Rückführbare Messungen zur Multielement-Spurenbestimmung metallischer und nichtmetallischer Analyten in Reinstmetallen mit dem neuen Glimmentladungs-Massenspektrometer Element-GD

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Abteilung I (Prof. U. Panne)

**Thermo Fisher Scientific

Content

- Why Primary Pure Standards?
- BAM System of Primary National Standards
  - Way of certification, some results
  - Need for GD-MS
- GD-MS and „Element GD“
  - Element-GD
  - Traceable results for metallic analytes
    - o Matrix zinc
    - o Matrix copper
    - o Matrix iron
  - Traceable results for non-metallic analytes
- Conclusions

➢ **Why Primary Pure Standards?**

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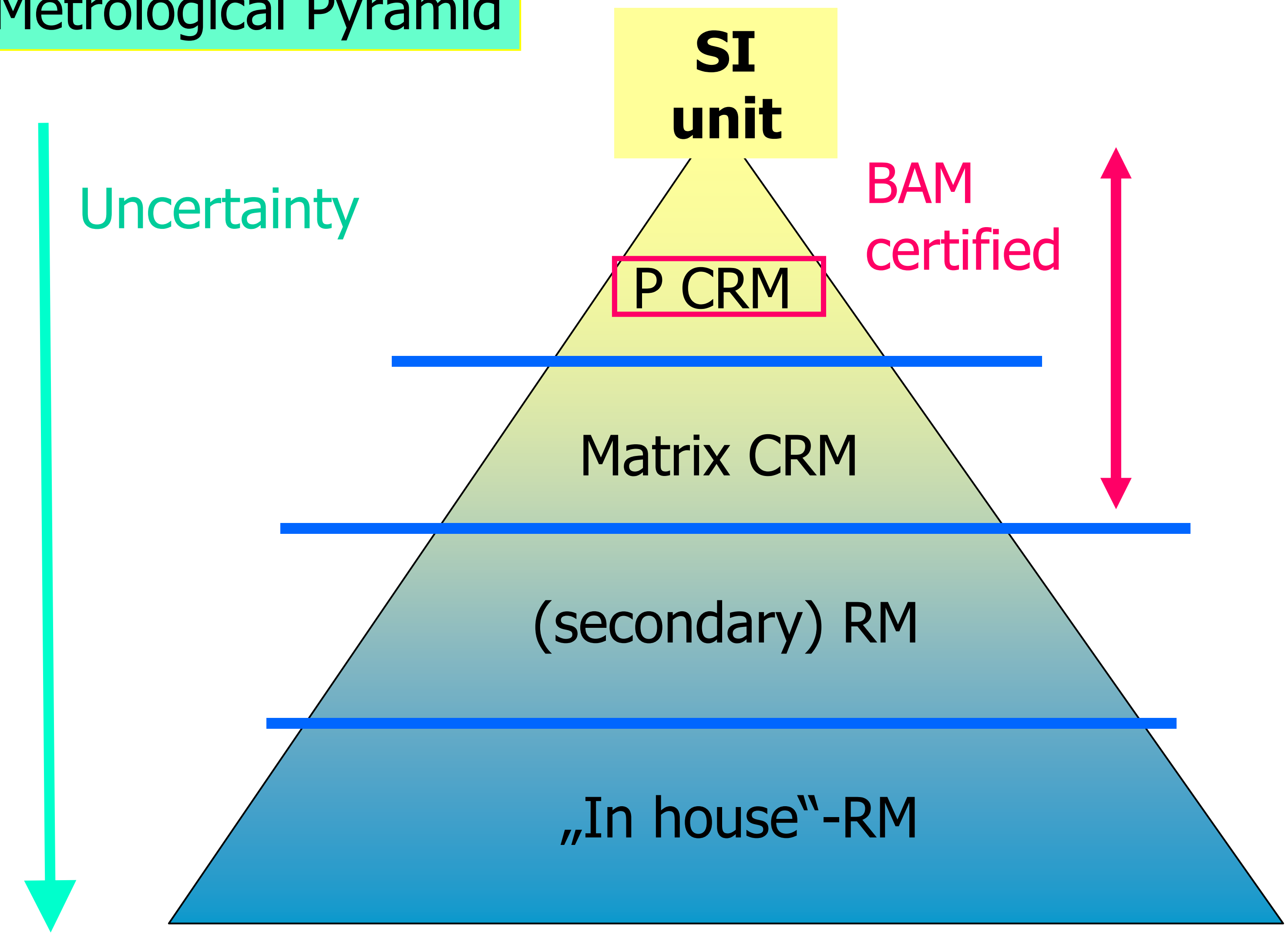
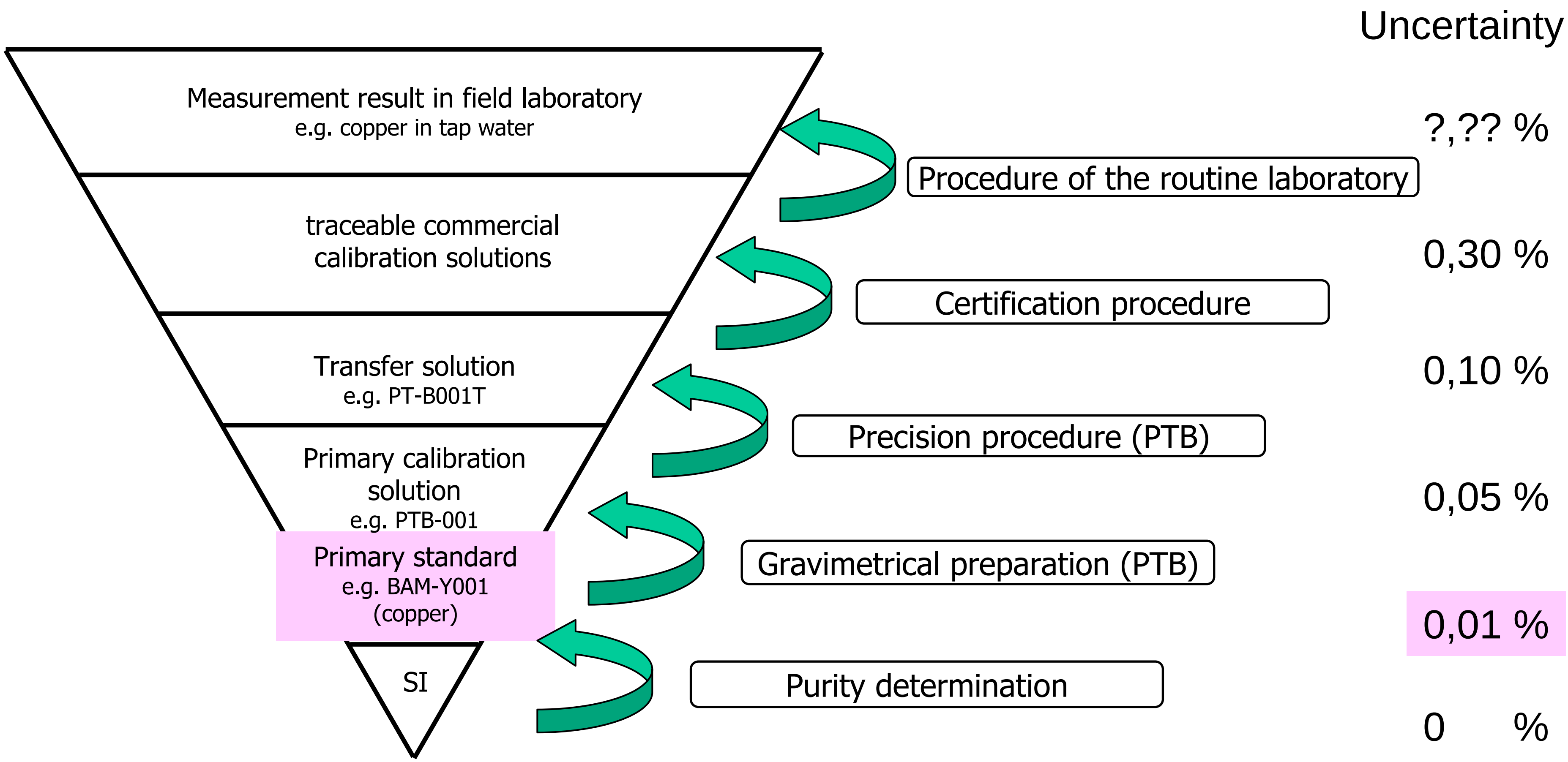
Metrological Pyramid

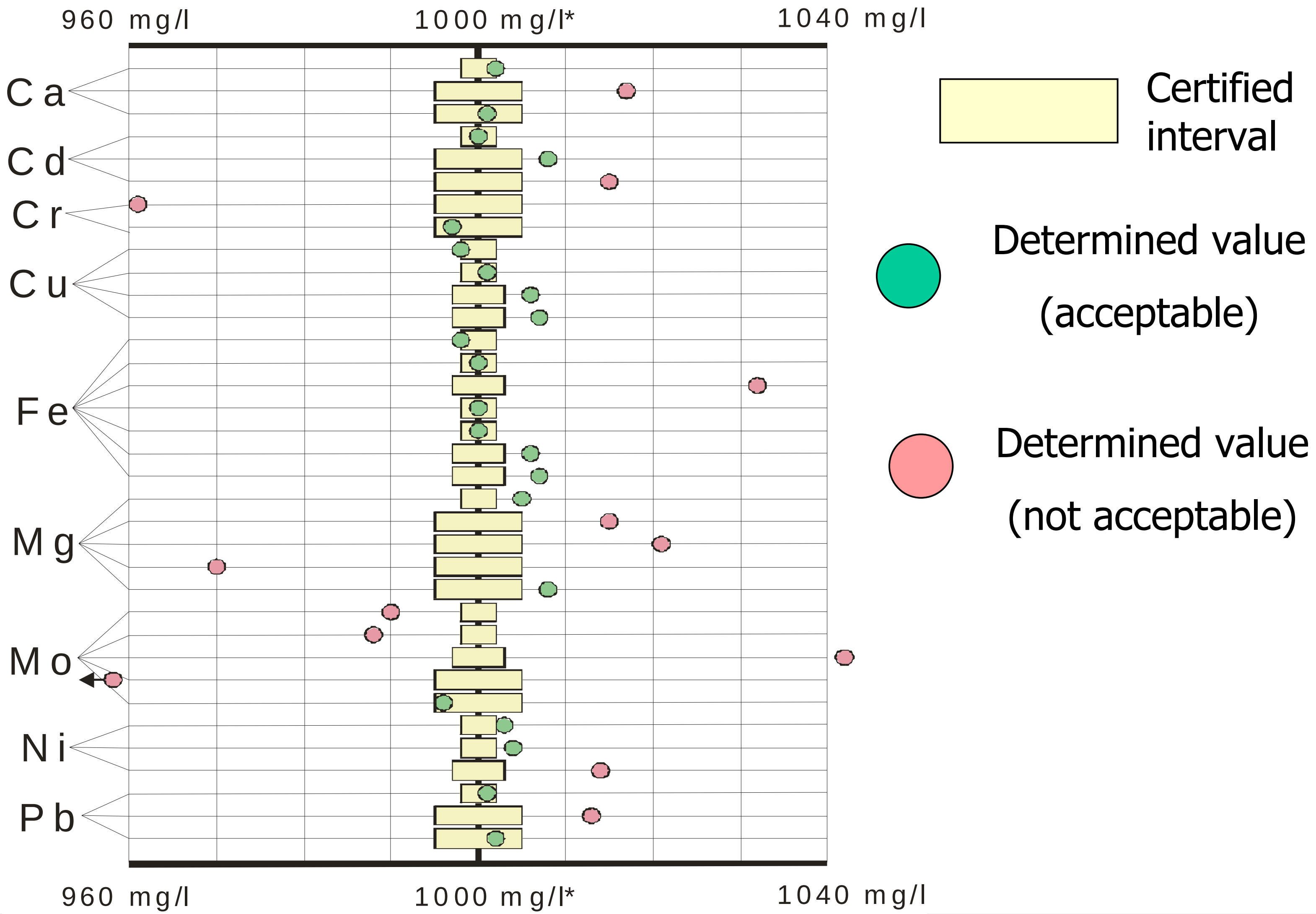


Dissemination of primary standards



Reality: Accuracy of different commercial calibration solutions

(according measurements by EMPA)



Materials certified for total purity ...

... hardly exist

... usually incompletely characterised using semi-quantitative measurement techniques

... no uncertainty statement

Typical example for this problem: Copper

purity	BAM-B-primary-	BAM-A-primary-Cu-1
‘nominal metallic’	0.999 999 (m6N)	0.999 9 (m4N)
‘metallic' based (by BAM)	0.999 997 ± 0.000 002	0.999 978 ± 0.000 010
total (certified by BAM)	0.999 44 (t3N5) ± 0.000 17	0.999 969 (t4N7) ± 0.000 010

Target: Primary standards ...

... of high metrological quality

... small uncertainty according to GUM

... serve as National Standards for
Elemental Analysis in Germany
(with PTB)

... can serve as primary back-spikes for IDMS
in European JEPPIM-project

... can serve as transfer standard in thermometry,
co-operation with PTB, NMIJ

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Primary standards of Type A ...

... intended for analyte calibration
(i.e. element amount standard)

... certified for the mass fraction of the matrix element in a ‘pure’ material (e. g. copper mass fraction of a pure copper material)

... for use within the NMIs
multiplication to the field via cooperation

Primary standards of type A

... Mass fraction ***w*(E)** known better than 0.01%

... approach: 100 % - **ΣImpurities**

... measurement of **all** impurity
elements (including non metals...)

... measurement of total impuritiy
content (bulk and surface after defined etching)

A Primary Standard of type A:

Trace contents and certification of primary copper (type A) BAM-Y001

Mass fractions above LOQ ; Sum: 9.95 ± 3.61 mg / kg

Mass fractions below LOQ ; Sum: 22.38 ± 3.84 mg / kg

Mass fractions estimated

Certified mass fraction:

99.9970 ± 0.0010 % (*U*, *k*= 2)

H < 2.1																	He < 0.001
Li < 0.31	Be < 1.1											B < 3.2	C 0.04	N 0.2	O 1	F < 2	Ne < 0.001
Na 0.002	Mg < 0.05											Al < 0.07	Si < 0.002	P < 2	S 5.4	Cl < 0.6	Ar < 0.001
K < 0.002	Ca 0.1	Sc < 0.06	Ti < 0.32	V < 0.04	Cr 0.07	Mn 0.01	Fe < 5	Co < 0.11	Ni 1.64	Cu matrix	Zn 0.057	Ga < 0.11	Ge < 0.12	As 0.5	Se 0.22	Br < 0.014	Kr < 0.001
Rb < 0.05	Sr < 0.014	Y < 0.03	Zr < 0.015	Nb < 0.02	Mo < 0.06	Tc < 0.001	Ru < 0.03	Rh < 1.6	Pd < 0.014	Ag 11.3	Cd < 0.015	In < 0.05	Sn 0.14	Sb 1	Te < 0.22	I < 0.09	Xe < 0.001
Cs < 0.0057	Ba < 0.017	La < 0.002	Hf < 0.003	Ta < 0.003	W < 0.12	Re < 0.009	Os < 0.004	Ir < 0.007	Pt < 0.007	Au < 0.008	Hg < 0.03	Tl < 0.005	Pb 0.47	Bi 0.23	Po < 0.001	At < 0.001	Rn < 0.001
Fr < 0.001	Ra < 0.001	Ac < 0.001															
			Ce < 0.0057	Pr < 0.002	Nd < 0.21	Pm < 0.001	Sm < 0.007	Eu < 0.003	Gd < 0.001	Tb < 0.001	Dy < 0.001	Ho < 0.001	Er < 0.001	Tm < 0.001	Yb < 0.001	Lu < 0.002	
			Th < 0.02	Pa < 0.001	U < 0.001												

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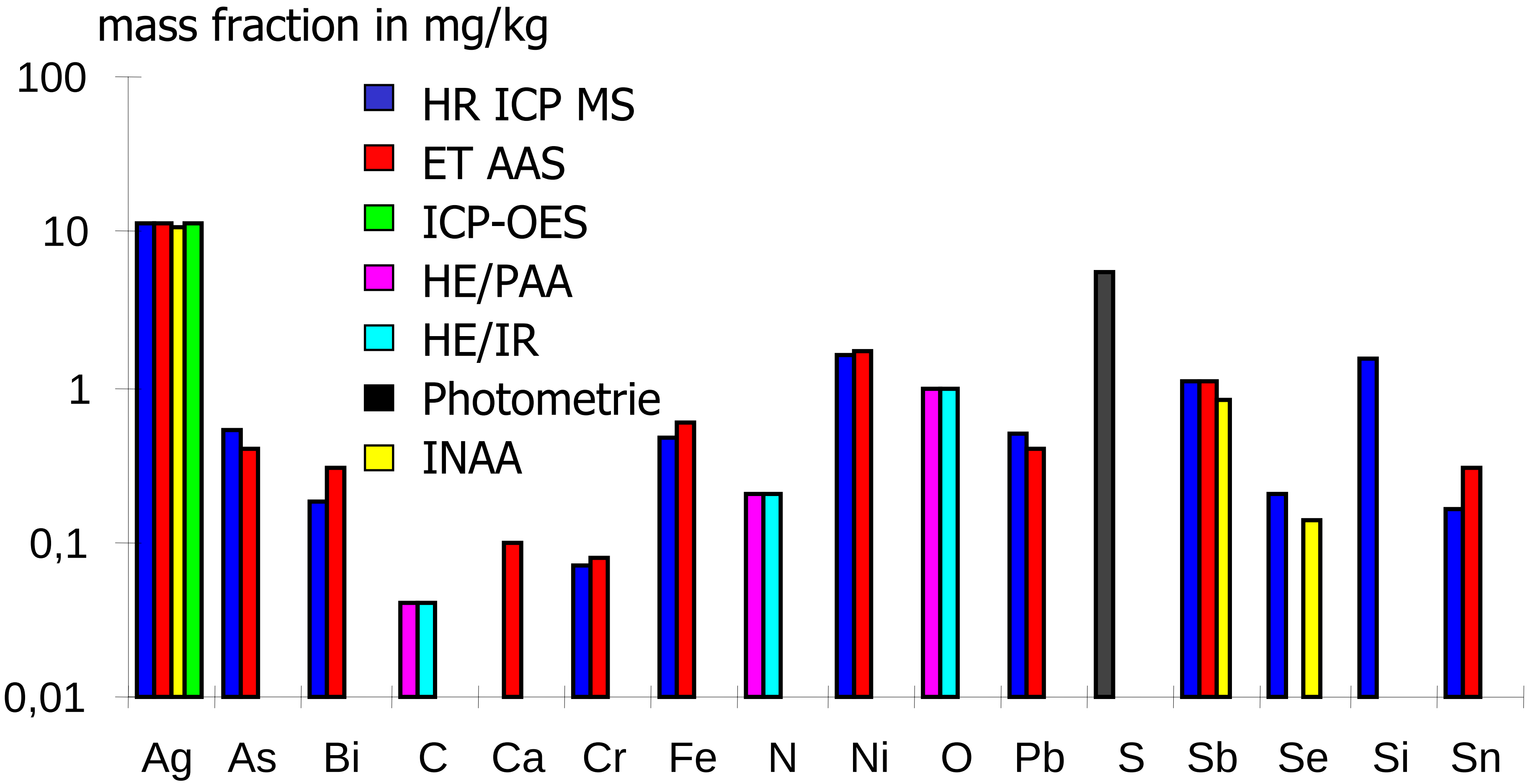
Measurements using different methods (BAM Y001)



BAM

BAM/HKi/01-27

I.1902

April 2004

Certification of the
mass fraction of copper
in Primary Reference Material
BAM-Y001

CERTIFICATION REPORT

Version of 2004-06-09

edited by Heinrich Kipphardt

Bundesanstalt für Materialforschung und -prüfung
Richard-Willstätterstr. 11
12489 Berlin
Germany

BAM-Y001 certification report

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Certification approach

BAM

ET and HG AAS

validation
additional information
consistency check

HR ICP MS

continuous
Nebulization
(all metallic analytes)

LA-ICP MS

check of
dissolution step

ICP OES, (INAA)

validation
additional information

?

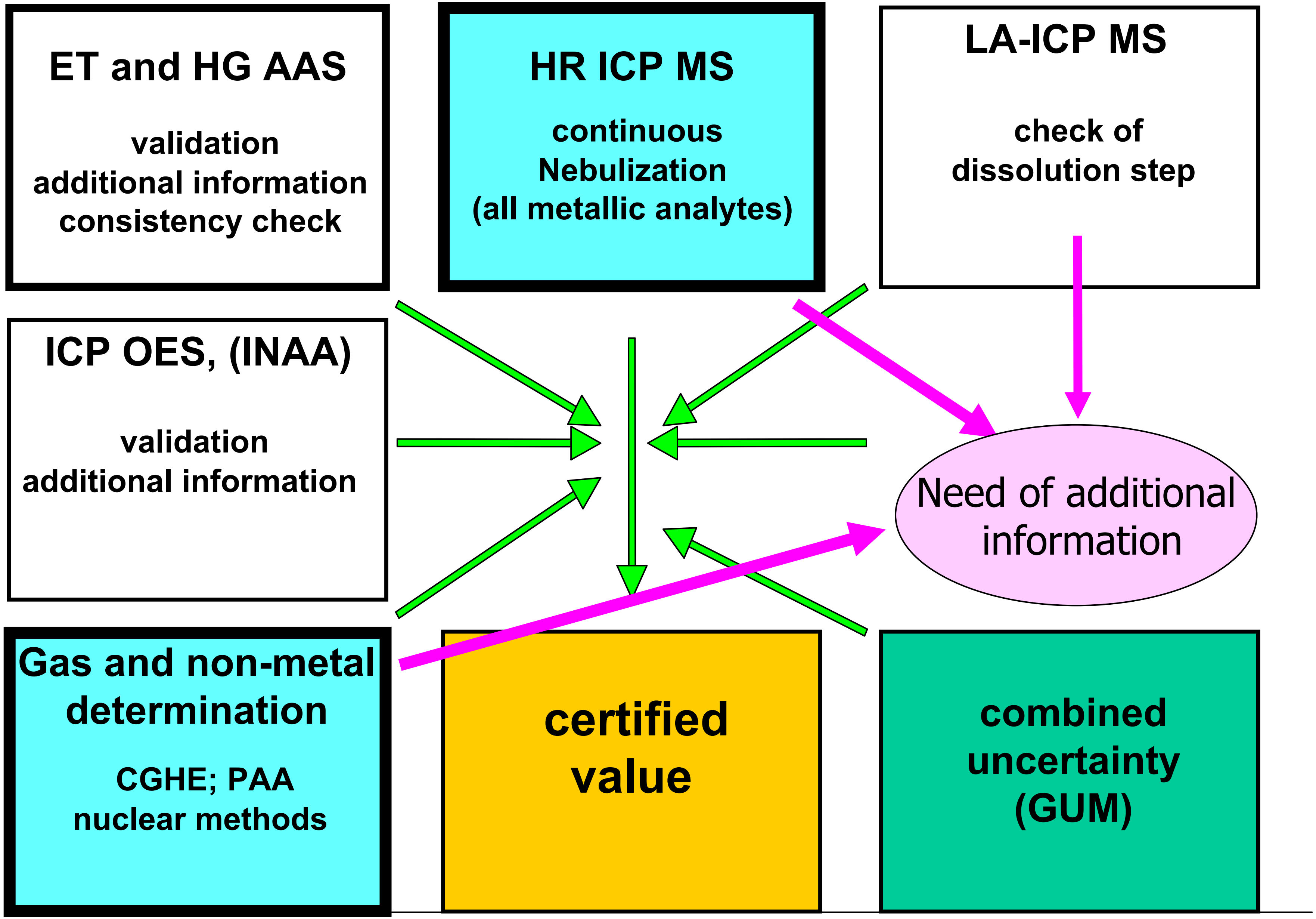
Gas and non-metal determination

CGHE; PAA
nuclear methods

certified value

combined uncertainty (GUM)

Certification approach



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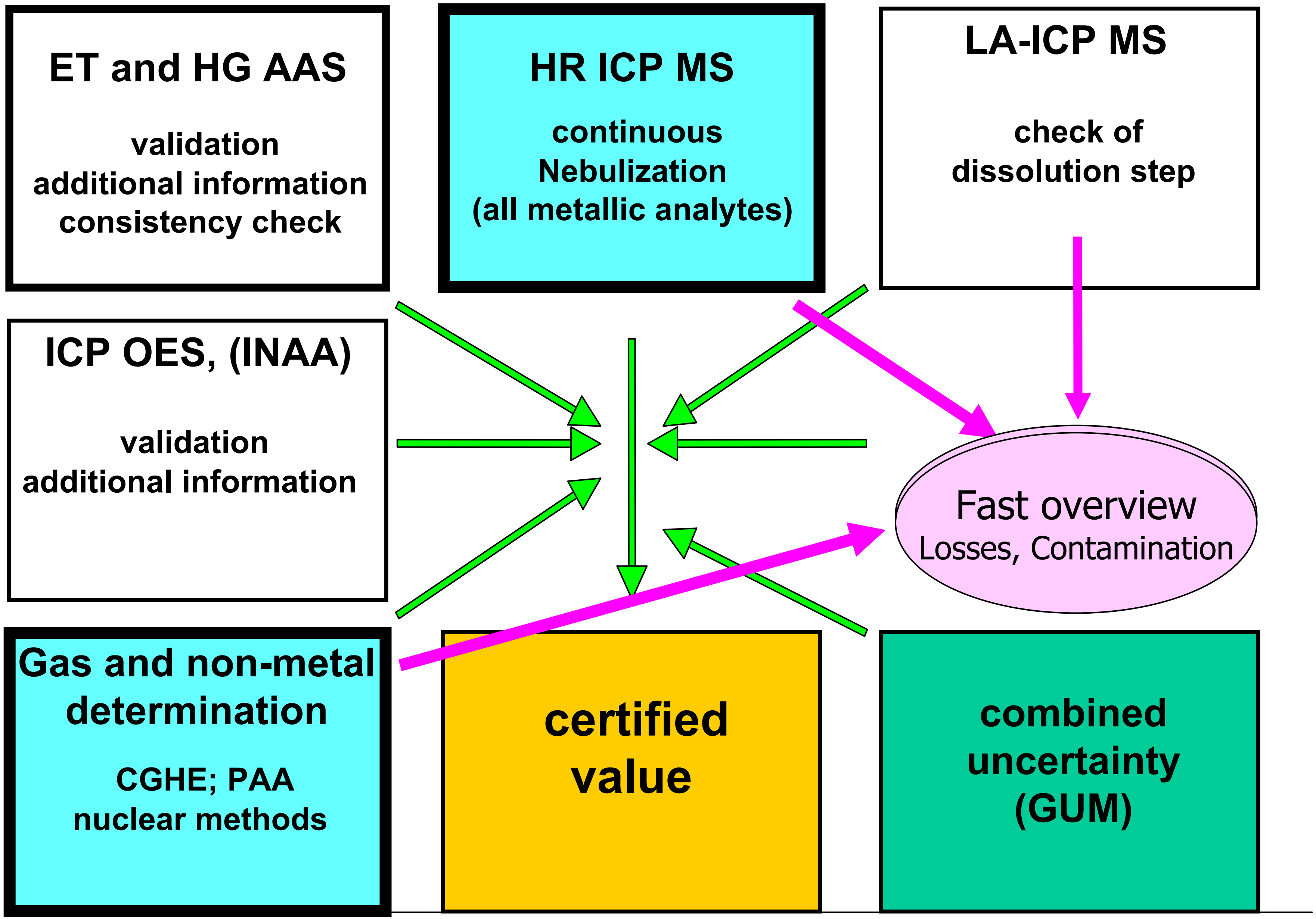

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GD-MS
Glow discharge
Mass spectrometry

Gas and non-metal determination

CGHE; PAA
nuclear methods

certified value

combined uncertainty (GUM)

Task of GD MS in context of PCRM

Liquid sampling methods (such as HR ICP-MS):

- **time consuming**
- **have analyte losses or contamination in some cases**
- **need to be supported by faster independent direct solid sampling methods** →

Glow discharge mass spectrometry (GD-MS):

- **solid sampling method**
- **with very low limits of quantification (LOQ).**

The question is:

- **how to use the new generation of fast GD-MS (Thermo ELEMENT GD) for this purpose ?**
- **how can it be calibrated for achieving reliable results which are traceable to SI ?**

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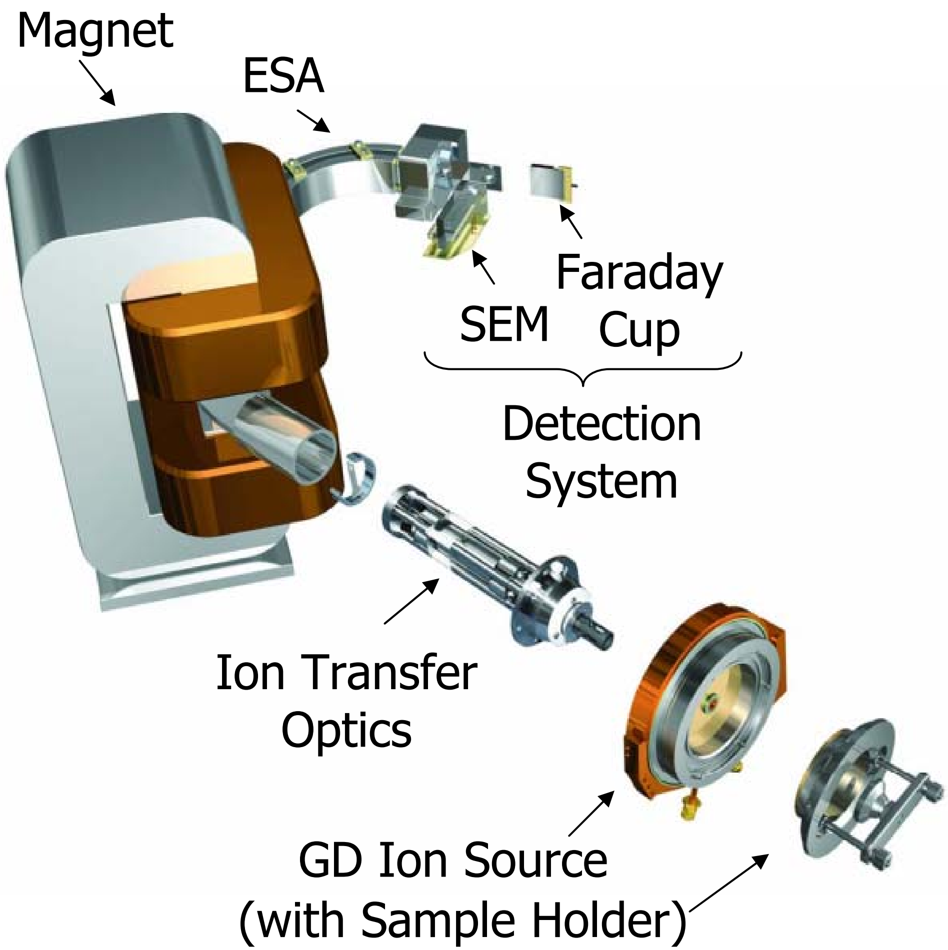
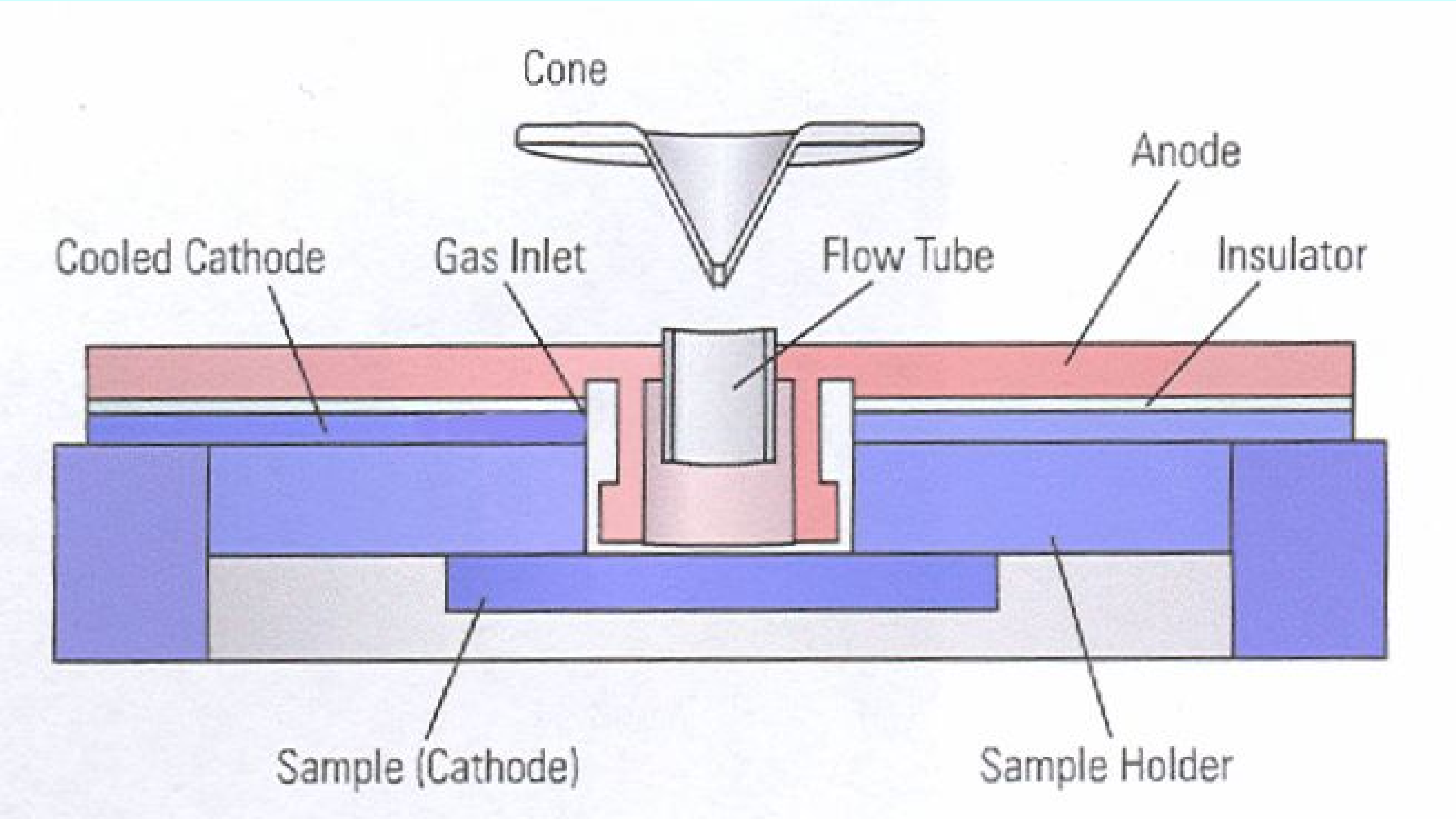
Main advantages of Finnigan ELEMENT GD
(Thermo Fisher Scientific)

