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CHALLENGES IN 999.9 GOLD ASSAYING BY CUPELLATION

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HILTON BANGALORE
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CHALLENGES IN 999.9 GOLD ASSAYING BY CUPELLATION

Standard	Analytical method	Au Range		Target Repeatability (2 replicates)	Repeatability on Au 999.9 ‰
		From (‰)	To (‰)		
ASTM E1335-08:2017	Fire Assay	5	998,0	Au <995‰ : 0.5 ‰ 995.0‰ ≥ Au < 999.5‰: 0.16 ‰	**NA**
ISO 11426:2021	Fire Assay	100	999,5	Au <995‰ : 0.5 ‰ 995.0‰ ≥ Au < 999.5‰: 0.16 ‰	**NA**
ISO 15093:2020	ICP-OES	999,0		10% of the total impurities	**0.1 ‰**
ISO 18214:2024	Spark-OES	999,0		Au ≥999.9: 0.01‰ 999 < Au < 999.9: 0.05 ‰	**0.01 ‰**
ISO 5724:2023	ICP-MS	999,99		25% of the total impurities	**NA**

NA = Out of scope

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Normative	Method	(0‰)	5‰	100‰	500‰	900‰	950‰	998‰	Au ‰ 998.5‰	999‰	999.5‰	999.9‰	999.99‰	(1000 ‰)
ASTM E1335-08 :2017	Fire Assay													
ISO 11426:2021	Fire Assay													
ISO 15093:2020	ICP-OES													
ISO 18214:2024	Spark-OES													
ISO 5724:2023	ICP-MS													

Overlapping area

In some cases the range of use is defined as «preferably»

Can a small range extension in fire assay analysis be considered?

Yes but… uncertainty must be evaluated very carefully!

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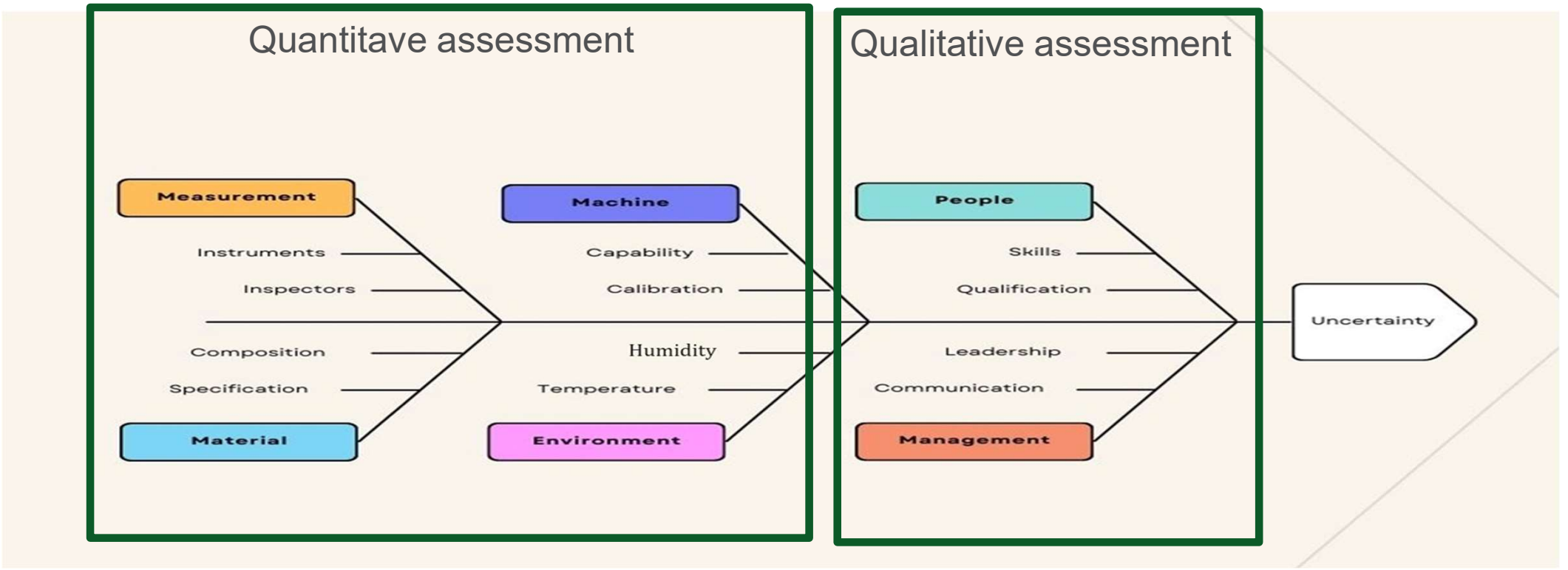
QUANTITATIVE / QUALITATIVE ASSESSMENT



