Effect of Pulsing on Hydrogen Analysis with GD-OES

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Content

- Instrumental and pulsing parameters used
- Depth profiles in coated steels, where H is present
- Variations in H signal/background as a function of pulse and source parameters
- Some further observations related to H and background signals
- Variation in signal/background of a few other elements and spectral lines
- Discussion and Conclusions

Instrumental parameters

- Leco GDS 850 GD-OES spectrometer with dual 75 cm polychromators.
- RF source operated in constant true power (TP) – constant voltage mode by active pressure regulation.
- RF source pulsed by means of custom-made electronics and an external function generator generator.
- Pulse frequencies 30 and 1000 Hz, duty cycle 50%.

- Additional work using a Spectruma GDS 750 GD-OES spectrometer; RF source operated in constant voltage – constant pressure mode; pulse frequency 30 – 3000 Hz, pulse duty cycle 20 - 80%.

Main spectral lines used

H 121,5 nm

O 130,2 nm

C 156,1 nm

P 177,5 nm

Zn 330,3 nm

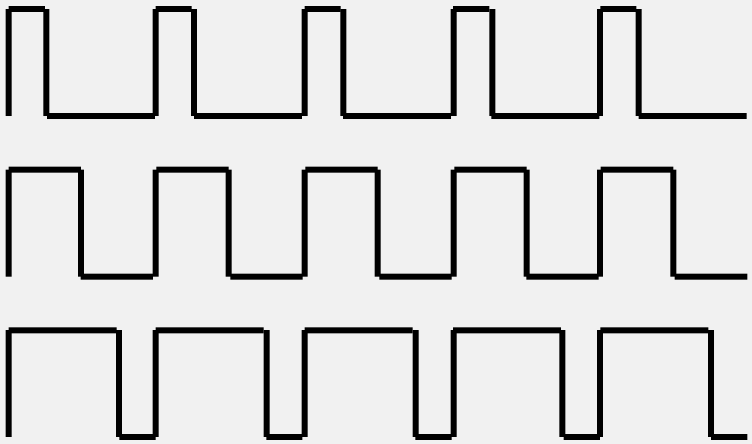
Fe 249,3 nm

Si 288,2 nm

Mo 386,4 nm

Cu 327,4 nm

Pulse parameters to vary….



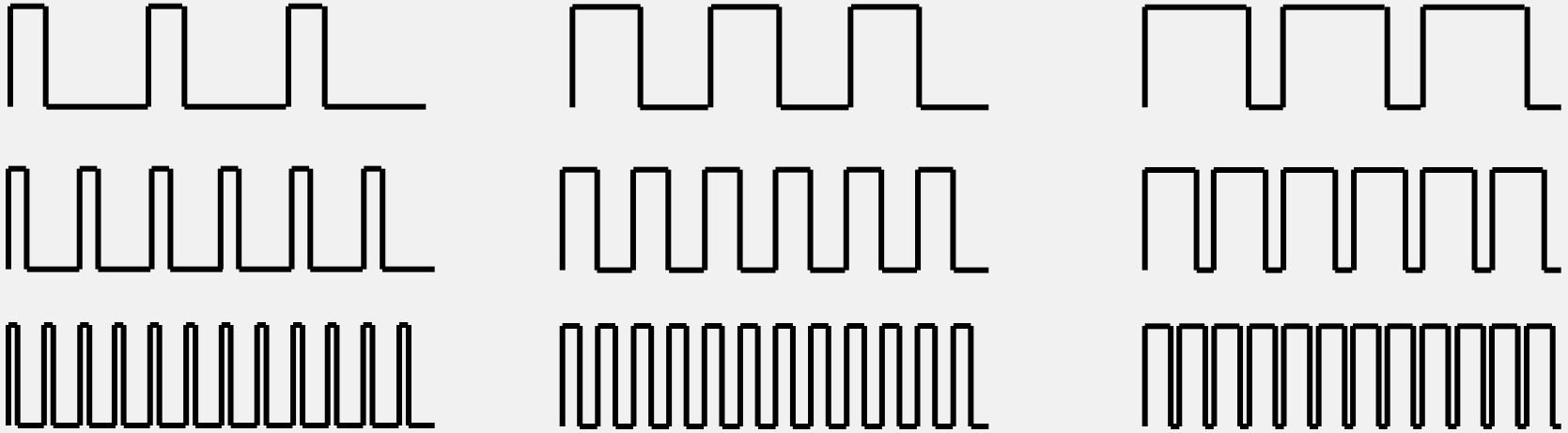
Duty cycle 25%

Duty cycle 50%

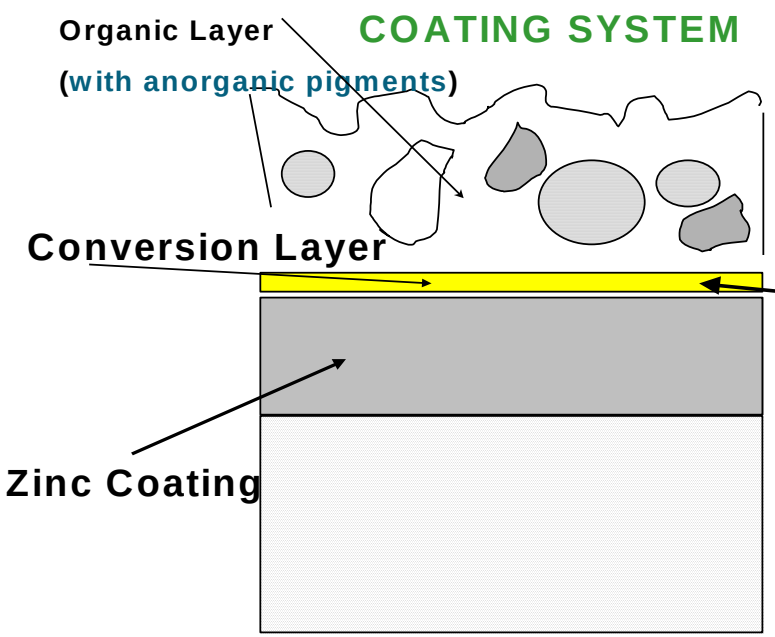
Duty cycle 75%

The higher the duty cycle, the higher the average power and the temperature of the sample

Pulse length can also be varied by pulse frequency at constant duty cycle



Coated steel sheet ”Gardoprotect (GP)”



2 Coating Systems:

a) Zn (pure)

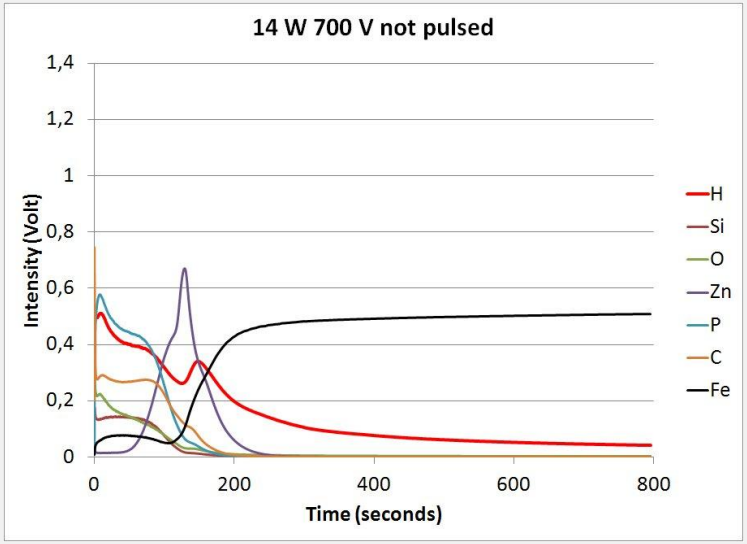
b) Fe-Phosphid

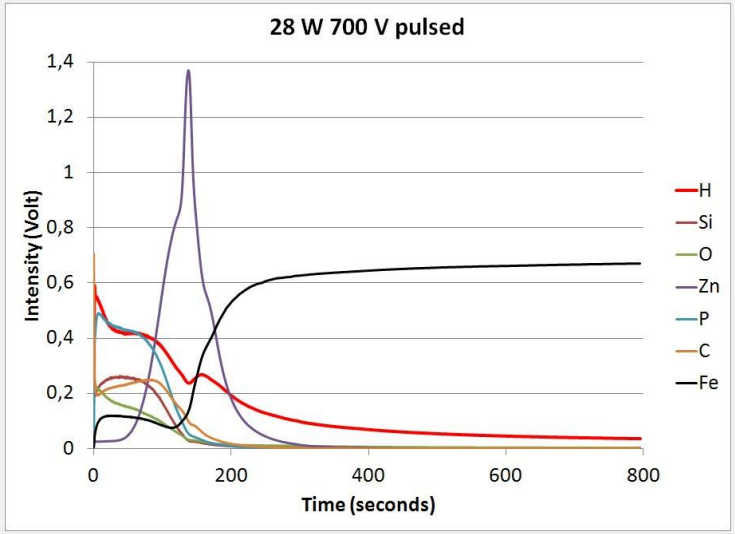
Ti, Mn, Zr (chromate-free conversion layer)