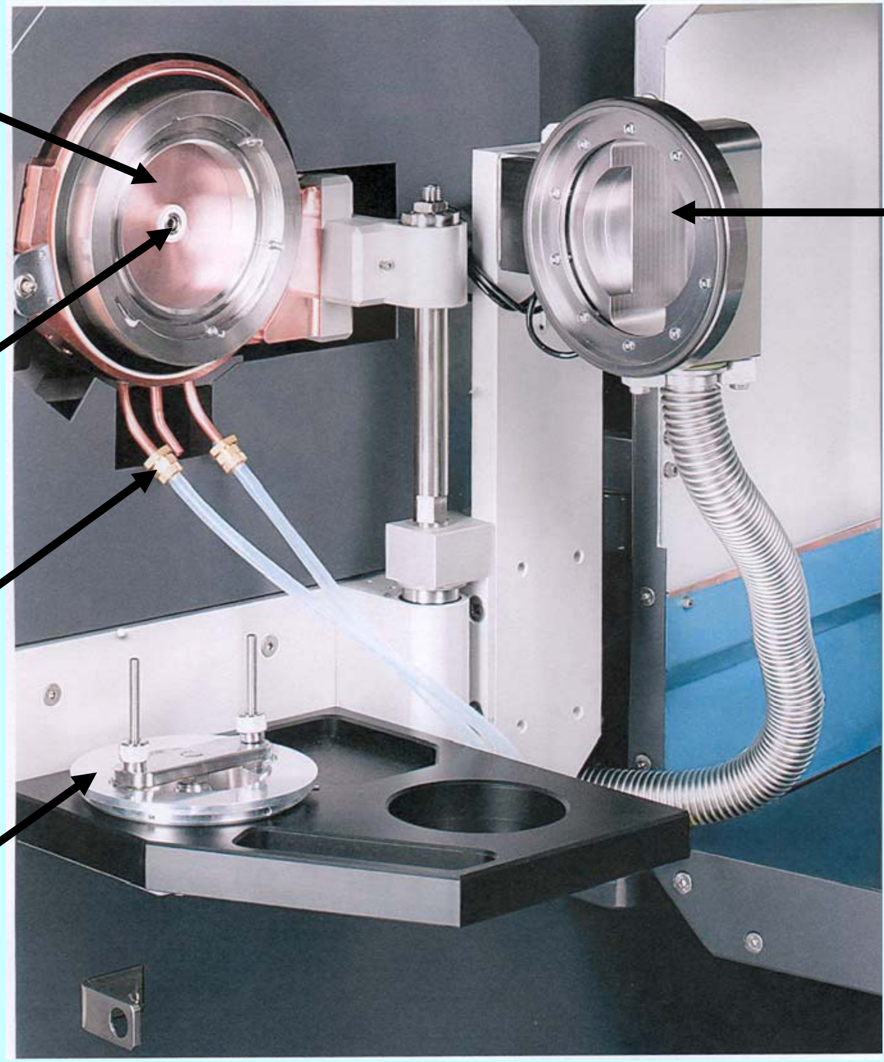


- **Grimm-type ion source**
- **High sputter rate**, **short analysis time**
- **High sample throughput** (6 Samples per hour)
- **More than 12 orders of magnitude automatic detection system**
- **Complete determination of matrix and trace elements** (up to ng/kg)
- **Extremely high SBR** (Signal to Background Ratio)
- **Double focussing mass spectrometer** (Resolution up to 10000)

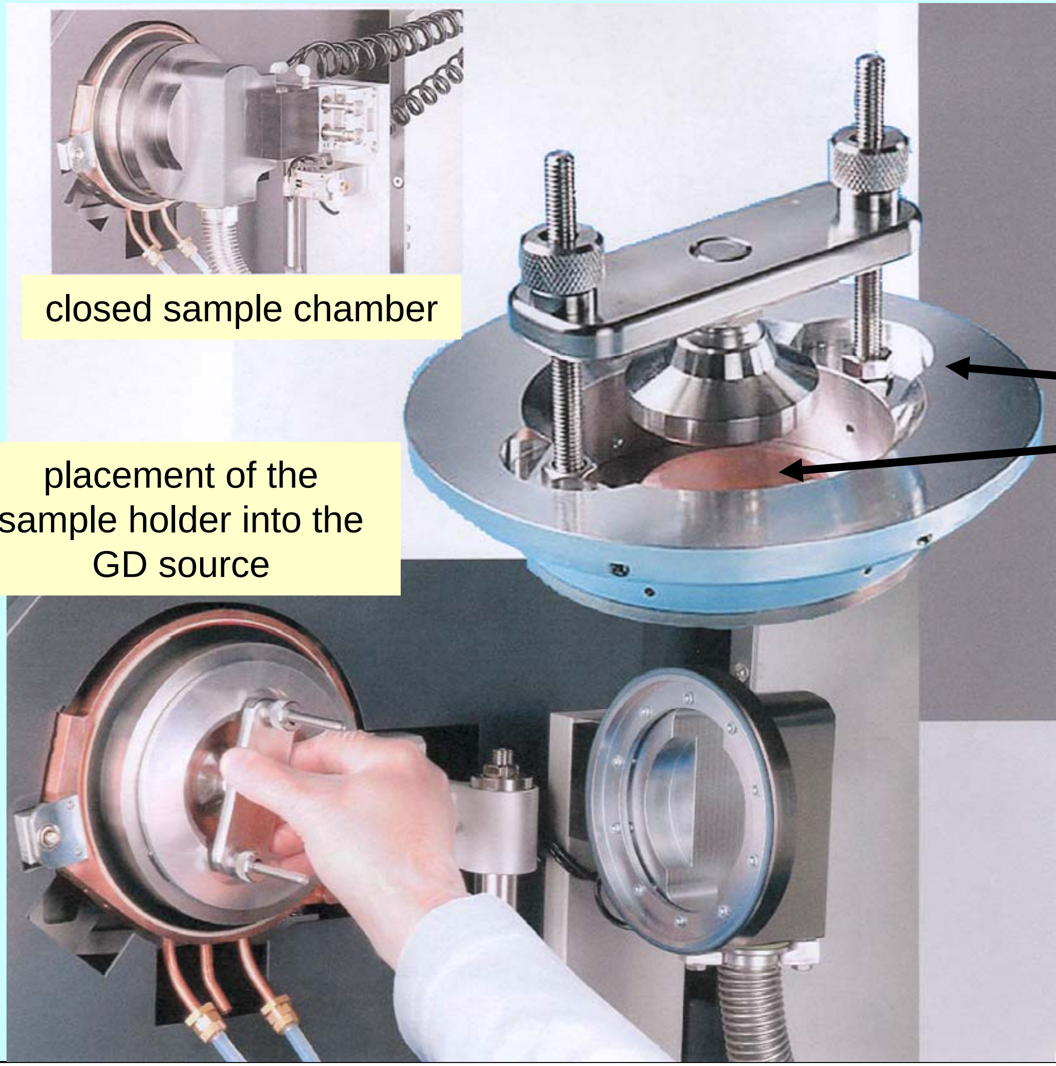
Principle Constructional Diagram of the Grimm Type Glow Discharge



Opened sample chamber of Finnigan GD Element



Placement of sample and sample holder



Problems of GD-MS

- GD-MS as solid sampling method needs calibration by solid samples similar to the samples to be analyzed.
- For most tasks of PCRMs adequate matrix CRMs do not exist

  ➡ external calibrations often cannot be carried out.
- Additionally, even if calibration materials would exist, those measurements would not be directly traceable to SI unit.
- In GD-MS mainly analyses are carried out based on:
- Element and matrix specific relative sensitive factors (RSFs, inaccuracy: ~ factor 2or higher), not directly traceable to SI unit
- Standard RSF values (SRSF), for semi-quanzitative analysis
- Both groups of values do not completely exist for the new GD-MS spectrometer Element GD with its new GD cell of Grimm type in opposite to the many RSF and SRSF values collected world wide for the former VG9000, results not traceable to SI

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How to get traceable results down to µg/kg level by GD-MS?

- Preparation of powder samples of pure metal matrix doped with graduated contents of trace elements down to the ppb-level (µg/kg)

-Pressing the powders at high pressure to metallic pellets of a size appropriate for the sample holder of GD-MS cell and compact enough to be sputtered by GD-MS without to be decayed.

-Measurement of isotope ions of the analytes in medium mass resolution and simultaneous measurement of the signal of the matrix element. Calculation of the ion beam ratios (IBRs) of all measured isotopes related to the ion strength of the matrix.

-Checking the linearity or monotony of the calibration curves based on these measurements. This is carried out for different sets of measurement values, starting with the lowest part of the calibration curve and ending with the curve including all contents, also the highest ones.

-The best calibration curve for one special analysis includes only one point above the unknown content of the analytical sample.

Quantification with Element GD

BAM

- **Semiquantitative**
  - **IBR**

    $$IBR = \frac{I_E / H_E}{I_M / H_M} \approx \frac{w_E}{w_M}$$

  - **Standard RSF**

    $$Std.RSF_{Fe}^{y} = \frac{RSF_{Zn}^{y}}{RSF_{Zn}^{Fe}}$$

- **Quantitative**
  - **Standard RSF**
  - **RSF**

    $$RSF_E = \frac{w_E^{SRM}}{IBR_E}$$

  - **Traceable to SI**
    - **Indirect** → **Calibration with RM**
    - **Direct** → **Calibration with doped pellets**

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Sample preparation of pressed powder pellets by doping with liquid standards (example Zn matrix)

R. Matschat, J. Hinrichs and H. Kipphardt,
Anal. Bioanal. Chem. **386:125 (2006)**

Doping
99,999% Zn powder
52 elements
1% HNO_3

→

Mix

Shaking in three dimensions of space

→

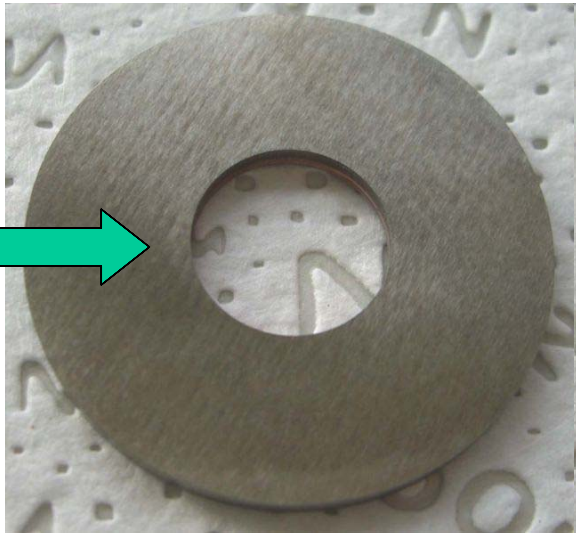
→

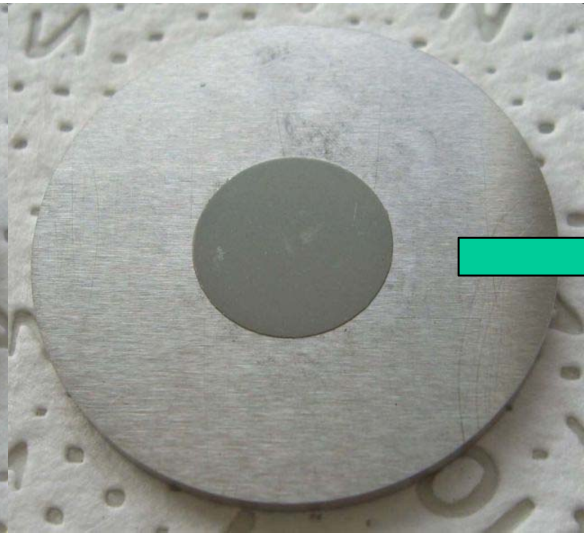
Press of ~ 1 g powder in steel-rings under 90 kN/cm²
Sample diameter ≈ 12 mm
Thickness ≈ 2 mm

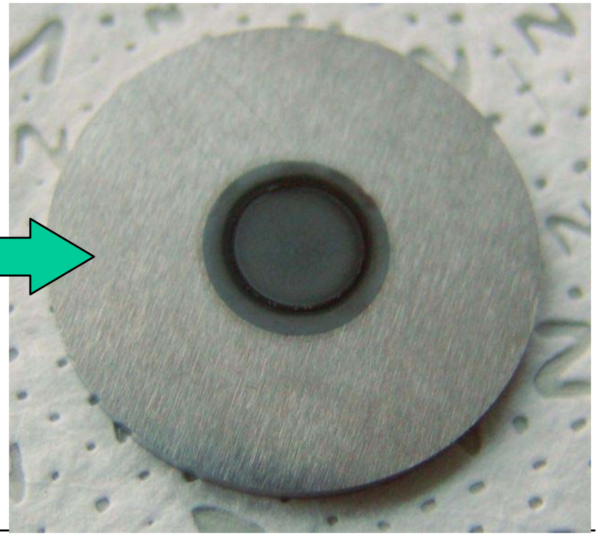
→

Analysis

Sample preparation of pressed powder pellets by doping with liquid standards (example Zn matrix)

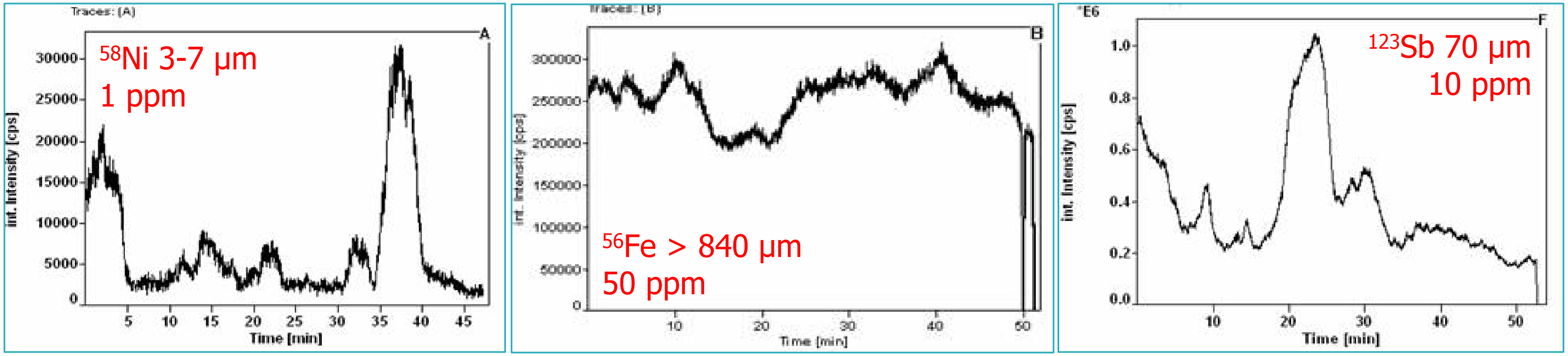




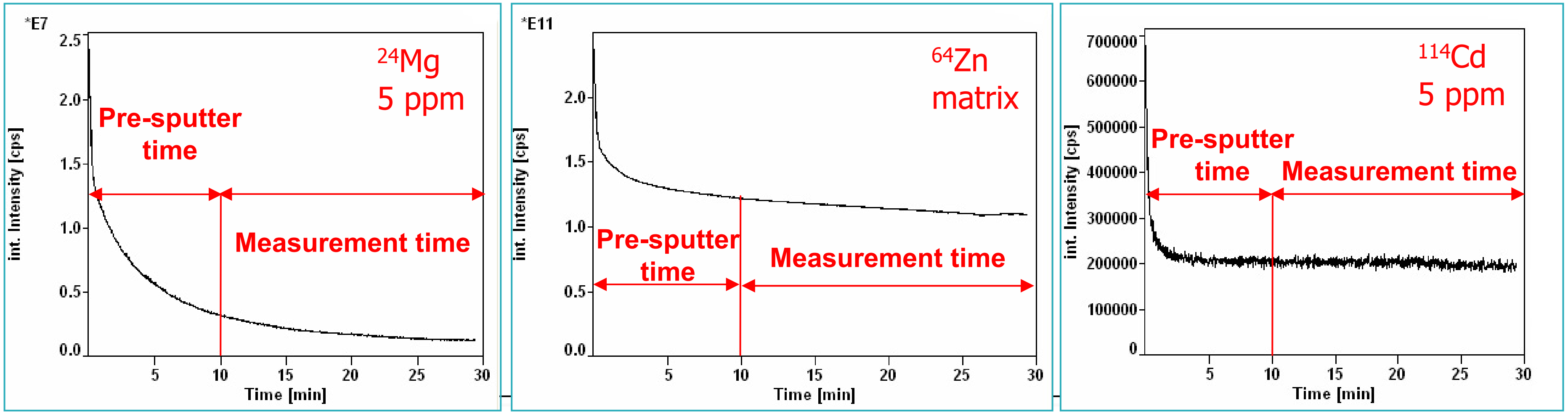


Observation of intensity-time behaviour of different elements

Doped with powders: grain size between 3 and 900 µm



Doped with liquids

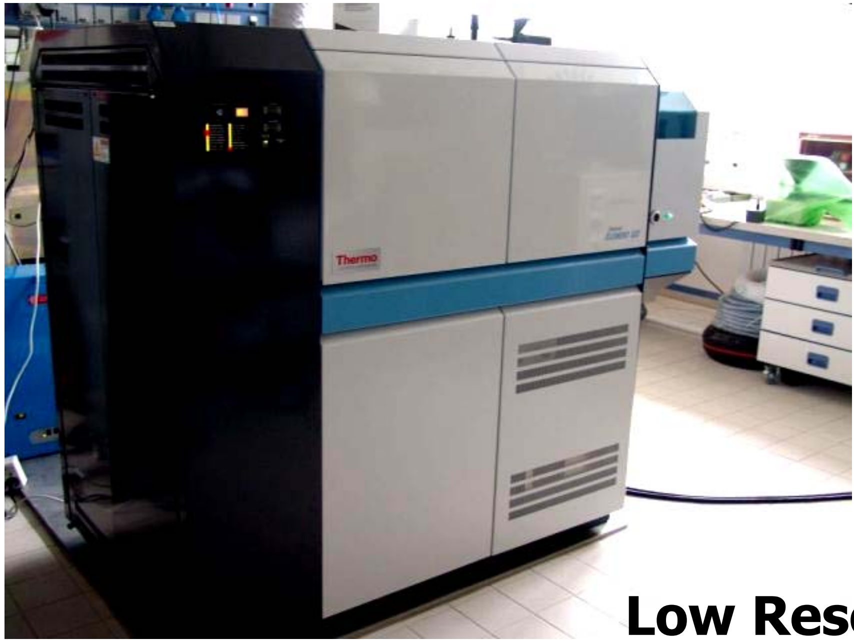


Analytical parameters with Zn matrix

Mass fractions of trace elements in the pellets

10 mg/kg; 5 mg/kg; 1 mg/kg; 500 µg/kg; 100 µg/kg; 50 µg/kg; 10 µg/kg; 5 µg/kg; blank

Zn powder 99,999% pure
<150 µm



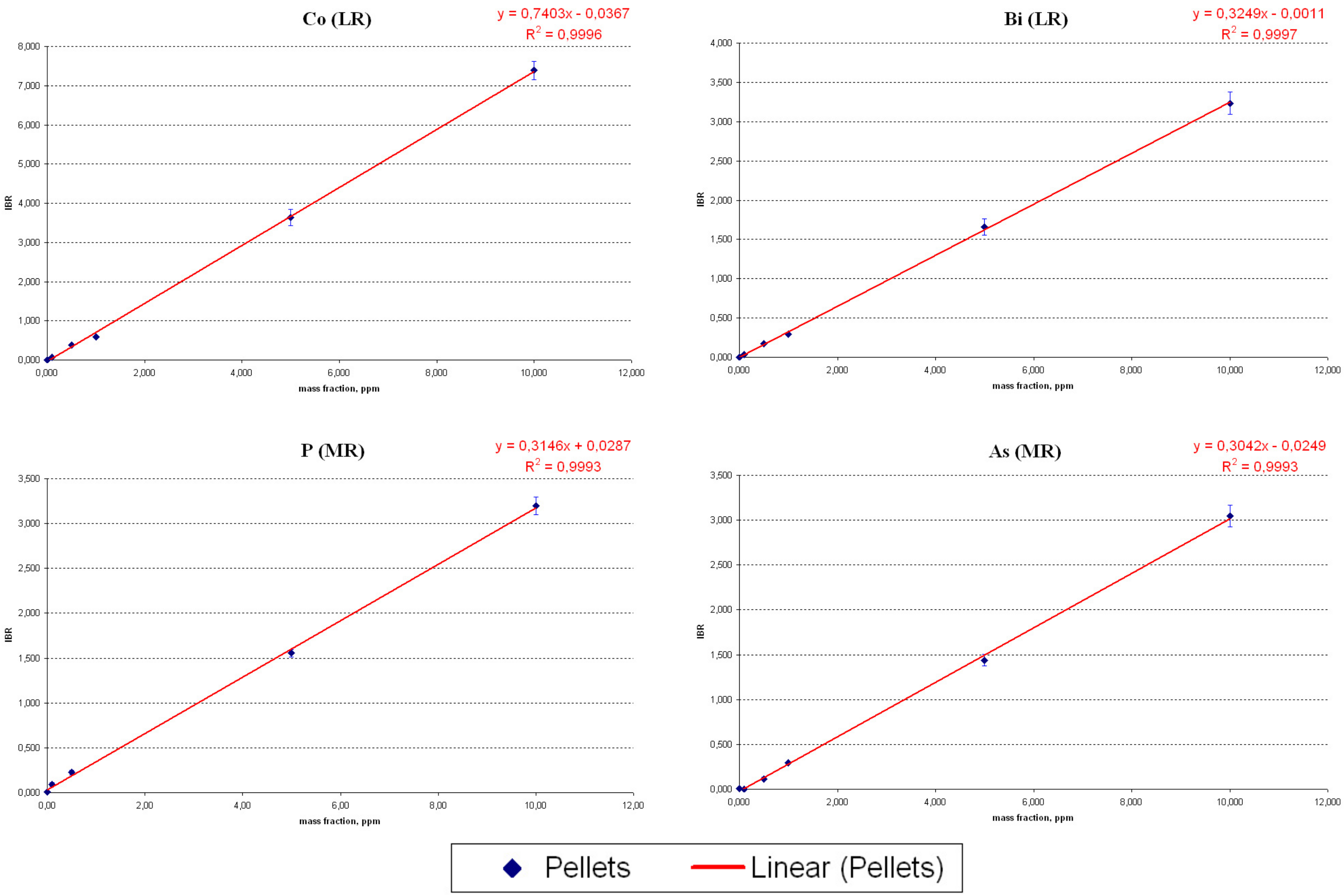
Parameters

Voltage	**~500 V**
Current	**20 mA**
Ar Gas Flow	**375 ml/min**
Peltier Cooling	**20 °C**

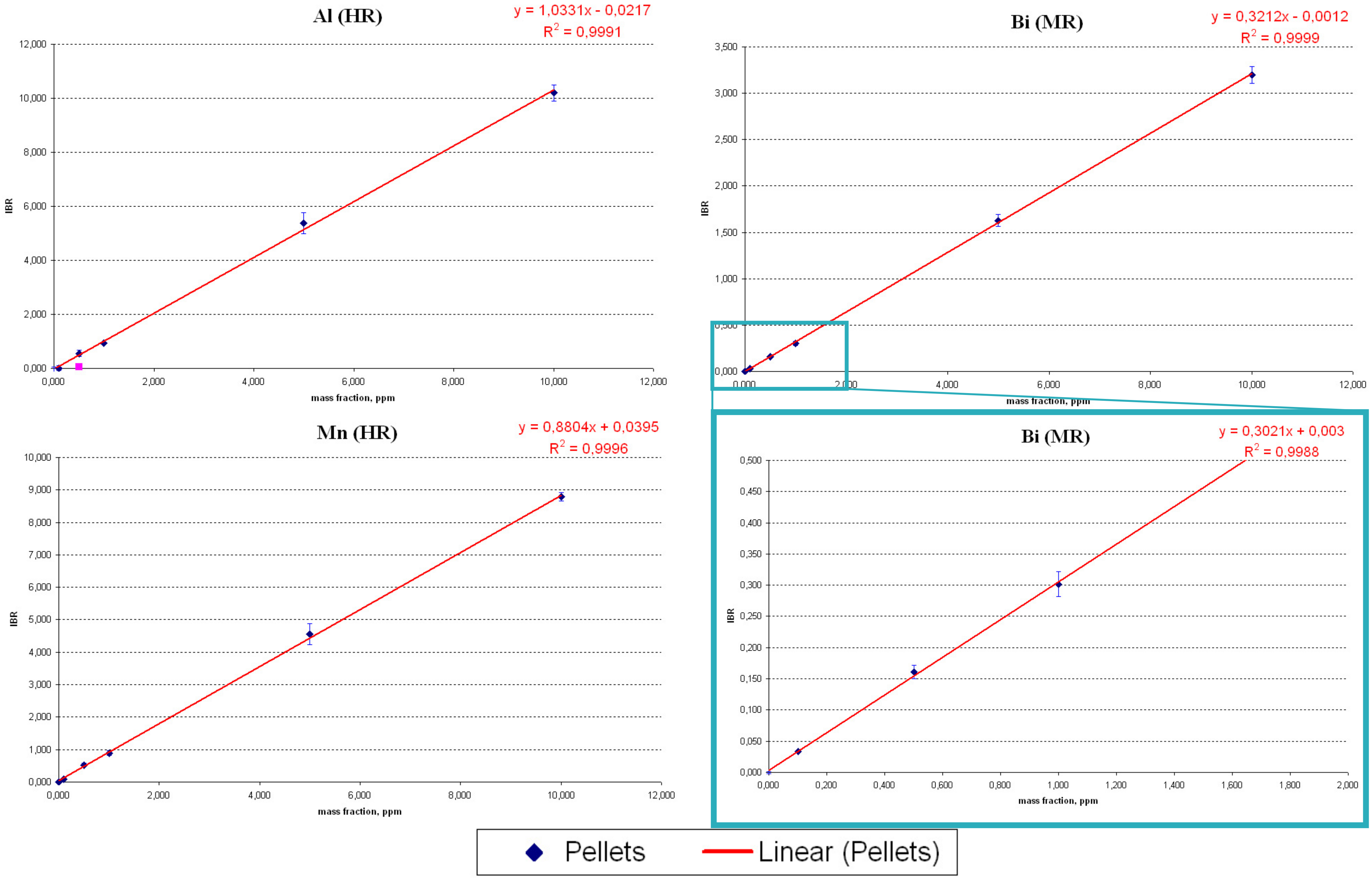
Low Resolution (LR) ≈ 400
Medium Resolution (MR) ≈ 4000
High Resolution (HR) ≈ 10000

Calibration with doped pellets

BAM



Calibration with doped pellets

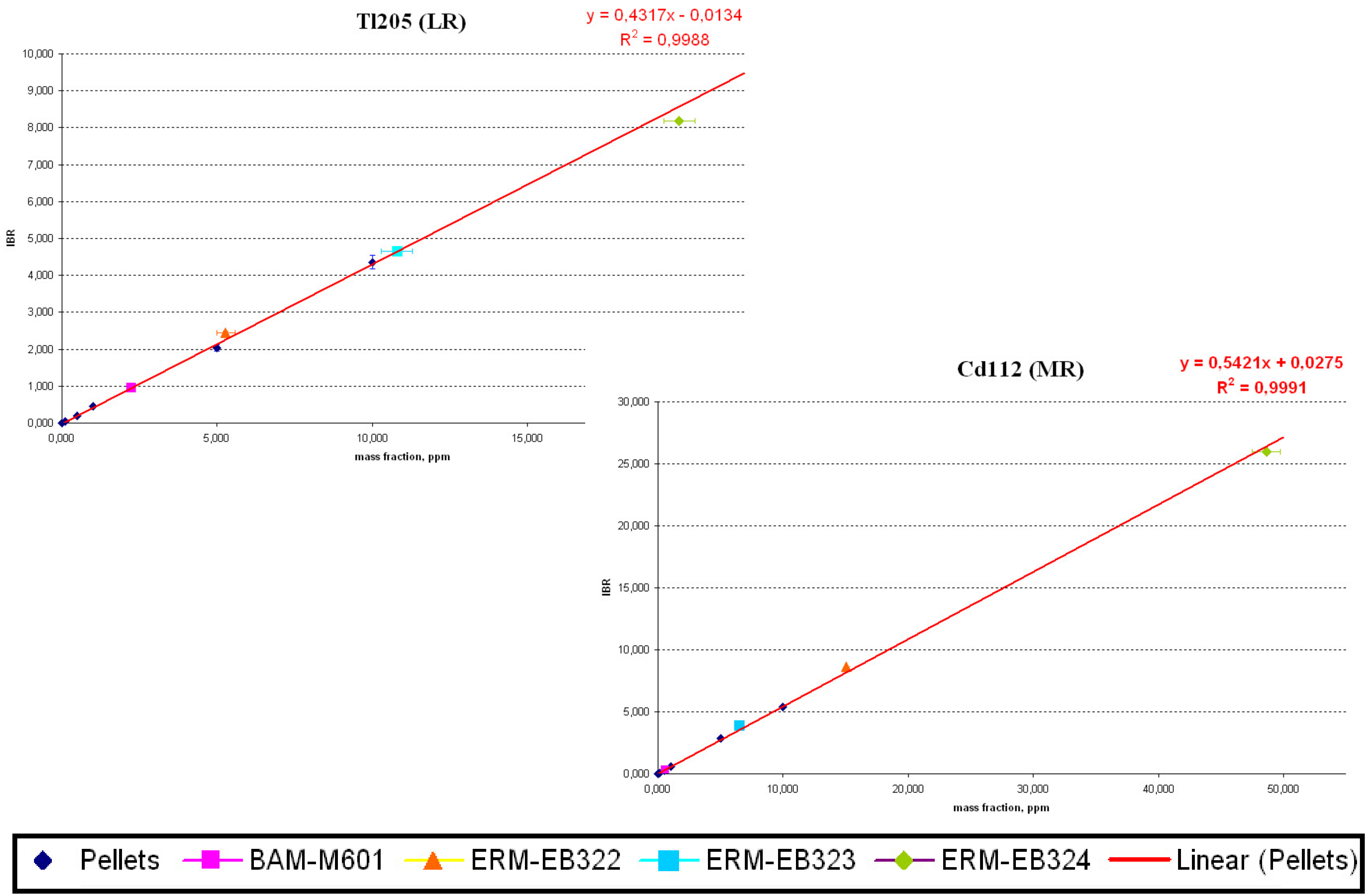


Zn Certified Reference Materials

Trace element mass fraction in mg/kg ± uncertainty mg/kg

	BAM-M601	ERM-EB322	ERM-EB323	ERM-EB324
Cd	**0.55** ± 0.06	**15.08** ± 0.30	**6.51** ± 0.21	**48.6** ± 1.1
Fe	**2.20** ± 0.09	**19.1** ± 0.8	**11.3** ± 0.7	**58.5** ± 1.6
Cu	**1.89** ± 0.11	**5.89** ± 0.15	**18.9** ± 0.4	**9.87** ± 0.18
Tl	**2.25** ± 0.09	**5.28** ± 0.30	**10.8** ± 0.5	**19.9** ± 0.5
Pb	**15.7** ± 0.03	**15.0** ± 0.5	**48.6** ± 0.9	**26.1** ± 0.5

