ARGOR-HERAEUS

QUANTITATIVE DETERMINATION OF SILVER CONTENT USING FIRE ASSAY: NEW PROPOSAL FOR ISO TC174

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LBMA Assaying & Refining Conference

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47 Ag

ANALYTICAL METHODS FOR DETERMINING SILVER PURITY: A WIDE RANGE OF CHOICE

Metallurgical Analysis

- Cupellation (Fire Assay)

Spectrometric Analysis

- X-Ray Fluorescence Spectrometry (WDXRF / EDXRF)
- Inductively Coupled Plasma Optical EmissionSpectrometry (ICP-OES)
- Spark-Optical Emission Spectrometry (Spark-OES/ LA-Spark)
- Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

Volumetric Analysis

- Potentiometric Titration
- Titration with indicator : Gay-Lussac, Mohr, Volhard, Fajans..

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Method	Sample	Pros	Cons	Range	Cost
Cupellation method (fire assay)	solid	Historical and well-established method	Destructive, affected by the presence of other metals	400‰ - 999‰ (proposed)	Low (if Au by fire assay is in place)
X-Ray Fluorescence Spectrometry (EDXRF)	solid	Non-destructive, quick, easy to use	Limited sensitivity for light elements, expensive for equipment	Intended for jewellery products (800‰-958‰)	Medium/HI
Spark-OES	solid	High sensitivity, easy to use	Expensive, requires sample preparation	>999‰ for trace determination	HI
ICP-OES	liquid	Extremely sensitive, trace detection	Expensive, complex to operate	>999 ‰ for trace determination	HI
Volumetric Methods	liquid	Good precision, relatively simple	Requires specific reagents, less suitable for complex samples, affected by the presence of other metals	100 ‰ to 999‰	Quite low

ALTERNATIVES TO SILVER ASSAYING BY CUPELLATION

		Ag‰									
Method	Standard	0	5‰	100‰	200‰	400‰	800‰	925‰	958‰	999‰	(1000‰)
Fire assay	Various										
Titration	ISO 11427:2024										
ED-XRF	ISO 23345:2021										
ICP-OES	ISO 15096:2020										
Spark-OES	ISO 18214:2024										

Overlapping area ?

Can we still consider Silver assaying by cuppelation an «up to date» method?
Yes but… repeatability & uncertainty must be evaluated very carefully!

National bodies that have standardized the method Ag via fire assay

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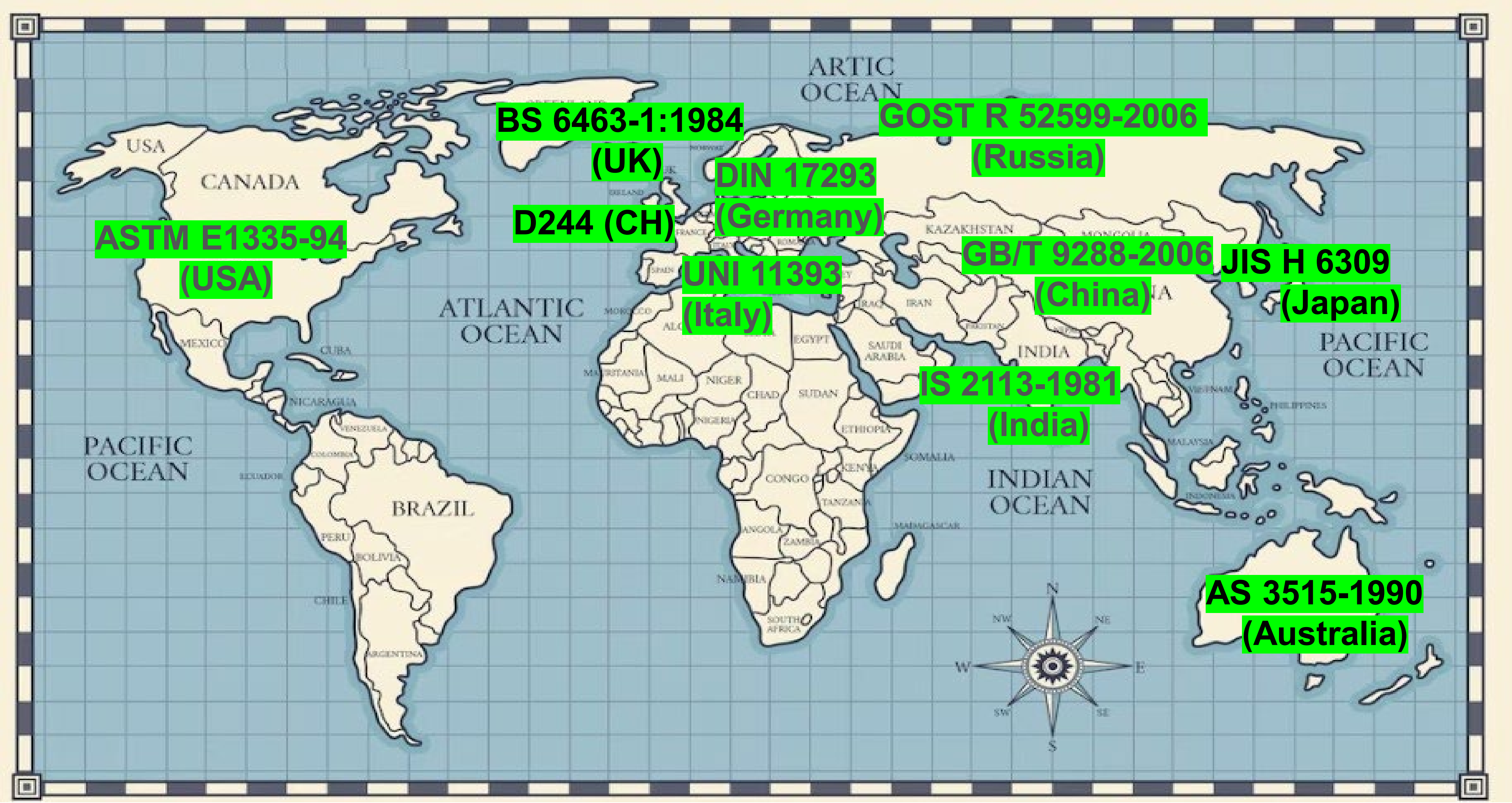


