

ISO TC 174 – WG 1 and Daily work with- ISO 15093 and ISO 15096

- Stefan Zorn
- Head of Laboratories Agosi/ Umicore BU JIM



Agenda

- ISO TC 174
- ISO TC 174 – Published standards
- ISO TC 174 – Round Robins
- ISO 15093 – ISO 15096 in the daily work
- LOD and LOQ, calibration and spectra
- Conclusion

Scope of ISO/TC 174

Standardization in the field of jewellery

Chairman and secretariat

Chairman: Dr. Jonathan Jodry, Switzerland until end of 2022

Secretary: Petra Bischoff, DIN , Germany

Structure of ISO/TC 174

ISO/TC 174 has two working groups

WG 1 Methods for determining fineness

Convenor: Stefan Zorn

P-member / O-member

PARTICIPATING

P-members are required to **play an active role** in the work of a committee, as well as **vote on all official committee ballots**. They are also expected **to base their positions on the consensus of national stakeholders**, preferably through national mirror committees.

OBSERVING

O-members **follow the development of a standard**, and possibly contribute to the work, without committing themselves to active participation.

Membership

The membership of ISO/TC 174 is as follows:

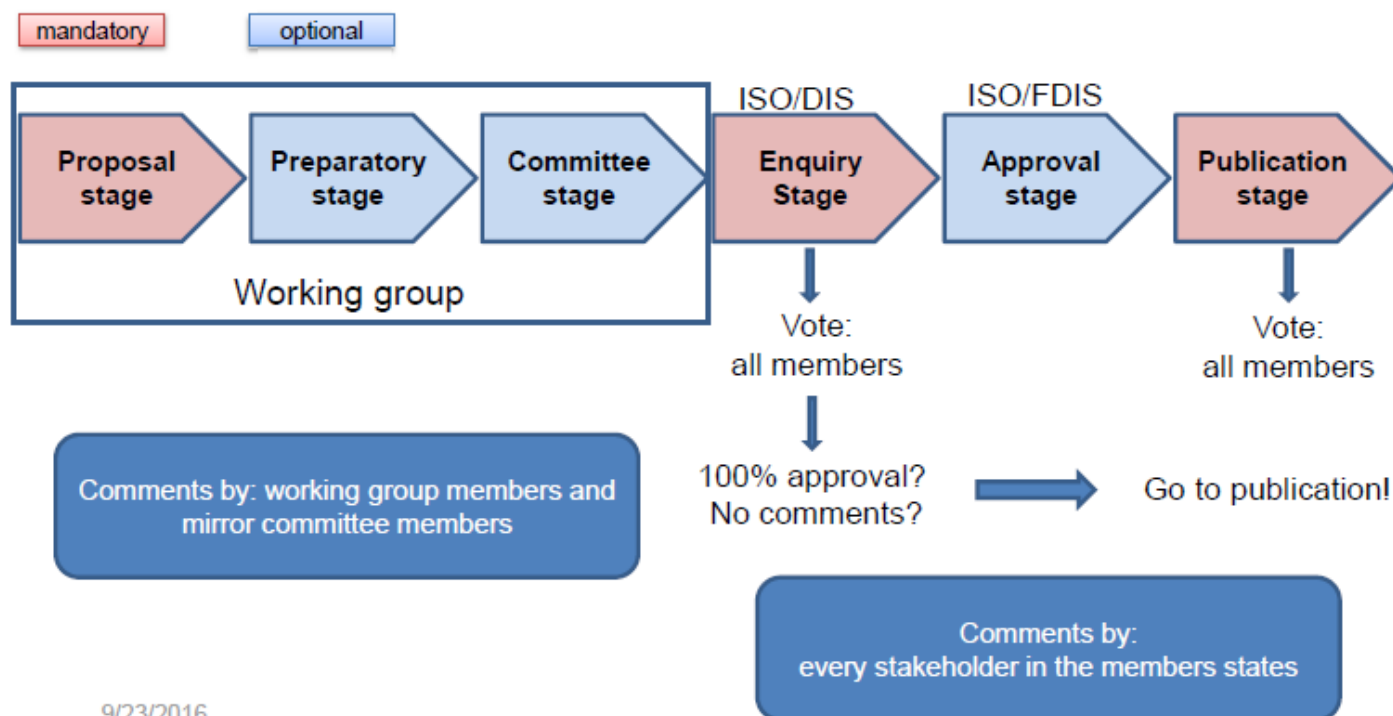
P-Members (20)

Armenia (SARM)
Austria (ASI)
Belgium (NBN)
Bulgaria (BDS)
China (SAC)
Czech Republic (UNMZ)
France (AFNOR)
Germany (DIN) - secretary
India (BIS)
Iran, Islamic Republic of (ISIRI)
Ireland (NSAI)
Israel (SII)
Italy (UNI)
Japan (JISC)
Norway (SN)
Peru (INACAL)
Russian Federation (GOST R)
Spain (AENOR)
Switzerland (SNV)
United Kingdom (BSI)

O-Members (17)

Hong Kong (ITCHKSAR) (Correspondent member)
Hungary (MSZT)
Iraq (COSQC)
Kenya (KEBS)
Korea, Republic of (KATS)
Lithuania (LST)
Mongolia (MASM)
Oman (DGSM)
Poland (PKN)
Romania (ASRO)
Slovakia (SOSMT)
South Africa (SABS)
Thailand (TISI)
Tunisia (INNORPI)
Turkey (TSE)
Zambia (ZABS) (Correspondent member)

Development of a standard- stages



9/23/2016

Published Standards – ISO TC 174

ISO 9202:2014, Jewellery -- Fineness of precious metal alloys 60.60

ISO 11210:2014, Jewellery -- Determination of platinum in platinum jewellery alloys -- Gravimetric method after precipitation of diammonium hexachloroplatinate 60.60

ISO 11426:2014, Jewellery -- Determination of gold in gold jewellery alloys -- Cupellation method (fire assay) 60.60

ISO 11427:2014, Jewellery -- Determination of silver in silver jewellery alloys -- Volumetric (potentiometric) method using potassium bromide 60.60

ISO 11489:1995, Determination of platinum in platinum jewellery alloys -- Gravimetric determination by reduction with mercury(I) chloride 90.93

ISO 11490:2015, Jewellery -- Determination of palladium in palladium jewellery alloys -- Gravimetric determination with dimethylglyoxime 60.60

ISO 11494:2014, Jewellery -- Determination of platinum in platinum jewellery alloys -- ICP-OES method using yttrium as internal standard element 60.60

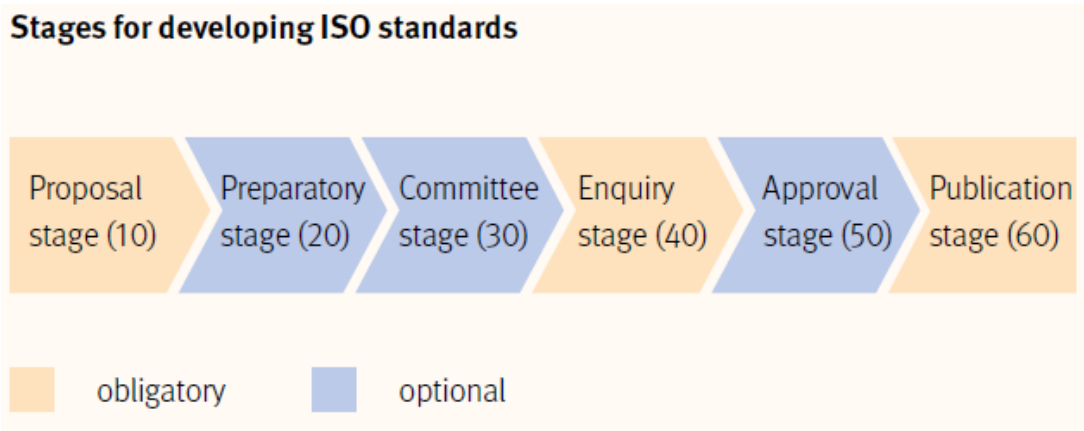
ISO 11495:2014, Jewellery -- Determination of palladium in palladium jewellery alloys -- ICP-OES method using yttrium as internal standard element 60.60

