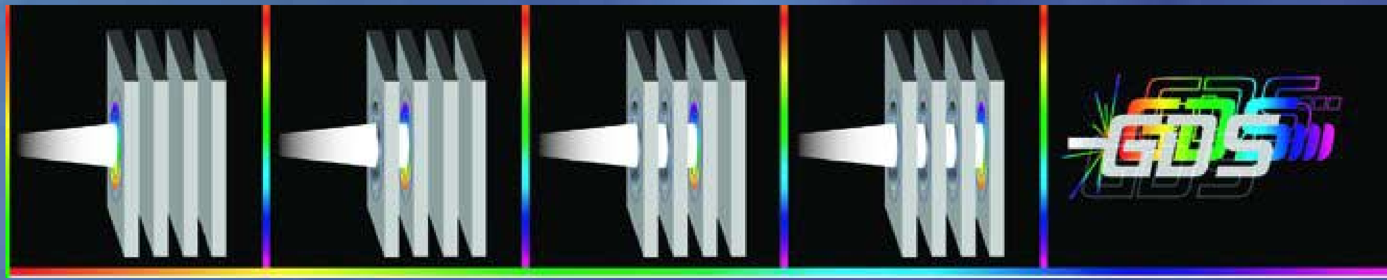
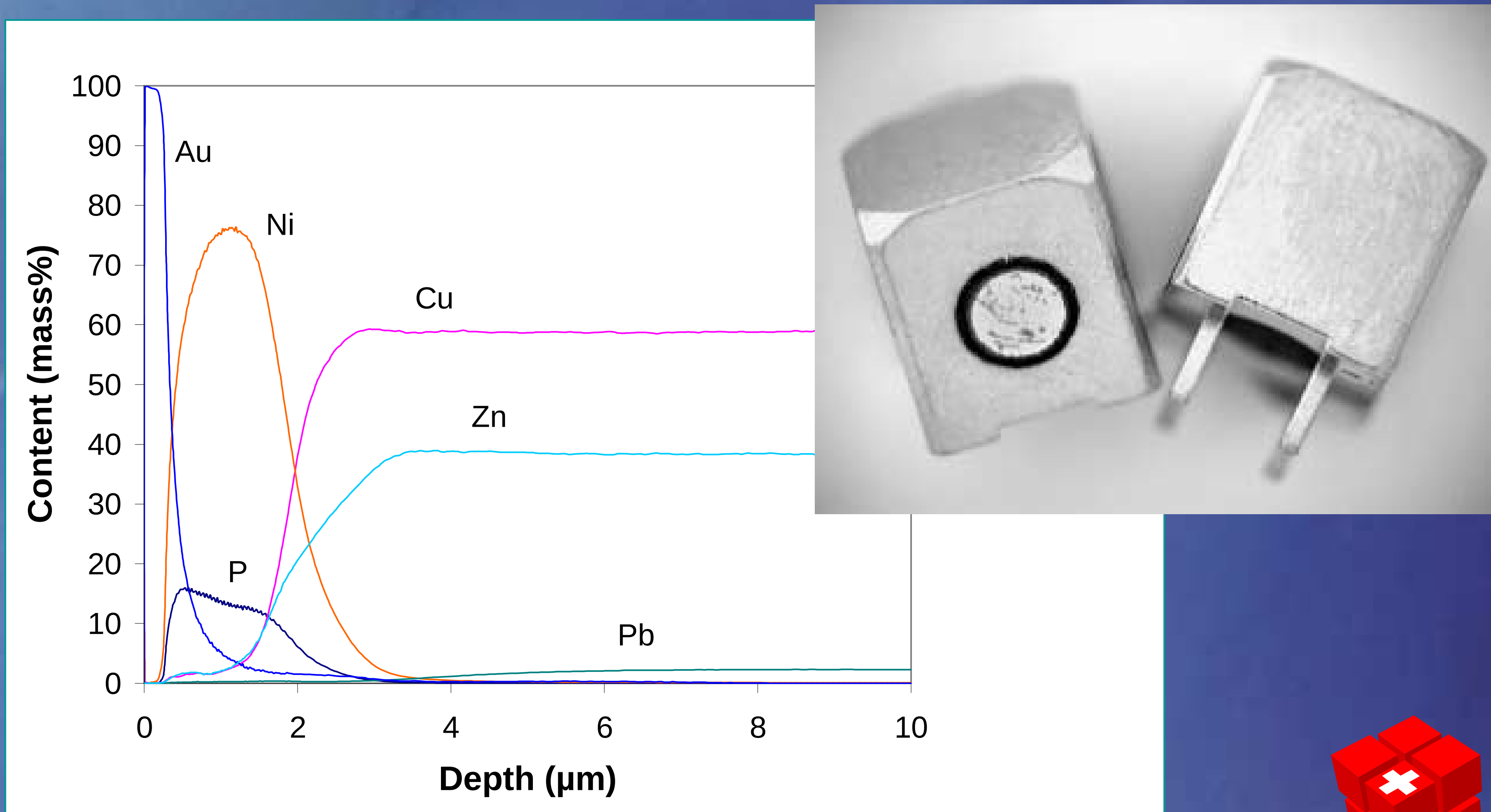


