SPECTRO | AMETEK MATERIALS ANALYSIS DIVISION

LBMA ASSAYING & REFINING Conference 2023

Improving the sensitivity, precision and accuracy of ICP-OES analyses to fulfill standardization regulations

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ISO/TC 174 - Jewellery and precious metals

Created 1978

Secretary: DIN Germany

Chairperson: Ph.D. Jonathan J. Jodry, Switzerland

ISO/TC 174/WG 1 Methods for determining fineness

ISO/TC 174/WG 2 Diamonds, gemstones and related products

18 Participating members (countries)

23 Observing members (countries)

20 published ISO standards, under the direct responsibility of ISO/TC 174

8 ISO standards under development, under the direct responsibility of ISO/TC 174

ISO/TC 174/WG 1 Methods for determining fineness

ISO 9202 –Fineness of precious metal alloys

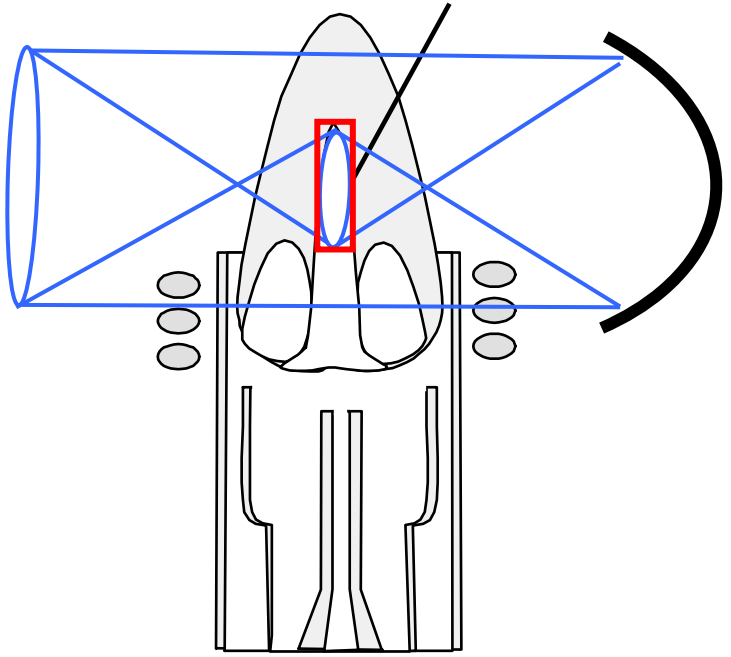
Precious metal	Fineness ‰	Recommended method
Ag	50 - 990	ISO NP 19919 (DIN 32562)
	333 - 990	ISO 11427 + 13756
	800 - 990	ISO 11427 + 13756
	≥ 999	ISO 15096
	999.9	ISO 15096
	999.99	ISO 15096
Au	100 - 999	ISO 11426
	≥ 999	ISO 15093
	999.9	ISO 15093
	999.99	ISO 15093
	999.999	under development (ICP-MS and GD-MS)
Pt	50 - 990	ISO 11210
	≤ 990	ISO 11494
	≥ 999	ISO 15093
Pd	50 - 990	ISO 11490
	≤ 990	ISO 11495
	≥ 999	ISO 15093

Dual Side-On Interface – Principle

- Since the light emitted into two directions is transferred into the optical system the sensitivity is in average improved by a factor of two

- In addition, the vertical torch provides high stability and freedom from matrix effects since the affected zones in the plasma are blanked out

Viewing volume x 2



- Pros and Cons:

  - **High stability**
  - **High matrix tolerance**
  - **High linear dynamic range**
  - **Freedom from matrix effects**
  - **All with ONE measurement**

  - Only a somewhat lower (factor 2) sensitivity compared to a direct light path axial plasma observation

ISO 15093 - DSOI - Limit of detection in 2 % Gold

Element	LOD in solution mg/l	LOD solid material mg/kg	Element	LOD in solution mg/l	LOD solid material mg/kg
Ag 328.068	0,014	0,70 (10)	Mo 202.095	0,0025	0,13
Al 167.078	0,0002	0,01	Ni 221.648	0,0007	0,04 (3)
As 193.759	0,013	0,65 (30)	P 177.495	0,0017	0,09
B 182.641	0,0022	0,11	Pb 168.215	0,0018	0,09 (10)
Ba 455.404	0,0003	0,02	Pd 324.270	0,013	0,65 (10)
Be 313.042	0,00005	0,003	Pt 177.708	0,012	0,6
Bi 223.061	0,013	0,65 (10)	Rh 343.489	0,033	1,65
Ca 396.847	0,001	0,05	Ru 240.272	0,005	0,25
Cd 228.802	0,0005	0,03	S 182.034	0,0095	0,48
Co 230.786	0,0001	0,005	Sb 206.833	0,0054	0,27
Cr 283.563	0,0013	0,07 (3)	Se 196.090	0,0047	0,235
Cu 324.754	0,0026	0,13 (10)	Sn 189.991	0,0036	0,18 (10)
			Si 251.612	0,0054	0,27 (10)
Fe 239.562	0,001	0,05 (10)	Sr 421.552	0,0002	0,009
Ge 164.919	0,003	0,15	Ti 334.941	0,00037	0,02
Hg 194.227	0,0039	0,20	Tl 190.864	0,009	0,45
Ir 183.250	0,0038	0,19	V 292.402	0,001	0,05
Li 670.780	0,004	0,2	W 239.709	0,03	1,5
Mg 280.270	0,00034	0,02 (10)	Zn 213.856	0,0003	0,02
Mn 259.373	0,00022	0,01 (3)	Zr 343.823	0,0037	0,19