ISO NP 25643

Jewellery and precious metals- Determination of silver- Cupellation method (fire assay)

Technical committee: ISO/TC 174 Jewellery and precious metals

«Cupellation method for the determination of silver on most types of silver samples of materials considered homogeneous in the range 400 ‰ - 999 ‰»
The method is also intended for the determination of fineness in jewellery alloys covered by ISO 9202

The method is designed to be used even in the presence of other precious or base metals below a specific concentration.

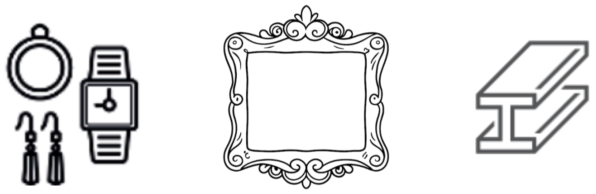
79 Au 78 Pt 46 Pd Allowed

ISO NP 25643

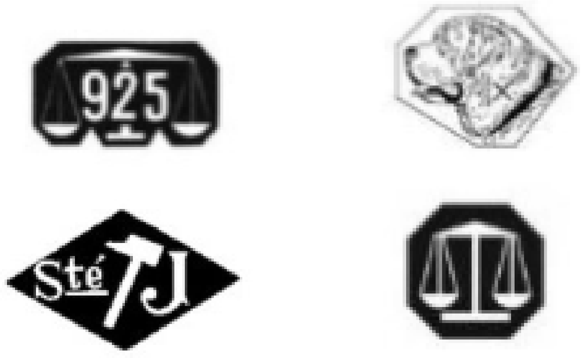
intended to be used along the value chain of the precious metals.