Analysis of conducting materials by JY RF-GD-OES

Christophe Deraed

Introduction example



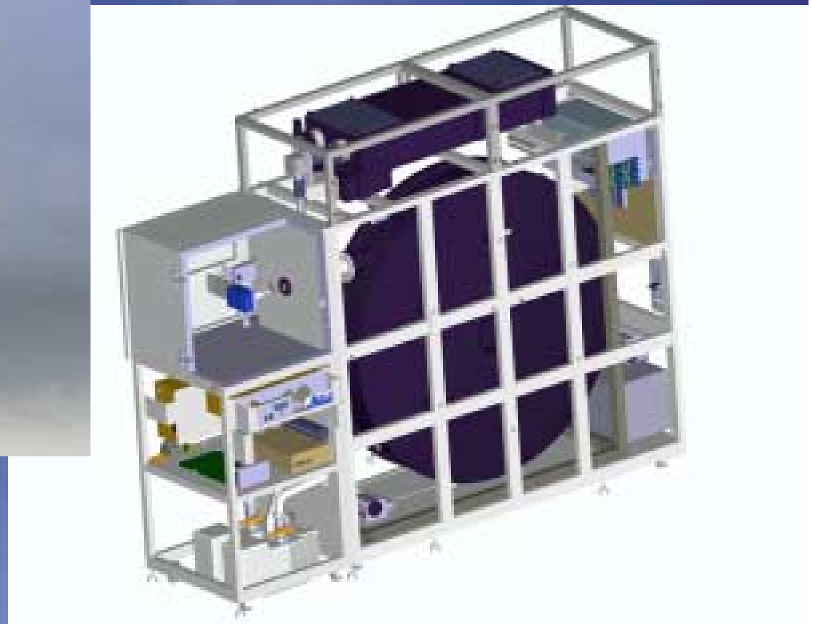
Courtesy of EMPA

Optical Spectrometer and RF powered Glow Discharge Source

- GD-PROFILER
- 50cm Polychromator with up to 46 detectors
- 64cm Monochromator

- GD-PROFILER HR
- 1m Polychromator with up to 64 detectors
- 1m Monochromator

Optical Spectrometer and RF powered Glow Discharge Source



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Spacious analysis chamber

Large samples

Automatic cleaning

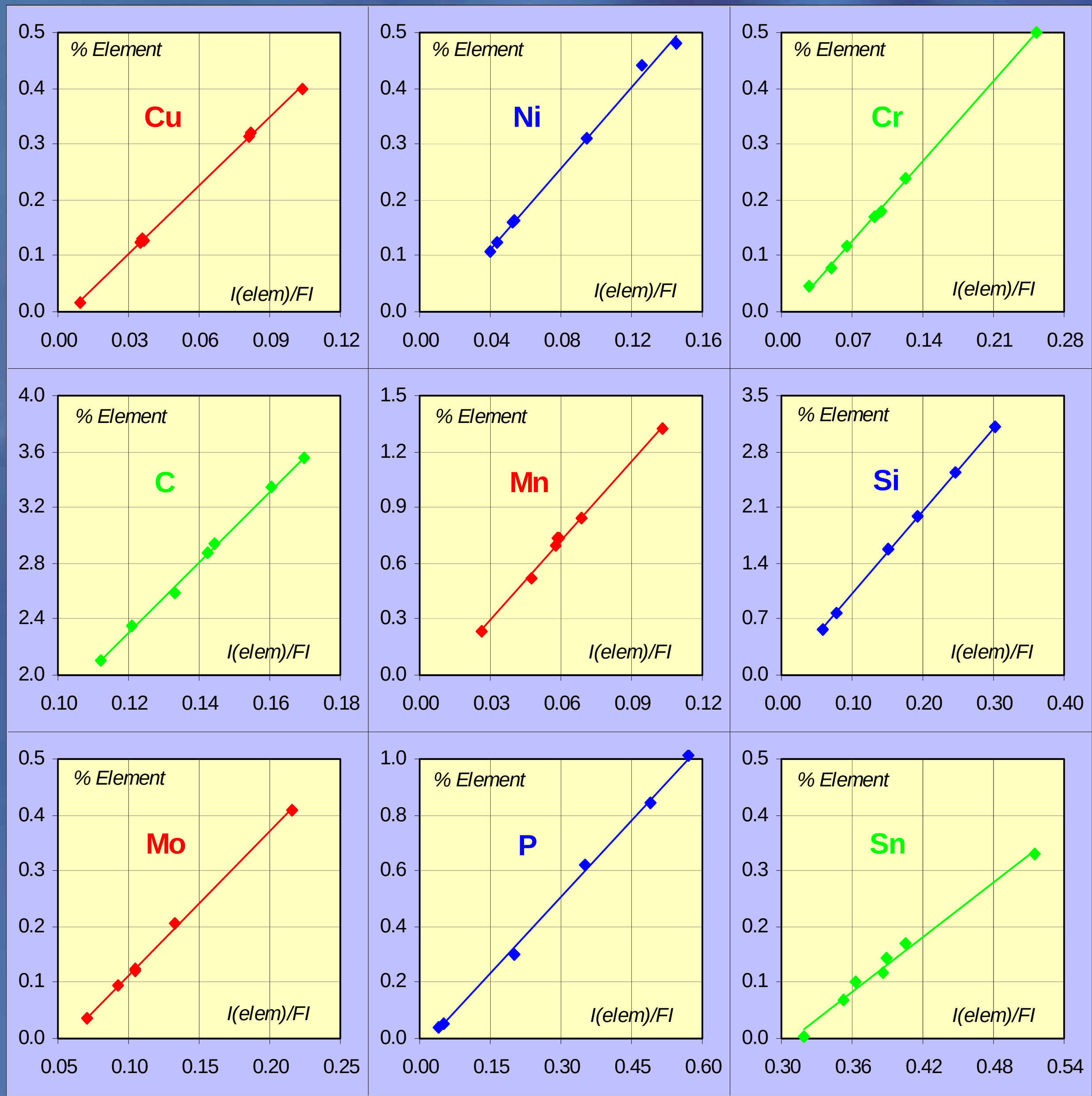
Centrelite for precise positionning

GD-Profiler with a large (A4) sample directly placed on the lamp

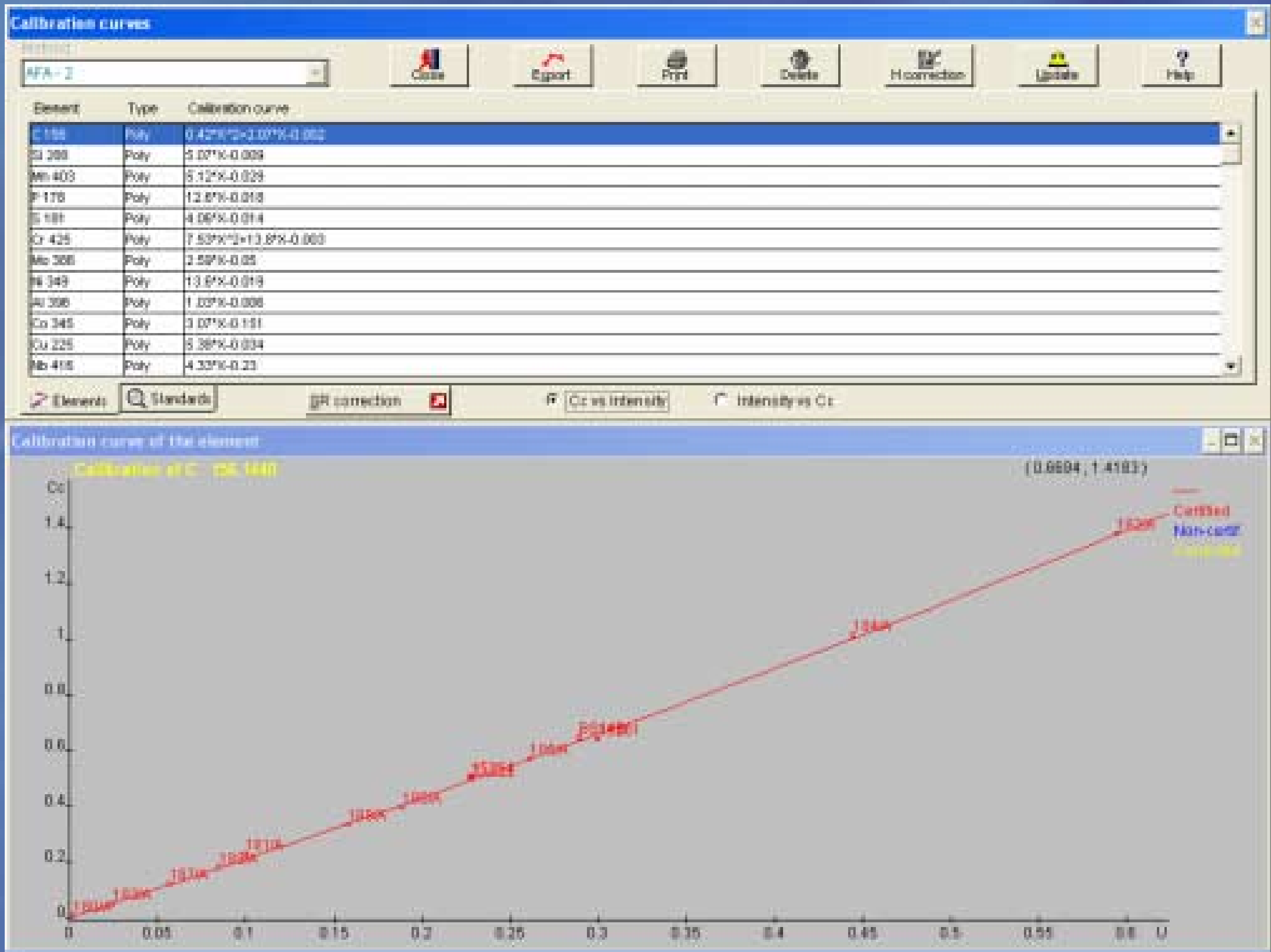
RF-GDOES CDP for conducting materials

- Quantitative Compositional Depth Profiling is like a series of ordinary bulk analyses repeated quickly on the same sample, same spot
  - With the addition of multimatrix and depth information
  - We first need to check whether bulk analysis is possible with RF-GDOES

Bulk analysis



Calibration curves



Analytical methods

relative mode best for bulk analysis in most cases

Analytical function

$$\left(c_i / c_{maj}\right) = f\left([a_i]; I_i / I_{maj}\right)$$

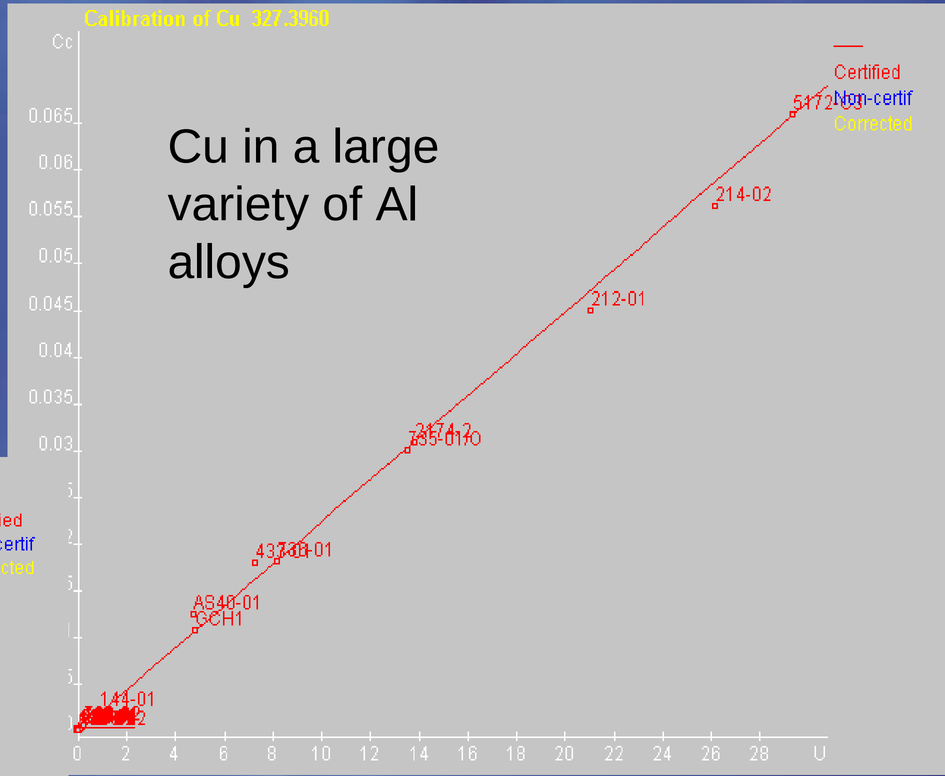
$$c_{maj}^{rel} = \frac{1}{1 + \sum c_i / c_{maj}}$$