Published Standards – ISO TC 174

ISO 13756:2015, Jewellery -- Determination of silver in silver jewellery alloys -- Volumetric (potentiometric) method using sodium chloride or potassium chloride 60.60

ISO 15093:2015, Jewellery -- Determination of precious metals in 999 0/00 gold, platinum and palladium jewellery alloys -- Difference method using ICP-OES 60.60

ISO 15096:2014, Jewellery -- Determination of silver in 999 0/00 silver jewellery alloys -- Difference method using ICP-OES 60.60



ISO - Jewellery — Fineness of precious metal alloys 9202

Precious metal	Fineness a min	Recommended method
Gold	333 - 990	ISO 11426
	999	ISO 11426 or ISO 15093
Platinum	500 990	ISO 11210
		ISO 11494
	999	ISO 15093
Palladium	500 - 990	ISO 11490
		ISO 11495
	999	ISO 15093
Silver	800 - 990	ISO 11427
		ISO 13756
	999	ISO 15096

ISO/TC 174/WG 1 N 262



Schweizerische Eidgenossenschaft
Confédération suisse
Confederazione Svizzera
Confederaziun svizra

Swiss Confederation

Federal Department of Finance FDF
Federal Customs Administration FCA
Central office for precious metals control

Round Robin ISO/TC-174

Determination of Platinum by ISO 11494

Determination of Gold by ISO 15093

Determination of Silver by ISO 15096

Final report

ISO 15093- Jewellery - Determination of precious metals in 999 0/00 gold, platinum and palladium jewellery alloys -- Difference method using ICP-OES

Scope

This International Standard specifies an analytical procedure for the determination of either platinum in platinum jewellery alloys, gold in gold jewellery alloys, or palladium in palladium jewellery alloys, with a nominal content of each precious metal of 999 ‰ (parts per thousand) by measuring specific elements. (See Tables A.1, A.2, and A.3.)

Principle

The samples of the precious metal alloy are weighed and dissolved in aqua regia to prepare a 10 g/l solution. The impurities are determined by ICP-OES, and the precious metals content is obtained by subtraction of the total content of impurities in the sample from 1 000 ‰.

Results – round robin ISO – 15093 -Au



Conclusion round robin ISO 15093

Problems with calibration

Problems with detection from non present metals (cross contamination)

This round robin was very interesting and provided a lot of information about the handling of the ISO-norms. The comments from the participants are very important for new revisions and improvement for a better handling in the daily work.

Element	Average	Range
Ag	228,38 ppm	+/- 65,14 ppm
Cu	101,33 ppm	+/- 14,07 ppm
Fe	7,09 ppm	+/- 14,36 ppm
Pd	8,67 ppm	+/- 1,22 ppm

ISO 15096 Jewellery -- Determination of silver in 999 0/00 silver jewellery alloys -- Difference method using ICP-OES

Scope

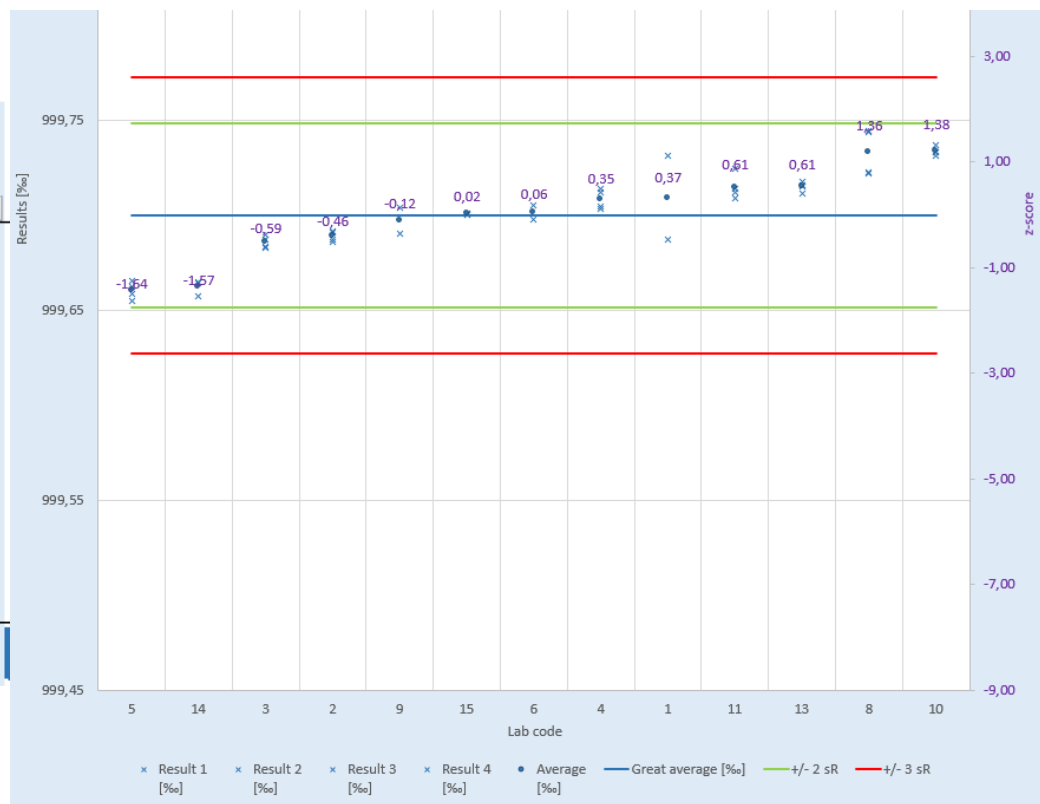
This International Standard specifies the analytical procedure for the determination of silver with a nominal content of at least 999 ‰ (parts per thousand) by measuring specific elements listed in Table A.1.

Principle

The sample is weighed and dissolved in nitric acid to prepare a 10 g/l solution. The suspension, which can be present in that solution, is isolated by centrifugation or microfiltration and dissolved in aqua regia. Both solutions are analysed separately by ICP-OES and the total content of each impurity (see Table A.1.) in the sample is obtained by adding together the results of the two analyses. The silver content is obtained by subtraction of the total content of impurities in the sample from 1 000 ‰.

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



Conclusion round robin ISO 15096

Problems with calibration and blanks

Problems with the separation from the nitric acid suspension.

Problems with detection from non present metals

This round robin was very interesting and provided a lot of information about the handling of the ISO-norms. The comments from the participants are very important for new revisions and improvement for a better handling in the daily work.

Element	Average	Range
Au	32,15	+/- 18,11 ppm
Bi	5,86	+/- 7,11 ppm
Ca	1,52	+/- 3,42 ppm
Cu	186,05	+/- 8,74 ppm
Fe	9,71	+/- 6,64 ppm
Ni	12,81	+/- 1,64 ppm
Sn	4,54	+/- 2,63 ppm
Te	3,14	+/- 2,44 ppm

Thanks to

Mr. Steeve Humbert

Head of Procedures and Technology
Central office for precious metals control

for fantastic statistical evaluation of the results,
support and organization of the round robins.

Mrs. Petra Bischoff

Project manager
Standards Committee Manager NAFuO
DIN , Germany

for the permanent support and help.

