La spectroscopie à décharge luminescente (GDOES) pour l'analyse de traitements thermiques et autres……

SURF –THERM
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Tel: 00 49 177 841 5661
Christophe.deraed@ametek.com

Techniques d’analyse pour les métaux

Spectrométrie d’étincelle

Rayons X

MEB + EDX

C/S, N/O/H

ICP

GDOES

Quelles sont les questions auxquelles la GDOES apporte une réponse ?

Quels éléments sont présents dans l'échantillon ? N O C S H F Cl et tous les autres

À quelle concentration ?

L'échantillon est-il homogène?

Y a t'il des couches sur la surface?

Y a t'il eu traitements thermiques ?

Ces traitements ont-ils été faits correctement?

D'où peuvent provenir des défauts de surface ?

Y a t'il une contamination à l'interface?

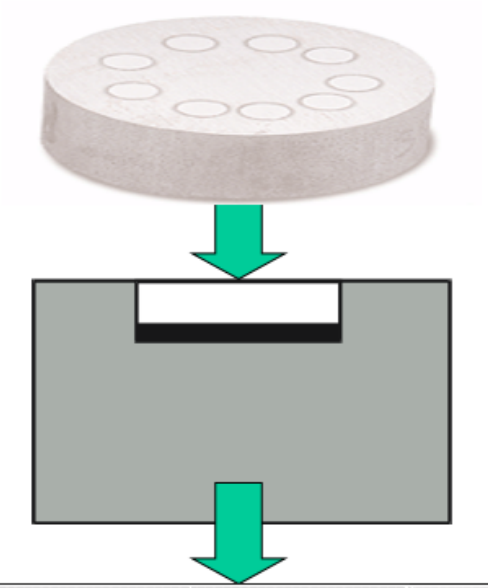
Y a t'il une oxidation ? Ou une diffusion dans une couche?

Que fait la concurrence?

En tout cela en quelques minutes !

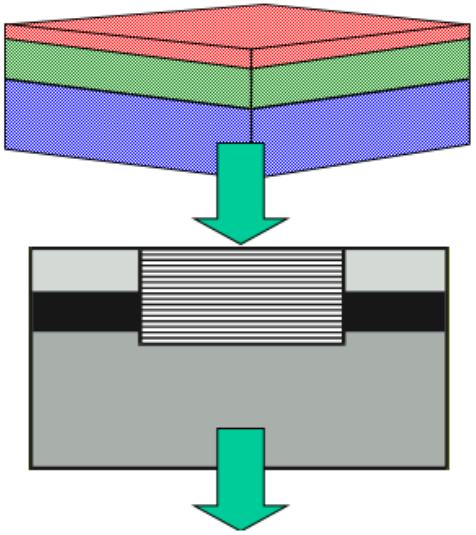
Comment ca marche ?