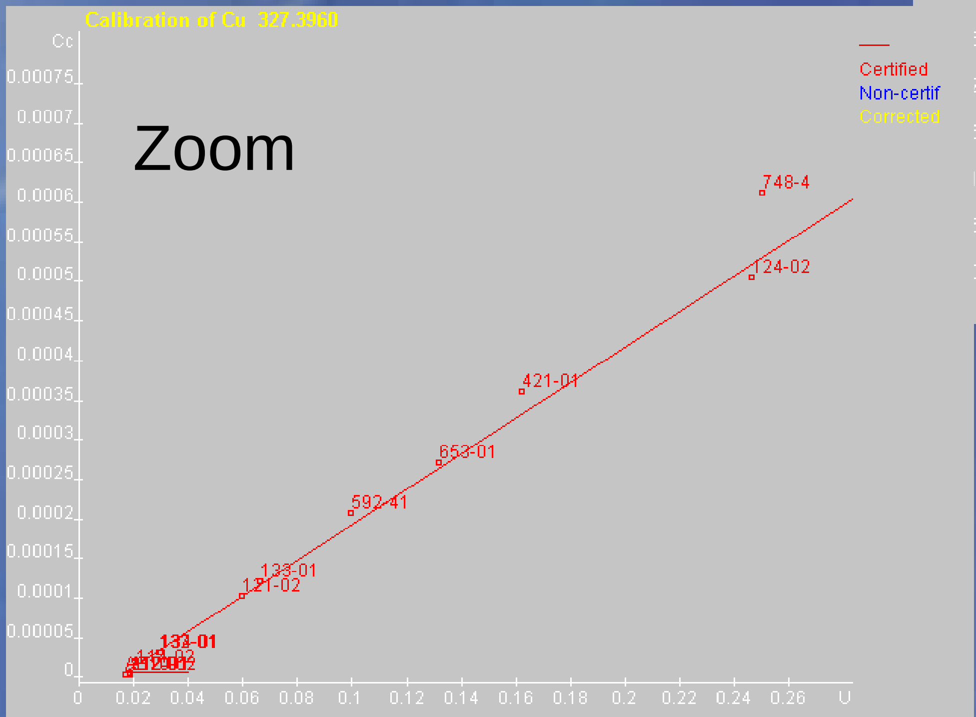
Major element content

All elements except major

$$c_i = \left(c_i / c_{maj}\right) \bullet c_{maj}^{rel}$$

Relative method Al matrix





Bulk Analysis: Steel

Element	Certified (mass %)	Measured (mass %)	SD (mass %)
Fe	70.8	71.3	0.01
Cr	17.3	17.5	0.05
Ni	9.2	9.1	0.04
Mn	1.38	1.38	0.01
Si	0.40	0.39	0.01
Cu	0.098	0.091	0.008
Mo	0.092	0.087	0.004
C	0.066	0.066	0.003
P	0.021	0.021	0.002
S	0.012	0.012	0.001

Table 2. RF-GD-OES Analysis of Stainless Steel 465/1

Bulk: Pure Pt data

Calibration curves of the method elements Method: Metalor Platines - 0 Method type: Normal Internal Std: Pt 225			
Element	Type	Calibration curve	Estimated LD
Pt 225	Poly	-	
Ag 338	Poly	1.22*X-0.001	<1ppm
Au 268	Poly	12.5*X-0.006	1ppm
Co 387	Poly	3.96*X-0.002	<1ppm
Cr 425	Poly	0.165*X-2e-04	<1ppm
Cu 325	Poly	0.655*X-0.002	<1ppm
Fe 302	Poly	18.3*X-0.005	1ppm
Ir 204	Poly	9.79*X-0.015	2ppm
Mn 403	Poly	0.519*X-8e-04	<1ppm
Ni 362	Poly	0.646*X-0.001	1ppm
P 178	Poly	1.45*X-1e-04	1ppm
Pd 340	Poly	0.885*X-8e-04	<1ppm
Rh 343	Poly	1.28*X-7e-04	<1ppm
Sn 318	Poly	5.5*X-0.04	4ppm
Al 394	Poly	0.411*X-7e-04	<1ppm
B 250	Poly	0.04*X-6e-05	1ppm
Bi 307	Poly	9.65*X-0.056	5ppm
Ca 397	Poly	0.032*X-6e-04	<1ppm
Cd 361	Poly	5.59*X-0.004	<1ppm
Li 671	Poly	0.064*X-3e-04	<1ppm
Mg 285	Poly	0.241*X-1e-04	<1ppm
Pb 406	Poly	3.31*X-0.01	3ppm
Si 288	Poly	1.44*X-0.001	1ppm
Te 214	Poly	27.8*X-0.017	3ppm
Ti 369	Poly	0.904*X-0.002	1ppm
Zn 335	Poly	4.09*X-0.015	3ppm
Zr 469	Poly	3.72*X-0.037	3ppm

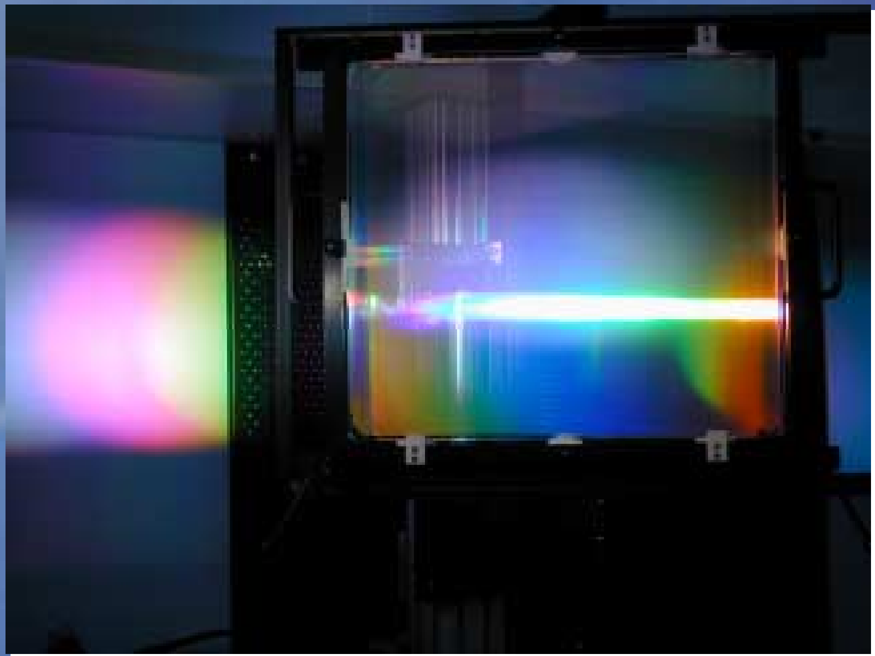
Most elements are very good

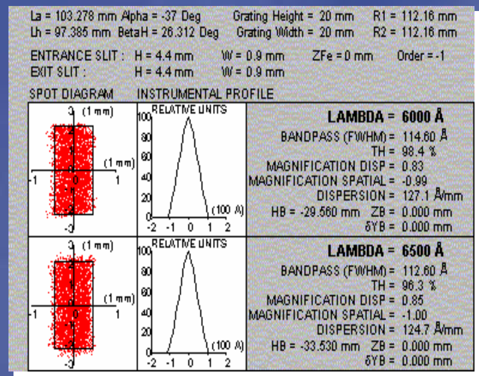
Bi 307 : special care required in sample handling (line close to an OH molecular band)

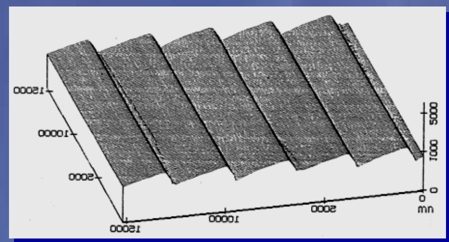
Bulk analysis

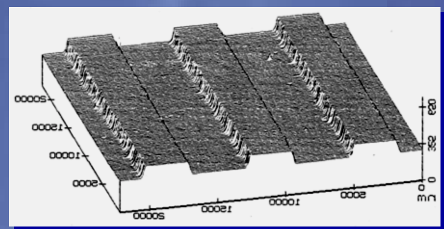
- Bulk analysis of conducting material is possible with RF-GDOES
  - The qualtity of CDP will most likely not be better than the quality of Bulk analyis
    - A few important features

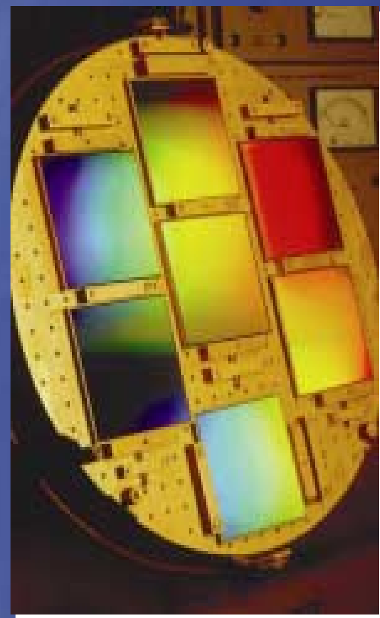
Optics : Diffraction gratings











HJY Very High Quality Optical Components

Up to 64 channels (on HR).

Blazed UV grating corrected for aberrations.

