Hohlkathode in Kombination mit einer Grimmschen Glimmentladung zur Spurenanalyse von Reinstmetallen

T. Gusarova, V.-D. Hodoroaba, H. Kipphardt, R. Matschat, U. Panne (BAM, Berlin)

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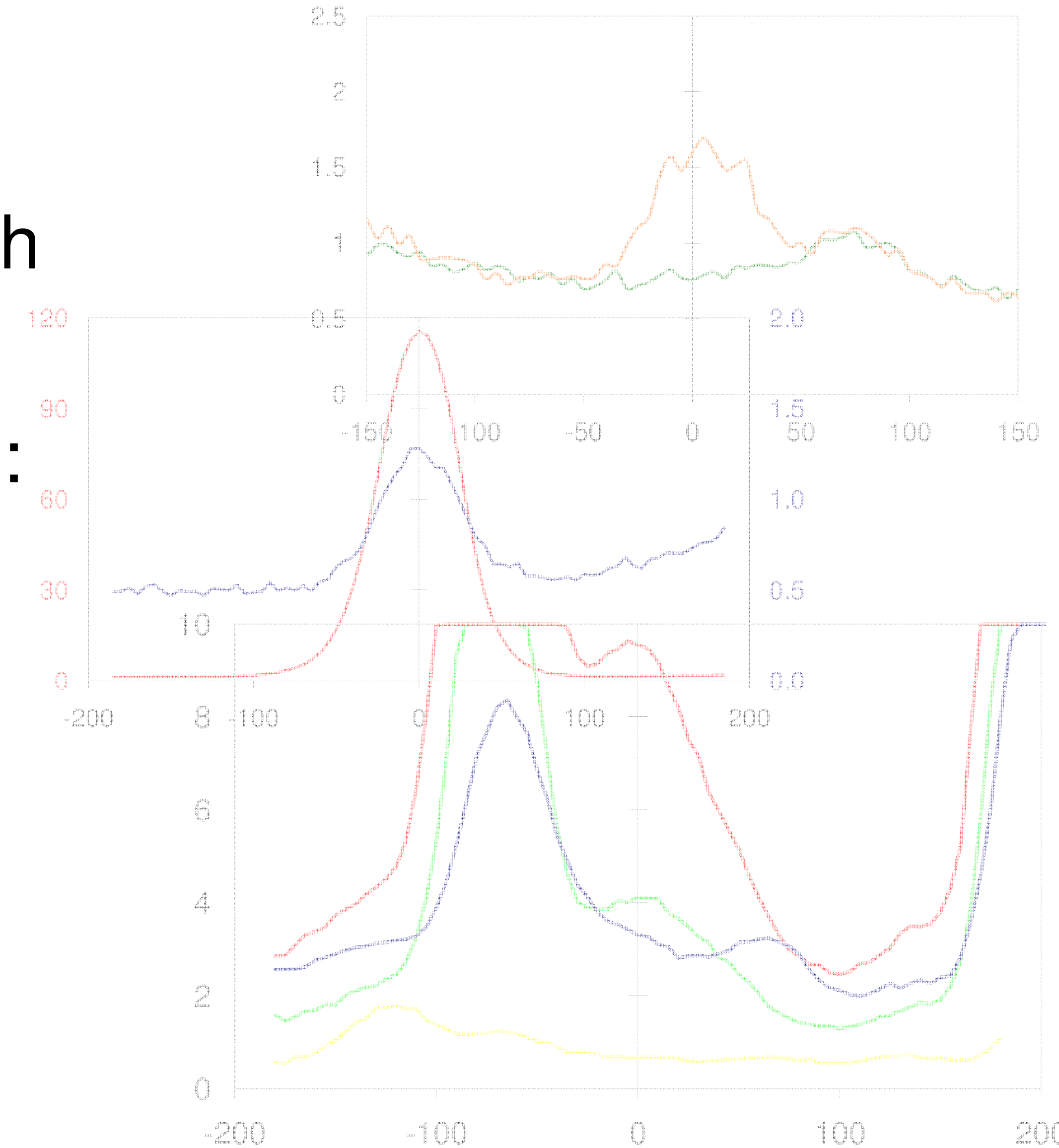


Motivation

- PTB – pure metals for definition of the fix points of the international temperature scale (Zn, In)
- Consistency check of the GD-MS results
- Grimm-type GD-OES – high limits of detection rel. to GD-MS

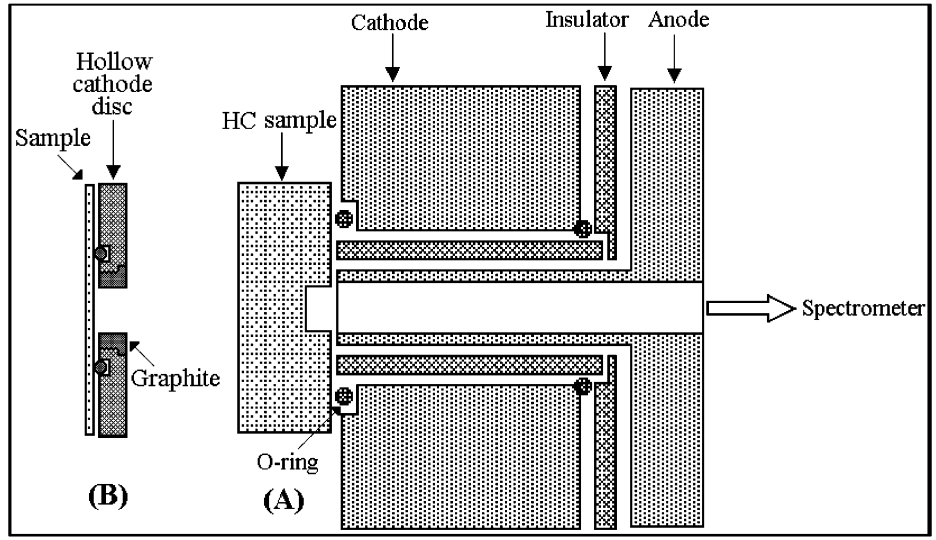
Hollow cathode effect + Grimm-type GD-OES