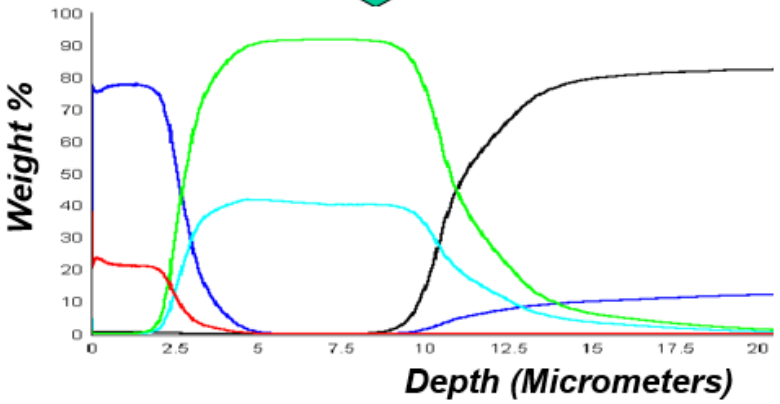
Bulk Analysis

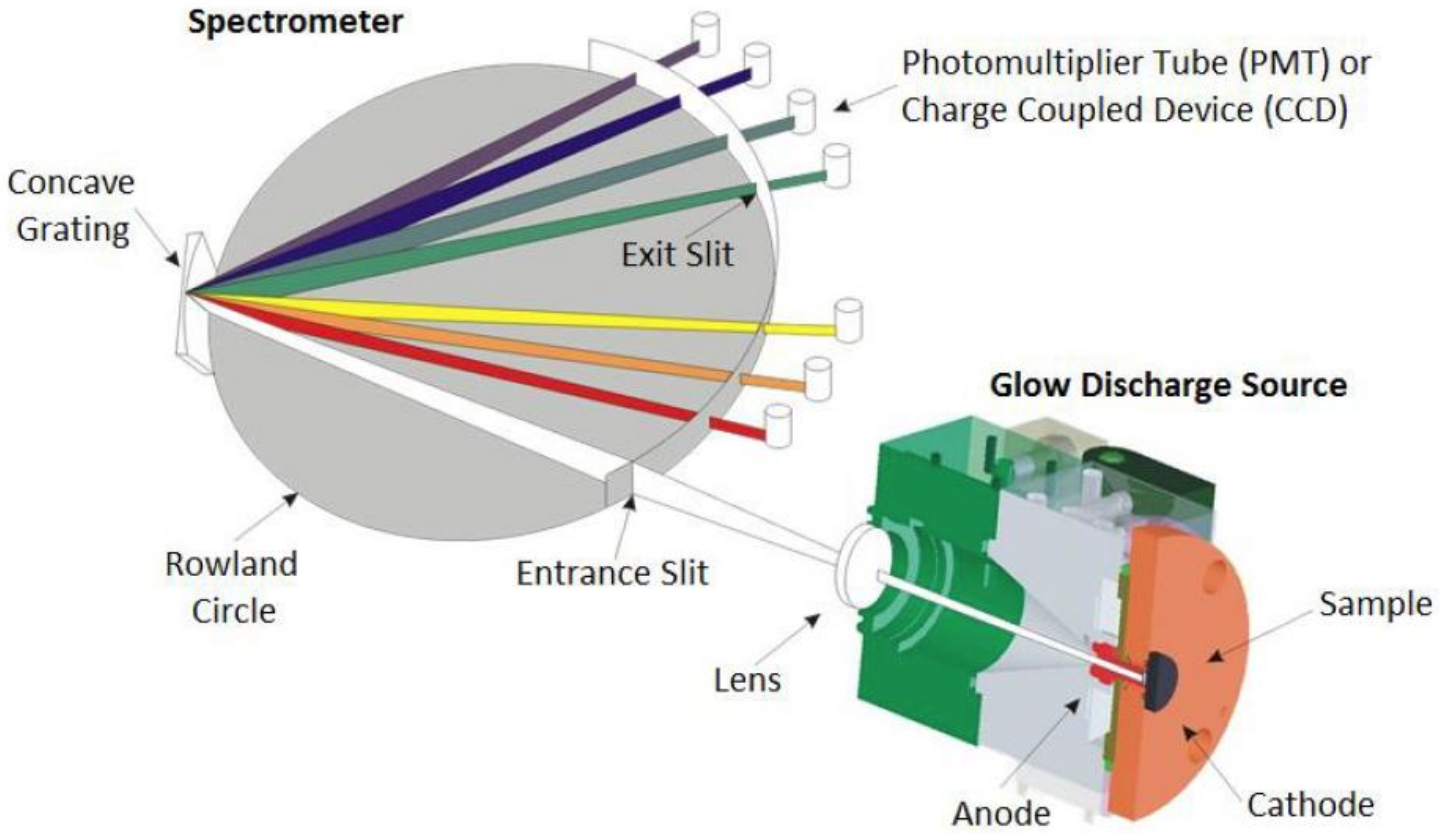


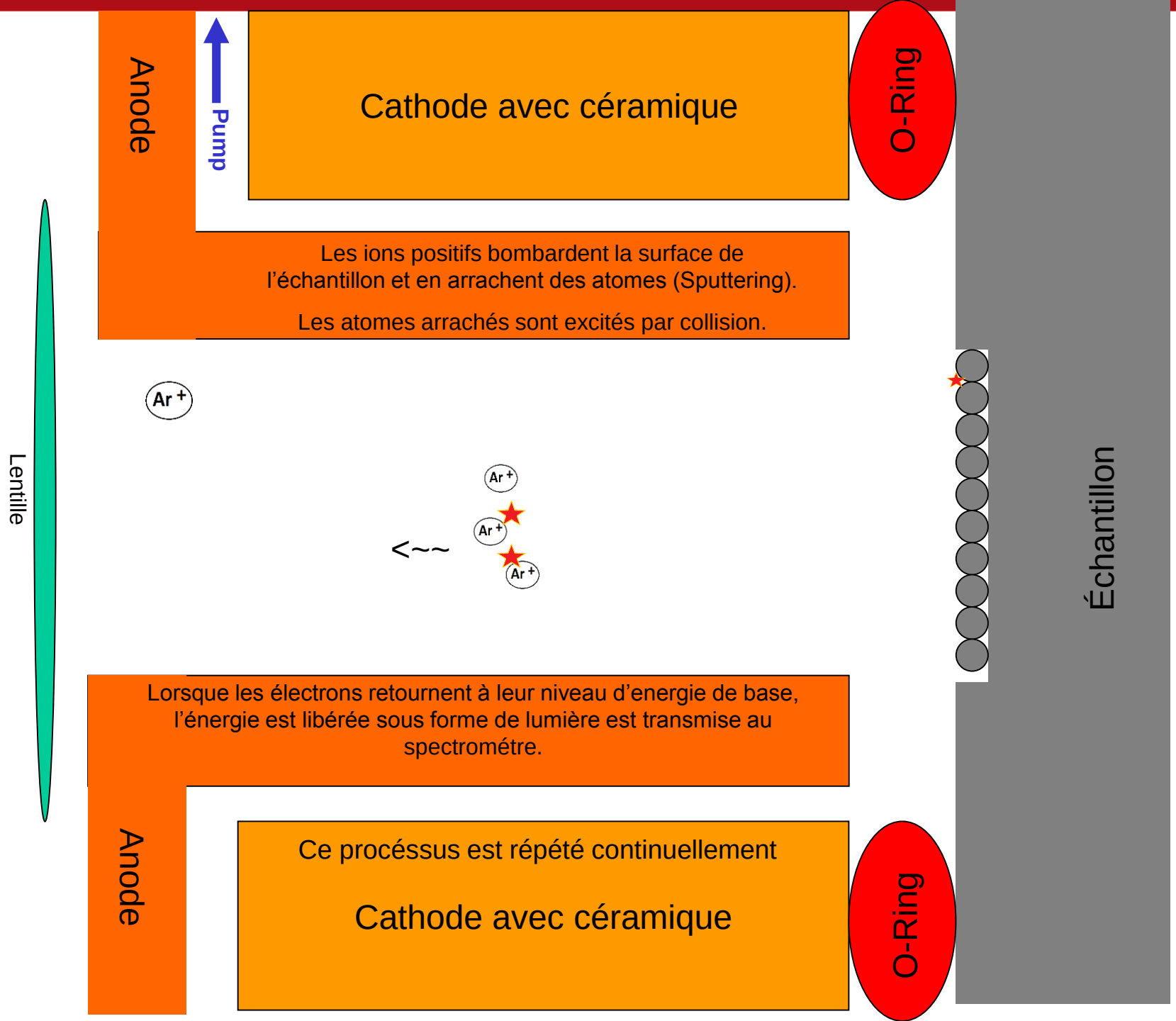
	Burn 1	Burn 2	AVG
C	0.159	0.160	0.160
P	0.00469	0.00470	0.00470
S	0.00451	0.00466	0.00460
Si	0.0112	0.0113	0.0112
Mn	0.0287	0.0286	0.0286