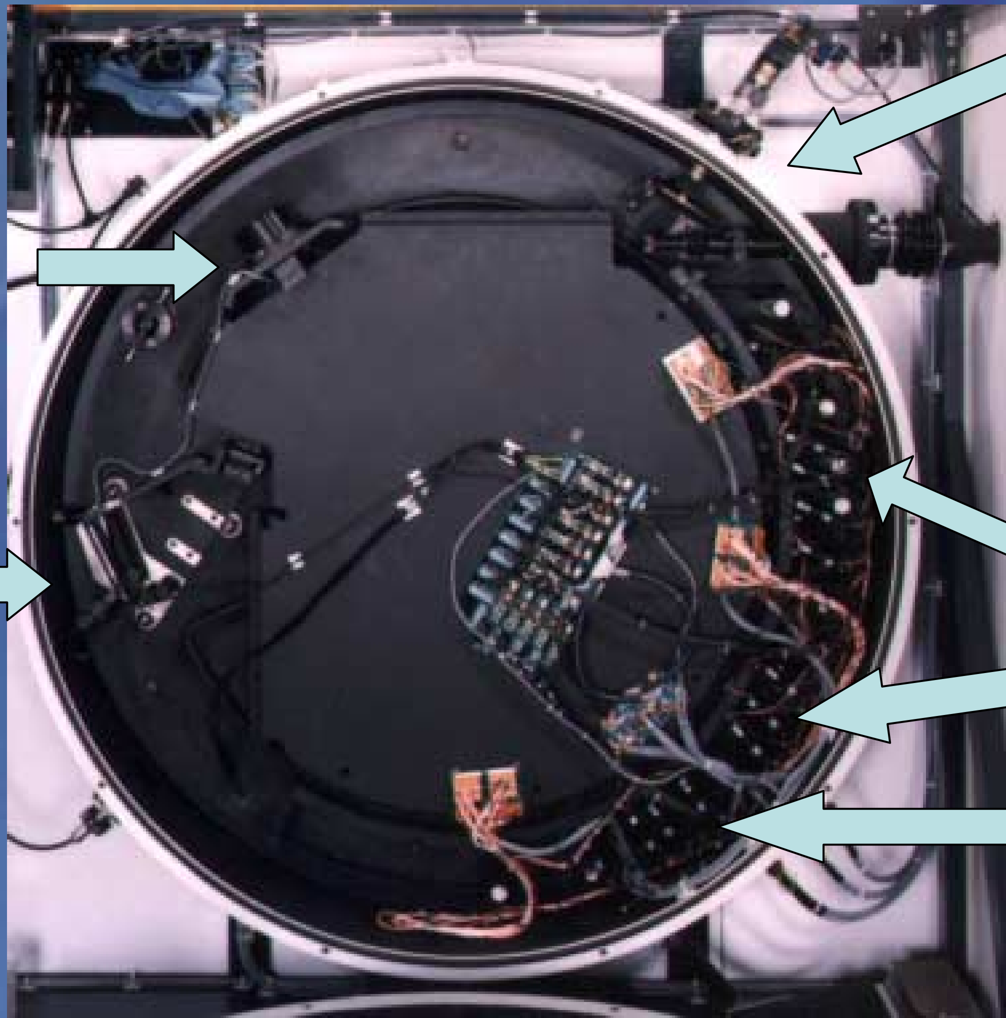
Paschen Runge mounting

Additional Flat field mount with IR grating for alcali

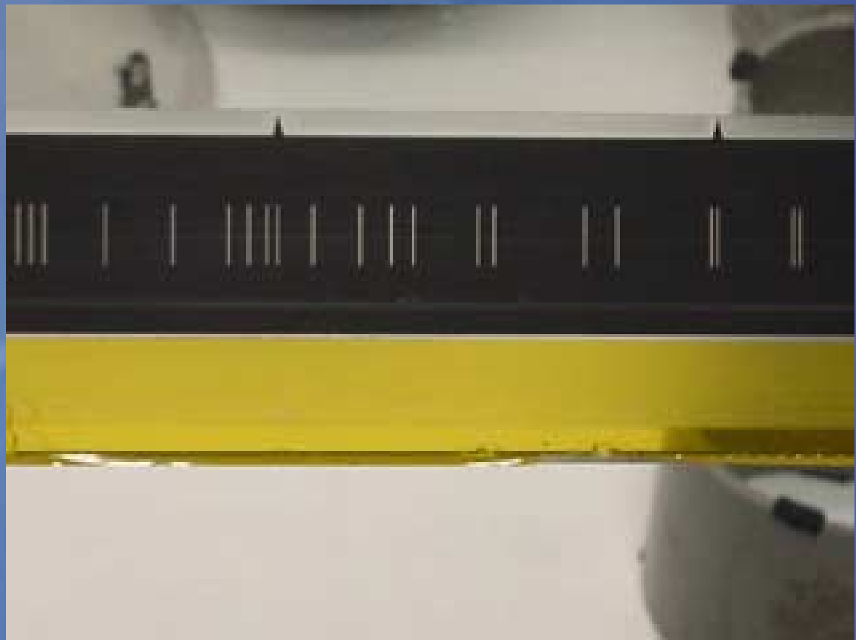
Mask for flexibility

Very High Resolution

High resolution poly (GD-Profiler HR)

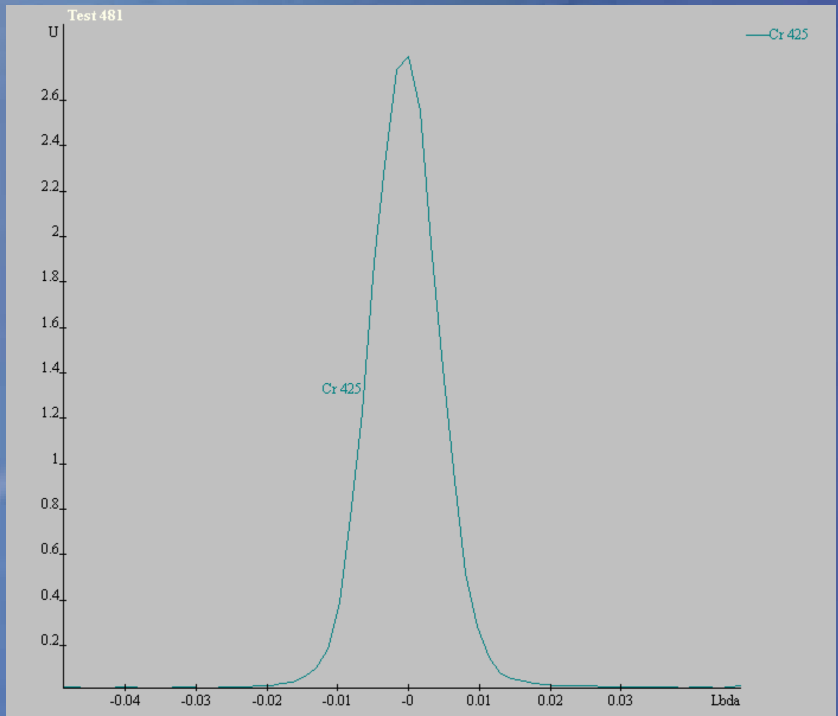


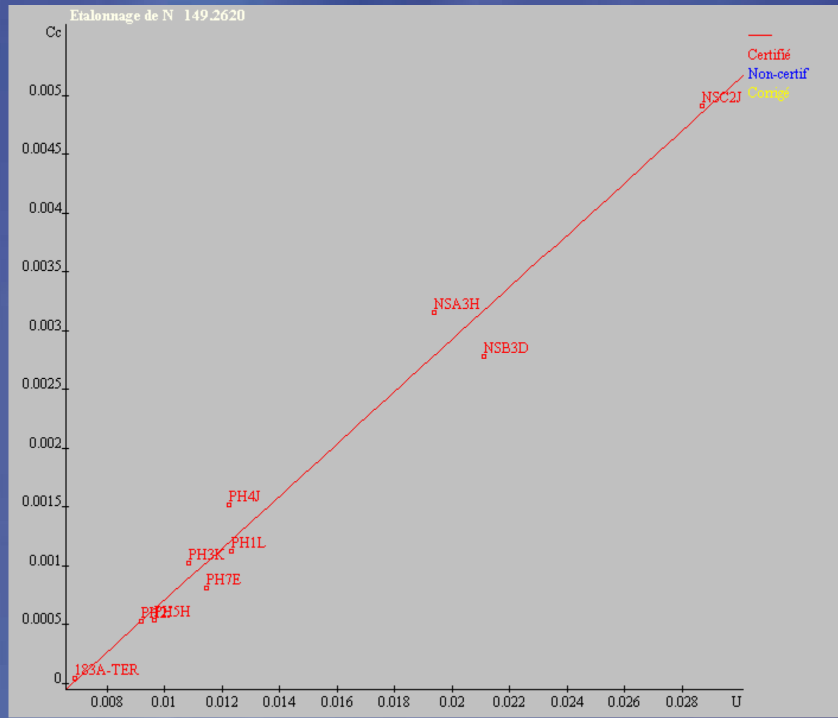
Flexibility of line selection



- Partial view of the mask with the secondary slits.
- The full mask is 1.2m long. Wavelengths positions are corrected for temperature (poly is thermoregulated).
- Mask produced by electrodeposition. Very high dimensional precision. Pure Ni with a thin Cu layer on top of it oxidized for darkness.
- Only the lines of interest will be kept open, others will be covered. On site modification or extension is possible.

