Metalor Technologies S.A.

Optimisation of fire assay analytical conditions for gold determination in industrial environment

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Optimisation of fire assay conditions for gold determination

- Fire assay method for gold determination is an old well known analytical method which is clearly described in ISO 11426-1997.
- This method covers the determination of gold in bullion estimated to contain from 0.5‰ up to 999‰ gold. Accuracy and precision of this method is also well known.
- In Switzerland, control of precious metals is managed by a law and supervised by BCMP (Bureau de Contrôle des Métaux Précieux) and all laboratories are accredited according to ISO 17025.
- Today, for refining companies, the increasing of gold market price requires a **more accurate determination of gold in alloys in order to reduce the financial risk in an industrial environment**.

Optimisation of fire assay conditions for gold determination

- **Evolution of gold price over 35 years.**
- From **http://goldprice.org/gold-price-history.html**

Optimisation of fire assay conditions for gold determination

- For this main reason, we have studied in detail the effect of the most significant parameters which affect the gold content in terms of precision and accuracy and try to correct them.
- Various standards were used. Mainly :
  - ISO 11426-1997
  - ISO 5725 (1 to 6)
  - Eurachem guide incertitude
- Various statistical methods were used to contribute to the improvement of the results :
  - Grubbs algorithm
  - Excel solver
  - PCA

Alternative analytical methods for gold determination

- Gravimetric method, after dissolution of the sample, by reduction of $HAuCl_4$ with SO_2 or oxalic acid
- Electro-gravimetry
- X-Ray fluorescence method
- Spectrometric method by AAS and ICP-OES
- Spectrometric method in solid state by Spark-OES
- Methods are generally direct chemical methods (by difference if Au>990‰ with ICP-OES and Spark-OES method).
- In practice, cupellation is the most efficient method in terms of cost, accuracy, precision and robustness when the composition of the alloy is not too complex.

Discussion of fire assay method

- For gold assays by cupellation, the alloys are inquarted with silver, compounded with lead (and Cu for high purity alloys) and cupelled in a cupellation furnace until a precious metal button is obtained. After flattening and rolling, silver is extracted in nitric acid and gold weighed.
- Possible systematic errors in the procedure are largely eliminated by assaying synthetic proof samples in parallel but in industrial environment, assays cannot be corrected by a large number of proof samples.
- Bias have various origins : loss of gold by volatilisation and by diffusion of gold inside the cupel (roots), during the handling of the button : brushing, flattening and rolling of the button.

Optimisation of fire assay conditions for gold determination

- Overweight of silver in the button due to not fully quantitative dissolution of Ag in nitric acid
- Residue of common metals of the alloy in the button
- Presence of slag due to common metals as Ni
- Residue of lead and lead oxide in the button
- Presence of PGMs : Pt, Pd, Rh, Ir, Ru.
- Difference of composition between the sample and the proof sample.

- Globally, the bias is resumed to the balance between silver overweight (and traces of common metals) and loss of gold.

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Fire assay parameters studied

These parameters are well known and are discussed in a lot of various papers and books. From our experience, we have retained the following 20 parameters :

1. Balance
2. Assay weight
3. Composition of the assay (Au, Ag, Pt, Pd, Cu, common metals)
4. Inquartation ratio
5. Mass of Cu and Pb added to the assay before the fire assay
6. Cupel type (supplier)
7. Cupel pre-burn
8. Furnace temperature and temperature control

Optimisation of fire assay conditions for gold determination

9. Fire assay duration
10. Position of the cupel inside the furnace
11. Local temperature inside the furnace
12. Casting of the assay
13. Brushing of the button
14. Flattening of the button
15. Button rolling and lamination thickness
16. Thermal treatment of the assay to improve the assay rolling
17. Effect of the common metals
18. Composition and number of proof samples
19. Position of the proof samples
20. Algorithm used for proof sample correction

Optimisation of fire assay conditions for gold determination

Experimental study

Study was divided into three steps :

1. First experiment plan to evaluate the sensitivity of gold content to various parameters, 400 assays performed with only proof samples (series of 9 to 15 assays).
2. Second experiment plan for the simultaneous determination of correction coefficients with Excel solver and PCA method, 300 assays performed with only proof samples.
3. Third plan with 300 assays to validate the correction model with real alloys 995, 750, 575 and 375‰.