PM Refiners

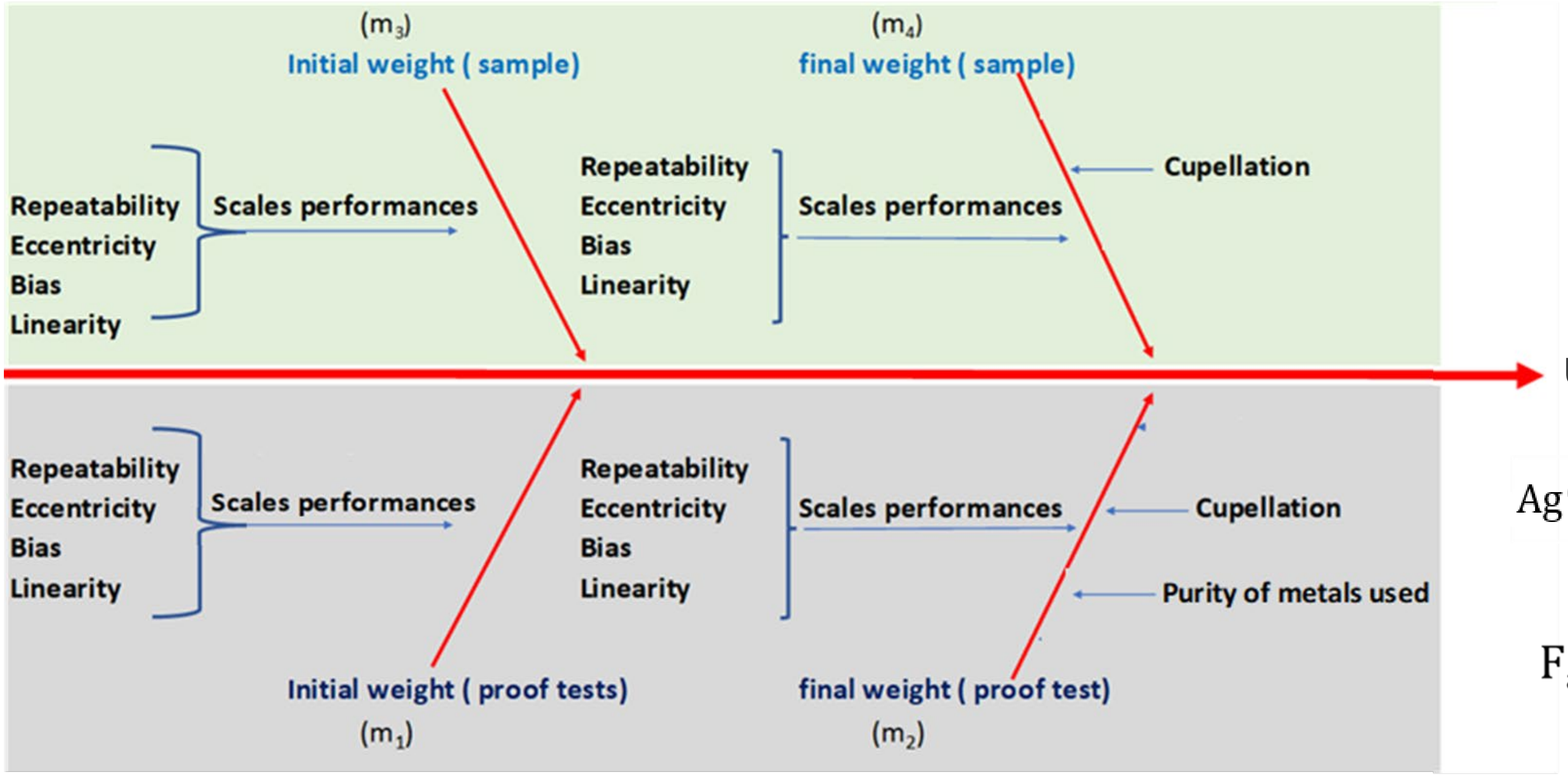
Jewellery producers Finished-semi finished products



Assay offices & customs



CHALLENGES IN SILVER ASSAYING BY CUPELLATION



UNCERTAINTY

$$Ag‰ = \frac{m4 * F}{m3} * 10^3$$

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

Au, Pt Pd affect the determination and must be quantified , they also have an effect on uncertainty

COMBINED UNCERTAINTY

Ag

Contributions to Uncertainty on Ag determination		
Id	**Description**	**Uncertainty**
A	Contribution due to the repeatability of the lab on Ag determination	µA
B	Contribution due to Au determination	µB
C	Contribution due to Pt determination	µC
D	Contribution due to Pd determination	µD