Mr. Jonathan Jodry

Head of Laboratories
Metalor

for support and organization of the round robins

and

The working group ISO TC 174 WG1



Subject area for the next ISO meeting – ISO TC 174 WG 1

ISO/PWI 11494, Jewellery — Determination of platinum in platinum jewellery alloys — ICP-OES method using yttrium as internal standard element

ISO/PWI 11495, Jewellery — Determination of palladium in palladium jewellery alloys — ICP-OES method using yttrium as internal standard element

ISO/PWI 15096, Jewellery — Determination of silver in 999 ‰ silver jewellery alloys — Difference method using ICP-OES

ISO/PWI 15093, Jewellery — Determination of precious metals in 999 ‰ gold, platinum and palladium jewellery alloys — Difference method using ICP-OES

New round robins on ISO 11494, ISO 11495, ISO 15093 and ISO 15096

Preliminary work item (PWI) on Standard on XRF

Daily work with- ISO 15093 and ISO 15096

- Stefan Zorn
- Head of Laboratories Agosi/ Umicore BU JIM



Required equipment

- 50 mL PP Vessels graduated
- Stock solutions in different concentration.
- Reference materials: gold or silver of 999,9 ‰ minimum purity; for 999,9 ‰ determination, gold and silver of 999,99 ‰ purity. The content of each impurity shall be specified.
- ICP-OES with EOP plasma observation
- Di-water <0,1 µS/cm conductivity
- 0,45 µm MCE filters
- Hydrochloric acid, approximately 30 % to 37 % hydrochloric acid (mass fraction) with recognized analytical grade.
- Nitric acid, approximately 65 % to 70 % nitric acid (mass fraction) with recognized analytical grade.

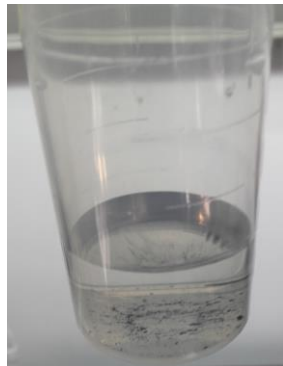
Sample preparation for fine gold analyze

- Dissolving 0,5 g sample in a 50 mL PP vessel with aqua regia .
- For standards dissolve 0,5 g Au 99,999 % the same way as the sample for each standard



Sample preparation fine silver

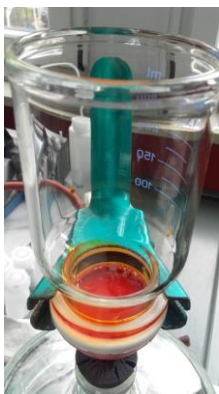
- Dissolving 0,5 g sample in a 50 mL PP vessel with nitric acid and di-water.
- For standards dissolve 0,5 g Ag 99,999 % the same way as the sample for each standard.



After dissolving elements like Au or Sn remain in the residue.

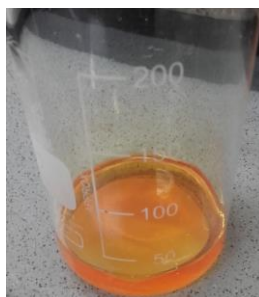
filtration

Filter the sample with a vacuum pump and a 0,45 μm MCE filter



For the purpose of demonstration
the solution was dyed red.

After filtration the silver nitrate solution can be measured with the ICP-OES



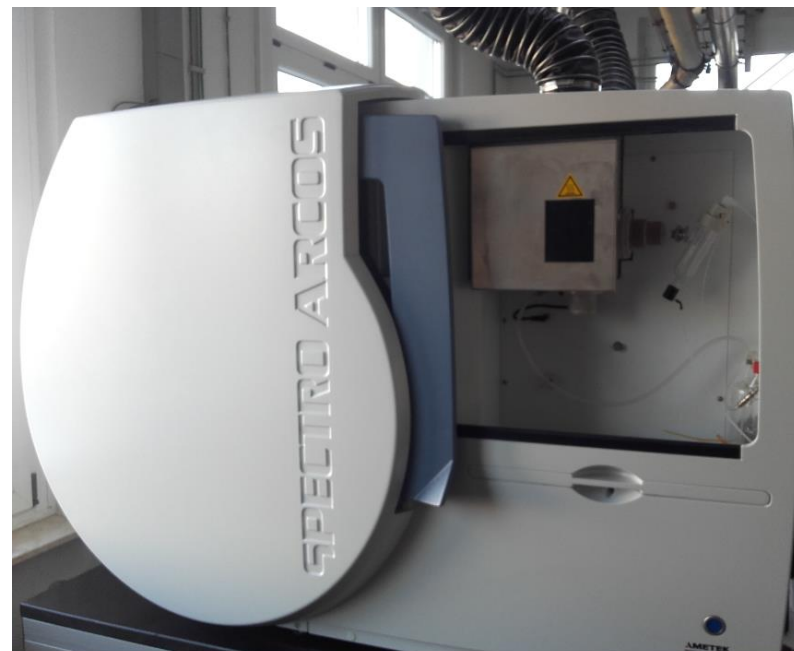
The residue remains on the filter. This filter can be dissolved in aqua regia

Used ICP-OES

Varian Vista Pro EOP



Spectro Arcos MV EOP mode



Sample introduction system

- Cyclonic spray chamber without internal pipe
- Concentric nebuliser

Measurement conditions

Optimized background correction for each element

Plasma condition should be adjusted for every type of ICP-OES

Used wavelength at Agosi

For fine gold determination

Element	WL			
Ag	328,068	338,289		
Al	167,019	237,312	396,152	
As	188,98	193,696		
Au	204,459	389,789		
B	182,577	208,956	249,678	249,772
Ba	233,527	455,403	493,408	
Be	313,042	313,107		
Bi	223,061	222,821	306,771	
Ca	393,366	396,847	422,673	
Cd	214,439	226,502	228,802	361,051
Co	228,615	230,786	238,892	
Cr	205,56	206,158	267,716	
Cu	324,754	327,395		
Fe	234,35	238,204	259,94	
Ga	287,423	294,363	417,204	
Hg	184,887	194,164		
In	230,606	303,936	325,609	
Ir	215,278	205,116	183,074	205,116
K	404,721	766,491	769,897	
Li	460,289	610,365	670,783	
Mg	279,553	280,27	285,213	
Mn	257,61	259,372	260,568	
Na	568,821	588,995	589,592	
Ni	216,555	221,648	231,604	352,454
P	177,434	213,618		
Pb	182,143	217,00	220,353	168,22

Element	WL			
Pd	340,458	360,955	324,27	
Pt	265,945	299,796	306,471	203,646
Rh	343,488	369,236		
Ru	240,272	267,876		
Sb	206,834	217,582	231,146	
Se	196,026			
Si	250,69	251,611	288,158	
Sn	189,925	189,989		
Sr	216,596	407,771	421,552	
Te	214,282			
Ti	334,941	336,122		
Tl	190,794	276,789	351,923	
Zn	202,548	206,2	213,857	
Zr	339,198	343,823	349,619	

ISO 15093

Used wavelength at Agosi

For fine silver determination

Element	WL			
Al	167,019	237,312	396,152	
As	188,98	193,696		
Au	242,794	267,594		
B	234,984	208,956	249,678	
Ba	233,527	455,403	493,408	
Be	313,042	313,107		
Bi	223,061	222,821	306,771	
Ca	393,366	396,847	422,673	
Cd	214,439	226,502	228,802	361,051
Co	228,615	230,786	238,892	
Cr	205,56	206,158	267,716	283,563
Cu	324,754	327,395		
Fe	234,35	238,204	259,94	
Ga	287,423	294,363	417,204	
Hg	184,887	194,164		
In	230,606	303,936	325,609	
Ir	215,278	205,116	183,074	205,116
K	404,721	766,491	769,897	
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Se	196,026	185,52		
Si	250,69	251,611	288,158	
Sn	189,925	189,989		
Sr	216,596	407,771	421,552	
Te	214,282	238,578		
Ti	334,941	336,122		
Tl	190,794	276,789	351,923	
Zn	202,548	206,2	213,857	
Zr	339,198	343,823	349,619	

ISO 15096

LOD and LOQ definition

LOD = Limit of detection

is the minimum concentration of an element required for the detection of the element but the concentration can not be defined.