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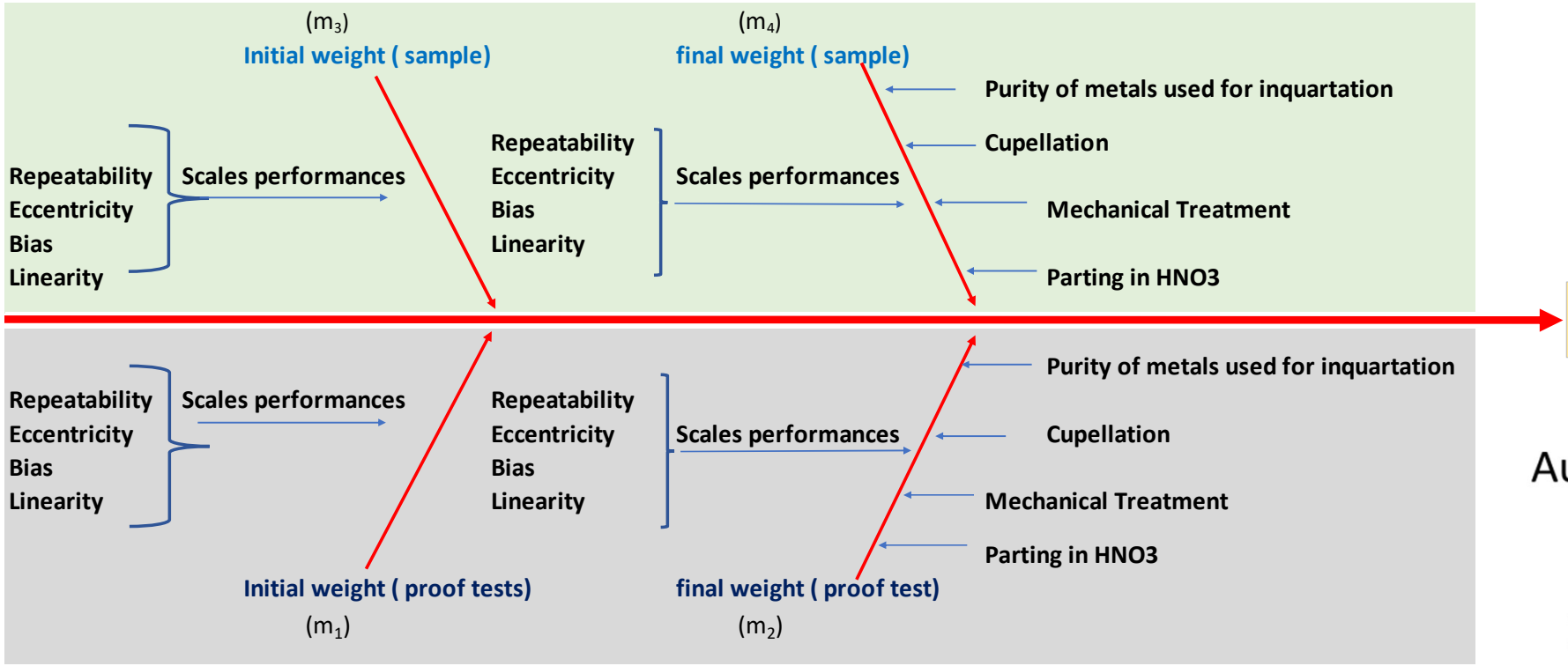

