How to measure trace amounts of sample by X-ray fluorescence analysis

Satoshi Ikeda*

1. Introduction

Figure 1 shows typical sample preparation methods for X-ray fluorescence analysis. In general, the shadowed methods are the most popular. Quality control analysis, which requires high precision, normally requires large samples as much as 20 mm–30 mm in diameter. However, in many cases it is difficult to prepare samples large enough or in sufficient quantity for R&D or troubleshooting. Because these samples are precious, there is a strong requirement to recover them after XRF analysis for other analysis methods. This paper introduces sample preparation methods useful for trace sample (small pieces, small amounts of powder, etc.) analysis.

2. Selection of sample preparation method, and precautions for measuring conditions

There are various sample preparation methods for trace amounts of sample depending on the sample size and amount. Figure 2 shows the sample preparation methods discussed in this paper. Choice of sample preparation method should be made in a comprehensive manner, considering the need to recover the sample, the purpose of the analysis (qualitative or quantitative) and the equipment specifications (measurement diameter, measurement atmosphere).

The method of sample embedded in a base material (sample embedded method) is popular when-sample recovery is not necessary. Although this method makes it difficult or impossible to recover and reuse the sample, it is an easy sample preparation technique if pressing dies can be used. On the other hand, if sample recovery is necessary, accessories such as thin film, sample cell, etc. to prevent spillage of sample powder will be required.

If only qualitative analysis is required, selection of an easy sample holding method according to sample size and amount may be accepted. If the sample powder area is smaller than the measuring area in the sample embedded method, it is essential to perform a measurement without sample (blank measurement) to

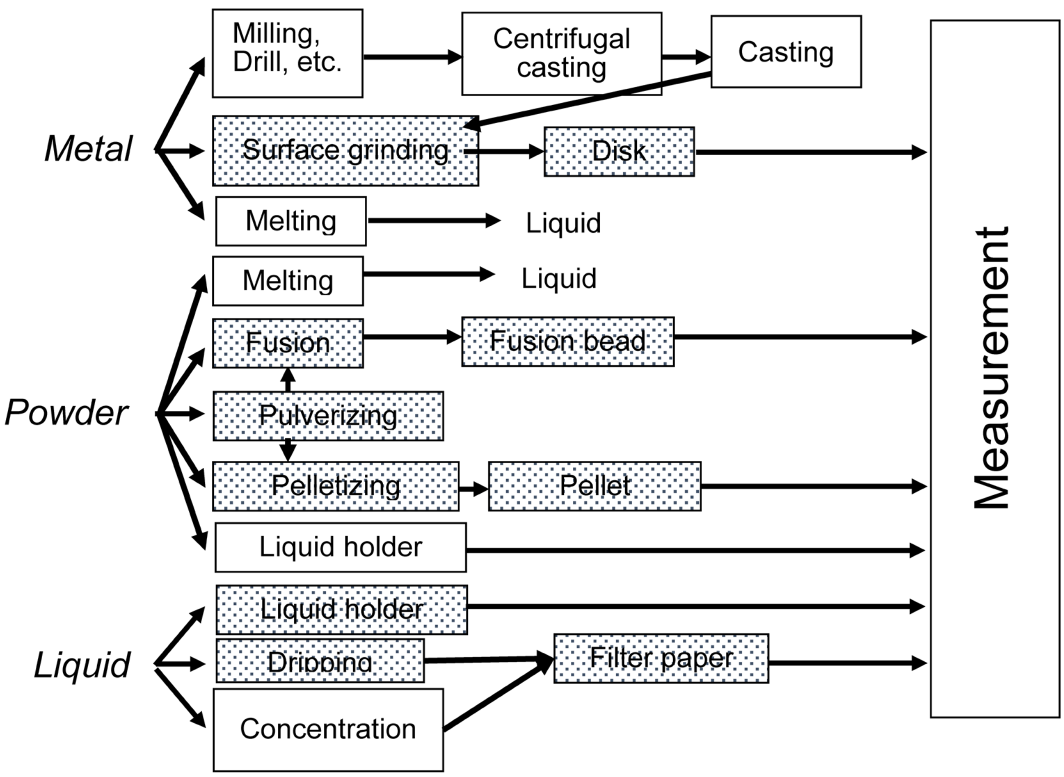

Fig. 1. Typical sample preparation methods.