CRMs measurements



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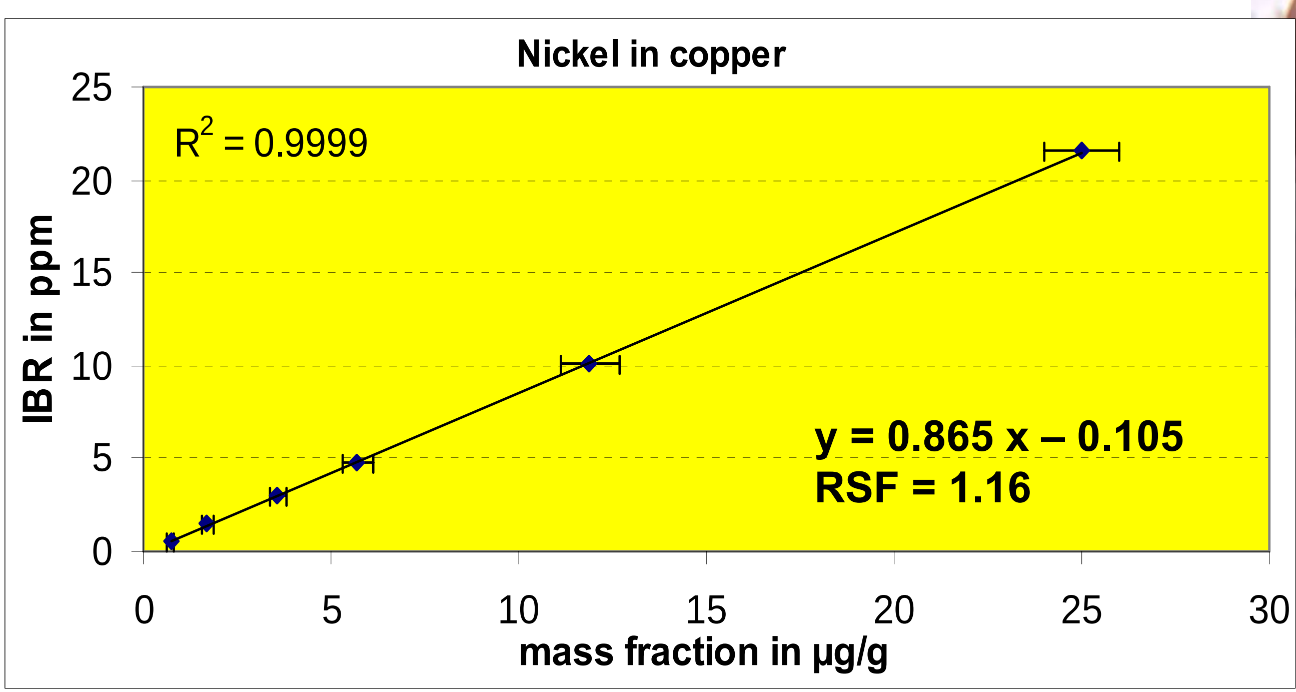
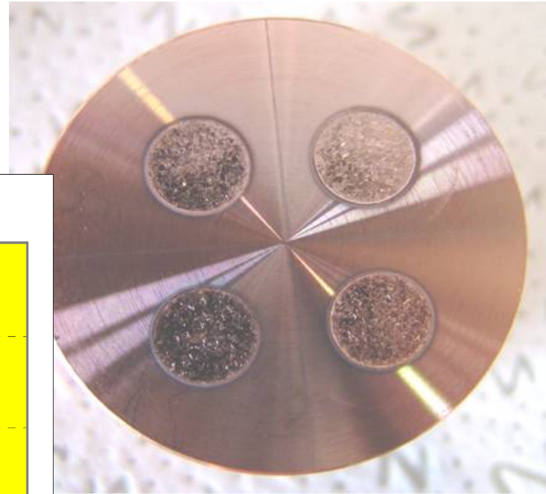
Quantification by Calibration with CRM

Pure copper calibration set BAM-M381 - 386

Ni mass fraction from 0.73 µg/g to 25 µg/g

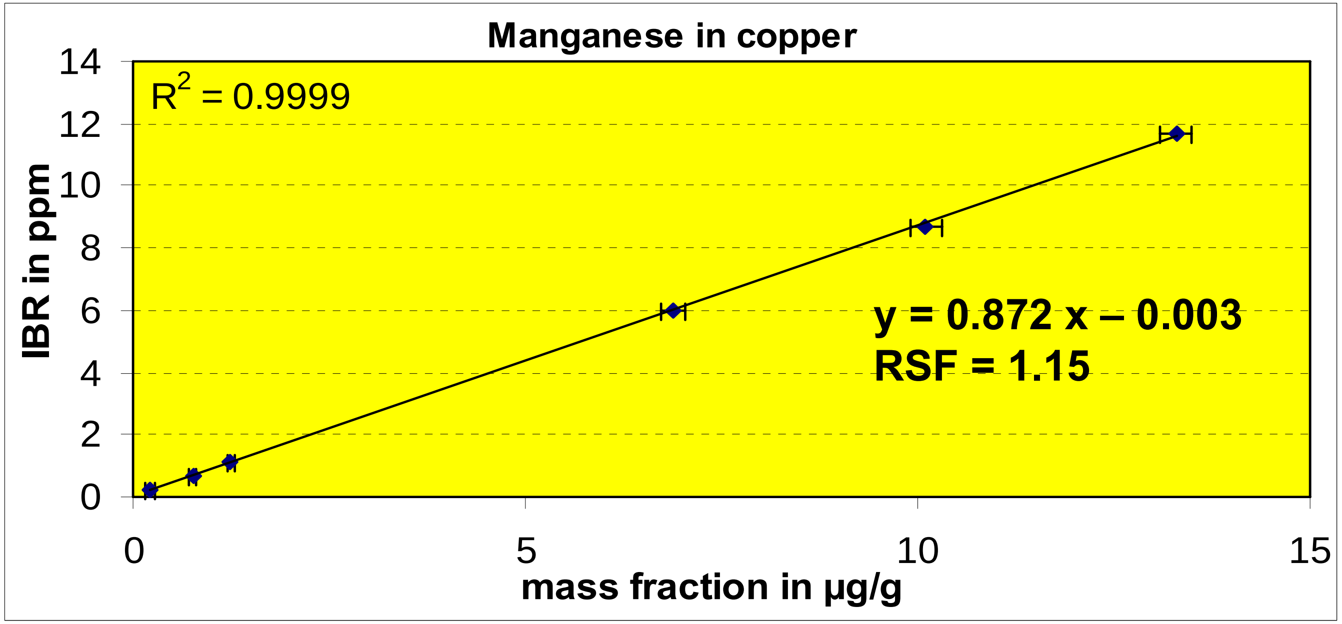




	certified [µg/g]	measured [µg/g]
BCR 074A	1.04 ± 0.11	0.96 ± 0.14
BCR 075A	1.45 ± 0.10	1.47 ± 0.05

Quantification by Calibration with CRM

Mn mass fraction from 0.22 µg/g bis 13.3 µg/g



	certified [µg/g]	measured [µg/g]
BCR 074A	1.27 ± 0.05	1.17 ± 0.04
BCR 075A	3.23 ± 0.19	3.23 ± 0.29

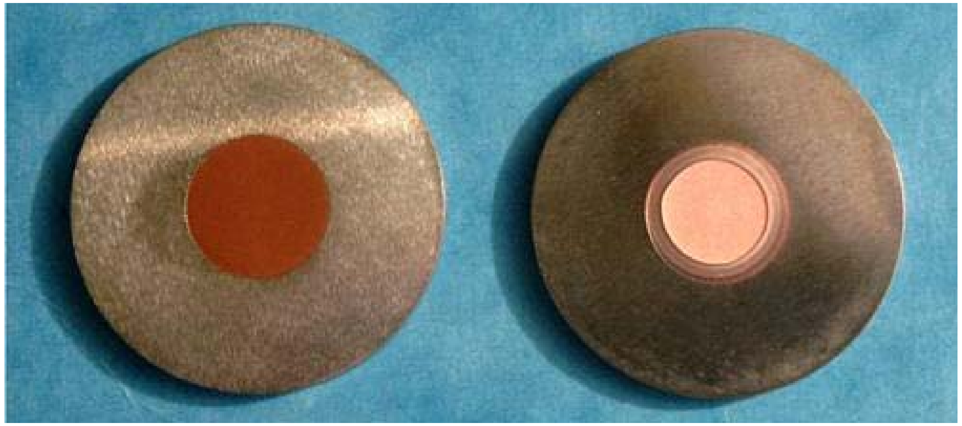
Quantification by Calibration with CRM

<u>drawbacks:</u>

- Indirectly traceable to SI (via measurement)
- only a few matrices availible especially for alloys
- often not availible in the necessary mass fraction range, especially mass fractions below 1 ppm are not accurately certified

→ **Use of doped and pressed powder samples**

- **doped with powders**
- **doped with solutions**

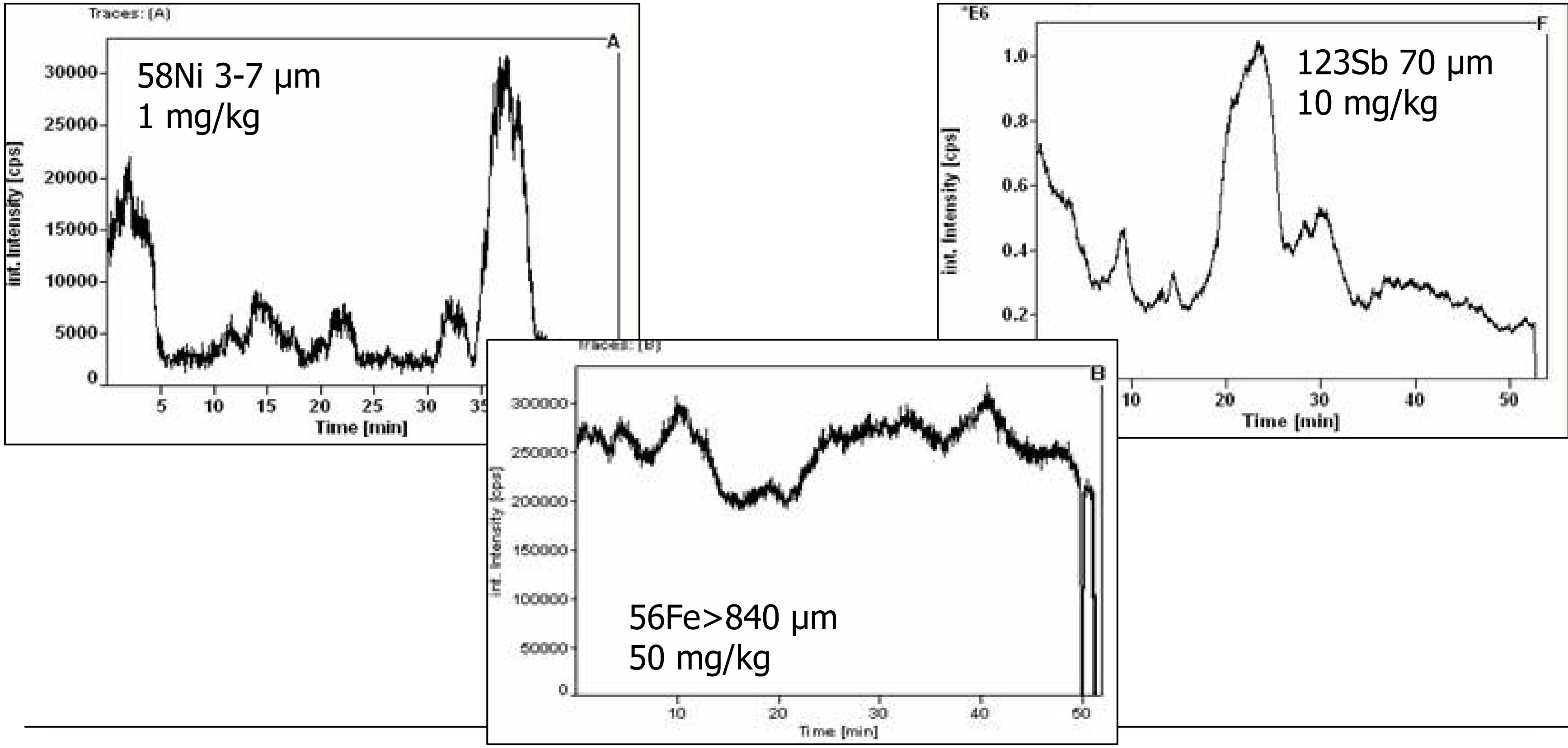


Quantification by Calibration with doped pellets

Homogeneity

Observation of intensity-time behaviour of different elements

Doped with powders: grain size between 3 and 900 micrometer



Mass fractions of analytes in the pressed copper and iron pellet samples doped with solutions:

Samples of series A :

0 – 10 – 50 – 100 – 1000 – 10 000 µg/kg (ppb): Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Fe, Ga, In, K, Li, Mg, Mn, Na, Ni, Pb, Sr, Tl, Zn

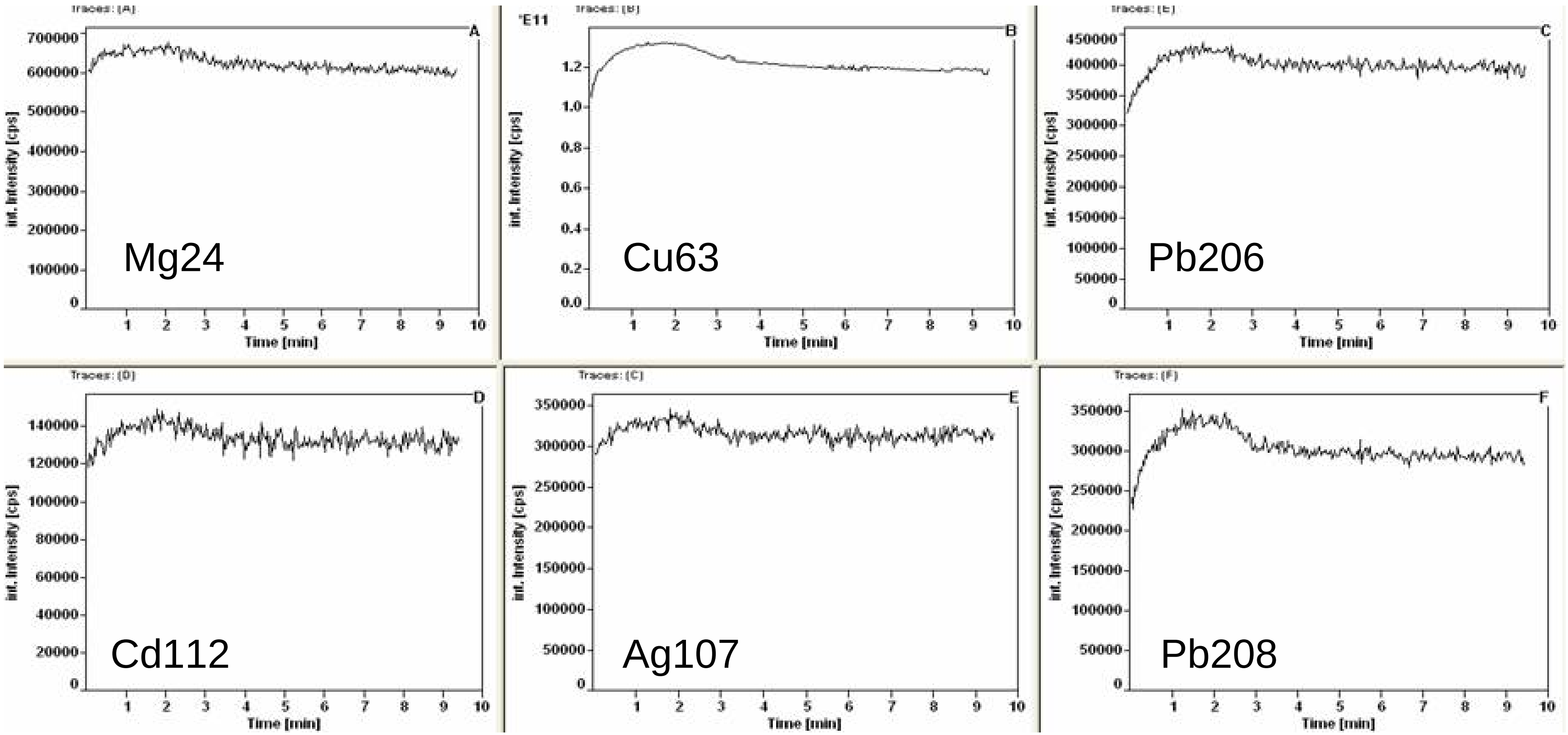
0 – 1 – 5 – 10 – 50 – 100 – 1000 µg/kg (ppb): Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Th, Tm, Y, Yb

Samples of series B :

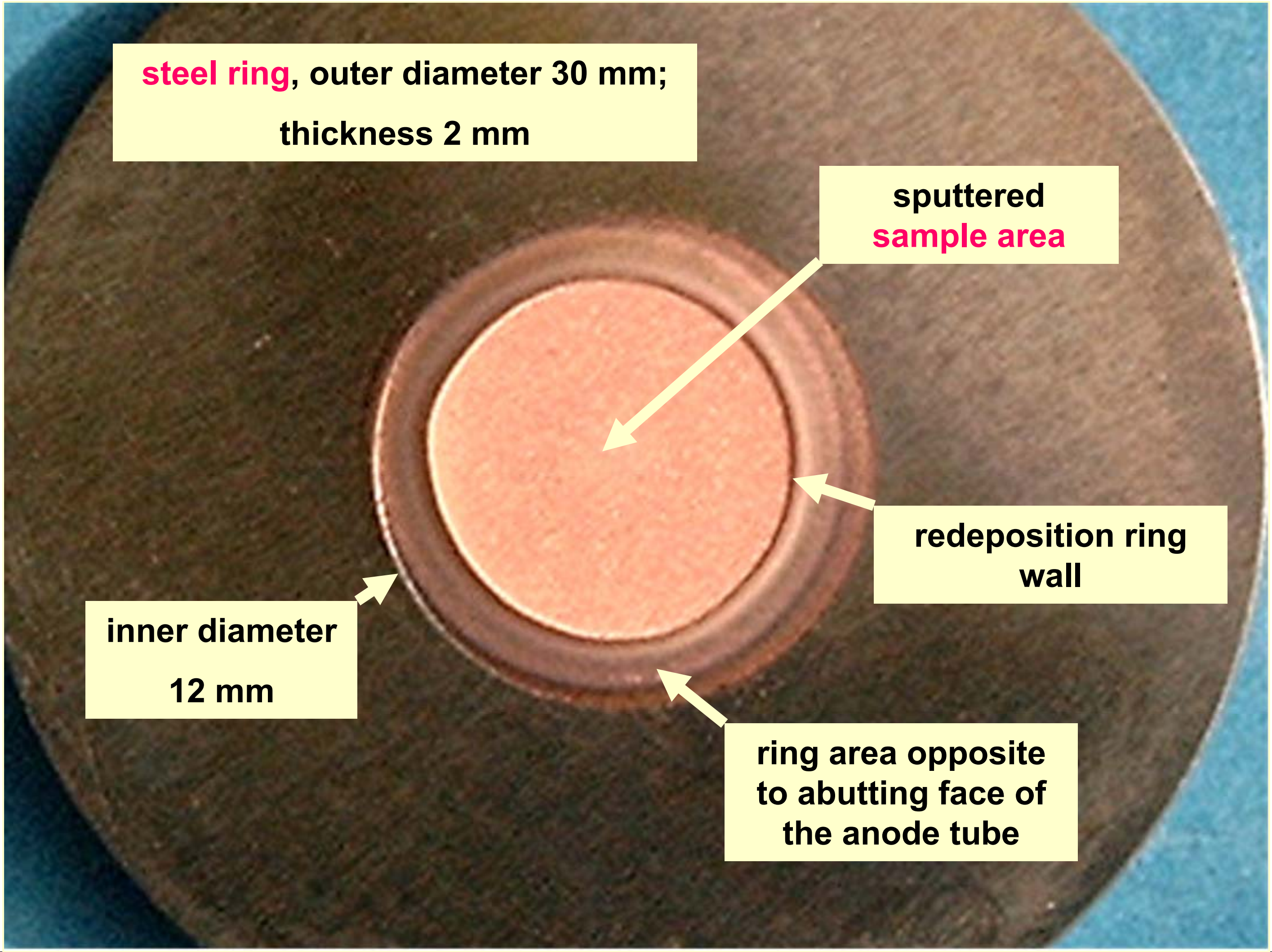
0 – 10 – 100 – 1000 µg/kg (ppb): As, Au, Hf, Ir, Mo, Nb, Os, Pd, Pt, Rh, Ru, Sb, Se, Sn, Ta, Te, Ti, V,

Quantification by Calibration with doped pellets

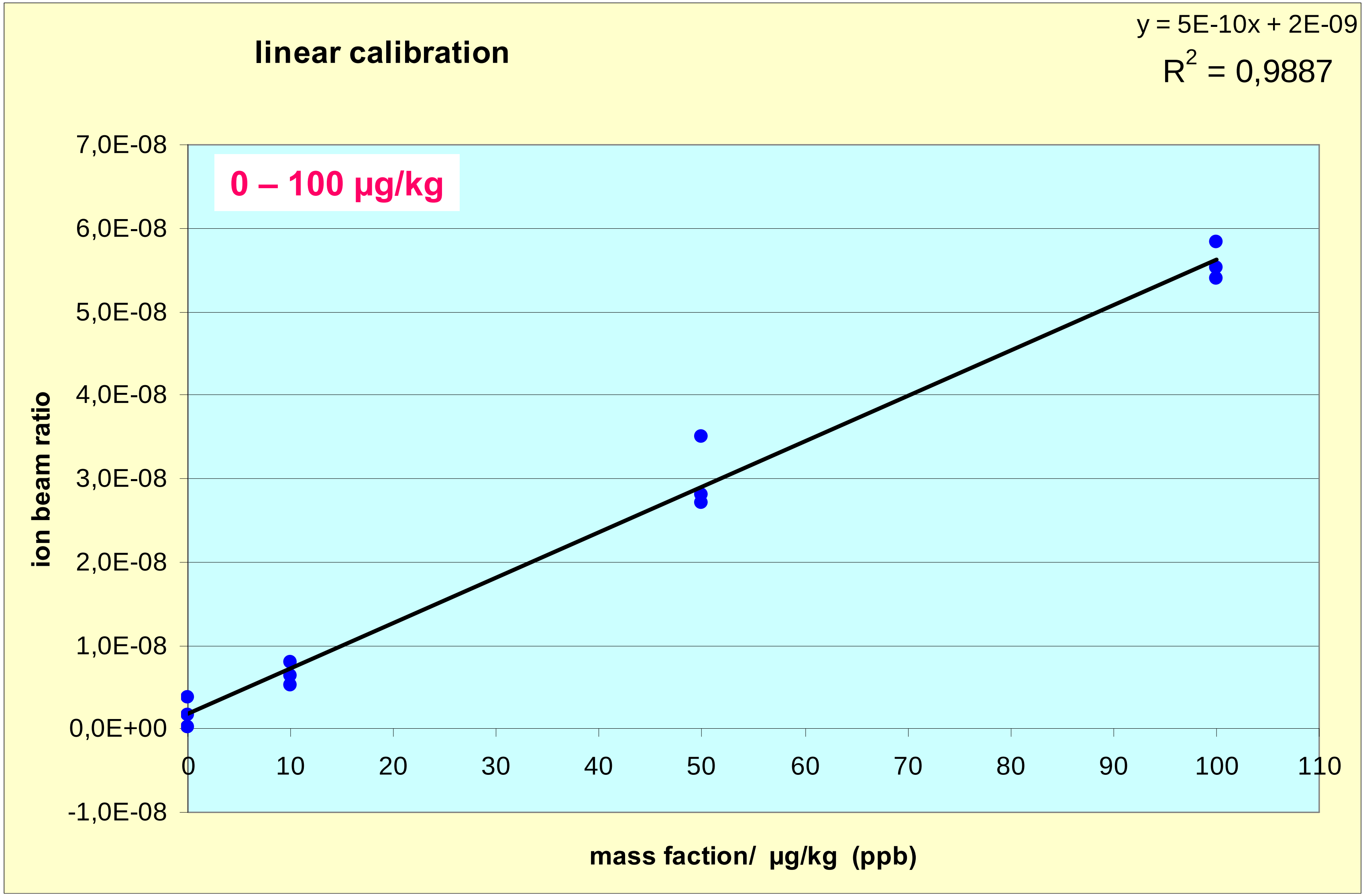
Doped with solutions: standard solutions in diluted HNO_3



Copper matrix: Pressed multielement copper sample after GD analysis



Calibration Function of ^{205}Tl in Copper Matrix



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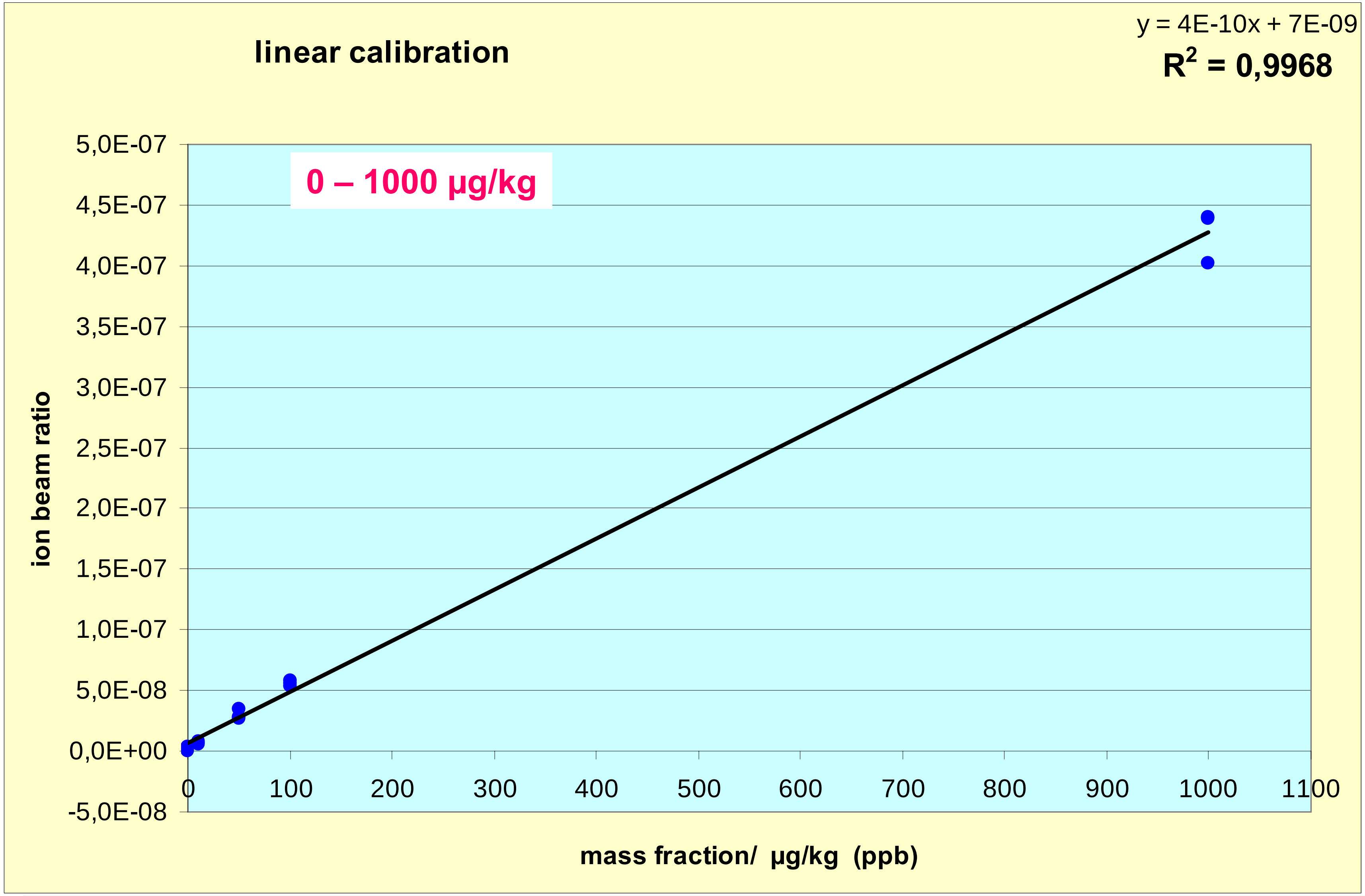