$$Au‰ = \frac{m4 * F}{m3} * 10^3$$

$$F_{avg} = \frac{m1}{m2}$$

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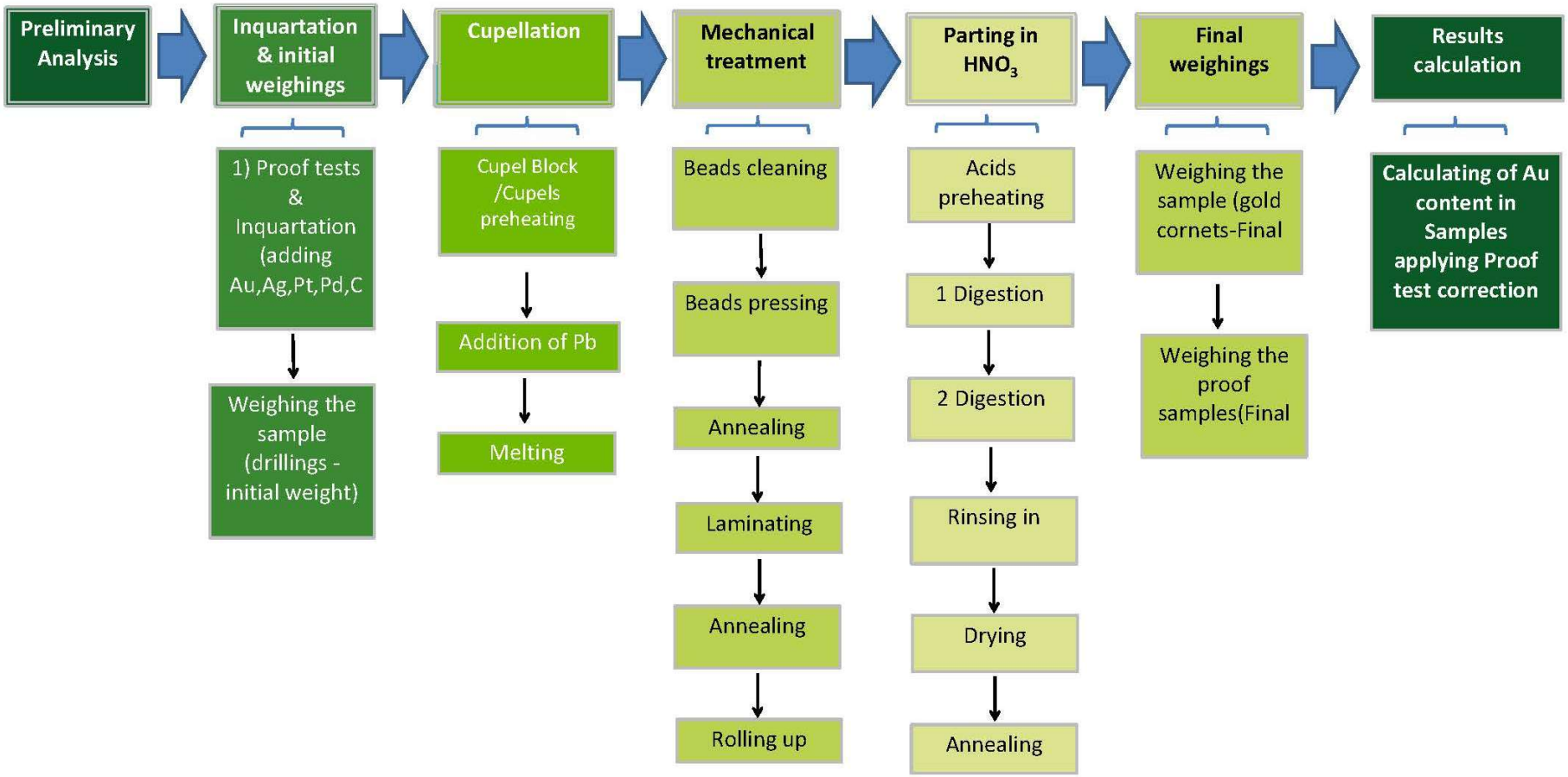
AU CONTENT DETERMINATION VIA FIRE ASSAY - GENERAL PROCESS



