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XRF SPECTROMETER SAMPLE PREPARATION BY USING FUSED BEADS TECHNIQUE

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ABSTRACT
Sample preparation is an very important procedure in X-ray fluorescence analysis, and this stars with the initial sample selection and subsequent preparation (i.e. crushing and milling of consolidated materials) with the final product being a fine-grained (ideally < 63 μm) powder. There are many methods for materials preparation for XRF analysis. The most important are fused beads preparation and the pressed pellets preparation. Fused beads is the method where the sample is mixed with suitable flux, which is then fused into a glass with specific diameter. Pressed pellet is the method where the sample powder, with or without binding agent, is compressed in order to get a solid tablet of powder. All presented results in this article are obtained mesuring samples as pressed powder and fused beads. Obtained results are compared with reference laboratory results.
Keywords: XRF (X-ray fluorescence) spectrometer, pressed pellet, fused bead, reference value

1. FUSED BEADS PREPARATION
The most important fusion method for x-ray fluorescence (XRF) analysis involves the fusion of a test portion of a prepared sample with lithium metaborate or lithium tetraborate at a temperature between 900°C and 1200°C, depending on the material type, in a 95% platinum/5% gold crucible.
About 1.0 g of material is heated in a platinum crucible for 10 minutes at 975 °C $\pm$ 10 °C according to DIN EN 196 Part 2 (10 min at 1050 °C $\pm$ 10 °C is also possible). After cooling down of the sample in a desiccator 0.7000 g of standard mixture and 6.3000 g of flux are mixed (ratio of 1:9, the total amount of the mixture can be different depending on the size of the fused beads). The amount mentioned above is valid for fused beads with a diameter of 34 mm. For fused beads with a diameter of only 30 mm, 0.5000 g of sample and 4.5000 g of flux are often sufficient.
The mixture is then transferred in a platinum crucible and after addition of 2 drops of a 5% LiBr solution heated in a furnace at 1050 °C $\pm$ 10 °C for 6 minutes. Subsequently the melt is removed from the furnace and mixed manually to ensure a homogenous and clear bead. Then the crucible is put on a tripod with a clay triangle and cooled down with a fan. By weighing the crucible the loss on ignition (LOI 2) is determined. This LOI 2 is mainly caused by a loss of weight of the flux.

2. TEMPERATURE
The fusion temperature should always be kept as low as possible in order to avoid losses by volatilization of important elements from the sample or the flux. A temperature between 1000 and 1050ºC is sufficient to melt borate fluxes and dissolve oxides. In a fusion context, the flux must melt

and then, the sample will dissolve into the molten flux. It is not necessary to reach a temperature that would melt the sample. As long as the flux itself is a liquid, the sample will dissolve in it. It is also important to note that some species, like SO_3 and alkaline oxides, are somewhat volatile and tend to be lost by volatilization if the temperature is too high. Therefore, short low temperature fusions (< 1050°C) are recommended because only the flux needs to mels, not the sample.

3. ADVANTAGES OF USING FUSED BEADS

The advantages of fusion to prepare samples are numerous. The first advantage is undoubtedly the power to dissolve difficult samples that sometimes represent such a big challenge for analysts. The power of fusion to dissolve oxides is far above the conventional acid attack, which generally consists in a long and tedious process. Conventional acid attack will often lead to partial dissolutions, while fusion allows a complete dissolution even for resistant oxides such as silica, alumina, zirconia and a lot of others.

Fusion also leads to high accuracy measurements. This represents another important advantage. We all know how the industries of the second millennium are becoming more demanding for more reliable results. It is therefore obvious that a complete dissolution without losses represents an efficient way to reach this goal.

Another advantage of preparing samples by fusion is the time and money factor. A typical fusion takes less than 10 minutes while conventional acid attacks take hours of laborious work. Time is often a crucial factor for labs and obviously time is linked to money. In general, fusions are very simple to achieve and do not require any complex procedures or the use of hazardous reagents. Especially when performed with an automated apparatus, it truly is a very safe and simple technique. Finally, fusion is certainly a very clean technique that does not involve hazardous acids or reagents. In a general context, it also represents an energy saving method, since the time and the energy required performing dissolution by fusion is lower than with any other conventional technique.

4. EXPERIMENT AND RESULS

One part of cement sample (CEM II/B-W 42,5N) was sent to the reference laboratory, second part of the same sample was measured on XRF spectrometer as pressed pellet on appropriate calibration and the third part was measured as fused bead also on appropriate calibration for fused bead samples. Measuring was focused on main oxides in cement SiO_2, Al_2O_3, CaO and MgO.