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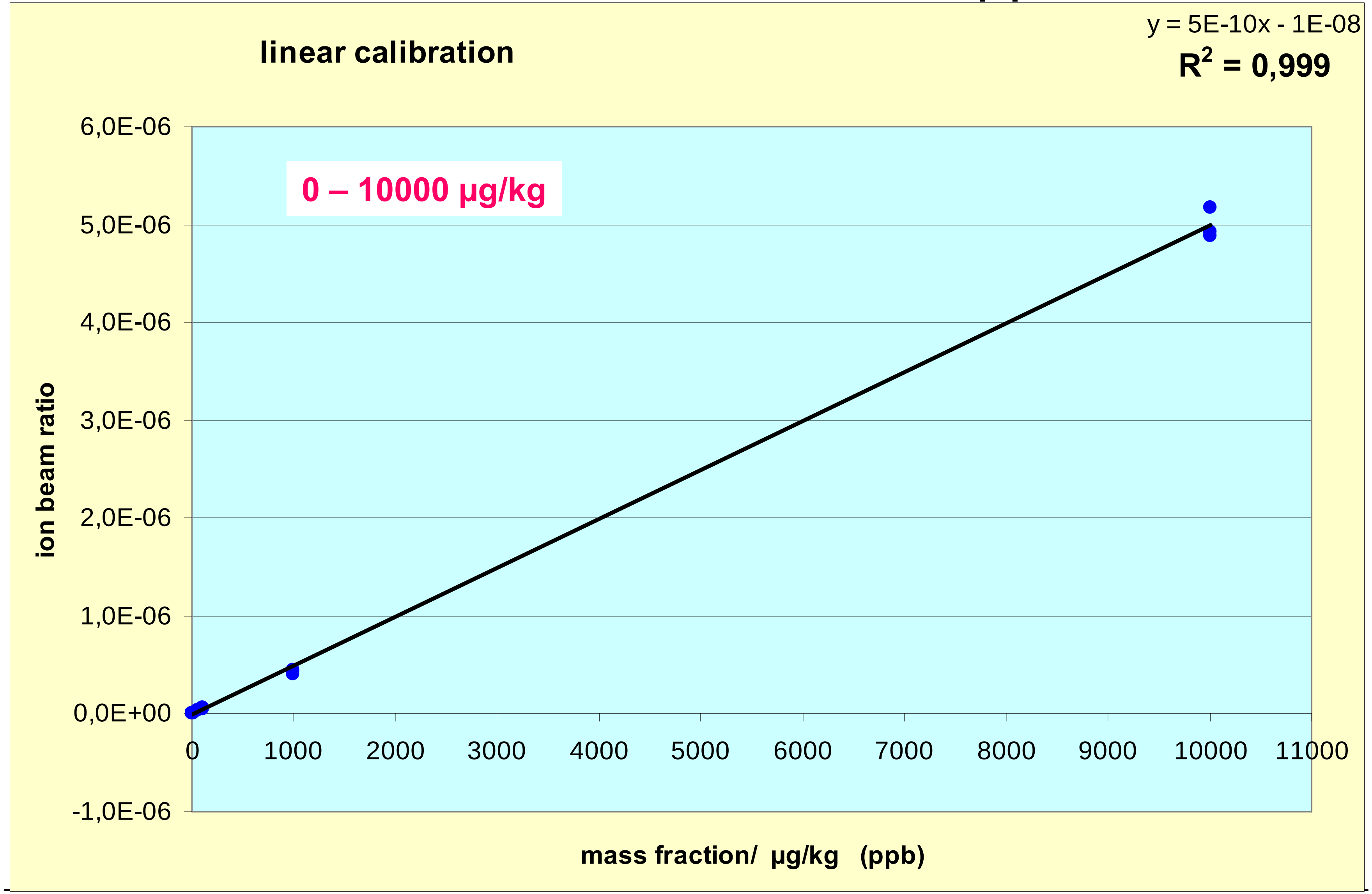
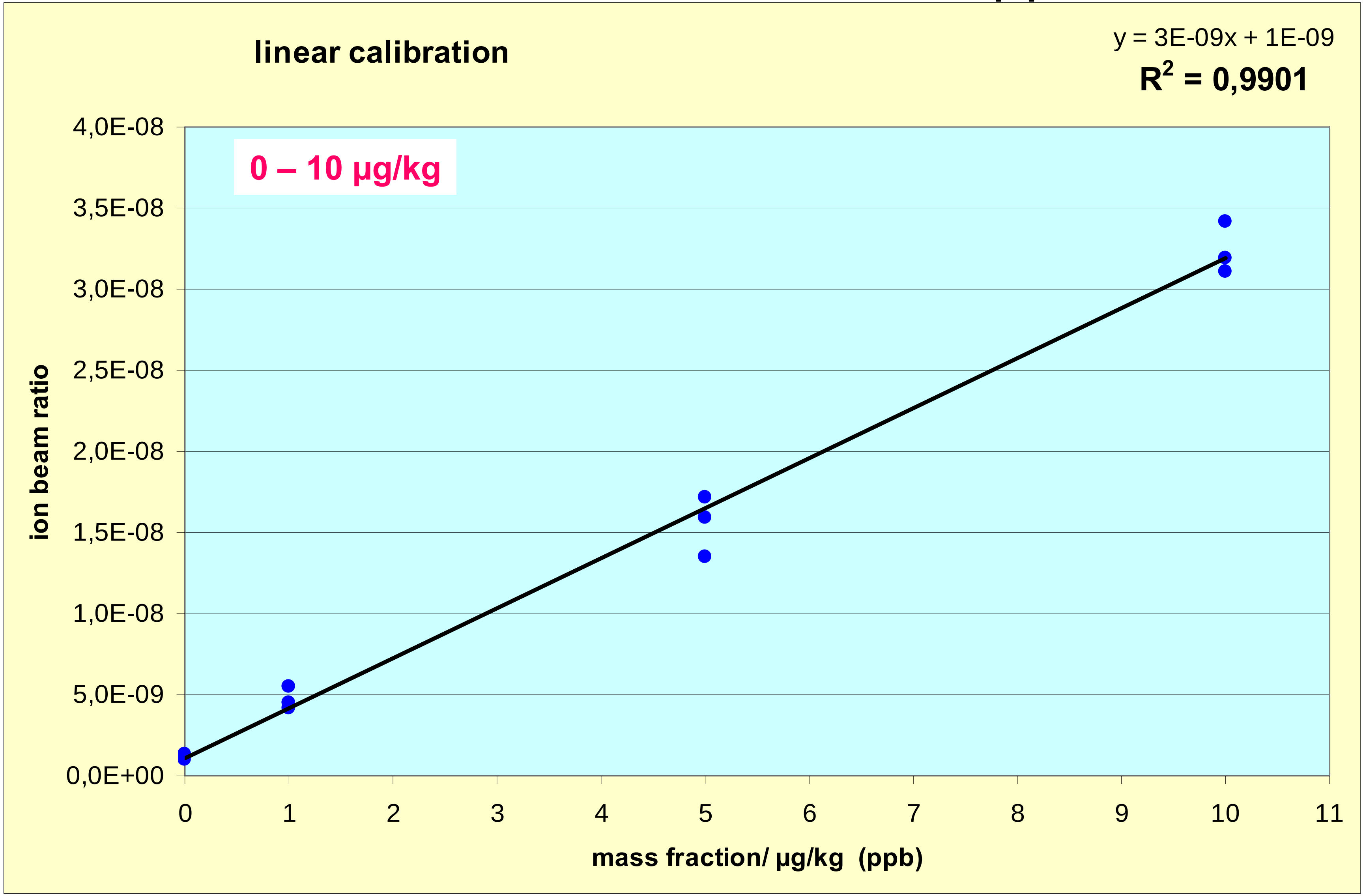
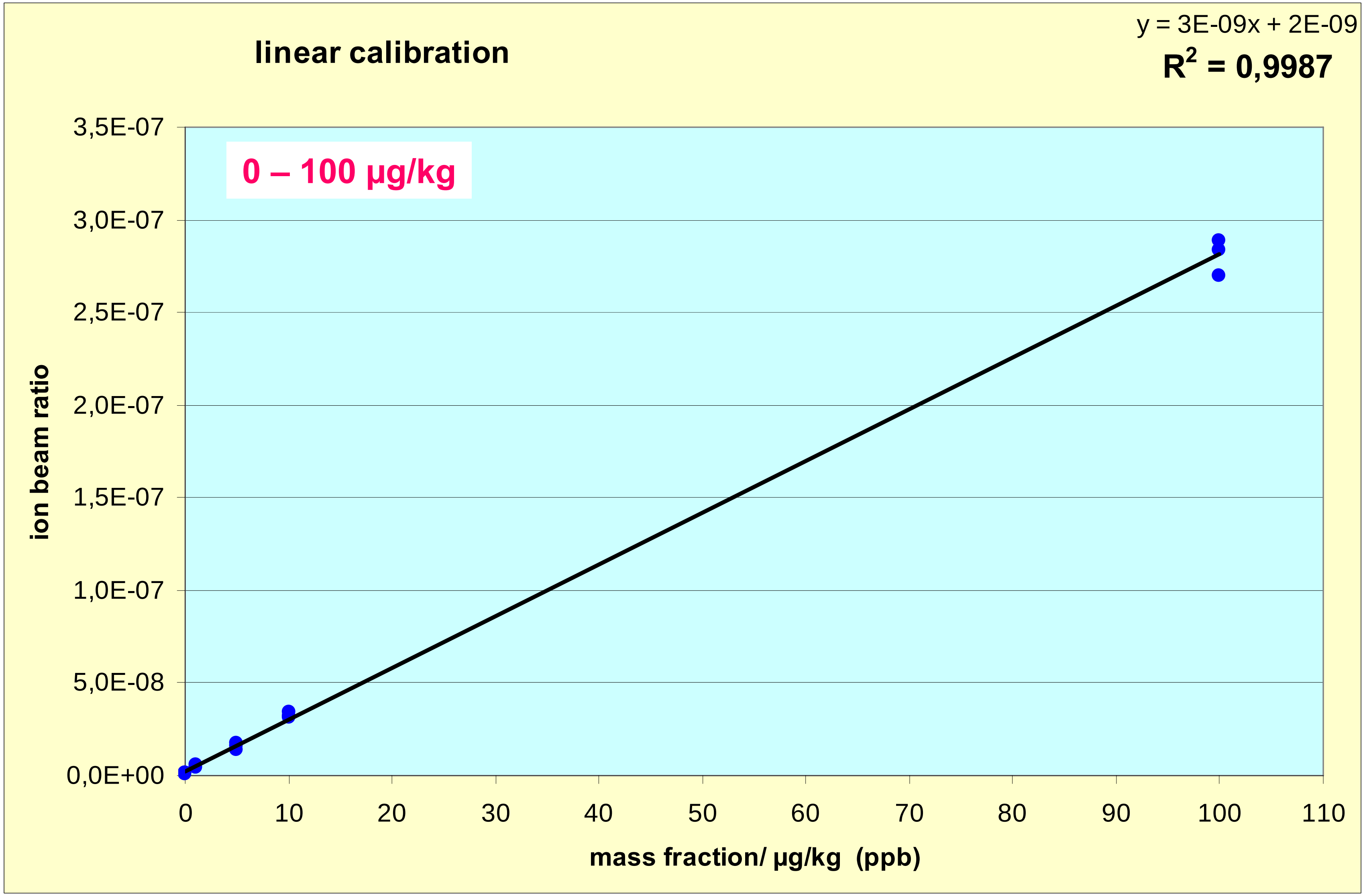


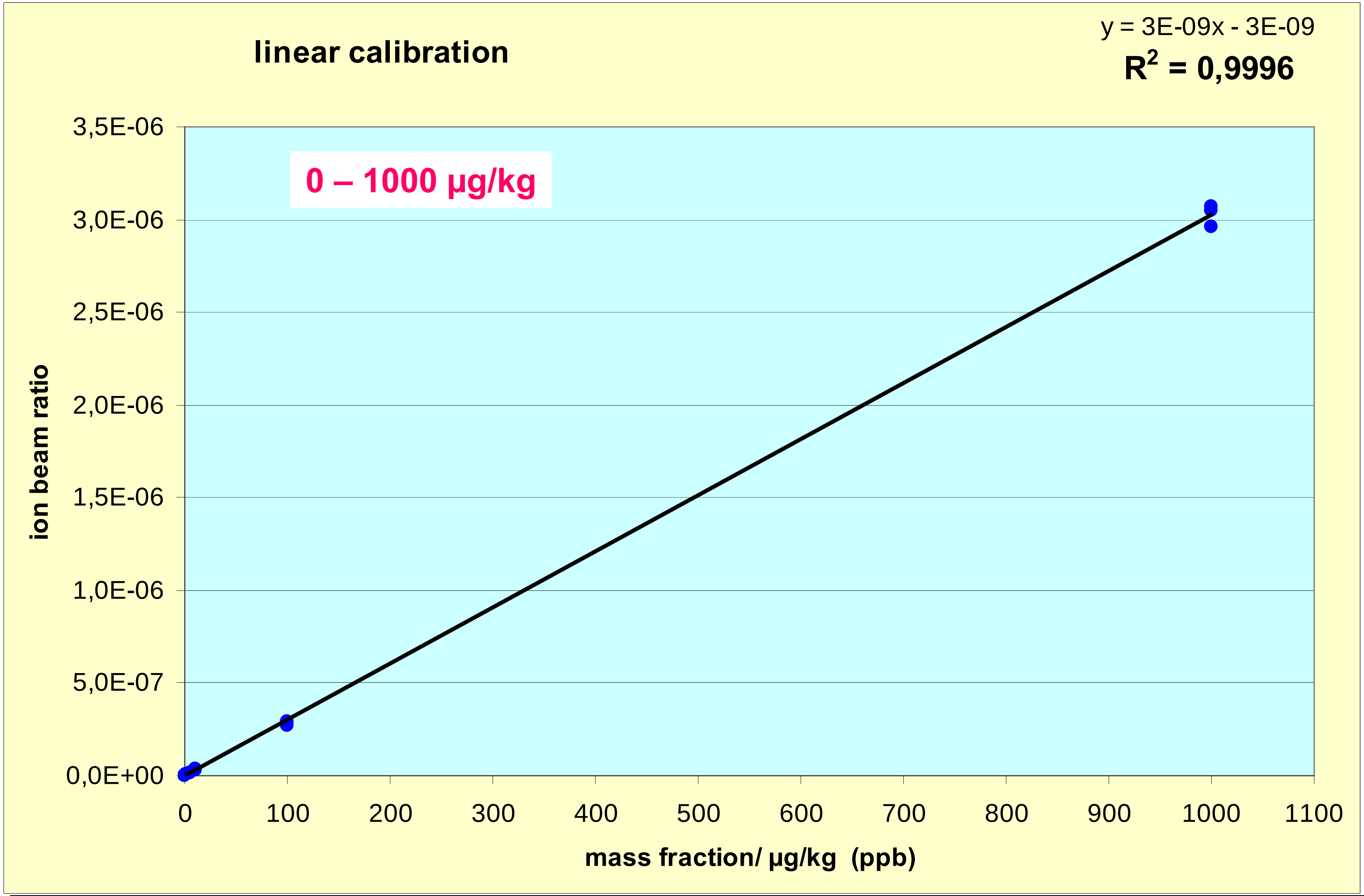
Calibration Function of ^{45}Sc in Copper Matrix



Calibration Function of ^{45}Sc in Copper Matrix

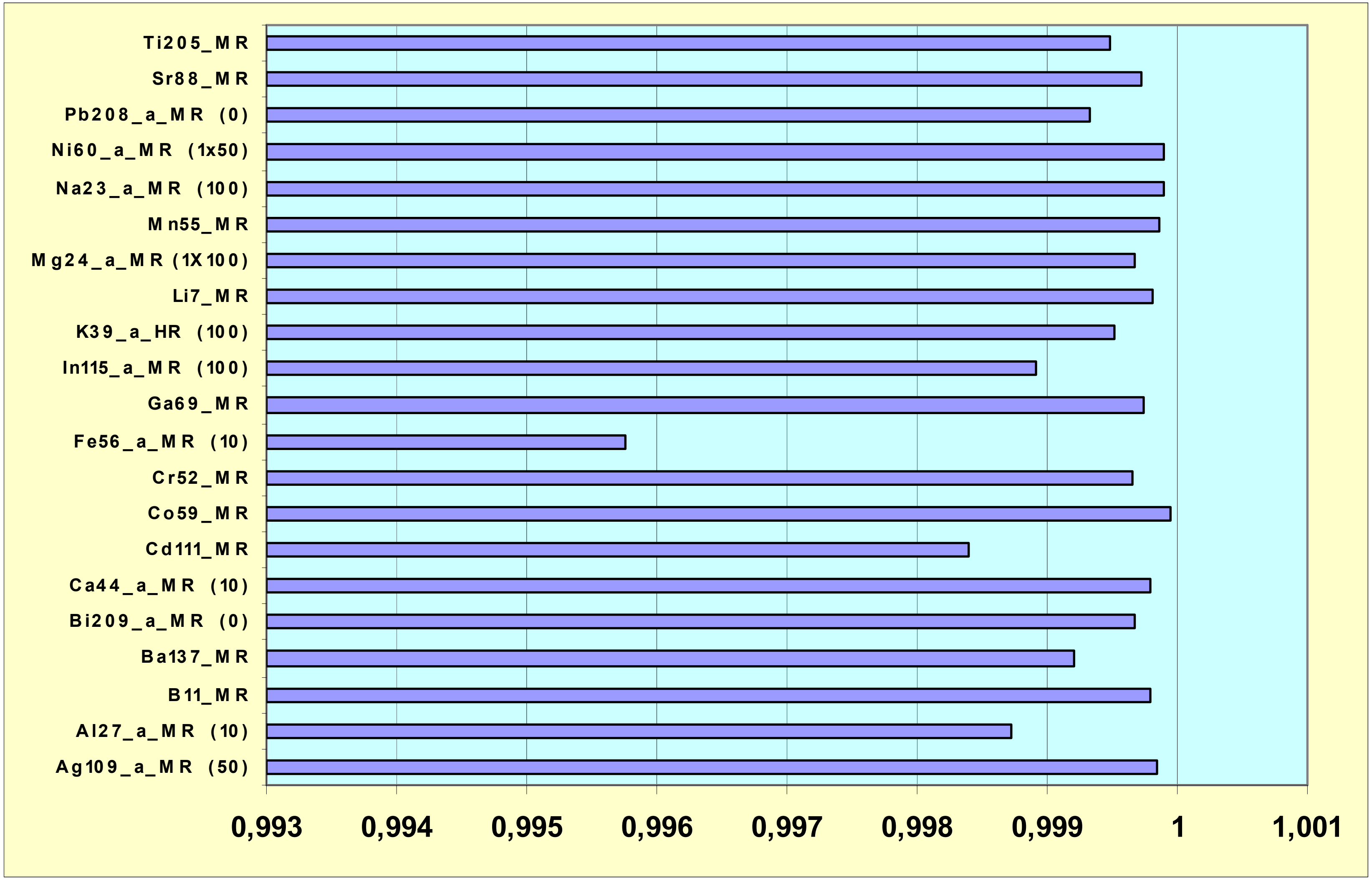


Calibration Function of ^{45}Sc in Copper Matrix



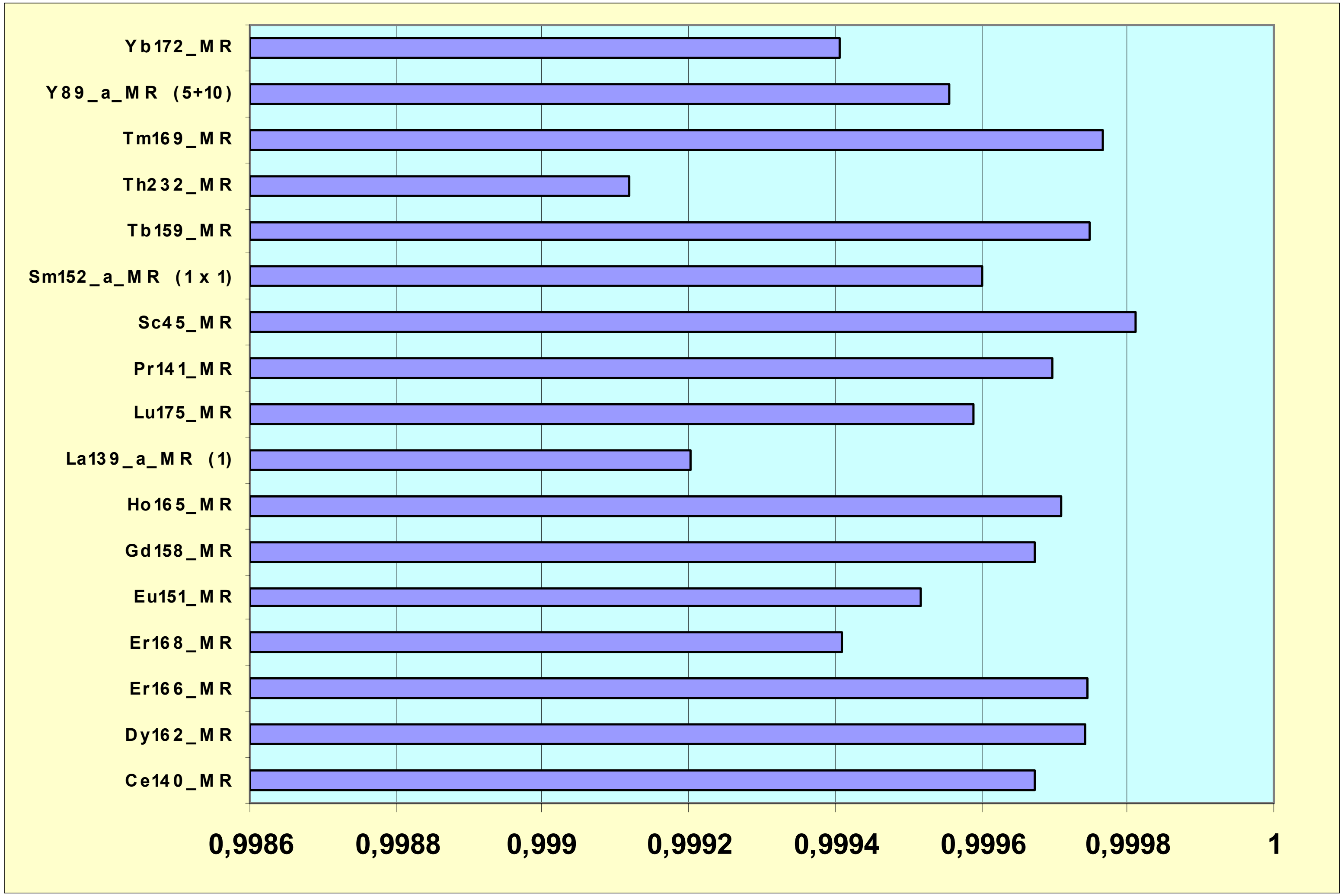
Linear correlation coefficients of calibration curves

Matrix: Copper, 0 – 10 mg/kg (ppm)



Linear correlation coefficients of calibration curves

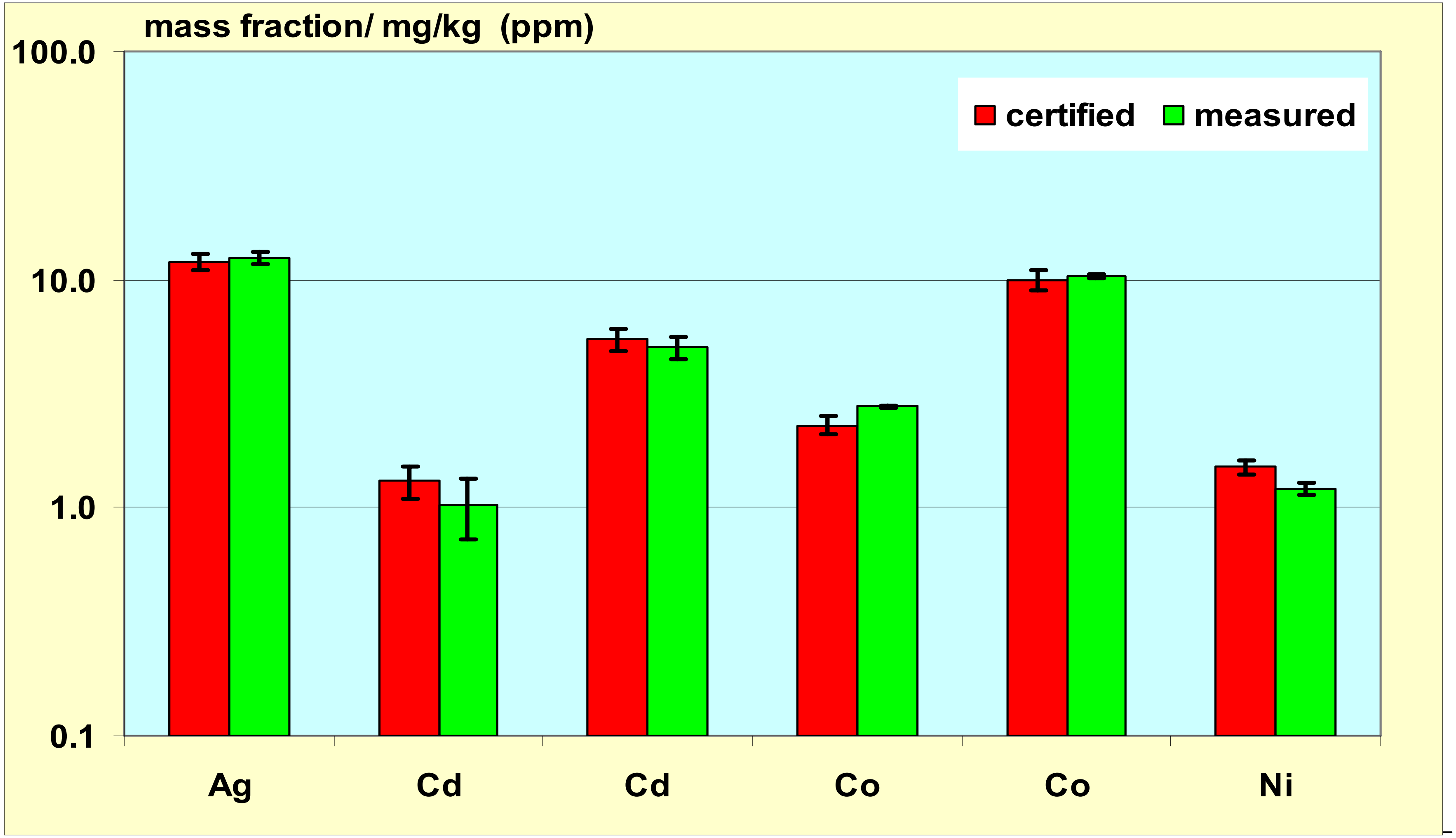
Matrix: Copper, 0 – 1000 µg/kg (ppb)



Comparison of certified and measured values

Matrix: Copper, FNE*) CRMs Cu II/6, Cu II/8, Cu I/X

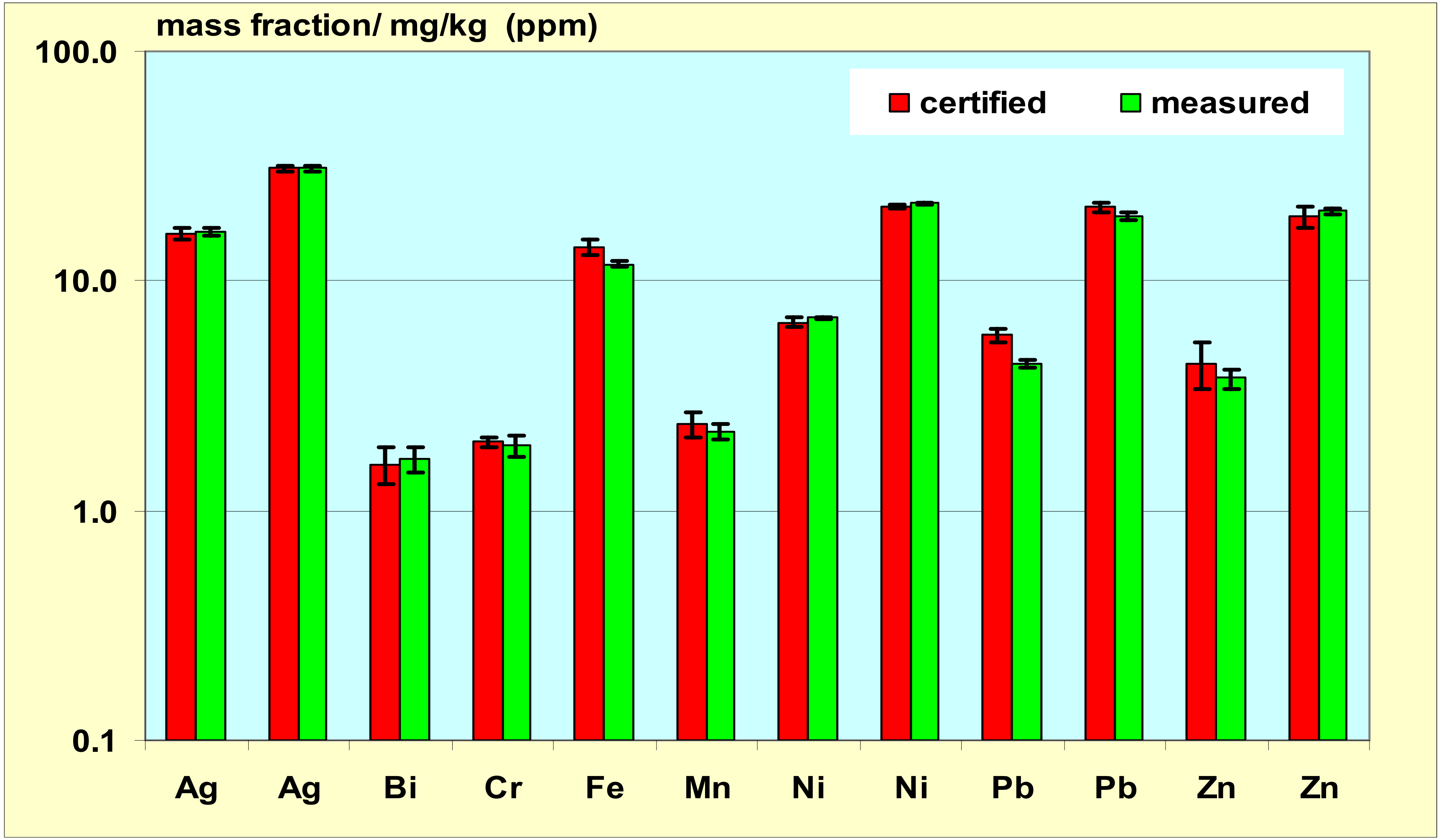
***) Research Institute for Nonferrous Metals, Mansfeld, Germany**



Comparison of certified and measured values

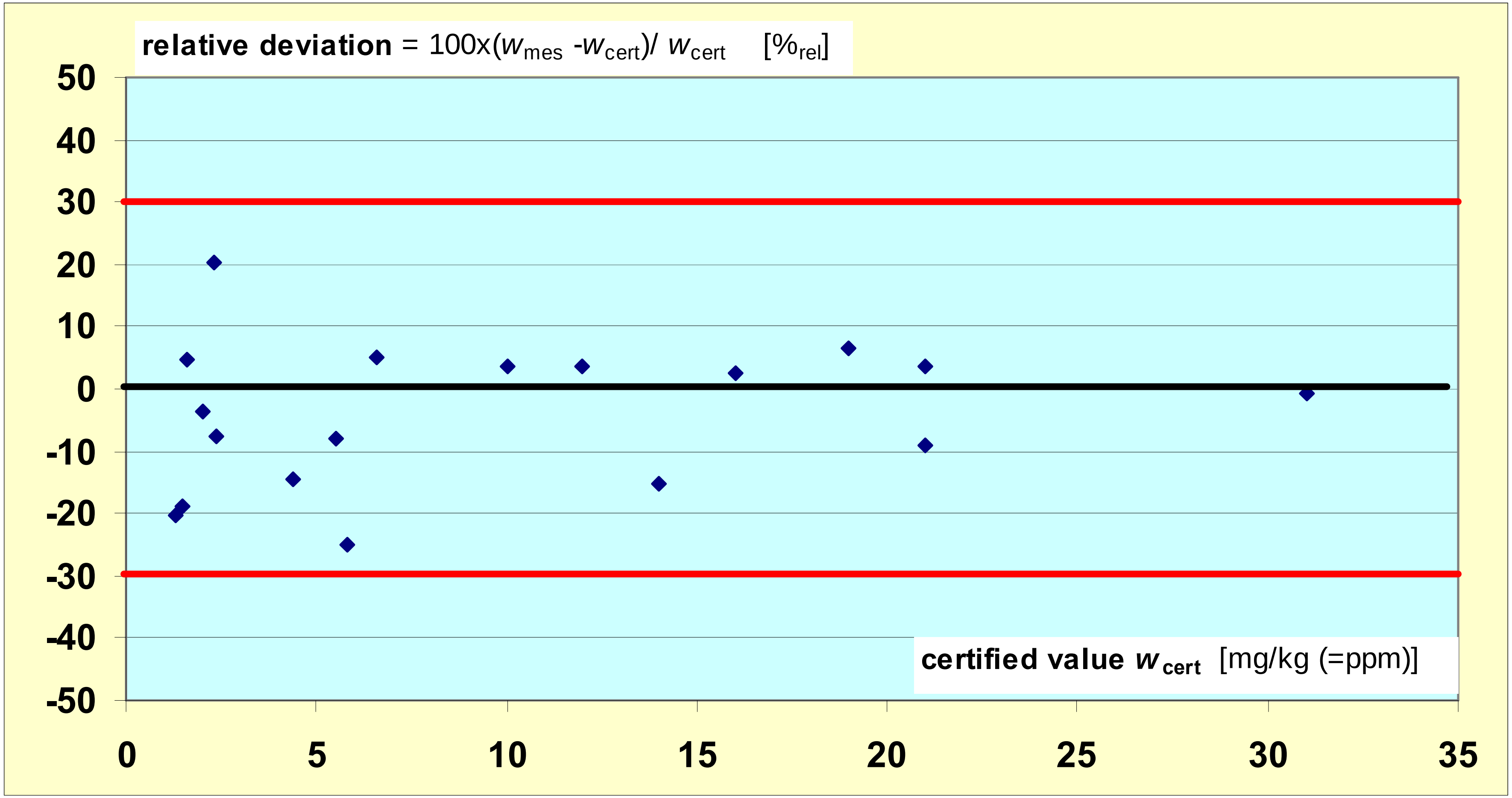
Matrix: Copper, FNE*) CRMs CuI/VI, Cu I/VIII