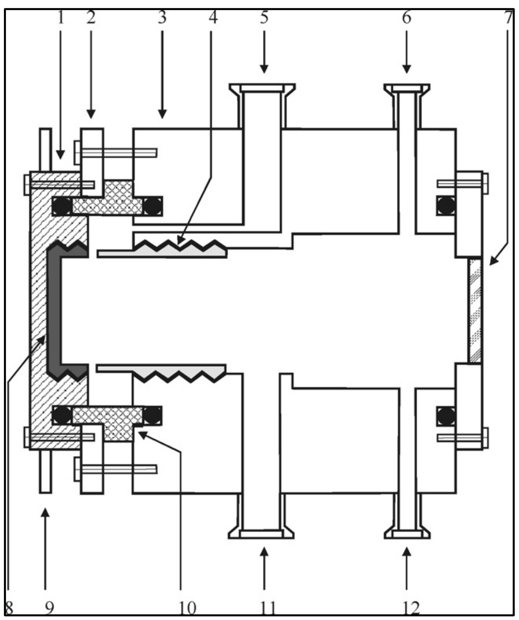
Previous research

- C. Yang, W.W. Harrison

Spectrochimica Acta Part B56 (2001), 1195-1208

  - Pulsed GD-AES; 10 µs, 1.8 kV, 3-torr
  - Cavity Ø 3 mm x 2 mm
  - Cu atomic and ionic lines enhancement (up to factor 18)



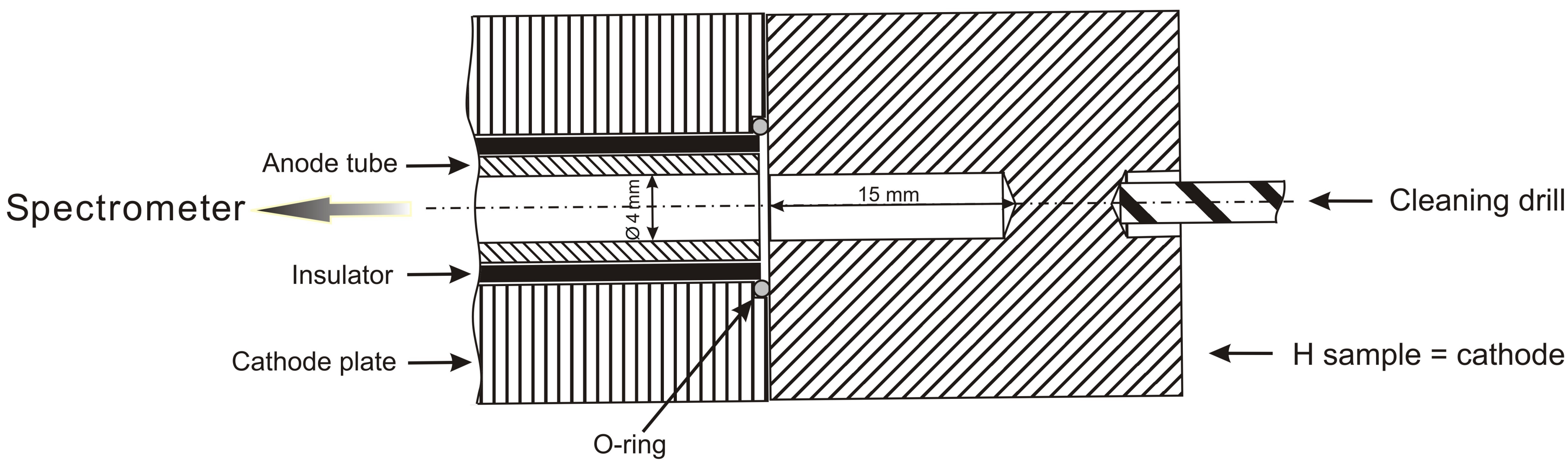


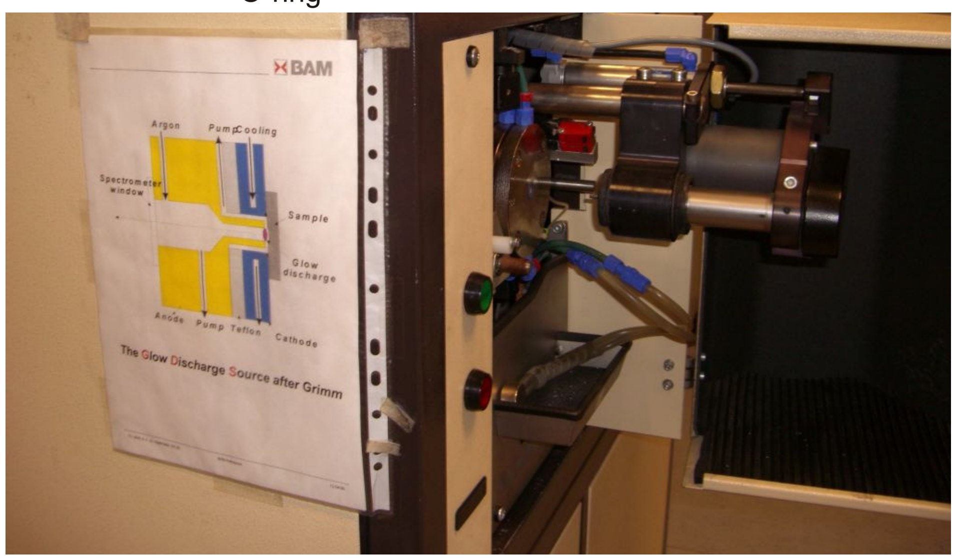
- A. Qayyum, M.I. Mahmood

Analytica Chimica Acta 606 (2008), 108-111

  - DC Grimm GD-AES; 130 mA, 400V, 4mbar
  - Cavity Ø 6 mm x 2.5 mm, water cooled
  - Cu atomic and ionic lines enhancement (up to factor 3) at about half of the input electrical power as compared to planar cathode

