

Analysis of conducting materials by JY RF-GD-OES

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Introduction example



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Courtesy of EMPA

Explore the future

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

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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 HORIBAJOBIN YVON



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

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Calibration curves

			-	1	~		9	. 1	-	BC.	4		?
M-2				Close	Egport	Pr Pr	91	Delete	Hoa	rector	Update	_	PB4
Benerit	Type	Calibration ourve	1	1.1.1								·	- 28
155	Paty	0.42*8*2+3.00*%	0.002										•
1 208	Poly	\$ 07"K-0.009											2
m 403	Poly	5.12*X-0.029											
178	Poly	12.6%-0.018											
1時	Poly	4.06*X-0.014											
r 425	Poty	7.53*X*2+13.8*X	0.003										
to 30E	Poly	2.50 ⁴ K-0.05											1.2
349	Poly	13.6*X-0.019											
1 396	Poty	1.03*%-0.008											
o 345	Poly	3.07*8-0.151											
u 225	Poly	5.38*%-0.034											
b 415	Poly	4.33*%-0.23											
Section in the											(0.0694, 1	41833	
Co 1.4 1.2										_	(0.6604, 1	A183)	Cettined Non-cetti
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Ce 14. 1.2. 1. 0.0. 0.4. 0.2.			1889		Sand	Eluent	_	_	-	/	(0.6604, 1	4183)	Certified

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Analytical methods

relative mode best for bulk analysis in most cases

Analytical function

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

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

Major element content

All elements except major

$$c_{i} = (c_{i}/c_{maj}) \bullet c_{maj}^{rel}$$

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Relative method AI matrix





Bulk Analysis: Steel

Element	Certified	Measured	SD
	(mass %)	(mass %)	(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
С	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

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Bulk: Pure Pt data

Calibration curves of the method elements Method: Metalor Platines - 0 Method type: Normal Internal Std: Pt 225

Element	Туре	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
lr 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
AI 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)

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Bulk analysis

 Bulk analysis of conducting material is possible with RF-GDOES

 The quality of CDP will most likely not be better than the quality of Bulk analyis

• A few important features

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Optics : Diffraction gratings











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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

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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.

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Resolution and sensitivity



Line profile of Cr (1 order) :

Resolution 12pm (on HR) HORIBAJOBIN YVON

Calibration of N in steels BEC 200ppm, LQ 10ppm

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Principle of Polyscan

N T K

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Erray be advartageous to explore the spectrum on either side of the line, either over a short detance, to their spectral elignment, or over a medium distance, to assess the influence of the emission background, or over a larger distance to use other emission background.

Let's remember that the radiation from a sit contains both the analytical line and the spectral background, made up of the continuous background and the wings of the near and intense lines. When the background is not corrected, the analysis result is erconous, to analyze traces, this error should be eliminated by measuring the intensity on either table of the line to measure the background and deduct it.

To explore the spectrum, it is simpler to increase the entrance skit, either optically or mechanically. This way, the spectrum can be scenned simultaneously around all the analytical lives of the optical programme.

To optically ocan the image of the entrance silt, a parable lace black is placed behind the silt. By rotating the black, the image of the silt moves, However, this rotation delocates the testers and only allows briefed spectral explorations.

#Disame 3 6 3 6 8 8 3 Storgen er une In. Stand Foreful 31. @Precher of entern.



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Applicable to BULK only

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Direct observation with a monochromator





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Signal / Background Ratio larger for smaller spectral band pass



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Three basic processes

- Erosion (sputtering)
 - Ion Bombardment
 - Secondary **Electron Emission**
 - Particle erosion

- Excitation \bullet (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

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Sputtering rate correction

We can calibrate and calculate the depth





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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

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 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



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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

 $\sum C_i = 1;$

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

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CDP : the quantification chain



Calibration curve: simple









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Analytical methods relative calibration mode for CDP

Basic idea :

- For many applications we do not need a real multimatrix 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.

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Analytical methods

relative mode

'cq' mode

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

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

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

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



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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

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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



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This is the end

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