What purity level can be assessed by ICP-OES ?

$$\sum LOD < 10\ mg/kg$$

99.999

ASTM B 562 - 95

$$\sum LOD < 4\ mg/kg$$

99.9996

*(5) maximum Limits ASTM 99.995

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39 elements versus 13 elements

ISO 15096 – DSOI - Limit of detection in 5 % Silver

Element	LOD in solution	LOD solid material	Element	LOD in solution	LOD solid material
	mg/l	mg/kg		mg/l	mg/kg
Al 167,078	0,0006	0,01	Mo 202,095	0,0007	0,01
As 189.042	0,003	0,07	Nb 316,340	0,002	0,05
Au 174.050	0,008	0,15	Ni 231.604	0,005	0,09
B 249.773	0,0013	0,03	P 177.495	0,002	0,04
Ba 233.527	0,0003	0,006	**Pb 168.215**	**0,002**	**0,04 (10)**
Be 234.861	0,000006	0,0001	**Pd 324.270**	**0,025**	**0,50 (10)**
Bi 223.061	**0,005**	**0,09 (5)**	Pt 214.423	0,002	0,05
Ca 396.847	0,002	0,05	Rh 233.477	0,015	0,30
Cd 214.438	0,0003	0,005	*Ru 240.272	0,024	0,47
Co 238.892	0,006	0,12	S 182.034	0,005	0,09
Cr 267.716	0,001	0,02	Sb 217.581	0,004	0,08
Cu 219.226	**0,004**	**0,08 (100)**	**Se 196.090**	**0,004**	**0,07 (5)**
Fe 259.941	**0,0006**	**0,01 (10)**	Sn 189.991	0,001	0,03
Ga 141.444	0,007	0,14	Sr 407.771	0,00008	0,002
Ge 164.919	0,004	0,08	Ta 226.230	0,004	0,09
Hf 264,141	0,002	0,04	**Te 214.281**	**0,004**	**0,08 (5)**
Hg 184.950	0,002	0,03	Ti 334,187	0,001	0,03
In 158.637	0,005	0,09	Tl 190.864	0,004	0,09
*Ir 183.250	0,002	0,05	V 292.402	0,001	0,03
Li 670.780	0,001	0,03	W 220.448	0,005	0,10
Mg 279.553	0,0004	0,008	Zn 213.856	0,0006	0,01
Mn 260.569	0,0003	0,005	Zr 339.198	0,002	0,04

What purity level can be assessed by ICP-OES ?

