



Recent developments in GD Optical Spectroscopy

Arne Bengtson

SWERIM AB, Isafjordsgatan 28A, Kista, Sweden

Presented at CANAS 2019, Freiberg, September 23 – 26, 2019



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Universität Münster, Isafjordsgatan 28A, Kista, Sweden

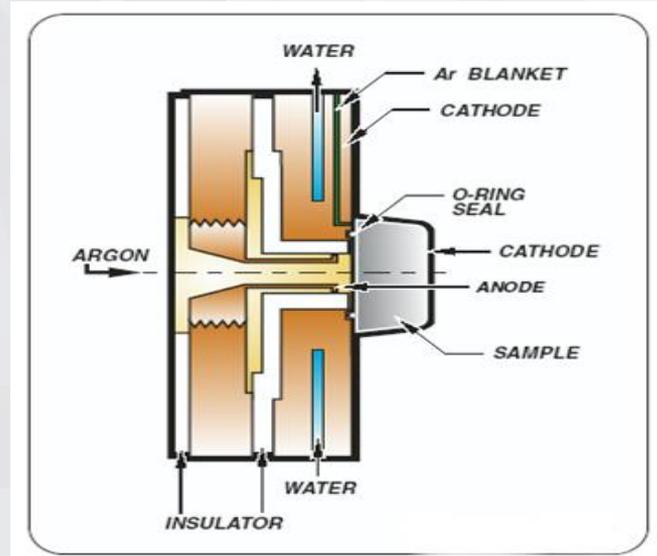
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Definition of Glow Discharge

- ***A glow discharge (GD) is a plasma formed by the passage of electric current through a gas.***
- A GD is often created by applying a voltage between two electrodes in a vessel containing a low-pressure gas. However, a glow discharge can also be sustained by applying a radio frequency (RF) voltage to the electrodes.
- Furthermore, glow discharges can also run at atmospheric pressure in some devices.
- *The main reason why glow discharges are highly useful analytical devices is the “cathodic sputtering” – material from the cathode is atomized in the plasma hence amenable to spectral analysis!*
- **Historical note: The first mentions in the literature of GD devices are from Grove (1852); Geissler (1857); Plücker and Hittorf (1858).**

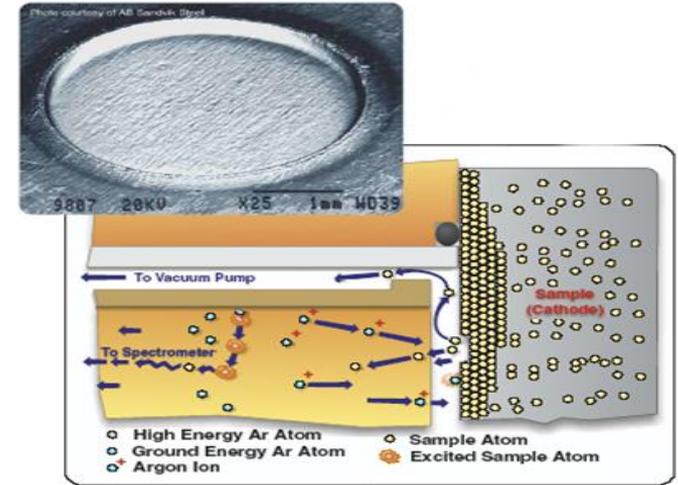
More recent history of GD-OES

- In 1968, Grimm designed a “hollow anode” glow discharge lamp for flat samples. His basic design has formed the standard for all commercial GD-OES instruments ever since.
- In 1973, Greene and Whelan published the first paper on the use of GD-OES for depth profiling.
- Starting in 1975, Berneron et.al. developed GD-OES for fast depth profiling based on the Grimm lamp.
- The first commercial GD-OES instrument was introduced in 1968 (RSV). Today, a number of instrument companies offer a wide variety of GD-OES instruments for both bulk and depth profiling applications.



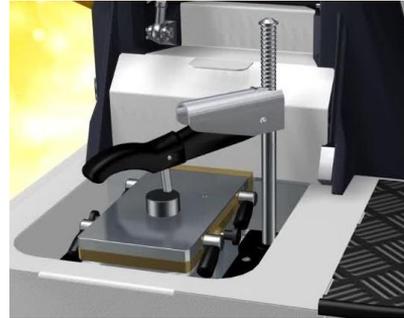
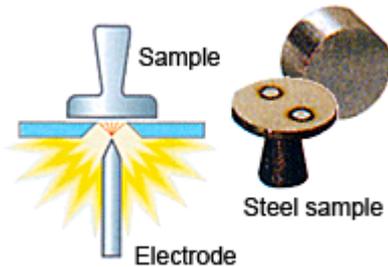
Applications of GD-OES

- Grimm's GDL was intended as an alternative to the spark for bulk analysis of metallurgical samples (hopefully with better performance).
- Due to the even sputtering of the surface, Compositional Depth Profiling (CDP) has emerged as the main field of applications.
- The introduction of a radio frequency (RF) powered Grimm source in 1987 enabled analyses of non-conductive surface layers.
- In addition to CDP, there is a number of applications to bulk analysis of complex alloys where the GD has some advantages over the spark.



Why is spark OES still the (by far!) most common instrument for bulk metallurgical analysis?

- The spark stand is a simpler, more robust device than a GD.



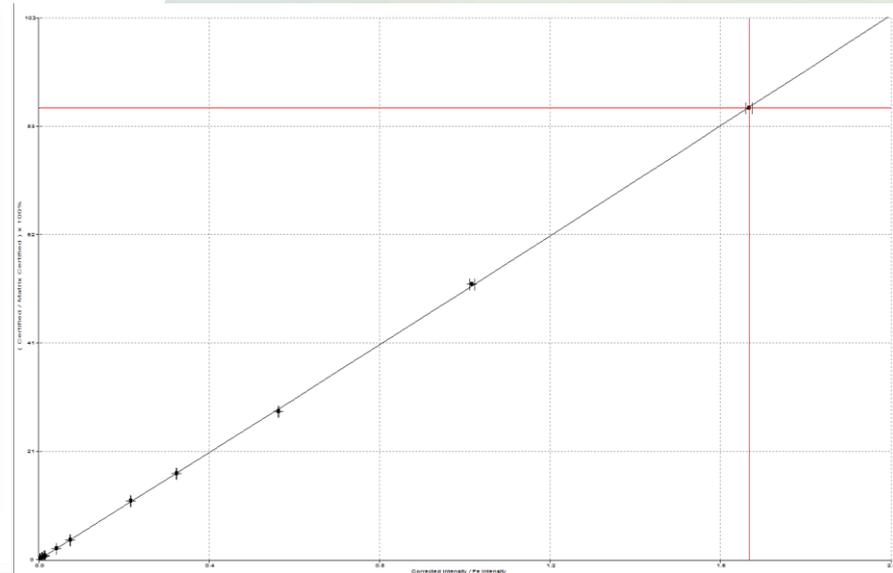
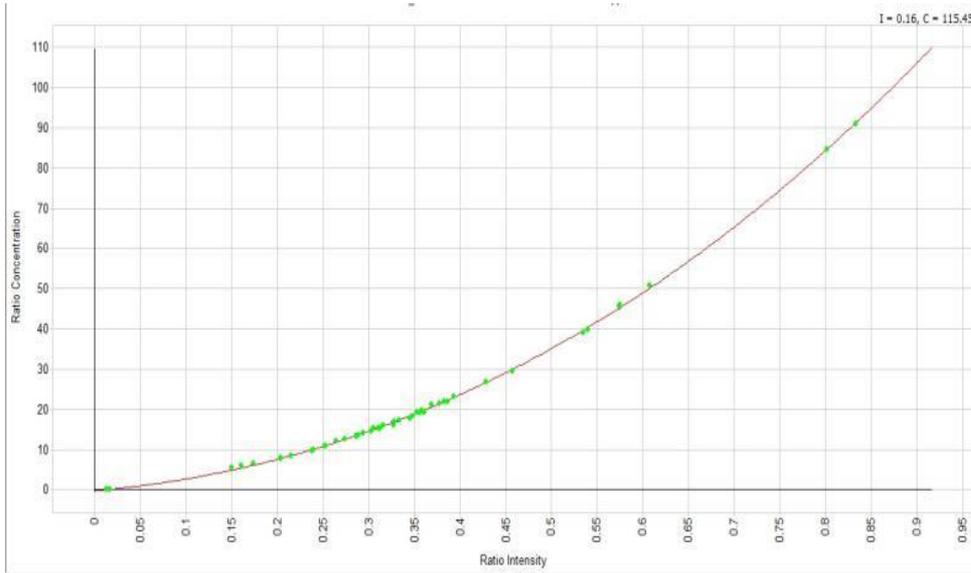
No vacuum,
No o-ring seal!