Grimm-type GD-OES with hollow cathode configuration

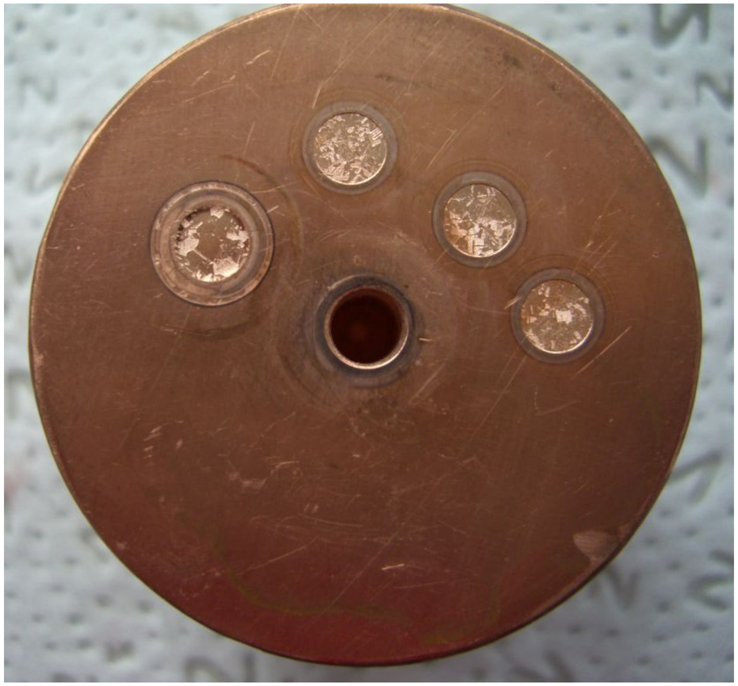




LECO SDP-750

GD-OES: Cu matrix

Preheating of the H-sample at 300 V and 270 mA for better plasma ignition



H-sample = hollow cathode sample
P-sample = planar sample

CRMs	Plasma parameters	
BAM-M381; BAM-M382; BAM-M383; BAM-M384; ERM-EB385; ERM-EB386	P-sample usual P-sample = H-sample H-sample optimal P-sample maximal	700 V 20 mA 380 V 118 mA or 300 V 50 mA 450 V 250 mA 500 V 100 mA

GD-OES: Cu matrix
P-sample parameter optimisation

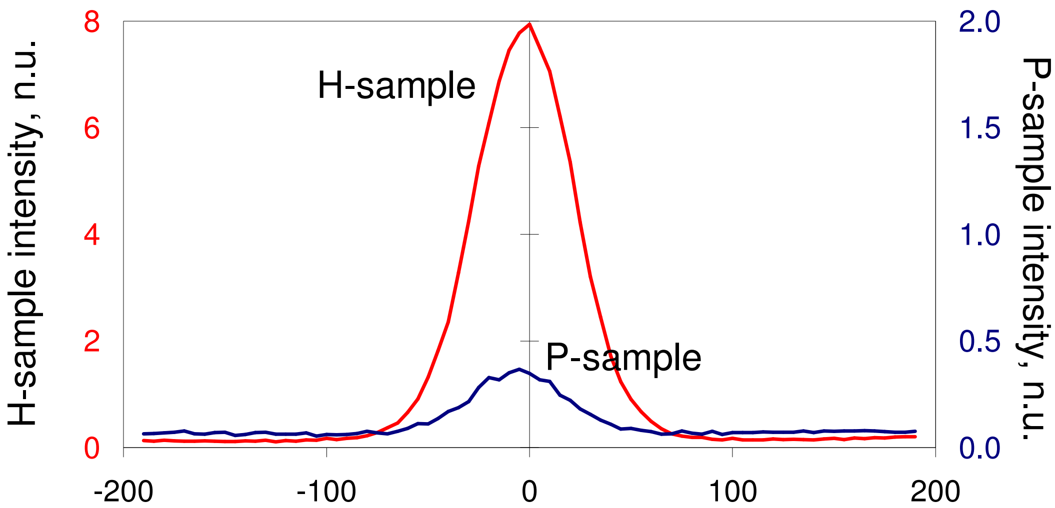
ERM-EB386 (with 29.1 mg·kg^{-1} Mg)
SBR = Signal to background ratios of the magnesium line 383.83 nm

		Voltage, V			
		500	700	900	1100
Current, mA	20	SBR=0.39	SBR=0.34*)	SBR=0.38	unstable
	50	SBR=0.55	SBR=0.60	SBR=0.63	unstable
	100	SBR=0.73**)	SBR=0.66	unstable	unstable

*) Parameters normally used for copper sample analysis ("P-sample usual")
**) Optimal parameters found ("P-sample maximal")

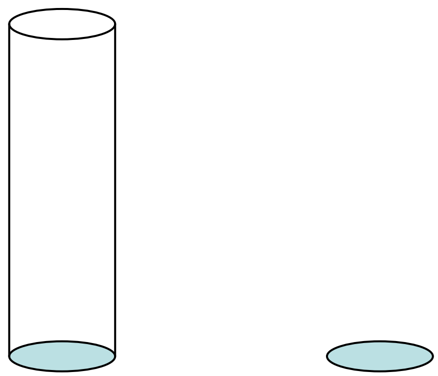
GD-OES: Cu matrix

Si atomic line (λ=288.157 nm) in ERM-EB386 (14.3 mg·kg^{-1} Si)