Resolution and sensitivity





Line profile of Cr (1 order) :

Resolution 12pm (on HR)

Calibration of N in steels

BEC 200ppm, LQ 10ppm

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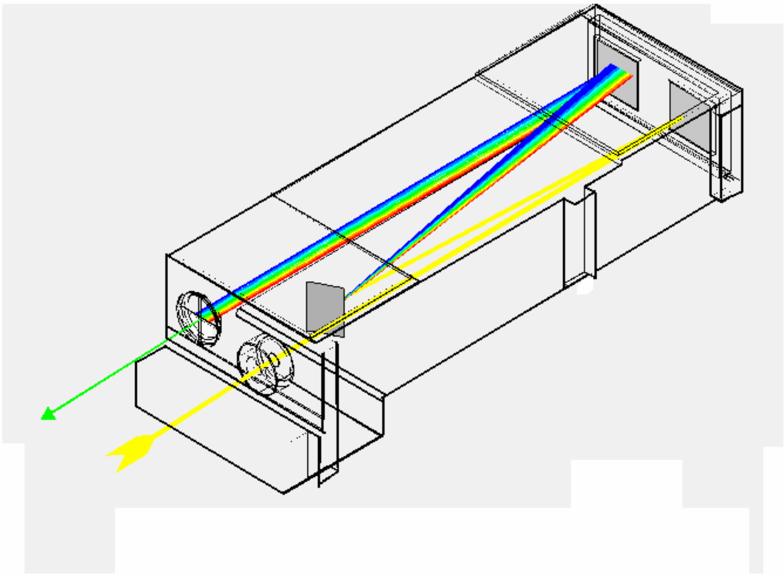
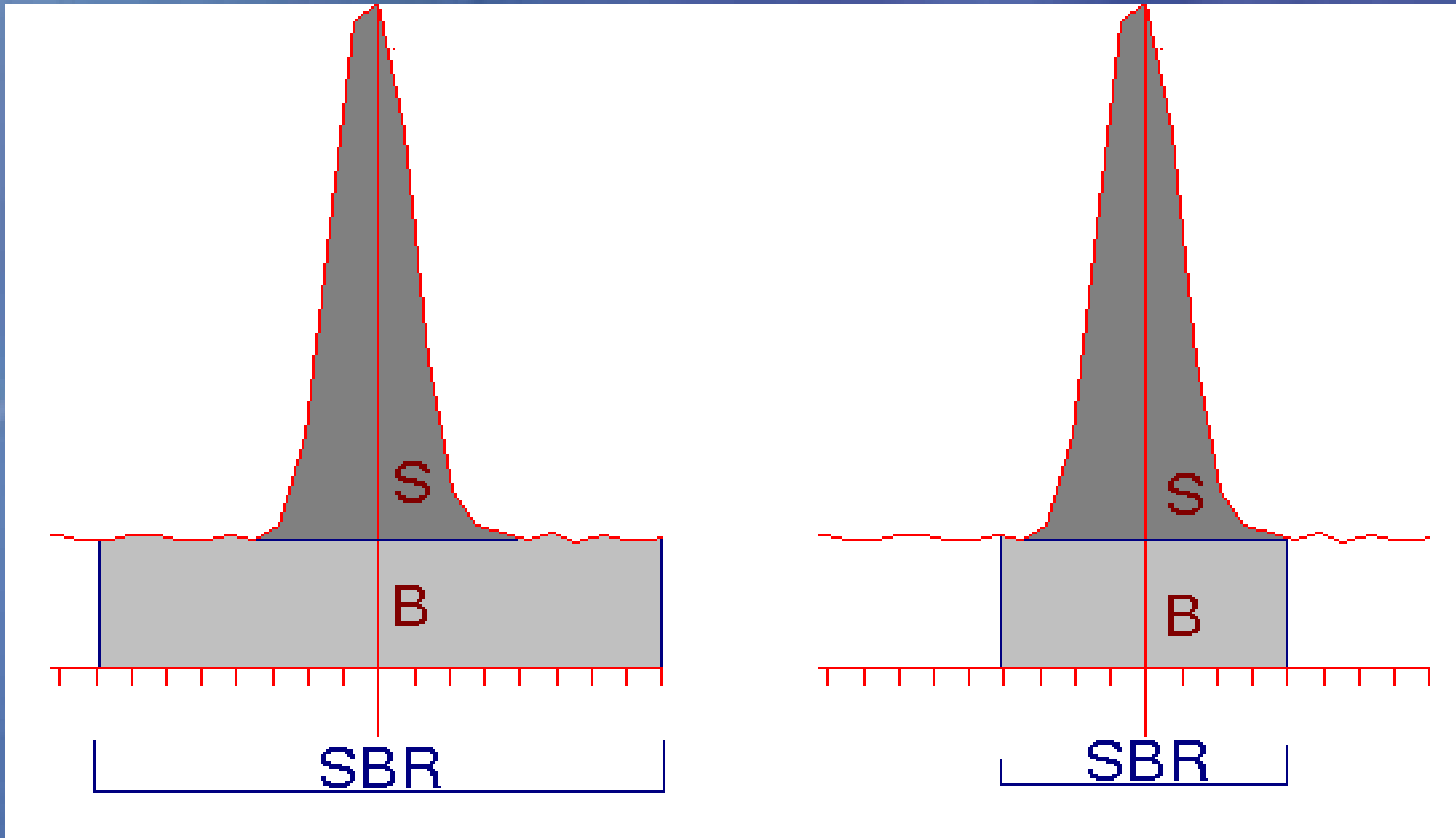
Principle of Polyscan

Applicable to BULK only

Direct observation with a monochromator

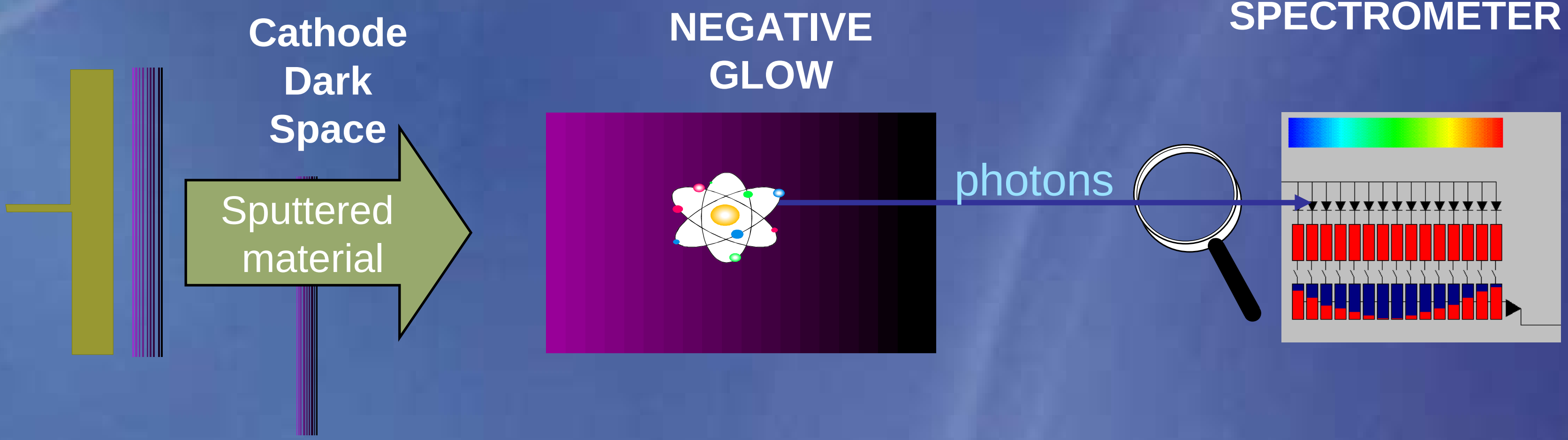


Signal / Background Ratio
larger for smaller spectral band pass



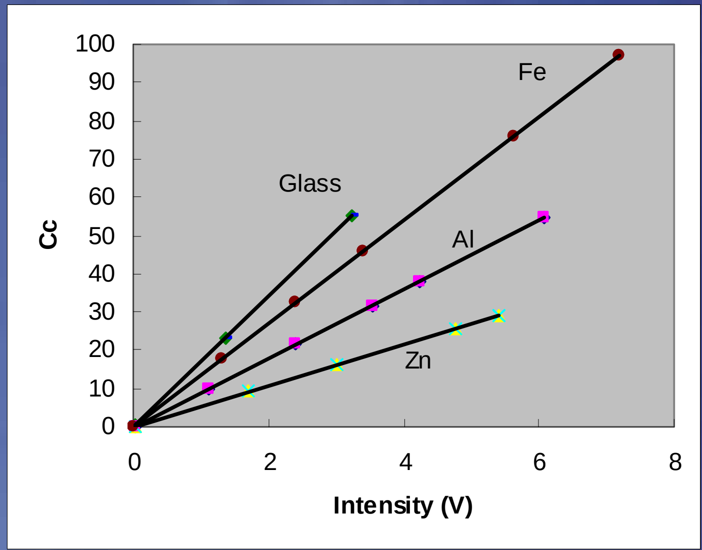
Three basic processes

- Erosion (sputtering)
  - Ion Bombardment
  - Secondary Electron Emission
  - Particle erosion
- Excitation (emission)
  - Collision
  - Excitation
  - Light Emission
- Detection and light collection