   Assays were performed by 6 operators, on 3 furnaces, with 4 tanks for acid dissolution (robots) and over one year.

Optimisation of fire assay conditions for gold determination

- First, gold results were filtered with Grubbs algorithm to reject significant (95% level) outliers in series.
- Next, sensitivity to each parameter, corresponding to our cupellation parameters and to the materials we are analyzing in routine.
- Then contribution of each parameter was evaluated with : Principal Component Analysis (PCA method). This method is a mathematical procedure that uses an orthogonal transformation to convert a set of observations of possibly correlated variables into a set of values of uncorrelated variables called principal components.

Optimisation of fire assay conditions for gold determination

This transformation is defined in such a way that the first principal component has as high a variance as possible.

- Next Excel solver was used after implementation of a mathematical model for the parameters. This Excel tool allows to perform multivariable calculations.
- The assays were realised using : Au 999.99‰, Ag 999.99, Cu 999.9‰, Pb 999‰ (without any traces of Au, Ag, Pt, Pd) and Pt 999.8‰ and Pd 999.7‰ for additional evaluations. All these metals were analysed by ICP-OES in order to evaluate accurately bias.

Optimisation of fire assay conditions for gold determination

- Covariance between sample and proof sample response was studied using Excel functions.
- Correlation between button overweight (positive or negative) and Ag content in the buttons (analysis by ICP-OES).
- After then, results obtained with the solver were studied in details to guarantee the convergence of the algorithms after iterations.
- Verification and validation of the algorithms was performed according to “Eurolab guidance for the management of computers and software” in reference to ISO/IEC 17025 (Technical Report N° 2/2006).
- Accuracy (trueness and precision) of the results was evaluated according to ISO 5725 (1 to 6)

Optimisation of fire assay conditions for gold determination

Experiments

1. **Assay composition (Au, Ag, Pt, Pd, common metals)**

- An assays plan was realised with various content of PMs (Au, Ag, Pt, Pd) and CMs (Cu, Zn, Ni, Sn, Pb, As, Sb, Mo, W, Al, Cr, Mn, Ti, Se, Te, Bi) corresponding to the materials we analyse in routine. The effect is a complex behaviour approximated by linear or quadratic corrections for all elements
- Nevertheless, in this study, we consider only assays with Au, Ag, Cu and relatively low content of alloying elements (not more than 20‰ in order to limit the complexity of the calculation).
- Assays were performed first with fine common metals (999 to 999.99‰) and proof samples, next with real alloys.

Optimisation of fire assay conditions for gold determination

2. Study of sensitivity to each parameter

- Sensitivity to each parameter X_1, X_2, …, X_i, … ,X_n was evaluated from an experiment plan taking into account a realistic range for each parameter corresponding to our cupellation parameters and to the materials we are analyzing in routine.
- The sensitivity to various parameters may be fitted by linear or quadratic equations.
- From this study, the main identified parameters are the local temperature inside the furnace and the efficiency of the nitric dissolution in the tanks. Four other parameters exhibit a significant effect.

Optimisation of fire assay conditions for gold determination

3. Effect of furnace temperature

- A specific tool was built including a stand with thermo-sensors at the position of the cupels. Temperature was then accurately measured inside the furnace all over the cupellation cycle with an acquisition data processor (not during the cupellation to protect the sensors).
- Results shows a good correlation between the temperature and the position (quadratic polynomial fit for the three furnaces) as between the gold content and the position during the cupellation.