Depth Profiling

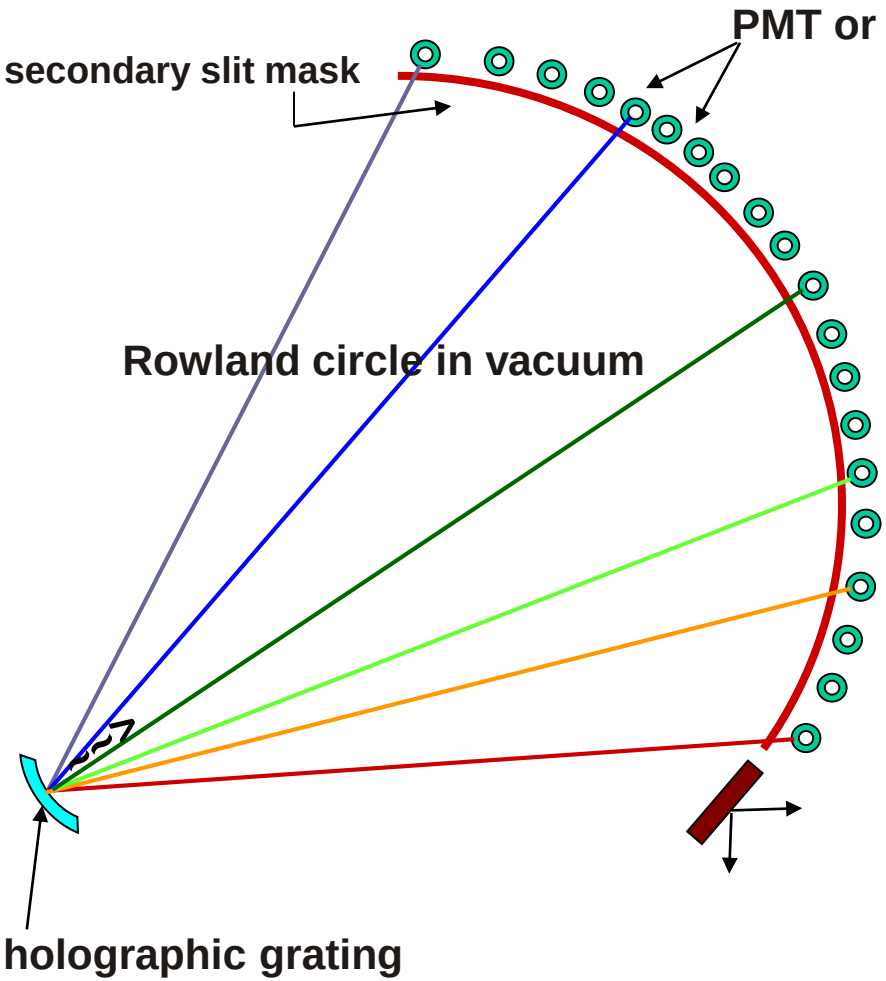





Spectrometer
Photomultiplier Tube (PMT) or
Charge Coupled Device (CCD)
Concave
Grating
Exit Slit
Glow Discharge Source
Rowland
Circle
Entrance Slit
Lens
Sample
Anode
Cathode


Anode
Pump
Cathode avec céramique
O-Ring
Les ions positifs bombardent la surface de l'échantillon et en arrachent des atomes (Sputtering).
Les atomes arrachés sont excités par collision.
Ar +
Lentille
<~~
Ar +
Ar +
Ar +
Échantillon
Lorsque les électrons retournent à leur niveau d'energie de base, l'énergie est libérée sous forme de lumière est transmise au spectrométre.
Anode
Ce procéssus est répété continuellement
Cathode avec céramique
O-Ring

simplified



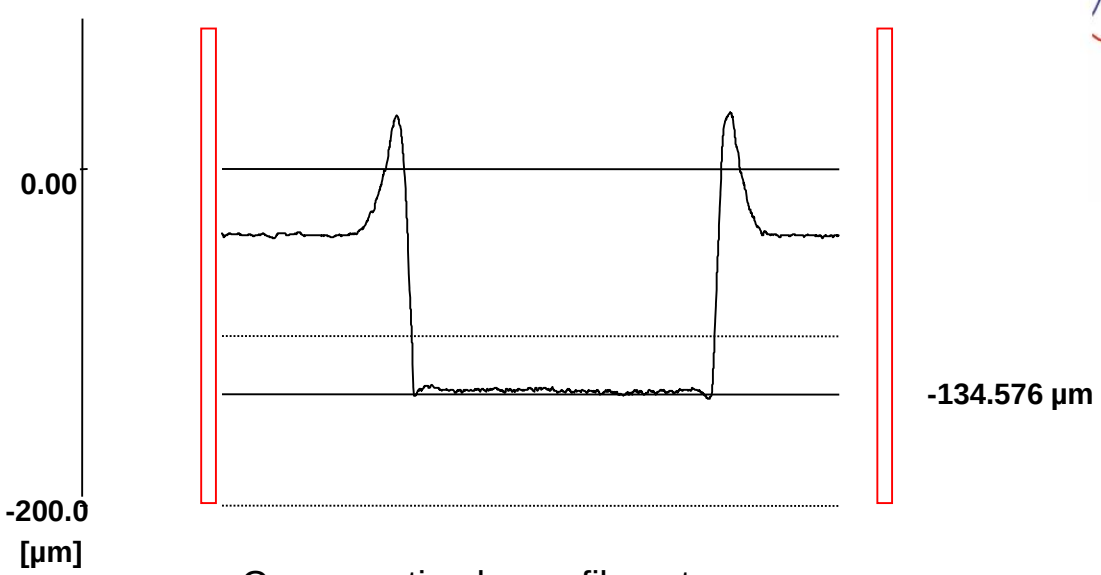
La lumière émise est diffractée par le réseau en différentes longueurs d'onde .