*) Research Institute for Nonferrous Metals, Mansfeld, Germany

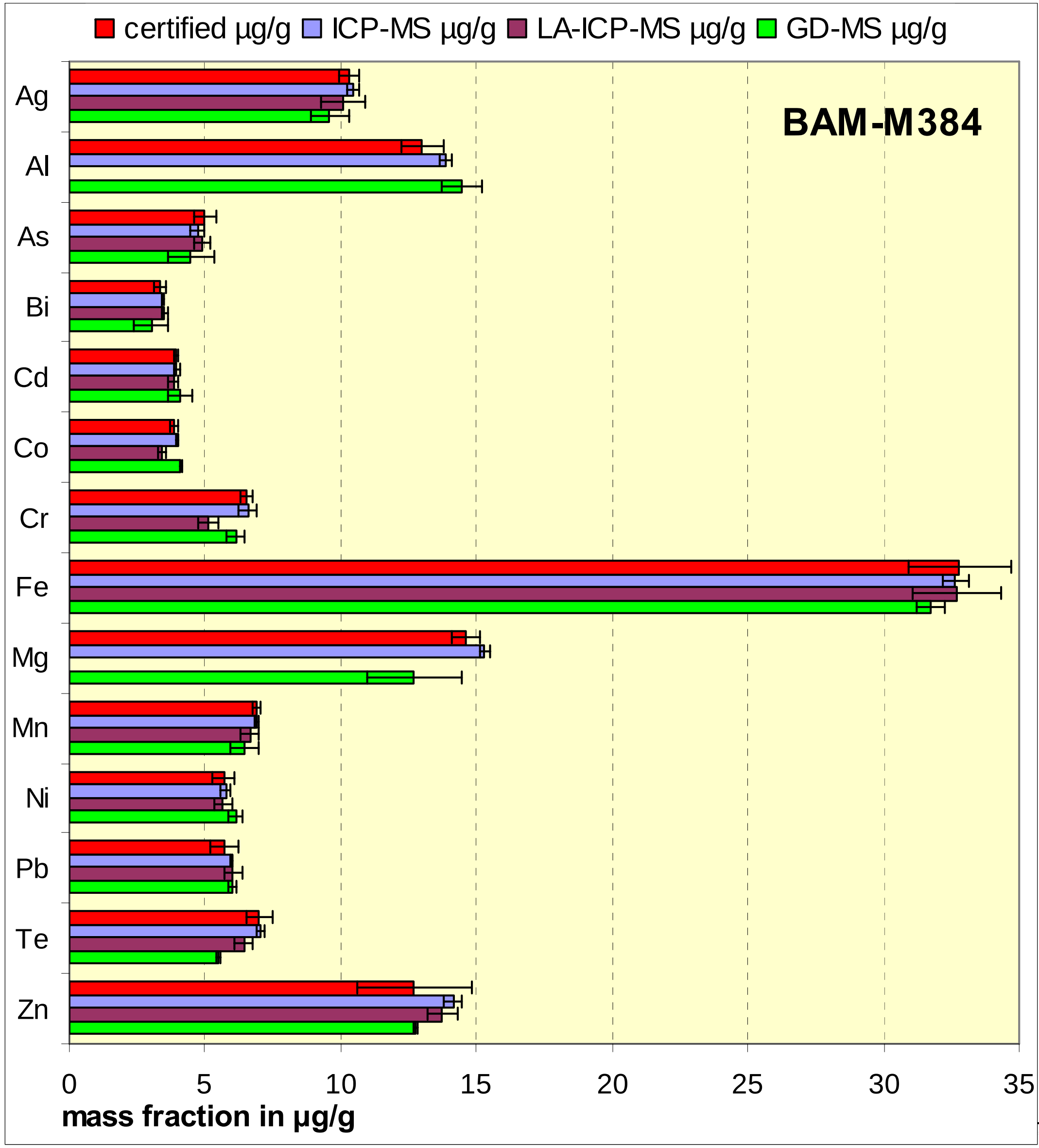


Comparison of certified and measured values

Matrix: Copper, all measurements of FNE samples

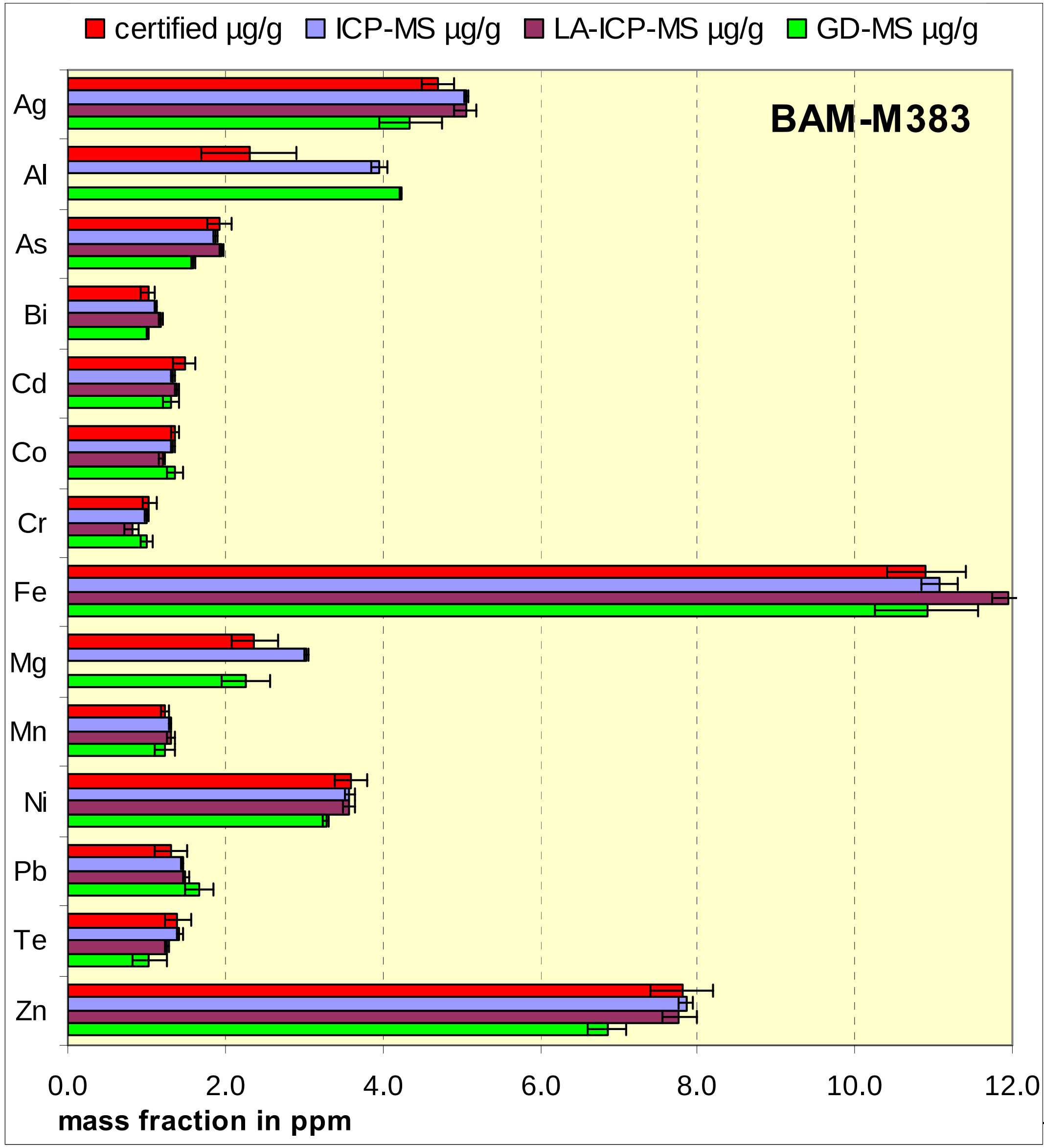


Quantification by Calibration with doped pellets using BAM CRMs as analytical samples



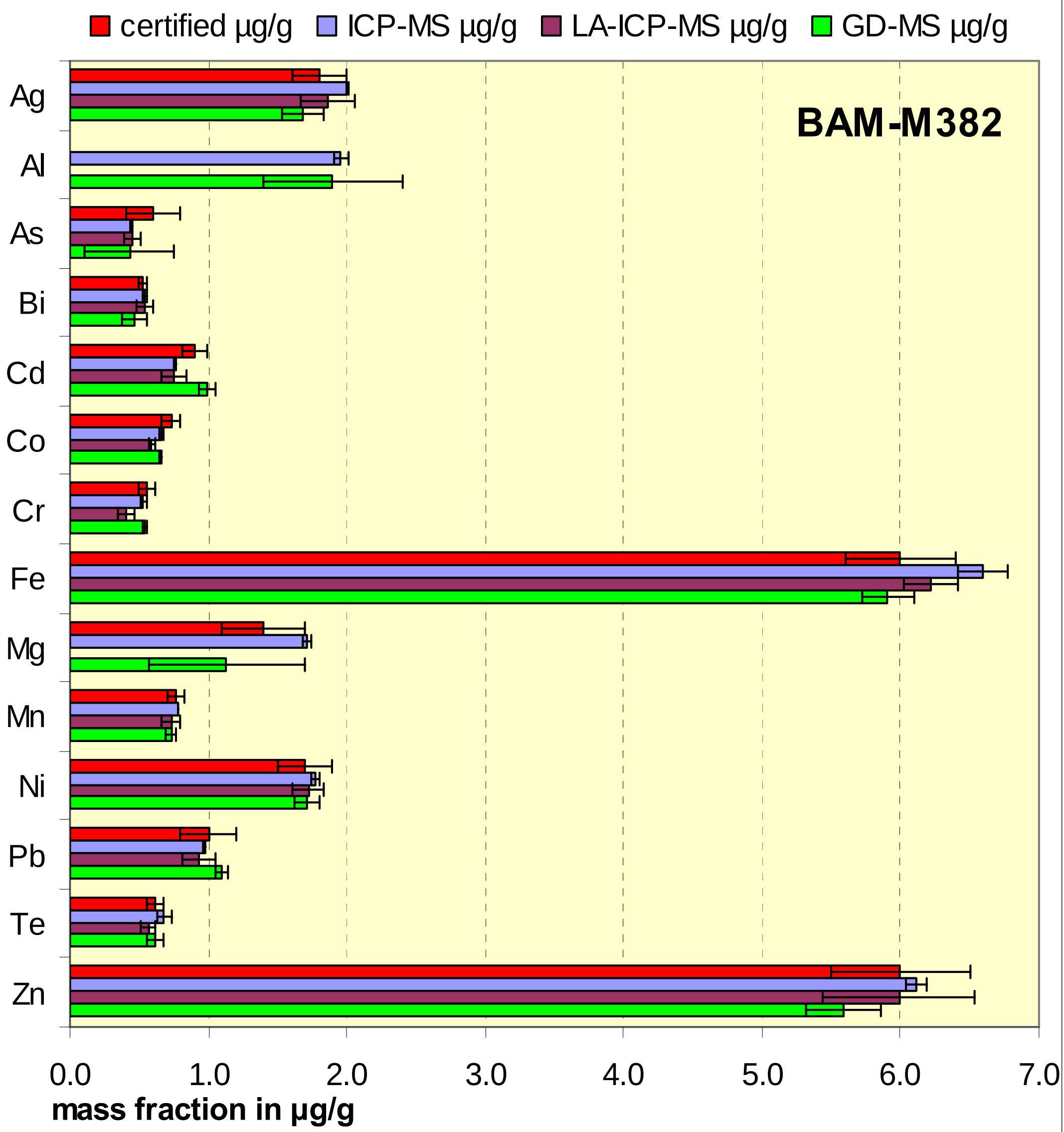
	certified µg/g	ICP-MS µg/g	LA-ICP-MS µg/g	GD-MS µg/g
Ag	10.3	10.44	10.10	9.59
Al	13	13.88		14.48
As	5	4.74	4.90	4.46
Bi	3.34	3.43	3.52	3.03
Cd	3.95	3.95	3.84	4.06
Co	3.88	3.97	3.39	4.09
Cr	6.53	6.58	5.13	6.12
Fe	32.8	32.66	32.70	31.73
Mg	14.6	15.29		12.71
Mn	6.88	6.88	6.65	6.46
Ni	5.7	5.75	5.66	6.14
Pb	5.7	5.98	6.02	6.01
Te	7	7.02	6.43	5.50
Zn	[12.7]	14.13	13.75	12.75

Quantification by Calibration with doped pellets



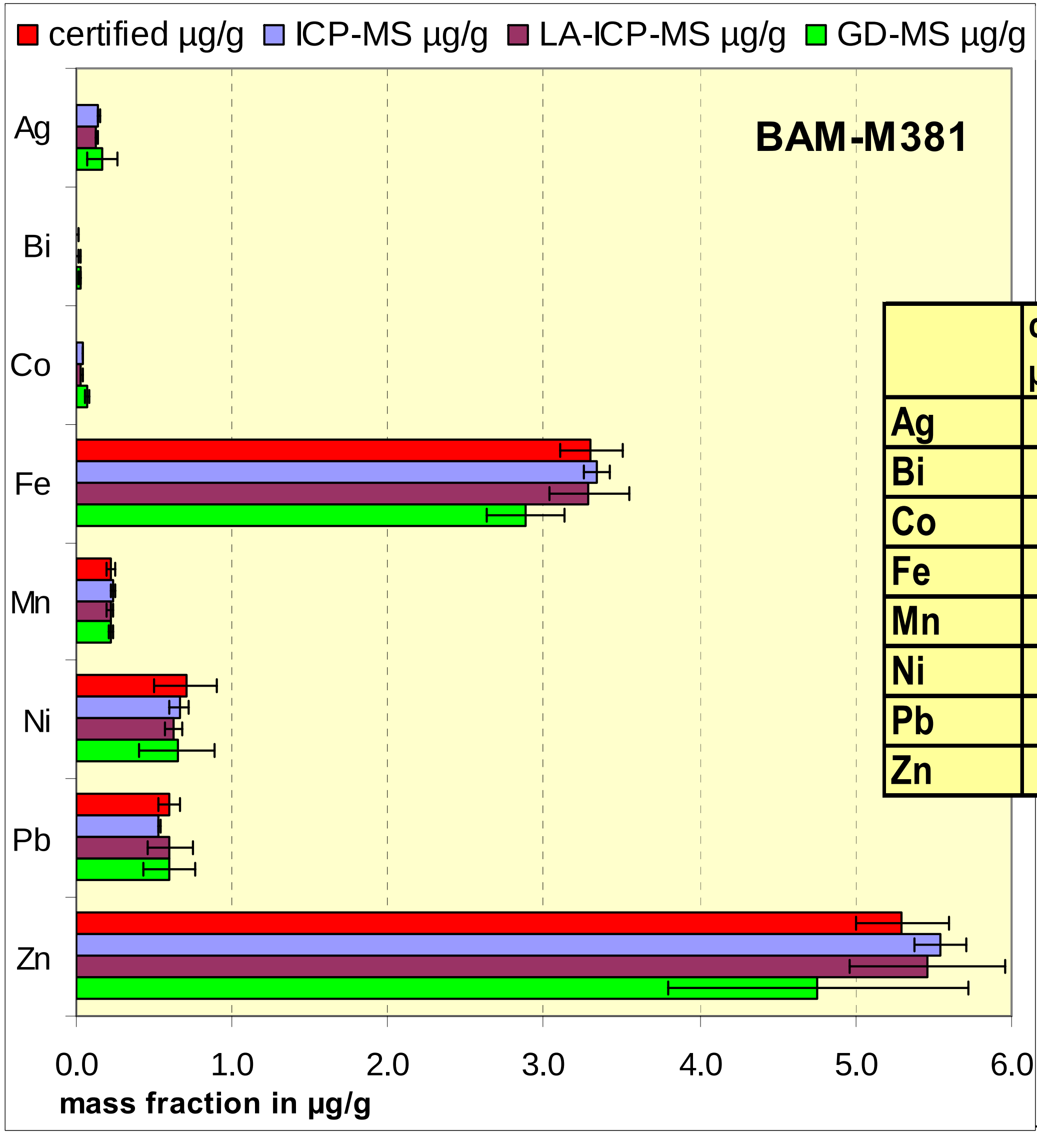
	certified µg/g	ICP-MS µg/g	LA-ICP-MS µg/g	GD-MS µg/g
Ag	4.7	5.07	5.05	4.35
Al	[2.3]	3.95		4.23
As	1.93	1.88	1.95	1.60
Bi	1.02	1.11	1.19	1.01
Cd	1.48	1.33	1.39	1.31
Co	1.37	1.34	1.20	1.36
Cr	1.03	1.00	0.81	1.00
Fe	10.9	11.07	11.96	10.91
Mg	2.37	3.03		2.27
Mn	1.24	1.30	1.31	1.24
Ni	3.59	3.58	3.57	3.28
Pb	1.31	1.46	1.50	1.67
Te	1.4	1.42	1.26	1.04
Zn	[7.8]	7.86	7.77	6.85

Quantification by Calibration with doped pellets



	certified µg/g	ICP-MS µg/g	LA-ICP-MS µg/g	GD-MS µg/g
Ag	1.8	2.00	1.86	1.68
Al	< 2,5	1.96		1.90
As	[0.6]	0.44	0.45	0.43
Bi	0.53	0.54	0.54	0.47
Cd	0.9	0.76	0.75	0.99
Co	0.73	0.66	0.59	0.66
Cr	0.56	0.53	0.41	0.54
Fe	6	6.59	6.22	5.91
Mg	[1.4]	1.71		1.13
Mn	0.76	0.78	0.73	0.73
Ni	1.7	1.77	1.72	1.71
Pb	1	0.97	0.93	1.10
Te	0.61	0.68	0.57	0.62
Zn	6	6.11	5.99	5.59

Quantification by Calibration with doped pellets



	certified µg/g	ICP-MS µg/g	LA-ICP-MS µg/g	GD-MS µg/g
Ag	< 1	0.14	0.13	0.16
Bi	< 0.3	0.02	0.02	0.02
Co	< 0,4	0.04	0.03	0.06
Fe	3.3	3.34	3.29	2.88
Mn	0.22	0.23	0.22	0.22
Ni	0.7	0.66	0.62	0.64
Pb	0.59	0.53	0.60	0.60
Zn	5.3	5.54	5.46	4.76

Content

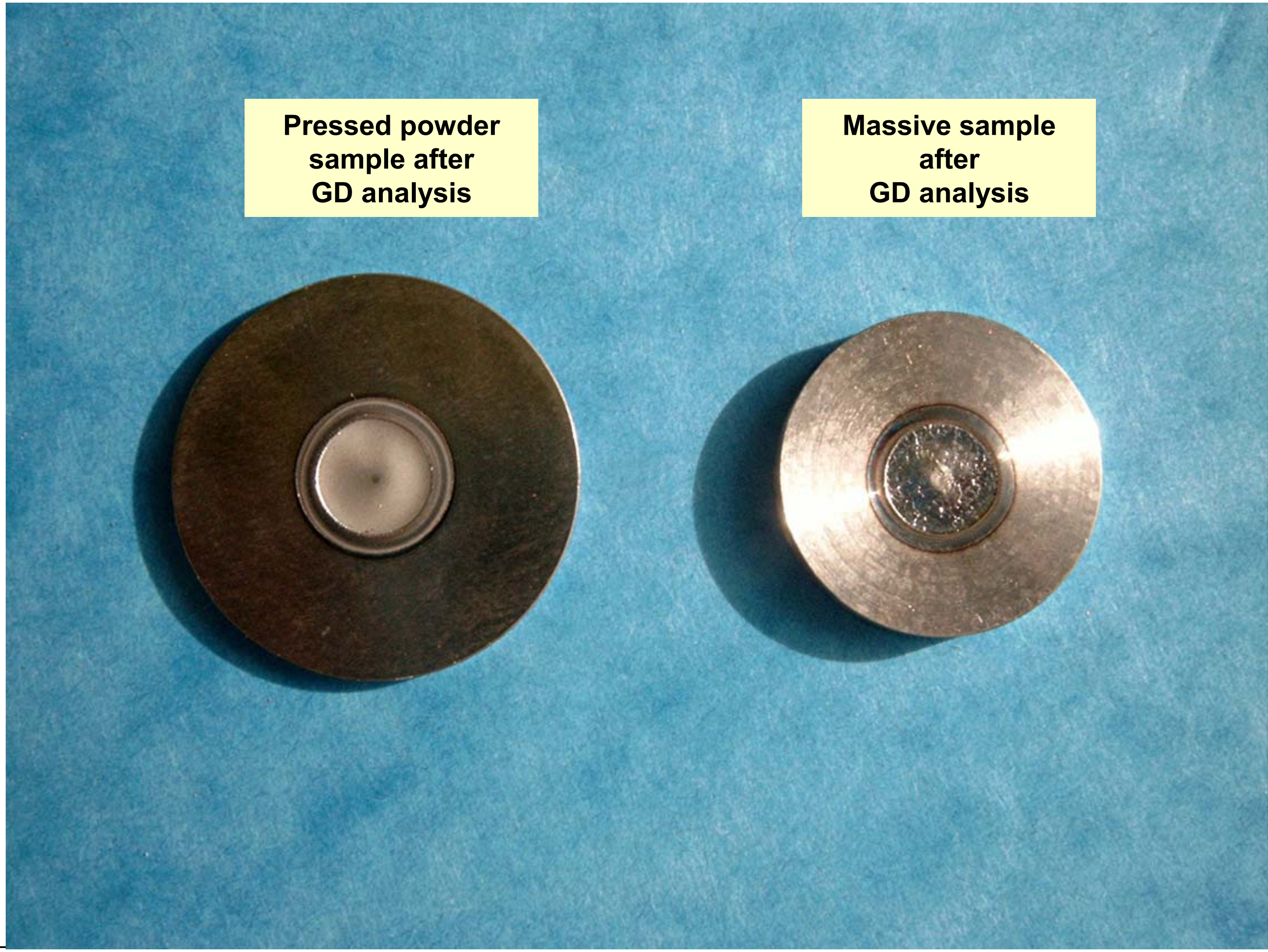
- Why Primary Pure Standards?

- BAM System of Primary National Standards
  - Way of certification, some results
  - Need for GD-MS

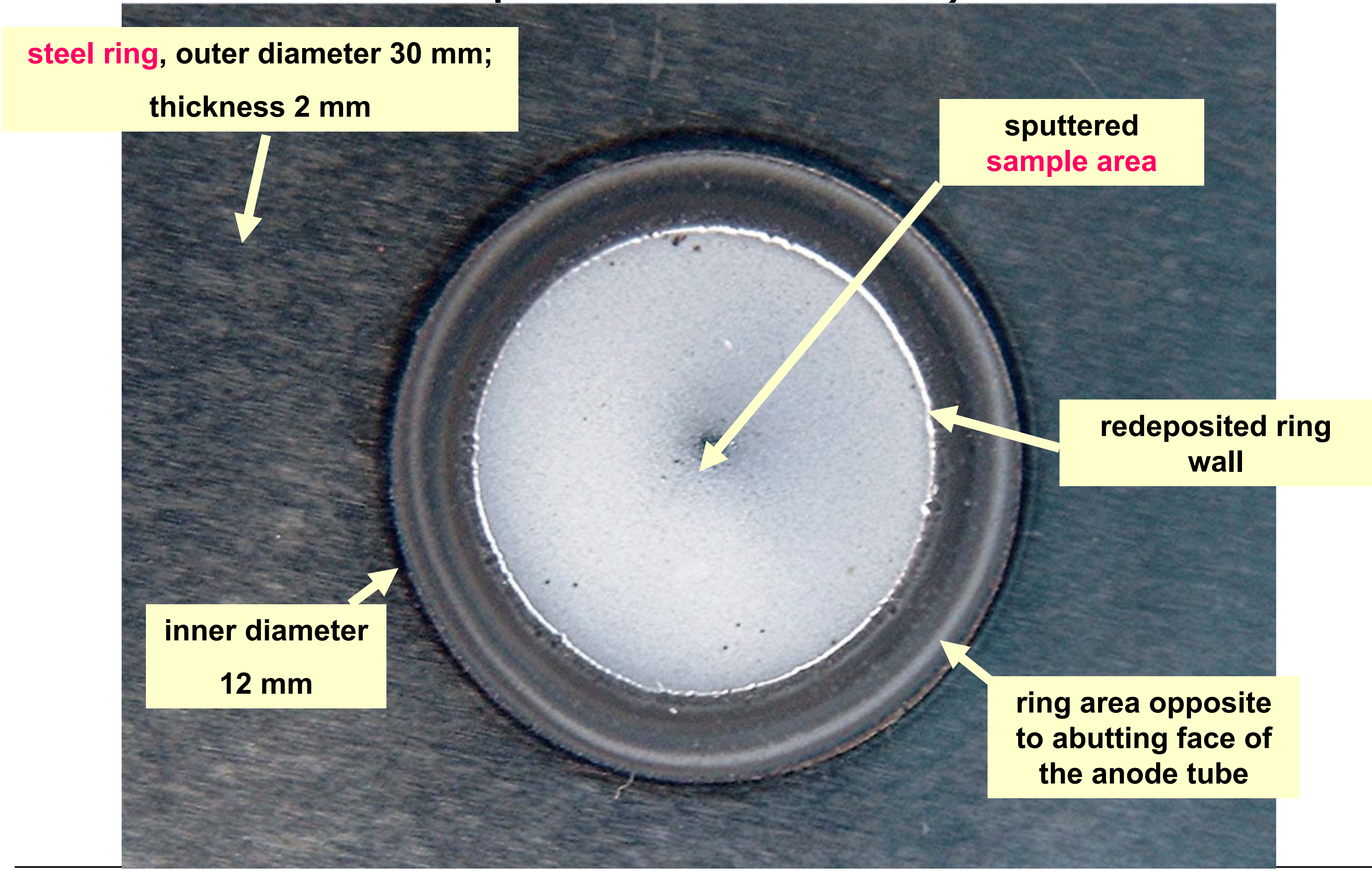
- GD-MS and „Element GD"
  - Element-GD
  - Traceable results for metallic analytes
    - o Matrix zinc
    - o Matrix copper
    - o **Matrix iron**
  - Traceable results for non-metallic analytes

- Conclusions

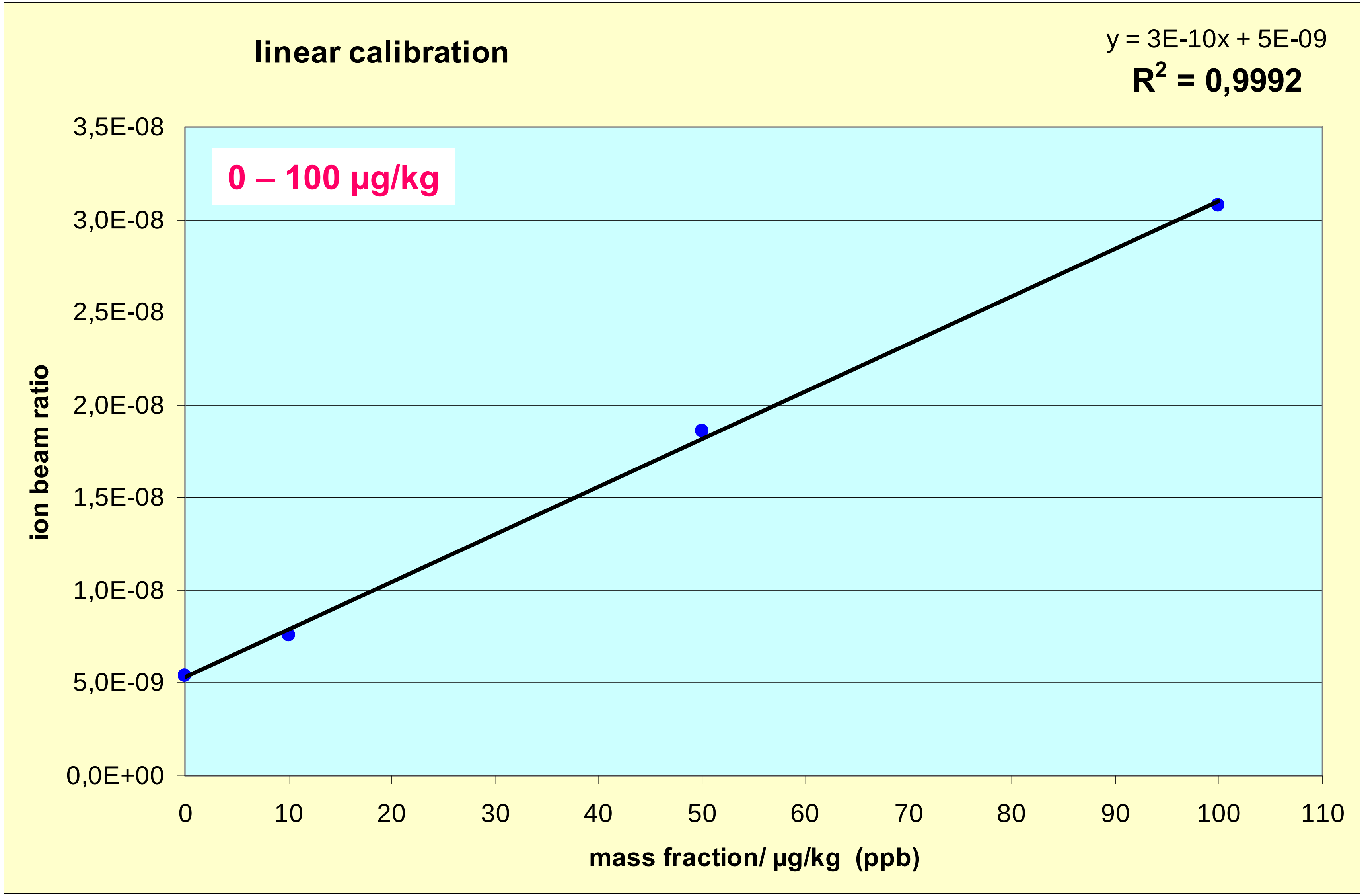
Iron matrix: Pressed multielement sample and ultrapure massive sample



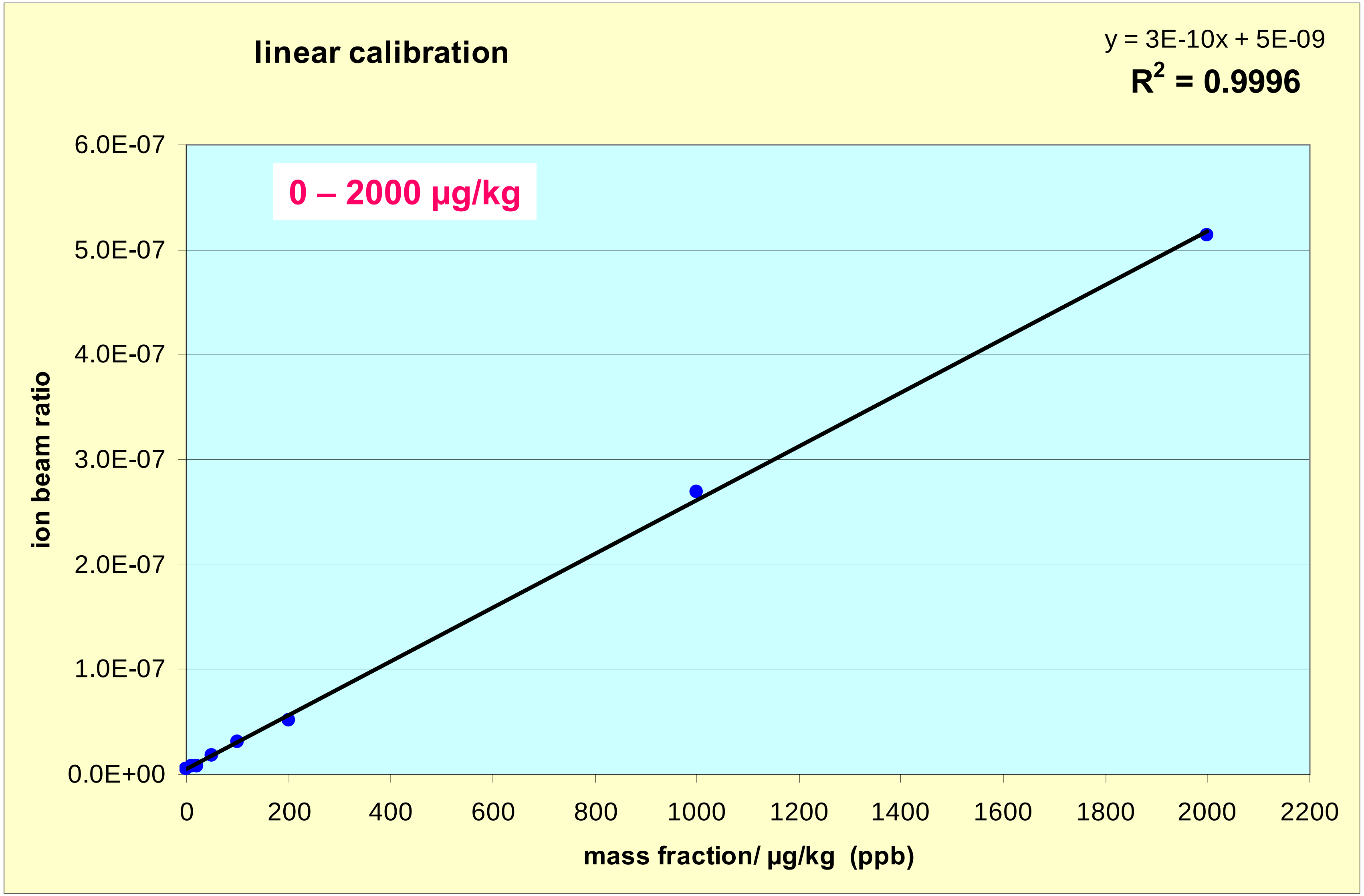
Iron matrix: Pressed multielement iron sample after GD analysis