- The spark is considerably faster than a GD – a complete analysis takes less than 10s, including preburn.
- The simple design of the spark stand lends itself very well to automation.

Common "myths" about GD vs spark for bulk analysis of metals

- The GD outperforms the spark in terms of analytical figures of merit – *wrong*, they are rather evenly matched.
- The more linear calibration curves of the GD results in better accuracy for high alloy materials – *wrong*, a modest non-linearity is no problem for accuracy.
- The GD has more narrow emission lines, allowing easier separation from interfering lines – basically true, but you need single picometer spectral resolution to take advantage of this. This is not available in commercial instruments, so the argument is irrelevant.
- There is no more R&D advancing spark OES technology – *wrong*, recent work on digitally controlled spark sources, advanced time resolved spectroscopy (TRS) etc. steadily improves the outstanding performance of spark OES.

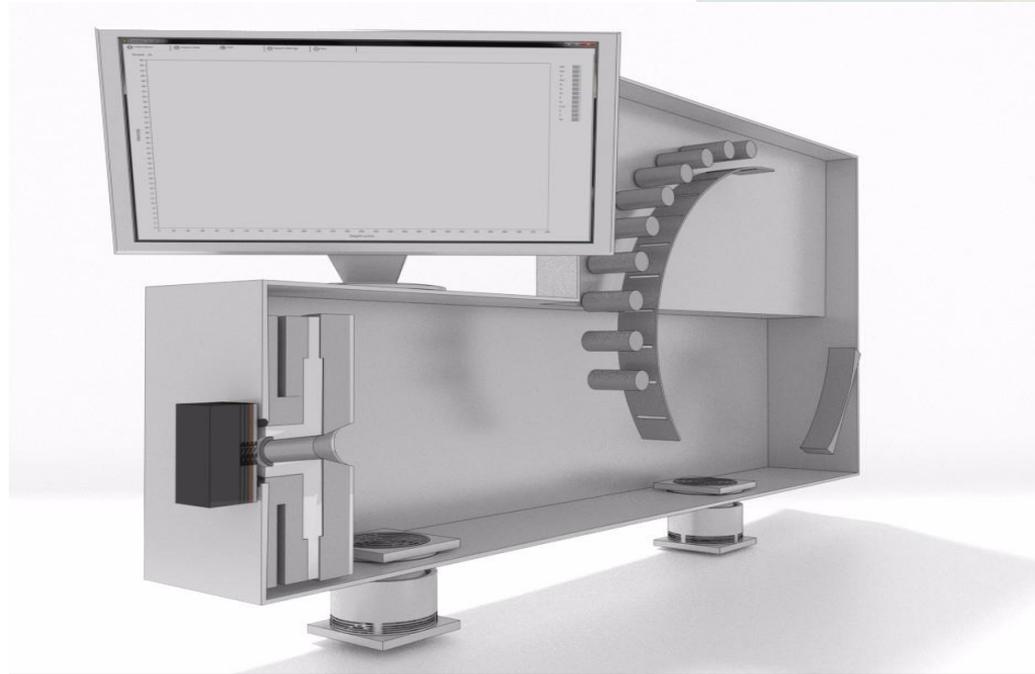
Ni calibration curves spark - GDL



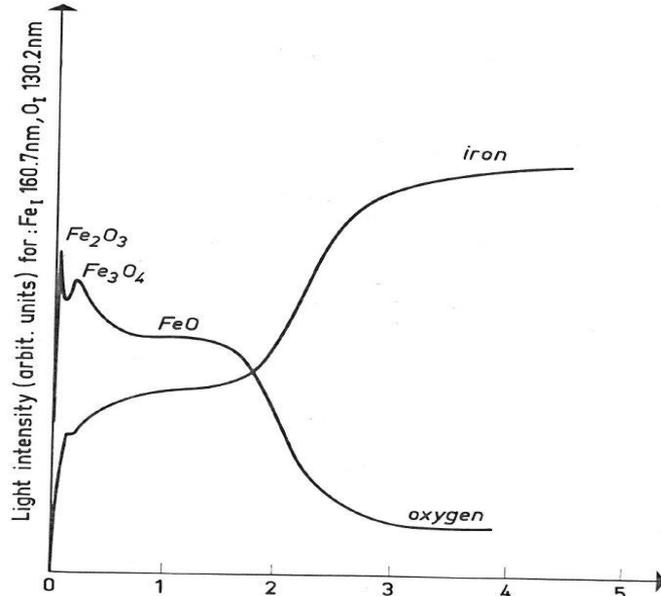
Spark calibration Ni II 243.79 nm Fe I ref 249.33 nm

GDL calibration Ni II 225.39 nm Fe II ref 249.33 nm

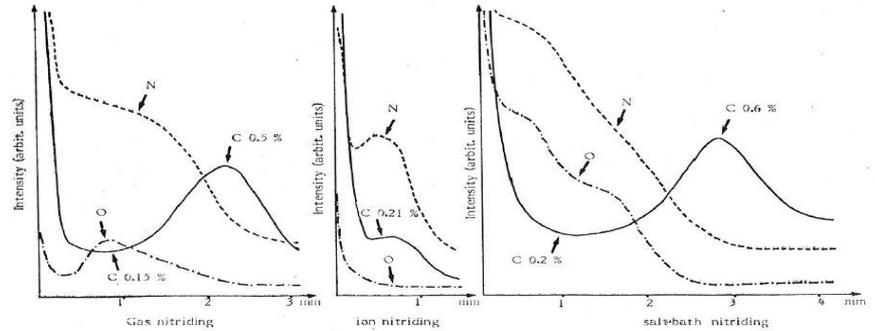
What GD-OES does best - compositional depth profiling



GD-OES depth profiles from R. Berneron, IRSID, 1980



Hot rolled steel



Carbonitrided steels

Topics related to CDP GD-OES

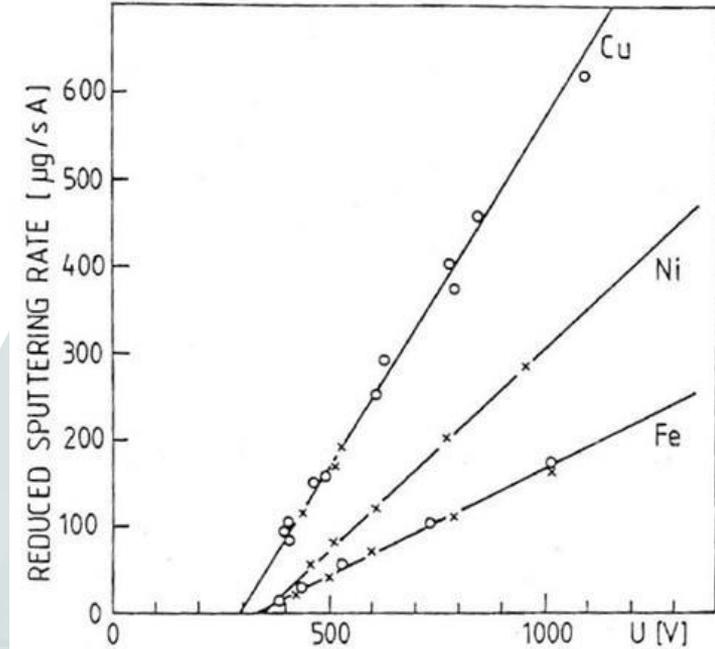
- Sputtering rates in different materials
- The emission yield (EM) as a basis for quantification
- Calibration and quantification in CDP
- Influence of the plasma parameters on the EY
- Examples of applications of CDP

Sputtering rates Sr_M in different materials

Boumans' equation: $Sr_M = k_M * i * (U - U_0)$

Reduced Sr $Sr_M/i = k_M * (U - U_0)$

Where i is the current, U is the voltage



Note that there is a threshold voltage for sputtering at approx. 300 V

Examples of sputtering rates in different materials at different source conditions

4 mm anode

700V 20 mA 1000 V 40 mA

LA steel 3,0 µg/s 10,5 µg/s
30 nm/s 105 nm/s

Brass 13 µg/s (46 µg/s)
110 nm/s (400 nm/s)

2 mm anode

700V 10 mA 1000 V 15 mA

LA steel 1,5 µg/s 3,9 µg/s
60 nm/s 160 nm/s

Brass 6,8 µg/s (18 µg/s)
230 nm/s (600 nm/s)

This is a very fast technique for CDP analysis!