Les détecteurs captent et mesurent l'intensité des raies

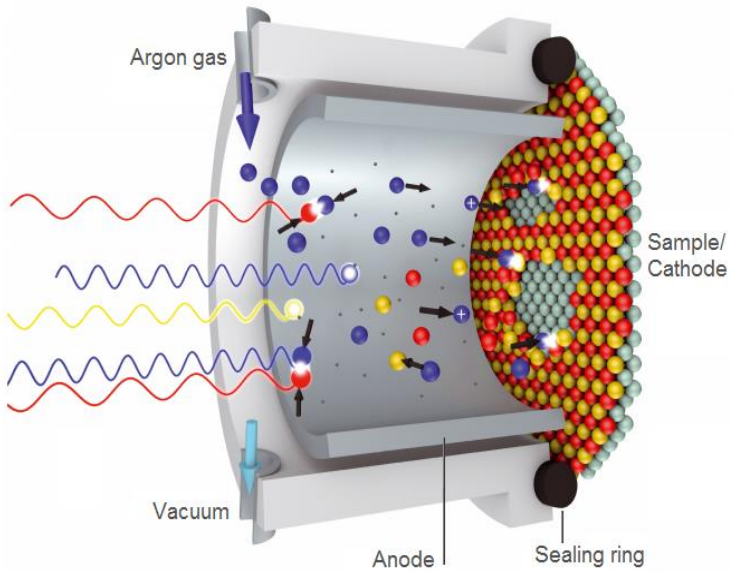
simplified

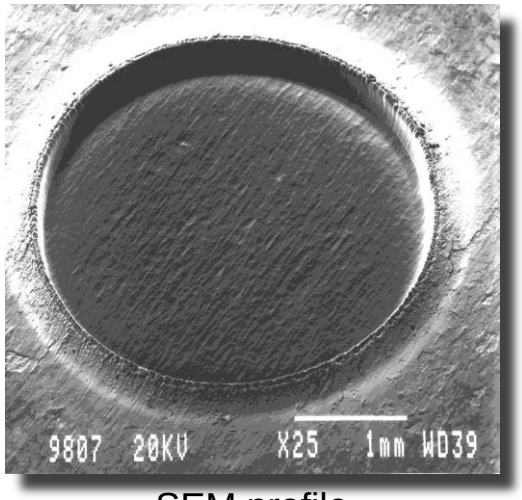
Analyse en Profondeur

- des parois de cratère rectilignes
- fond de cratère plat, pour une meilleure resolution en profondeur



Cross section by profilometer





SEM profile

Différents instruments

GDA Alpha

GDA 150 HR/ 650 HR

GDA 550 HR/ 750 HR

- Échantillons conducteurs ou non
- Épaisseur des couches <> 0,1 µm
- Limites de détection désirées notamment pour H O N

- PMT ou CCD ou les deux
- Taille de l'optique
- Source Courant Continu (DC) ou source HF (Pulsée)

GD - CCD
Haute sensibilité / Flexibilité dans les canaux

SPECTRO | AMETEK MATERIALS ANALYSIS DIVISION

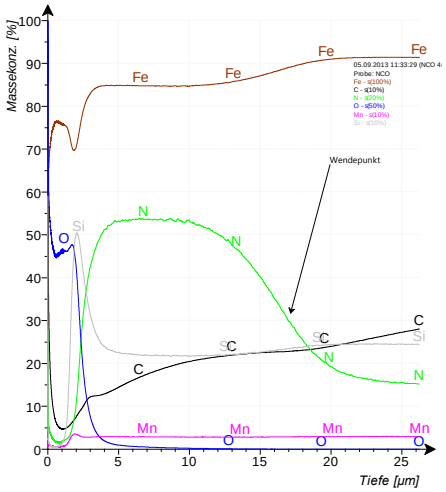
GDA-Alpha

Physical dimensions	GDA-Alpha
Length	950 mm
Width	390 mm
Height	675 mm
Weight	95 kg

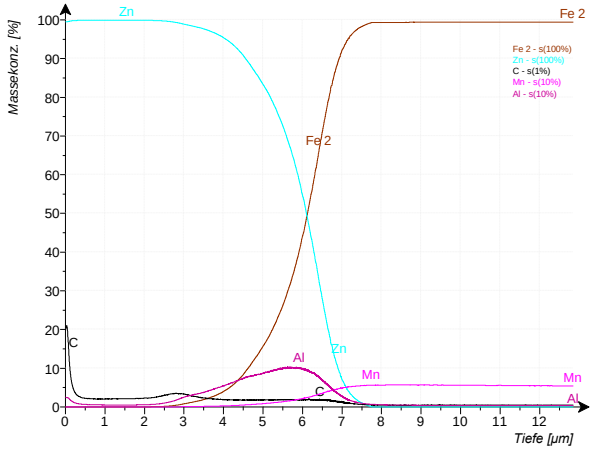
The GDA-Alpha is a user friendly and compact instrument. The same sensors and other components like the big instruments are used.
The GDA-Alpha is perfectly suitable for production and quality controls. Application fields range from bulk analysis of complex alloys up to depth profile analysis of coated materials.