4.1. SiO_2 measuring

Table 1. Content of SiO_2 in tested cement samples

Method	Tested cement samples				
	U1	U2	U3	U4	U5
Reference value	24,30	24,80	25,40	26,00	26,30
Pressed pellet value	26,04	26,30	26,56	26,69	26,99
Fused bead value	24,24	24,85	25,47	25,72	26,41

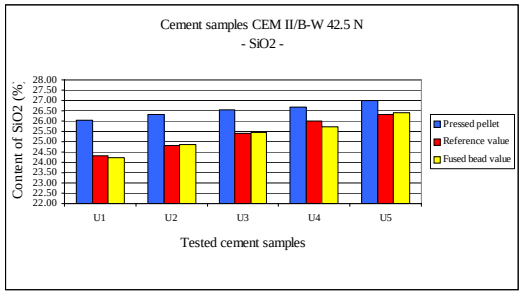

Figure 1. Comparation between pressed pellet, fused bead and reference value for SiO_2

4.2. Al_2O_3 measuring

Table 2. Content of Al_2O_3 in tested cement samples

Method	Tested cement samples				
	U1	U2	U3	U4	U5
Reference value	8,06	8,36	8,74	9,08	9,23
Pressed pellet value	7,76	7,83	7,91	7,95	8,03
Fused bead value	8,18	8,50	8,89	9,08	9,45

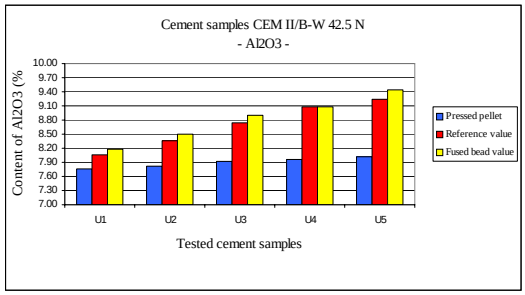

Figure 2. Comparation between pressed pellet, fused bead and reference value for Al_2O_3

4.3. CaO measuring

Table 3. Content of CaO in tested cement samples

Method	Tested cement samples				
	U1	U2	U3	U4	U5
Reference value	56,70	55,70	54,60	53,70	52,70
Pressed pellet value	55,32	54,77	53,99	53,43	52,89
Fused bead value	56,93	56,11	54,91	54,08	53,28

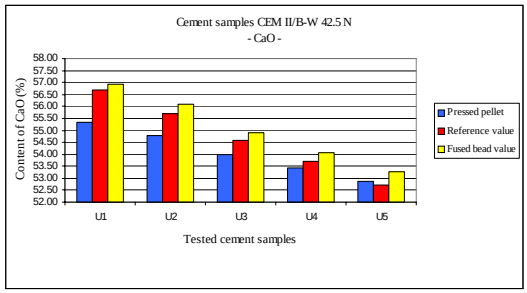

Figure 3. Comparation between pressed pellet, fused bead and reference value for CaO

4.4. MgO measuring

Table 4. Content of MgO in tested cement samples

Method	Tested cement samples				
	U1	U2	U3	U4	U5
Reference value	1,38	1,39	1,43	1,46	1,47
Pressed pellet value	1,19	1,29	1,35	1,35	1,40
Fused bead value	1,42	1,45	1,48	1,45	1,47

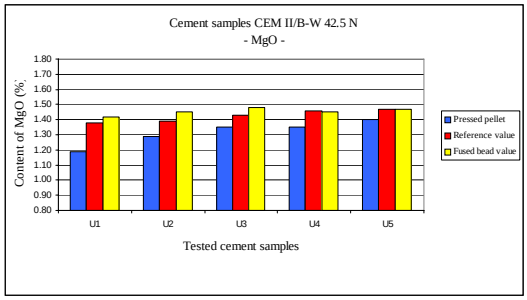

Figure 4. Comparation between pressed pellet, fused bead and reference value for MgO

5. CONCLUSION

As we can see from the table and figure 1 values of SiO_2 for all five samples measured as fused bead are closer to the reference values than values obtained measuring samples as pressed pellets. Concerning Al_2O_3 from the table and figure 2 we can see that the situation is the same as for SiO_2, it means all five samples measured as fused bead are closer to the reference value. Table and figure 3 show as that CaO values for samples U1, U2 and U3 are better measuring samples as fused bead and samples U4 and U5 are better measuring samples as pressed pellet. The same as for SiO_2 and Al_2O_3, in the case of MgO all five samples measured as fused bead are closer to the reference value. According to these presented values it is obviously that more accurate results are obtained by using fused bead technique than pressed pellet.

6. REFERENCE

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