The Emission Yield (EY) concept as a basis for quantification of depth profiles

The Emission Yield (EY) is defined as:

The amount of emitted light (number of photons) per unit sputtered weight of an element, given for a specific wavelength (emission line).

It is well documented that the EY is **matrix-independent**, at least to a first approximation.

The basic equation for the intensity of element i at wavelength λ :

$$I_{i\lambda} = EY_{i\lambda} * c_i * Sr_M$$

Where c_i is the mass fraction ("concentration") of element i and Sr_M is the sputtering rate of the sample M .

Sputter rate corrected multi-matrix calibration (“standard method”)

$$c * q = R * I$$

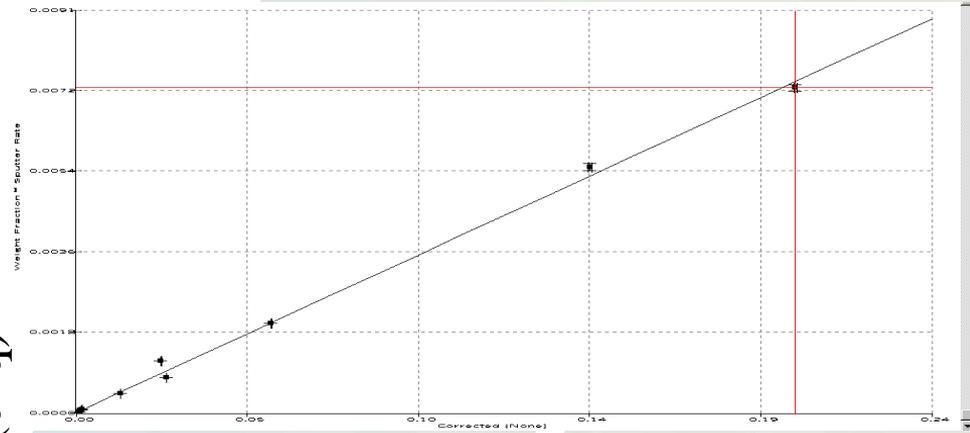
I= emitted light intensity

q= sputtering rate [$\mu\text{g/s}$]

c= concentration

R= the inverse emission yield

Concentration *
sputtering rate
(c*q)

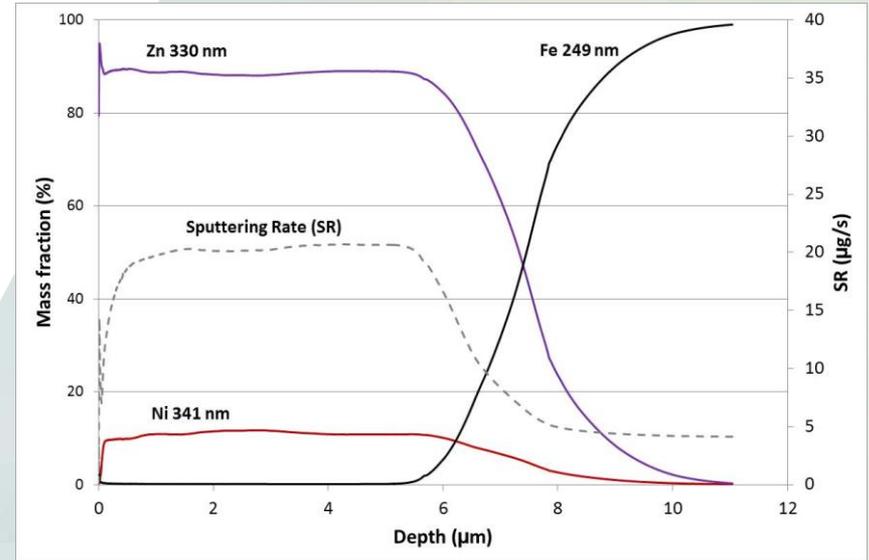
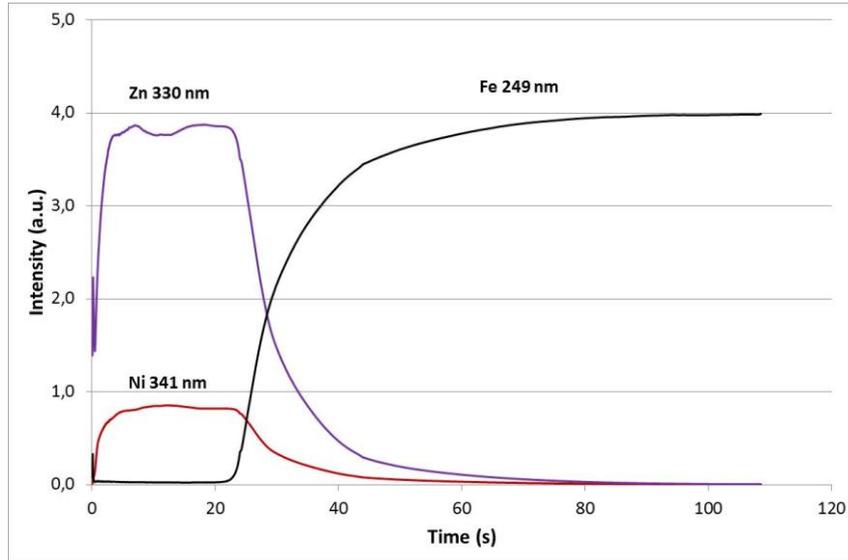


Intensity (I)

Calculations steps in quantitative CDP

- When measuring an unknown, the primary data obtained from the calibration is $c_i * Sr_{sample}$ for each element i .
- In each time (depth) increment, the sputtered mass Δm_i is obtained by multiplying $c_i * Sr_{sample}$ with the time increment. The corresponding total sputtered mass ΔM is obtained by summing over all elements.
- The concentrations in each time (depth) increment are obtained by sum normalisation of the elemental masses to 100%:
$$c_i = 100 * \Delta m_i / \Delta M \text{ (in weight\%)}$$
- The depth is calculated by converting total mass to volume by means of the density (*calculated from the concentrations or manual input*).

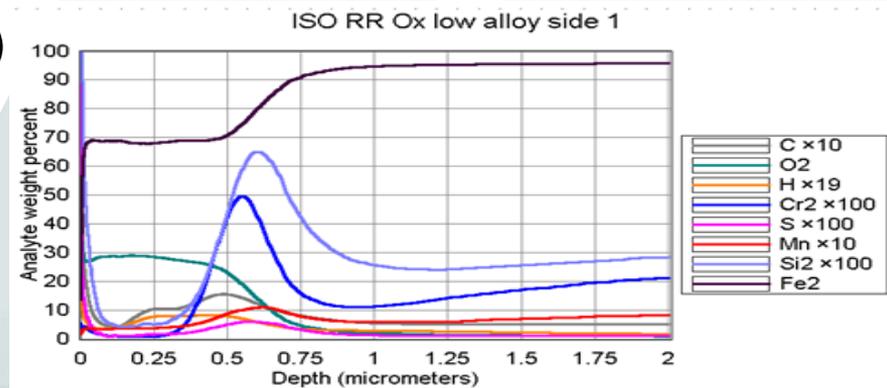
From time-intensity diagram to fully quantified depth profile



