Methods for Au 995‰ and Ag 999‰ analysis

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Various methods are used by Metalor for Au and/or Ag determination

- Fire assay method: for Au
- Gravimetric method: for Au
- Potentiometric method: for Ag
- X-Ray Fluorescence method: for Au
- Spectrometric method after acid dissolution by AAS and ICP-OES for Au and Ag
- Spectrometric method in solid state by Spark-OES for Au and Ag

The three first methods are direct chemical methods. The three last methods are indirect methods where the main element is determinated by difference to 1000 ‰. The goal of this study is to compare these methods.
Choice of the method

For direct methods, the analyst has to evaluate:
- Which precision, accuracy can be routinely achieved for such a high grade?
- What are the chemical and/or physical interferences (co-precipitation, electrochemical, adsorption, oxides, solubility limit, ...)?
- What kind of corrections have to be applied?
- Is it required to dissolve the sponge (gravimetry) for trace analysis?

For indirect methods as Spark-OES or ICP-OES methods:
- Which precision and accuracy can be routinely achieved in the determination of trace elements?
- Which elements may be present in the precious metal?
- Which elements are routinely analysed and/or statistically analysed?
- What are the detection limits of the elements routinely and/or statistically analysed?
- What are the spectral interferences for trace analysis?
- What are the possible contaminants?

Choice of the corrections

The choice and the number of corrections is depending of the level of precision and accuracy to be achieved for direct or indirect methods. Here are some examples.

- AAS or ICP methods to correct the residual solubility of the complex HAuCl₄ after reduction by H₂SO₃ and separation of metallic gold by filtration, and to evaluate the content of impurities in the sponge.
- Gas analysis (C, S, N, O) by combustion, for corrections to be applied to gravimetric determination (filter residue, oxides or sulphide traces) or for direct analysis of the raw material.
- Ionic chromatography for anion determination (Cl⁻, NH₄⁺, ...).
- Spectrometric determination by AAS and ICP to correct direct methods.
- Proof samples are used for fire assay series in order to correct parameter variations.
- Various mathematical models are used for corrections to calibrate XRF and OES spectrometers (Traill-Lachance, Cola, ...) and to correct analytical results.
Calculation of Au or Ag content for indirect methods

For indirect methods as Spark-OES or ICP-OES methods, the fine metal content is evaluated by the formula:

\[ \text{MP} \% = 1000 - 0.001 \times \sum_{i=1}^{n} C_i \]

where:
- \( C_i \) is the concentration of the measured trace elements (unit mg/kg) for \( n \) measured trace elements.

In fact, if an element is not detected, the zero concentration may be replaced by the detection limit (LoD) of the element measured with a spectral analytical line.

Logically, the maximum of trace elements would be measured to avoid bias. In routine, the analysis is limited to the determination of the elements of interest (defined by the standards, the experience of the laboratory and the efficiency of the various refinery process).

Bias in normalised analytical methods

The bias can be defined as the sum of:

- The bias due to the uncertainty in the determination of the measured and detected elements.

- The bias due to the elements which are measured but not detected. This bias is therefore depending of the detection limits of the elements which are routinely measured.

- The bias due to elements which are not measured. It depends of the non-routinely measured elements and of their detection limits (generally, they are not measured because they are never detected).
Identification of bias for indirect ICP method

- With modern ICP spectrometers, the number of elements and lines which can be measured is generally not limited (for example 255 lines on Varian or Perkin-Elmer instruments).

- For rare elements, not routinely analysed, standard reference solutions are available on the market, from which additional calibration solutions may be easily prepared to calibrate the missing elements.

- For example, what are the detection limits of elements in Ag base:
  1. 32 elements are measured in routine by Metalor: Cu, Fe, Bi, Se, Te, Pb, Pd, P, Au, Ni, Sb, Si, Sn, Zn, As, Cd, Na, K, Ca, Mg, Cr, Al, Rh, Co, Mn, Mo, B, Ti, In, Ti, Pb, Pt with 3.9 mg/kg as result of the sum of the LoD.
  2. 30 additional elements are not measured routinely but can be easily evaluated with an ICP: Ir, Ru, Os, Sc, Rb, Nb, La, Er, Ho, Tm, Y, Ta, Hg, Nd, Tb, Sm, Yb, Eu, Ce, Dy, Li, Be, V, Ga, Ge, Sr, Zr, Ba, W, Re with 1.0 mg/kg as result of the sum of the LoD.

