ARGOR-HERAEUS SA

The golden link

Uncertainty and Fineness Marking of Bars

Alessandro Ruffoni, London, 10th march 2015

High-tech precious metals processing

Overview

Since the time of the pharaohs, precious metals deliveries are object of careful acceptance checking and of disputes on their purity.

Since biblical times the mankind has learned to assay them, and throughout the centuries the bars have begun to be marked quite like they are today.

Overview

Centuries before the establishment of universally recognized authorities the recipients of the gold and silver bars certainly already had a precise opinion about the reliability of their declared quality.

Nowadays, anyway, the global market can take advantage of

- clear guidelines, like the Good Delivery Rules and the national regulations
- precise assay methods
- established regulatory and control authorities

Although not all regulations fully overlap, the globalization has led in the recent decades to largely shared rules.

Precision and Accuracy

Numerous speeches held during this conference cycle and during the previous ones have underlined a number of crucial aspects of the assaying:

- the achievable precision of the different assaying techniques, represented by the level of their statistical uncertainty
- the existing ways to assure the accuracy (trueness) of the assay results, basing on the use of certified reference standards and on the participation in proficiency testing programs.
- the involvement in the certification and in the accreditation of the production and of the assay laboratory in order to continuously assure and improve the quality of the company's products.

Besides of the uncertainty related to the assaying methods and procedures, further factors possibly determining whether the fineness marked on the bars is correct or not need to be identified and considered.

Precision and Accuracy

In the need to keep the uncertainty under proper control, two kinds of contributions have to be distinguished:

(1) the ones related to the statistical error

They cannot be avoided, but they can be controlled and reduced

(2) the ones related to systematic errors

They can have a significant and critical influence on the quality of the product (in our case on the fineness to be marked on the bar).
It is necessary to identify them so that can be avoided.

Leaving apart the systematic errors possibly related to the work of the analytical laboratory, considered elsewhere, it is important to focus our attention onto the sampling.

Sampling

Which kind of sampling?

FINAL PRODUCT

The fineness marked on the bars is obviously related to the finished product.

It is less obvious, inversely, to analyze the finished bars because:

- fire assay and ICP require drillings
- Spark-OES leaves noticeable marks on the metal surface
- XRF, despite of being non-destructive, has a number of requirements that make its use basically impossible with finished bars

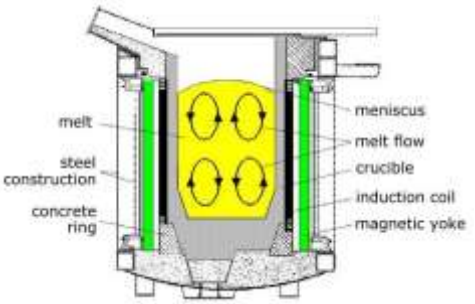
Sampling

MELT

Once the starting material has been completely melted and the obtained melt homogenized by proper stirring, the right sample for the batch can be drawn.

Pin samples or disk samples obtained by suction from the melt, or disks obtained by transferring a portion of the melt into a small mould using a ladle are appropriate.

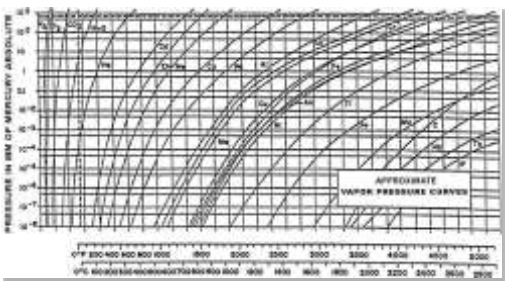
Proper stirring of the melt is achieved by the action of the electromagnetic field when using induction furnaces.



Sampling

Of course, accidental contamination downstream has to be prevented.

In the case of strong overheating and long pouring time the lower boiling elements present in the melt tend to escape, determining a deviation of the fineness of the cast metal in comparison to the one of the drawn sample. In refined metals and by atmospheric pressure the extent of this effect is however limited.



Sampling

STARTING MATERIAL

When using tunnel furnaces each bar - may it be a 100-grams gold bar or a 1000-ounces silver Good Delivery bar - has to be considered as a "batch" on its own.

Since the assaying of the finished bar, as discussed before, is not feasible, one has to rely on the analysis of the starting material.

Two different technical approaches exist:

- melting of previously melted and cast material (in the form of granules or of raw metal blocks)

→ the assay of the originating melt will be valid for the whole corresponding lot

- melting of crystals (cathodic deposit)

This approach allows to avoid one melting operation and would therefore be preferable from an economical and from an ecological point of view.