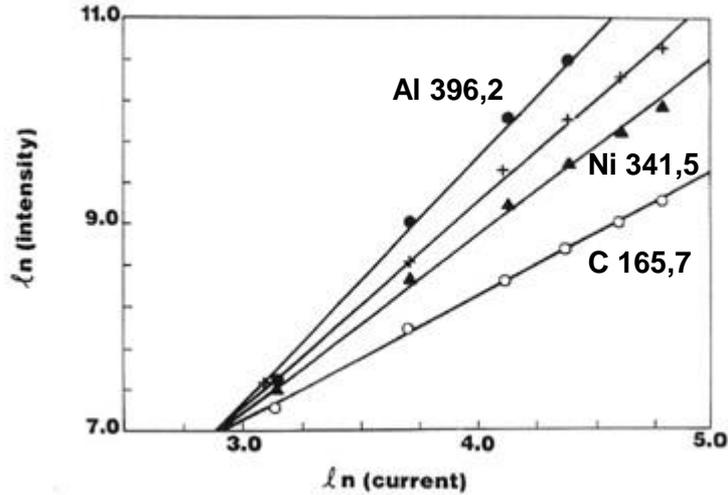
Electroplated ZnNi coating on steel

Characteristics of GD-OES CDP

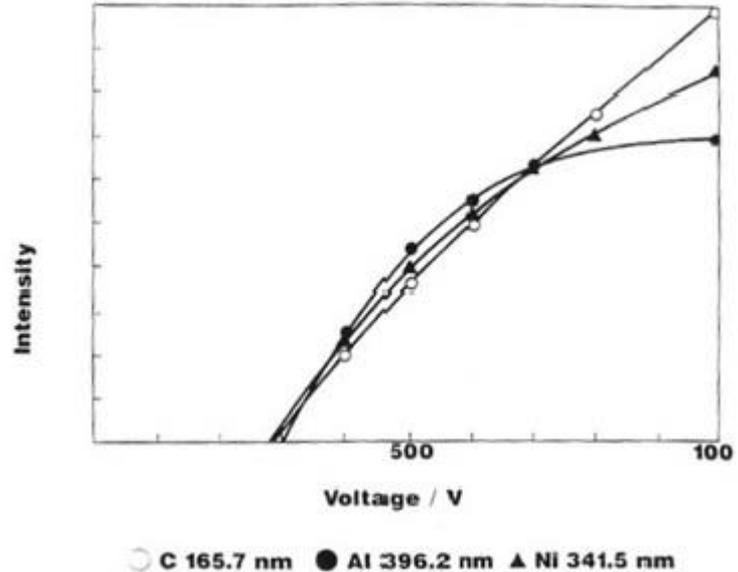
- Quantified elemental depth profiling of conductive and non-conductive surface layers.
- Range of analysis depth 1 nm - 100 μm
- Rapid analysis ($\approx 2 \mu\text{m}/\text{min}$ in steel)
- Mass fraction range 10 ppm-100%.
- Quantification accuracy better than 10% relative error.
- *Analysis of the light elements H, C, O, N.*



Current and voltage influence on emission intensities (and thereby the EY)

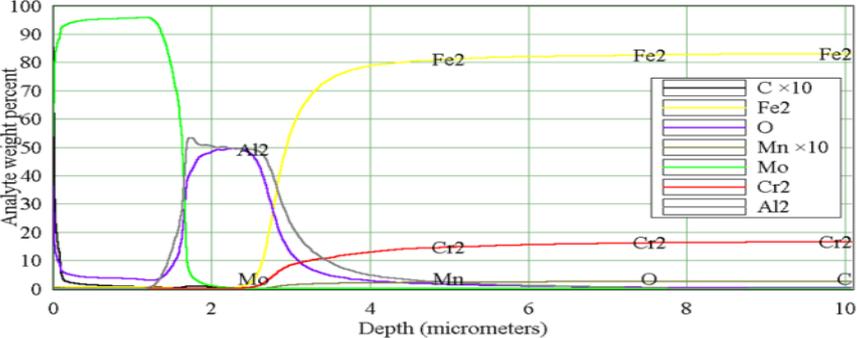


Intensity vs current in a log – log diagram. The slope is close to 2 (quadratic) for several spectral lines.

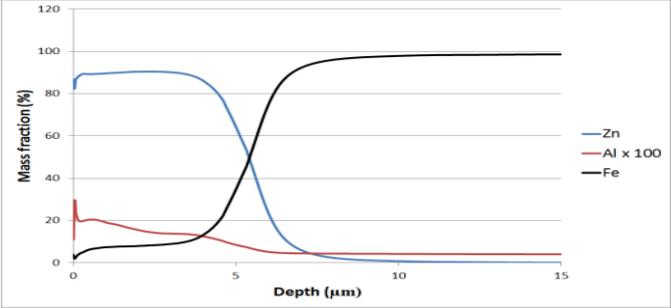


Intensity vs voltage. Note that the threshold voltage for sputtering also is seen in the emission signals.