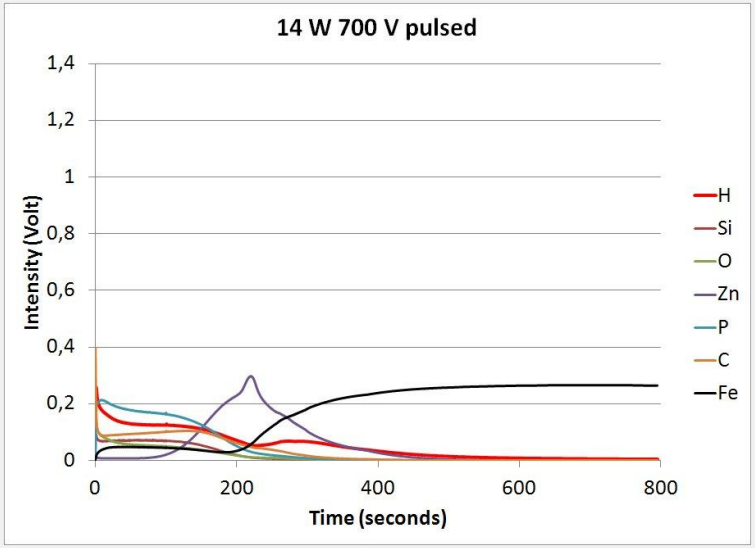
Experimental conditions for work on the coated steel samples with the Leco GDS 850

- RF conditions: 14W and 28W (TP), 700V by pressure regulation.
- Duty cycle: 50%
- Frequencies: 30 and 1000 Hz
- At 14W RF power, the average power is reduced to 7W in pulsed mode.
- At 28W RF power, the average power stays at 14W in pulsed mode.
- By retaining the RF voltage at 700V, the electrical parameter that changes with the power is the effective current, which doubles from 20 to 40 mA.
- The reason to only vary the current is 1) to simplify the interpretation of the results 2) It is well known that the current increases the emission yield for most analytical spectral lines, while the voltage generally has the opposite effect.

Time – intensity depth profiles at 14 W and 28 W; 700 V; pulsed at 1000 Hz

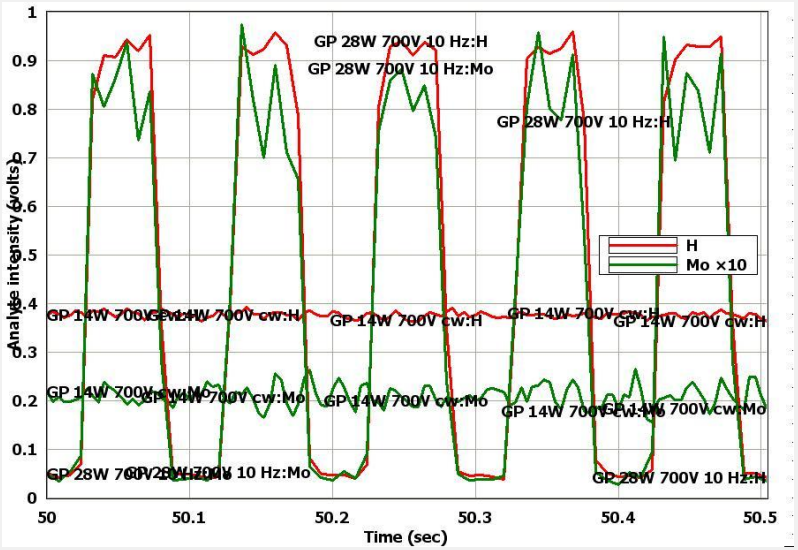


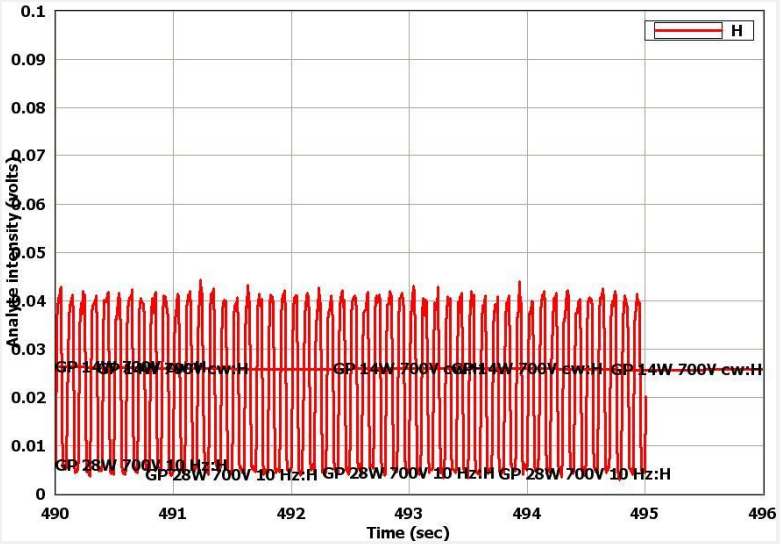




ThyssenKrupp Steel Europe

Some details of the effect of pulsing at constant average power of 14 W and constant voltage at 700 V (10 Hz)