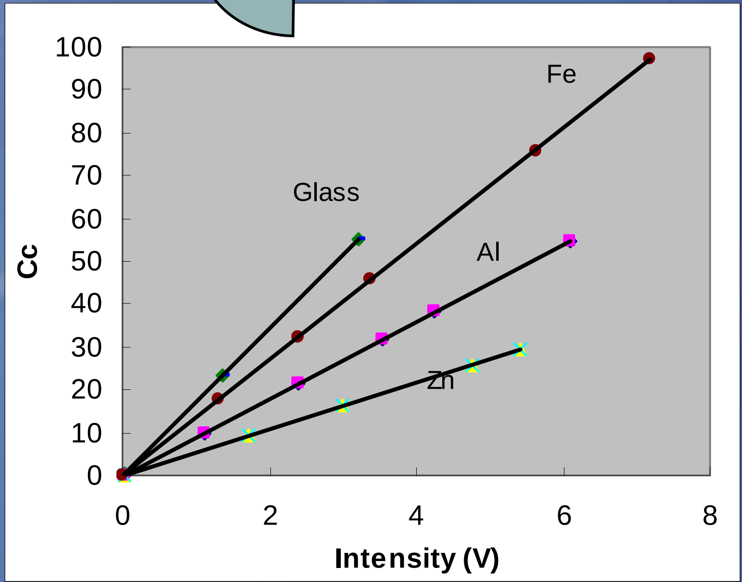
CDP Calibration

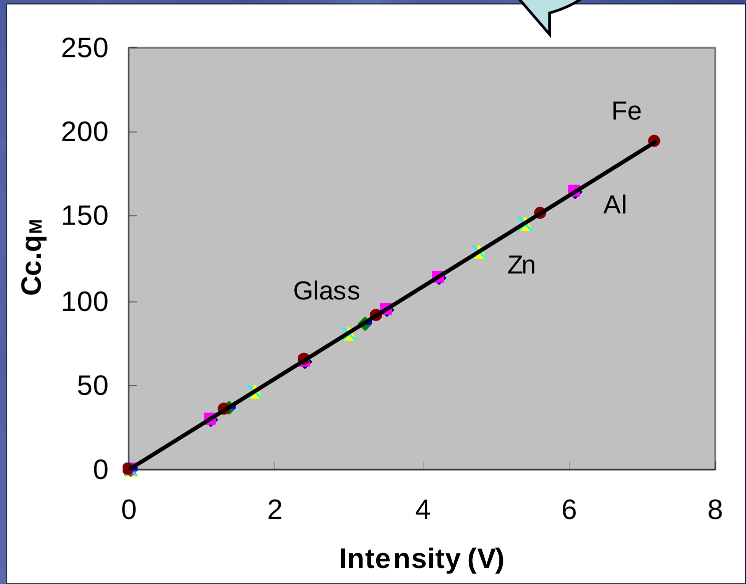
- Calibration : we want to create a functional relationship between the observed signals and a elemental composition of the sample
- The detector actually records the light emitted by the plasma, the sample itself does not emit any light.
- If we neglect this we would get in the best case the following result
- each type of material leads to one straight line
- in worst case we have a calibration cloud



Sputtering rate correction

We can calibrate and calculate the depth





Composition of the plasma

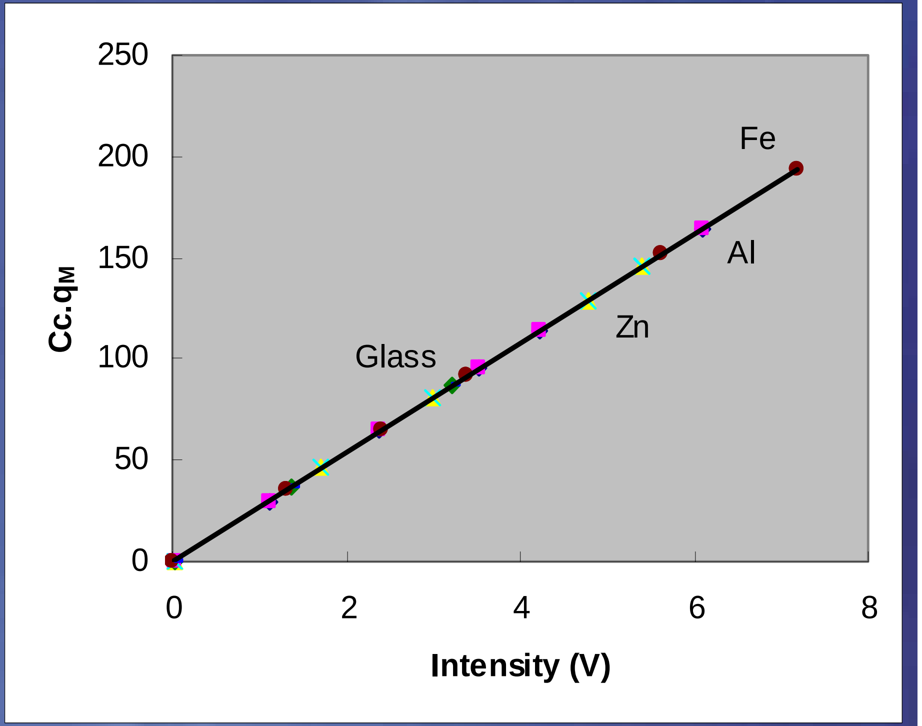
- The plasma contains mainly argon, the discharge carrier gas.
- Constituents of the plasma other then argon should come from the sample through sputtering
- A steady process of sputtering material and pumping it away

- The elemental composition of the plasma is proportional to the product of sputtering rate *q* and the composition of the sputtered sample surface c_i

- The composition of the plasma is equivalent to the composition of the samples surface multiplied by the sputtering rate

The 'cq' calibration line

- the analytical curve gives the concentration corrected by the sputtering rate as a function of the measured intensities
- For a given concentration : if the sputtering rate increases, the observed signal increases.
- If the concentration increases at the sample surface at constant sputter rate the signal will increase



Normalisation to 100%

- We need to know the chemical composition of the sample and not so much the composition of the plasma.
- If we assume all elements are analysed, the sum of all elements must be 100%
- Now we know the sputter rate
- and can calculate the elemental content in the sample