300 V, 50 mA
for H- and P-sample

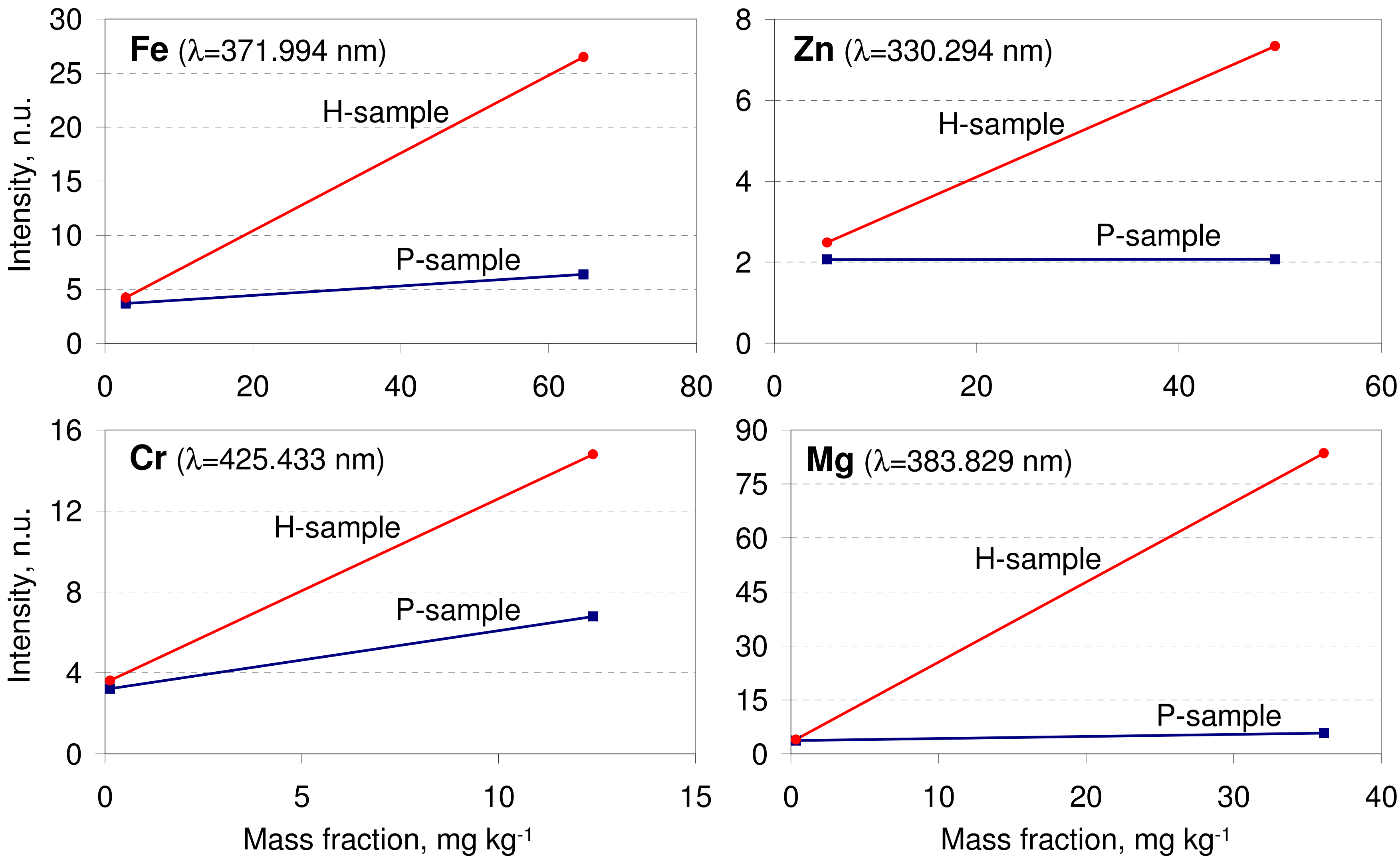
Signal enhancement of about factor of **25**



Surface magnification (H/F)
= only factor 16

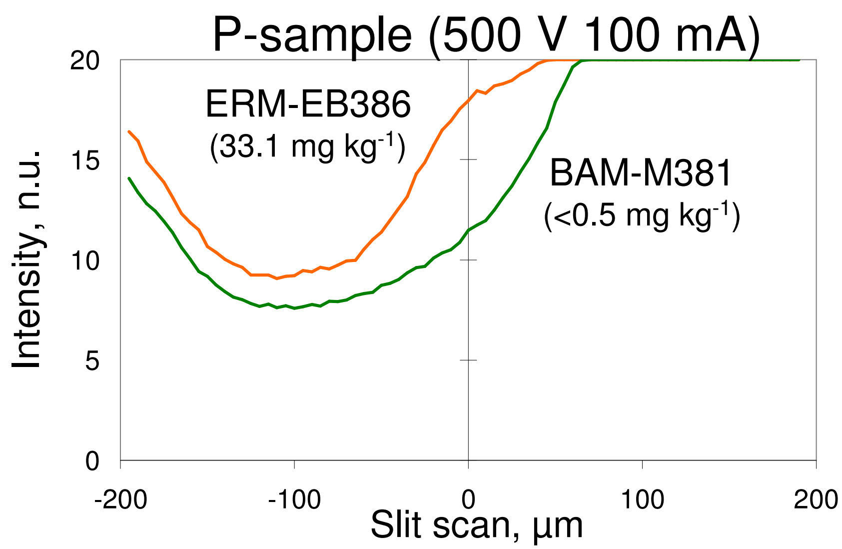
GD-OES: Cu matrix

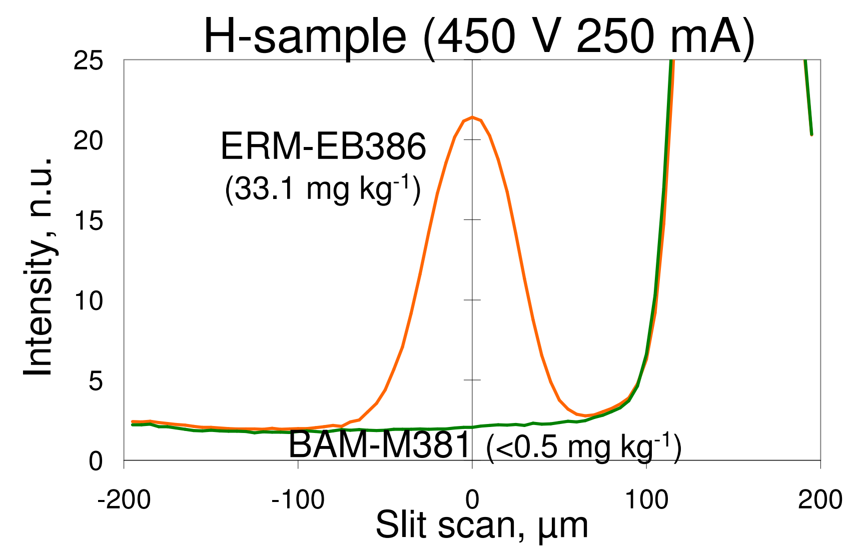
Calibration curves (380 V, 118 mA)

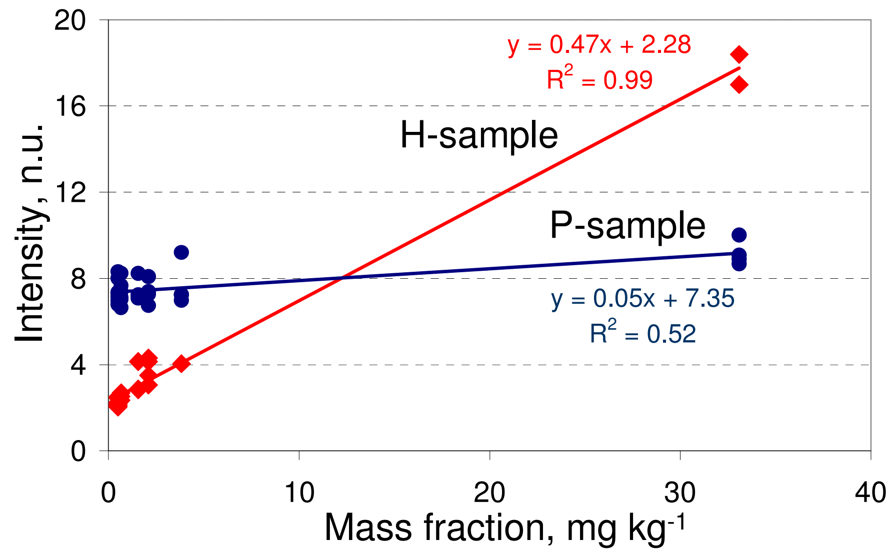


GD-OES: Cu matrix
Better separation from spectral interferences

Ti atomic line (λ=365.350 nm)