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

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

Where Uc is the Combined Standard Uncertainty

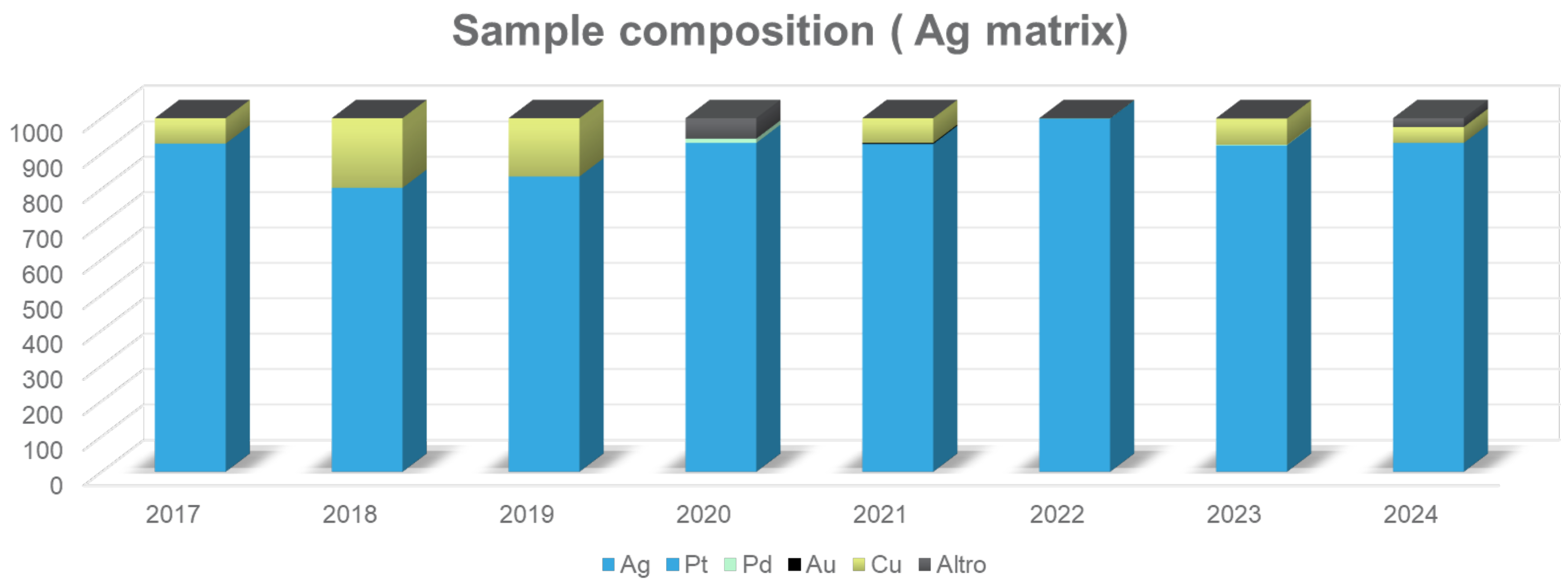
Starting from Uc we can calculate the **expanded uncertainty U** taking into account a confindence level:

U=K*Uc

K=2 (95 % of confidence)

K=3 (99 % of confidence)

ISO NP 25643 - Performances check - Proficiency Testing : a starting point



year	Au ‰	Ag ‰	Pt ‰	Pd ‰	Cu ‰	Other ‰
2017	0	928	0	0	72	0
2018	0	803	0	0	197	0
2019	0	835	0	0	165	0
2020	0	930	0	12	0	58
2021	3	927	0	0	70	0
2022	0.260	998.77	0.265	0.230	0.415	0.07
2023	0	923	0	2	74	1
2024	0	930	0	0	45	25

Case 1 (No AuPtPd)

composition : Ag rest Cu

year	Au ‰	Ag‰	Pt‰	Pd‰	Cu‰	Other ‰
2017	0	928	0	0	72	0
2018	0	803	0	0	197	0
2019	0	835	0	0	165	0

year	**Ag AVG**	Ag REF value	Participants	replicates	**Ag maxRange ‰**
2017	**928.2**	928.52	11	4	**2.95**
2018	**802.7**	802.98	9	4	**1.16**
2019	**835.1**	835.43	12	4	**1.62**

Case 2 (Ag, AuPtPd)

composition : Ag , Au&Pd

year	Au ‰	Ag‰	Pt‰	Pd‰	Cu‰	Other ‰
2021	3	927	0	0	70	0
2022	0.260	998.77	0.265	0.230	0.415	0.07
2023	0	923	0	2	74	1

year	**Ag AVG**	Ag REF value	Participants	Replicates	**Ag maxRange ‰**
2021	**926.9**	926.64	14	4	**1.49**
2022	**998.6**	998.85	12	4	**2.28**
2023	**923.5**	923.07	12	4	**1.28**

Case 3 (Ag, Pd & common metals)