$$\sum LOD < 4\ mg/kg$$

99.9996

ASTM B413-97a

$$\sum LOD < 1\ mg/kg$$

99.9999

*(5) maximum Limits ASTM 99.99

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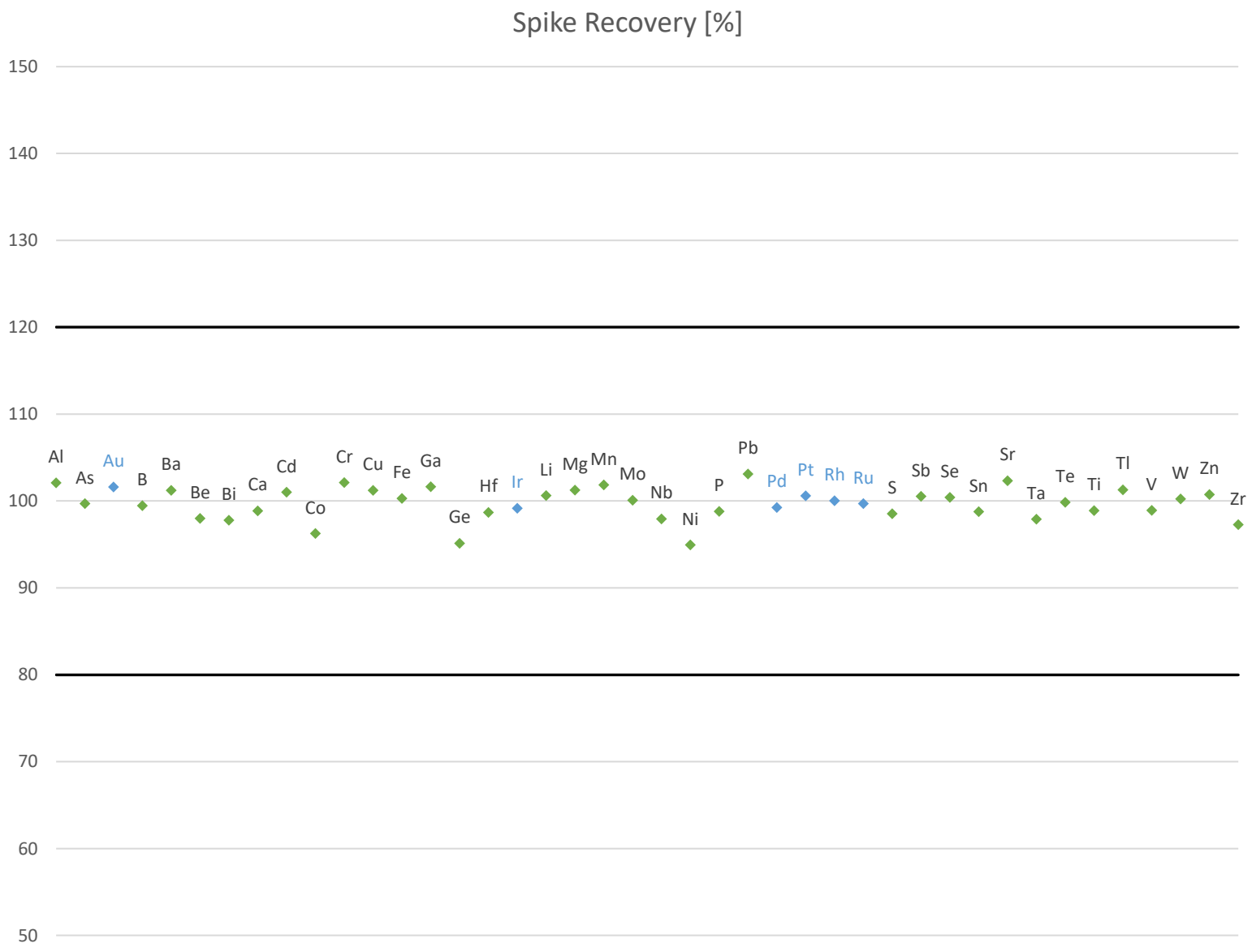
44 elements versus 7 elements

ISO 15096 - DSOI – Spike Recovery in 5 % Silver



Spike Recovery Multi Element Standards

- **CCS 2** **1,0mg/l ≙ 20 mg/kg**
- **CCS 5** **0,25mg/l ≙ 5 mg/kg**
- **Merck VI** **0,025mg/l ≙ 0,5 mg/kg**

Results – round robin ISO 15096 - Ag

Average [‰]	s [‰]	z-score with outliers	z-score without outliers
999.662	0.005	-1.62	-1.64
999.664	0.004	-1.56	-1.57
999.688	0.003	-0.60	-0.59
999.691	0.003	-0.48	-0.46
999.699	0.009	-0.15	-0.12
999.703	0.001	-0.01	0.02
999.703	0.005	0.03	0.06
999.710	0.005	0.31	0.35
999.711	0.031	0.34	0.37
999.717	0.007	0.56	0.61
999.717	0.003	0.57	0.61
999.735	0.013	1.30	1.36
999.736	0.003	1.32	1.38
	Great average	999.703	999.702

ISO 15093 - DSOI - Limit of detection in 2 % Paladium

Element	LOD in solution	LOD solid material	Element	LOD in solution	LOD solid material
	mg/l	mg/kg		mg/l	mg/kg
Ag 328.068	**0,003**	**0,13 (100)**	Mo 281.615	0,003	0,16
Al 167.078	**0,003**	**0,16 (50)**	Nb 269.706	0,003	0,14
As 228.812	0,014	0,68	**Ni 221.648**	**0,001**	**0,06 (50)**
Au 201.265	**0,006**	**0,28 (100)**	P 213.618	0,010	0,48
B 249.773	0,003	0,15	**Pb 168.215**	**0,042**	**2,10 (50)**
Ba 455.404	0,0004	0,02	**Pt 177.708**	**0,004**	**0,21**
Be 313.042	0,00001	0,0003	Re 227.525	0,004	0,19
Bi 223.061	0,013	0,64	**Rh 343.489**	**0,025**	**1,27**
Ca 393.366	**0,001**	**0,04 (50)**	**Ru 240.272**	**0,007**	**0,37**
Cd 214.438	0,001	0,03	S 182.034	0,006	0,29
Co 230.786	**0,002**	**0,08 (10)**	**Sb 217.581**	**0,010**	**0,49 (20)**
Cr 267.716	**0,002**	**0,10 (10)**	Se 196.090	0,063	3,13
Cu 327.396	**0,004**	**0,21 (50)**	**Si 251.612**	**0,012**	**0,58 (50)**
Fe 261.187	**0,004**	**0,18 (50)**	**Sn 147.516**	**0,058**	**2,92 (50)**
Ga 141.444	0,021	1,03	Sr 407.771	0,0001	0,01
Ge 209.426	0,011	0,55	Ta 240.063	0,011	0,55
Hf 277.336	0,004	0,18	Te 214.281	0,010	0,49
Hg 194.227	0,002	0,11	Ti 336.121	0,001	0,06
In 158.637	0,017	0,87	Tl 132.171	0,070	3,49
Ir 183.250	**0,005**	**0,25**	V 292.402	0,001	0,06
Li 670.780	0,003	0,13	W 207.911	0,004	0,21
Mg 279.553	**0,002**	**0,08 (50)**	**Zn 213.856**	**0,0004**	**0,02 (25)**
Mn 260.569	**0,0004**	**0,02 (10)**	Zr 343.823	0,002	0,08