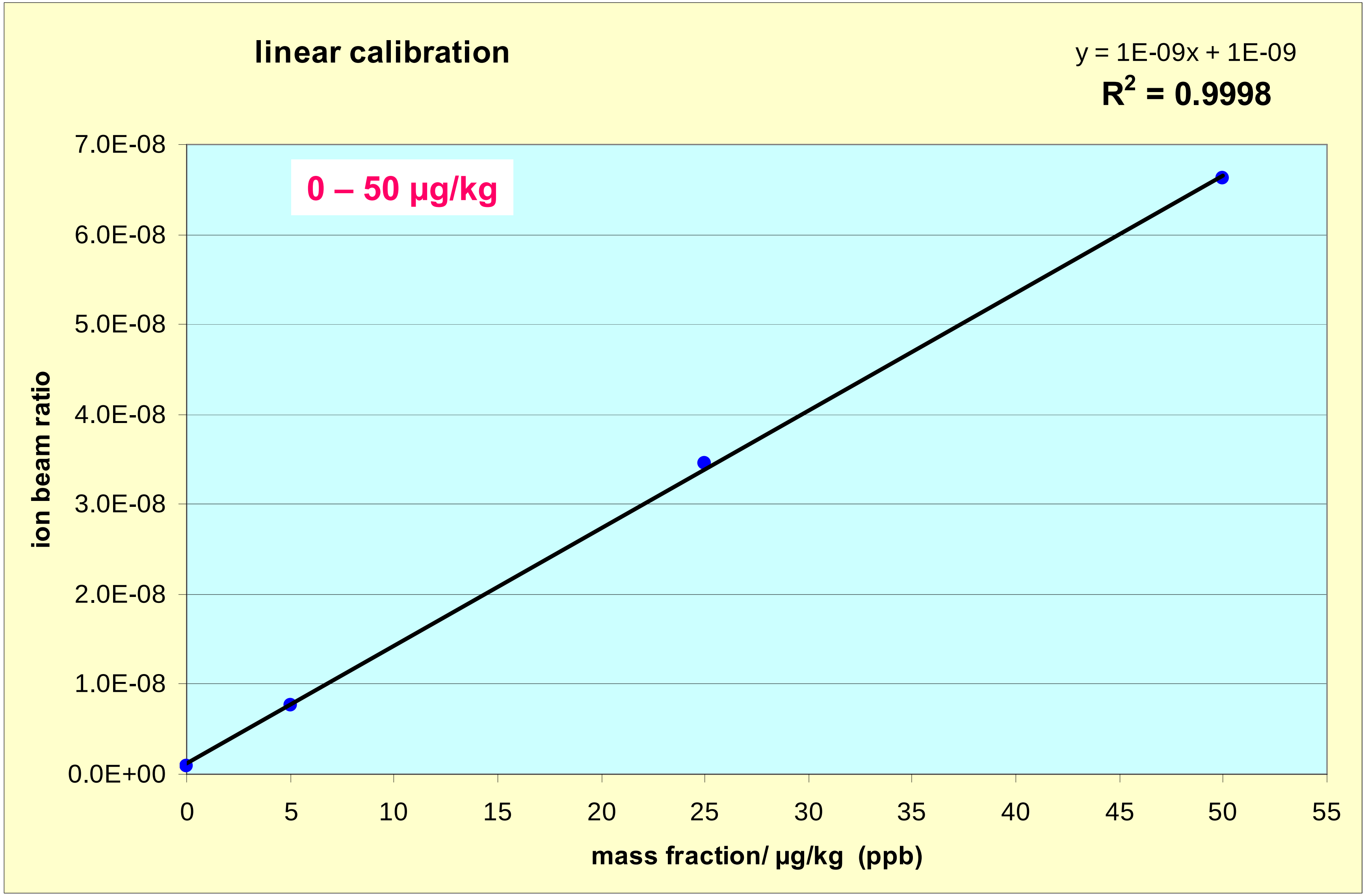
Calibration Function of ^{109}Ag in Iron Matrix



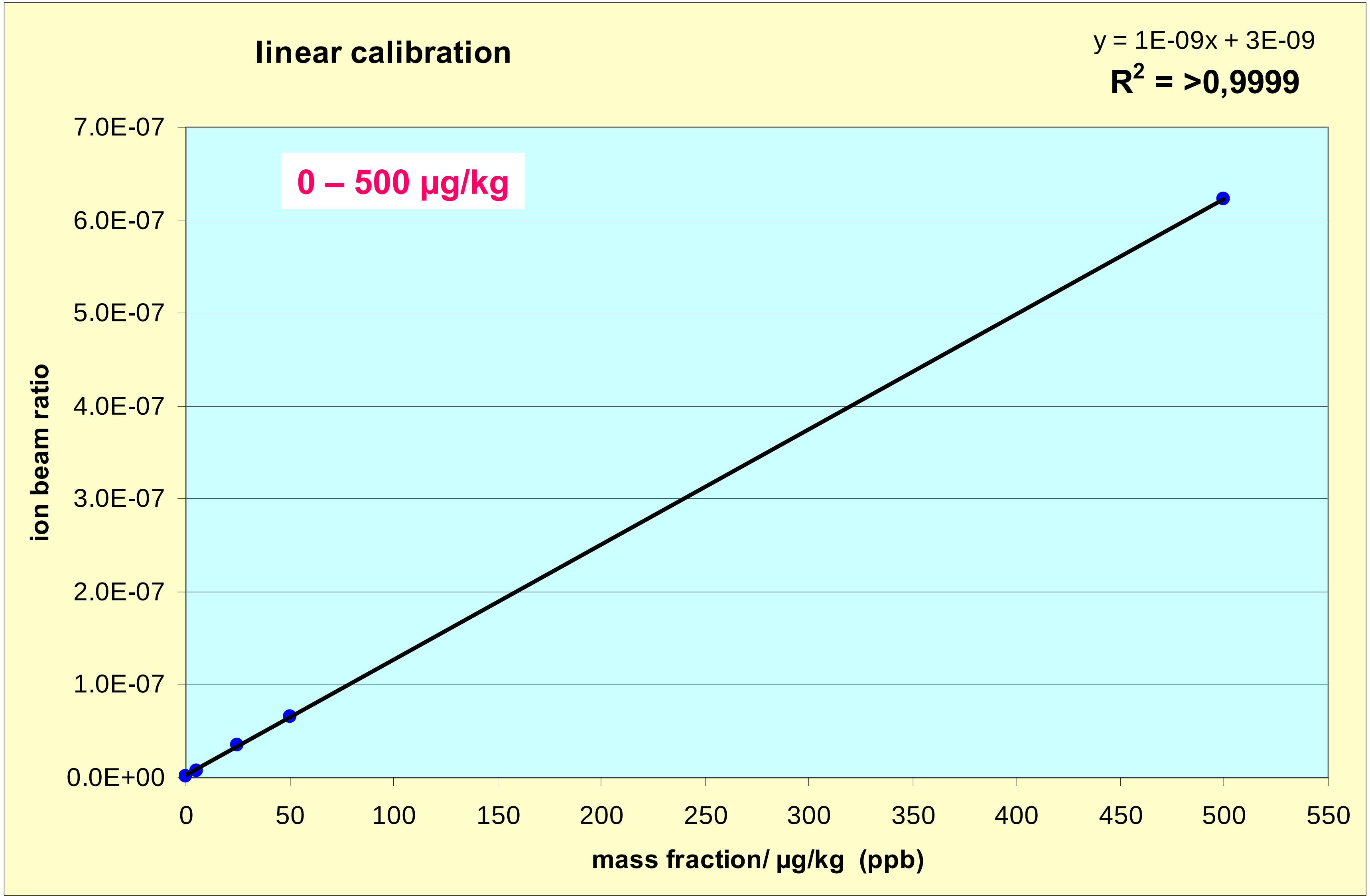
Calibration Function of ^{109}Ag in Iron Matrix



Calibration Function of ^{165}Ho in Iron Matrix

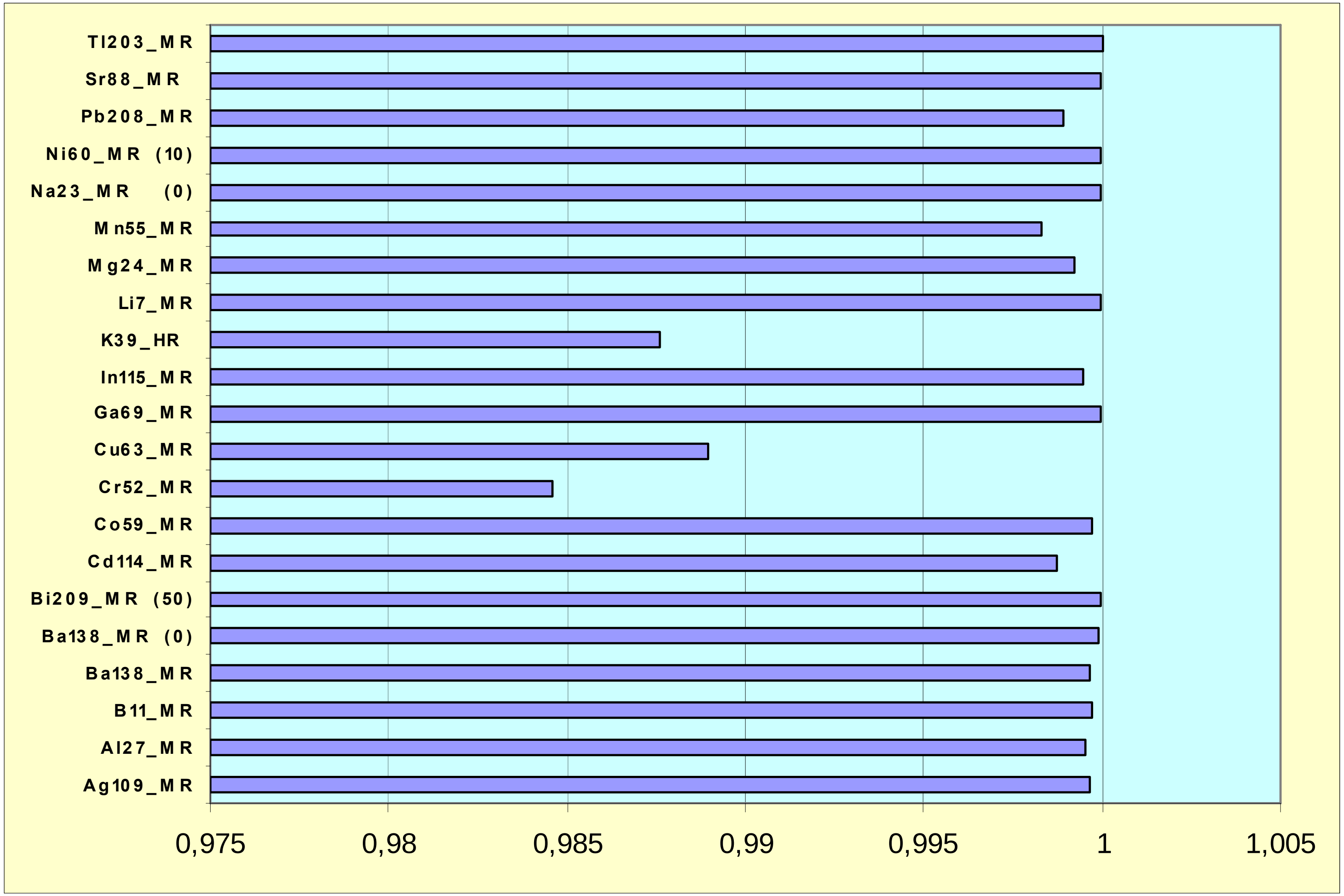


Calibration Function of ^{165}Ho in Iron Matrix



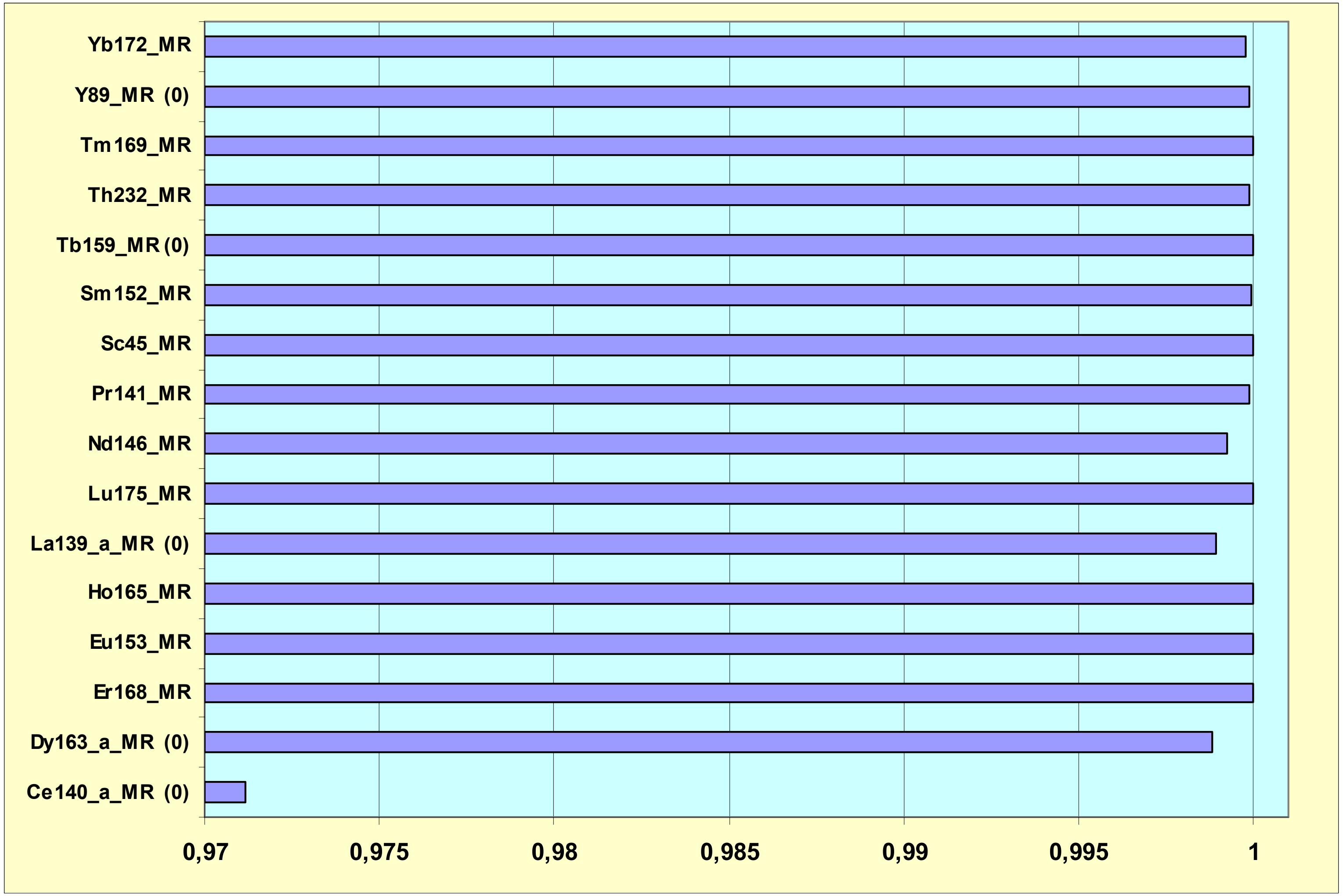
Linear correlation coefficients of calibration curves

Matrix: Iron, 0 – 1000 (4000) µg/kg (ppb)



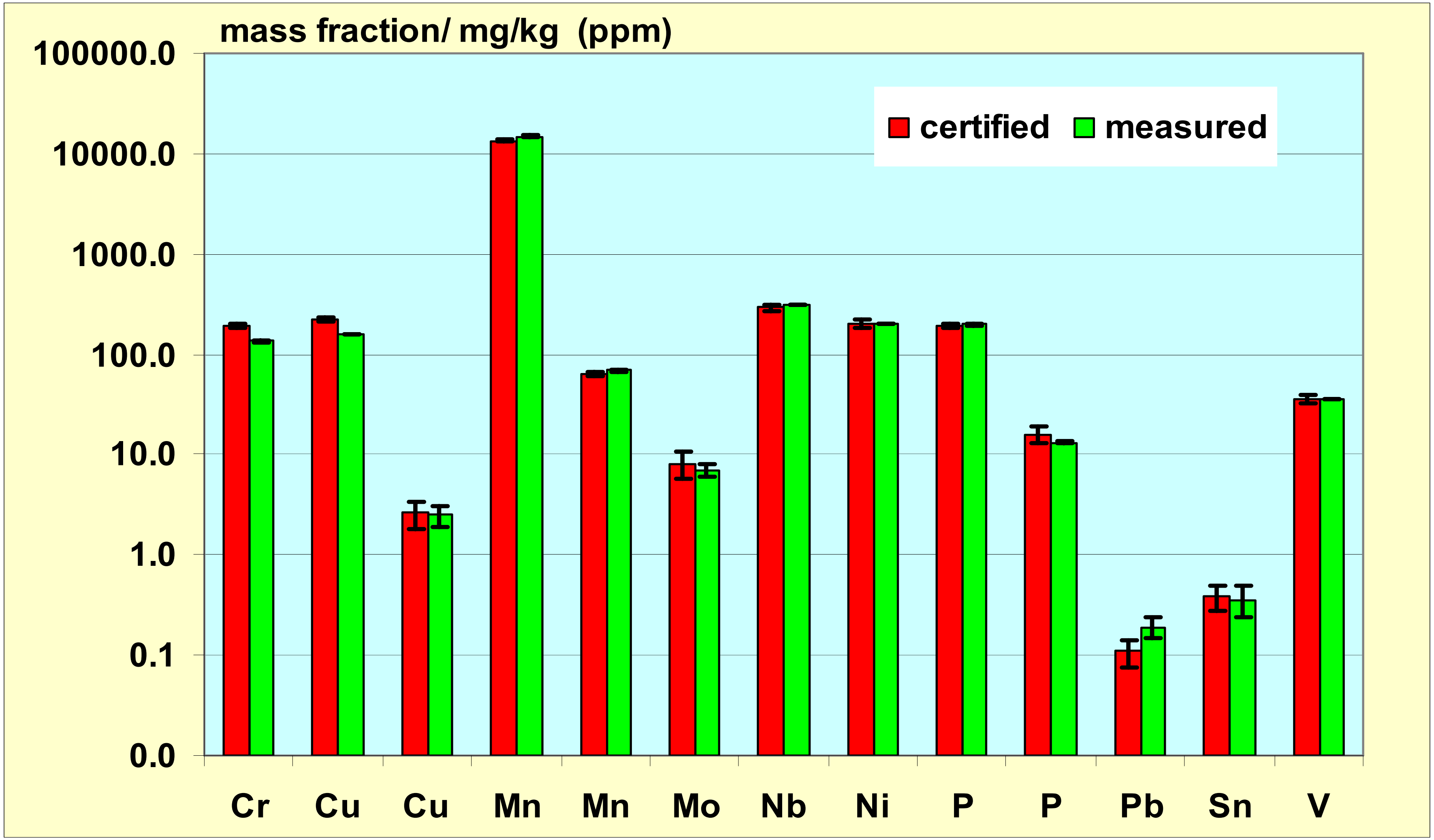
Linear correlation coefficients of calibration curves

Matrix: Iron, 0 – 500 µg/kg (ppb)



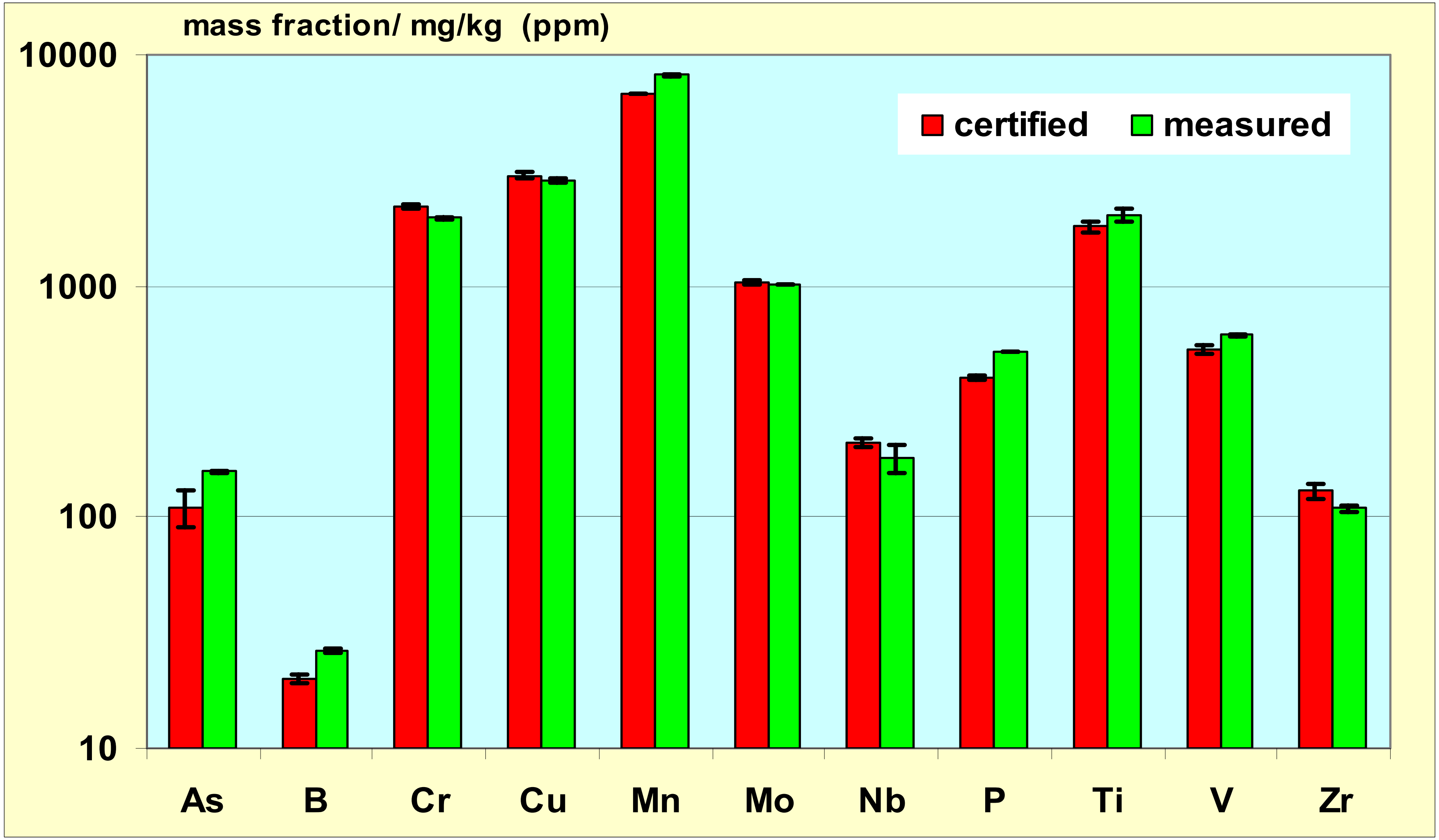
Comparison of certified and measured values

Matrix: Iron, ECRMs 096-1, 097-1, 098-1



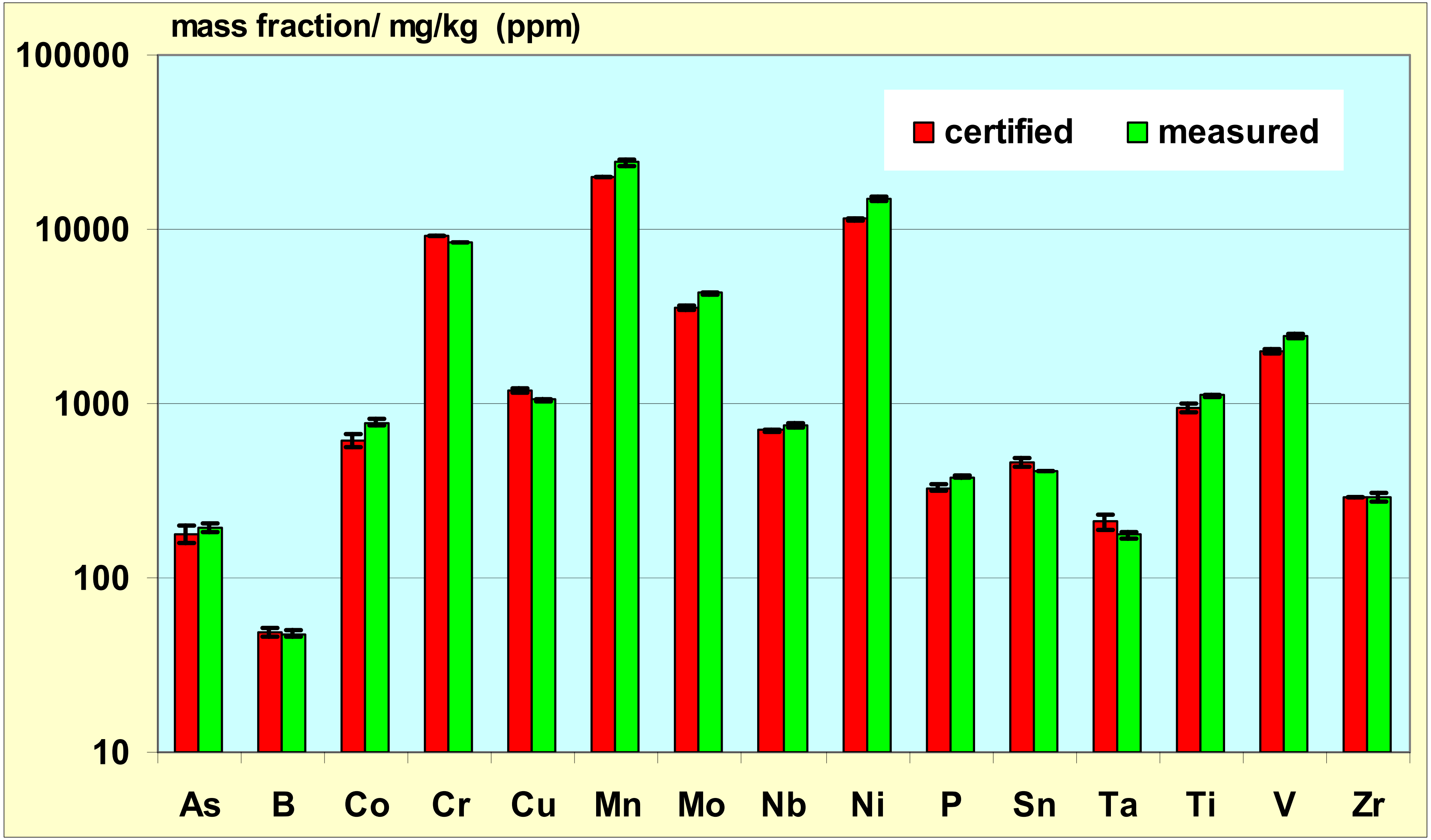
Comparison of certified and measured values

Matrix: Iron, SRM 1761



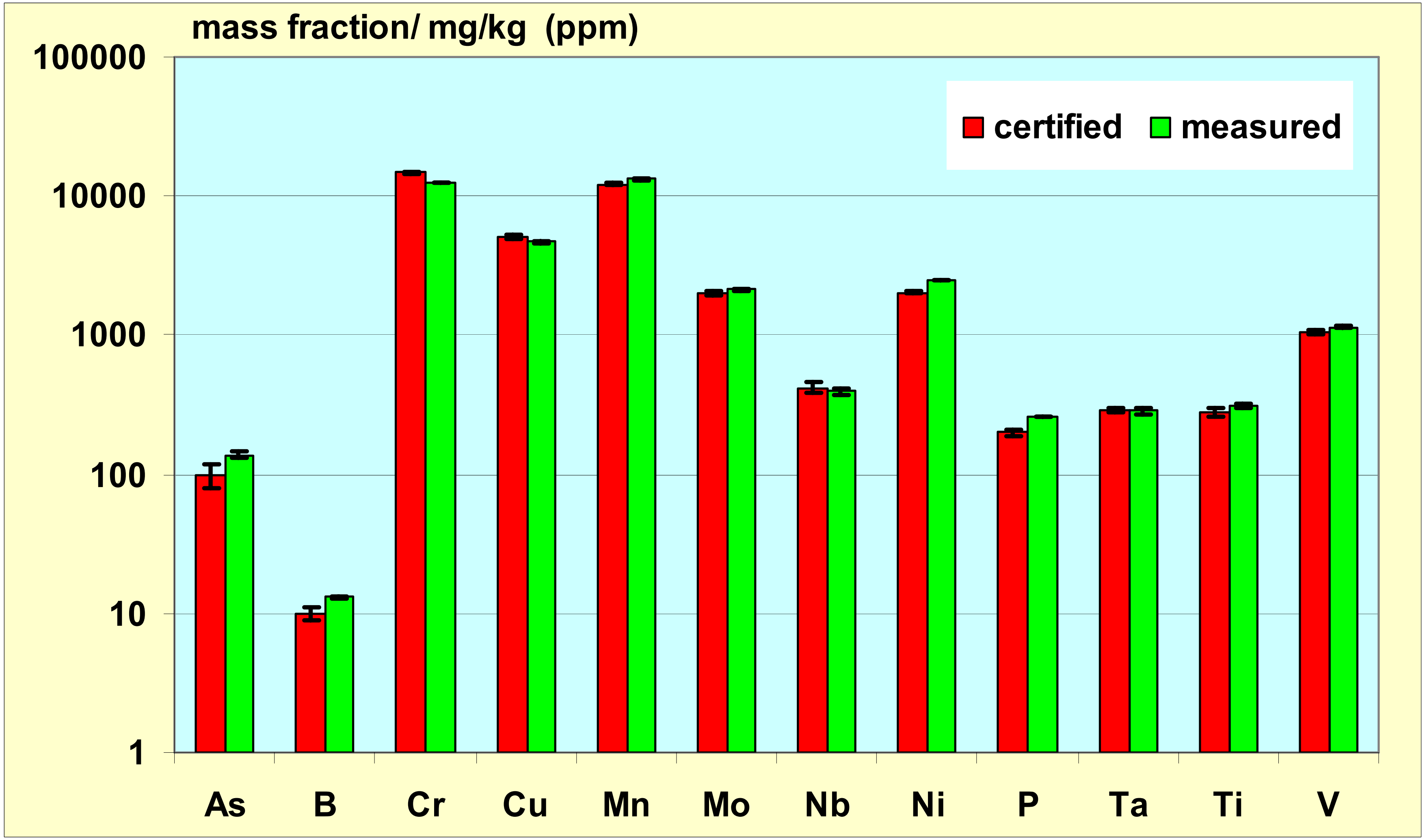
Comparison of certified and measured values

Matrix: Iron, SRM 1762



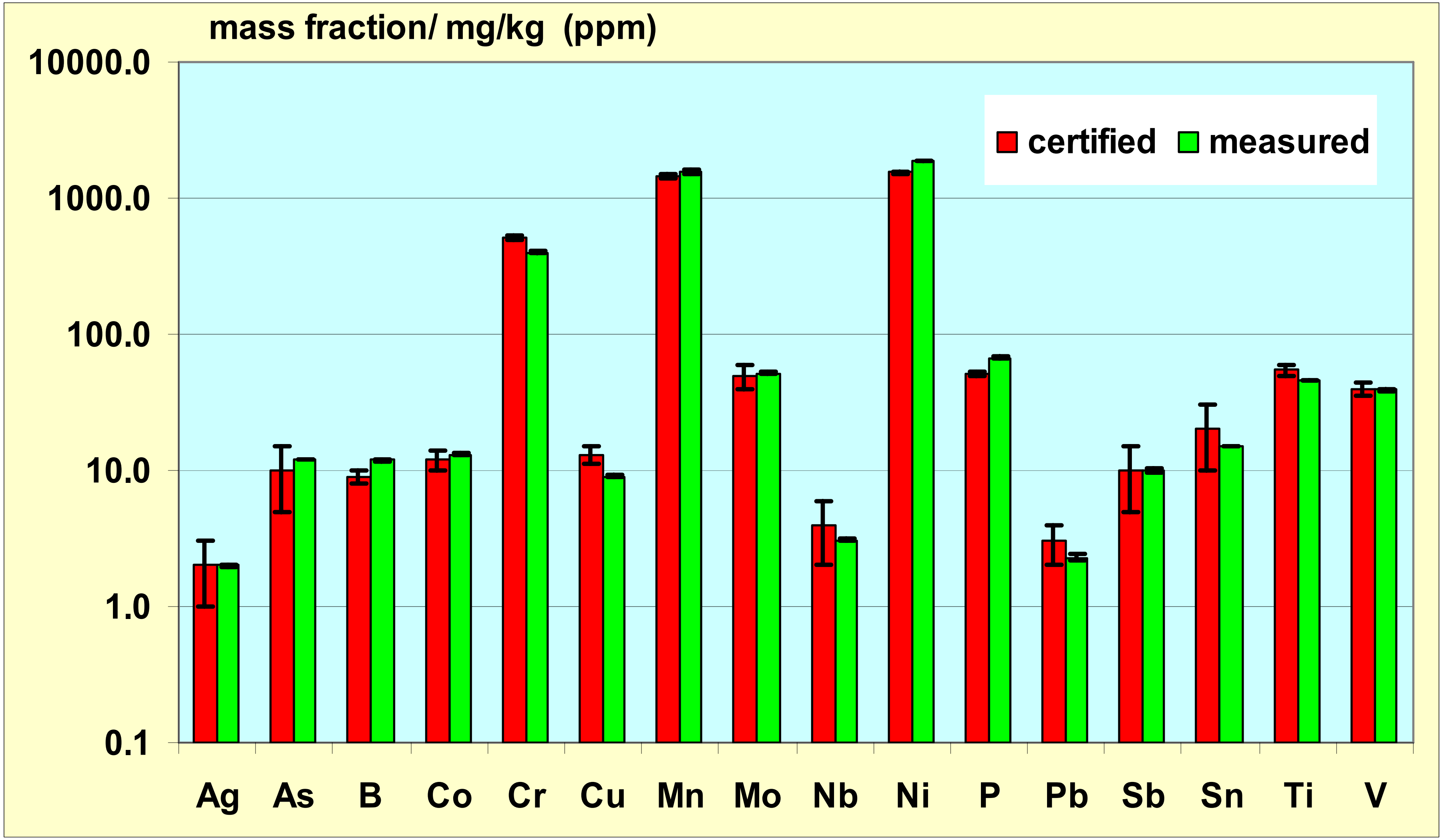
Comparison of certified and measured values