LOQ = Limit of quantification

is the minimum concentration of an element required to determine the concentration of the element

Calculation of LOD and LOQ

Calculation with average – method 1

$$LOD = \text{average blanc from 10 measures} \\ + (3 \cdot sd \text{ of the 10 blanc measures })$$

$$LOQ = \text{average blanc from 10 measures} \\ + (10 \cdot sd \text{ of the 10 blanc measures })$$

Calculation without average – method 2

$$LOD = 3 \cdot sd \text{ of the 10 blanc measures}$$

$$LOQ = 10 \cdot sd \text{ of the 10 blanc measures}$$

Limits in 10 g/L Au solution

Calculation method 1

Probe	LOD	LOQ	LOQ
Typ	mg/L	mg/L	ppm
Ag 328,068	0,003	0,008	0,80
Al 167,078	0,002	0,003	0,30
As 189,042	0,005	0,014	1,37
Bi 223,061	0,003	0,008	0,77
Cd 214,438	0,000	0,001	0,12
Co 228,616	0,000	0,001	0,07
Cr 205,618	0,001	0,002	0,18
Cu 324,754	0,004	0,007	0,72
Fe 259,941	0,003	0,008	0,77
Ga 417,206	0,003	0,007	0,72
In 325,609	0,003	0,008	0,78
Ir 205,222	0,005	0,016	1,58
K 769,896	0,004	0,011	1,07
Li 670,780	0,000	0,000	0,02
Mg 279,553	0,000	0,001	0,12
Mn 257,611	0,001	0,001	0,10

Calculation method 2

Probe	LOD	LOQ	LOQ
Typ	mg/L	mg/L	ppm
Ag 328,068	0,002	0,007	0,72
Al 167,078	0,001	0,002	0,21
As 189,042	0,005	0,013	1,30
Bi 223,061	0,002	0,007	0,71
Cd 214,438	0,000	0,001	0,11
Co 228,616	0,000	0,001	0,07
Cr 205,618	0,000	0,001	0,13
Cu 324,754	0,002	0,005	0,53
Fe 259,941	0,002	0,006	0,63
Ga 417,206	0,002	0,006	0,62
In 325,609	0,002	0,008	0,76
Ir 205,222	0,005	0,015	1,52
K 769,896	0,003	0,010	1,02
Li 670,780	0,000	0,000	0,01
Mg 279,553	0,000	0,001	0,11
Mn 257,611	0,000	0,000	0,04