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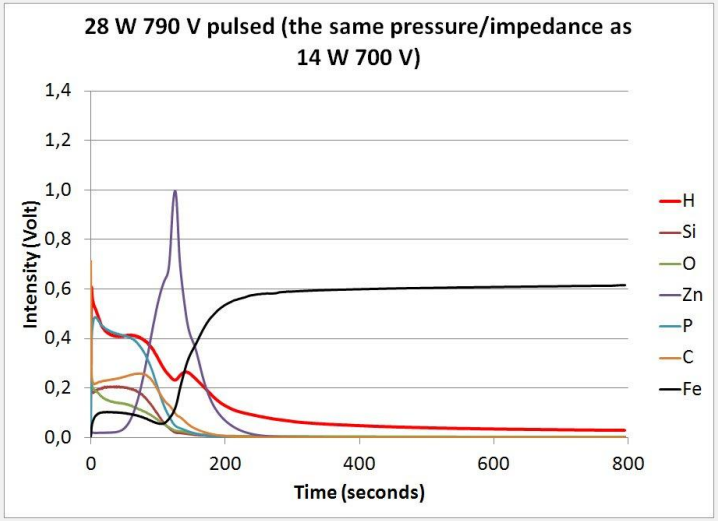
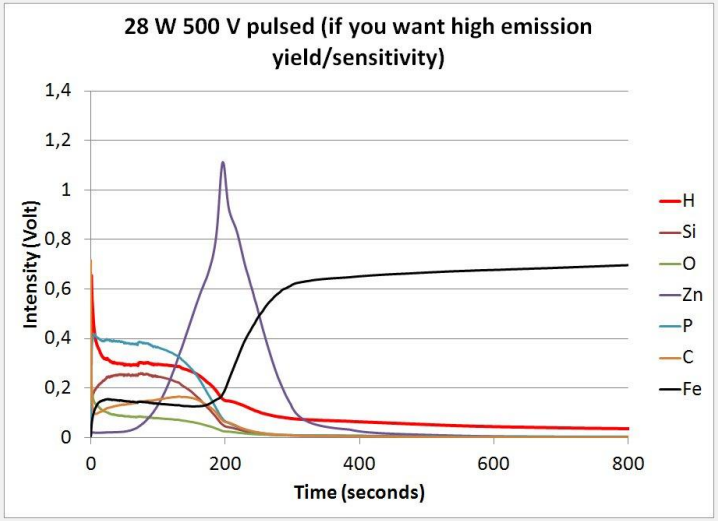
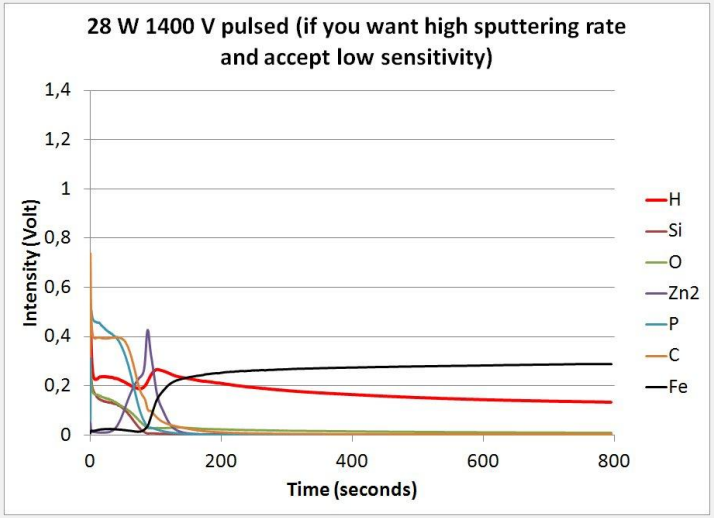
Time – intensity depth profiles at 14 W and 28 W; Varying voltages; pulsed at 1000 Hz







Comments: At 500 V, the H profile looks more ”credible” in shape.

At 1400 V, the H profile is a disaster!

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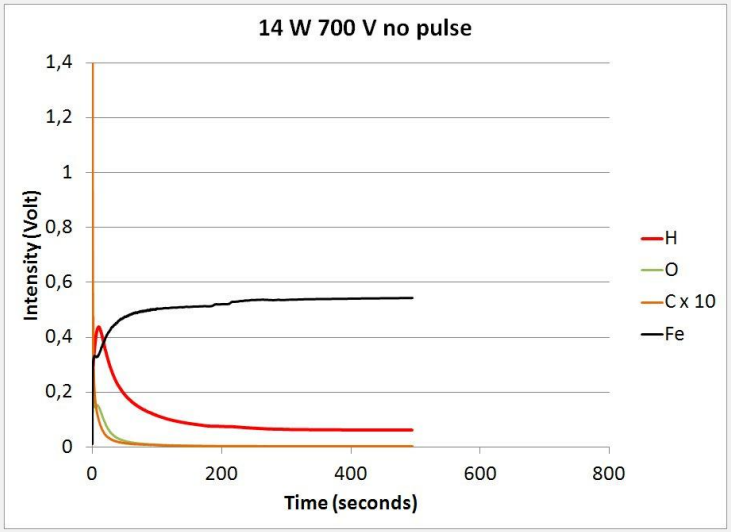
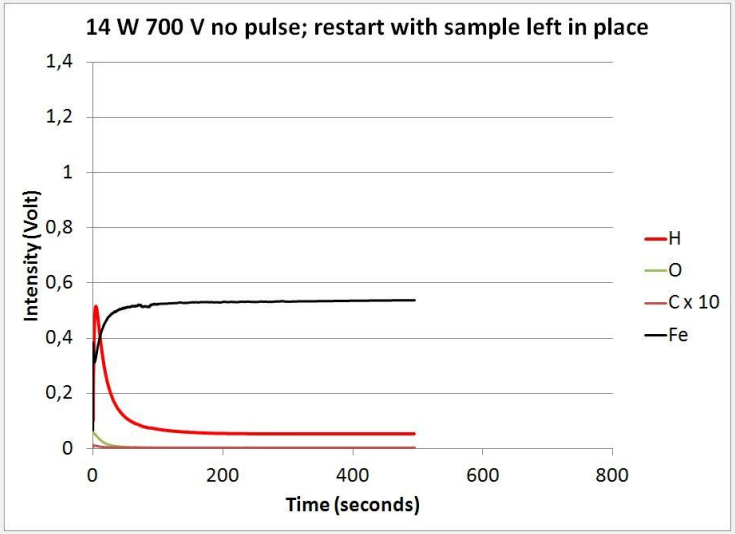
Background signals in high purity iron (hydrogen free!)





The initial H background is substantial – and you can't get rid of it!

On restart in the same spot, the O background is significantly reduced,
the C background almost disappears – but the H signal is nearly unchanged!

Conclusion: The H background is not from pump oil or other hydrocarbons.
It can be water, the initial O background probably comes from both surface oxide and/or organic contamination as well as water.

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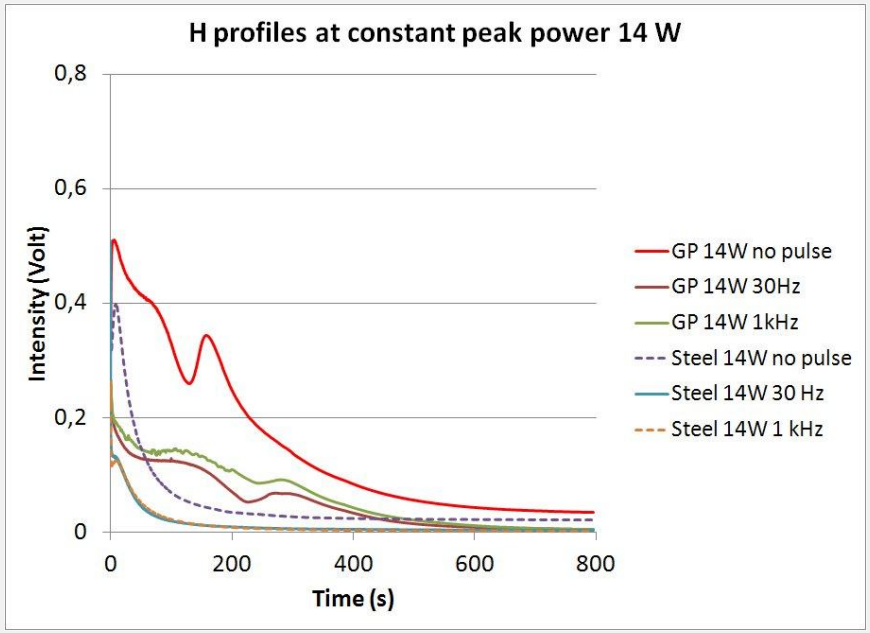
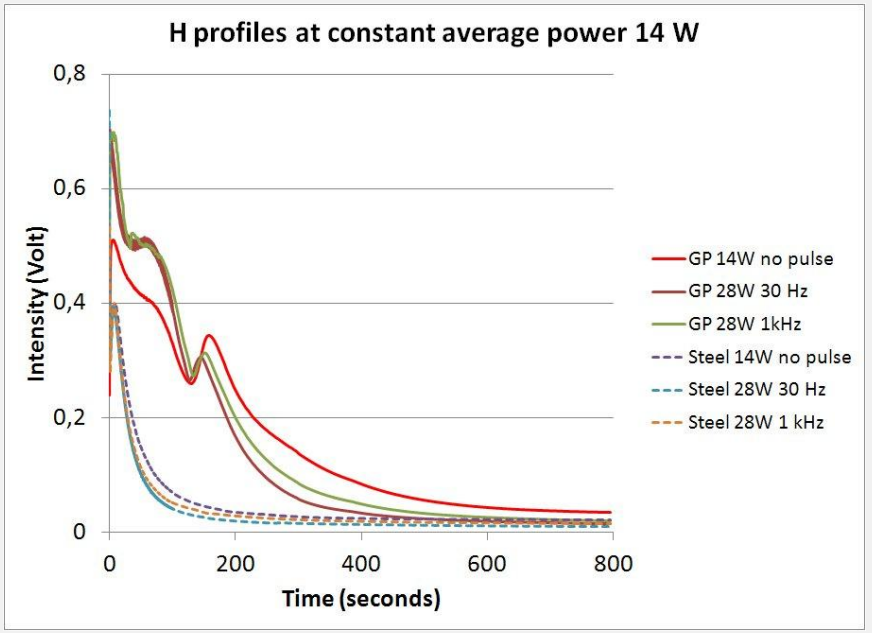
H profiles in Gardoprotect and steel at different power/pulse conditions