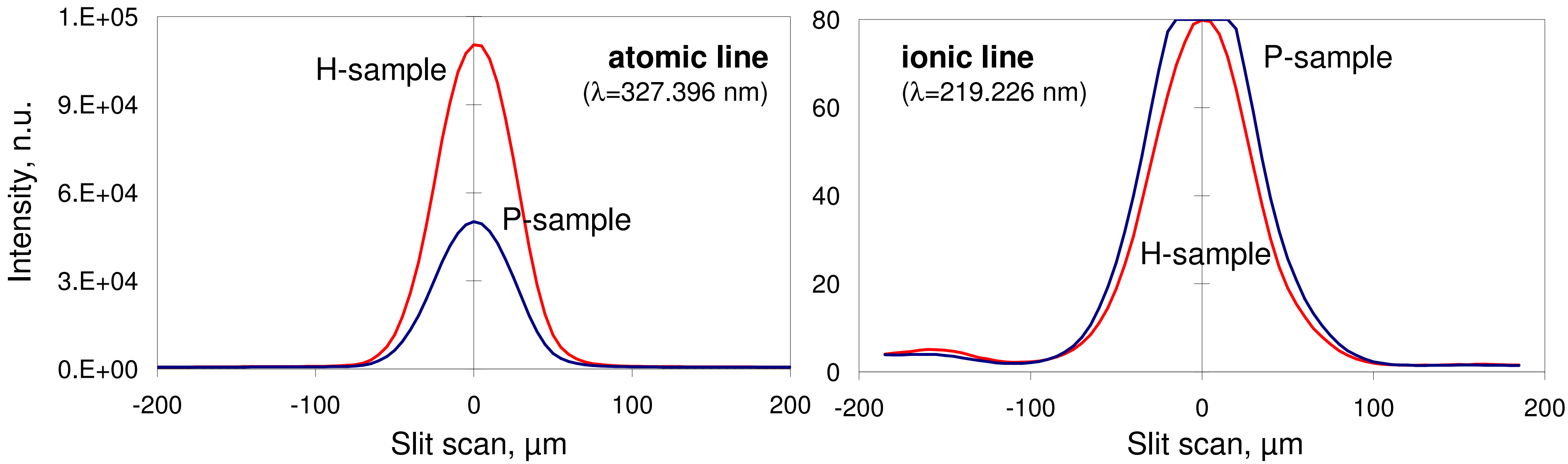






GD-OES: Cu matrix
Enhancement of atomic line intensity and rather reduction of ionic line intensity

Spectra of copper atomic and ionic lines of ERM-EB386 (300 V 50 mA)