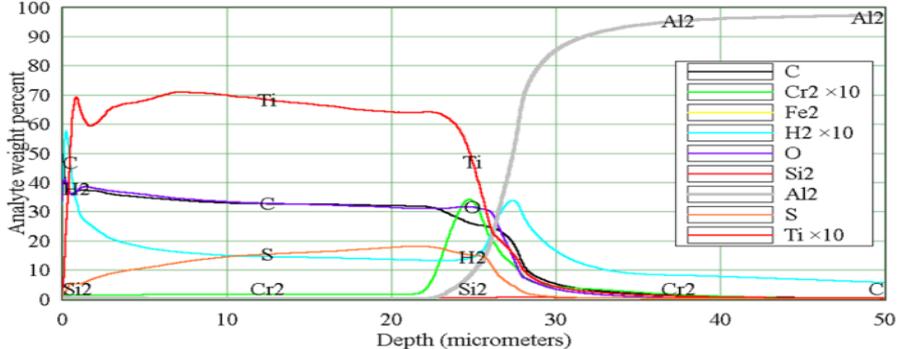
Examples of GD-OES depth profiles



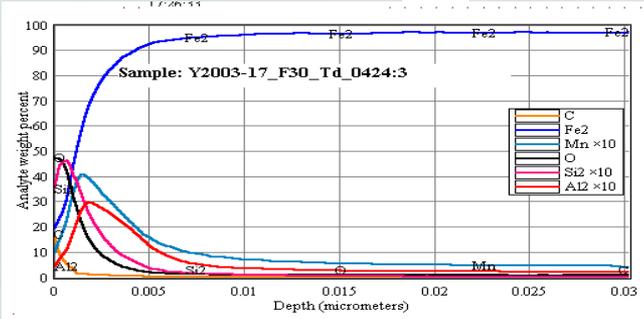
Double coating system on chromium steel



ZnFe "Galvanneal" coating on steel

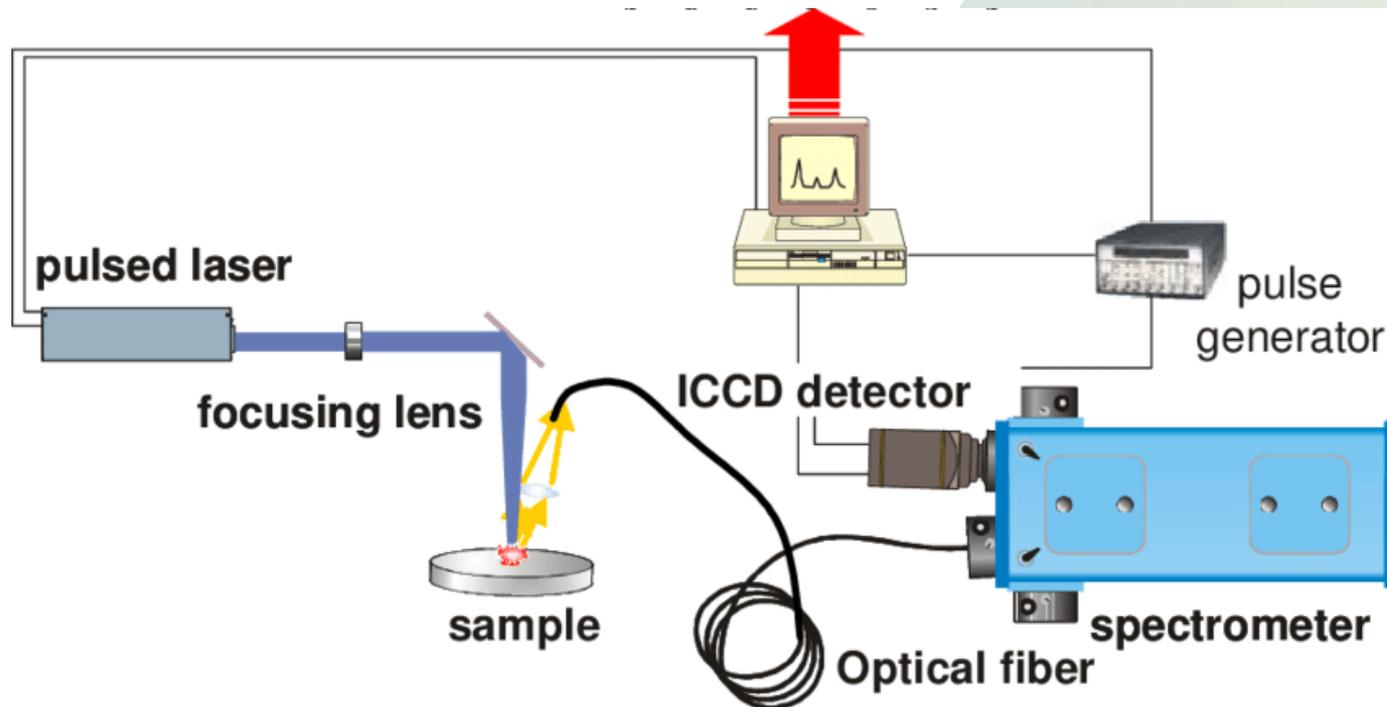


PE coating on Al sheet



Steel sheet annealed in reducing atmosphere

Alternative for CDP - Laser Induced Breakdown Spectroscopy (LIBS)



LIBS for CDP analysis

- A laser can be adjusted to remove a very thin layer with each shot, LIBS is therefore also used for CDP analysis.
- In order to achieve good depth resolution, it is necessary to shape the laser beam to "flat top" fluence distribution.
- In contrast to GD-OES; LIBS CDP can be done in air and on samples of greatly varying composition and shape.
- LIBS CDP is currently being developed by several groups, and we are likely to see further advances in the near future.

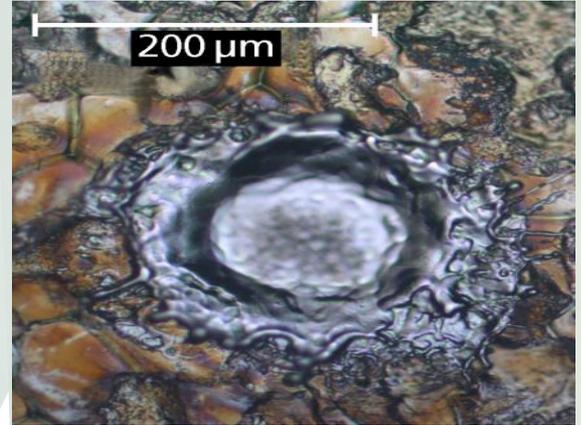
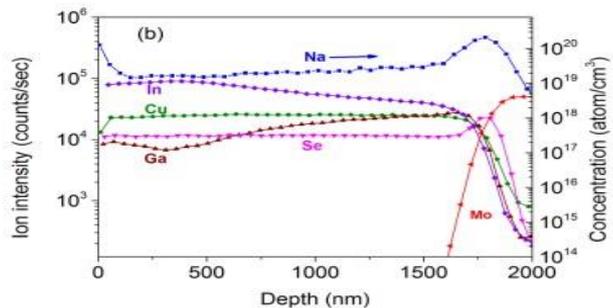
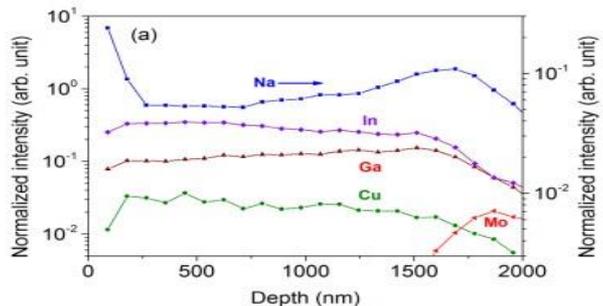
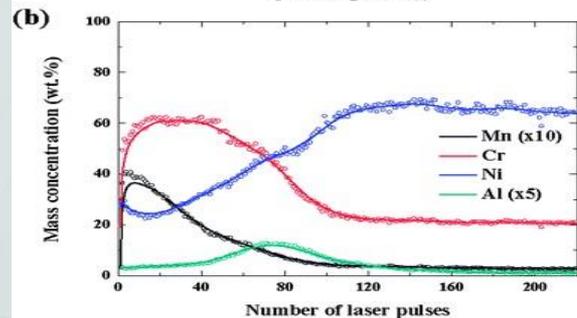
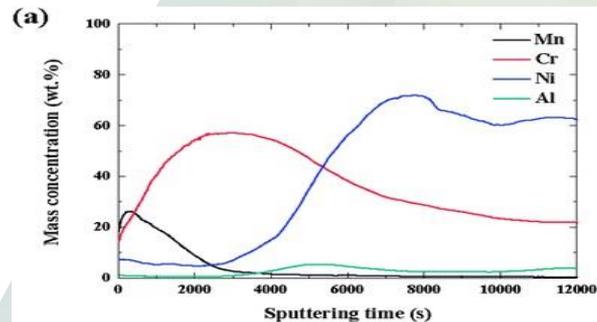


Photo from ILT, Aachen, Germany

Examples of LIBS depth profiles



Depth profile of CIGS layer;
LIBS top SIMS bottom.



Depth profile of a 5 μm oxide layer on a
Ni alloy, SIMS? top, LIBS bottom

Pros and Cons of GD and LIBS CDP analysis

GD

- **Pros:**
- Robust and fairly easy to operate, high sample throughput (fast).
- Very large dynamic range in both depth and mass fraction, low DL's.
- Very well developed and proven quantification method.
- **Cons:**
- Nearly no lateral resolution.
- Vacuum system, sample must seal against O – ring.
- Restrictions on sample shape and composition.

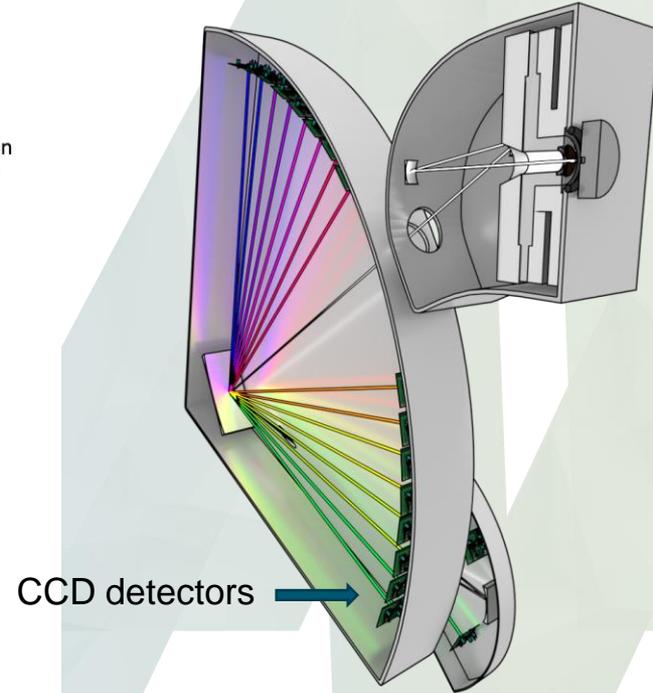
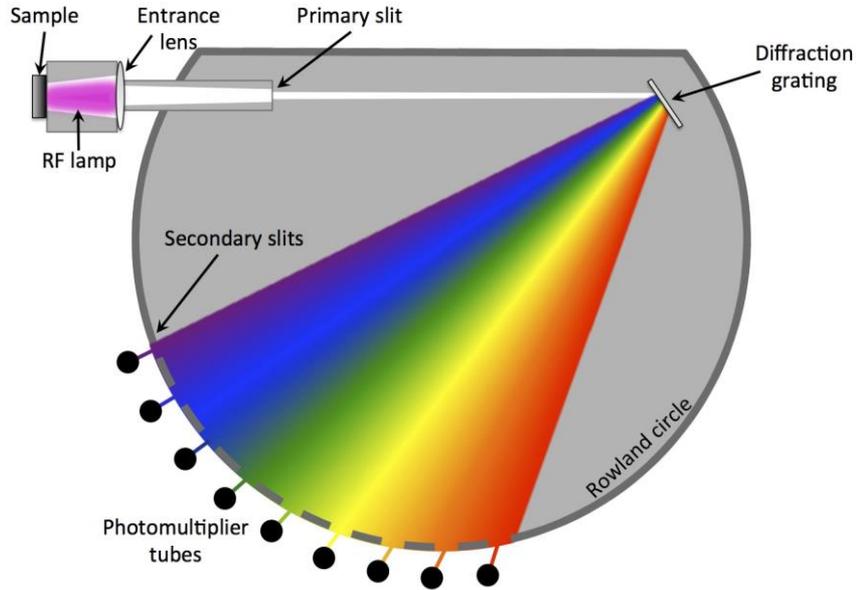
LIBS