Determination of gas elements C, S, N, O in the frame of this study:

- Ag 999‰: O = 35 mg/kg; C, S, N < 2 mg/kg

  The correction of this significant bias should be considered

- Au 995‰: O 2 mg/kg; C 3 mg/kg; S, N < 2 mg/kg

  In this case the correction is negligible
Bias Origins

- For fire assay: equilibrium between Au loss and Ag overweight during the fire assay process depending on the alloy composition, furnace temperature and configuration, fire assay duration, cupel type, correction by the proof samples made by different ways, ...
- For gravimetry: Au loss, Ag coprecipitation, residual Au solubility, imperfect correction by the blank, traces of O and C in the sponge, ...
- For potentiometry: accuracy of Ag content of the standard used for KBr solution calibration, $N_2O_4$ electrochemical interferences, algorithm to evaluate the equivalent point, ...
- For XRF analysis: presence of impurities which cannot be evaluated at this concentration level, preparation of the sample, stability of the spectrometer, not measured elements, ...
- For ICP-OES analysis: contaminations, imperfect blank correction, spectral interferences, instrument drift, not measured elements, ...
- For Spark-OES: contamination during sample preparation (by abrasive paper or drilling machine), spectral interferences, instrument drift, not measured elements, ...

Elements which can be measured by various methods

<table>
<thead>
<tr>
<th></th>
<th>H</th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
<th>Ne</th>
<th>Mg</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cl</th>
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<tbody>
<tr>
<td>Na</td>
<td>K</td>
<td>Ca</td>
<td>Sc</td>
<td>Ti</td>
<td>V</td>
<td>Cr</td>
<td>Mn</td>
<td>Fe</td>
<td>Co</td>
<td>Ni</td>
<td>Cu</td>
<td>Zn</td>
<td>Ga</td>
<td>Ge</td>
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<td>Rb</td>
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<td>Zr</td>
<td>Nb</td>
<td>Mo</td>
<td>Tc</td>
<td>Ru</td>
<td>Rh</td>
<td>Pd</td>
<td>Ag</td>
<td>Cd</td>
<td>In</td>
<td>Sn</td>
<td>Te</td>
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<tr>
<td>Cs</td>
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<td>La</td>
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<td>Eu</td>
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<td>Yb</td>
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<td>Th</td>
<td>Pa</td>
<td>U</td>
<td>Np</td>
<td>Pu</td>
<td>Am</td>
<td>Cm</td>
<td>Bk</td>
<td>Cf</td>
<td>Es</td>
<td>Fm</td>
<td>Md</td>
<td>No</td>
<td>Lr</td>
</tr>
</tbody>
</table>

70 Elements covered by ICP methods (green)
5 Elements covered by gas methods (blue)
4 Elements covered by ionic chromatography (pink)
LoD in Ag 999‰ for elements relating to various methods

Unit [mg/kg] - ICP (green), Gas (blue), IC (pink), Not evaluated (yellow)

### Comparison of analytical methods

**Analysis performed on a real production sample**

<table>
<thead>
<tr>
<th>Analytical method</th>
<th>Estimation [%]</th>
<th>Precision [%] (1 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal composition</td>
<td>995.17</td>
<td>0.015</td>
</tr>
<tr>
<td>Fire assay</td>
<td>995.14</td>
<td>0.040</td>
</tr>
<tr>
<td>Gravimetry (H\textsubscript{2}SO\textsubscript{3})</td>
<td>995.10</td>
<td>0.11</td>
</tr>
<tr>
<td>XRF spectrometry</td>
<td>995.15</td>
<td>0.032</td>
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<tr>
<td>Spark OES</td>
<td>995.22</td>
<td>0.029</td>
</tr>
<tr>
<td>HP ICP OES</td>
<td>995.16</td>
<td>0.008</td>
</tr>
</tbody>
</table>
Discussion of the differences between methods:

- Gold gravimetry: small loss of gold during the evaporation of acids and/or distillation of HAuCl₄.
- Spark OES: uncertainty of Ag and/or Cu calibration curves and/or small variation of the analytical gap between W electrode and the flat surface of the sample and/or weak uncorrected matrix effect due to the multi-elements standards, …
Ag 999‰ - Accuracy and precision

Comparison of analytical methods

Analysis performed on a laboratory sample (400 g)

<table>
<thead>
<tr>
<th>Analytical method</th>
<th>Estimation [‰]</th>
<th>Precision [‰] (1 s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nominal composition</td>
<td>999.12</td>
<td>0.025</td>
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<tr>
<td>Potentiometry</td>
<td>999.43</td>
<td>0.34</td>
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<tr>
<td>Indirect Spark OES</td>
<td>999.18</td>
<td>0.02</td>
</tr>
<tr>
<td>Indirect HP ICP OES</td>
<td>999.11</td>
<td>0.04</td>
</tr>
</tbody>
</table>

Distribution of analytical results
Conclusions

• The analytical methods evaluated for Au 995‰ and Ag 999 ‰ determination do not exhibit significant bias and confirm the accuracy of recommended LBMA methods. Some methods are complementary, they guarantee a better accuracy of the results.

• Accuracy and precision are generally higher for indirect methods in comparison with direct methods when the metal content is higher than 980-995 ‰. This is also true for high grade Pt, Pd and Rh.

• For indirect methods, the analyst has to pay attention to the presence of unusual elements and to the spectral interferences.

• Additional methods as gas analysis are recommended for easily oxidizable metals as Ag, Pd and Rh.