$$\sum C_i = 1;$$

$$\sum C_i q = \left(\sum C_i\right) q = q$$

$$C_i = \frac{(C_i q)}{q}$$

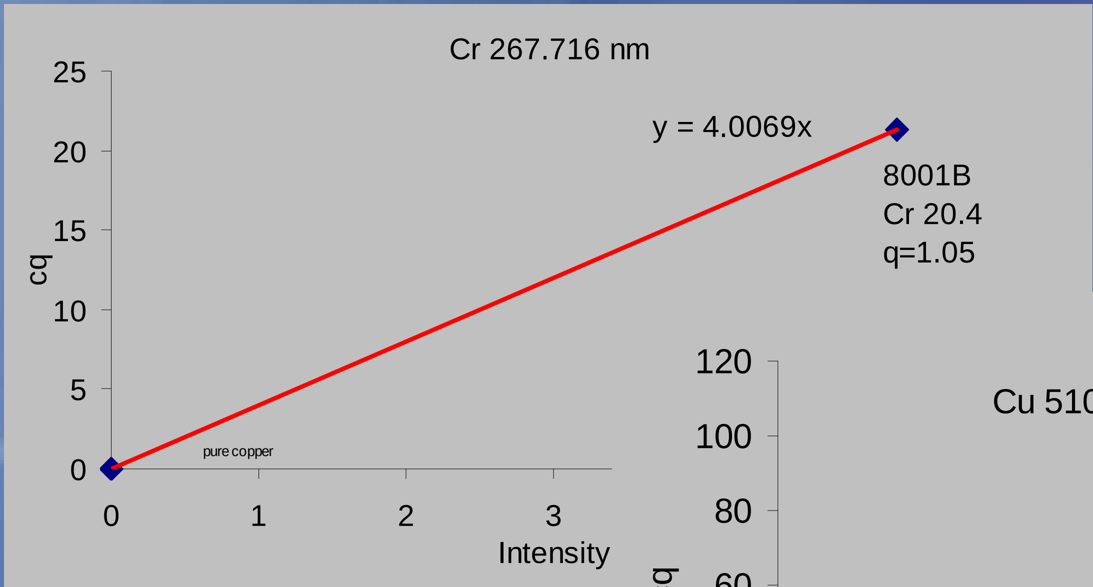
CDP : the quantification chain

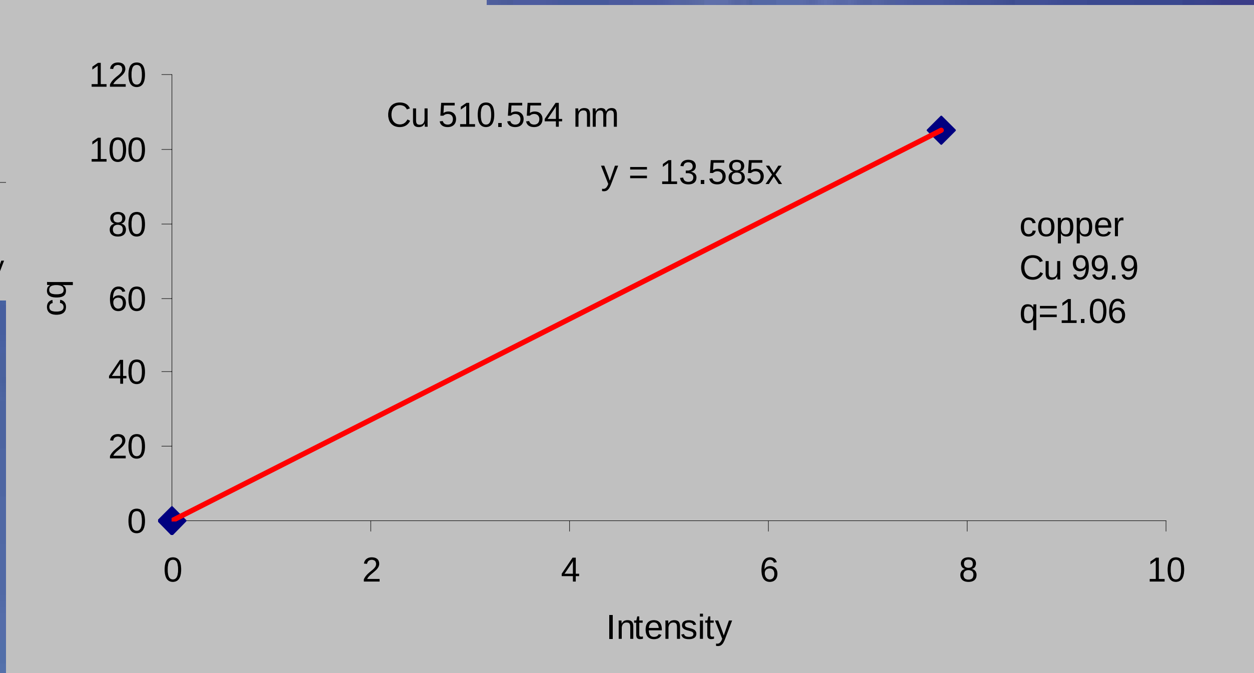
- Measure of intensities
- Calibration curves
- Get $c_i q$'s
- Sum of $c_i q$'s gives q
- Calculation of c_i's
- Estimation of density
- Depth

$$c_i\left(q_M / q_{\mathrm{Re}\,f}\right) = k_i^{(1)} R_i I_i + K^{(é)} (R_i I_i)^2 + b_i$$

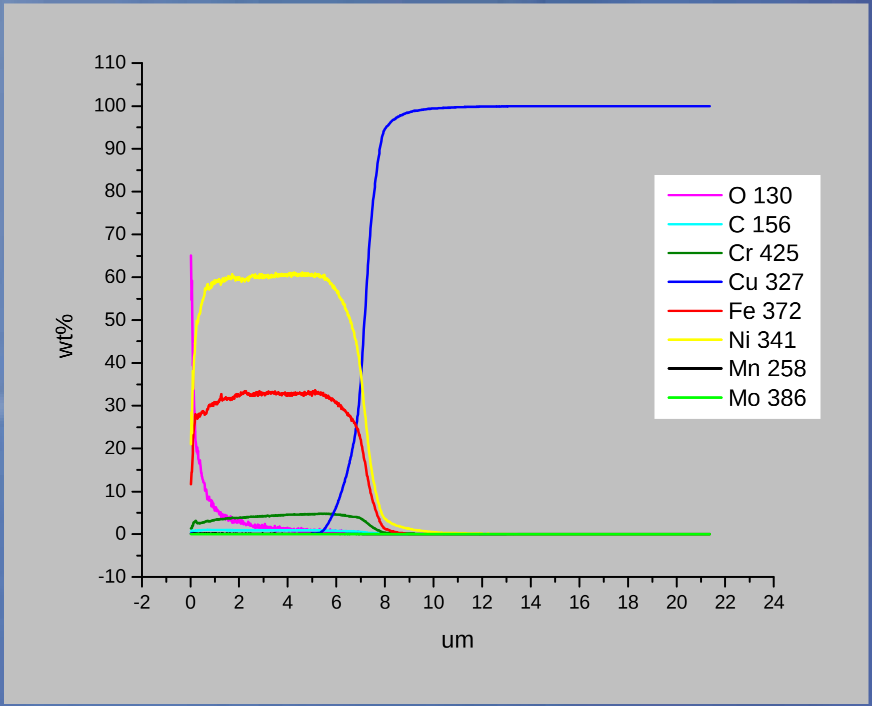
$$R_i = 1 + r_i (V - V_0)$$

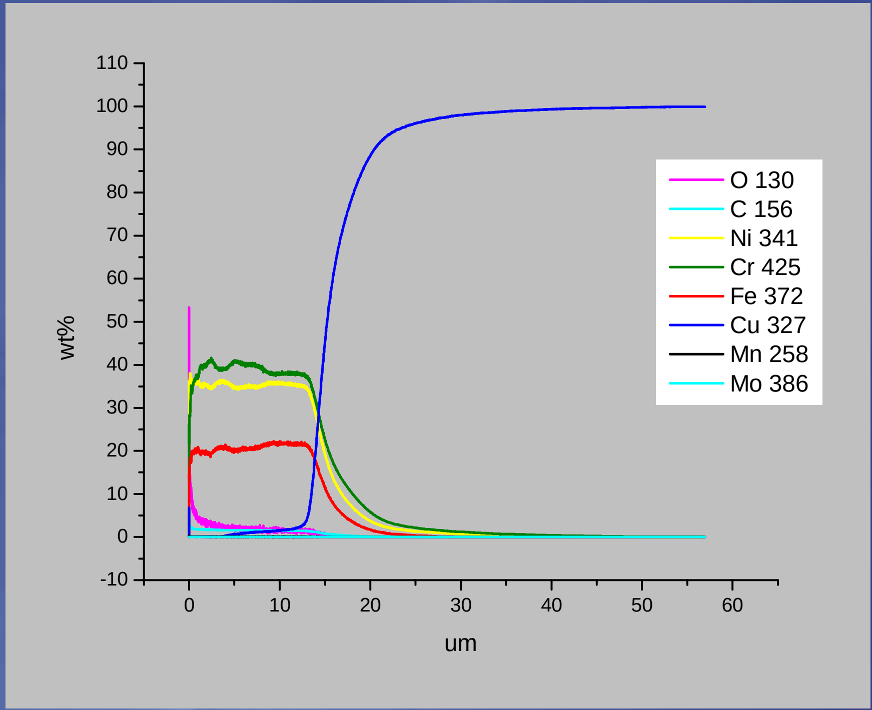
Calibration curve: simple





Application electrochemical deposition of steel on Cu





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Analytical methods
relative calibration mode for CDP

Basic idea :

- For many applications we do not need a real multi-matrix calibration : cladding, heat treatment, Oxidisation…
- It is sufficient to use the ‘virtual’ calibration mode for all elements but the major. Only the major is calibrated in the ‘cq’ mode.

Analytical methods

relative mode

$$\left(c_i / c_{maj}\right) = f\left(\left[a_i\right]; I_i / I_{maj}\right)$$

$$c_{maj}^{rel} = \frac{1}{1 + \sum c_i / c_{maj}}$$

$$c_i = \left(c_i / c_{maj}\right) \bullet c_{maj}^{rel}$$

‘cq’ mode

$$c_{maj} q_{rel} = f\left(\left[a\right]; \left[I_{maj}\right]\right)$$

$$q = {c_{maj} \cdot q} \Big/ {c_{maj}^{rel}}$$

Analytical methods

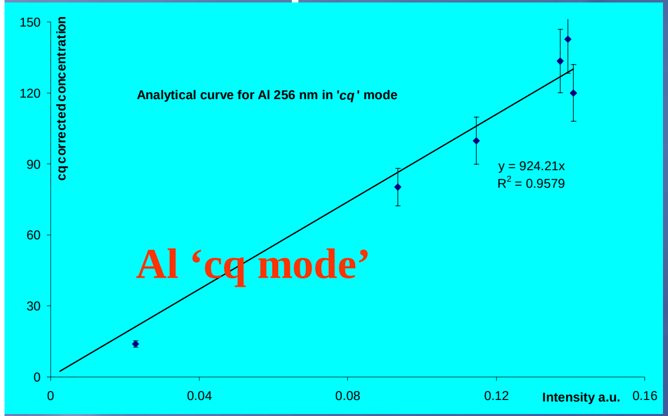
relative calibration mode for CDP

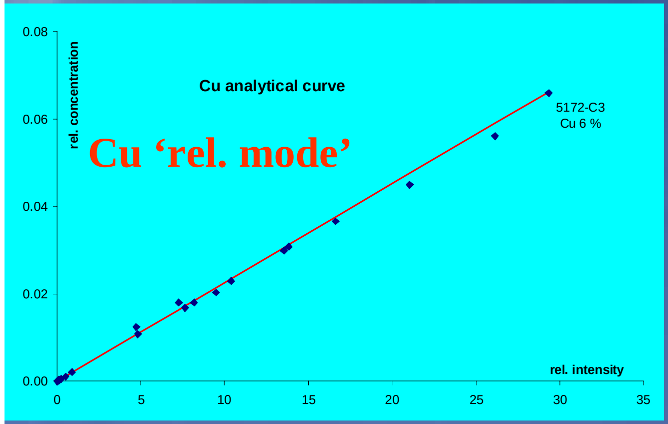
Advantages :