Matrix: Iron, SRM 1764



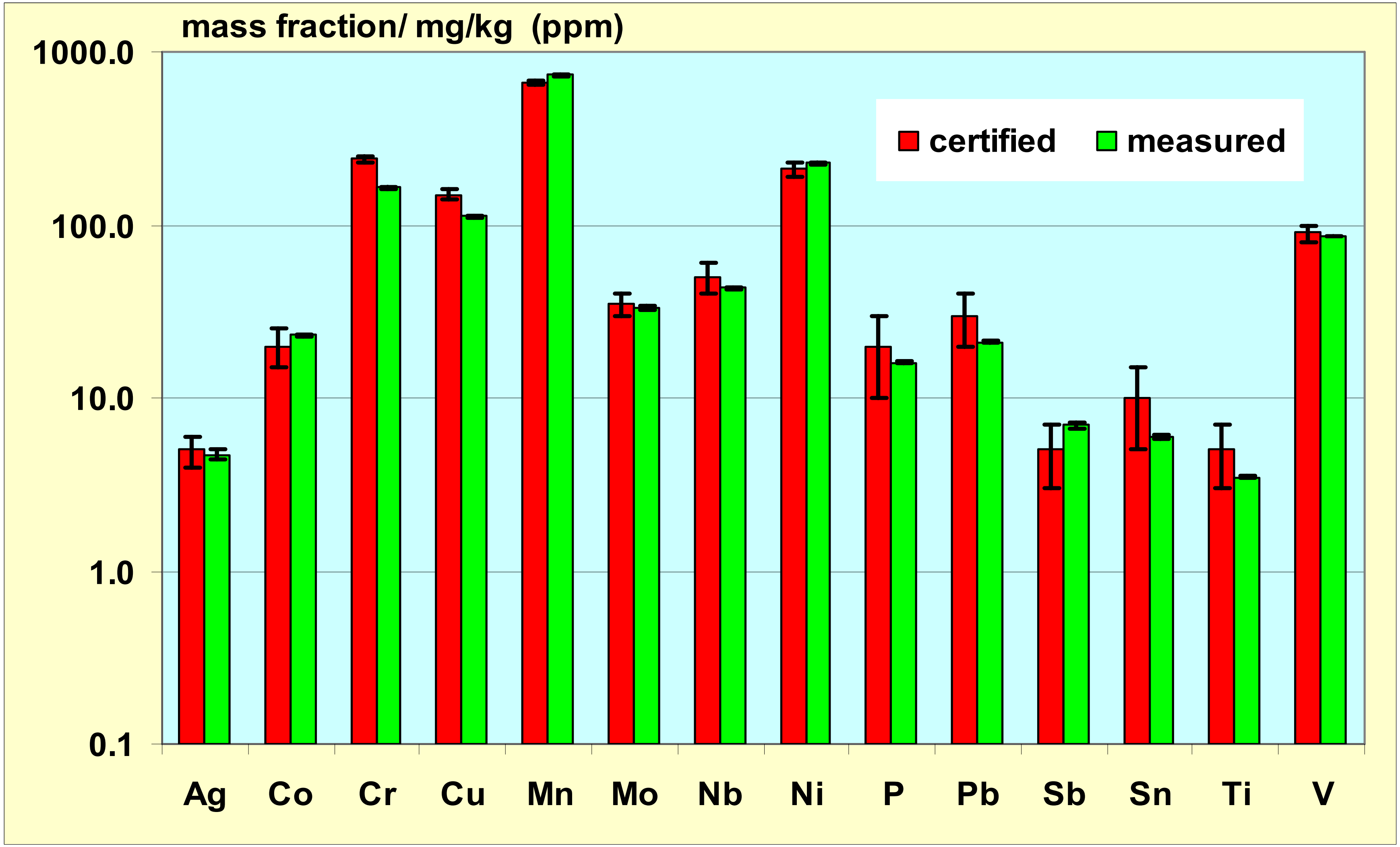
Comparison of certified and measured values

Matrix: Iron, SRM 1765



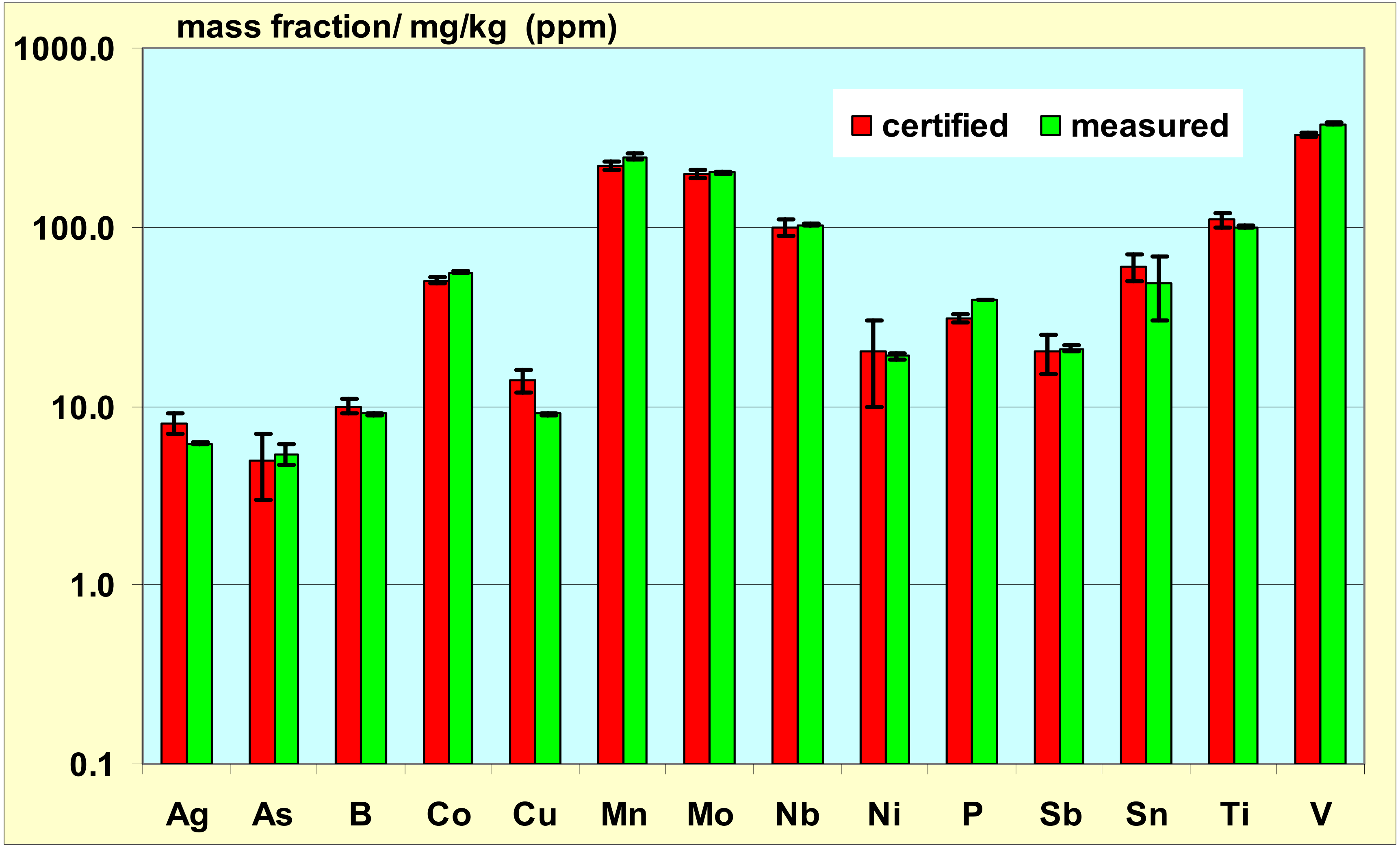
Comparison of certified and measured values

Matrix: Iron, SRM 1766



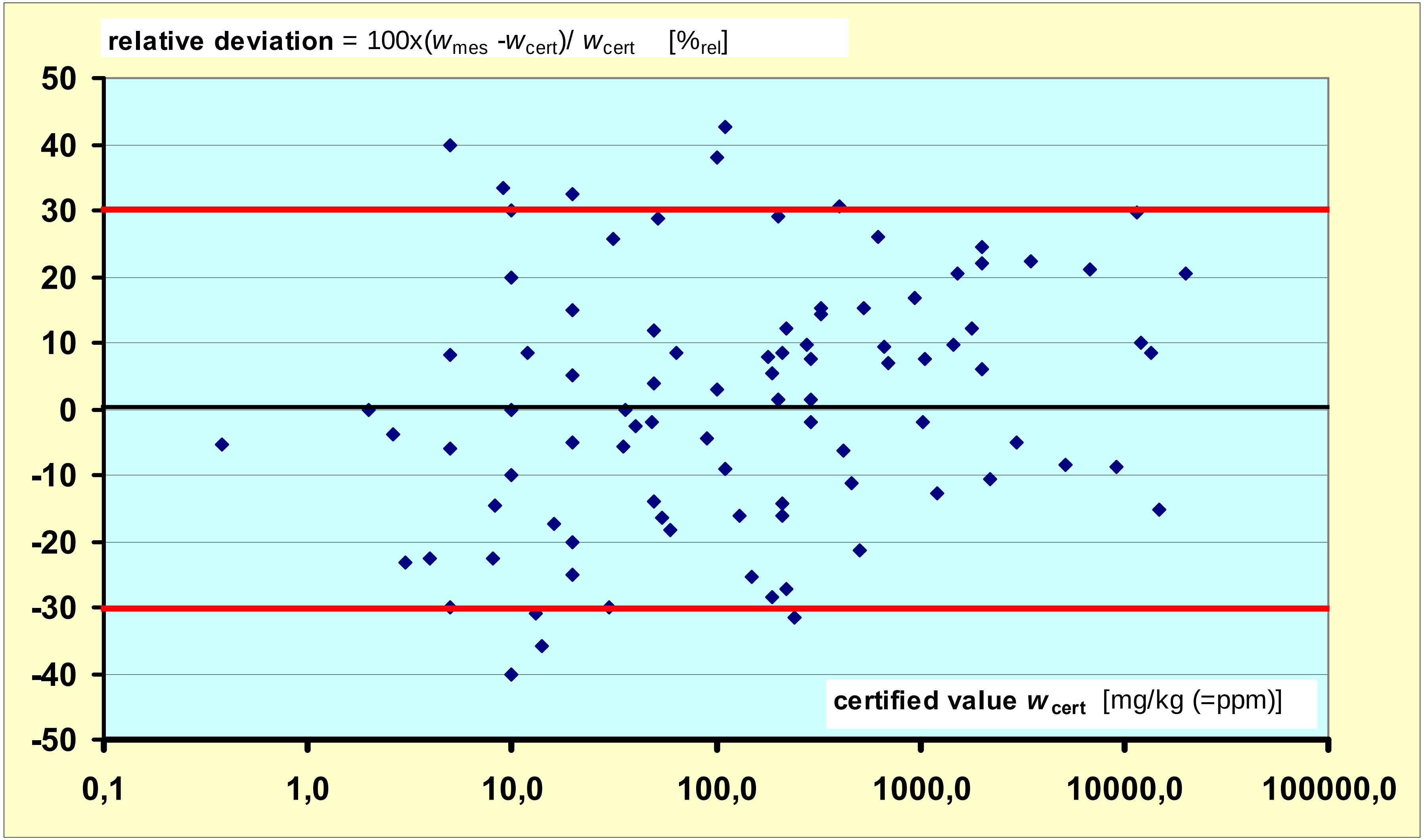
Comparison of certified and measured values

Matrix: Iron, SRM 1767



Comparison of certified and measured values

Matrix: Iron, all measurements



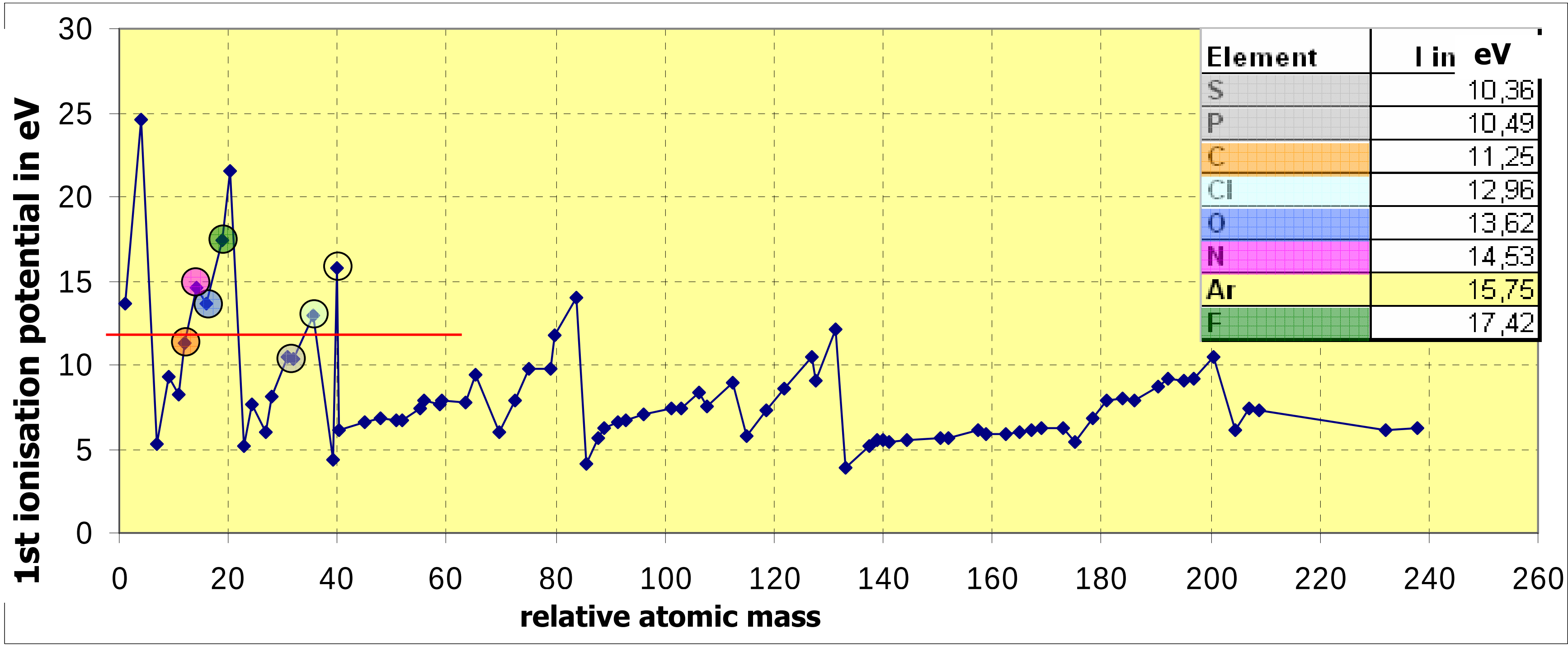
Content

- Why Primary Pure Standards?
- BAM System of Primary National Standards
  - Way of certification, some results
  - Need for GD-MS
- GD-MS and „Element GD“
  - Element-GD
  - Traceable results for metallic analytes
    - o Matrix zinc
    - o Matrix copper
    - o Matrix iron
  - **Traceable results for non-metallic analytes**
- Conclusions

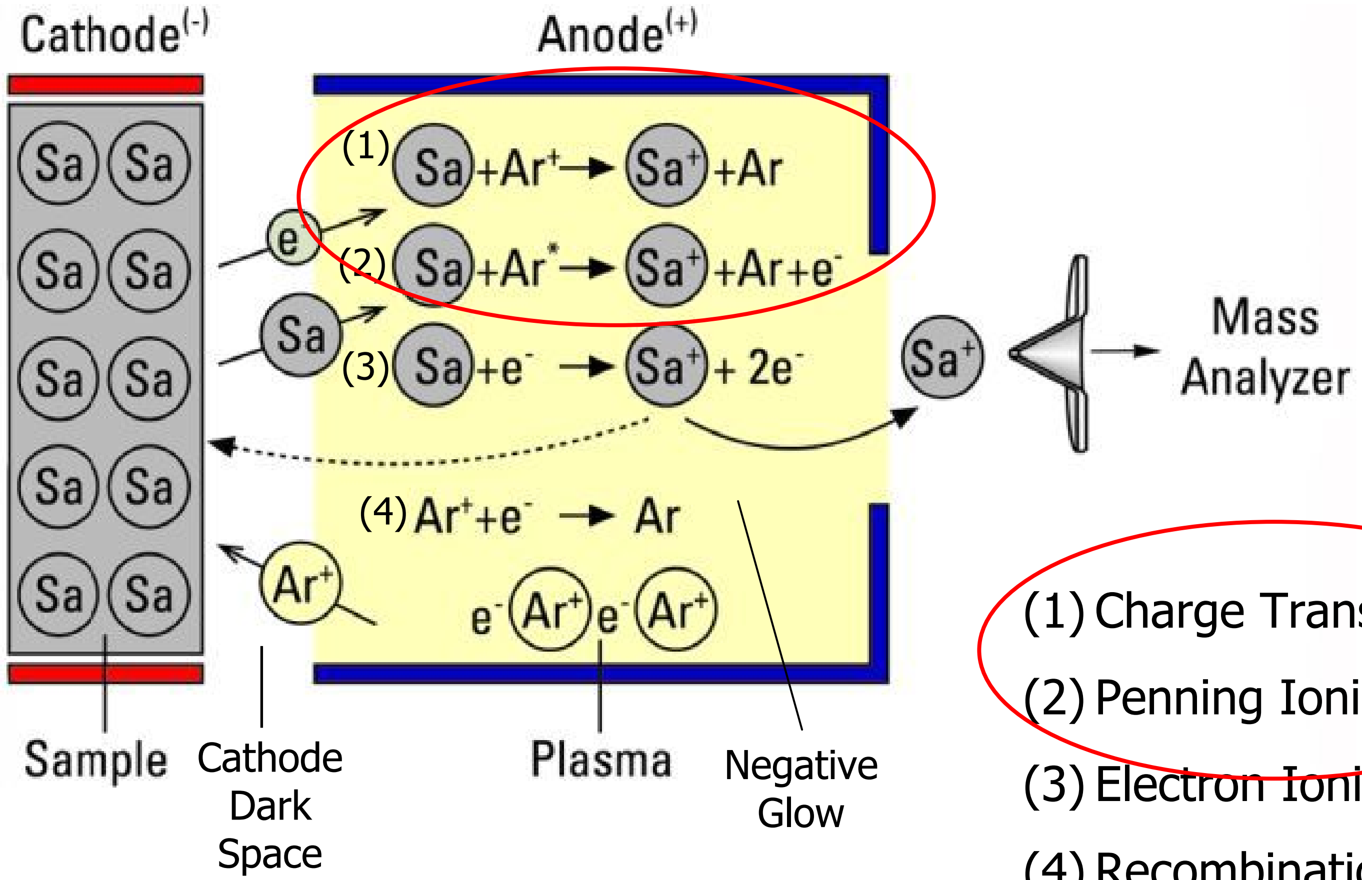
Determination of non-metals by GD-MS – Why is it a problem?

- Determination of non-metallic analytes is much less sensitive than of metallic ones

Reason: **Their higher ionisation energies** in comparison with metallic analytes



Ionisation processes in GD-MS



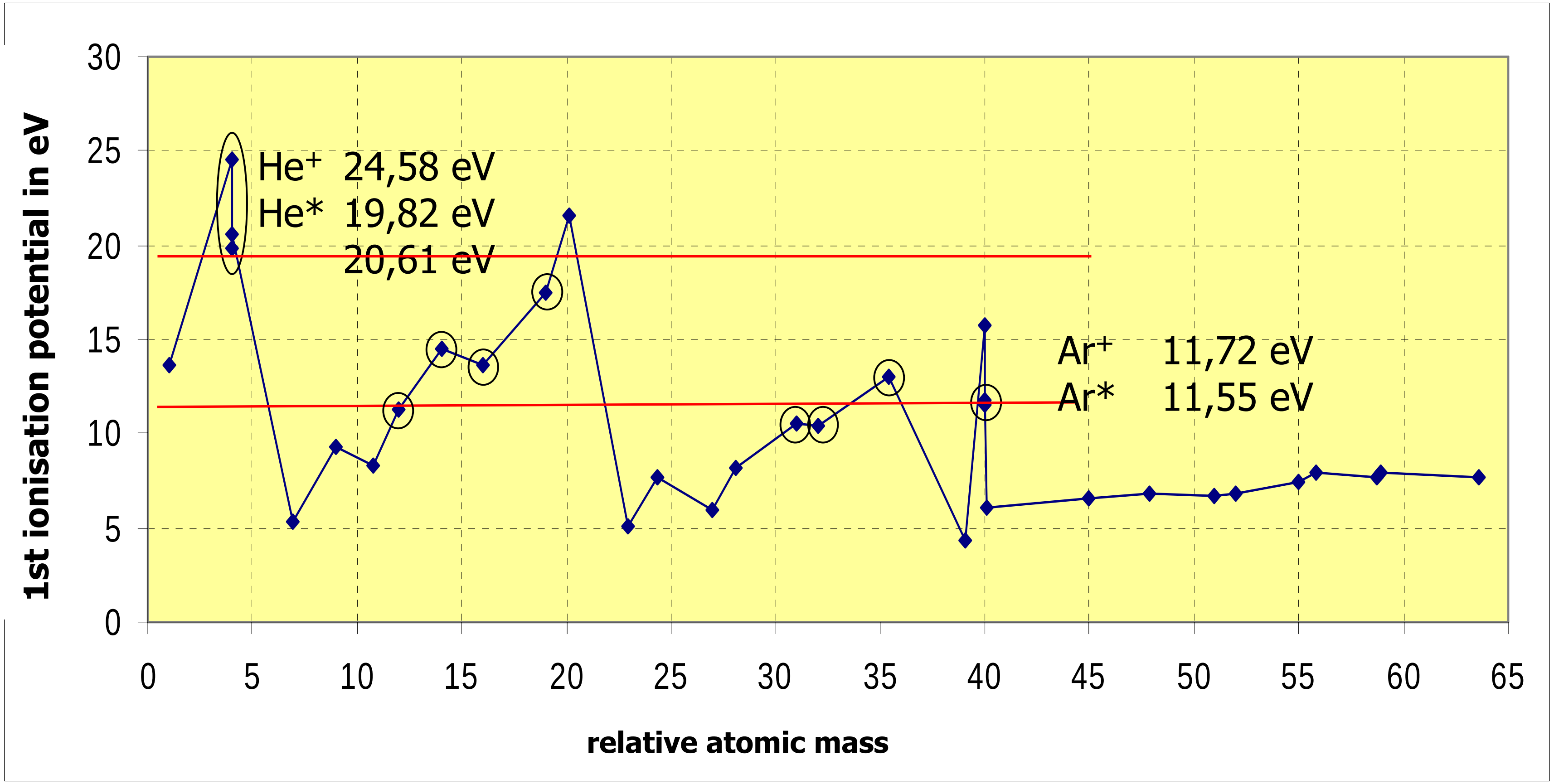
(1) Charge Transfer

(2) Penning Ionisation

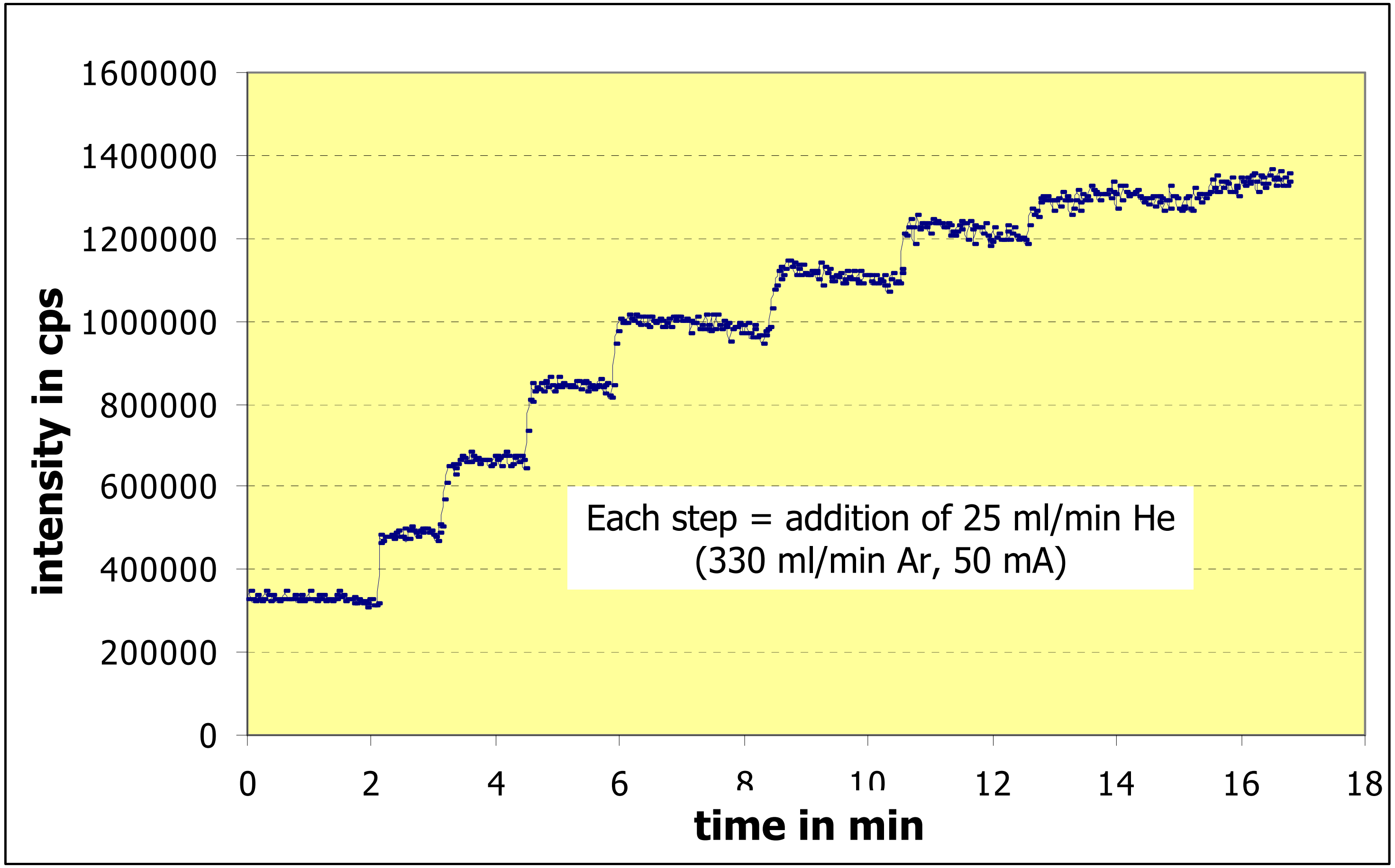
(3) Electron Ionisation

(4) Recombination

Ionisation potential and metastable energies of He and Ar

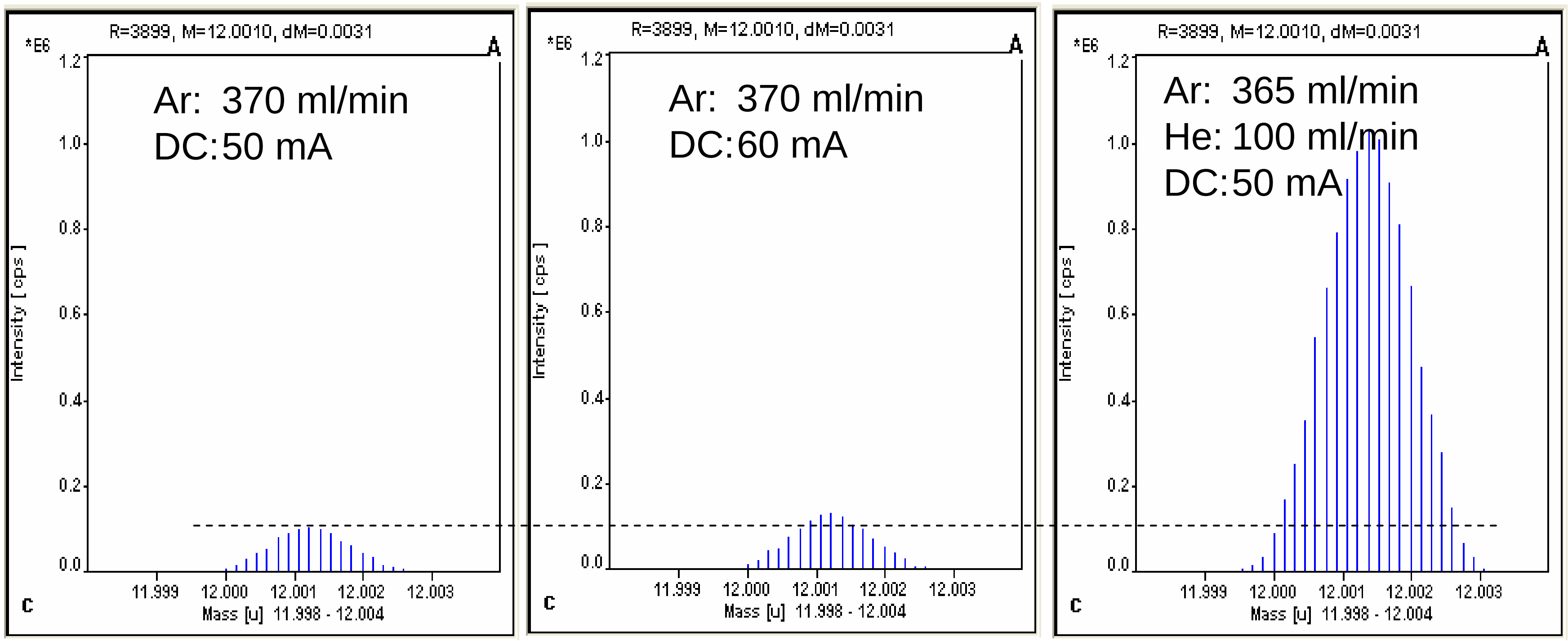


Enhancement of analytical signals of phosphorus in copper by addition of **He gas** to the Ar plasma gas



Signal enhancement by changing discharge current or discharge gas

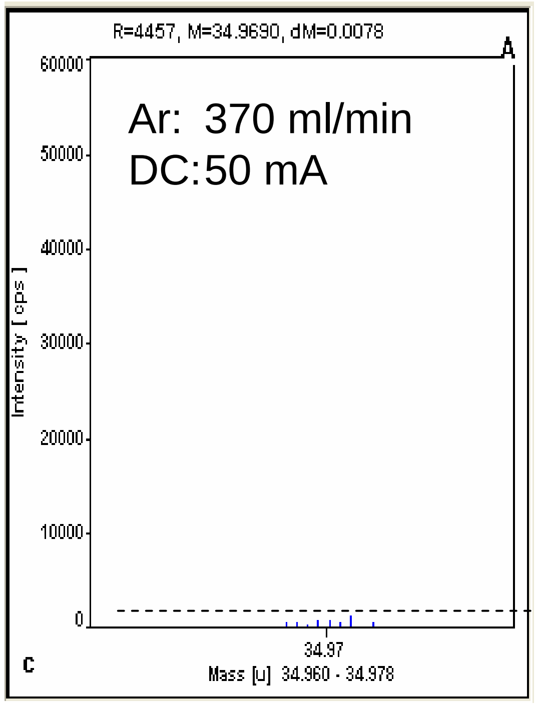
Carbon (IP 11.25 eV):

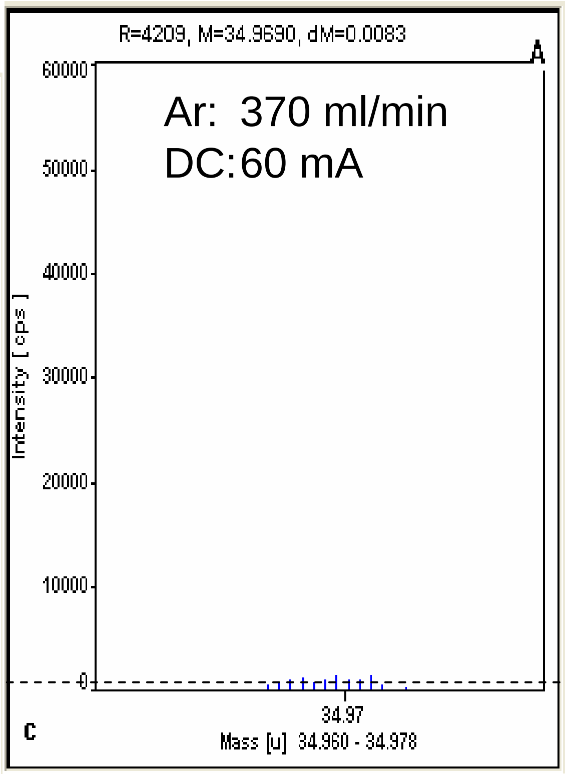


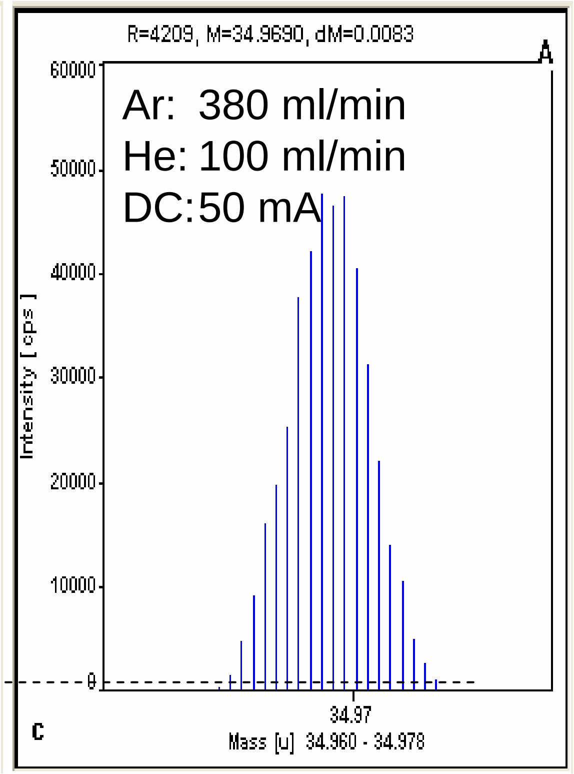
Increase of peak about:	25 %	1500 %

Signal enhancement by changing discharge current or discharge gas

Chlorine (IP 12,96 eV):