What purity level can be assessed by ICP-OES ?

$$\sum LOD < 23\ mg/kg$$

99.997

ASTM B589-94

$$\sum LOD < 10\ mg/kg$$

99.999

*(25) maximum Limits ASTM 999.5

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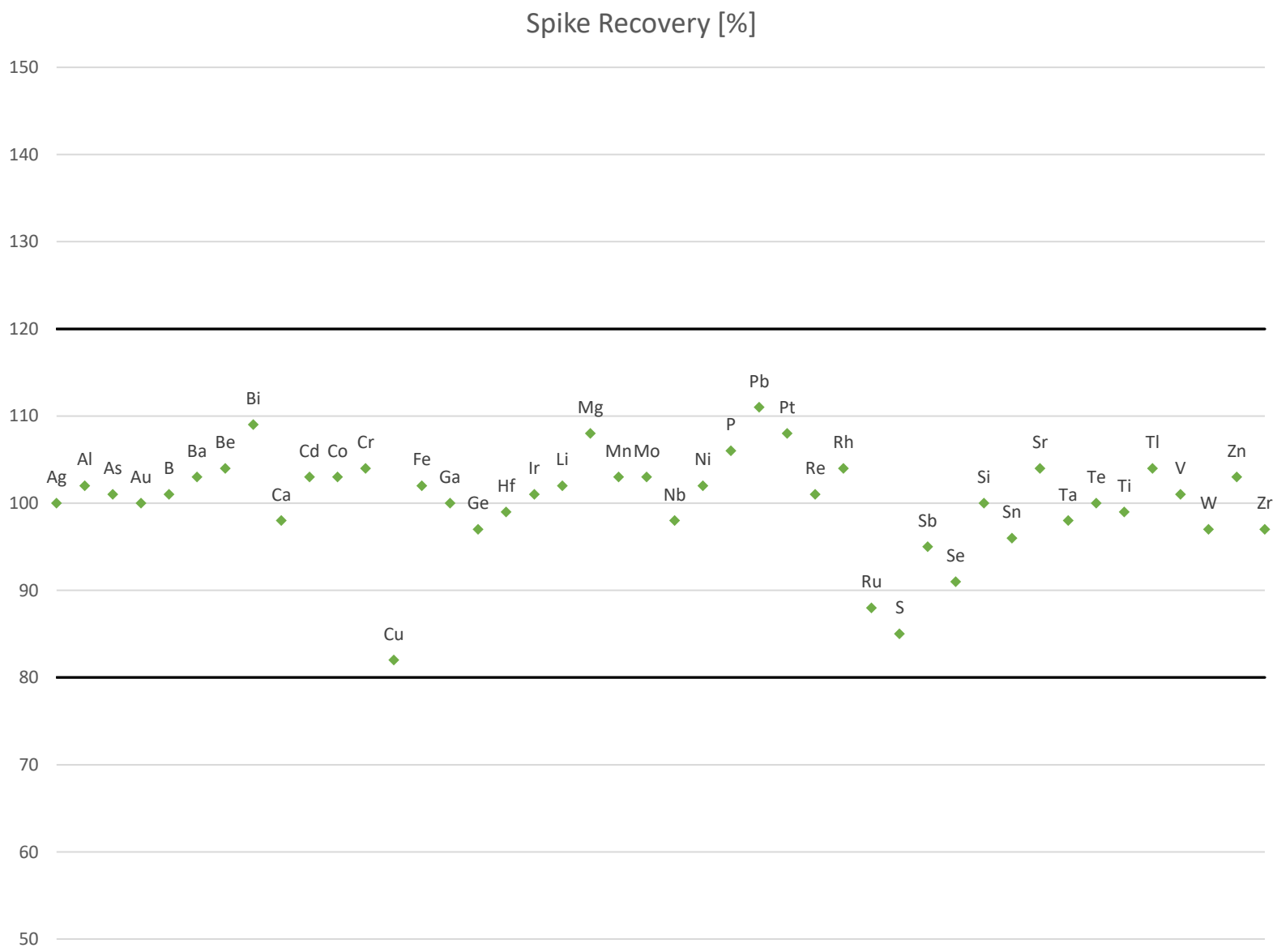
42 elements versus 20 elements

ISO 15093 - DSOI – Spike Recovery in 2 % Platinum



Spike Recovery Multi Element Standards

- **CCS 2 0,025mg/l ≙ 1,25 mg/kg**
- **CCS 5 0,025mg/l ≙ 1,25 mg/kg**
- **Merck VI 0,025mg/l ≙ 1,25 mg/kg**