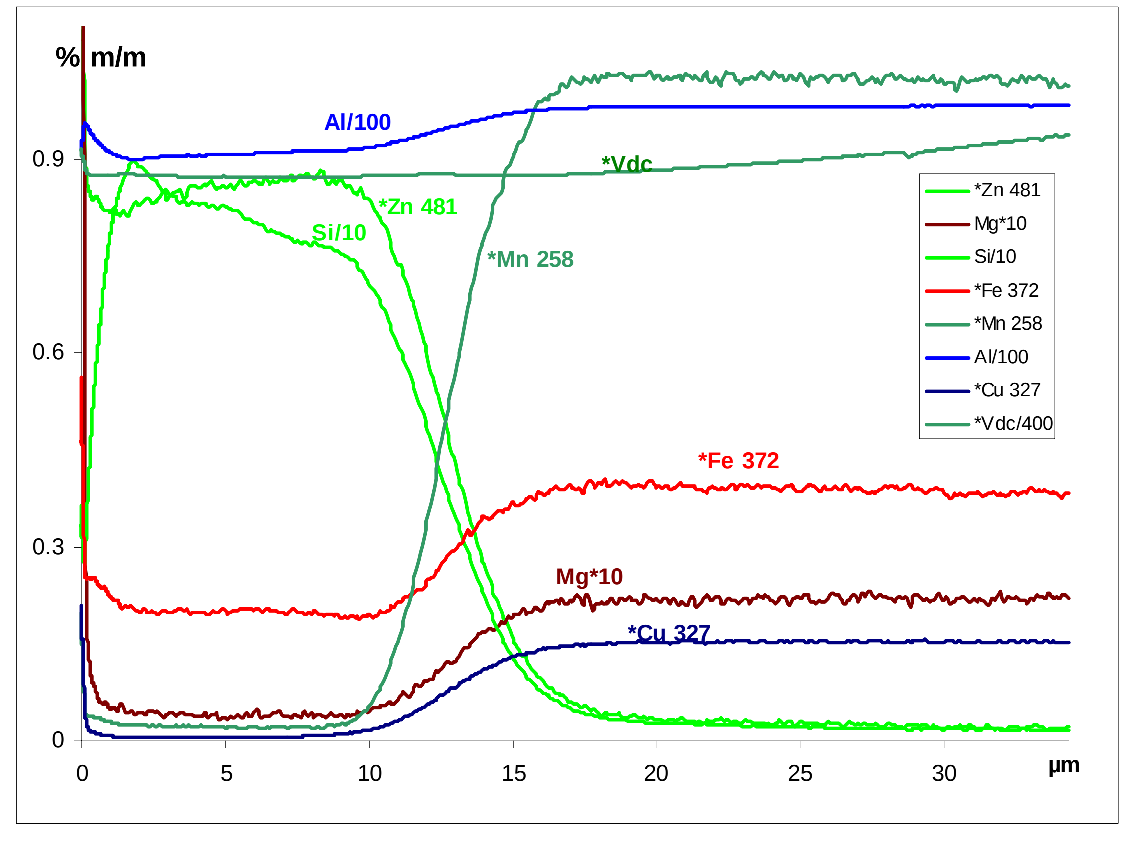
- Only few CRM with known sputtering rate are needed.
- More CRM can be included in the calibration
- The major source of uncertainty is excluded from the calculation of the chemical content

Analytical methods
relative calibration mode for CDP

example : Cladded aluminium sheet







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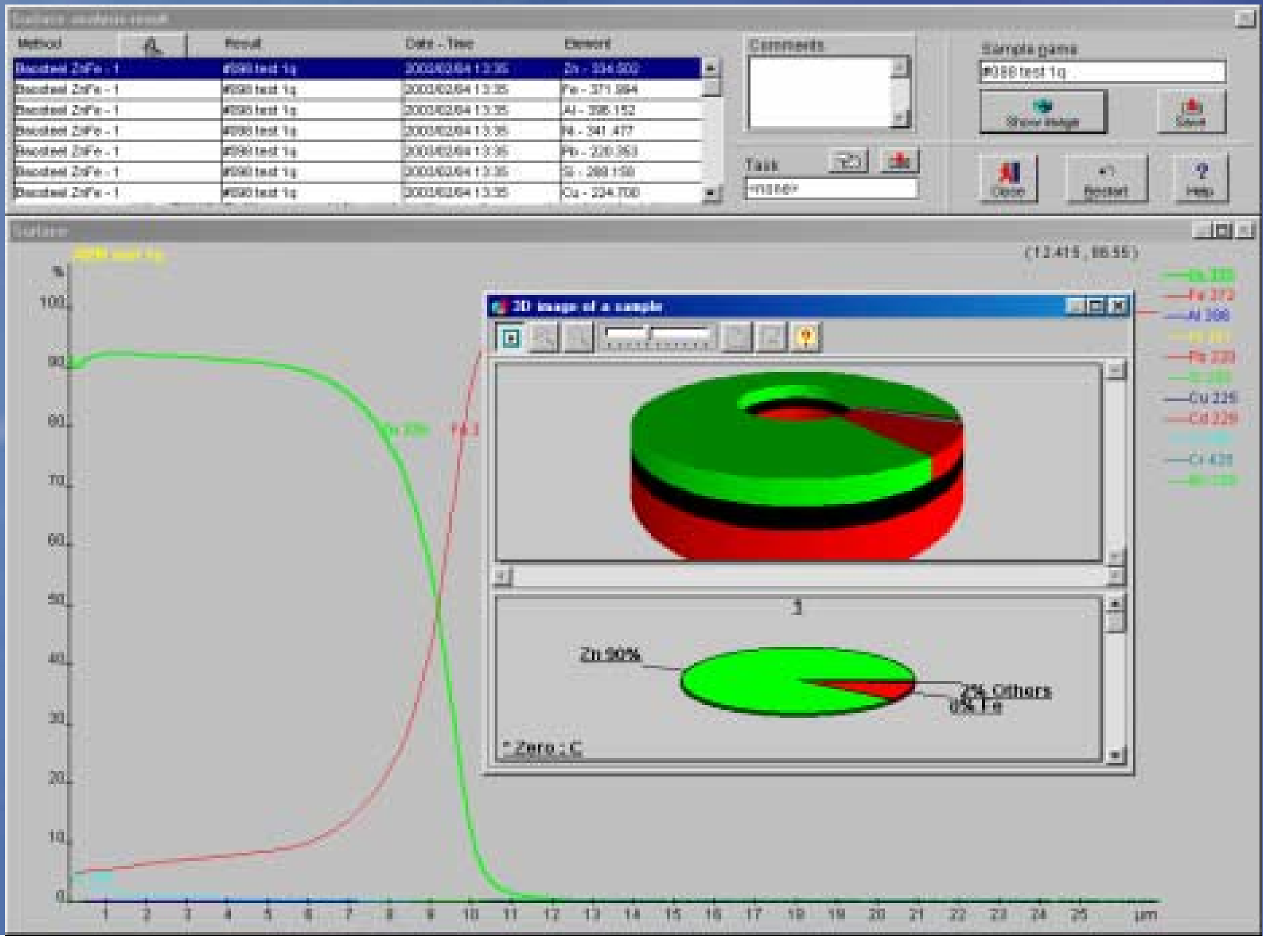
Depth profiling: ZnFe coating on Steel



Control of coating weights

Control of process defects

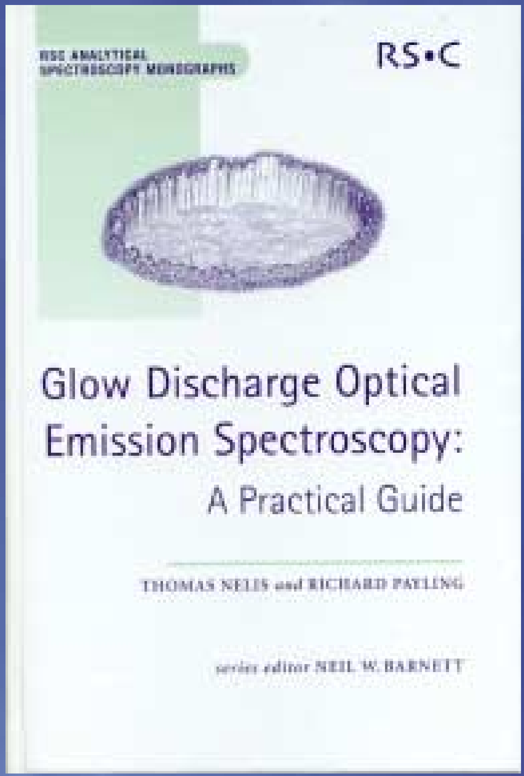
NEWS NEWS

ISO 16962

GD recent books

Marcus:
"Glow Discharge Plasmas in Analytical Spectrometry"
Wiley, November 2002

Nelis and Payling:
"Practical Guide to Glow Discharge Optical Emission Spectroscopy"
Royal Society of Chemistry, Cambridge, 2004



This is the end