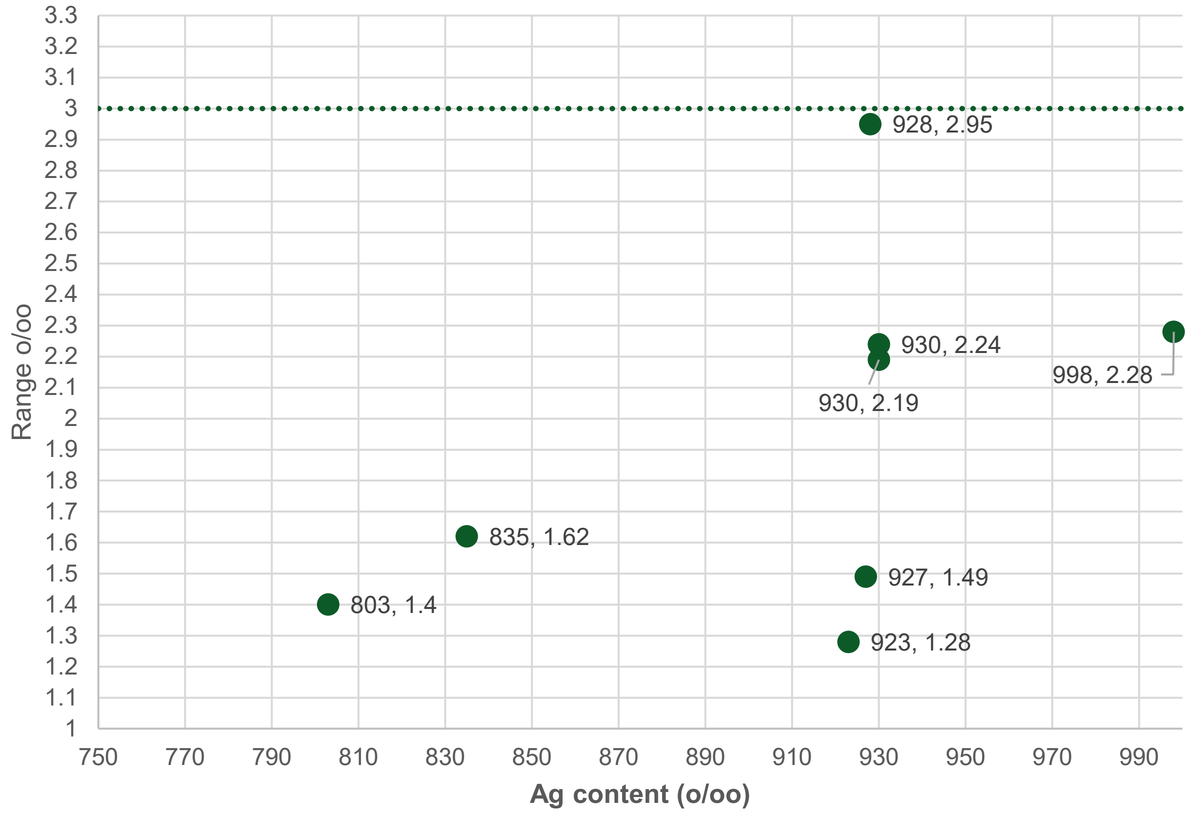
composition : Ag Pd , In Zn

year	Au ‰	Ag‰	Pt‰	Pd‰	Cu‰	Other ‰
2020	0	930	0	12	0	(In Zn)58
2024	0	930	0	0	45	(Zn) 25

year	**Ag AVG**	Ag REF value	Participants	replicates	**Ag maxRange ‰**
2020	**934.0**	933.16	16	4	**2.19**
2024	**932.4**	930	11	4	**2.24**

9.3 Repeatability

Ag ‰	Au ‰	Pt ‰	Pd ‰	Cu ‰	Other ‰	Repeatability (o/oo) Range (n=4)
803				197		1.4
835				165		1.62
923			2	74	1	1.28
927	3			70		1.49
928				72		2.95
930			12		58	2.19
930				45	25	2.24
998	0.2		0.2	0.4		2.28



