# Sample preparation for X-ray fluorescence analysis IV. Fusion bead method—part 1 basic principals

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## 1. Introduction

For the analysis of powders by XRF, sample inhomogeneity due to segregation, grain size and mineralogical effects influence X-ray intensity and can cause analysis errors. It is therefore recommended to analyze powder samples after fine pulverizing as described in "Sample Preparation for X-ray Fluorescence Analysis II. Pulverizing methods of powder samples(1)." However, when inhomogeneity can not be sufficiently removed by pulverization and more accurate analysis is required, fusion bead (Fig. 1) method is advisable.

The fusion bead method first established in the 1950s(2), has since progressed such that it is not only applicable to powders as oxides but also to non-oxides such as metals, carbides, sulfides which had previously been considered to be difficult(3),(4). Characteristics of the fusion bead method are that (a) analysis error due to grain size and mineralogical effects can be removed, (b) matrix effect is reduced due to dilution, (c) standard samples can be prepared by mixing of reagents. Characteristics of fusion bead and pressed powder methods are compared in Table 1.

In this article, general preparation methods, equipment, reagents and other important considerations for powders with typical grain size and drying conditions are described. If analysis must be performed in accordance to a specific standard test method, adhere to its prescribed conditions. In a following issue on fusion beads, various applications such as for ferroalloy, silicon carbide and copper concentrate samples will be reported.

## 2. Preparation method

Figure 2 shows the general procedure for preparing a fusion bead.

### 2.1. Weighing

Dry powder sample, flux, oxidizing agent are weighed to 0.1 mg precision.

### 2.2. Mixing

Transfer weighed sample and flux into a crucible. Be sure that the specimen is thoroughly mixed prior to fusion and add releasing agent if fusion bead is difficult to remove from the mold. Add oxidizing agent if oxidation of sample is required.

### 2.3. Oxidization/Calcination

Samples containing metals, carbides, sulfides are mixed with oxidizing agent and oxidized at around 600–800°C. In cement raw meal and limestone, CaO in sample can actually be present as $CaCO_3$. For such samples, sudden increase in temperature can cause significant foaming due to release of $CO_2$ caused by the chemical reaction $CaCO_3 \rightarrow CaO + CO_2$. Calcination at around 800°C before fusion reduces risk of sample overflow and air being trapped in the finished fusion bead.

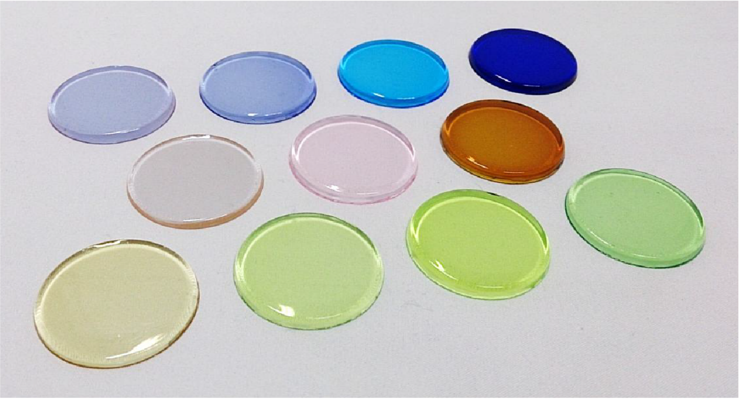

**Fig. 1.** Fusion beads.

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**Table 1.** Comparison between fusion bead method and pressed powder method.

| | Fusion bead method | Pressed powder method |
|---|---|---|
| Grain size effect | Not affected | Affected |
| Mineralogical effect | Not affected | Affected |
| Matrix effect | Reduced due to dilution | Affected by elemental composition |
| Standard sample | Possible to prepare by mixing reagents | Need to be similar to test sample |
| Grain size of sample | 106 $\mu$m (140 mesh) or less | 46 $\mu$m (330 mesh) or less |
| X-ray intensity | Reduced due to dilution | No change |
| Storage | In desiccator to avoid deliquescence | In desiccator |
| Handling | Easy since in glass form | Care required not to break |
| Preparation time | 15–30 min. including weighing | Several minutes |

