# ARGOR-HERAEUS SA

The golden link

## Uncertainty of Assaying Measurements

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High-tech precious metals processing

“If we begin with certainties, we shall end in doubts,
but if we begin with doubts, and are patient in them,
we shall end in certainties.”

Francis Bacon (1561-1626)
British philosopher, essayist and statesman

## uncertainty and error

UNCERTAINTY = a parameter associated with the result of a measurement that characterises the dispersion of the values that could be reasonably attributed to the measurand.

It does not imply doubt about the validity of a measurement - inversely, it implies increased confidence in the validity of a measurement result.

ERROR = difference between an individual result and the true value of the measurand.

Only if we know the true value of a measurand we can assess the error.

☞ The value of a known error can be used as a correction to the result; the uncertainty cannot.

☞ A result may be by chance very close to the true value, and therefore the error will be negligible. The uncertainty, however, may be still very large.

# types of error

random error

- It arises from unpredictable fluctuations of influence quantities.
- It cannot be compensated for, but it may be reduced.

systematic error

- An error which remains constant or varies in the time in a predictable way.
- It is independent of the number of measurement.
- If known, it can be compensated for.

spurious error

- It typically arises through human failure or instrument malfunction.
- It should be identified and the corresponding measurement result discarded.

## usefulness of the uncertainty

The knowledge of the measurement uncertainty, or rather of the confidence interval related to a reported value, is a valuable information that finds its use in the following fields:

- Compliance with specified limits.
  Are the results really within the limits?
- Assessment of analytical results.
  Are the results sufficiently reliable?
- Validation of analytical methods.
  Is the method fit for purpose?
- Screening of possible analytical methods.
  Which method is most promising?
- Improvement of existing analytical procedures.
  Where is place for improvement?
- Qualification of equipments and/or operators
  Do they meet the requirements?

## Step 1 : Specify the measurand

Specify which is the output value of the measurement.

## Step 2 : Identify the uncertainty sources

Specify how the output value, relates to the input values. In the case of the determination of the gold fineness by fire assay, this will be

$$X_{Au} = \frac{m_{1,S} - dm_P}{m_{0,S}} = \frac{m_{1,S} - (m_{1,P} - m_{0,P})}{m_{0,S}}$$

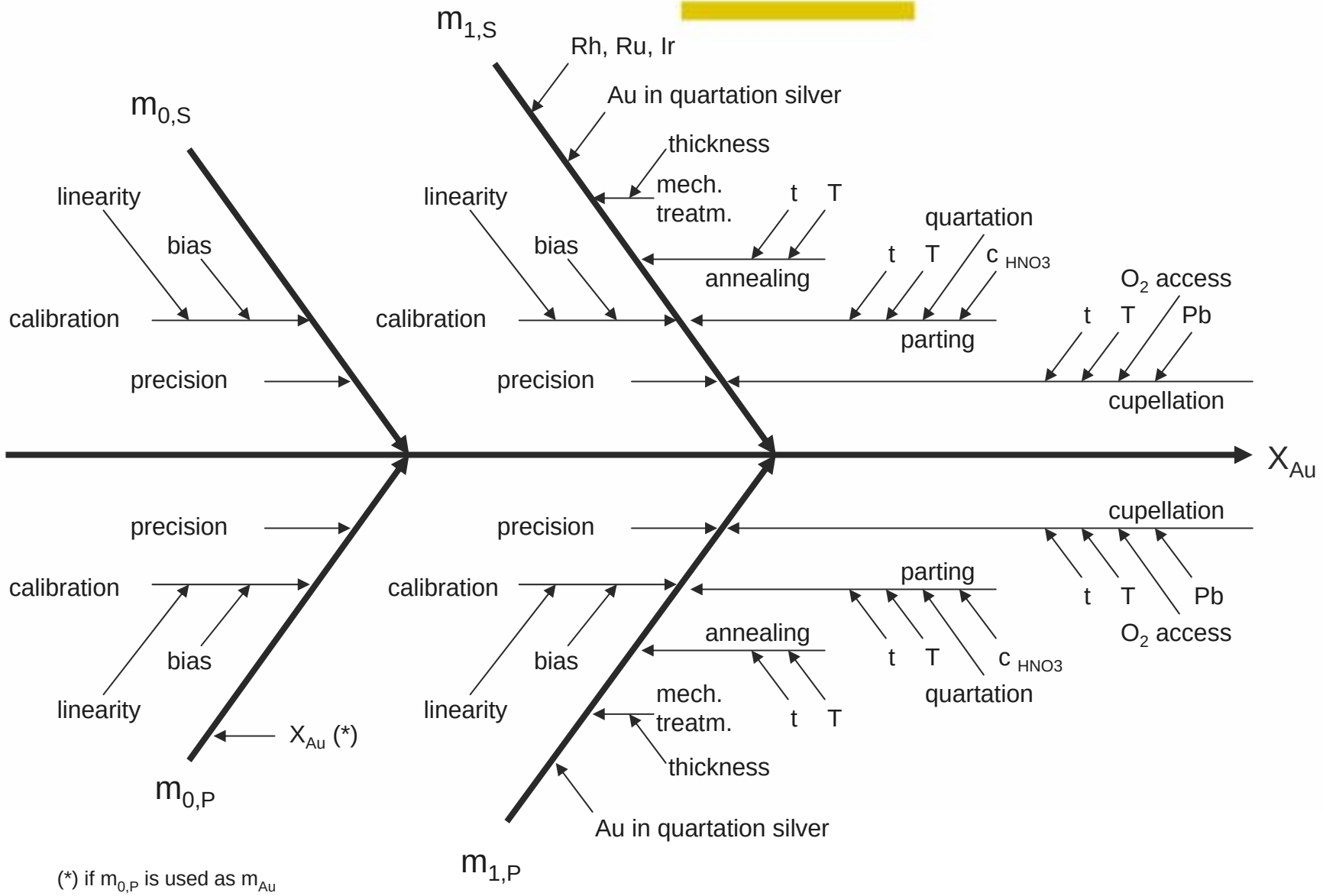
where
- $X_{Au}$ is the gold fineness
- $m_0$ is the initial weight of the sample ($m_{0,S}$) and of the proof ($m_{0,P}$)
- $m_1$ is the final weight of the sample ($m_{1,S}$) and of the proof ($m_{1,P}$)
- $dm_P$ is the weight excess of the proof after cupellation