Pressure (380 V 120 mA):
H-sample 0.0269 mbar
P-sample 0.0931 mbar

Penning ionization: $S + Ar^{*} \rightarrow S^{+} + Ar^{+} + e^{-}$

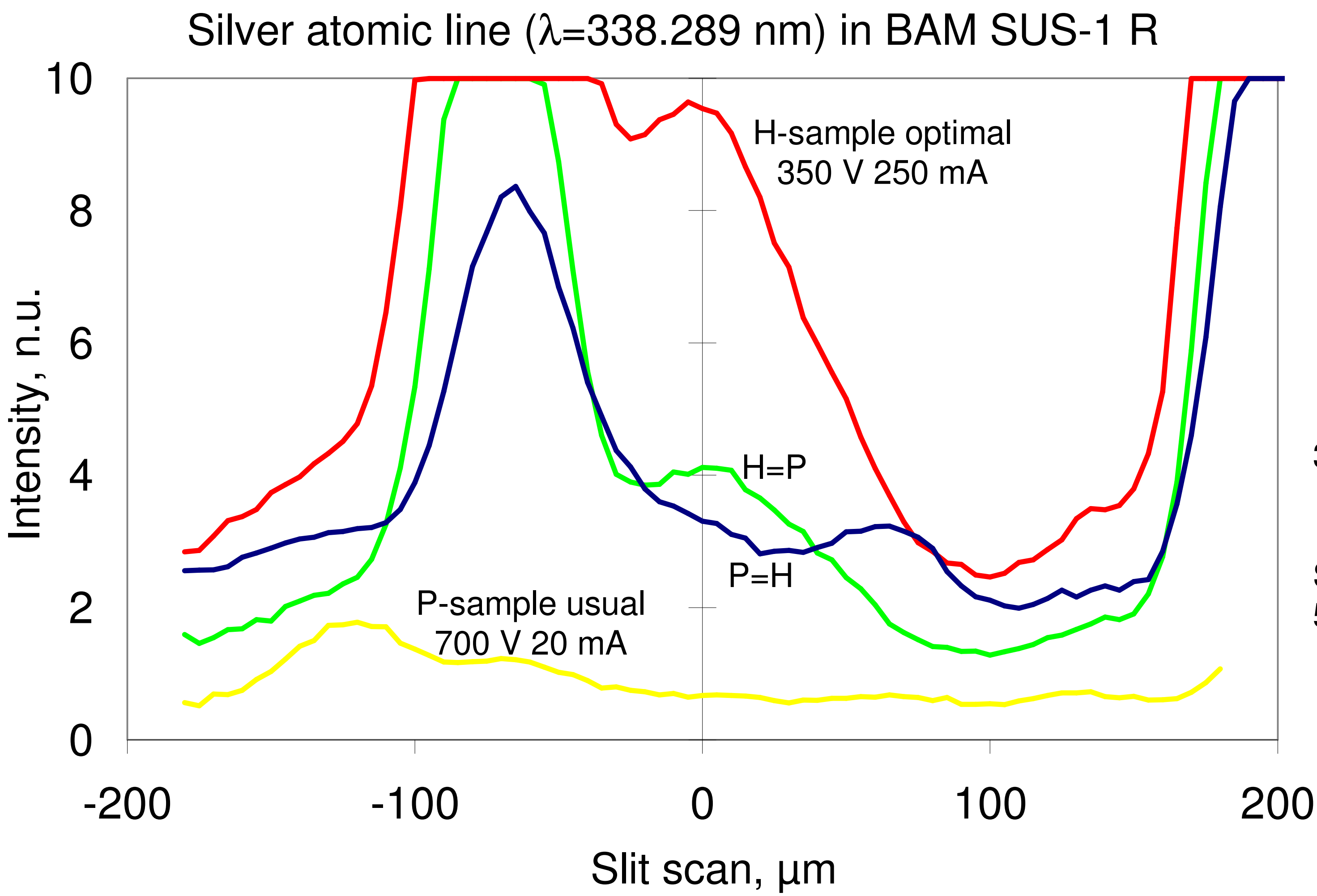
GD-OES: Steel matrix

Element	Certified value
Fe	matrix
Cu	0.7 %
Ni	2.9 %
Cr	1.7 %

CRMs	Plasma parameters	
BAM SUS-1 R	P-sample usual H-sample optimal Same power P-sample Same power H-sample	700 V 20 mA 350 V 250 mA 500 V 102 mA 300 V 170 mA

} 51 W

GD-OES: Steel matrix
Comparison at different parameters



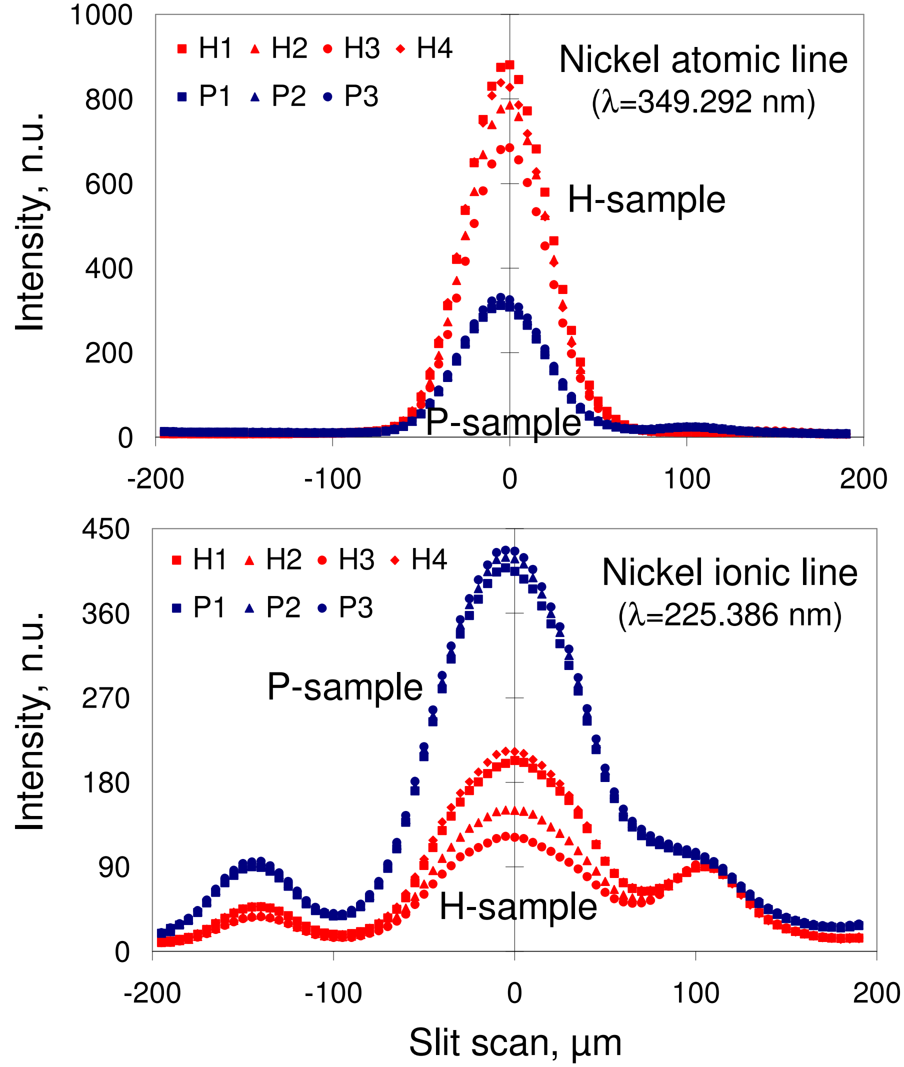
H=P
Same power H-sample
300 V, 170 mA

P=H
Same power P-sample
500 V, 102 mA

GD-OES: Steel matrix
Enhancement of atomic line intensity and rather reduction of ionic line intensity

H1, H2, H3, H4 – 1-4 independent measurements of H-sample at 300 V 170 mA
Pressure spread 11 %

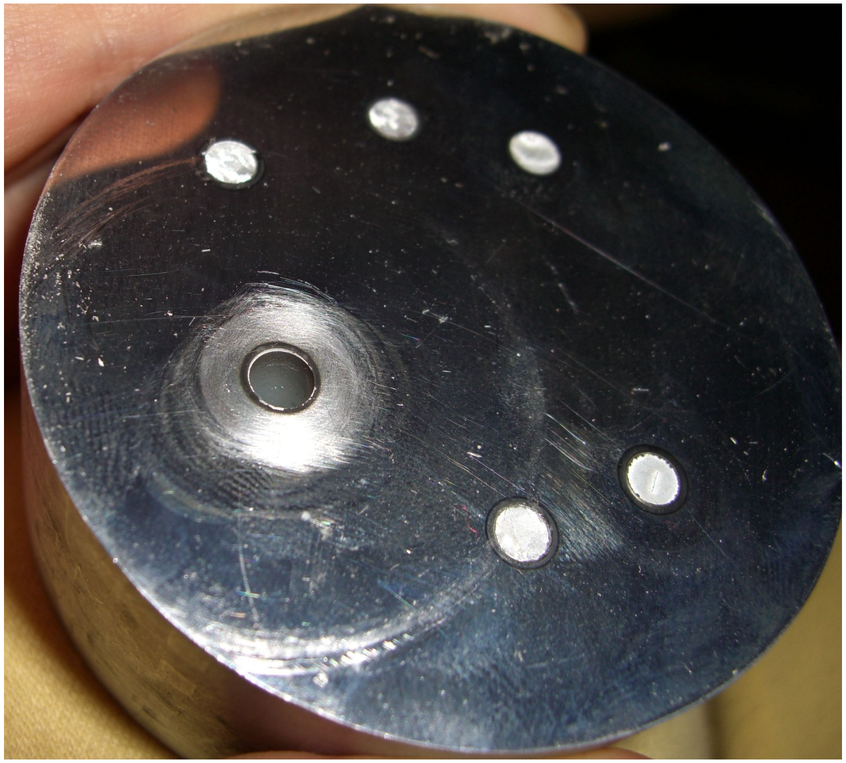
P1, P2, P3 – 1-3 independent measurements of P-sample at 500 V 102 mA
Pressure spread 0.5 %