- **A CCD option adds flexibility**
- Each wavelength can be defined for analysis
- Short-wave spectral lines like that of H and O can be detected
- Long-wave spectral lines like that of Na and Li can be detected
- Resolution 20 pm

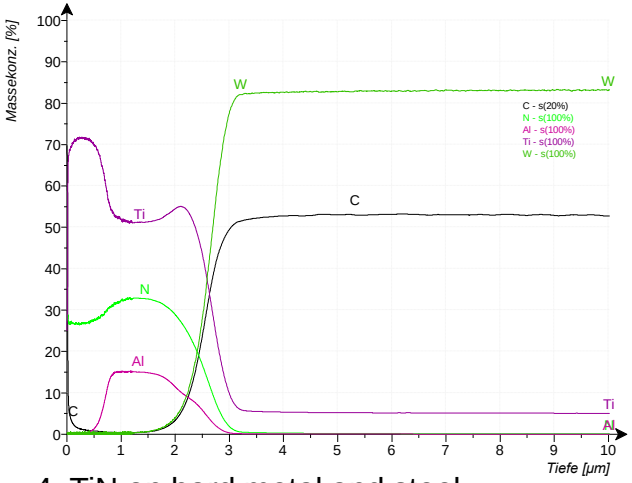
GDA-Alpha
Applications typiques..pour aujourd'hui ici à Yverdon