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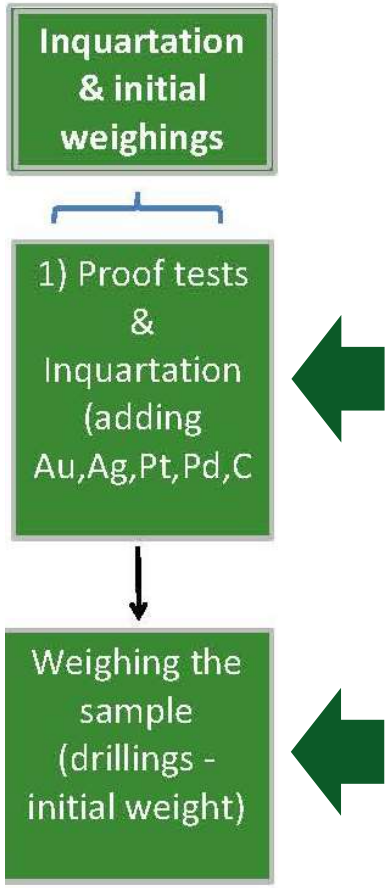
INQUARTATION



Inquartation

Au for proof samples min purity	999.99	‰
Ag for proof samples min purity	999.9	‰
Pb & Cu for proof samples min purity	999.9	‰

Scales

Accurancy : 0.001 mg
Sample weight: 500 mg (double the standard weight)
Environment: T & RH% under control

Check che performance of the scale stated on the certificate issued by the manufacturer!

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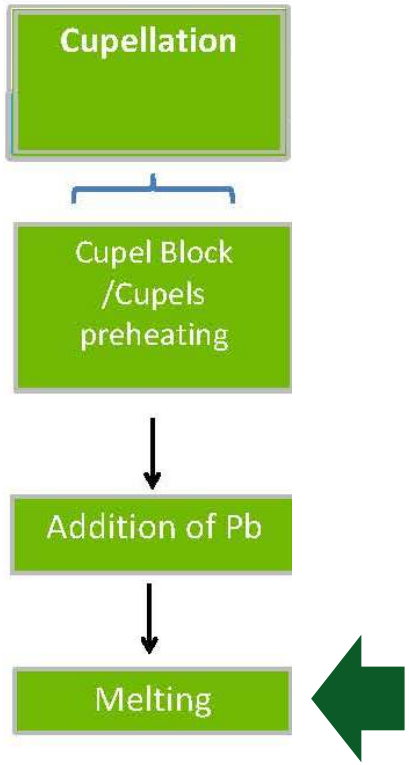
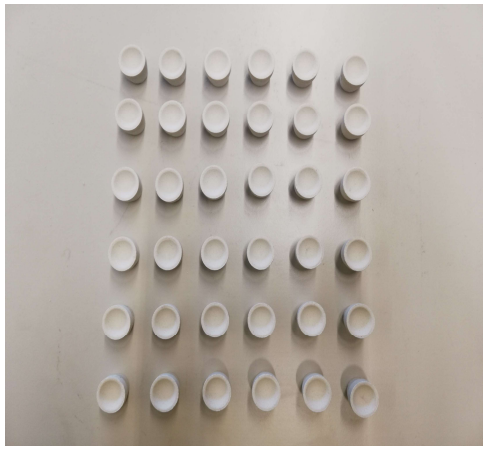
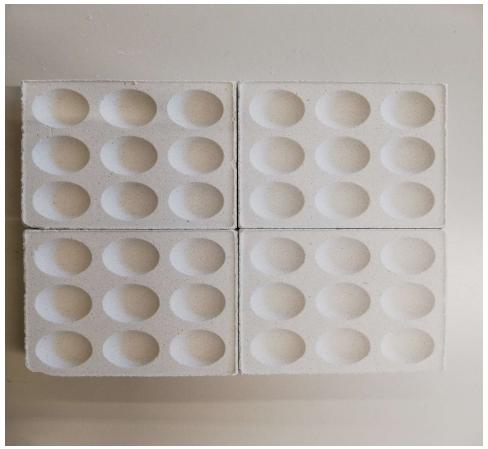
CUPELLATION



36 MgO single cupels



4 MgO blocks 3x3



The temperature inside the oven should be as homogeneous as possible, small variations are corrected by proof tests.

The use of an MgO blocks increases the position-related repeatability.