- **Pros:**
- Lateral resolution down to a few μm possible.
- No vacuum, can be used in air.
- Almost any sample shape and composition possible.
- **Cons:**
- Poor depth resolution, minimum information depth “large” ($> 10 \text{ nm}$?)
- Quantification methods poorly developed.
- Cannot do C, O, S, P, N; at least not with good sensitivity.

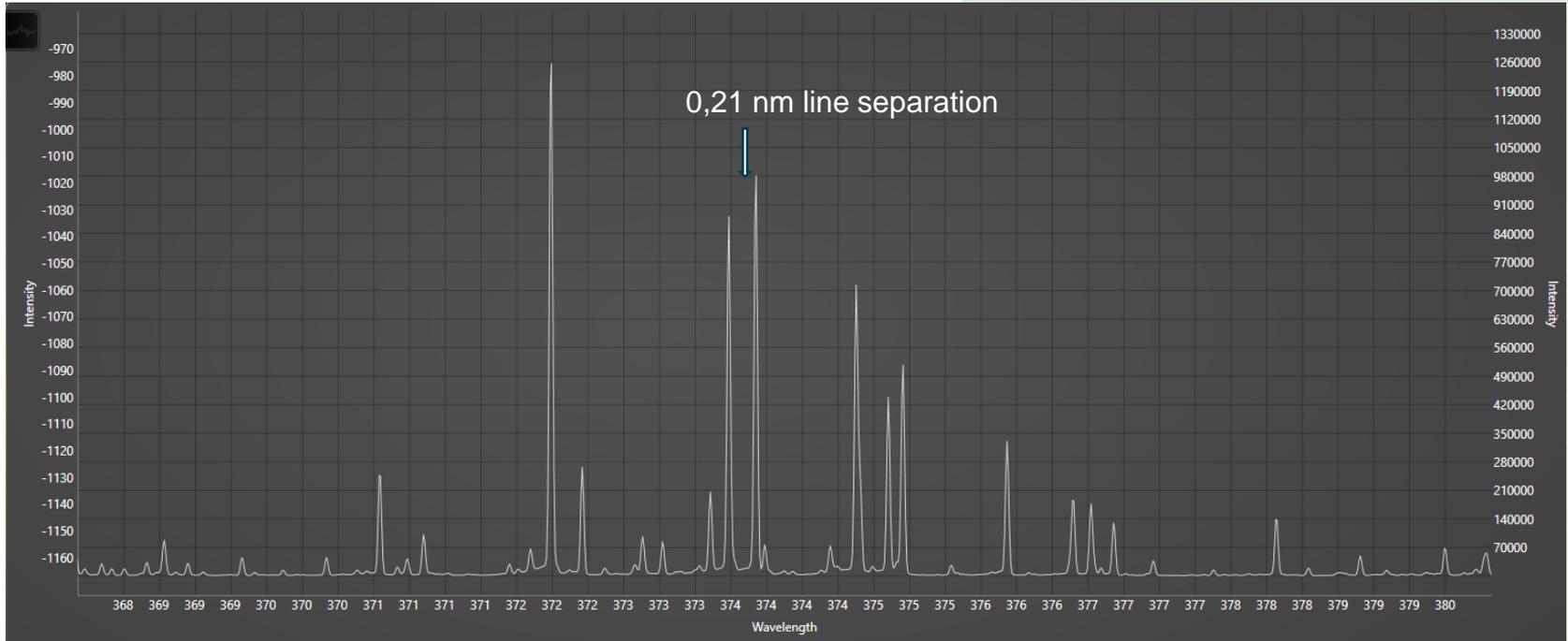
Recent developments in GD-OES

- Instruments with solid state array (CCD – CID) detectors
- Pulsed GD sources
- Real-time measurement of sputtering depth by optical methods
- Macroscopic mapping with large area GD
- The Solution Cathode GD for liquids analysis

PMT vs CCD spectrometer



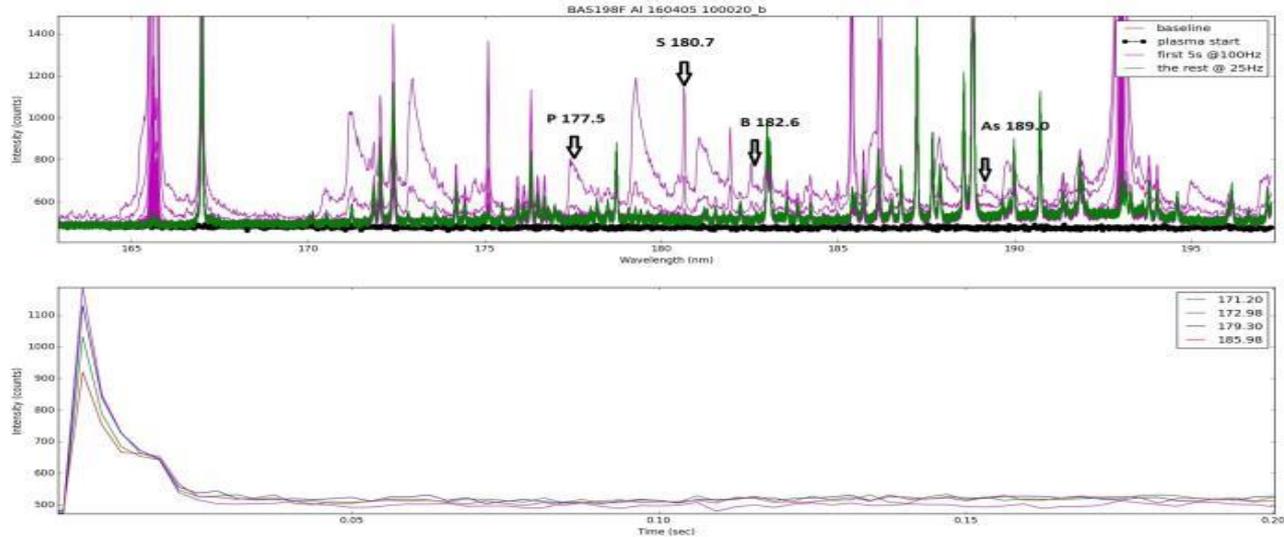
Example of spectrum from a high-performance GD-CCD spectrometer



Advantages of the CCD spectrometer

- “Unlimited” choice of elements and spectral lines
- “New” lines with better performance than those commonly used in PMT spectrometers can still be found
- Improved background and line interference subtraction
- Future prospect – increased precision and accuracy by making use of multiple lines/element