2. Heat treated material



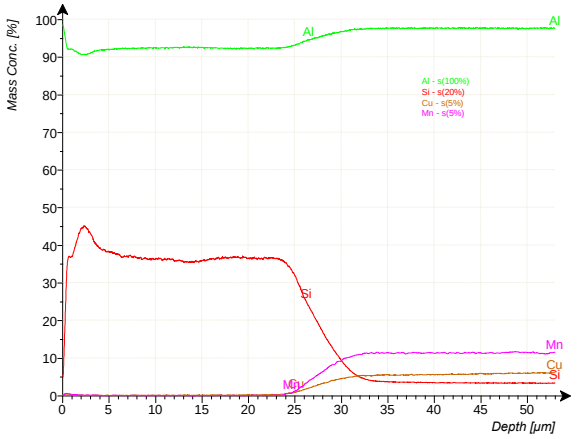
3. Galvanizing



4. TiN on hard metal and steel

Probe:	1763																	
Elemente:	Fe [%]	C [%]	Si [%]	Mn [%]	P [%]	S [%]	Cr [%]	Ni [%]	Al [%]	Cu [%]	Ti [%]	B [%]	Nb[%]	Co [%]	Mo [%]	V [%]	Zr [%]	
21.09. 16:40	95,12	0,201	0,691	1,514	0,012	0,021	0,481	0,503	0,046	0,041	0,313	0,005	0,102	0,086	0,481	0,302	0,044	
22.09. 8:33	95,09	0,199	0,651	1,541	0,012	0,019	0,512	0,499	0,048	0,042	0,338	0,005	0,098	0,089	0,508	0,303	0,044	
22.09. 9:18	95,09	0,198	0,683	1,539	0,012	0,019	0,490	0,511	0,047	0,042	0,307	0,005	0,100	0,088	0,499	0,301	0,042	
22.09. 10:05	95,17	0,198	0,692	1,487	0,012	0,019	0,499	0,507	0,047	0,041	0,334	0,005	0,101	0,088	0,489	0,301	0,041	
22.09. 11:23	95,17	0,198	0,685	1,502	0,011	0,020	0,501	0,503	0,046	0,041	0,313	0,006	0,104	0,093	0,516	0,315	0,043	
22.09. 12:20	95,16	0,199	0,667	1,494	0,011	0,019	0,490	0,510	0,046	0,041	0,315	0,006	0,103	0,095	0,515	0,315	0,045	
22.09. 13:22	95,05	0,207	0,656	1,457	0,012	0,019	0,499	0,508	0,045	0,041	0,318	0,006	0,107	0,094	0,507	0,307	0,045	
22.09. 14:02	95,18	0,205	0,652	1,472	0,012	0,019	0,488	0,503	0,045	0,040	0,329	0,006	0,104	0,094	0,517	0,315	0,044	
22.09. 15:00	95,13	0,203	0,645	1,523	0,012	0,019	0,495	0,511	0,046	0,041	0,336	0,006	0,102	0,094	0,514	0,319	0,045	
22.09. 16:15	95,10	0,201	0,641	1,561	0,012	0,019	0,490	0,510	0,046	0,040	0,315	0,006	0,107	0,092	0,505	0,316	0,045	
23.09. 8:50	95,14	0,195	0,682	1,468	0,012	0,019	0,510	0,503	0,047	0,041	0,326	0,006	0,099	0,084	0,510	0,304	0,041	
23.09. 14:53	95,13	0,197	0,678	1,472	0,012	0,020	0,517	0,511	0,047	0,041	0,325	0,006	0,102	0,087	0,530	0,313	0,043	
24.09. 8:35	95,15	0,200	0,666	1,481	0,012	0,020	0,508	0,503	0,047	0,042	0,319	0,006	0,102	0,092	0,505	0,306	0,046	
24.09. 15:20	95,02	0,204	0,629	1,587	0,012	0,021	0,502	0,510	0,048	0,043	0,308	0,005	0,100	0,094	0,508	0,300	0,044	
25.09. 8:12	95,10	0,199	0,661	1,491	0,012	0,020	0,526	0,502	0,046	0,041	0,324	0,0054	0,103	0,089	0,524	0,318	0,044	
Mittelwert	**95,12**	**0,200**	**0,665**	**1,506**	**0,012**	**0,020**	**0,501**	**0,506**	**0,046**	**0,041**	**0,321**	**0,006**	**0,102**	**0,091**	**0,509**	**0,309**	**0,044**	
Std.Abw.	0,04598	0,00326	0,01950	0,03759	0,00036	0,00076	0,01226	0,00411	0,00092	0,00077	0,00990	0,00017	0,00258	0,00350	0,01242	0,00700	0,00149	
rel.Std.Abw. [%]	0,05	1,63	2,93	2,50	3,06	3,88	2,45	0,81	1,97	1,88	3,08	3,09	2,52	3,86	2,44	2,27	3,40	
Std.Abw. lt Zert.[%]		0,99	3,17	1,90	8,33	4,35	2,00	1,96	6,98	4,65	3,23	1,85	5,00	5,26	2,00	3,33	6,82	