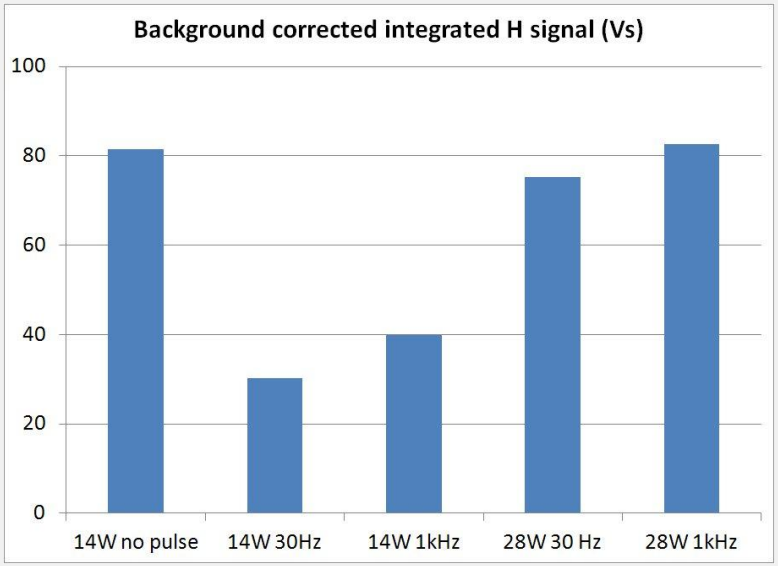


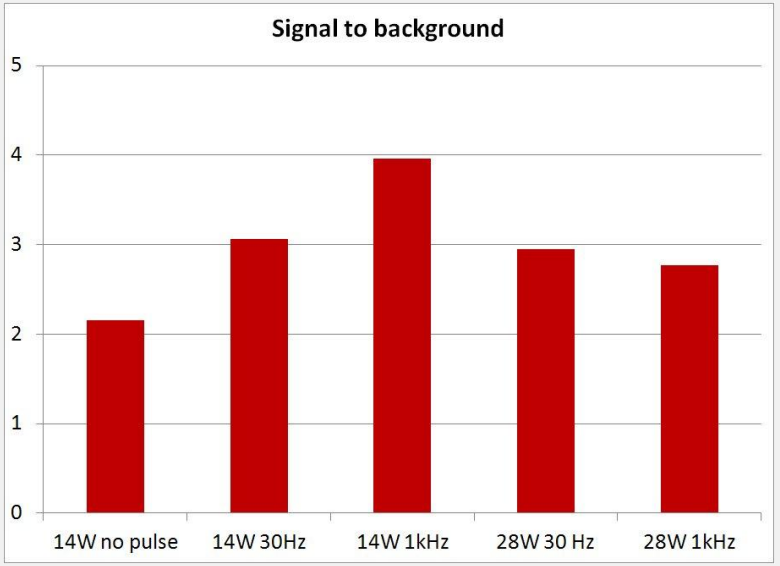


On ”visual inspection”, it appears that the backgrounds are reduced to a larger extent than the signal when pulsing the source.

At constant average power, pulsing gives slightly increased peak signal.

H signal to background in Gardoprotect coating

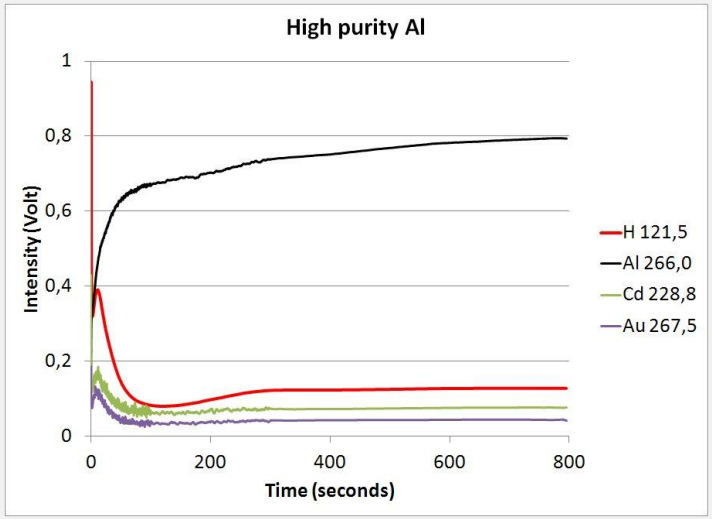


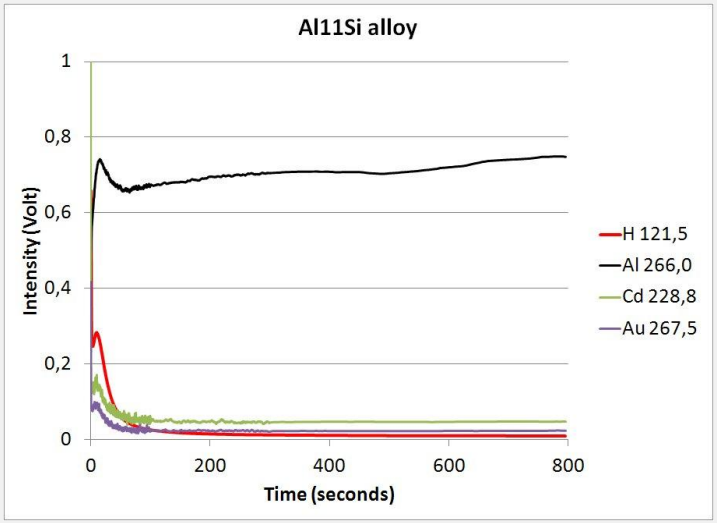


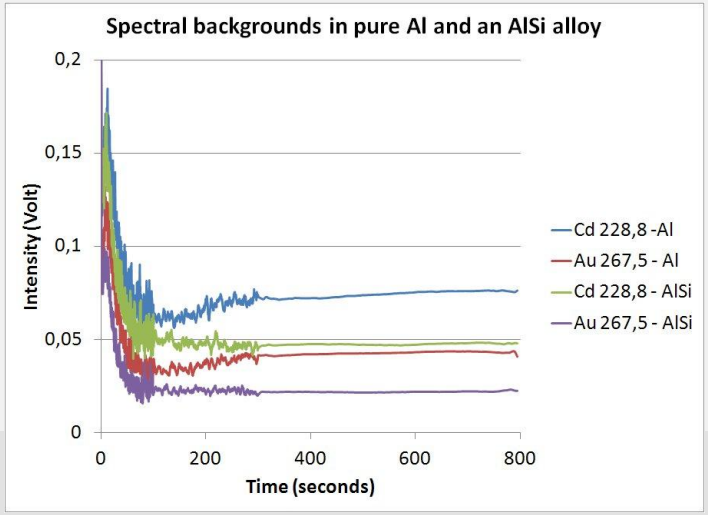
The background is here defined as the integrated background from the low alloy steel sample.

Pulsing gives a slightly improved signal/background ratio, but ”slow” or ”fast” pulsing seems to make little/inclonclusive difference.