ISO 15093 - DSOI - Limit of detection in 2 % Platinum

Element	LOD in solution	LOD solid material	Element	LOD in solution	LOD solid material
	mg/l	mg/kg		mg/l	mg/kg
Ag 338.289	**0,014**	**0,72 (30)**	**Mo 281.615**	**0,004**	**0,19 (40)**
Al 396.152	**0,016**	**0,78 (40)**	Nb 316.340	0,004	0,18
As 197.262	**0,034**	**1,72 (20)**	**Ni 231.604**	**0,002**	**0,11 (10)**
Au 267.595	**0,007**	**0,34 (50)**	P 213.618	0,018	0,90
B 249.677	0,005	0,26	**Pb 220.353**	**0,015**	**0,74 (10)**
Ba 455.404	0,0004	0,02	**Pd 340.458**	**0,017**	**0,87 (50)**
Be 313.042	0,000004	0,0002	**Rh 343.489**	**0,040**	**2,01 (50)**
Bi 223.061	**0,017**	**0,87 (20)**	**Ru 245.644**	**0,012**	**0,59 (20)**
Ca 396.847	**0,001**	**0,04 (30)**	S 182.034	0,011	0,57
Cd 226.502	**0,001**	**0,04**	**Sb 217.581**	**0,030**	**1,50 (20)**
Co 238.892	0,002	0,10	Se 196.090	0,012	0,60
Cr 283.563	**0,001**	**0,06 (10)**	**Sn 147.516**	**0,012**	**0,61 (20)**
Cu 327.396	**0,004**	**0,21 (40)**	Sr 421.552	0,0002	0,01
Fe 261.187	**0,004**	**0,22 (50)**	Ta 240.063	0,006	0,31
Ga 417.206	0,032	1,61	**Te 214.281**	**0,030**	**1,52 (40)**
Ge 164.919	0,011	0,56	Ti 334.941	0,001	0,03
Hg 194.227	0,009	0,46	Tl 132.171	0,070	3,48
Ir 183.250	**0,009**	**0,47 (50)**	V 292.402	0,001	0,07
Li 670.780	0,002	0,09	W 220.448	0,009	0,46
Mg 280.270	**0,001**	**0,07 (30)**	**Zn 213.856**	**0,001**	**0,07 (20)**
Mn 257.611	**0,0004**	**0,02 (10)**	Zr 339.198	0,001	0,07

What purity level can be assessed by ICP-OES ?

$$\sum LOD < 24\ mg/kg$$

99.997

ASTM B561-94

$$\sum LOD < 14\ mg/kg$$

99.998

*(25) maximum Limits ASTM 999.9

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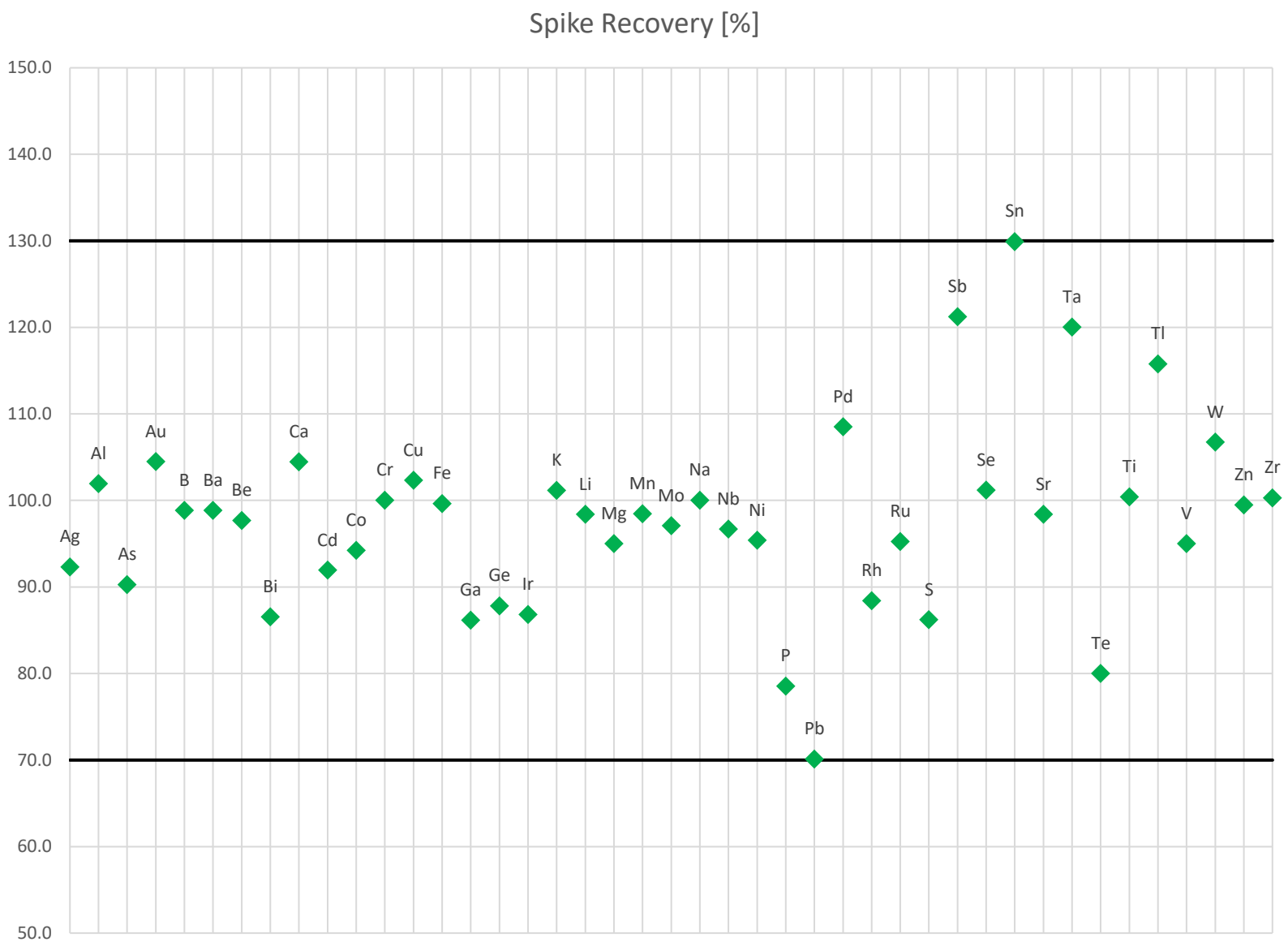
42 elements versus 24 elements