Optimisation of fire assay conditions for gold determination

4. Data processing with Excel solver

- After evaluation of the sensitivity of 20 parameters, the plan was reduced to height parameters and Excel solver was used to solve a system of 500 equations with 28 independent variables. The fit between real and calculated data was evaluated by minimization of the global standard error of estimate. After corrections of the data, its value is 0.12‰ and variance is reduced by 60%

Optimisation of fire assay conditions for gold determination

5. PCA method

PCA was applied to about 900 gold assays. Cumulative Results are :

FIT MEASURES

COMPONENTS	E-Value	Prop.	CumProp
PC1	11.52291	**0.76819**	0.76819
PC2	1.93249	**0.12883**	0.89703
PC3	0.60898	**0.04060**	0.93763
PC4	0.22867	0.01524	0.95287
PC5	0.17709	0.01181	0.96468
PC6	0.11712	0.00781	0.97248

Optimisation of fire assay conditions for gold determination

- The first component PC_1 was identified as the **local temperature inside the furnace** with Prop. = 76.8%
- The second one PC_2 was identified as the **efficiency of the dissolution in nitric acid** with Prop. = 12.9%
- All the other components PC_i represent only Prop. = 10.3%
- This means that about 90% of the variance is explained by only two parameters. In theory, the standard error may be improved by a factor 3.

Optimisation of fire assay conditions for gold determination

6. Evaluation of the bias of gold content

- Laboratory uncertainty is depending of the repeatability of the method and of the number of assays. We have verified that, after corrections by proof samples, the distribution is normal. Then, according to ISO 5725-4, uncertainty bias Δ_m is given by formula :
- $\Delta_m / 1.84 \geq 1.96 \sigma_r / \sqrt{n} <$ where Δ_m is the amplitude of the bias that the analyst want to detect.
- We consider that the accurate value for gold content is the value given by ICP. For the proof samples Au 999.99‰ calculation gives as uncertainty bias Δ_m = 13 ppm for cupellation when ICP-OES gives Δ_m = 2 ppm

Optimisation of fire assay conditions for gold determination

7. Composition of materials used for proof samples

With modern ICP spectrometers, the number of elements and lines which can be measured is generally not limited. (255 lines on Varian or Thermo 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.

32 elements are routinely measured in gold : Ag, Cu, Fe, Bi, Se, Te, Pb, Pd, P, Ni, Sb, Si, Sn, Zn, As, Cd, Na, K, Ca, Mg, Cr, Al, Rh, Co, Mn, Mo, B, Tl, In, Ti, Pb, Pt very low LoD.

Optimisation of fire assay conditions for gold determination

8. Application to synthetic and real samples

- 9 ct alloy (synthetic sample) 375.0 ± 0.11 ‰
- 14 ct alloy (synthetic sample.) 575.0 ± 0.09‰
- 18 ct alloy (synthetic sample) 750.0 ± 0.07‰
- 22 ct alloy (synthetic sample) 917.0 ± 0.07‰
- 995 alloy (real sample) 995.0 ± 0.07‰
- Fine gold (real sample) 1000.0 ± 0.06‰
- 18 ct alloy (real sample) 751.42 ± 0.09‰
- 14 ct alloy (real sample) 575.40 ± 0.09‰

Optimisation of fire assay conditions for gold determination

9. Comparison of analytical methods for 995 analysis

Analysis performed on a real Au 995‰ production sample

Analytical method	Estimation [‰]	Precision [‰] (1 s)
Nominal composition	995.17	0.015
Fire assay	995.14	0.040
Gravimetry (H_2SO_3)	995.13	0.090
XRF spectrometry	995.15	0.032
Spark OES	995.22	0.029
HP ICP OES	995.16	0.008

Optimisation of fire assay conditions for gold determination

10. Conclusion

This study demonstrates :

- The efficiency of statistical methods to improve performances of analytical methods and to reduce the financial risk.
- The potential of improvement for the fire assay method. The application of this method in our laboratories, shows that about 90% of the variance is explained (and may be corrected) by thermal effect inside the furnace and by the efficiency of the acid dissolution in tanks. The other PC_i are negligible and cannot be simply identified.
- The simplification of the corrections with proof samples. One or two proof samples are enough to correct a full series when the composition of samples are not too different.