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

Table 1. Base materials commonly used.

Base material	Remarks
Boric-acid (Composition formula: H_3BO_3)	・Applicable for both flat type dies and cylinder type dies. ・Unsuitable for the analysis of boron and oxygen, which are major components. ・Drying is recommended before forming or measurement because of its high hygroscopic nature. ・It may be difficult to hold sample due to large grain size of boric-acid. Pulverization of the material with an agate mortar will solve this problem.
Cellulose powder (Composition formula: $C_6H_{10}O_5$)	・Sample embedding is much easier than with boric-acid. ・As the bulk density is low, flat type dies are not suitable for making pellet but cylinder type is suitable. ・Unsuitable for the analysis of carbon and oxygen, which are major components. ・Drying is recommended before forming or measurement because of its high hygroscopic nature.

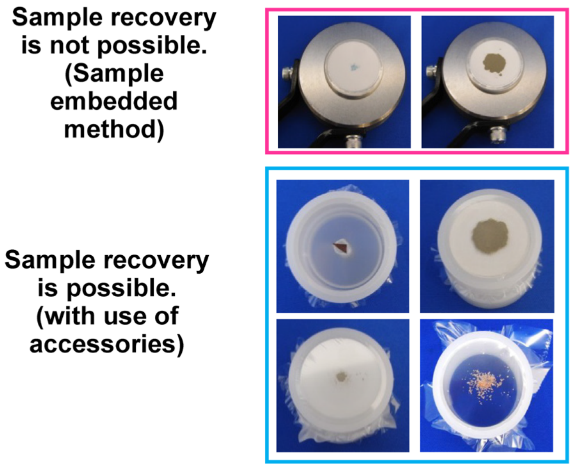

Fig. 2. Sample preparation methods discussed in this paper.

determine components detected from the base material. A blank measurement is also necessary when the sample is a thin film. Attention should be paid not to make a gap on the analysis surface in the case of quantitative analysis (including semi-quantitative analyses such as SQX), and it is recommended to select a smaller measurement area than the embedded sample size. From this perspective, trace amount quantitative analysis is difficult for equipment that does not have a diaphragm for the small diameter analysis area.

3. Sample preparation method for trace sample amount

3.1. When sample recovery is not necessary

Sample embedded method

This method can be used for pieces of solids and for small amounts of powder. The sample is embedded onto the base material by pressing lightly, and then pressed thoroughly to hold the sample. As this method embeds sample onto the base material directly, recovery of the sample is very difficult or almost impossible. However, when the necessary tools for pressing samples are available, it is easy to make pellets by preparing only base material.

A material that has good formability and does not contain analyte elements is optimum as the base material. For example, boric acid reagent and cellulose powder for column chromatography are commonly used

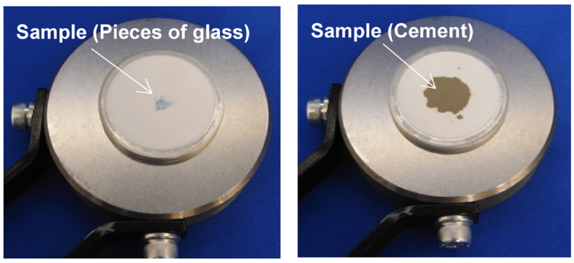

Fig. 3. Example of use of flat type dies.

as base materials because of their low concentrations of impurity (Table 1). An example of the sample embedded method with flat type dies is shown in Fig. 3. Pieces of broken glass and several hundred milligrams of cement powder are embedded onto boric-acid. The outer frame of the base material is an aluminum ring (32 mm inner diameter). First, fill the boric acid into an aluminum ring on a flat type die and press it lightly at around 40 kN. Then place the sample at the center of the ring and apply pressure at around 100 kN. It is recommended to cover the sample with a thin film to prevent spillage of sample powder.