GD-OES: Zn matrix

BAM

Preheating of the H-sample at 300 V and 80 mA for better plasma ignition



CRMs	Plasma parameters	
BAM-M601; ERM-EB322; ERM-EB323; ERM-EB324	P-sample usual P-sample = H-sample H-sample optimal	700 V 20 mA 300 V 50 mA 330 V 250 mA

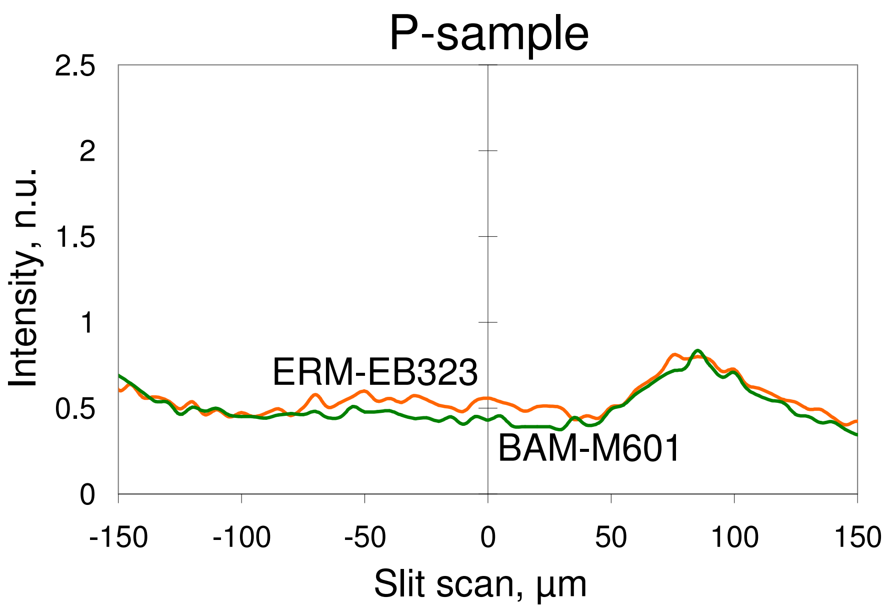
GD-OES: Zn matrix
Signal enhancement

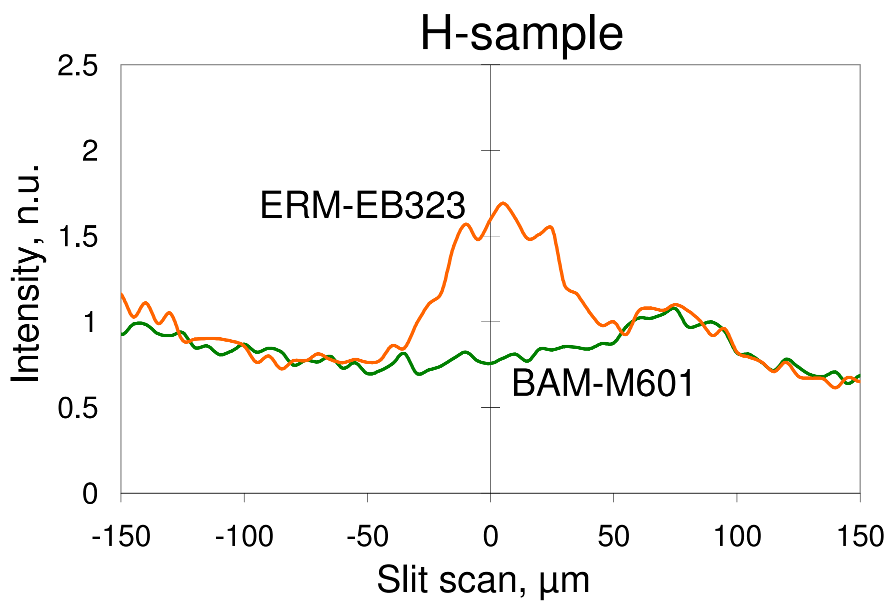
Comparison of SBRs (signal to background ratios)
for certified elements obtained for P- and H-sample measurements
at the same and at the optimal parameters

Sample	**Parameter**	H-/P-sample	**Cu**	**Cu2**	**Fe**	**Fe2**	**Pb**	**Sn**	**Sn2**	**Zn**
ERM-EB324	300 V 50 mA	H	2	1	0.3	0	0	2	0	2
	300 V 50 mA	P	1	1	0.1	0	0	2	0	1
SBR Relationschip H-sample/P-sample			**3**	**1**	**4**	**-**	**-**	**1**	**-**	**2**
ERM-EB323	330 V 250 mA	H	26	1	7	2	1	5	0.2	3
	700 V 20 mA	P	2	1	1	9	0.2	10	0.1	2
SBR Relationschip H-sample/P-sample			**16**	**1**	**11**	**0.2**	**6**	**0.5**	**3**	**2**