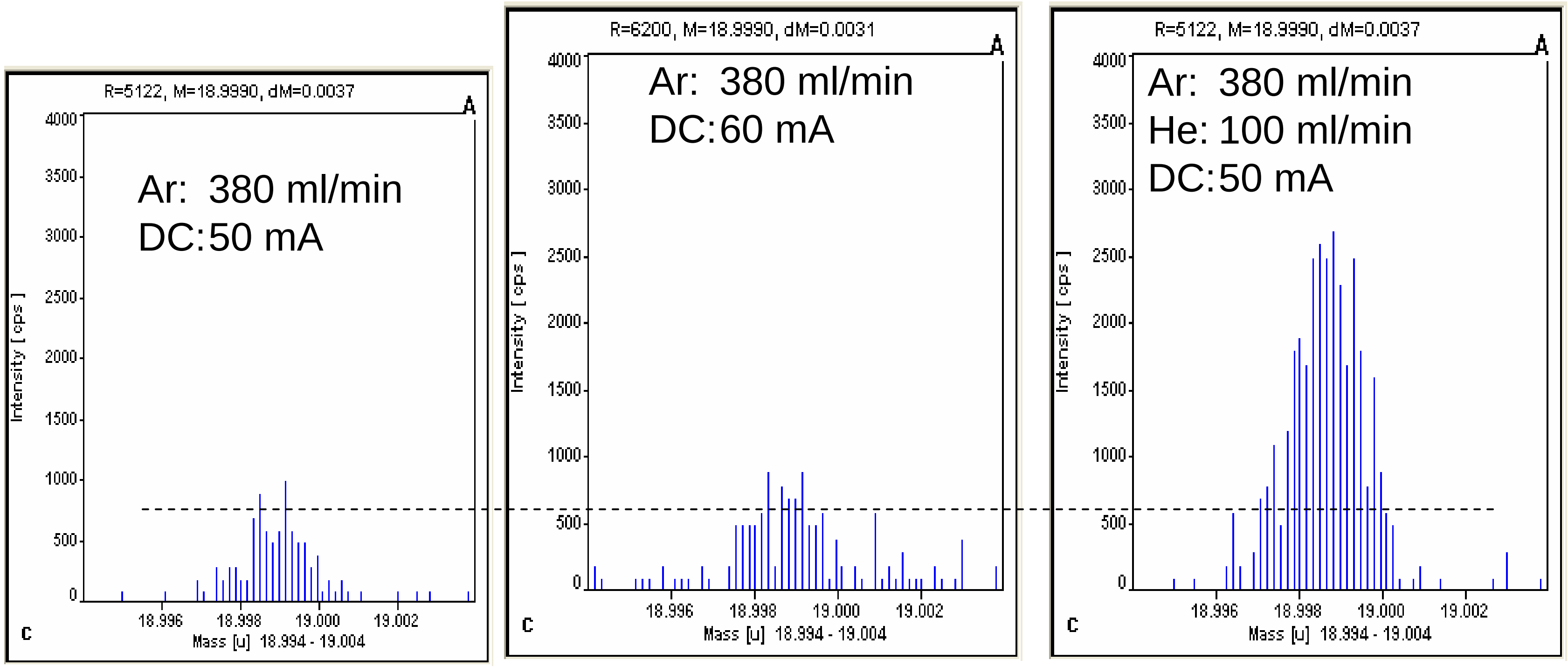




Increase of peak about: 40 % 4500 %

Signal enhancement by changing discharge current or discharge gas

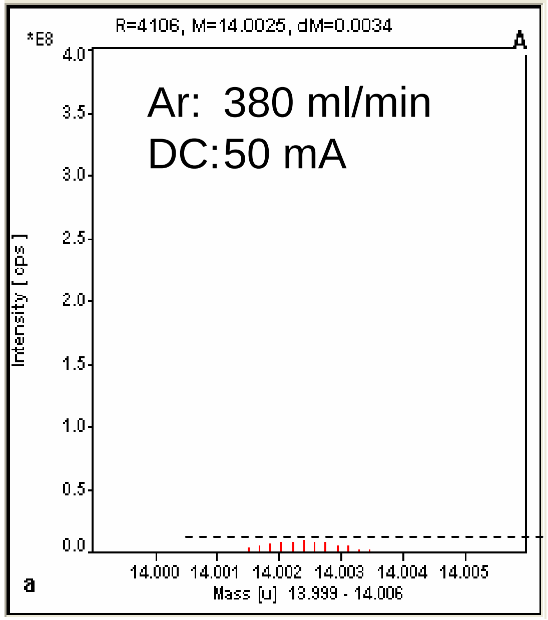
Fluorine (IP 17,42 eV):

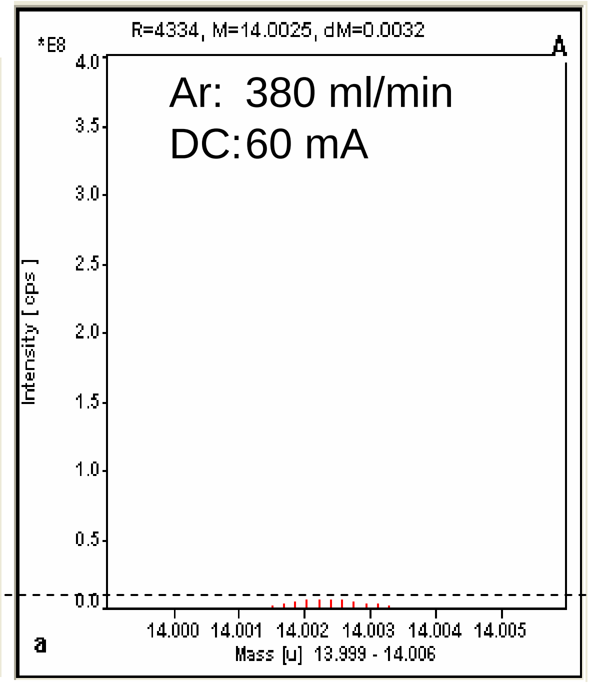


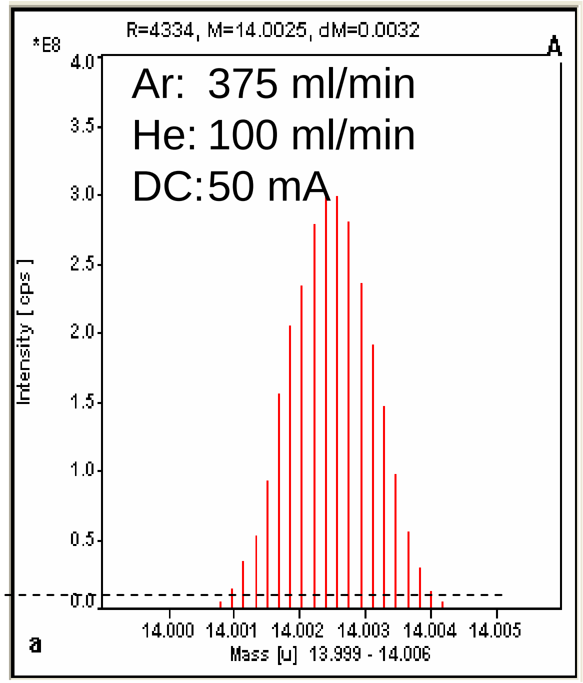
Increase of peak about:	40 %	350 %

Signal enhancement by changing discharge current or discharge gas

Nitrogen (IP 14,53 eV):



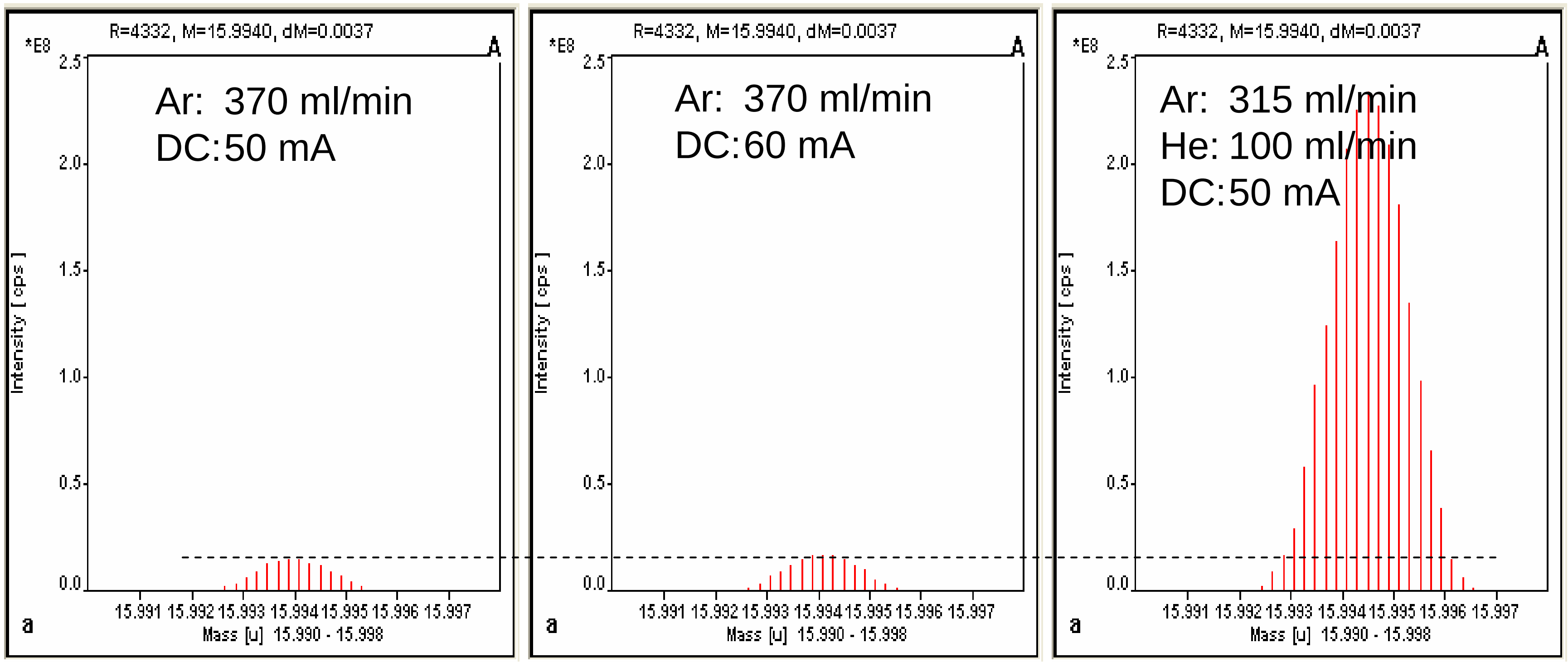




Increase of peak about: 20 % 4000 %

Signal enhancement by changing discharge current or discharge gas

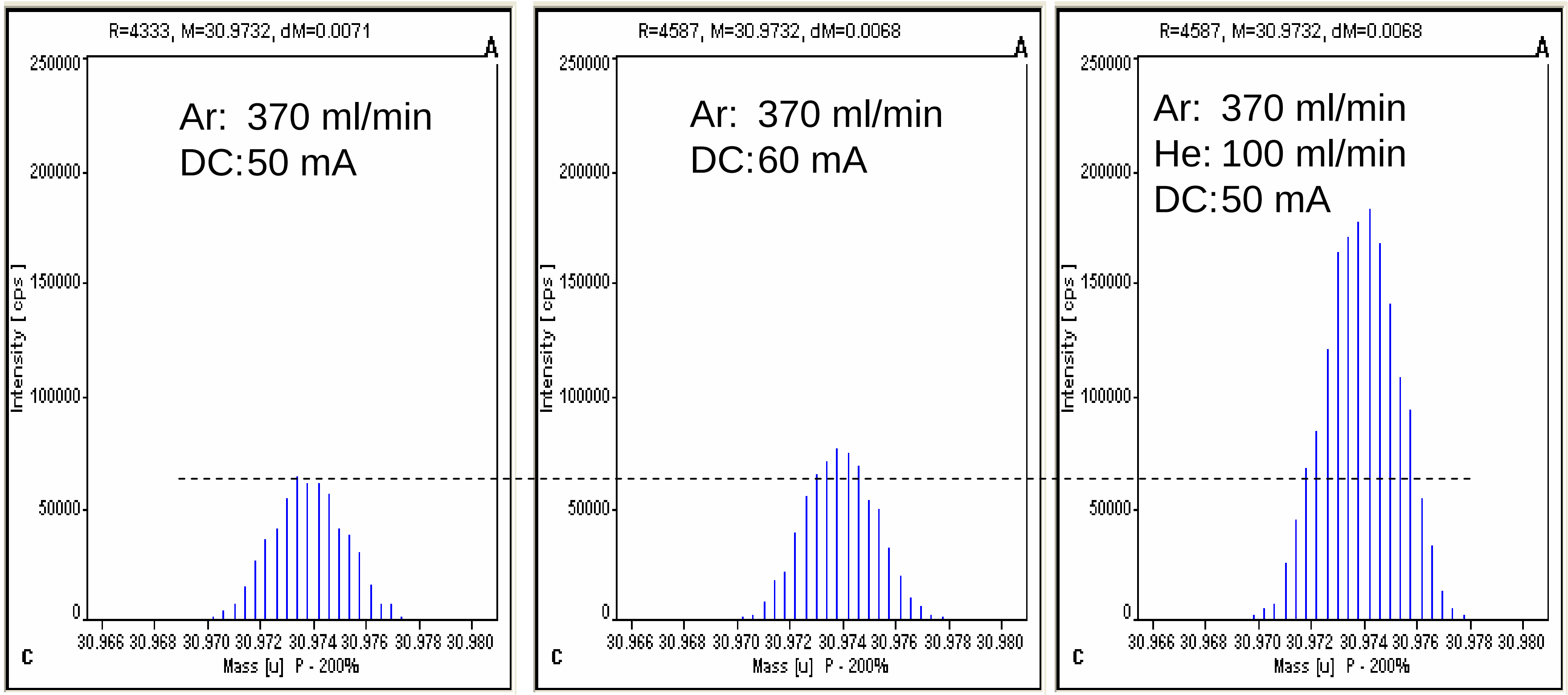
Oxygen (IP 13,62 eV):



Increase of peak about: 10 % 800 %

Signal enhancement by changing discharge current or discharge gas

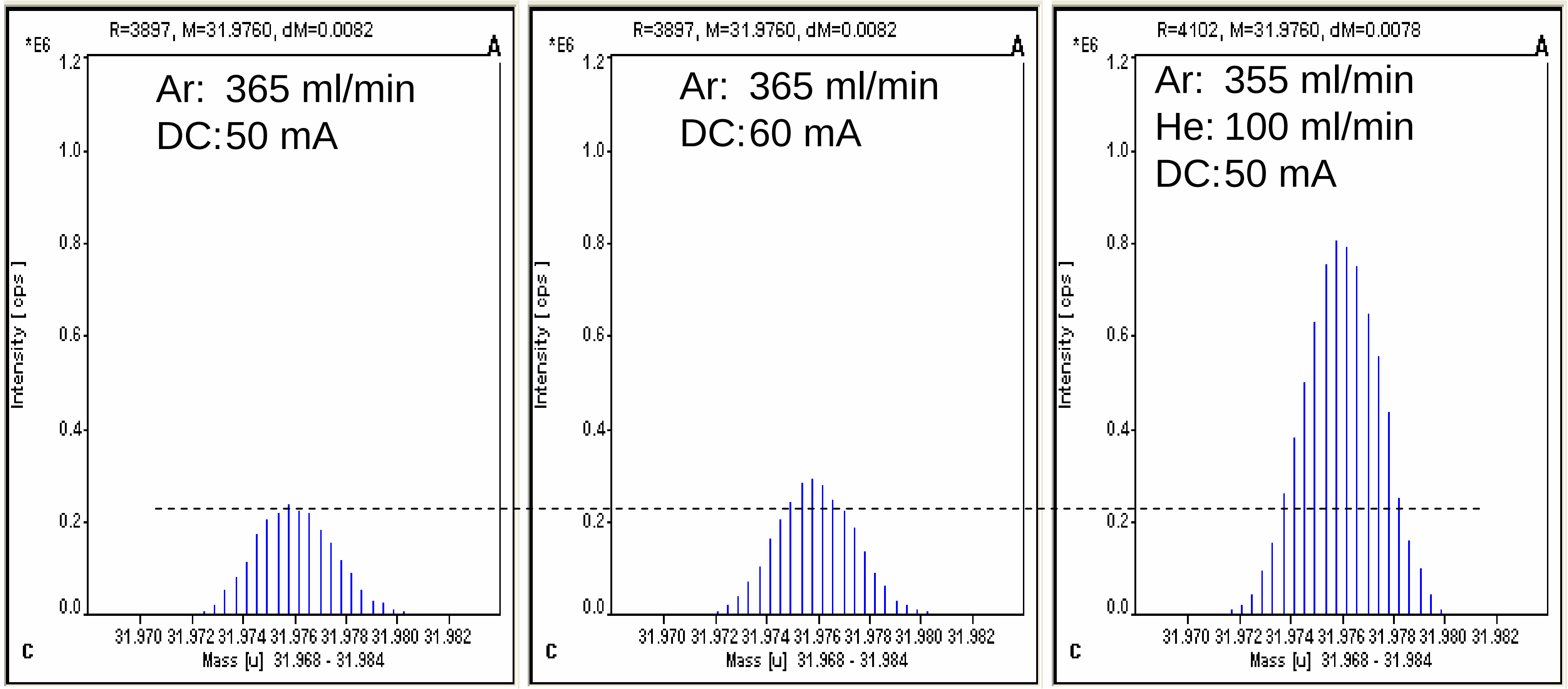
Phosphorus (IP 10,49 eV):



Increase of peak about: 30 % 200 %

Signal enhancement by changing discharge current or discharge gas

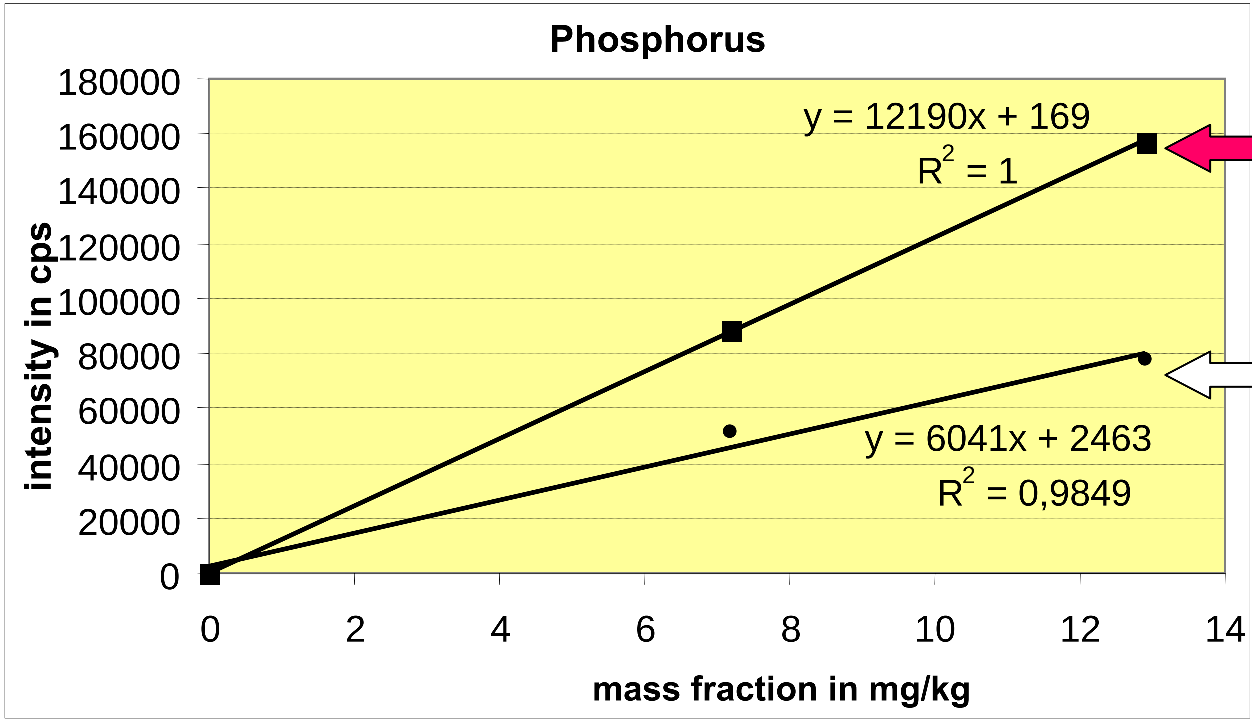
Sulphur (IP 10,36 eV):



Increase of peak about: 30 % 250 %

Comparison of CRM based calibration curves
with and without He discharge gas

phosphorus in copper matrix



Conditions:

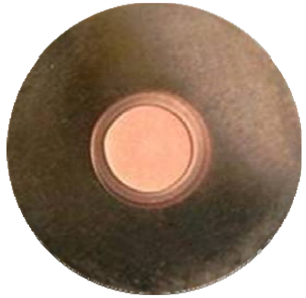
52 mA
325 ml/min Ar
90 ml/min He

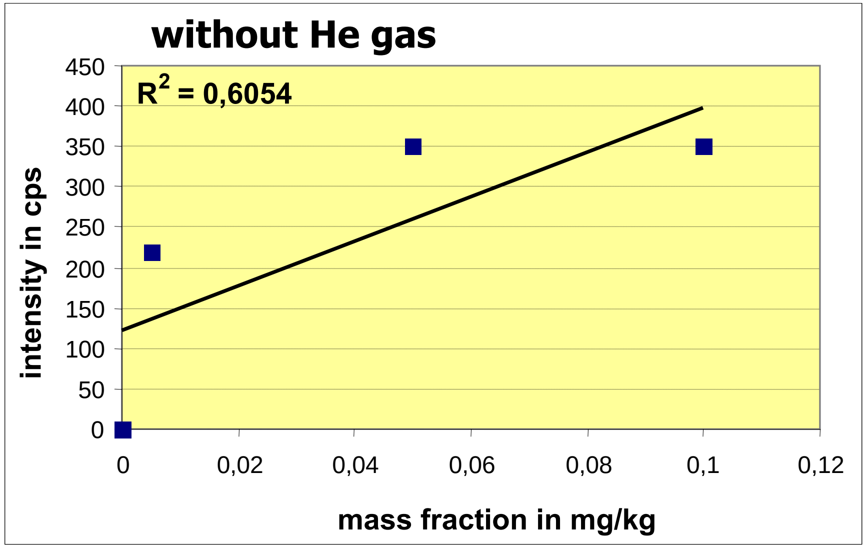
60 mA
370 ml/min Ar

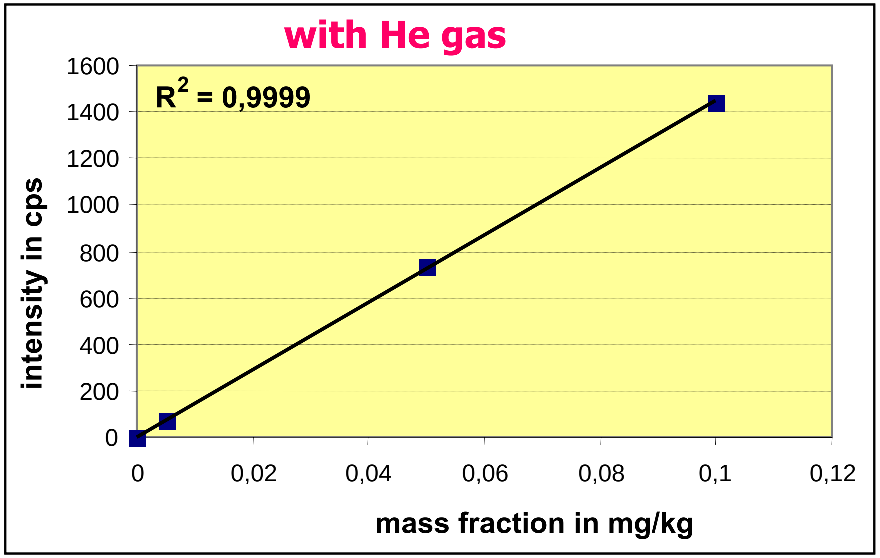
- increase of slope
- absolute sensitivity doubled
- calibration points meet the straight line

Comparison of calibration curves based on doped pressed powder pellets (5 µg/kg ...100 µg/kg) with and without He discharge gas

phosphorus in copper matrix

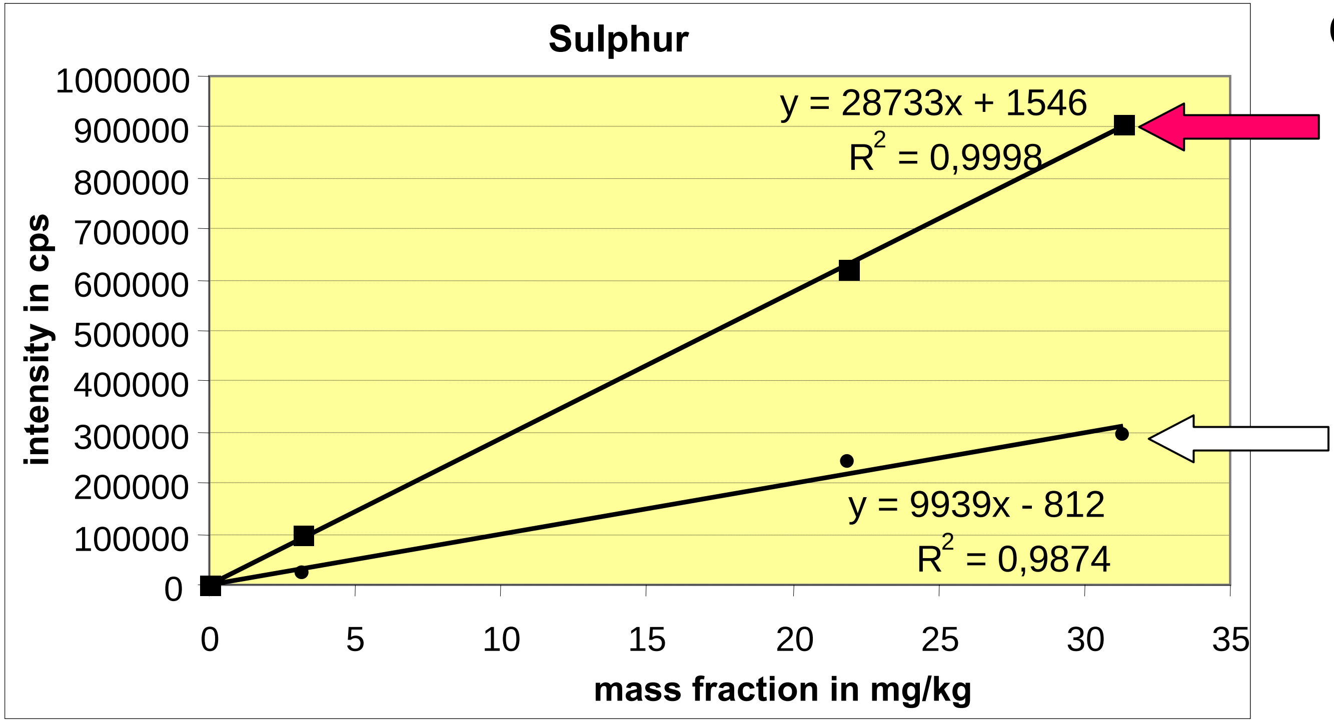






Comparison of CRM based calibration curves
with and without He discharge gas

sulphur in copper matrix



Conditions

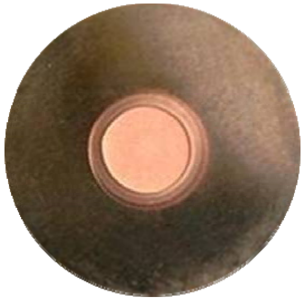
60 mA
310 ml/min Ar
140 ml/min He

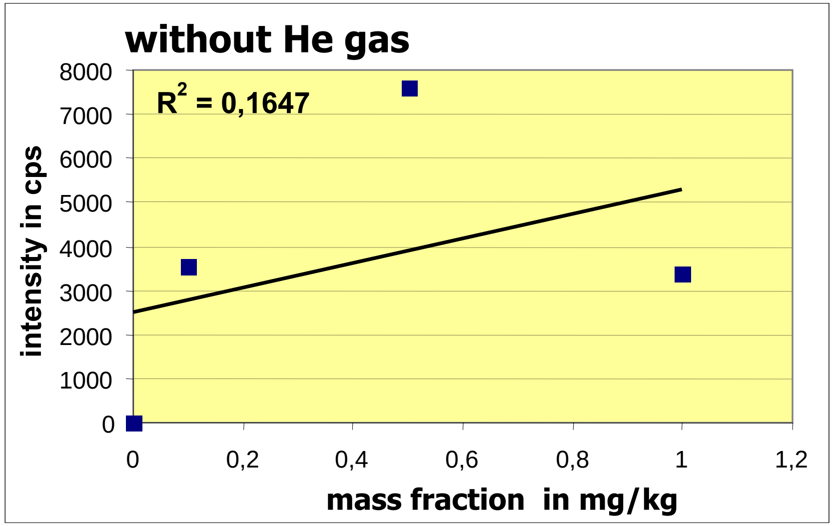
60 mA
355 ml/min Ar

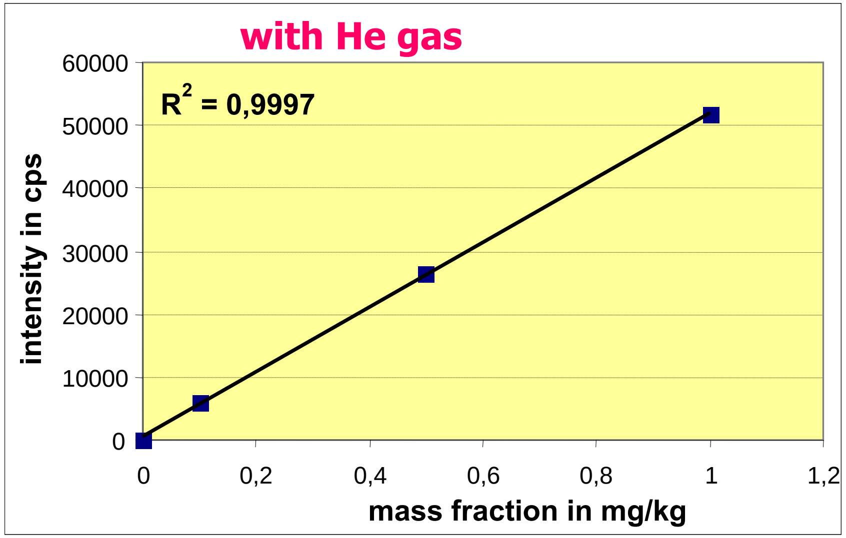
- increase of slope
- absolute sensitivity higher (nearly factor three)
- calibration points meet the straight line

Comparison of calibration curves based on doped pressed powder pellets (5 µg/kg …1000 µg/kg) with and without He discharge gas

sulphur in copper matrix







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    - o Matrix copper
    - o Matrix iron
  - Traceable results for non-metallic analytes
- **Conclusions**

Conclusion I

- **The necessity of Primary Pure CRMs as National Standards for Elemental Analysis is evident**

- **The BAM system of such materials is in progress together with a system for national dissimination (in co-operation with PTB)**

- **The materials will be only be distributed to NMIs or signatories of MRA**

Conclusion II

➢ **GD-MS is a powerful tool for multielement ultra-trace determination of metallic analytes and – using Ar/He mixtures as plasma gas - also for non-metallic analytes**

➢**The new ELEMENT GD spectrometer combined with the special preparation and application of doped pressed powder pellets offers an important completion to achieve traceable results for Primary Pure CRMs and other high purity metals**

The authors say many thanks to all concerned colleagues from BAM for their valuable contributions

...and thank you for your attention!