Sampling

However…

- single portions of the crystals may not be washed properly

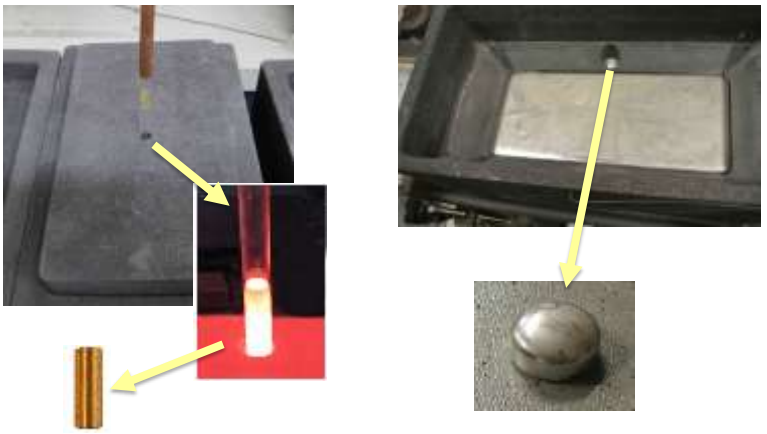
- crystals obtained at different times during the refining operation may differ in their purity due to the changes in the working conditions (electrolyte depletion, cell voltage or current density evolution)

- crystals obtained at the same time in different points of the cathodes may display varying levels of impurities due to local differences in the electrical field ("edge effect") and in mass transport towards the electrode (convection, diffusion)

This makes the use of crystals conceptually unsuitable for the quality assurance of small bars (up to kilobars) produced in large numbers using tunnel furnaces.

In the case of Good Delivery bars, in turn, technical solutions of this issue have been studied and developed.

Sampling

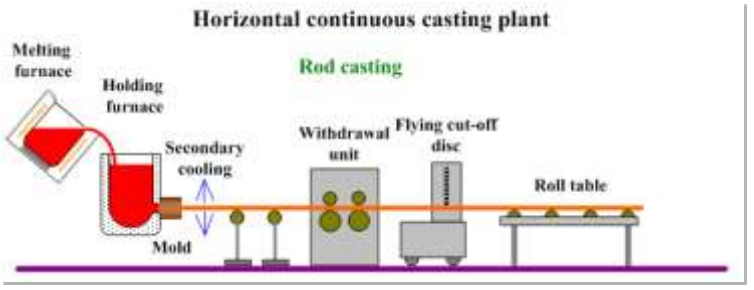


Dip sampling procedures available for the IKOI FLAMELESS TUNNEL® (*WORLDWIDE IKOI PATENT)*

Sampling

Which sampling scheme for the continuous casting?

In Continuous Casting the metal is prepared batchwise using a melting furnace, then poured into a holding furnace and drawn from it through a graphite mould in order to produce a rod with the desired section.



Sampling

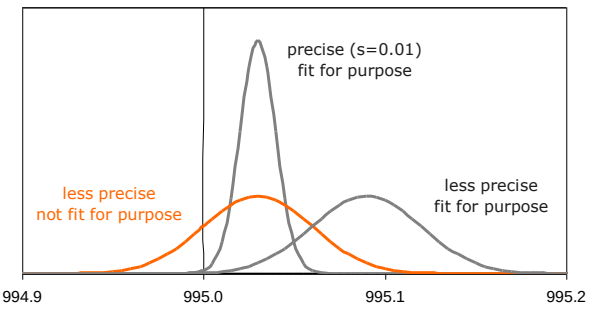
The produced rod is mainly an intermediate product; it can be cut into raw blocks which are further remelted to produce cast bars, or into strips that are rolled down and die-cut to produce minted bas. It can be also be cut and milled to produce Good Delivery bars.

If a rapid analysis is available, the fineness is checked before pouring the molten metal into the holding furnace. Spot sampling of the rod at the end of the production line is also possible, provided that the sampling interval includes a quantity of metal that does not exceed the size of the initial melting batches. Only in this way it is possible to spot accidentally produced off-standard material.

During its operation the holding furnace is never emptied completely before a new molten batch of metal is added. For this reason only certificates of conformity of the final product can be issued, whereas it is not possible to provide full analytical certificates correctly related to each individual bar.

Responsible decision

Now we have drawn the ultimate sample, and performed our best analysis. Our result is a Gold fineness of 995.03. Is this OK?



Provided that our result is accurate, the minimum fineness of 995.0 will be assured only if our precision is good enough

Conclusions

CONCLUSIONS

The recipe for a correct marking of the fineness of the gold and silver bars is the following:

• control and reduce statistical uncertainty, in the same time allowing a safety margin above the minimum required fineness corresponding to the uncertainty of the fineness determination

• use appropriate means of quality management in the analytical lab in order to assure the best possible accuracy of your assays: the purchase of Certified Reference Materials and the participation in Proficiency Testing will add reliability to your assays

• avoid the uncertainty related to systematic errors by proper process concept and by appropriate sampling; when inhomogeneity of the sampled material can be presumed, sample the material where its fineness can be expected to be lower.