3.2. When sample recovery is necessary

3.2.1. Analysis of a small piece of foreign substance

Minute sample cell [Cat. No. RS840]

This is suitable for holding a small piece of a foreign substance such as broken pieces of metal. Sample recovery is possible as it is held and fixed with double-sided tape or by placing it between thin film and inside board.

The accessory consists of a polyethylene cell covered with a thin film, a lid with a screw and an inside board (Fig. 4). Place the sample on the tip of the screw with double-sided tape. The height of the sample should be adjusted by turning the screw until the sample touches the thin film. The inside board can be used for supporting large samples. If the sample size is large and it can be firmly held by the sample holder mask, the thin film may be removed after using the screw to adjust the height.

3.2.2. Analysis of a trace amount of powder sample

(a) Sample cell for trace amount of powder sample [Cat. No. RS540]

This is suitable for holding powder samples of up to several hundred milligrams. Fill the sample pan with the powder sample and cover the surface with a thin film to prevent spillage. The sample can be easily recovered after analysis because no press forming is required.

The accessory consists of the sample pan, a polyethylene cell and a base cap (Fig. 5). Fill the depressed center of the sample pan with the powder sample and place it into the polyethylene cell and cover with thin film. As the bottom of the sample pan is a breathable filter paper, measurement in a vacuum can be made. Sample pans are available in sizes 12 and 23 mm inner diameter (i.d.), and depth 1 mm. As little as 100 mg of powder can be measured with the 12 mm i.d. sample pan.

(b) Sandwich type sample cell for trace amounts of sample [Cat. No. RS1340]

This is suitable for holding dust, flakes, etc. by placing them between two thin films (Sandwich method). It is used mostly for qualitative analysis.

The accessory consists of a polyethylene sample cell and an acrylic base plate (Fig. 6). Place the film and sample on the sample cell (inside), and make two pinholes in the film with a needle. Then, cover the sample with film and put the outer sample cell over the film so that the sample is held between the films. Pinholes in the thin film allow measurement under vacuum.

(c) Accessories useful for analysis of several tens of milligrams of powder sample

Powder samples in the amount of several tens of milligrams, which are not enough for the trace amount sample cell, can be measured by using a combination of accessories. Both qualitative and semi-quantitative analysis can be performed.

Accessories for this purpose are shown in Fig. 7. To assemble the sample cell, first place the plankton net (small) between the cylinder and the cap of sample cell CH3110 to form a surface on which to place the sample. Next, place sample cell CH1540 covered with film over CH3110. Finally, turn over and cover the bottom of CH1540 with the plankton net (large). Since the plankton net is used, measurement under vacuum condition is possible.

4. Selection of thin film

Because thin films are frequently used to prevent

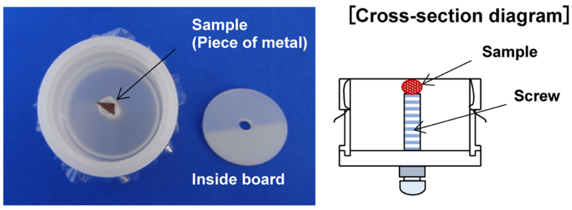

Fig. 4. Minute sample cell.

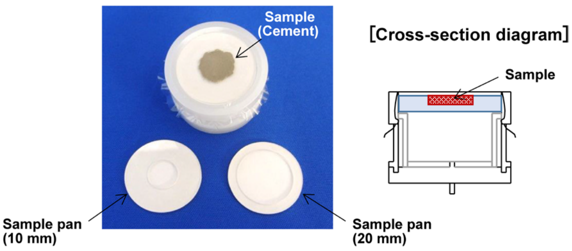

Fig. 5. Sample cell for trace amounts of powder sample.