ISO 15093 - DSOI – Spike Recovery in 2 % Platinum



Spike Recovery Multi Element Standards

- **CCS 2 0,025mg/l ≙ 1,25 mg/kg**
- **CCS 5 0,025mg/l ≙ 1,25 mg/kg**
- **Merck VI 0,025mg/l ≙ 1,25 mg/kg**

ARCOS EOP - Limit of detection in 5 % Gold

Element	LOD in solution	LOD solid material	Element	LOD in solution	LOD solid material
	mg/l	mg/kg		mg/l	mg/kg
Ag 328.068	0,0013	0,026	Mn 259.373	0,0003	0,006
Al 167.078	0,0006	0,01	Mo 202.095	0,0033	0,07
As 193.759	0,037	0,74	Ni 221.648	0,0021	0,04
B 182.641	0,0023	0,05	Pb 168.215	0,0104	0,21
Ba 455.404	0,0003	0,006	Pd 324.270	0,014	0,28
Bi 223.061	0,0113	0,23	Pt 177.708	0,0086	0,17
Cd 228.802	0,0008	0,02	Re 221.426	0,0041	0,08
Ce 413.765	0,017	0,34	Rh 343.489	0,0234	0,47
Co 230.786	0,0022	0,04	Ru 240.272	0,0072	0,14
Cr 283.563	0,0011	0,02	Sb 206.833	0,0102	0,20
Cu 324.754	0,0011	0,02	Sc 335.373	0,0007	0,01
Fe 239.562	0,0014	0,03	Se 196.090	0,0182	0,36
Ga 141.444	0,0111	0,22	Sn 189.991	0,0094	0,19
Ge 164.919	0,0082	0,16	Sr 407.771	0,0001	0,002
Hf 232.247	0,0036	0,07	Ta 268.517	0,012	0,24
Hg 184.950	0,0147	0,29	Te 214.281	0,031	0,62
In 158.637	0,0082	0,16	Ti 334.941	0,0006	0,01
Ir 183.250	0,0225	0,45	Tl 190.864	0,0204	0,41
Li 670.780	0,0034	0,07	Zn 206.200	0,0015	0,03
Mg 280.270	0,0001	0,002	Zr 343.823	0,0021	0,04

ISO NWIP : 99.9999 possible by ICP-OES ?

What purity level can be assessed by ICP-OES ?