Limits in 10 g/L Au solution

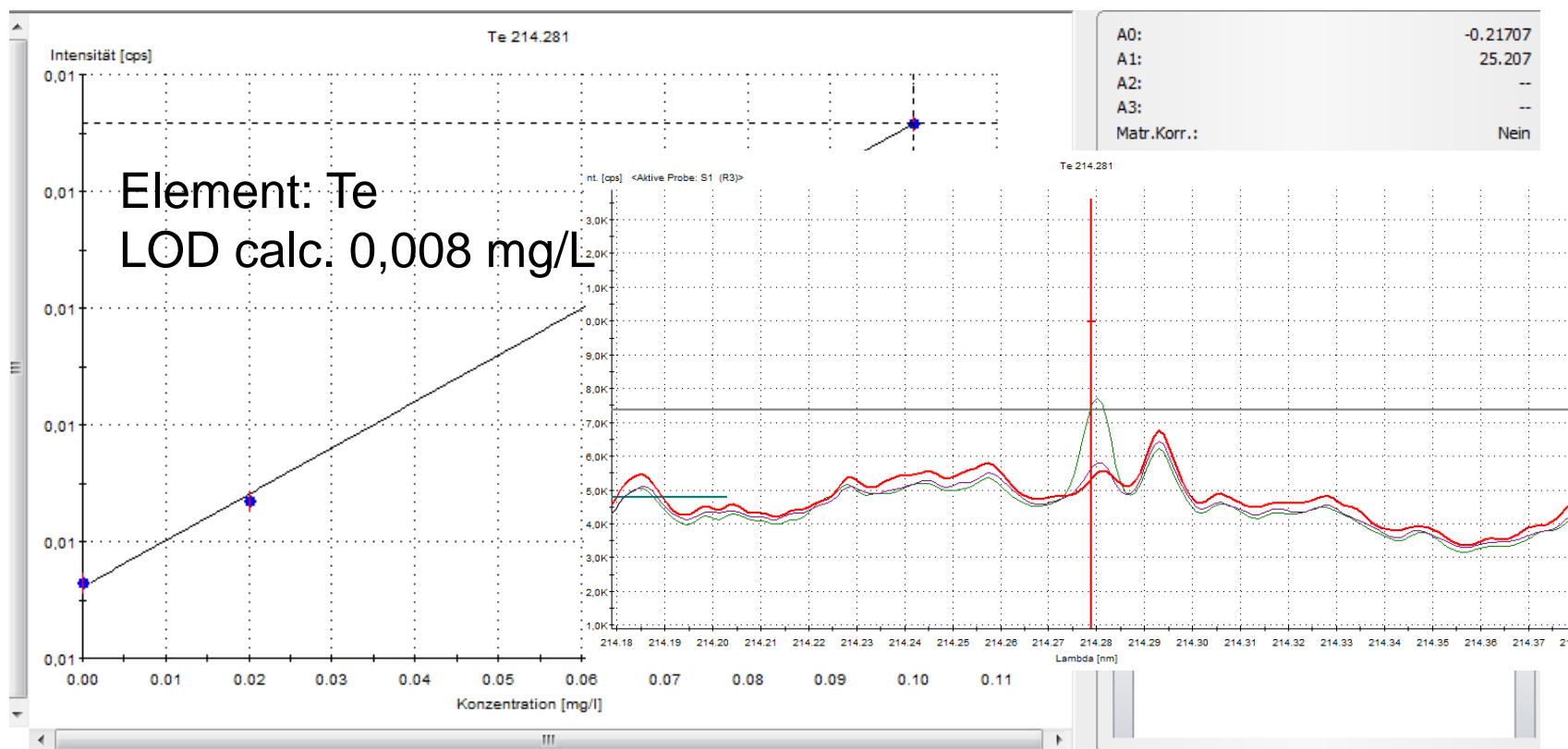
Calculation method 1

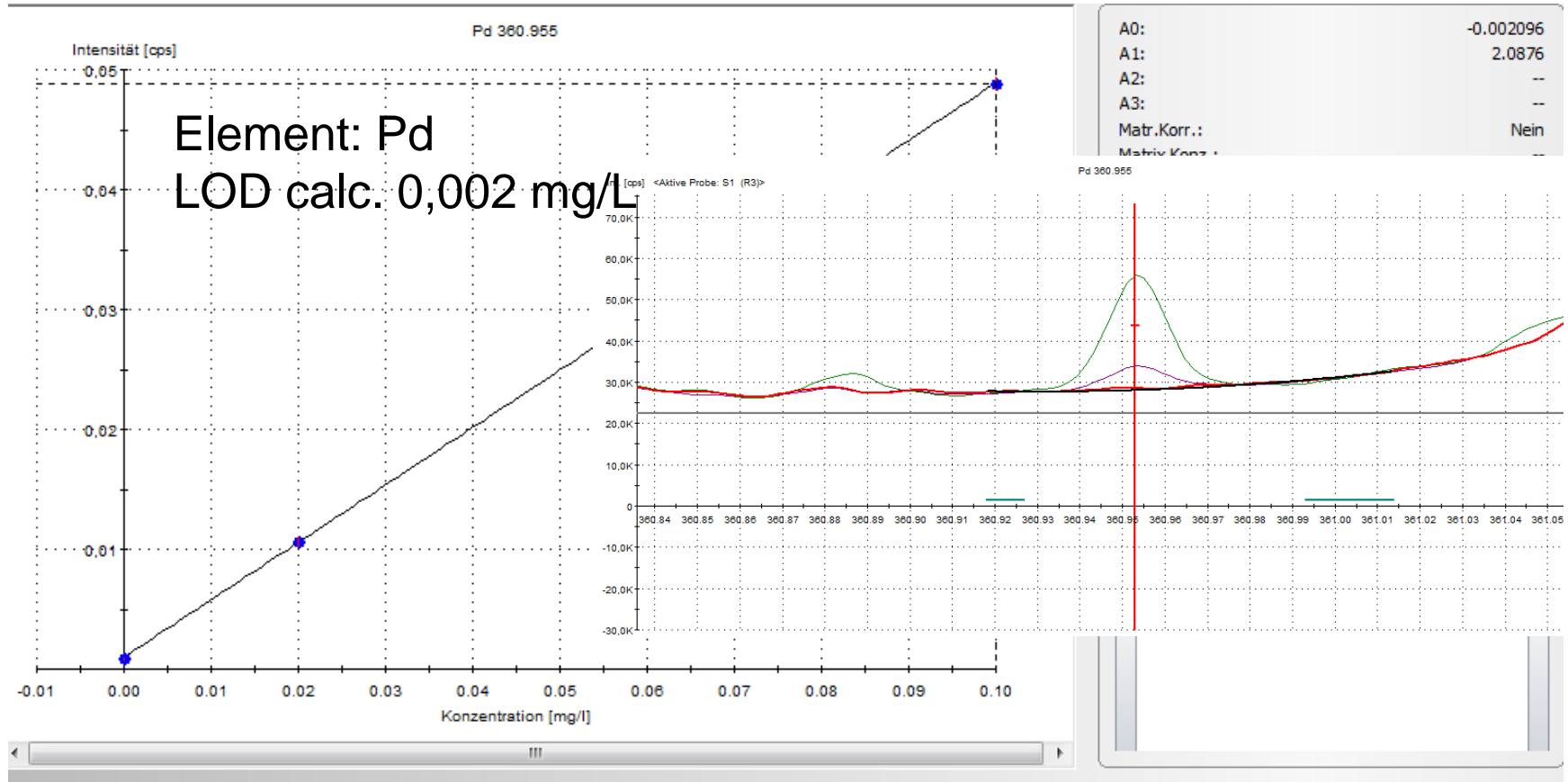
Probe	LOD	LOQ	LOQ
Typ	mg/L	mg/L	ppm
Mo 281,615	0,001	0,003	0,29
Ni 231,604	0,001	0,003	0,28
P 177,495	0,004	0,010	0,98
Pb 220,353	0,004	0,011	1,11
Pd 360,955	0,002	0,007	0,66
Pt 265,945	0,003	0,009	0,94
Rh 343,489	0,002	0,006	0,59
Ru 240,272	0,001	0,003	0,33
Sb 206,833	0,004	0,011	1,14
Se 196,090	0,009	0,022	2,21
Si 251,6_2	0,006	0,017	1,67
Sn 189,991	0,002	0,005	0,55
Sr 421,552	0,001	0,001	0,08
Te 214,281	0,008	0,025	2,51
Ti 336,121	0,000	0,001	0,10
Zn 213,856	0,001	0,002	0,22
Zr 343,823	0,000	0,001	0,08