Subtraction of background from molecular spectra in CDP



Spectrum of CO on lamp startup in a pure Al sample

Pulsed GD – parameters to vary



Duty cycle 25%



Duty cycle 50%

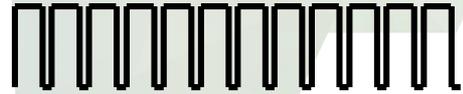


Duty cycle 75%



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

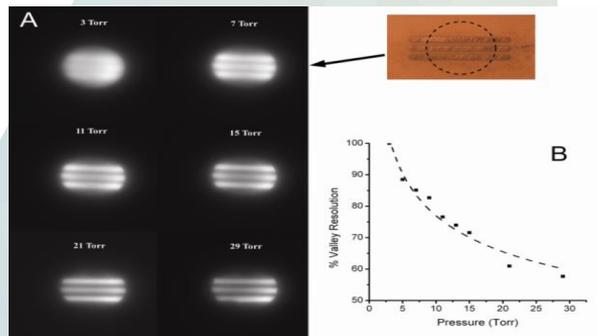
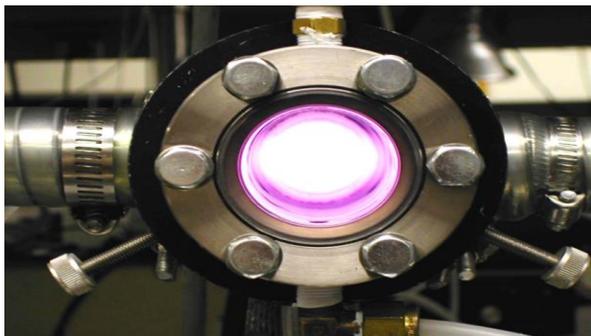


Results from investigation of pulsed GD in the GLADNET program

- Under the pulse conditions tested, the enhancement of emission yield (EY) by pulsing is marginal, even in the "most favourable" cases.
- Possibly, a combination of very short pulses and high instantaneous power can improve the EY significantly.
- Most likely, the major analytical benefit of pulsed operation remains less heating/thermal stress of small, thin and otherwise heat-sensitive samples.

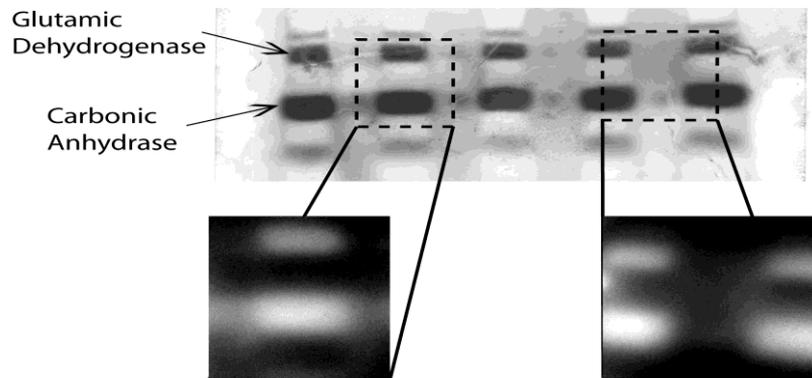
Large area GD-OES elemental mapping

- Lateral resolution typically limited by anode size
- Pulsed-GD allows lateral resolution within anode
- **Large areas mapped simultaneously!**
 - No 2D rastering = very fast ($> 10^3$ vs typical techniques)
 - Applications requiring lateral resolution $\geq 100\mu\text{m}$



GDOES Elemental Mapping Applications

- Protein analysis
 - Blotting membrane substrates
 - Identification and quantification mapping

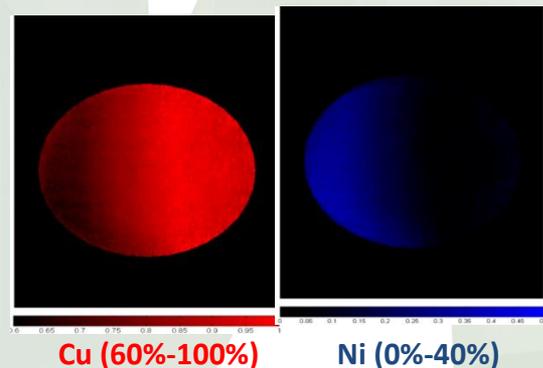


- Thin films
 - Stoichiometry
 - Contaminants, dopants, grain boundaries
 - Materials combinatorial libraries

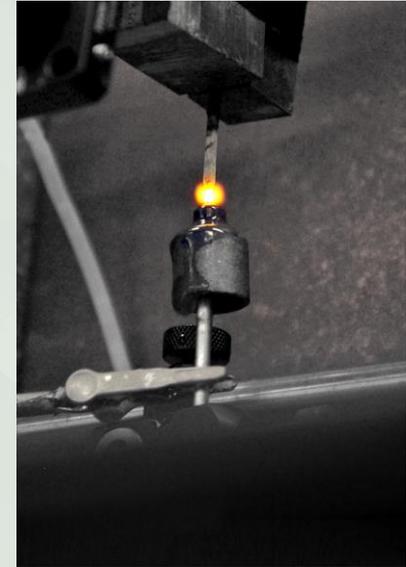
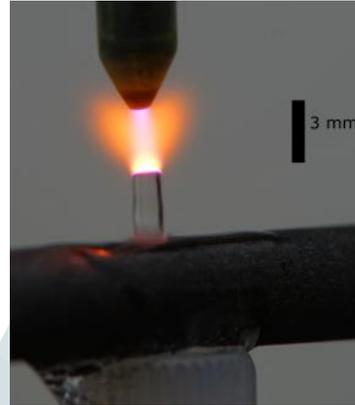
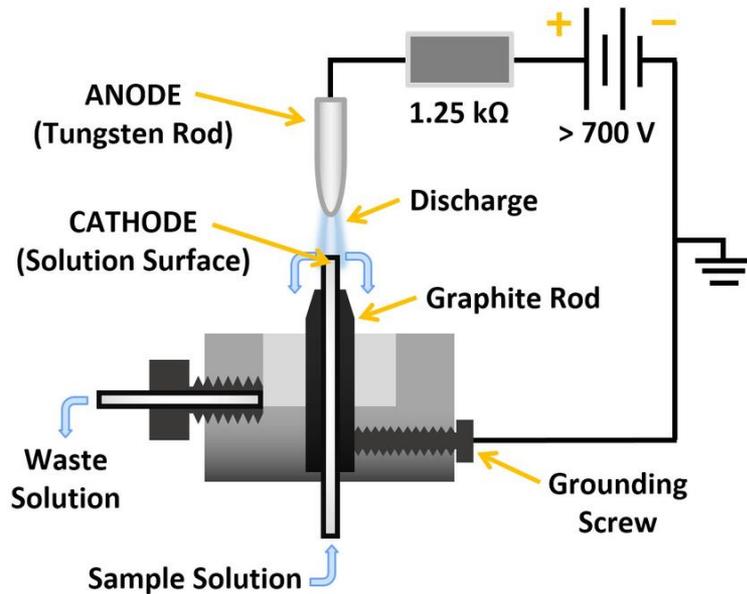
Composition gradient