Background of H and other elements in a pure Al and an AlSi alloy







-There are no measurable traces of H, Cd and Au in these materials (by GD-OES).
-Line overlap from Al cannot explain the higher backgrounds in pure Al.

The key to both the unusually high H signal and spectral backgrounds in pure Al?

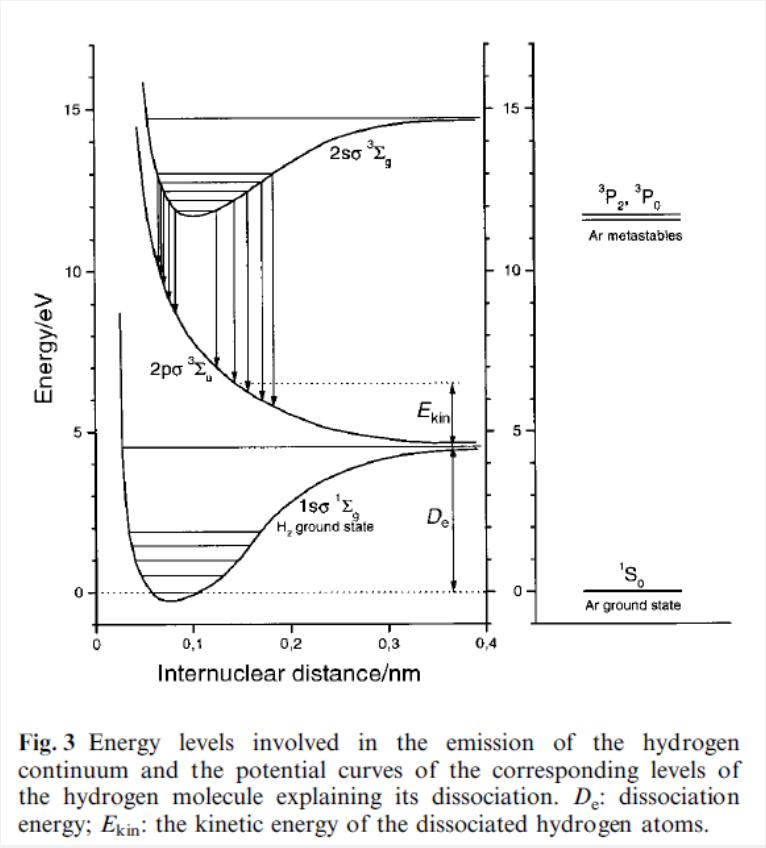


Fig. 3 Energy levels involved in the emission of the hydrogen continuum and the potential curves of the corresponding levels of the hydrogen molecule explaining its dissociation. D_e: dissociation energy; E_{kin}: the kinetic energy of the dissociated hydrogen atoms.

-Dissociating hydrogen molecules emit optical emission over a wide spectral range in the UV - VIS region.

-The process also puts more H atoms into the plasma.

-The observations can thus be understood if pure Al "catalyses" the H2 dissociation process.

From V.-D. Hodoroaba, V. Hoffmann, E. B. M. Steers, K. Wetzig, Investigations of the effect of hydrogen in an argon glow discharge, *J.Anal.At.Spectrom.*, 2000, **15,** 1075.

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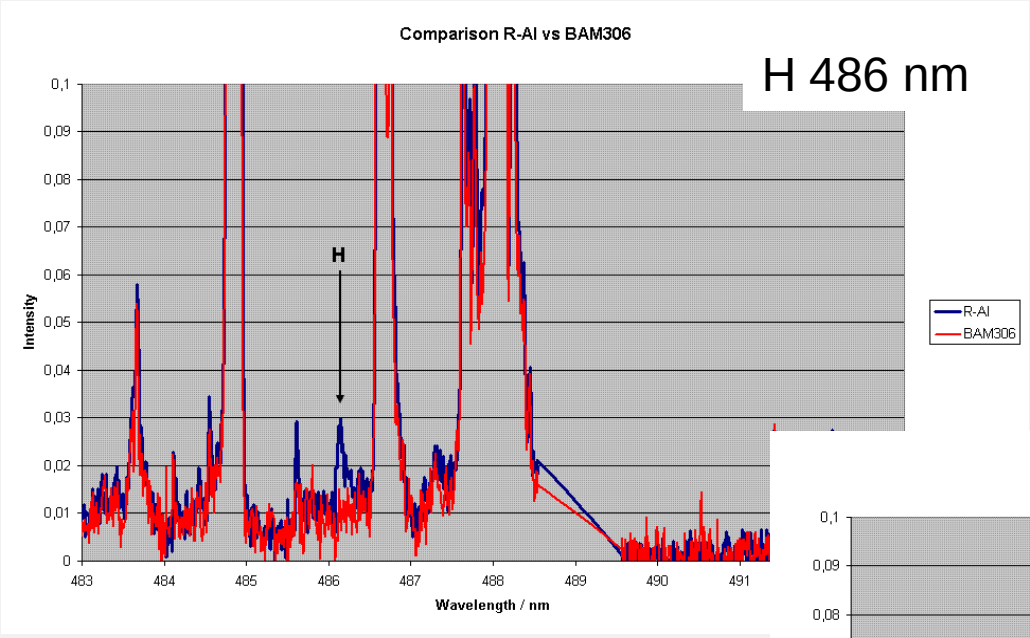
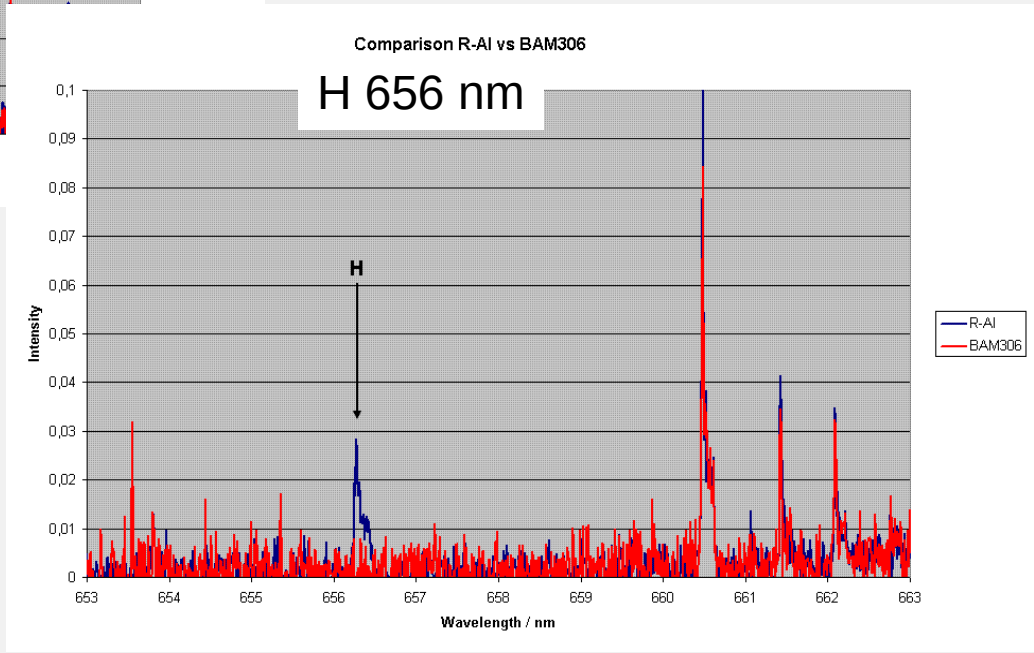
Hydrogen in pulsed GDOES….
…some extras

