Analysis of 999.9 fine gold by the fire assay method and common sources of error

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Technical Director & Chief Assayer
The majority of errors in the fire assay operation comes from three sources:

1. Imperfection in even the finest balance.

2. Non-matching matrices i.e. differences in composition between the controlling proof assay sample and the alloy under examination.

3. Variations in temperature in different parts of the cupellation muffle.

Other sources of error depend upon the skill of the worker who prepares the cupelled buttons for parting.

We will identify these sources of errors and discuss ways to minimise them.
Two Pan Mechanical Balance vs Electronic Balance
# Accuracy vs Weight

## Test Method | Recommendation | Why???
--- | --- | ---
Weighing step. | 999.9 fine gold - always weigh 500mg in quadruplicate. | Why 500mg?

<table>
<thead>
<tr>
<th>Initial wt. (mg)</th>
<th>Fineness (ppt.)</th>
<th>Final wt. (mg) [of 999.9 fine]</th>
<th>Final Wt. (mg) [Say 0.01 mg error occurred due to any reason]</th>
<th>Fineness (ppt.)</th>
<th>Diff. in fineness (+ side)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>999.9</td>
<td>99.99</td>
<td>100.000</td>
<td>1000.00</td>
<td>0.1 ppt</td>
</tr>
<tr>
<td>250</td>
<td>999.9</td>
<td>249.975</td>
<td>249.985</td>
<td>999.94</td>
<td>0.04 ppt</td>
</tr>
<tr>
<td>500</td>
<td>999.9</td>
<td>499.95</td>
<td>499.960</td>
<td>999.92</td>
<td>0.02 ppt</td>
</tr>
</tbody>
</table>

Higher the weight, better will be the accuracy
Literature search reveals

<table>
<thead>
<tr>
<th>Optimum ratio???</th>
</tr>
</thead>
<tbody>
<tr>
<td>What is the optimum Ag: Au ratio?</td>
</tr>
</tbody>
</table>

Higher the silver content, lower will be the absorption loss during cupellation


2. We conducted several experiments on a certified 999.9 fine gold taking Ag: Au ratio as 2.5:1, 2.17:1 and 2:1. No copper was added during experiment. Silver content in cornets were also checked by ICP-OES.

3. The best results (more uniform results) were obtained when Ag: Au ratio was 2.17:1. A ratio of 2 (Ag):1(Au) gives equally good results for 999.9 fine gold.
Is Your Silver Free From Gold?

<table>
<thead>
<tr>
<th>Sample Ref.</th>
<th>Value in %</th>
<th>Au Sample Weight</th>
<th>Silver added (Cupellation)</th>
<th>Effect in ppt.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wire cut of different dia. - pieces randomly taken from silver stock.</td>
<td>0.006</td>
<td>500mg</td>
<td>1000mg</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>0.032</td>
<td>500mg</td>
<td>1000 mg</td>
<td>0.64</td>
</tr>
</tbody>
</table>

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London 2017
## Copper Addition

<table>
<thead>
<tr>
<th>Test Method</th>
<th>Recommendation</th>
<th>Why?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper addition step</td>
<td>No copper added.</td>
<td>Why “no copper”?</td>
</tr>
</tbody>
</table>

### Copper is added:

1. To prevent “spitting” or “spurting” due to the escape of oxygen from the Au-Ag button.
2. To increase the malleability of the button for rolling and to remove last traces of lead.

**BUT:**

Copper enhances absorption loss.

1. “Spitting” or “spurting” does not take place if gold is present in the silver button to the extent of 33% or more, as solubility of oxygen in silver is lowered by alloying with gold.

   “Spitting” or “spurting” can also be controlled by allowing cupel to cool naturally in the muffle with door partially open and then withdrawing cupel gradually towards the door of the muffle and hold till button solidifies.

2. 999.9 fine gold alloy is already very malleable.
<table>
<thead>
<tr>
<th>Test Method</th>
<th>Recommended</th>
<th>Why?</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesia cupel</td>
<td>✔</td>
<td>The diffusivity of heat of magnesia cupels are far greater than those of bone-ash cupels. Cupellation is more uniform, so the surcharge is more trustworthy.</td>
</tr>
<tr>
<td>Bone Ash Cupel</td>
<td>✗</td>
<td></td>
</tr>
<tr>
<td>Single Cupel</td>
<td>✗</td>
<td>Single cupel - absorption loss will vary from cupel to cupel.</td>
</tr>
<tr>
<td>Multi hole Cupel</td>
<td>✔</td>
<td>Multi-holes cupel - Cupellation is more uniform, so the surcharge is more trustworthy.</td>
</tr>
</tbody>
</table>
Temperature Effect – Layout of Samples and Proof

- Furnace muffle temperature varies from front to back – highest at the back. This could result in variable surcharge.

Preferred Layout of samples in the individual cupel (10 in a block):

<table>
<thead>
<tr>
<th></th>
<th>P1</th>
<th>S1</th>
<th>P2</th>
<th>S2</th>
<th>Empty</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>P</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

S = Sample
P = Proof

![Image of furnace muffle with samples and proof in layout]

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Preparing Bead for Parting

Squeezed edgeways and subsequently squashed on a press. Why??
Flatten all beads so that they have approximately the same shape and thickness after rolling - Why??
Preparing Bead for Parting

Anneal the flattened beads in a muffle to red heat (700 °C) to obtain the same condition of recrystallization. - Why??
Preparing Bead for Parting

Annealing, rolling, annealing and rolling up into cornet
- dirty side face up – Why????

Platinum Tray vs Flask Parting

Best to use Parting Tray - **Why?**

Compared to individual flasks, parting is more uniform in parting tray so the proof correction is more trustworthy.
1. In the assay of high grade bullion, the silver retained is usually in excess of the gold lost, so surcharge should always be positive.

2. Surcharge varies from about +0.8 to +1.3 parts per 1000 for 500mg. The results will be less accurate if it is > +0.13

3. If it is negative then suspect something is wrong with the process and results may be less accurate.

4. MOU – 999.9 +/- 0.048 ppt. (Expanded. 95% confidence)
Any Questions...

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