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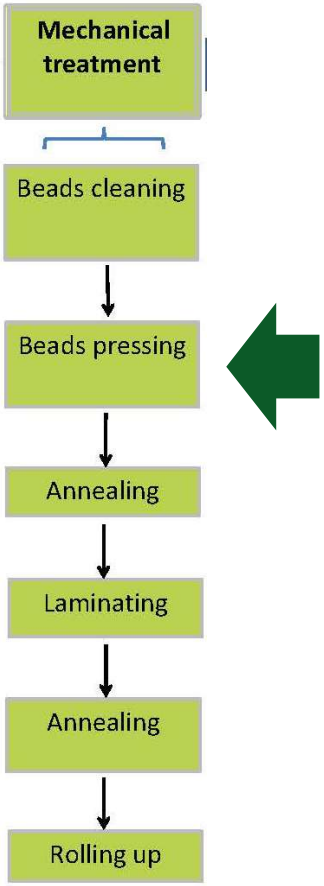
MECHANICAL TREATMENT, 1



Anvil & Hammer

Hydraulic Press

The bead resulting from cupellation must be cleaned and flattened before being rolled.
The use of anvil & hammer is historical but the surface of the hammer must be absolutely smooth and clean.
Using a press gives greater safety and repeatability

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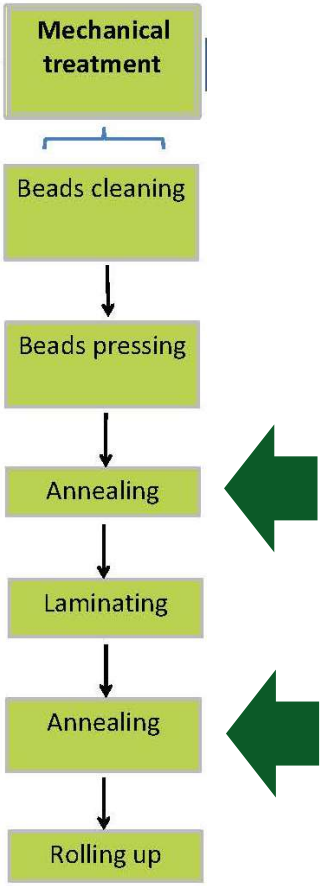
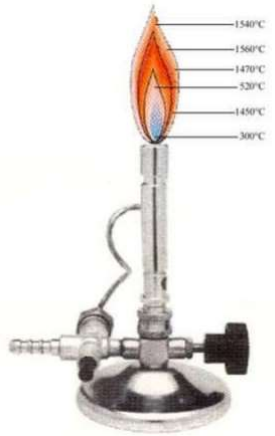
MECHANICAL TREATMENT, 2



Bunsen burner



Annealing oven

The bunsen burner does not allow an effective temperature control as an annealing oven.
Some areas of the flame are too hot , others too cold.
In addition, samples must be handled one at a time.
Samples may be damaged and have a loss of material then give results under what expected !

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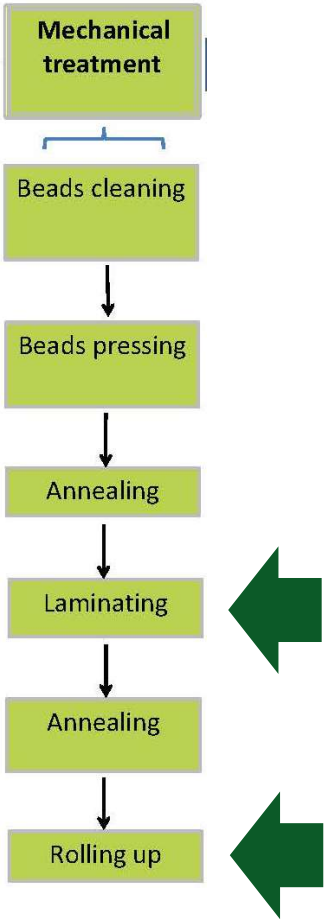
MECHANICAL TREATMENT, 3



Laminating

Gold beads should be prepared to a thickness of 0.12 to 0.15 mm and rolled fairly tightly but not too tightly so that HNO_3 solutions can act effectively.

Rolls type

«S» shape «B» shape «spiral» shape

All samples must have the same thickness !
All rolls must have the same shape !