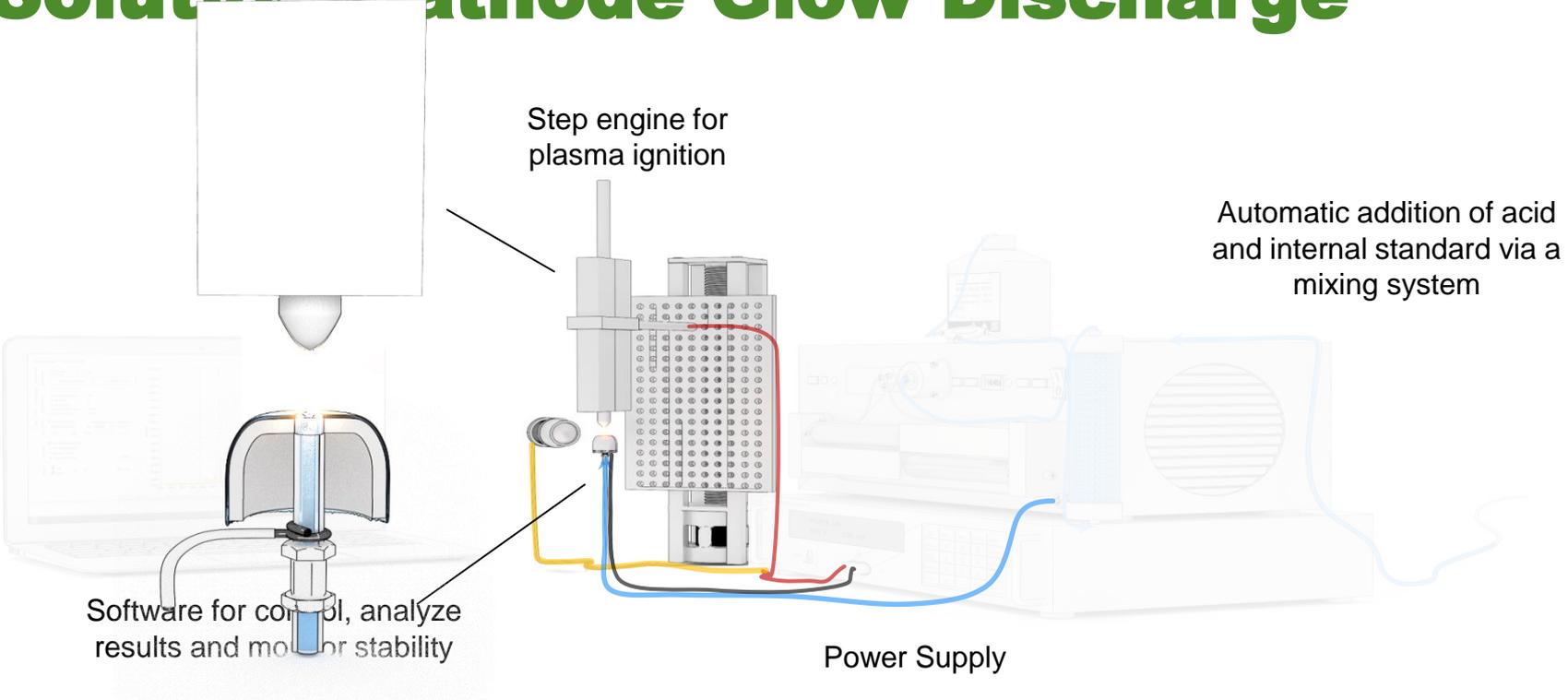
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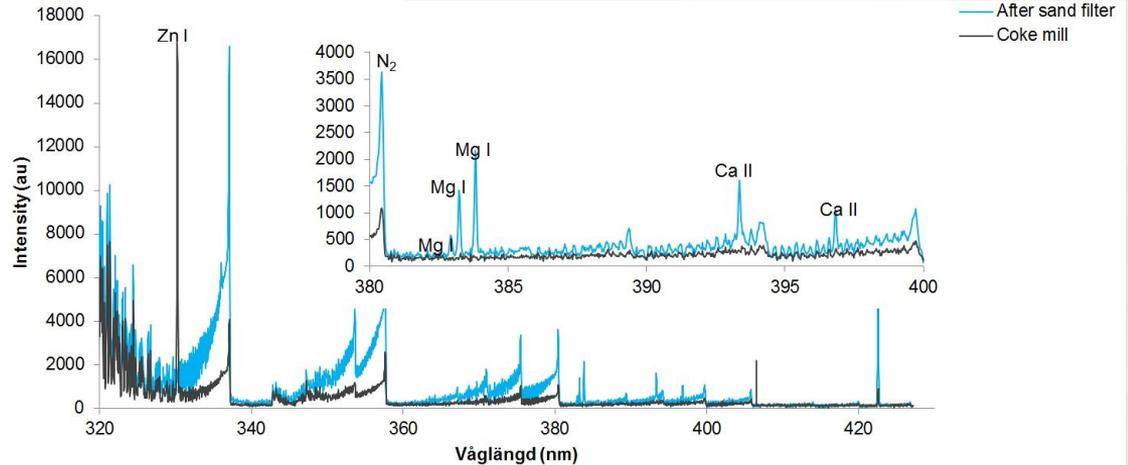
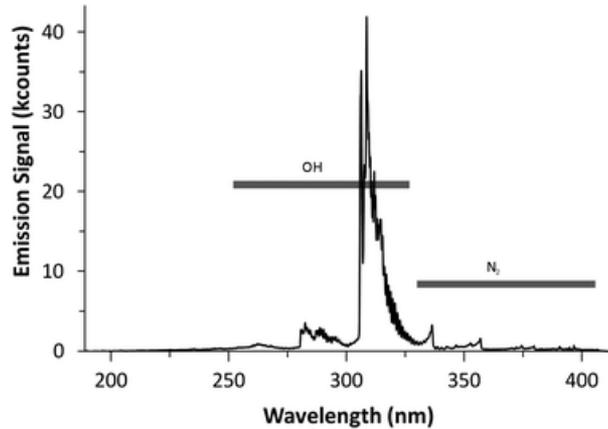
The Solution Cathode Glow Discharge – a novel device for analysis of liquids



Solution Cathode Glow Discharge



SCGD spectra



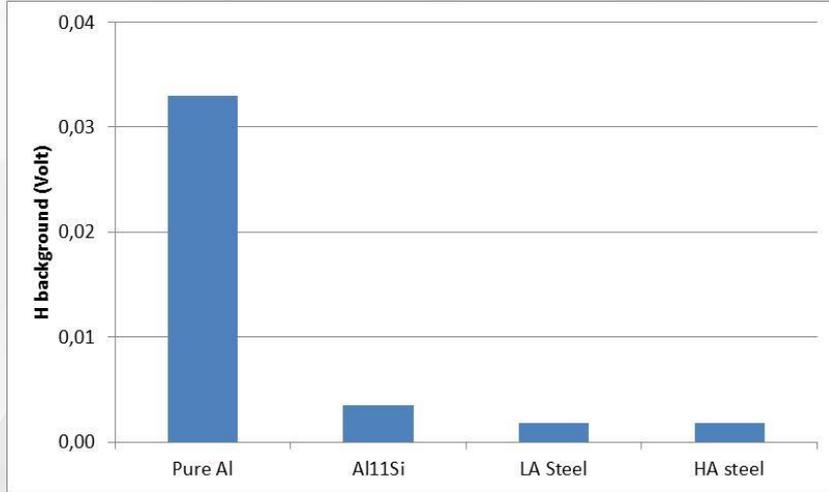
Blank spectrum dominated by OH and N₂ molecular bands

Spectra of industrial waste water before and after filtering

Suggestions for continued work to improve GD-OES

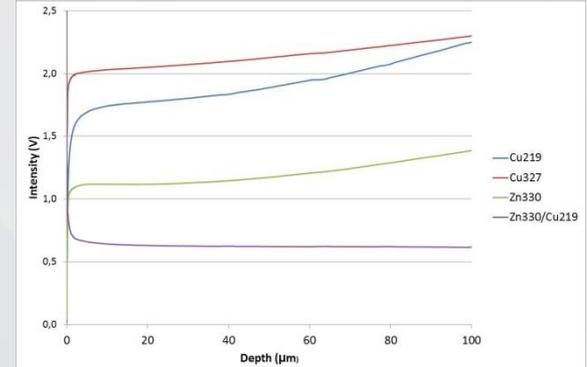
- Develop more advanced (chemometric?) quantification methods utilising the massive amount of information in CCD spectrometers
- Introduce time resolved detection in combination with pulsed GD's – improving detection limits similar to high end spark OES
- Advance the SCGD to robust, commercial systems for on-line monitoring of industrial processes

Finally, two little “mysteries” for the curious GD researcher

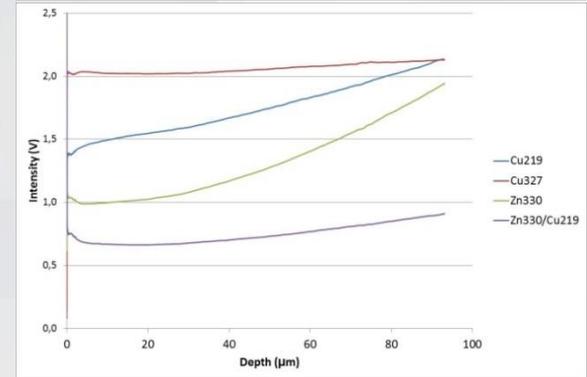


Background H intensity in different alloys

4 mm anode



2 mm anode



Spectral line dependent intensity variations with depth

Acknowledgements

- The organising committee for the invitation
- The Swedish Innovation Agency VINNOVA for financial support
- All colleagues at SWERIM AB for their contributions
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Thank all of you for your attention!