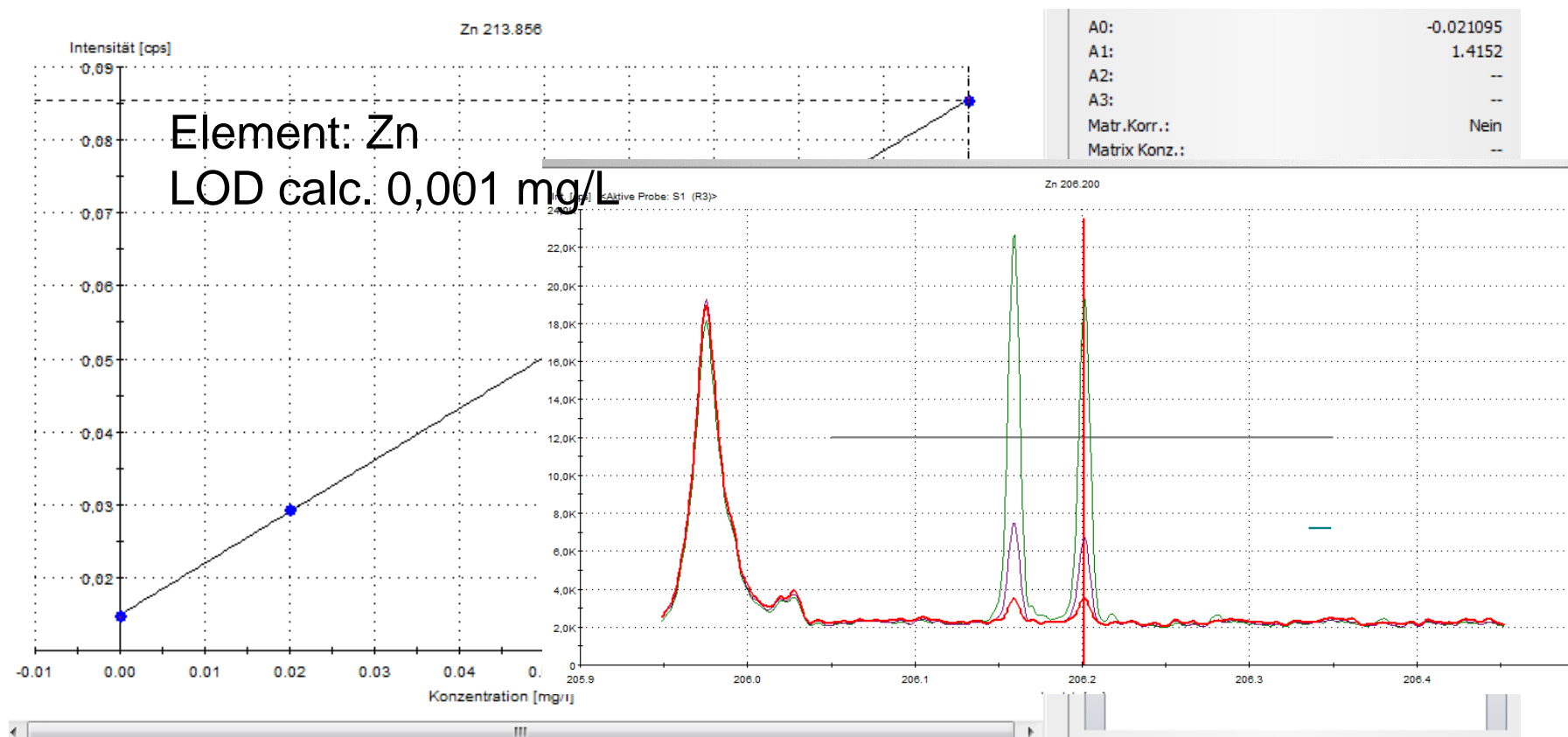
Calculation method 2

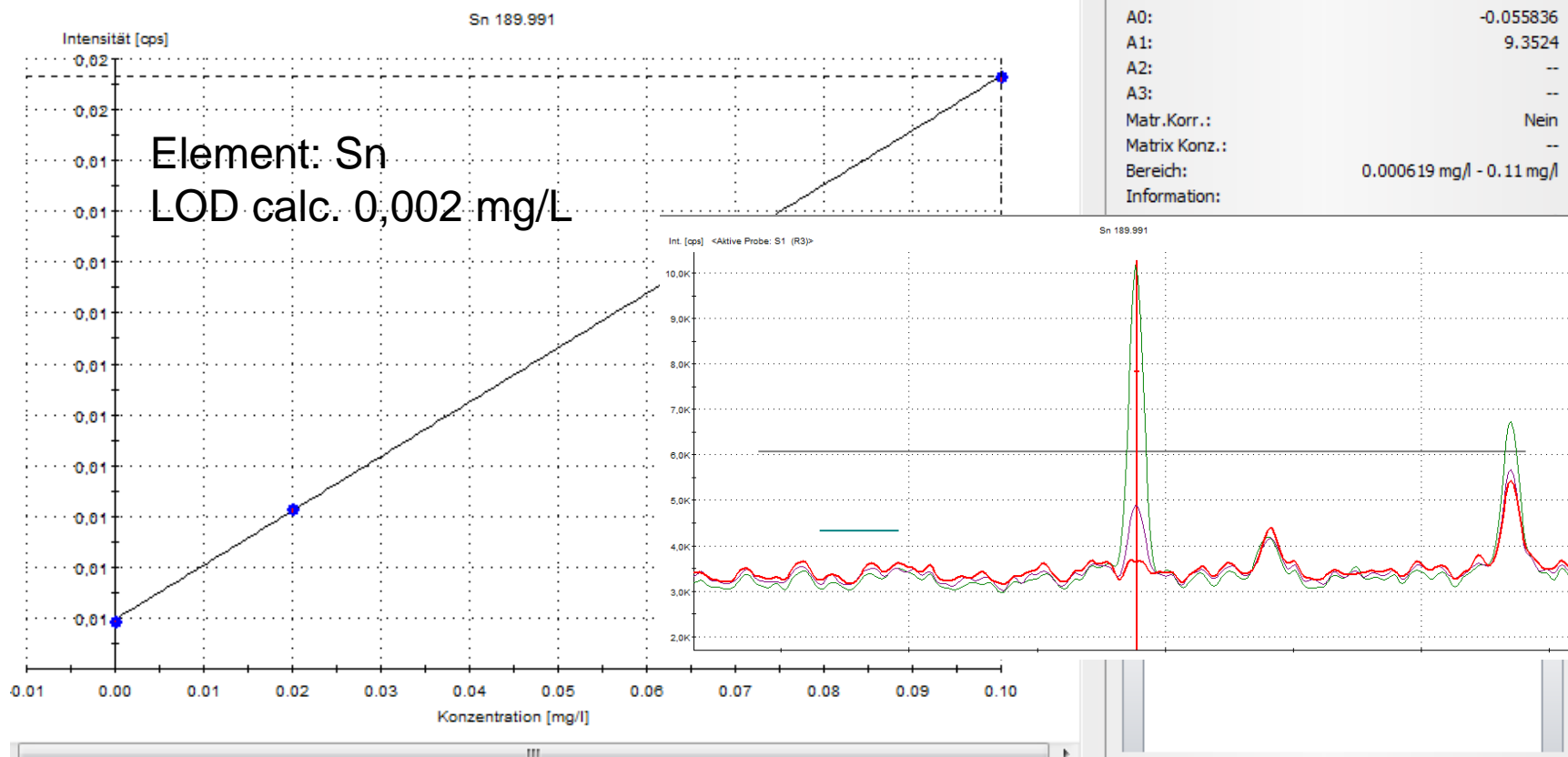
Probe	LOD	LOQ	LOQ
Typ	mg/L	mg/L	ppm
Mo 281,615	0,001	0,003	0,29
Ni 231,604	0,001	0,003	0,25
P 177,495	0,002	0,008	0,80
Pb 220,353	0,003	0,011	1,05
Pd 360,955	0,002	0,006	0,63
Pt 265,945	0,003	0,009	0,89
Rh 343,489	0,002	0,005	0,52
Ru 240,272	0,001	0,003	0,30
Sb 206,833	0,003	0,011	1,09
Se 196,090	0,006	0,019	1,90
Si 251,6_2	0,005	0,015	1,54
Sn 189,991	0,002	0,005	0,53
Sr 421,552	0,000	0,000	0,01
Te 214,281	0,008	0,025	2,50
Ti 336,121	0,000	0,001	0,09
Zn 213,856	0,001	0,002	0,20
Zr 343,823	0,000	0,001	0,06

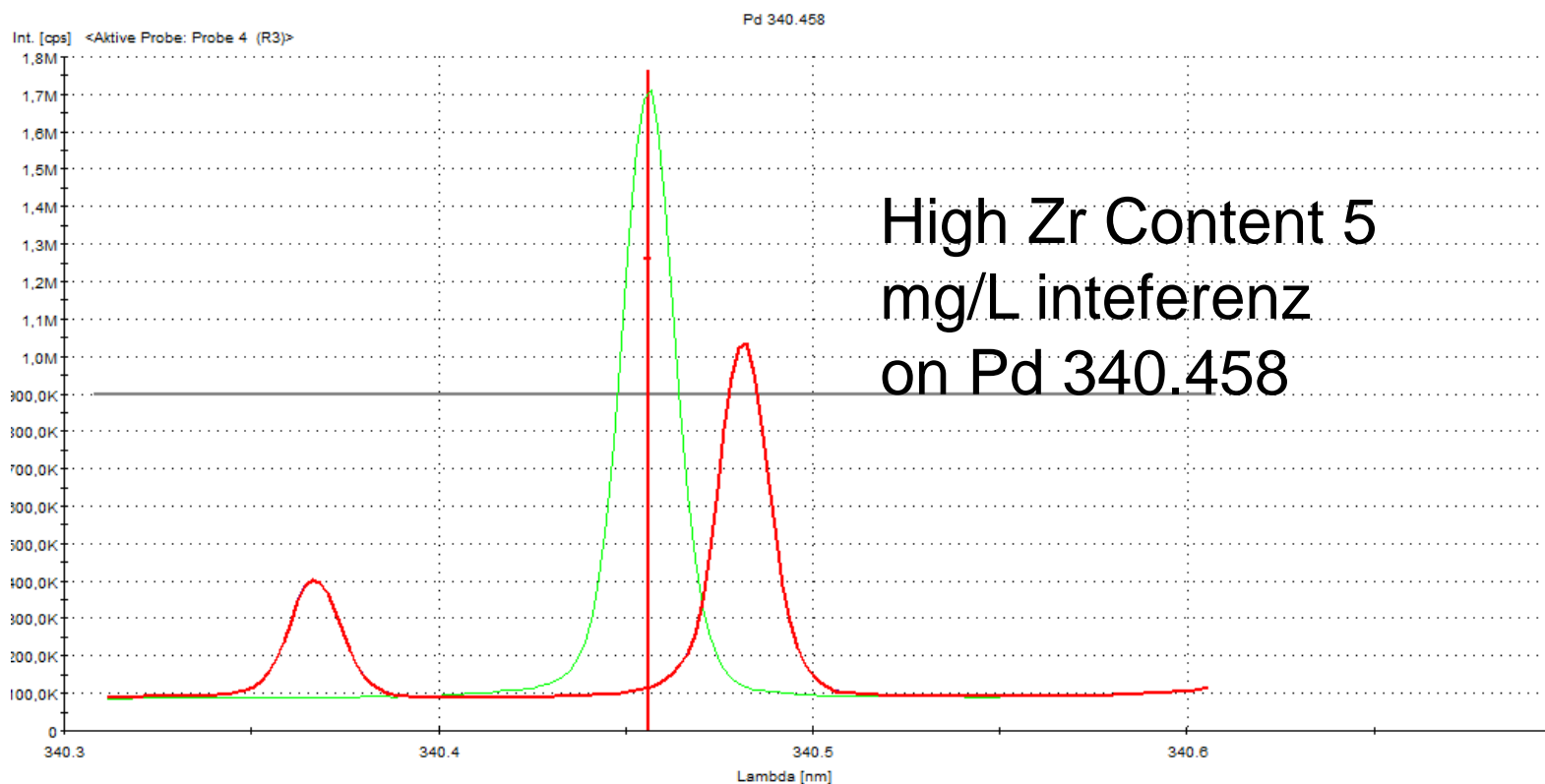
Calibrations and peaks of selected elements in 10 g/L Au solution