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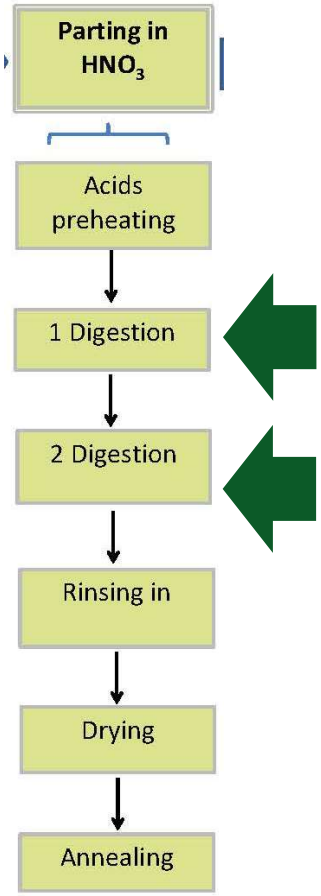
PARTING IN HNO_3



6 Kjeldahl flasks

6x6 Quartz basket

The use of a basket made of suitable material (quartz or platinum) instead of using traditional flasks could rationalize the HNO_3 separation operation.
It allows greater control of temperature distribution during the treatment.

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UNCERTAINTY

Contributes to Uncertainty		
Id	Description	Uncertainty
A	Contribute due to the Repeatability of the lab	µA
B	Contribute due to the Repeatability of F factor	µB
C	Contribute due to weighing uncertainty	µC
D	Contribute due to purity of Au for proof tests (999.99 ‰)	µD
E	Contributes due to purity of Ag for proof tests (999.9 ‰)	µE

Starting from Uc we can calculate the **expanded uncertainty U** taking into account a confindence level:

U=K*Uc

K=2 (95 % of confidence)

K=3 (99 % of confidence)

Accordingly to the law of propagation of the uncertainty, if the contributions are **not correlated** the variances add up with the formula:

$$Uc = \sqrt{\mu A^2 + \mu B^2 + \mu C^2 + \mu D^2 + \mu E^2}$$

Where Uc is the Combined Standard Uncertainty

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HOW TO REDUCE THE UNCERTAINTY ?

1) Reduce the uncertainty related to statistical & systematic errors :

Statistical errors : related to the standard deviations of the method
→ Improve the repeatability of the process

Systematic errors: related to an inaccurancy of the system
→ Check with Proficiency Testing and apply corrective actions

2) Increase the number of replicates

The standard uncertainty of mean value **Un** of **n** replicates is expressed this way:

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

Where **s** is the standard deviation of the method

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HOW MANY REPLICATES FOR SAMPLES AND PROOF TESTS?

e.g for a standard deviation of 0.07‰ (considering the same for samples and proof tests):