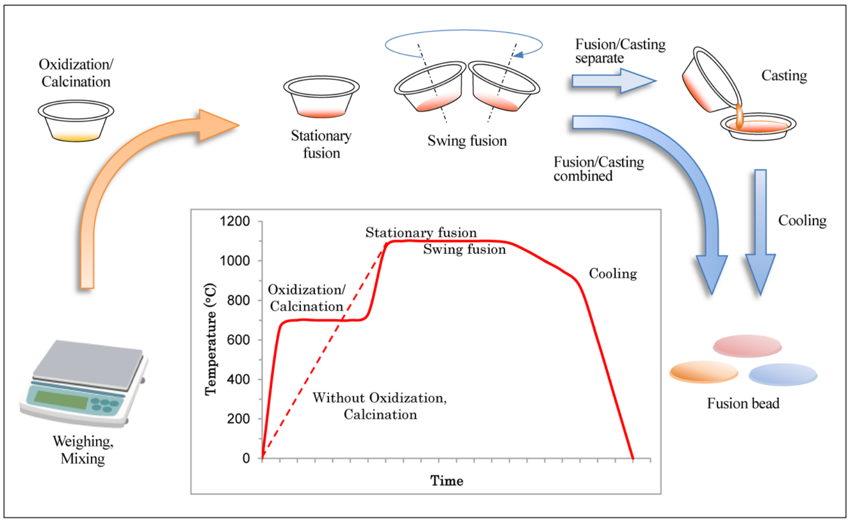

**Fig. 2.** General fusion bead preparation method.

## 2.4. Fusion

Samples are fused at 1000–1200°C for a certain period of time. Keep the crucible stationary until the sample and the flux melt, and then begin to swing to homogenize and remove air bubbles. The higher the temperature applied, the higher the fluidity during fusion, but can increase volatilization of flux and analytes, and decrease crucible lifetime. By keeping fusing time fixed, flux volatilization is consistent and therefore its effect can be ignored. However, to minimize variation in sample volatilization due to differences in sample composition, it is advisable to fuse at lower temperatures.

When the fusion is completed, stop swinging and keep the crucible horizontal for fusion/casting combined vessels, or pour the fused sample into a mold.

## 2.5. Cooling

It is important to cool down the fused sample while maintaining its property as a glass. Rapid cooling can cause the sample to crack, while cooling too slowly can cause crystallization. Because of this, initial passive slow cooling followed by active cooling is recommended. Cooling time will vary according to sample, flux type, dilution ratio. Figure 3 illustrates sample cool down timeline.

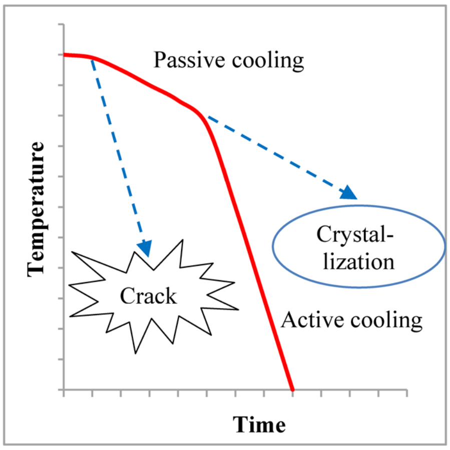

**Fig. 3.** Sample cool down timeline.

## 3. Instruments

### 3.1. Fusion types

There are three types of fusion machines for preparing fusion beads, namely high frequency (HF) induction, electric furnace and a gas burner types. Fusion temperature range slightly varies depending on type but is typically around 1000–1250°C and have a swing/cooling mechanism. Room ventilation is recommended especially when many fusion bead samples are prepared with oxidizers or releasing agent.

(a) HF induction type

Due to direct heating by high frequency coil, heating is efficient and rapid(5).

(b) Electric furnace type

There are muffle and non-muffle type electrical furnaces. It is necessary to turn power on before use and time is required to reach high enough temperatures.

(c) Gas burner type

Temperature is controlled by adjusting gas flow rate. Since combustible gases such as propane is used, environment needs to be carefully monitored.

### 3.2. Vessels (Crucible, Mold)

Regarding use of vessels, there are two different approaches for forming the fusion bead namely crucible/mold combined and separate types. The fusion instrument mentioned above uses combined type vessels (Fig. 4).

