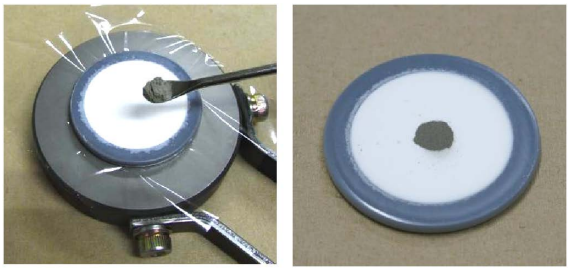
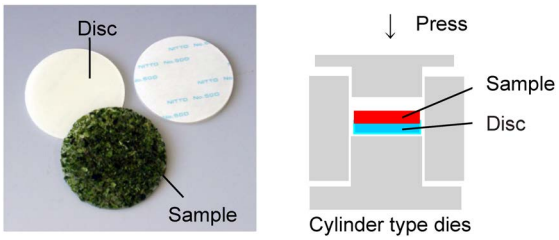


Fig. 12. Special pressed powder methods.



(a) Place sample (10 mg) in center of base pellet (b) Press the sample together with the base pellet

Fig. 13. Pelletization of small amount of sample.



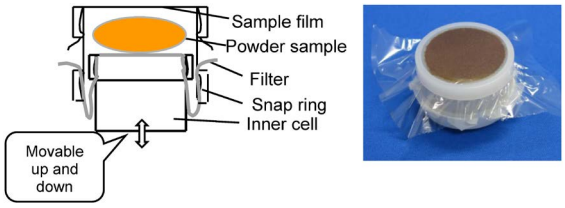
(a) Pressed sample (b) Sample setup

Fig. 14. Disc for grass samples [Cat. No. 3399J403].

vacuum (Fig. 14)[1].

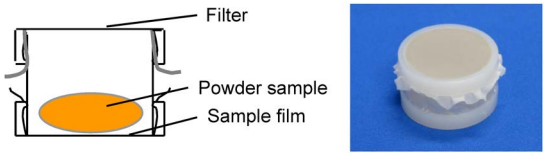
3. Loose powder method

When sample has to be recovered after measurement or powder samples such as graphite and mica which are difficult to form into pellets even using binders, the sample can be measured in vacuum atmosphere by the loose powder method using a special set of cells and films. Since the sample can be recovered after measurement, it can subsequently be analyzed by a different analytical method. Reproducibility of sample preparation however is not as high compared to pressed powder method. Therefore, it is recommended to check the reproducibility beforehand. Moreover, attention should be paid to the fact that the X-ray intensity decreases due to the sample film covering analysis surface. The sensitivities especially for light elements such as $_5$B–$_9$F decreases significantly and can not be measured when using sample film. Film characteristics such as X-ray transmittance will be discussed in a future issue "Sample Preparation for XRF (Liquid samples)." It is also recommended to check the impurities in the various films by making a blank measurement of the film itself.



(a) Structure of cell (b) Cell with sample

Fig. 15. Sample cell for tube above/below types [Cat. No. RS640] (Set including filter).



(a) Structure of cell (b) Cell with sample

Fig. 16. Cell for tube below type [Cat. No. CH1540] (Set without filter).

Great care should be taken that film does not break during measurement to prevent sample chamber contamination by the sample. For powder samples with sharply edged grains, preliminary check by placing the sample cell in a vacuum chamber prior to loading into the instrument to confirm that the film does not break will minimize contamination risk. Furthermore, since integrity of the film may deteriorate and break for long measurement times especially for high power instruments (3–4 kW), optimization of measurement conditions such as shortening measurement time, reduction of the X-ray power, and use of primary beam filters is recommended.

Figure 15 shows a sample cell where the loose powder sample is supported between a sample film attached to the sample cell and a semi-permeable (microporous) filter. This can be used for both X-ray tube above and below instruments. Figure 16 shows a sample cell for the tube below type instruments. The structure of the cell is much simpler than the cell shown in Fig. 15. There are many other cells for different sizes and shapes besides those shown in Figs. 15 and 16. The sample cells are reusable when thoroughly cleaned.

3.1. Sample preparation for very small quantities

Very small quantity (100 mg) of powder can be measured in vacuum atmosphere without pelletization. Two types of cells for such cases are available. A disc as shown in Fig. 17 with either 12 mm or 23 mm ID opening with 1 mm depth to insert the sample into can be used. Sample surface is covered with a sample film and the sample is supported by a breathable filter paper. The ventilation hole at the bottom of the cell must remain open during measurement.

4. Conclusion

Various sample preparation methods for powder samples have been described. It is recommended

(a) Structure of cell for small quantity powder sample

(b) Place sample in opening (Sample: 100 mg coal ash)

(c) Cell with sample

Fig. 17. Cell for very small quantity of powder sample [Cat. No. RS540] (Sample cell set).

to select the appropriate sample preparation and accessories depending on purpose of the analysis by considering target elements, required precision, accuracy and reproducibility of sample preparation

Reference

(1) *Sample Preparation Instruments and Accessories*, Rigaku Corporation, Rigaku Service Corporation (2014), 40−61.

(2) H. Honma: *Sample Preparation Method*, *Keiko Xsen bunseki no jissai*, Edited by Izumi Nakai, Asakura Shoten, (2005), 69−70, (in Japanese).

(3) H. Kohno: *X-ray Fluorescence spectroscopy Introduction and Applications*, Rigaku Corporation, (2011), 199, (in Japanese).