Hydrogen in Aluminium

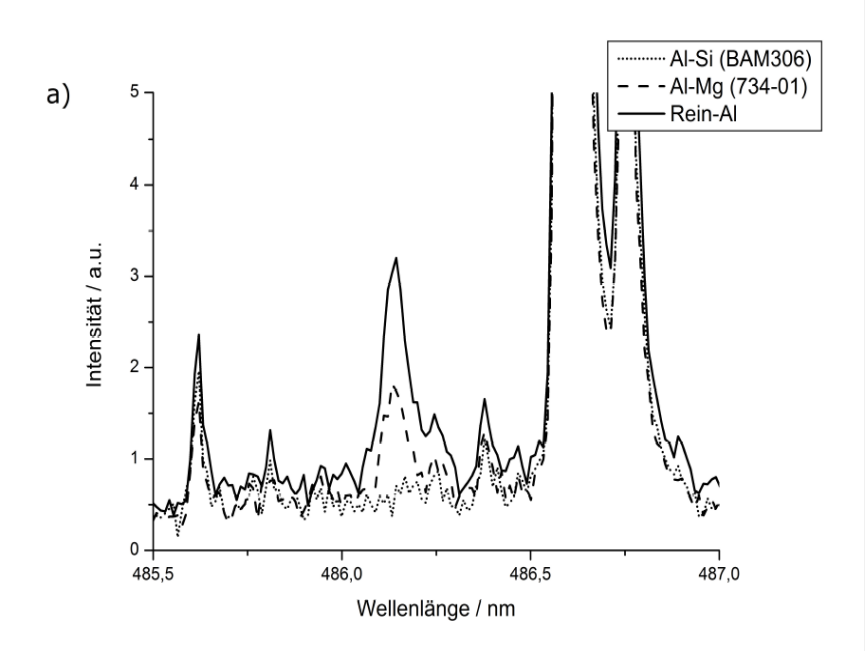


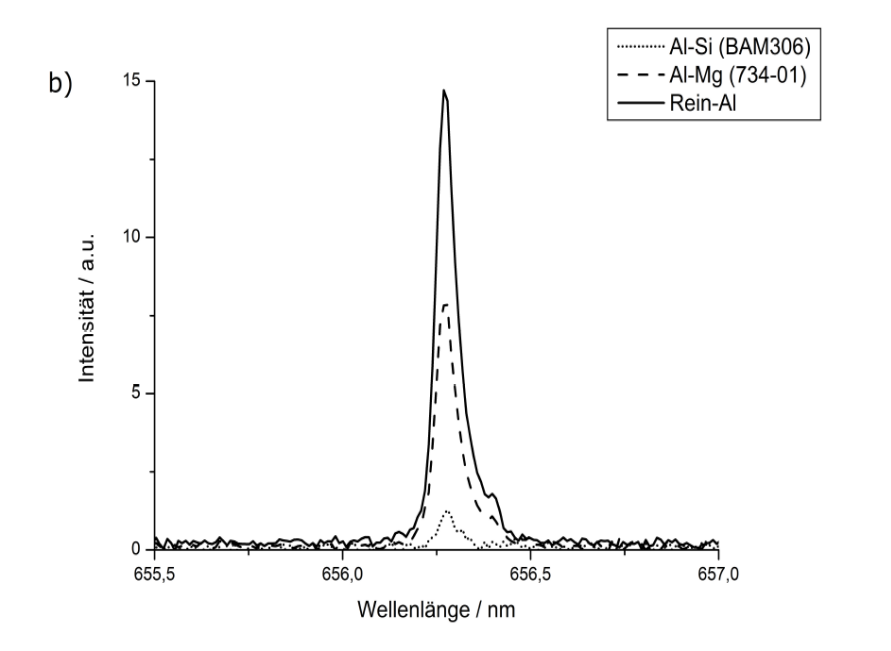
Higher intensities also at other spectral lines of hydrogen

➡ real effect that more hydrogen atoms are excited in the plasma

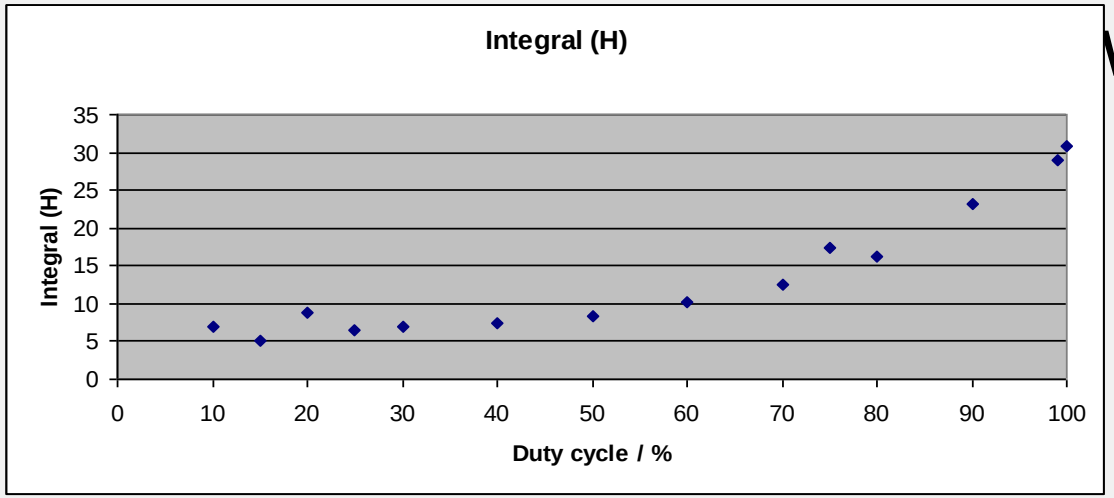


Hydrogen in Aluminium





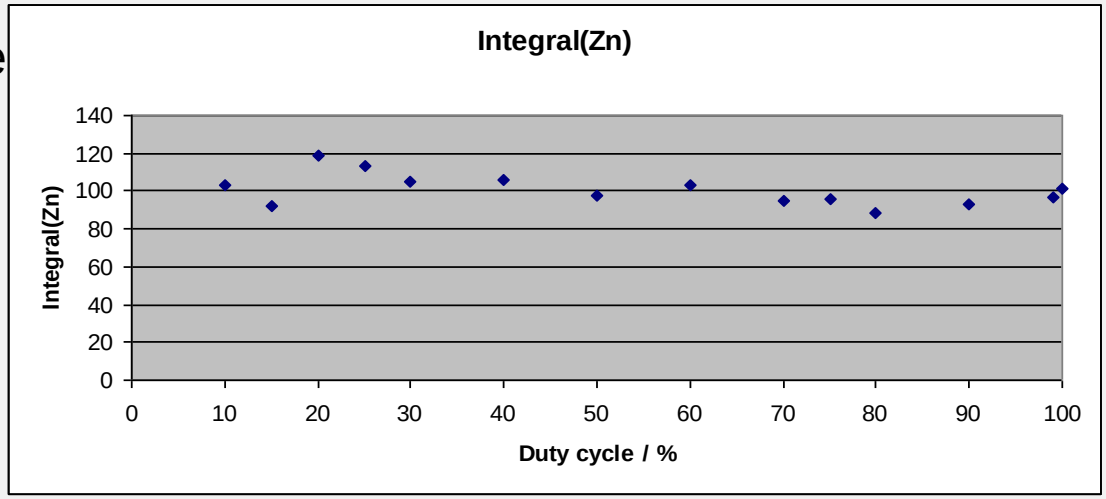
Electrolytic zinc coated steel: Integral over whole coating



An increasing duty cycle leads to:

- higher temperature of the sample
- increased H diffusion and more H in the GD plasma?

Integral (Zn) is constant: similar plasma conditions for different duty cycles



Electrolytic Zn coated steel
GDOES Dortmund Spectruma 750
RF 550 V – 2,5 hPa

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Results from experiments on Gardoprotect

Emission yield of some elements for different duty cycles:

With increasing duty cycle ….