(a) Crucible/mold combined

Sample is fused and cooled down in the crucible, where the crucible is also used as a mold.

**Fig. 4.** Crucible/mold in one type.

(b) Crucible/mold separate type

Sample is fused in the crucible and then transferred into a mold to form the fusion bead. Preheating the mold to around 800°C before pouring into the mold prevents cracking of the fusion bead.

Most vessels are made of platinum and gold (95 and 5 mass%) to assure release of the formed fusion bead. To improve hardness and prevent deformation, some have added rhodium and consist of reinforced platinum or platinum alloy. Whatever the material, the flatness of the mold's surface in contact with the sample is critical for sample detachment and should therefore also be mirror polished.

## 4. Analysis sample and reagents

### 4.1. Analysis sample

Analysis sample is pulverized to smaller than 106 $\mu$m particle size (140 mesh), dried for over two hours in 110±5°C air atmosphere, then cooled down and stored in a desiccator.

### 4.2. Flux

Flux is available as fine powders or in granular and globular forms, and some already contain releasing agents. In any case, it should not contain any water and depending on analysis requirement, the appropriate purity grade should be chosen.

Impurity levels can vary from lot to lot, so it is desirable to have a substantial amount of the same lot to minimize analysis error. Flux is a hygroscopic substance and therefore it should be dried before use. Place the flux in a platinum tray and heat in an electric furnace at 200–250°C below its melting point for 4 hours, and then cool down and store in a desiccator (for example, lithium tetraborate is dried at 650–700°C for 4 hours). Fusing temperature is typically 200–250°C higher than its melting point to improve fluidity. Table 2 shows the physical properties of various types of flux(6),(7).

(a) Lithium tetraborate $Li_2B_4O_7=Li_2O\cdot 2B_2O_3$

Lithium tetraborate is the most commonly used flux

**Table 2.** Physical properties of various fluxes.

| | Lithium tetraborate | Lithium metaborate | Mixed flux | Sodium tetraborate |
|---|---|---|---|---|
| Formula | $Li_2B_4O_7$ | $LiBO_2$ | $Li_2B_4O_7$, $LiBO_2$ | $Na_2B_4O_7$ |
| Melting point | 930°C | 845°C | 875°C (66 : 34)<br>870°C (50 : 50)<br>825°C (12 : 22)<br>840°C (20 : 80) | 741°C |
| Acid/Base | Acidic | Basic | Weak acid–Weak base | Acidic |
| Suitable sample | Lime stone<br>Cement | Silicate, Rock<br>Refractory | Silicate, Rock<br>Refractory | Metal, Mineral ore |
| Remarks | High melting point<br>High solubility for basic oxides | Crystalizes when cooled | Low melting point<br>High solubility for acidic oxides | Lowest melting point<br>High deliquescence<br>Na analysis not possible |

in XRF analysis. Since it is a relatively more acidic compound compared to lithium metaborate ($LiBO_2$), it is suitable for fusing samples such as lime stone and cement which contain basic oxides (CaO, MgO, $Na_2O$, $K_2O$, etc.). However, its 930°C melting point is the highest among the various flux types and consequently fusion temperature must be relatively high. Therefore, this flux requires special attention to sample and flux volatilization as well as damage to the vessel.

(b) Lithium metaborate $LiBO_2=Li_2O \cdot B_2O_3$

Lithium metaborate is a relatively more basic compound compared with lithium tetraborate, and is therefore suitable for fusing samples such as silicates, rocks and refractories which contain acidic oxides ($SiO_2$, $ZrO_2$, $TiO_2$, etc.). It has a low melting point of 845°C and tends to cause crystallization instead of vitrification when cooled. It is therefore not used by itself but rather in combination with lithium tetraborate as a mixed flux.

(c) Mixed flux (Lithium tetraborate $Li_2B_4O_7$, Lithium metaborate $LiBO_2$)

As this is a mixture of lithium tetraborate and lithium metaborate, its acidity/basicity can be adjusted by the mixing ratio. It also has the advantage of lowering the melting point for easier fusion compared to pure lithium tetraborate.

Lithium tetraborate to metaborate ratios are typically 66% to 34%, 50% to 50%, 35.3% to 64.7% (12 : 22 flux), 20% to 80%, respectively. The melting point of 12 : 22 flux is 825°C which is the lowest among the mixed types.