$$\sum LOD < 7\ mg/kg$$

99.9993

ASTM B 562 - 95

$$\sum LOD < 2\ mg/kg$$

99.9998

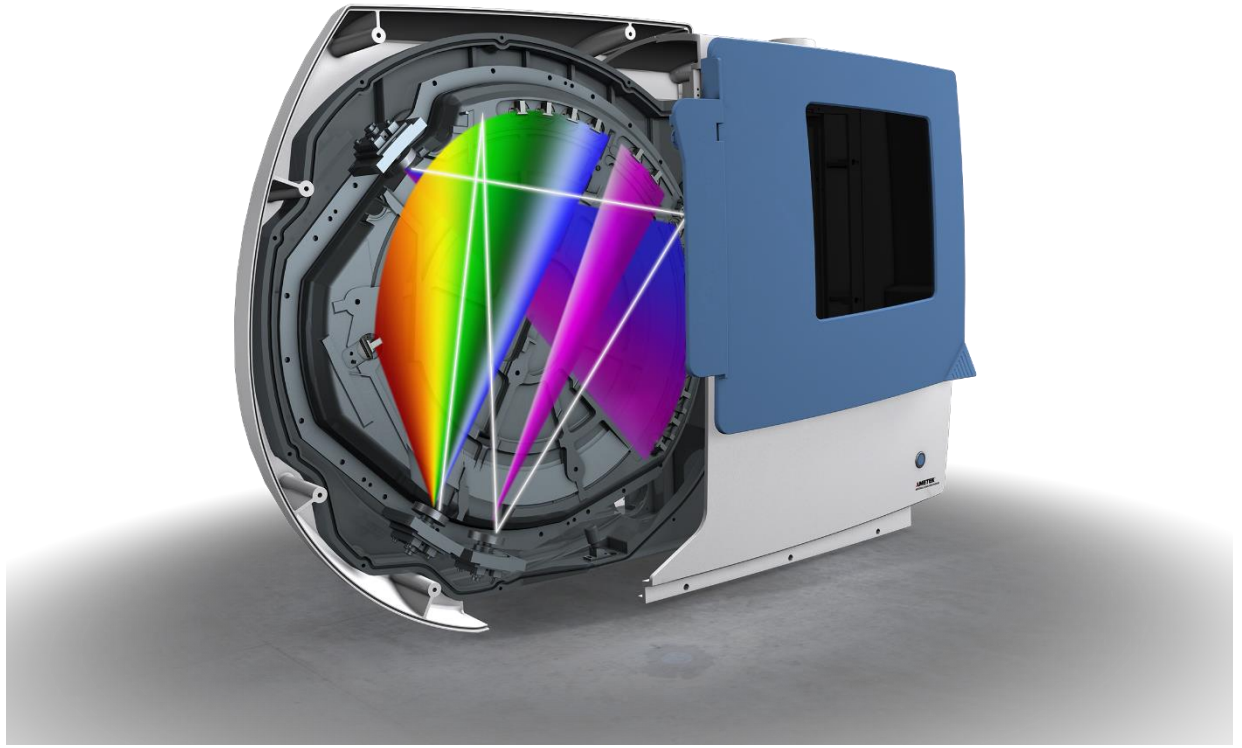
Bracketing - Highest precision and accuracy

Procedure described in :

- **ISO 11494 Platinum in alloys**
- **ISO 11495 Palladium in alloys**
- **ISO NP 19919 (DIN 32562) Silver in alloys**
- **NWIP Gold in alloys**

General requirements:

- Mandatory use of an internal standard.
- High precision, weight-based preparations (analyte and internal standard).
- Repeated measurements (“cycles”) of the sample and two standards of a slightly lower and higher concentration.



BRACKETING

BRACKETING

ISO 11494 - ARCOS DSOI - Bracketing

High precision for main components

Sample	Type	Pt 306.471	
		mg/l	
	1	173,535	
	2	173,559	
	3	173,597	
	4	173,565	
	5	173,541	
RRT Platinum (liquid)	**<x>**	**173,559**	
	sd	0,024	
	rsd	**0,014**	
EW (g)	*0,09128*		
Vol (ml)	*500*		
		Pt 306.471	
		%	
RRT Platinum (solid)		**95,070**	
	RSD(%)	**0,014**	

Consideration of the expanded uncertainty of measurement ISO 11494

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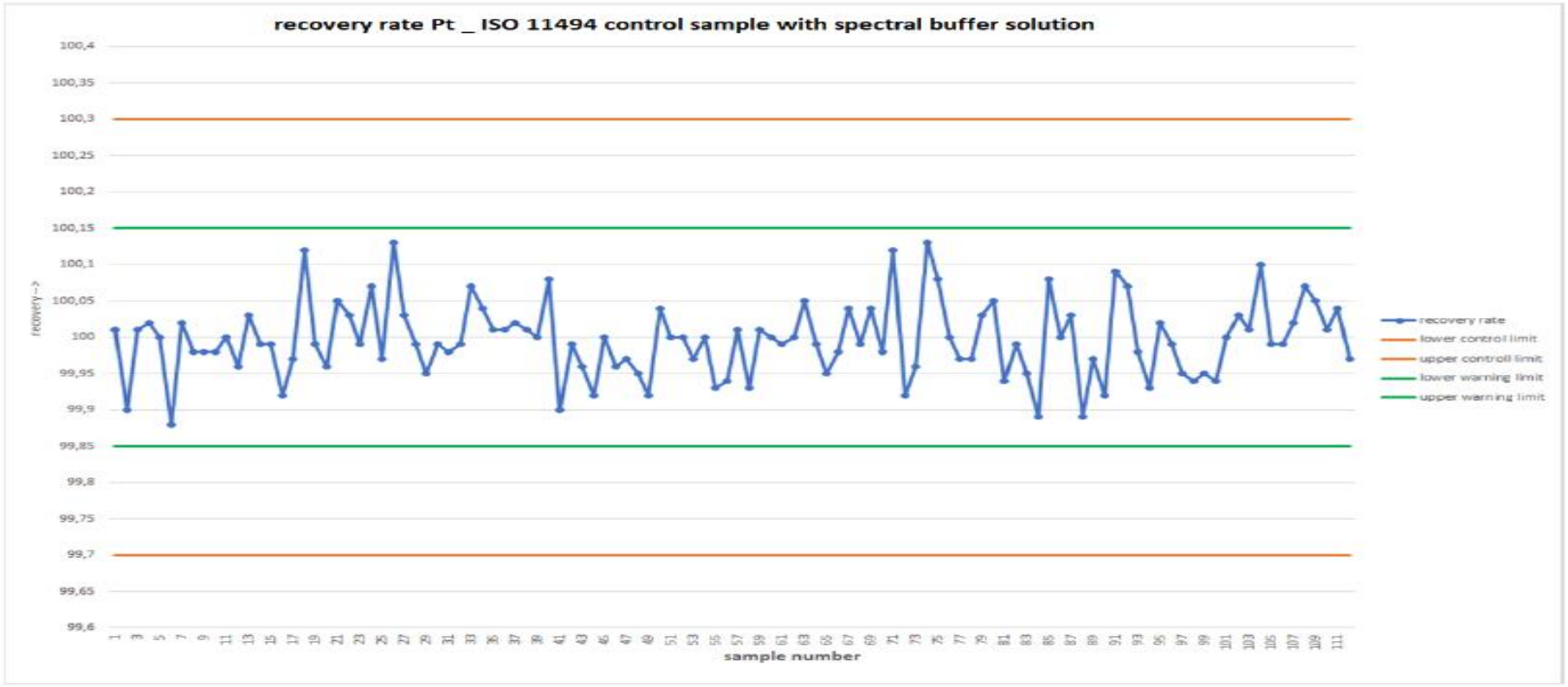
Part of Umicore