- …strong increase
- …increase
- ….slight increase
- …neutral/slight decrease

-> Signal intensity / emission yield seems to be dependent on excitation energy of the spectral lines

Element	Wavelength / nm	Degree of ionization	Excitation energy / eV
H	121,567		10,2
O	130,217	I	9,52
P	185,943	I	8,08
C	156,143	I	7,94
Zn2	330,258	I	7,78
S	180,731	I	6,85
Zn	213,856	I	5,8
Si	288,158	I	5,08
Ti	365,350	I	3,44
Mo	386,411	I	3,2
Ca	393,367	II	3,15

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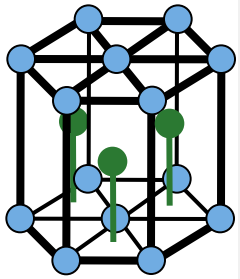
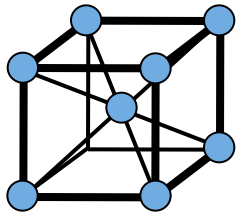
Calibration of H in titanium

- 10 titanium alloys of different composition
- H content varying from 15 - 130 ppm
- different crystal structures, most of them 95% α-Ti , 5% β-Ti

  (experimentally determined for every sample with XRD)

α-Ti: hex





β-Ti: krz

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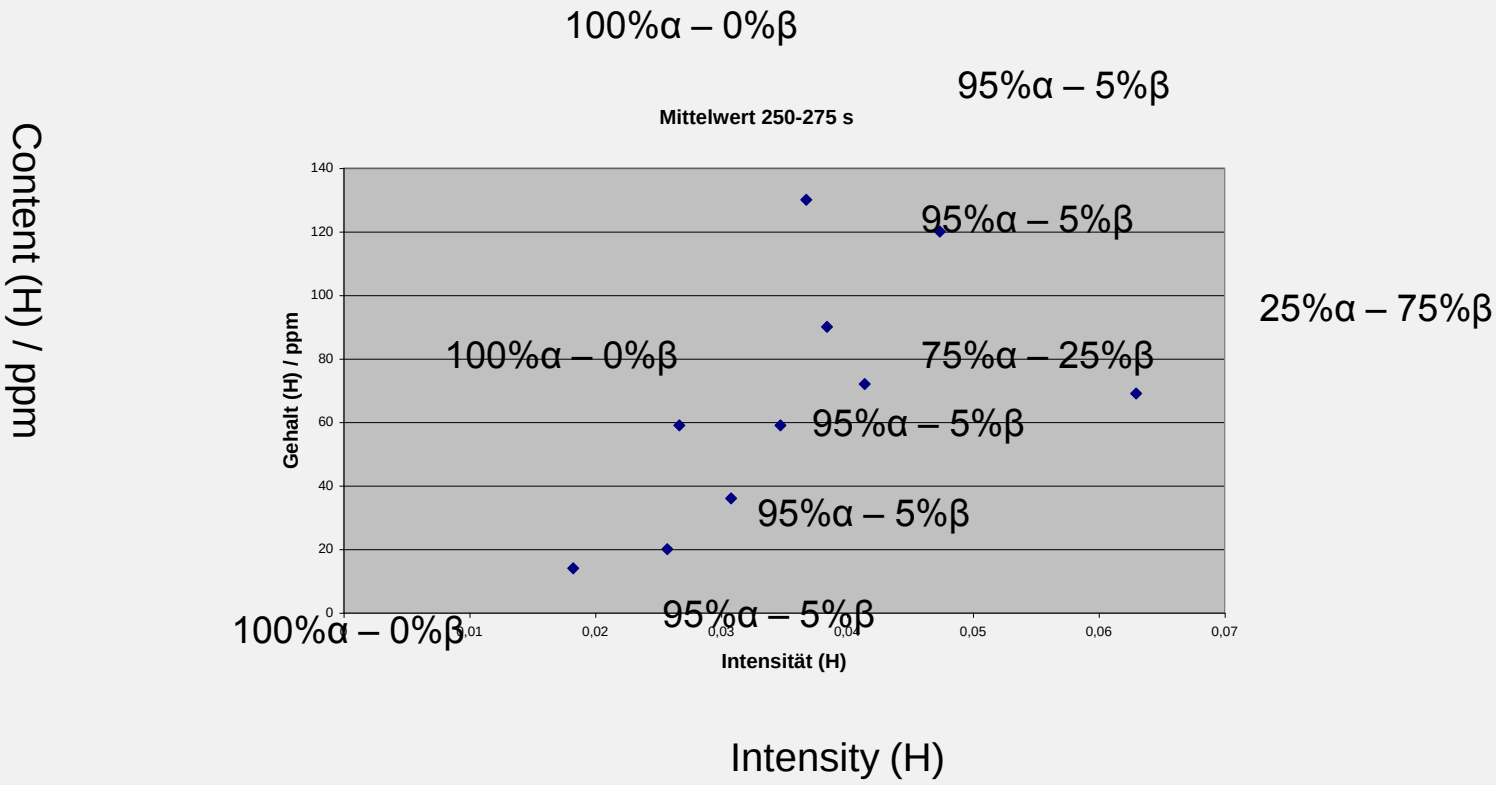
Comparison: Calibration H in Ti continuous vs pulsed RF-GD-OES, continuous sputtering

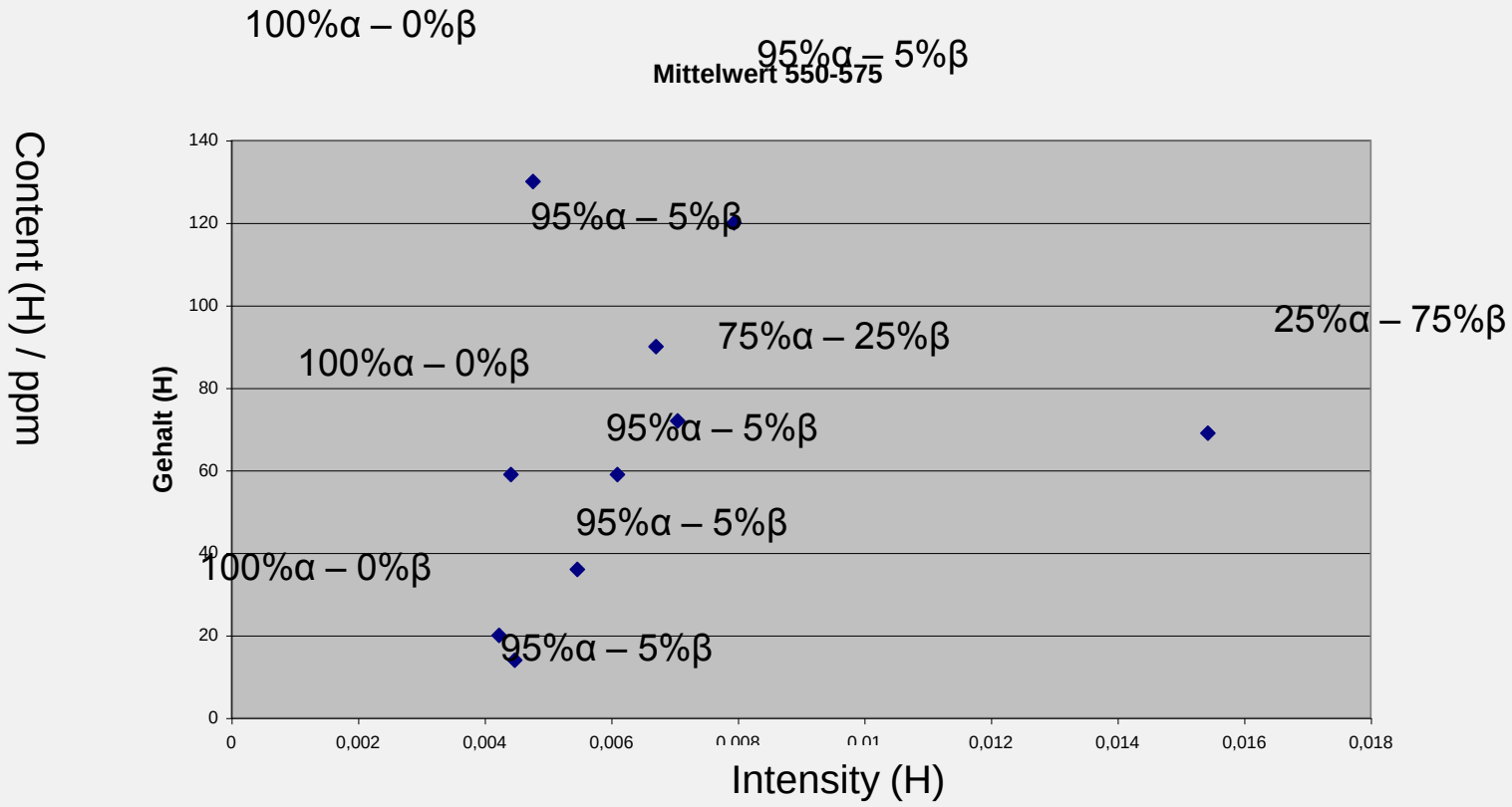
Averaged value 250-275 s (stabilized signal)



- Shows strong matrix-dependant effects (independent from sputtering rate)
- Possible reason: Difference in H diffusion in different phases of titanium?

