A QUICK AND RELIABLE FUSION METHOD FOR SILICON AND FERROSILICON

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ABSTRACT
Making glass disks for XRF analysis of silicon and its alloys represents a major problem of sample preparation. The reaction between silicon and platinum quickly leads to major corrosion or even complete destruction of the crucible. The new approach presented by the author last year at DXC2000 [1] paved the way to a new generation of fusion methods that give surprising results. Based on the same approach, a short and efficient chemical treatment has been found to oxidize silicon easily and rapidly, directly in the platinum crucible at low temperature, followed by fusion of the oxides. Using this method, the fusion leads to high quality glass disks; the unusual high sample/flux ratio is particularly interesting in the analysis of trace elements. Features of the new technique are: no crucible corrosion; simplicity, ease and speed; unusual high sample/flux ratios; easy trace analysis and easy XRF calibration using synthetic standards. This method has been developed particularly for silicon and ferrosilicon, but it has also been successfully applied to many other metals.

INTRODUCTION
Borate fusion of oxides is well recognized as the most accurate sample preparation method for XRF analysis [2]. Despite its great advantages, certain materials - particularly silicon and its alloys - have been kept away from borate fusions for many years. One reason is the quick alloying reaction that can occur between potentially unoxidized particles and the platinum crucible used to process the fusion [3]. To ensure a complete oxidation of a sample, long and tedious oxidation procedures in an oven are often required, without guarantee of success. Oxidations - using conventional solid oxidizers like nitrates and carbonates at low temperature - are also very risky in a production context. Their low efficiency to oxidize the silicon metal completely before the oxidizer has decomposed, gives alloying a chance to take place, leading to severe damage or even complete destruction of the platinum crucible [4,5].

OBJECTIVE
This paper intends to describe a quick and reliable procedure to efficiently oxidize metallic silicon prior to fusion. After oxidation, fusion is started and the produced silicates dissolve into a molten borate flux, yielding high quality glass disks. This paper also intends to show that a new generation of fusion techniques is appearing, allowing making fused beads from all kinds of metals and alloys, including previously difficult ones such as silicon and ferrosilicon.
THE PROPOSED METHOD

It has been observed that metallic silicon is readily oxidized by strong bases [6,7] such as lithium hydroxide according to the following reaction:

\[
\text{Si (s)} + 4 \text{LiOH (aq)} \rightarrow [\text{SiO}_4]^{4-} (\text{aq}) + 4 \text{Li}^+ (\text{aq}) + 2 \text{H}_2 (\text{g})
\]

The property of silicon to be efficiently oxidized by strong bases constitutes the heart of the strategy employed to produce glass disks from silicon metal by fusion. To minimize time, handling and contamination, the oxidation of silicon is achieved directly in the platinum crucible, just prior to fusion. That is achieved near ambient conditions, generally in less than five minutes. It is very important to mention that the proposed method employs a strong base LiOH.H_2O as the oxidizing agent. This hazardous compound is very poison, dangerous and extremely corrosive. May be fatal if swallowed or inhaled and causes burns to any area of contact. LiOH.H_2O must be handled with extreme care using the proper laboratory protective equipment such as goggles, laboratory coat, and proper gloves [8]. In addition to that, the oxidation reaction between metallic silicon and lithium hydroxide produces a considerable amount of hydrogen, which is potentially explosive. The procedure should therefore be done in a well-ventilated hood, with no sparks or flames present.

1. The first step consists in mixing the silicon sample and a solid strong base directly in the platinum crucible. Lithium hydroxide is selected as the most advantageous since lithium is a low absorber of X-rays. Lithium hydroxide is used in a solid form. The liquid form is not practical and present serious risks as it turns out to be too reactive during the oxidation reaction, which may become uncontrollable. The solid state is therefore preferred. The stable hydrate LiOH.H_2O is used. In this particular example, 500mg of metallic silicon and 5g of LiOH.H_2O are accurately weighted. Both compounds were obtained from a local supplier, and are 99%+ of purity.