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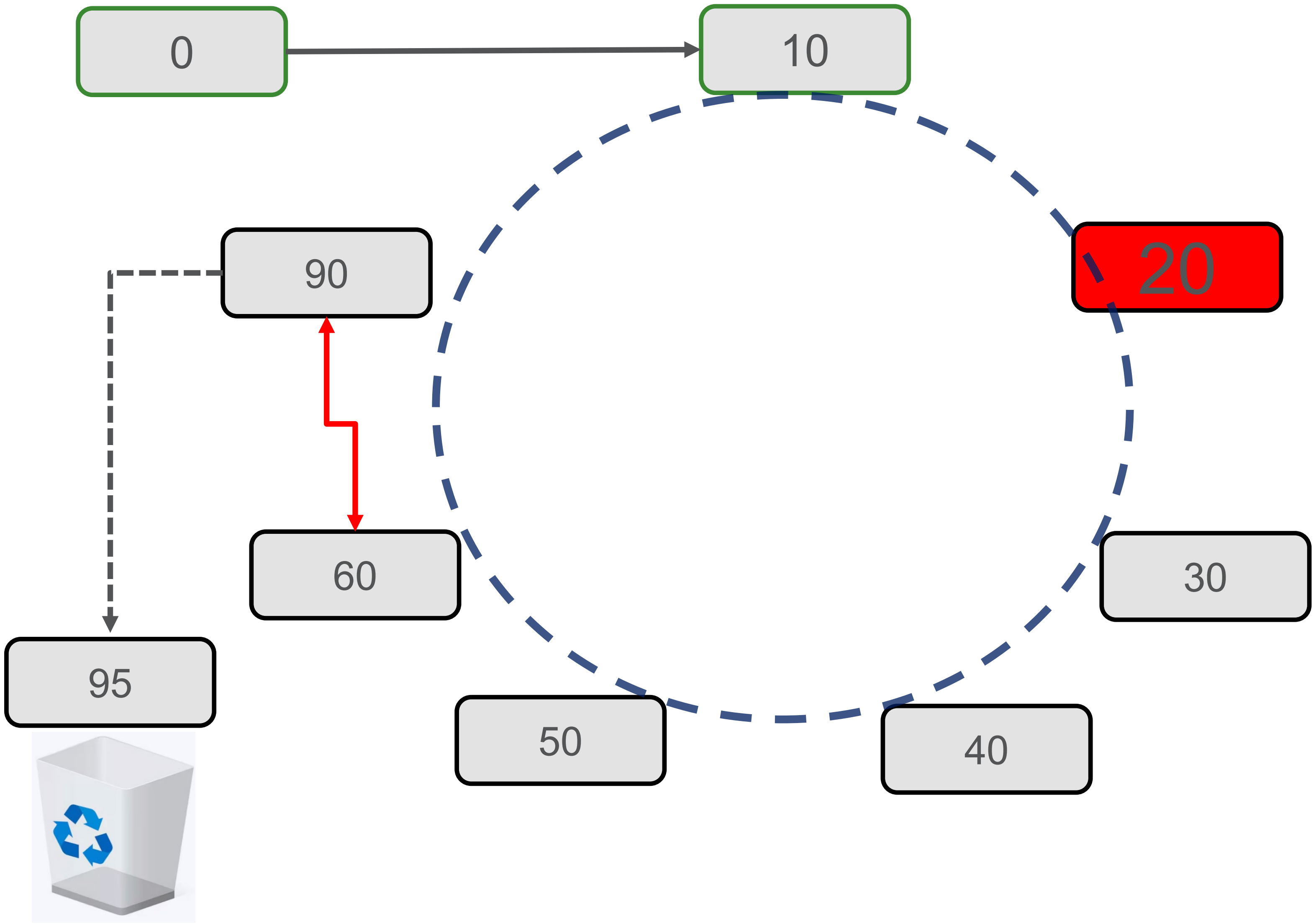
THE LIFE CYCLE OF AN ISO STANDARD



Status

0	Preliminary Stage
10	Proposal Stage
20	Preparatory
30	Commitee Stage
40	Enquiry Stage
50	Approval Stage
60	Publication Stage
90	Review
95	Withdrawal

CONCLUSIONS

1)The analysis of silver by cupellation in the range 800-998 has shown a good repeatability.

2) In future stages of the ISO standard, repeatability for concentrations < 800‰ will be assessed.

3) Fire assay analysis on Ag material with other PM(Au Pt Pd) can be used after careful assessment of the measurement uncertainty

References & Bibliography

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www.LBMA.org.uk Assaying & Refining Conference 2013-2015 Dr A .Ruffoni
www.eptis.bam.de/pts1025797 PT scheme database Argor-Heraeus

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