FUSED BEADS FROM METAL DRILLINGS AND CHIPS
EXAMPLE OF APPLICATION TO TIN-LEAD ALLOYS

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ABSTRACT
The objective of this paper is to introduce an easy and fast fusion procedure for metallic samples, in which oxidation of the sample uses specific acid solutions near ambient conditions. An example of application to tin-lead alloys will be described. It represents one example of the most critical cases, since tin-lead alloys melt at temperatures lower than most solid oxidizers, which will generally lead to complete destruction of the crucibles. Some advantages of this new technique are: no crucible protection layer to make; total elimination of crucible corrosion; simplicity, ease and speed; sample/flux ratio with significant increase of XRF intensities; oxidation in oven is not required; elimination of solid oxidizers and their contamination; easier analysis of trace elements.

INTRODUCTION
The borate fusion technique, which is directly applicable to oxides only, has become widely accepted, thanks to its simplicity and accuracy. This is not the case for metals and alloys. It has been shown that application of fusion to alloys can be made possible by mixing solid oxidizers with the sample or with the flux, and beginning the fusion with a low temperature heating step until the metal particles are completely oxidized, then proceeding to fusion as with oxides. Such techniques have been developed for ferro-alloys, and some have been tested successfully on other metals as well. However, they are not well known and they suffer two important limitations: a) difficulties of obtaining very fine powders from metallic samples without contaminating them and, b) necessity of making a protection coating of flux on the surface of the crucible.

OBJECTIVE
The objective of this research is to develop alternative wet chemical procedures for oxidizing metals before proceeding to fusion. Then, fine particles would not be required, and contamination could be easily avoided.

A CRUCIAL CASE
For the first application, the case of Sn-Pb alloys was chosen because usual sample preparation methods are rather unsatisfactory (polishing of solid metals) or inapplicable (fused beads):
   a) Particle size effects can be a major problem with solid metal samples, because the metal grains are nearly pure tin grains or highly concentrated lead grains of variable sizes.
   b) Polishing of Sn-Pb samples is difficult on account of smearing.
   c) Sn-Pb alloys start melting at 183°C. During heating, the alloy melts before the oxidizers and fluxes, and would destroy the crucible by alloying with it, even if a coating of flux protects the crucible.
THE PROPOSED METHOD
We have observed that a 200-mg sample of Sn-Pb "chips" dissolves readily in 1 ml of hydrobromic acid (HBr):
- in the crucible
- near ambient conditions
- in less than four minutes,
and that hydrogen peroxide can rapidly precipitate the dissolved elements as oxides.

The assumed reactions are:
\[
Pb^0 + Sn^0 + 4 HBr \rightarrow PbBr_2 + SnBr_2 + 2 H_2 ^\uparrow \\
PbBr_2 + SnBr_2 + 3 H_2O_2 \rightarrow PbO↓ + SnO_2↓ + 2 Br_2↑ + 3 H_2O
\]

The proposed procedure for oxidation consists in doing the reactions directly in the fusion crucible in order to minimize handling and time:
1. Put up to 200 mg of Sn-Pb chips into the Pt-Au crucible.
2. Add about 25 drops of hydrobromic acid (HBr).
3. Cover the crucible with a watch-glass;
4. Leave the crucible on a hot plate at <100°C until the formation of hydrogen gas has ceased.
5. Add 15 or 20 drops of 15% H_2O_2 solution; avoid too high a temperature that would result in spattering.
6. Agitate and reheat if necessary, in order to release the bromine; avoid the formation of a crust that would be too slow to dissolve during the fusion. Do not evaporate to dryness.

The procedure for fusion is similar to that for oxides. All fusions were done on a Claisse M4. In this particular case only, the flux could not be a Li borate because PbO is volatile above about 850°C. Sodium hexametaphosphate (NaPO_3)_6 has a melting point of 620°C and was found a satisfactory alternative. The detailed procedure is:
1. Pour 8 g of (NaPO_3)_6 over the wet oxidized alloy in the crucibles.
2. Add 75 mg of NH_4Br as a non-wetting agent.
3. Start heating and agitation slowly, and increase the temperature gradually until the melt is fluid and homogeneous.
4. Cast into hot moulds, cool in still air for one or two minutes, then accelerate cooling.

Results
The reliability of the technique was tested by measuring the reproducibility of line intensities on 30 identical fused beads. Results are given in Table 1. Most of the deviations can be attributed to weighing accuracy.

Table 1. Reproducibility of Sn and Pb line intensities on 30 fused beads of SRM 1131

<table>
<thead>
<tr>
<th></th>
<th>Sn Kα</th>
<th>Pb Lα</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal composition (w/o)</td>
<td>40</td>
<td>60</td>
</tr>
<tr>
<td>Average intensity (Kcps)</td>
<td>152.76</td>
<td>190.86</td>
</tr>
<tr>
<td>Relative standard deviation (%)</td>
<td>0.82</td>
<td>0.73</td>
</tr>
<tr>
<td>Precision on concentration, 90% confidence</td>
<td>±0.1%</td>
<td>±0.1%</td>
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</tbody>
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Features of the new technique
As compared to "fusion with oxidants in flux-coated crucibles" for fine metal particles, and/or "grinding and polishing" for solid metals, the advantages are great:
- simplicity, ease and speed;
- application to samples of various sizes and shapes;
- higher line intensities through greater oxidation efficiency;
- no contamination;
- no risk of crucible corrosion.

Next objectives
Several qualitative tests made on other metals and alloys of various shapes have resulted in high quality fused beads (Fig. 1). In all those cases, Li borate fluxes were used. One objective is to define the optimal conditions for various types of alloys.

Aluminum
(wires)

Ferroalloys
(FeCr, FeMn, FeMo, FeTi, etc.)

Copper
(tubing)

Complex metal
(paper clip)

Fig. 1: Example of application to metals

A second objective is to supplement the fusion technology with the accurate composition determination of the alloys after oxidation-fusion. The oxidation of metals is always accompanied with significant "GOF" (gain on fusion): 114% for Si, 32% for Fe, 27% for Sn and 8% for Pb. An FP (Fundamental Principle) software specifically designed for taking care of the difficult problems of unmeasured loss on fusion and gain on fusion has reached the final step of development, and will be tested shortly.
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