(d) Sodium tetraborate $Na_2B_4O_7$

This is an acid compound and has the lowest melting point of 741°C and samples can therefore easy be fused. However, its high deliquescence makes it unsuitable for long term use, and the Na in the flux restricts analysis of Na in sample.

## 4.3. Releasing agent

Halides such as iodides or bromides are used as releasing agents to facilitate removal of the cooled fusion bead from the mold. Addition of releasing agent increases surface tension of sample during fusion since halogen remains on the surface and therefore surface area of sample in contact with the vessel is reduced. As a result, the cooled fusion bead becomes easier to remove from the mold. In addition, it improves removal of air bubbles from the sample due to lower viscosity. Typical iodides are LiI, NaI, KI and $NH_4I$, and bromides are LiBr, NaBr and KBr.

Bromides compared to iodides act as stronger releasing agents and therefore can be effective in smaller quantities, but tend to remain in the fusion bead. Halogens remaining in the sample can interference analysis lines. Table 3 shows analysis and interference lines due to the releasing agent.

Releasing agent can be added before heating or during fusion. Consistent addition of releasing agent quantity can be difficult since typical amounts are less than 1 mg. By preparing 5–50% (w/v) solutions in advance and addition by a micropipette can improve consistency. The iodide solution should be kept in a light-resistant bottle as many iodide materials tend to liberate iodine due to air oxidation or light. Moreover, as described below, lithium fluoride in addition to acting as a releasing agent also lowers the viscosity during fusion.

When releasing agent quantity is insufficient, the sample's surface area in contact with mold's internal wall is relatively large and become difficult to remove. On the other hand, when too much is added, surface tension becomes too high such that sample does not fully cover the bottom of the vessel resulting in a crescent or ball shaped fusion bead. Effect of releasing agent quantity on sample surface tension is shown in Fig. 5 above. Adequate amount of the releasing agent depends on type of sample, dilution ratio, and surface condition of the mold.

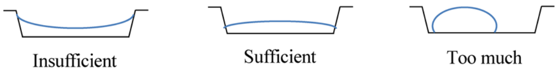

**Fig. 5.** Effect of releasing agent quantity on sample surface tension.

**Table 3.** Example of interference line from releasing agent.

| Releasing agent | Analysis line | Interference line |
|---|---|---|
| Bromide (Br) | Al-K$\alpha$ ($\lambda$=0.8340 nm) | Br-L$\alpha$ ($\lambda$=0.8375 nm) |
| Iodide (I) | Ti-K$\alpha$ ($\lambda$=0.2750 nm) | I-L$\beta_2$ ($\lambda$=0.2752 nm) |

**Table 4.** Physical properties of various oxidizing agents.

| Oxidizing agent | Lithium nitrate | Sodium nitrate | Potassium nitrate | Strontium nitrate | Ammonium nitrate | Lithium carbonate | Sodium carbonate | Vanadium oxide |
|---|---|---|---|---|---|---|---|---|
| Formula | $LiNO_3$ | $NaNO_3$ | $KNO_3$ | $Sr(NO_3)_2$ | $NH_4NO_3$ | $Li_2CO_3$ | $Na_2CO_3$ | $V_2O_5$ |
| Melting point | 264°C | 306.8°C | 339°C | 570°C | 169.6°C | 618°C | 851°C | 690°C |
| Decomposition temperature | 600°C | 380°C | 400°C | 570°C | 210°C | 618°C | 851°C | 1750°C |
| Deliquescence | Yes | Yes | Yes | Yes | Yes | No | No | No |
| Remarks | $NO_2$ originated | $NO_2$ originated | $NO_2$ originated | $NO_2$ originated | $NH_3$, $NO_2$ originated | $CO_2$ originated | $CO_2$ originated | Oxidation catalyst |

### 4.4. Oxidizing agent

Samples which include metals, carbon and sulfur are fused with oxidizing agent since they can react and form an alloy with the platinum in the vessel and cause irreversible damage. It is possible to oxidize the sample using a strong oxidant such as nitric acid and then dried prior to fusion. However, for some samples it may be easier to perform oxidization during the pre-heating stage prior to fusion. Typical oxidizing agents are nitrates such as $LiNO_3$, $NaNO_3$, $KNO_3$ and $Sr(NO_3)_2$ which cause oxidation at high temperatures. Since decomposition temperature varies depending on oxidizer, often times a mixture of several different nitrates are used.