$$Uc = \sqrt{\mu A^2 + \mu B^2}$$

Sample replicates (A)	Proof Tests replicates (B)	Uc ‰
2	1	0.09
4	2	0.06
8	4	0.04

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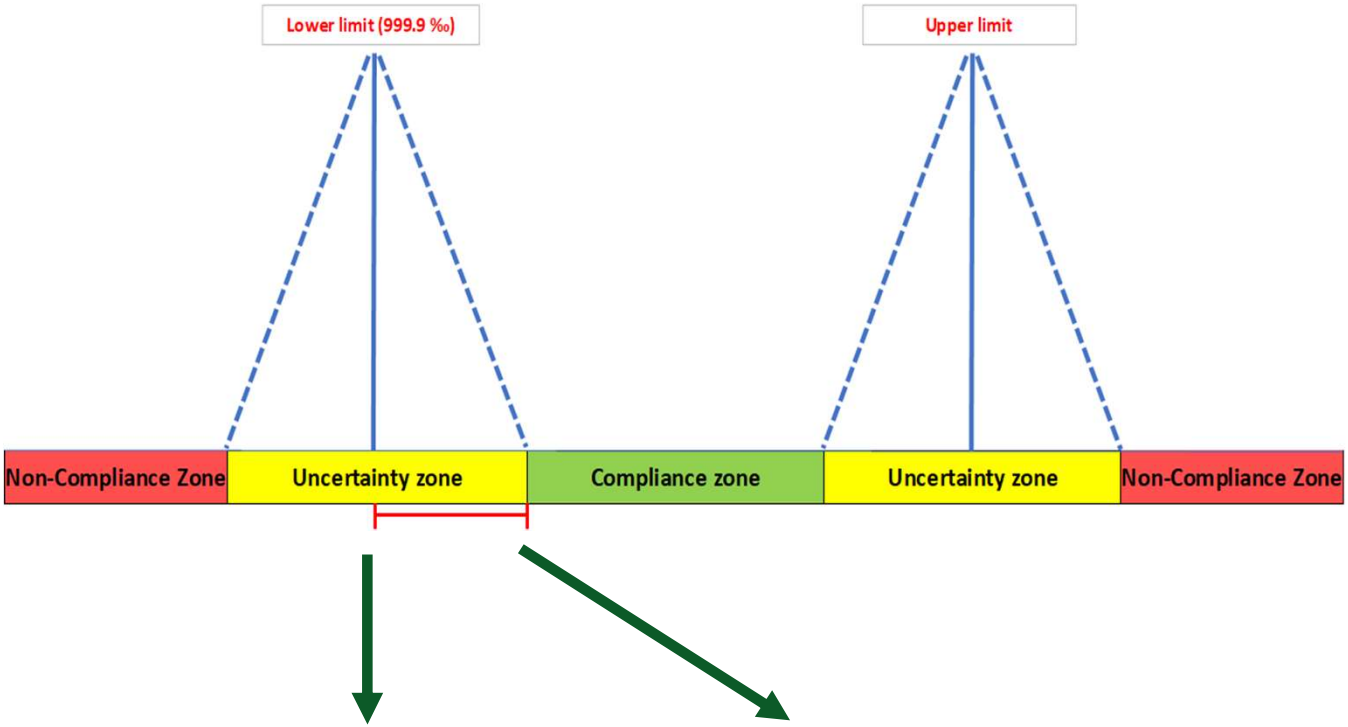
ISO APPROACH



Au $_{(min)}$ ‰ = 999.9 ‰ + Uncertainty (U =K*Uc)

ISO Approach

Measurement uncertainty must be covered by the party assuming the duty of proving conformity or non-conformity and consequently carries out the measurement

Uncertainty is a cost!

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CONCLUSIONS

1) Fire assay analysis on Au 999.9 ‰ can be considered as an alternative to spectrometric methods but only after **careful assessment of the measurement uncertainty**

2) An **increase in the number of standard repetitions** (e.g. ISO 11426, ASTM E1335-08) must be taken into consideration

References & Bibliography

www.ISO.org International Organization for Standardization
www.ASTM.org American Society for Testing and Materials International
www.eurachem.org Eurachem/Citac Guide 2012
www.LBMA.org.uk Assaying & Refining Conference 2013-2015 Dr A .Ruffoni

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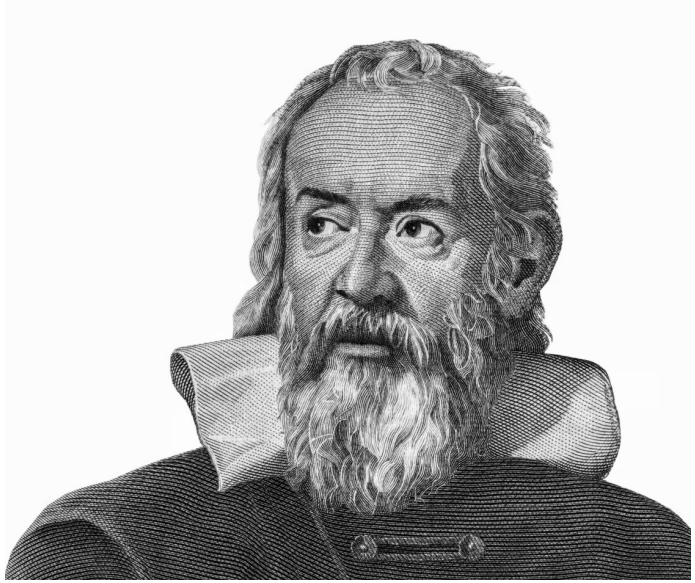
Thank you for your attention

“Count what is countable,
measure what is measurable
and make measurable what is not”

Galileo Galilei (1564-1642)



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