Consideration of the expanded uncertainty of measurement - ISO 11494



Epanded Uncertainty Ucs
UCS = 2* Uc = 0,10 %
Uc= combined uncerainty

umicore

Multi-element bracketing for alloys

Sample	Typ	Pt %	Pd %	Cu %	Total %
Sample 1-1	1	60.33	10.10	29.57	99.99
	2	60.32	10.09	29.58	100.00
	3	60.29	10.08	29.59	99.96
	4	60.31	10.10	29.59	99.99
	5	60.28	10.08	29.61	99.97
	<x>	**60.31**	**10.09**	**29.59**	**99.98**
	rsd	**0.033**	**0.102**	**0.072**	**0.046**
Sample 1-2	1	60.312	10.083	29.61	100.01
	2	60.31	10.108	29.58	100.00
	3	60.311	10.082	29.59	99.98
	4	60.32	10.101	29.59	100.01
	5	60.334	10.082	29.59	100.00
	<x>	**60.32**	**10.09**	**29.59**	**100.00**
	rsd	**0.017**	**0.124**	**0.018**	**0.012**
Sample 1-3	1	60.316	10.09	29.56	99.97
	2	60.331	10.125	29.55	100.01
	3	60.292	10.091	29.59	99.97
	4	60.294	10.111	29.57	99.98
	5	60.266	10.09	29.63	99.99
	<x>	**60.30**	**10.10**	**29.58**	**99.98**
	rsd	**0.05**	**0.155**	**0.088**	**0.022**

GDMB

RRT for 3 component alloy

Same procedure as in single element bracketing

	Pt %	Pd %	Cu %	Total %
Lab 1	60.31	10.09	29.59	99.99
Lab 2	60.38	10.04	29.58	100.00
Lab 3	60.33	10.08	29.59	100.00
Lab 4	60.37	10.05	29.51	99.93
Lab 5	60.4	10.00	29.63	100.03
Lab 6	60.32	10.12	29.62	100.06
Lab 7	60.28	10.12	29.62	100.02
Lab 8	60.33	10.08	29.58	99.99
mean	**60.34**	**10.07**	**29.59**	**100.00**
SD	**0.040**	**0.041**	**0.038**	**0.038**

Multi-element bracketing for alloys

Synthetic sample - Au 45 - Ag 845 -Pt 18 - Pd 22

Test measurements by means of a synthetic precious metal alloy using different spectral lines and measurement concentrations.

	Au			Ag			Pt			Pd		
Weight	100 mg	150 mg	300 mg	100 mg	150 mg	300 mg	100 mg	150 mg	300 mg	100 mg	150 mg	300 mg
Average [g/kg]	45,13	45,15	45,05	845,00	845,07	844,76	17,99	18,06	18,02	21,91	21,94	21,94
s [g/kg]	0,10	0,06	0,04	0,60	0,47	0,90	0,07	0,07	0,05	0,08	0,05	0,06
sr [%]	0,22 %	0,12 %	0,10 %	0,07 %	0,06 %	0,11 %	0,37 %	0,39 %	0,25 %	0,38 %	0,22 %	0,26 %
Wavelength [nm]	242	242	242	338	338	338	265	265	265	360	360	360
Measuring concentration [mg/L]	4,5	6	12	85	130	260	1,8	2,7	5,4	2,2	3,8	7,6

Multi-element bracketing for alloys

Example for precious metal scrap
same procedure as in single element bracketing

	Pt	Ag	Au	Pd	Ir	Rh	Ru
g/kg	**207,94**	**32,83**	**81,85**	**73,87**	**47,92**	**11,82**	**18,66**
mg/l	80,90	12,77	31,85	28,74	18,64	4,60	7,26
RSD	0,07	0,12	0,13	0,10	0,23	0,26	0,46

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