If constants, like curve parameters or physical constants, are included in the formula, their uncertainty has to be considered as well.

## Step 3 : Calculate the individual standard uncertainties, $u_i$

Consider each input value.
Consider each unit operation.

# evaluation of the uncertainty




(*) if $m_{0,P}$ is used as $m_{Au}$

Simplify wherever possible

- In particular cases, contributions to the uncertainty cancel out.

  This is possible, for example, when appropriate reference samples, or proofs, are included in the measurement series.

- Where appropriate, group uncertainty contributions.

  Often it is not easy to isolate and to evaluate individual contributions. If it is not necessary to consider them separately, as for example it is when a procedure needs to be optimised, it is reasonable to group them together.

In practice, it is usual to consider the uncertainty associated with elements of overall method performance, such as observable precision and bias measured with respect to appropriate reference materials.
These contributions generally form the dominant part of the uncertainty.

Collect data

- Type A evaluation : based on statistical analysis of series of observations.

  Depending on the information required, collect standard deviations representing the repeatability, or in other cases the intermediate precision.

- Type B evaluation : based on approaches other than Type A.

  The evaluation may include data taken from handbooks, manufacturer specifications, calibration data, interlaboratory comparisons, etc.

  This kind of approach allows, among other things, to assess the uncertainty related to procedures that are not yet implemented in one’s laboratory.

Step 4 : Calculate the combined standard uncertainty, $u_c$

Use the law of propagation of the uncertainty. If the individual components are not correlated, the variances simply add up:

$u_c^2 = \Sigma\, \mathbf{u_i^2}$ **or** $u_c = \sqrt{(\Sigma\, \mathbf{u_i^2})}$

Step 5 : Calculate the expanded uncertainty, U

The expanded uncertainty takes into account the desired confidence level. Normally, an expansion factor k=2 (for a confidence level of about 95%) or k=3 (for a confidence level greater than 99%) is used.

$U = k\, u_c$

The expansion factor (or the corresponding confidence level) has always to be mentioned when stating the uncertainty of a measurement result.

## HOW TO REDUCE THE UNCERTAINTY

Reduce the uncertainty related to the statistical errors

- by improving the procedure and/or the equipment
- by increasing the number of replicates

Reduce the uncertainty related to the systematic errors

- by using appropriate reference samples (e.g. proofs)
- by using certified reference materials
- by the information obtained through round robins

## HOW TO MANAGE THE UNCERTAINTY

Check the performance (e.g. using quality control cards)

- of the critical components
- of the operators
- of the whole process

☞ (Re-)calibration is a source of uncertainty

(Re-)calibration is essential to get accurate analytical results. However, it is subject to the same sources of error and uncertainty as the analysis itself. The uncertainty of the (re-)calibration, as well as that related to the use of proof samples, has therefore to be taken into account when calculating the combined uncertainty.

☞ Get lower uncertainty with less work

The standard uncertainty of the mean value of n replicates, $u_n$, can be expressed as

$$u_n = s / \sqrt{n}$$

**where s is the standard deviation of the analytical method**

**Therefore, if s = 0.10 ‰, the uncertainty becomes**

$$u_{n=1} = 0.10 ‰ \quad ; \quad u_{n=2} = 0.071 ‰ \quad ; \quad u_{n=4} = 0.050 ‰ \quad ; \quad u_{n=8} = 0.035 ‰$$

**If we perform a fire assay using two samples and one proof**

$$u_c = \sqrt{(u_S^2 + u_P^2)} = \sqrt{(u_{n=2}^2 + u_{n=1}^2)} = \sqrt{(0.071^2 + 0.10^2)} = 0.12\ ‰$$

**Similarly, for eight samples and one proof**

$$u_c = \sqrt{(0.035^2 + 0.10^2)} = 0.11\ ‰$$

**But for four samples only, and two proofs**

$u_c$ = **Ö (0.050 2 + 0.071 2) = 0.09 ‰**

... A better result with less work!

☞ Do not forget the sampling

The sampling of the material is also related to a certain level of uncertainty, which adds up with the uncertainty of the analytical result. It is therefore important to hold both aspects of the task in sight. Any improvement reached in the analytical laboratory will be useless if the uncertainty related to the sampling is not correspondingly low.

## CONCLUSIONS

Although the term bears in itself a negative connotation, the uncertainty of the measurement is a valuable source of confidence.

Its knowledge is not only important when stating the compliance with specified limits, but also allows among other things to assess the performance of new analytical procedures, and to optimise efficiently existing ones.

A good knowledge of its background allows to work more efficiently, ensuring optimum analytical performance and cost-effective operation at he same time.

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