2. Once the sample and the solid base are mixed together, a Pt-5%Rh crucible is put on a warm plate at low temperature (80 °C) for 1-2 minutes. This step ensures a proper heating to initiate and quicken the oxidation reaction that will follow.

3. The crucible is removed from the warm plate with great care. Then, in order to partially dissolve the strong base and to initiate the oxidation reaction between metallic silicon and LiOH.H_2O, 3 ml of distilled water at ambient temperature are gently added – dropwise – on top of the mixture, which is at about 80°C. This operation should be completed within about three minutes. It is recommended to spread it on the whole surface in order to cover the entire surface area. The oxidation reaction that takes place is strongly exothermic. The heat produced by the oxidation process quickly propagates to the entire mixture yielding an important temperature increase inside the crucible. That is why it is important to do not put the crucible on a warm plate or close to any source of heat during this step. The temperature could become too high and might eventually lead to the expulsion and losses of the mixture outside the platinum crucible. As already described, it is very important to use proper safety equipment and a well ventilated hood, with no sparks or flames present.

4. According to the chemical reaction shown previously, the silicon sample gets quickly oxidized into silicates. The mixture will continue to react and cool down for about five minutes. At this step, most of the metallic silicon is oxidized. The rest, if any, will be oxidized at the first step of the fusion process by the excess of lithium hydroxide still present in the mixture.
5. A borate flux and a non-wetting agent are put on top of the mixture. In this particular example, 6 g of lithium tetraborate and 3.6 g of boric acid (H$_3$BO$_3$) are added one after the other in the crucible to cover the oxidized mixture. Finally, 40 mg of lithium iodide (LiI) is used as non-wetting agent and put on top.

6. The fusion is carried out with an automatic fusion instrument. The fusion is started at low temperature (200-300 °C) for 5 minutes in order to get rid of the remaining liquid and, if needed, to complete the oxidation reaction. The temperature is then raised at 1000 °C for another 5 minutes.

7. The borate flux quickly melts and the silicates readily dissolves, yielding a perfect homogenous melt.

8. The resulting molten mixture is finally poured into a platinum mold.

9. After 5 minutes of cooling, a perfect homogenous and stable glass disk is obtained.

10. The crucible remains perfectly clean, without any corrosion.

The illustrations below show the 10-step procedure described above.

Fig. 1 to 10: Procedure for oxidation-fusion of silicon.
RESULTS
The reliability of the method was tested by measuring the repeatability of line intensities on six fused bead replicates. All fusions were done on a Claisse M4 fluxer, and the intensities were obtained using a Philips PW 2400. The results are given in table 1.

Table 1. Repeatability of Silicon Kα line intensities on six fused beads of pure silicon powder sample.

<table>
<thead>
<tr>
<th>Replicates</th>
<th>Intensity Si Kα (Kcps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>119.27</td>
</tr>
<tr>
<td>2</td>
<td>118.91</td>
</tr>
<tr>
<td>3</td>
<td>118.76</td>
</tr>
<tr>
<td>4</td>
<td>119.28</td>
</tr>
<tr>
<td>5</td>
<td>119.59</td>
</tr>
<tr>
<td>6</td>
<td>119.37</td>
</tr>
<tr>
<td>Average (Kcps)</td>
<td>119.20</td>
</tr>
<tr>
<td>Standard dev.</td>
<td>0.31</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>0.26</td>
</tr>
</tbody>
</table>

Using the weakness of silicon against alkaline attack, other silicon compounds such as ferrosilicon have been tested also using the same oxidation-fusion preparation method previously described (steps 1-10). In all cases, the procedure led to high quality glass disks. The ferrosilicon results are shown in table 2.

Table 2. Repeatability of Si Kα and Fe Kα line intensities on six fused beads of steel plant ferrosilicon sample.