GD-OES: Zn matrix
Lower limits of detection

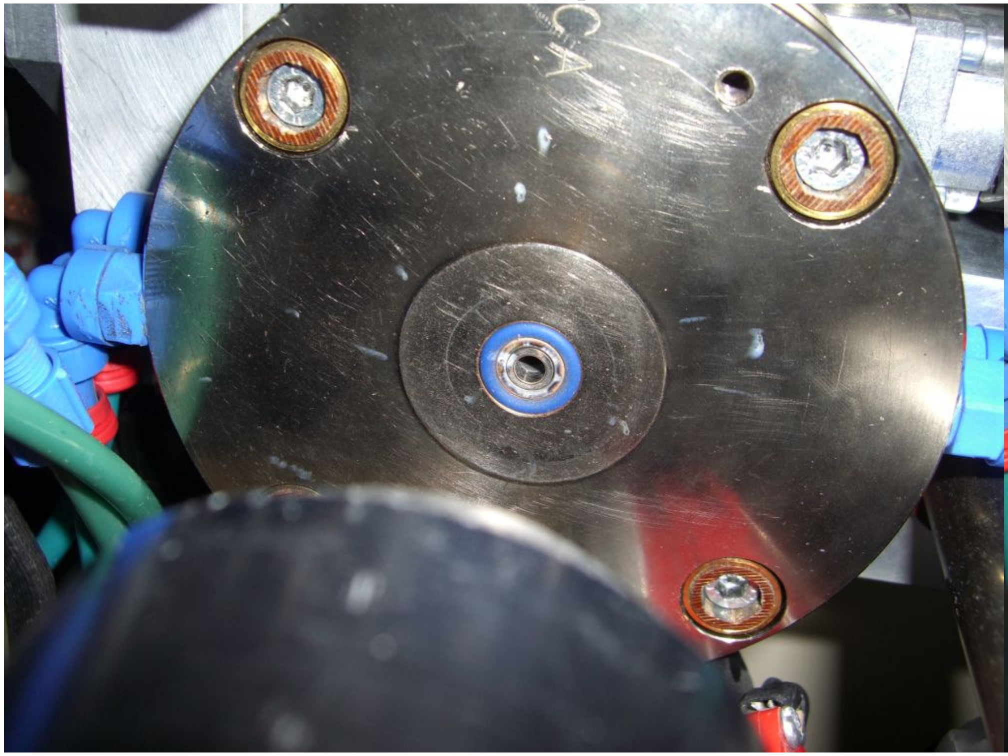
Nickel atomic line (λ=349.292 nm) in BAM-M601 and ERM-EB323



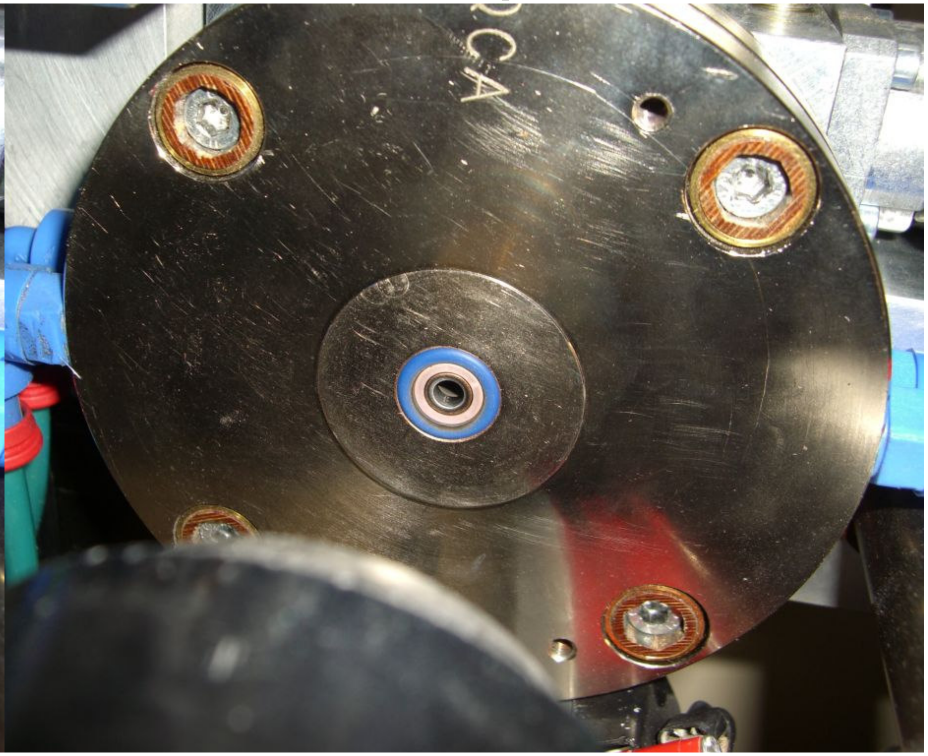


Sputtering

P-sample

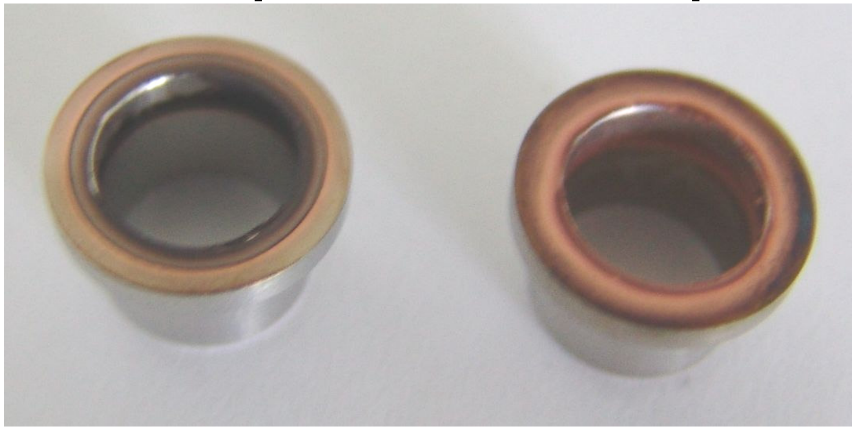


H-sample



GD-MS: Cu matrix

H-sample **P-sample**



Conclusions

H-sample in comparison to P-sample:

- ✓ Signal enhancement; same background level – high SBRs
- ✓ Better separation of spectral interferences

"Use of the hot hollow cathode effect for sensitivity enhancement of Grimm-type DC Glow Discharge Optical Emission Spectroscopy"
T. Gusarova, V.-D.-Hodoroaba, R. Matschat, H. Kipphardt and U. Panne

- ✓ Lower sputtered material deposition also in GD-MS. Lower Intensities than by P-sample measurement

Improvement of the Grimm-type GD-OES (signal enhancement up to factor 150) without additional construction changes of the commercial instrument - easy replacement of P- and H-samples without productivity losses is ensured.

Thank you for your attention

GD-OES: Steel matrix