Limits in 10 g/L Ag solution

Calculation method 1

	LOD	LOQ	LOQ
	mg/L	mg/L	ppm
Al 167,078	0,003	0,007	0,73
As 189,042	0,009	0,028	2,75
Bi 223,061	0,003	0,007	0,65
Ca 396,847	0,002	0,006	0,63
Cd 214,438	0,001	0,003	0,32
Co 238,892	0,005	0,015	1,54
Cr 267,716	0,002	0,005	0,45
Cu 324,754	0,002	0,006	0,60
Fe 259,941	0,003	0,006	0,61
Ga 294,364	0,006	0,017	1,70
In 325,609	0,010	0,039	3,90
K 769,896	0,006	0,042	4,16
Li 670,780	0,000	0,000	0,03
Mg 280,270	0,000	0,001	0,08
Mn 259,373	0,000	0,001	0,08

Calculation method 2

	LOD	LOQ	LOQ
	mg/L	mg/L	ppm
Al 167,078	0,002	0,006	0,62
As 189,042	0,008	0,027	2,65
Bi 223,061	0,033	0,007	0,65
Ca 396,847	0,002	0,006	0,59
Cd 214,438	0,001	0,003	0,31
Co 238,892	0,005	0,015	1,51
Cr 267,716	0,001	0,004	0,38
Cu 324,754	0,002	0,006	0,60
Fe 259,941	0,002	0,005	0,50
Ga 294,364	0,005	0,018	1,78
In 325,609	0,010	0,039	3,90
K 769,896	0,011	0,036	3,64
Li 670,780	0,000	0,000	0,02
Mg 280,270	0,000	0,001	0,08
Mn 259,373	0,000	0,001	0,07