Comparison: Calibration H in Ti continuous vs pulsed RF-GD-OES, pulsed – 300Hz, dutv cvcle 7%

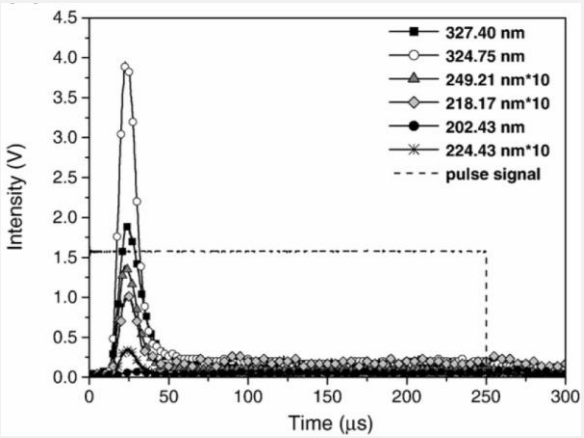
Averaged value 550-575 s (stabilized signal)

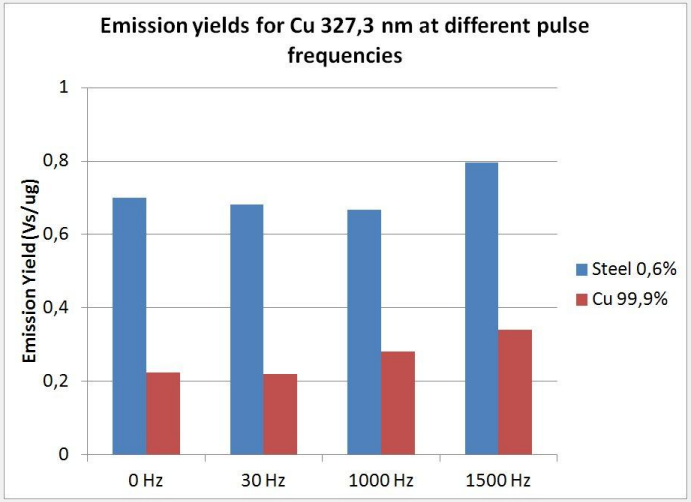


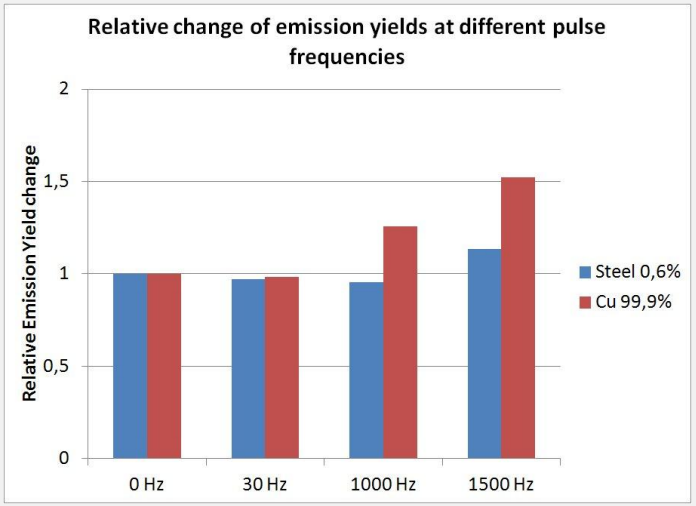
- Pulsed mode does not reduce (rather increases) matrix dependant effects – Why?

Change of Cu 327,3 nm emission yield as a function of pulse frequency

”Prepeak” in Cu resonance lines; pure Cu



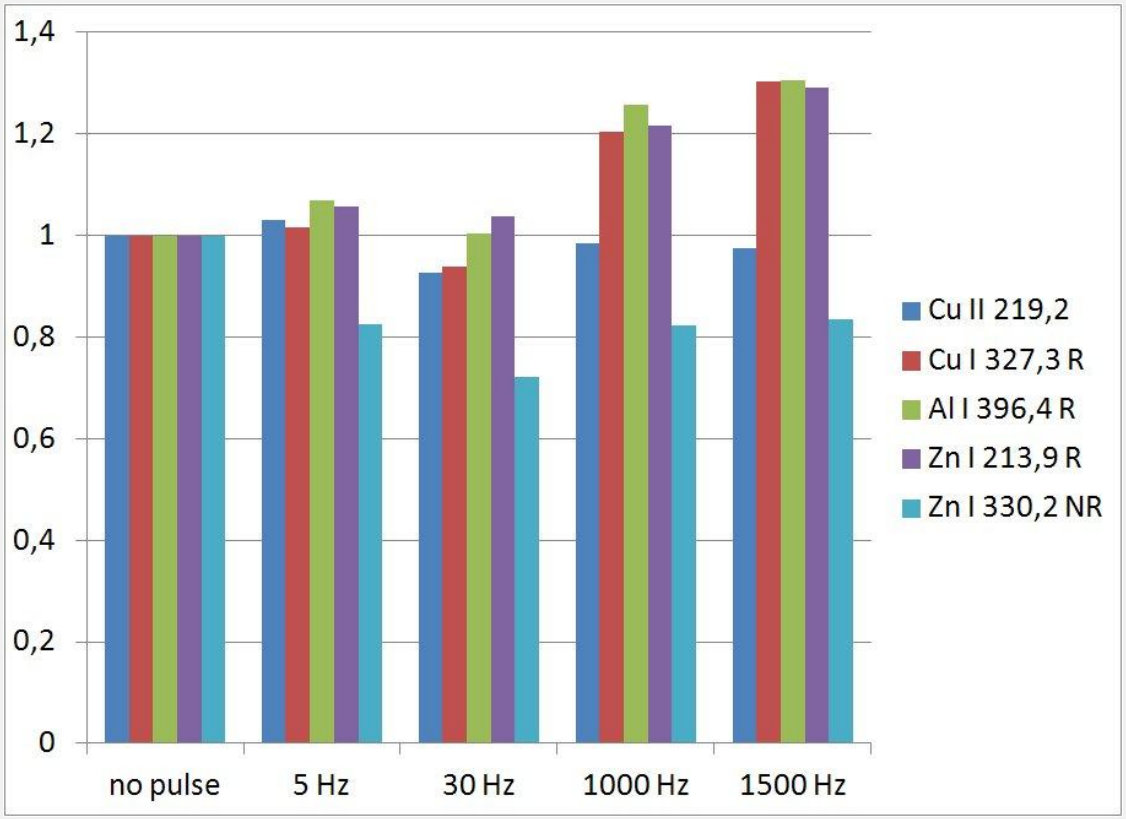




These observations support the suggestion that the prepeak is due to reduced self – absorption

BUT……

Relative intensity changes as a function of pulse frequency (length) in brass



Cu 61,5%; Zn 34,0%; Al 1,54% (very little self-absorption)
- Perhaps the prepeak for atomic resonance lines is more due to transient excitation conditions than reduced self-absorption?

Acknowledgements

- The member companies of Swerea KIMAB and the EU steel research program (RFCS) for financial support
- The EU Marie Curie program for a fellowship for Simone Weyler (GLADNET)
- Leco corporation for putting specially designed equipment for the GDS 850 at our disposal