<table>
<thead>
<tr>
<th>Replicates</th>
<th>Intensity Fe Kα (Kcps)</th>
<th>Intensity Si Kα (Kcps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>128.23</td>
<td>54.88</td>
</tr>
<tr>
<td>2</td>
<td>129.13</td>
<td>54.84</td>
</tr>
<tr>
<td>3</td>
<td>126.51</td>
<td>54.58</td>
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<td>4</td>
<td>128.05</td>
<td>55.05</td>
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<tr>
<td>5</td>
<td>127.00</td>
<td>54.54</td>
</tr>
<tr>
<td>6</td>
<td>127.78</td>
<td>54.70</td>
</tr>
<tr>
<td>Average (Kcps)</td>
<td>127.78</td>
<td>54.77</td>
</tr>
<tr>
<td>Standard dev.</td>
<td>0.93</td>
<td>0.19</td>
</tr>
<tr>
<td>RSD (%)</td>
<td>0.73</td>
<td>0.35</td>
</tr>
</tbody>
</table>
FEATURES OF THE NEW TECHNIQUE
As compared to “fusion with oxidants in flux-coated crucibles” and/or “grinding and polishing” solid metals, the advantages are great:
- simplicity, ease and speed;
- easy XRF calibration using synthetic standards (mixtures of oxides)
- elimination of crucible corrosion;
- unusual high sample/flux ratios attainable;
- easy trace analysis
- high precision and accuracy
- efficient and complete oxidation

GLASS STABILITY AND MAXIMAL RATIOS TESTED
The oxidation of metallic silicon in the sample produces silica, which has a very benefic stabilizing effect on the glass beads [2]. These are very solid and do not tend to crack or shatter. The glass disks produced are slightly hygroscopic; silica tends to lower this property. The use of desiccators for storage is highly recommended. Silica is highly soluble in borate fluxes, which allows dissolving interesting amounts of sample. When expressed as oxides, the maximal sample/flux ratios tested for metallic silicon sample was 1:4, and 1:6 regarding ferrosilicon sample. The described method allows reaching very interesting ratios, which is highly benefic for trace analysis.

APPLICATION TO OTHER METALS
Several qualitative tests on other metals and alloys of various shapes have resulted in high quality glass disks. Often, the sample does not need to be ground and can be taken directly as metal drillings, chips, or even as an entire piece. Minor modifications in the procedure can be required for processing certain metals according to their shape and size, but the general principle remains basically the same. An example is shown below (Fig.11) where a 200-mg piece of aluminum foil has been taken and processed using the procedure described in this paper with a minor change however. This change consists in inserting three simple steps between step 4 and step 5 of the procedure described previously. These three extra steps are:

4.a. Once the crucible and mixture have cooled down, gently add 1.5 ml of distilled water dropwise in the mixture. This operation should be completed within 2-3 minutes.
4.b. Put the crucible on a warm plate at low temperature (50 °C) for about 10 minutes in order to complete and make sure that all the metallic aluminum has been oxidized into aluminates. If the mixture tends to splatter outside of the crucible, the temperature should be lowered or the crucible should be totally removed from the warm plate.
4.c. Remove the crucible from the warm plate and let it cool for five minutes.

At this point, it is very important recalling to always apply all the security procedures with great care, using the proper protective equipment as described earlier in this paper.
Using this modified procedure, the qualitative tests led to high quality glass disks (Fig. 12) as shown below.

![Fig. 11: Aluminum foil sample.](image1)

![Fig. 12: Glass disk resulting from the oxidation-fusion procedure.](image2)

CONCLUSION

Silicon metal and most of its alloys are efficiently oxidized by strong bases near ambient temperature, directly in platinum crucibles, followed by fusion of the oxides. The complete procedures, from weighing to obtaining the final cooled glass disks, are normally achieved in less than half an hour and obviously, more than one sample can be processed at the same time on a multi-position fluxer. Alkaline attack represents therefore a very efficient technique for certain hard-to-oxidize samples. The fused beads preparation of silicon and most of its alloys as well as many other metals is therefore accessible in routine laboratory procedures, and XRF analysis will gain from the high precision and accuracy obtainable with homogeneous specimens.

ACKNOWLEDGEMENTS

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REFERENCES