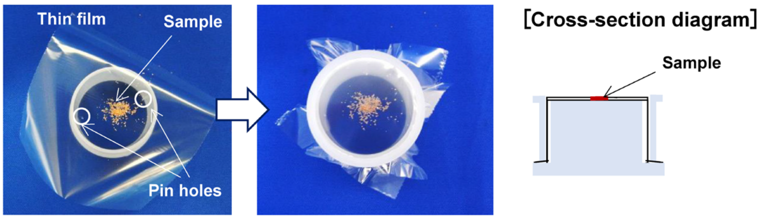

Fig. 6. SW type sample cell for trace amounts of sample.

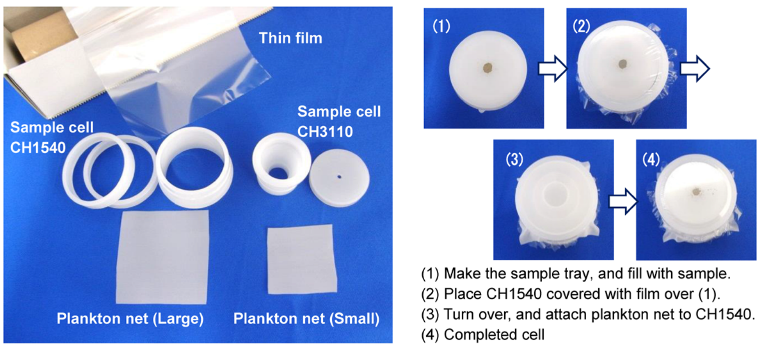

Fig. 7. Accessories useful for analysis of several tens of milligrams of powder samples.

spillage when measuring a trace amount of sample, considerations for the selection of film type are described.

Available thin films types are polyester, polypropylene, polyimide, etc. with thicknesses of around several μm–10μm. Polypropylene, which has a high X-ray transmission rate and low levels of impurities, is normally suitable for the analysis of small pieces of foreign substance and small amounts of powder sample. However, different films may be chosen to take advantage of their respective properties. X-ray transmission rate, durability against X-ray irradiation (including heat radiation), impurities, etc., should all be taken into consideration when selecting a thin film. The transmission rate of fluorescence X-rays differs depending on the film material. Fluorescence X-rays of lower atomic number elements have lower transmission rates, and the analyzable element range is Na–U when thin film is used. X-ray transmission rates of polypropylene film (6μm), polyester film (6μm) and polyimide film (7.5μm) are shown in Fig. 8. It can be seen that polypropylene has relatively higher transmission rates for low atomic number elements. Regarding damage due to X-ray irradiation, polyimide is the most durable, followed by polyester and polypropylene. Although impurities (Si, P, S, Ca, etc.) can vary even between rolls of the same film type, polypropylene has the lowest impurity level, followed by polyester and polyimide. Considering these film properties, polyester 6μm and polypropylene 6μm films are generally the most commonly used.

In many cases, polypropylene film is preferred due to having a high X-ray transmission rate and low impurities. However, because its durability against X-ray irradiation is relatively low, the measurement time should be limited to below around 15 minutes when a high-power X-ray tube (4 kW maximum) is used. Lowering the X-ray tube power to around 2 kW can significantly reduce damage to the film. Use of a primary X-ray beam filter is also very effective.

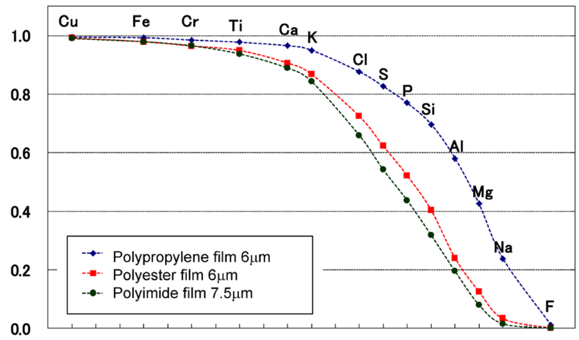

Fig. 8. X-ray transmission rates of various films.

If the analytes are mostly heavy elements, either polyester or polyimide film can be used.

5. Summary

Sample preparation methods for measurement of trace amounts of sample by XRF have been described. It was shown that by using special accessories in combination with sample preparation equipment and unique preparation methods, challenges due to small sample amount can be overcome for routine analysis.