Other than ammonium nitrate, elements in the oxidizer remain in the fusion bead and therefore a consistent amount should be added. Generally, since nitrates easily dissolve in water, preparation of oxides as water solution in advance and addition by a micropipette improves consistent addition of a homogeneous mixture.

Carbonate is occasionally used as another type of oxidizing agent. Since carbonate has higher melting point and decomposition temperature compared with nitride, it is mostly used for oxidization of ferroalloy or metal sample. Vanadium oxide works as an oxidation catalyst for the oxidization of sample by oxygen in the air. Table 4 is a compilation of the physical properties of various oxidizing agents$^{(8)}$.

### 4.5. Other reagents

(a) Lithium fluoride

Lithium fluoride works not only as a releasing agent but also acts to lower the viscosity and melting temperature. For mixed flux of lithium tetraborate 90% and lithium fluoride 10%, the melting point is as low as 780°C, and therefore volatilization of sample and flux can be reduced drastically. Adhesion to the vessel is low as its fluidity is very high.

(b) Oxide of heavy element

In case of wide elemental concentration range such for geological samples, addition of heavy element based oxides ($La_2O_3$, $CeO_2$, etc.) further reduces absorption/excitation effects due to matrix, and the linearity of the calibration line is improved (Heavy element dilution effect)$^{(9)}$.

## 5. Other sample preparation considerations

### 5.1. Trapped air

As mentioned above, samples having high concentration of Ca such as limestone, cement raw meal etc. cause significant foaming when fused, and they air may be trapped in the fusion bead. Calcination at lower temperature prior to fusion can reduce the air being trapped in the fusion bead.

### 5.2. Residual sample unfused

Sample with high quartz concentration such as high silica materials are difficult to fuse completely, and the unfused residual causes analysis error. Thoroughly mixing sample and flux before fusion is advisable in this case. When unfused residue is observed, change the flux type considering the acid-base, or fuse it again. Pulverization of samples can also reduce residuals since coarse powders require longer fusion time.

## 6. Vessel maintenance

Fragments of fusion bead attached to the vessel and difficult to remove are soluble in 30% (w/v) citric acid solutions. Heated citric acid solutions or diluted hydrochloric acid can speed up removal.

Thermal stress from repeated use of the vessel can cause mosaic-like patterns to appear on the surface due to sample, oxidizer or releasing agent residue in the micro-cracks. This not only can lead to the fusion bead to crack during cooling and make releasing sample difficult, but also can be a cause of analysis error. In such cases, polish the vessel surface with a cloth or fibrous buff with alumina paste or diamond paste with particle size less than 1 $\mu$m.

Polishing allows repeat use of the vessel, but eventually the bottom surface begins to deform making preparation of flat samples difficult. When the damage to the vessel surface increases, problems such as cracking, air being trapped and releasing become more serious. In such cases, recasting of vessel may be required.

## 7. Standard

Following standards regarding XRF analysis by fusion bead method are published, and detailed sample preparation methods are also described$^{(10)}$.

JIS M 8205:2000 Iron ores—X-ray fluorescence spectrometric analysis
JIS R 2216:2005 Methods for X-ray fluorescence spectrometric analysis of refractory products
JIS R 5204:2002 Chemical analysis method of cement by x-ray fluorescence
ISO 4503:1978 Hardmetals—Determination of contents of metallic elements by X-ray fluorescence—Fusion method
ISO 9516-1:2003 Iron ores—Determination of various elements by X-ray fluorescence spectrometry—Part 1: Comprehensive procedure
ISO 12677:2011 Chemical analysis of refractory products by X-ray fluorescence (XRF) —Fused cast-bead method
ISO 29581-2:2010 Cement—Test methods—Part 2: Chemical analysis by X-ray fluorescence

## 8. Summary

This article describes general principles of fusion bead preparation regarding operation, instruments, reagents and precaution. In a following issue regarding fusion beads, various fusion bead preparation methods with practical application examples will be discussed.

### References

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