Limits in 10 g/L Ag solution

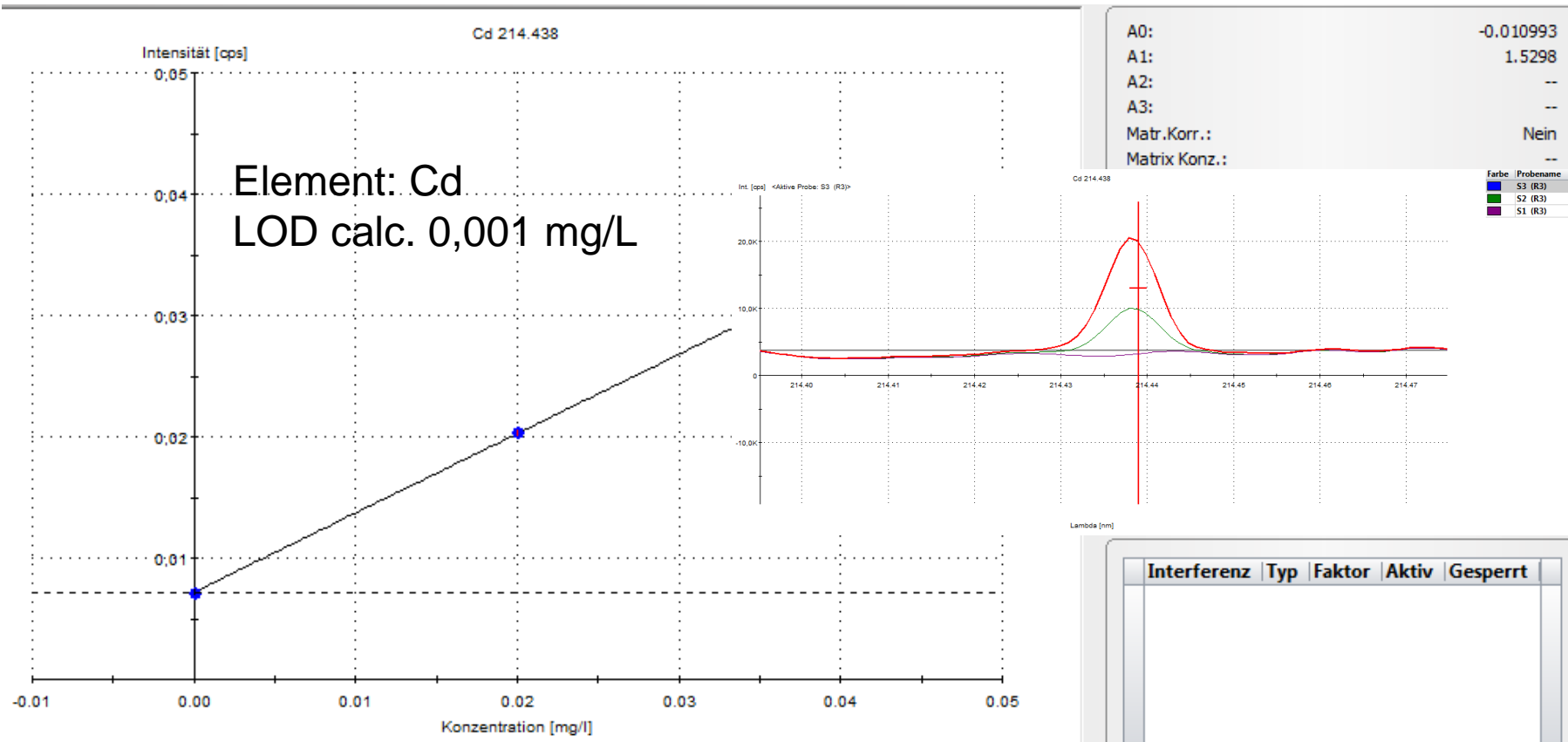
Calculation method 1

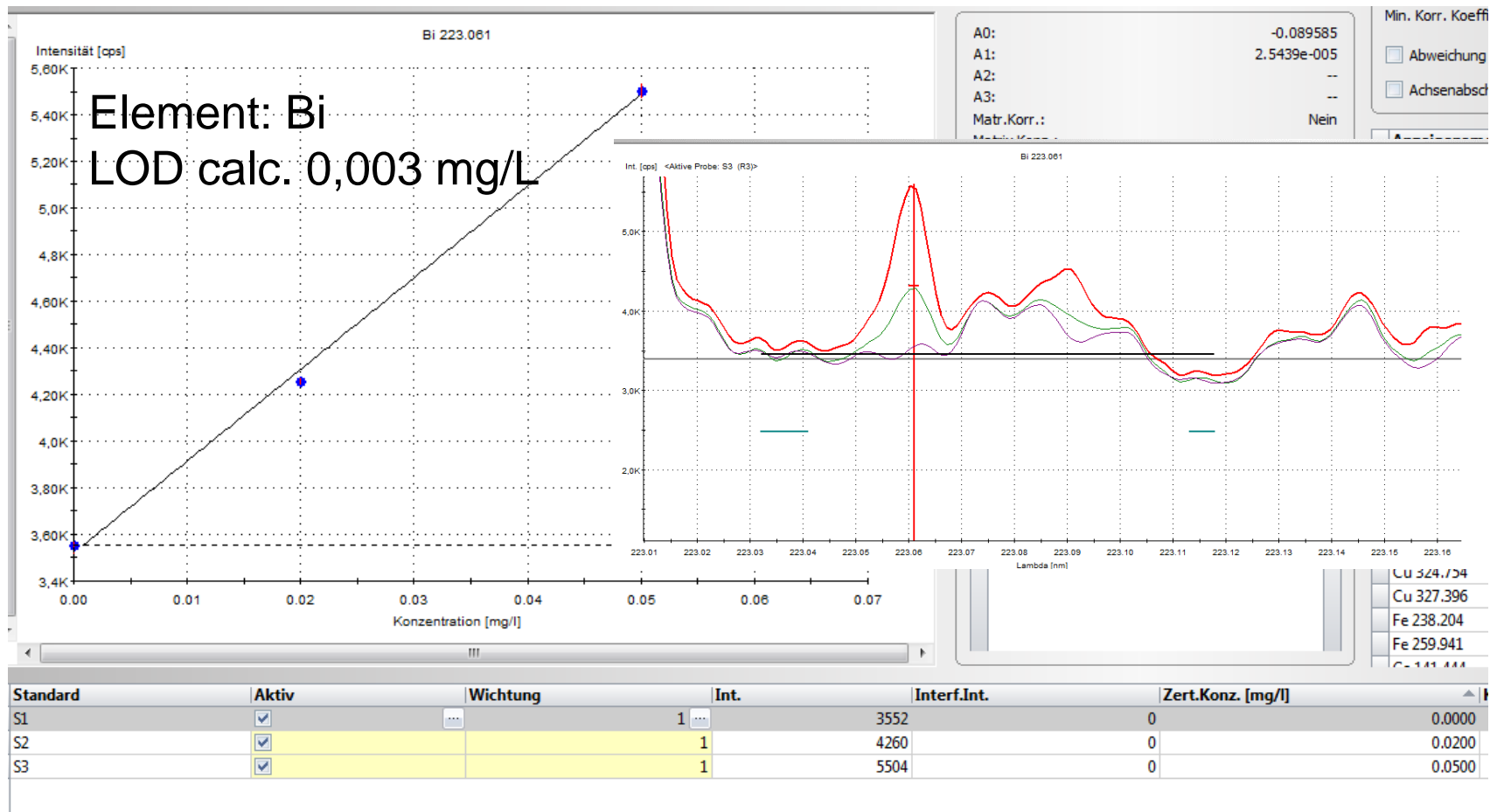
	LOD	LOQ	LOQ
	mg/L	mg/L	ppm
Mo 281,615	0,004	0,011	1,13
Ni 221,648	0,016	0,028	2,78
P 177,495	0,002	0,006	0,59
Pb 220,353	0,010	0,030	3,00
Pd 360,955	0,003	0,008	0,81
Sb 217,581	0,009	0,025	2,45
Se 196,090	0,007	0,019	1,91
Sr 421,552	0,000	0,001	0,08
Te 214,281	0,013	0,032	3,19
Ti 336,121	0,002	0,006	0,55
Tl 190,864	0,006	0,016	1,57
Zn 213,856	0,001	0,004	0,40

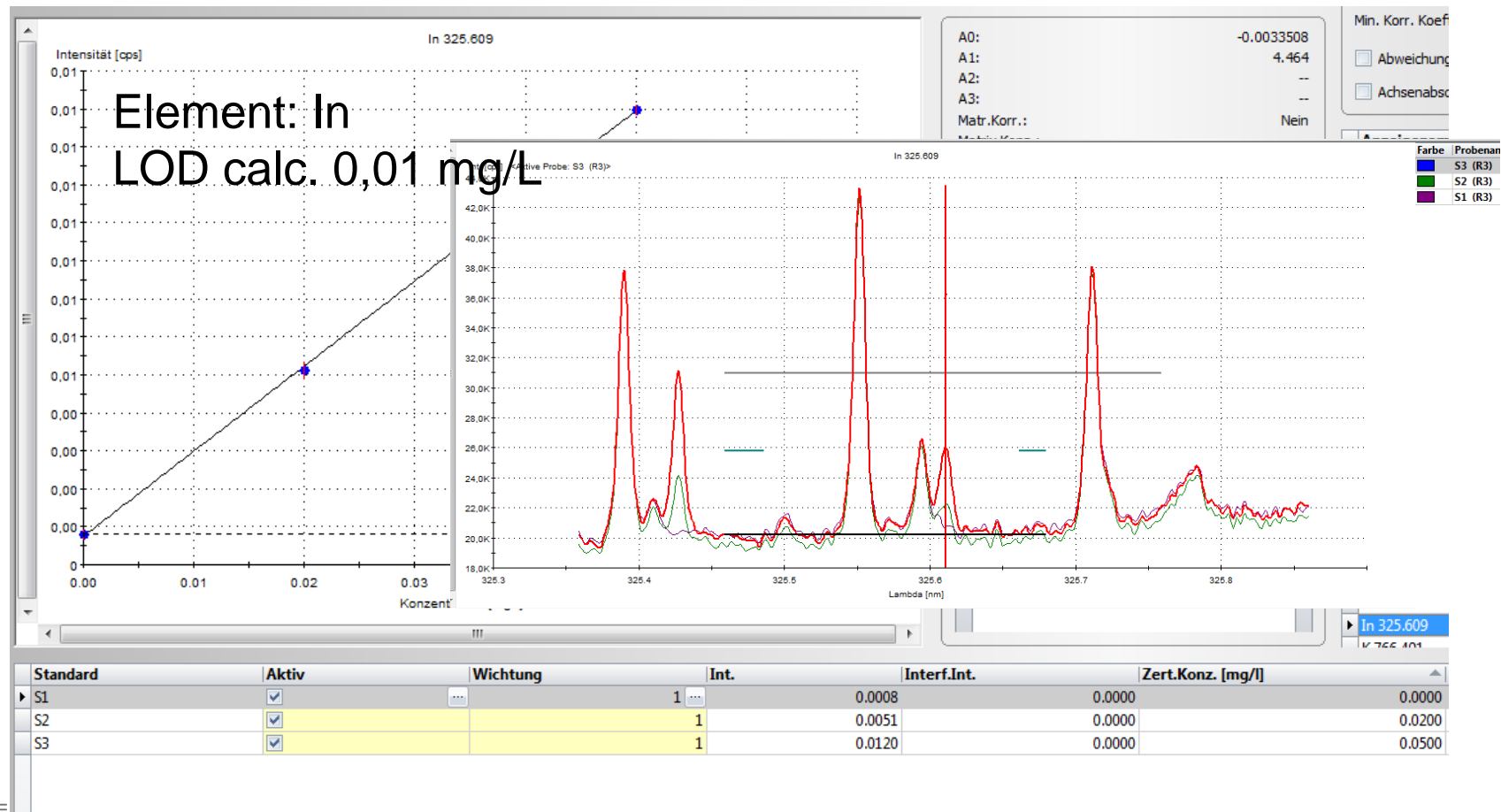
Calculation method 2

	LOD	LOQ	LOQ
	mg/L	mg/L	ppm
Mo 281,615	0,003	0,011	1,10
Ni 221,648	0,016	0,028	2,80
P 177,495	0,001	0,005	0,49
Pb 220,353	0,010	0,030	3,00
Pd 360,955	0,002	0,007	0,73
Sb 217,581	0,007	0,022	2,20
Se 196,090	0,005	0,017	1,68
Sr 421,552	0,000	0,001	0,07
Te 214,281	0,017	0,057	5,72
Ti 336,121	0,002	0,005	0,53
Tl 190,864	0,004	0,014	1,40
Zn 213,856	0,001	0,004	0,37

Calibrations and peaks of selected elements in 10 g/L Ag solution







Attention should be paid to

- Background correction for each element in each sample must be used
- Impurities in the 99,999 % fine metals for matrix matching should be considered
- Calculations of LOD and LOQ have to be done in real matrix (10 g/L Au and Ag)

Conclusion

- LOD must be known.
- LOQ must be well - defined.
- QC - samples must be used to check the calibration, the chemicals and the spectrometer.
- It should be possible to analyze Au, Ag, Pt and Pd above 999 ‰ fineness with these methods.