1. Bulk analysis



5. Aluminum cladding and others

GDA-Alpha
Application typique : Bulk

Probe:	1763																	
Elemente:	Fe [%]	C [%]	Si [%]	Mn [%]	P [%]	S [%]	Cr [%]	Ni [%]	Al [%]	Cu [%]	Ti [%]	B [%]	Nb[%]	Co [%]	Mo [%]	V [%]	Zr [%]
21.09. 16:40	95,12	0,201	0,691	1,514	0,012	0,021	0,481	0,503	0,046	0,041	0,313	0,005	0,102	0,086	0,481	0,302	0,044
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22.09. 10:05	95,17	0,198	0,692	1,487	0,012	0,019	0,499	0,507	0,047	0,041	0,334	0,005	0,101	0,088	0,489	0,301	0,041
22.09. 11:23	95,17	0,198	0,685	1,502	0,011	0,020	0,501	0,503	0,046	0,041	0,313	0,006	0,104	0,093	0,516	0,315	0,043
22.09. 12:20	95,16	0,199	0,667	1,494	0,011	0,019	0,490	0,510	0,046	0,041	0,315	0,006	0,103	0,095	0,515	0,315	0,045
22.09. 13:22	95,05	0,207	0,656	1,457	0,012	0,019	0,499	0,508	0,045	0,041	0,318	0,006	0,107	0,094	0,507	0,307	0,045
22.09. 14:02	95,18	0,205	0,652	1,472	0,012	0,019	0,488	0,503	0,045	0,040	0,329	0,006	0,104	0,094	0,517	0,315	0,044
22.09. 15:00	95,13	0,203	0,645	1,523	0,012	0,019	0,495	0,511	0,046	0,041	0,336	0,006	0,102	0,094	0,514	0,319	0,045
22.09. 16:15	95,10	0,201	0,641	1,561	0,012	0,019	0,490	0,510	0,046	0,040	0,315	0,006	0,107	0,092	0,505	0,316	0,045
23.09. 8:50	95,14	0,195	0,682	1,468	0,012	0,019	0,510	0,503	0,047	0,041	0,326	0,006	0,099	0,084	0,510	0,304	0,041
23.09. 14:53	95,13	0,197	0,678	1,472	0,012	0,020	0,517	0,511	0,047	0,041	0,325	0,006	0,102	0,087	0,530	0,313	0,043
24.09. 8:35	95,15	0,200	0,666	1,481	0,012	0,020	0,508	0,503	0,047	0,042	0,319	0,006	0,102	0,092	0,505	0,306	0,046
24.09. 15:20	95,02	0,204	0,629	1,587	0,012	0,021	0,502	0,510	0,048	0,043	0,308	0,005	0,100	0,094	0,508	0,300	0,044
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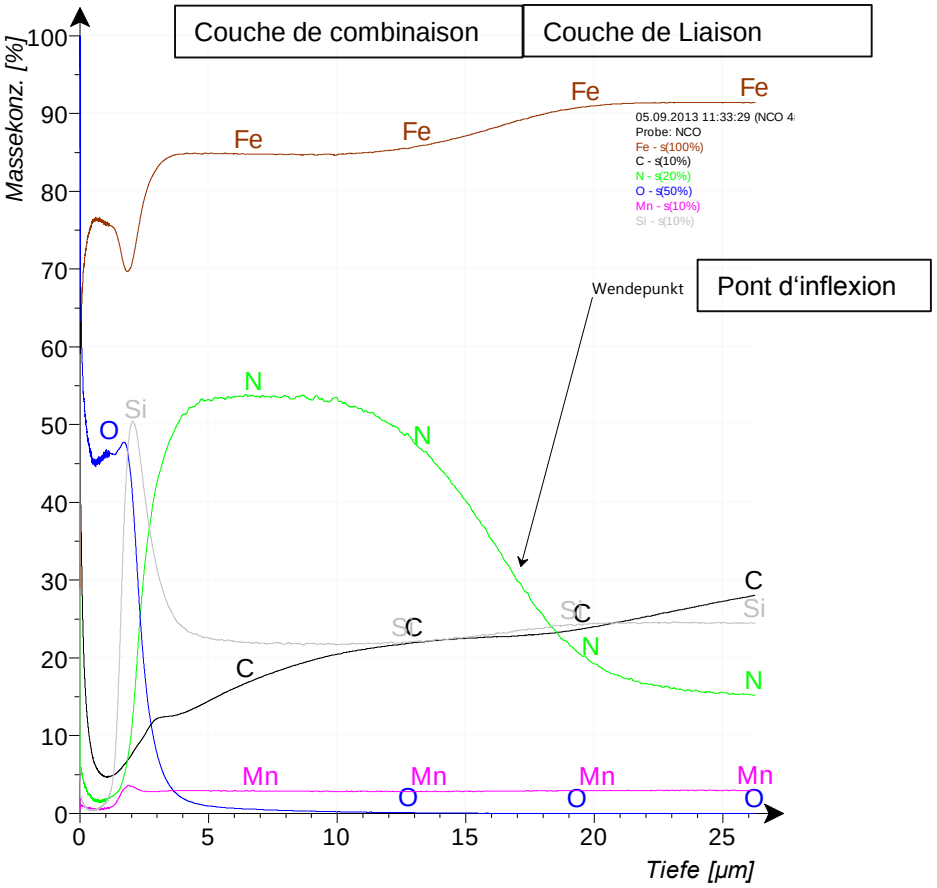
Mittelwert	**95,12**	**0,200**	**0,665**	**1,506**	**0,012**	**0,020**	**0,501**	**0,506**	**0,046**	**0,041**	**0,321**	**0,006**	**0,102**	**0,091**	**0,509**	**0,309**	**0,044**
Std.Abw.	0,04598	0,00326	0,01950	0,03759	0,00036	0,00076	0,01226	0,00411	0,00092	0,00077	0,00990	0,00017	0,00258	0,00350	0,01242	0,00700	0,00149
rel.Std.Abw. [%]	0,05	1,63	2,93	2,50	3,06	3,88	2,45	0,81	1,97	1,88	3,08	3,09	2,52	3,86	2,44	2,27	3,40
Std.Abw. lt Zert.[%]		0,99	3,17	1,90	8,33	4,35	2,00	1,96	6,98	4,65	3,23	1,85	5,00	5,26	2,00	3,33	6,82

…spécialement pour les métaux Précieux…..

GDA-Alpha
Application typique : Traitements Thermiques

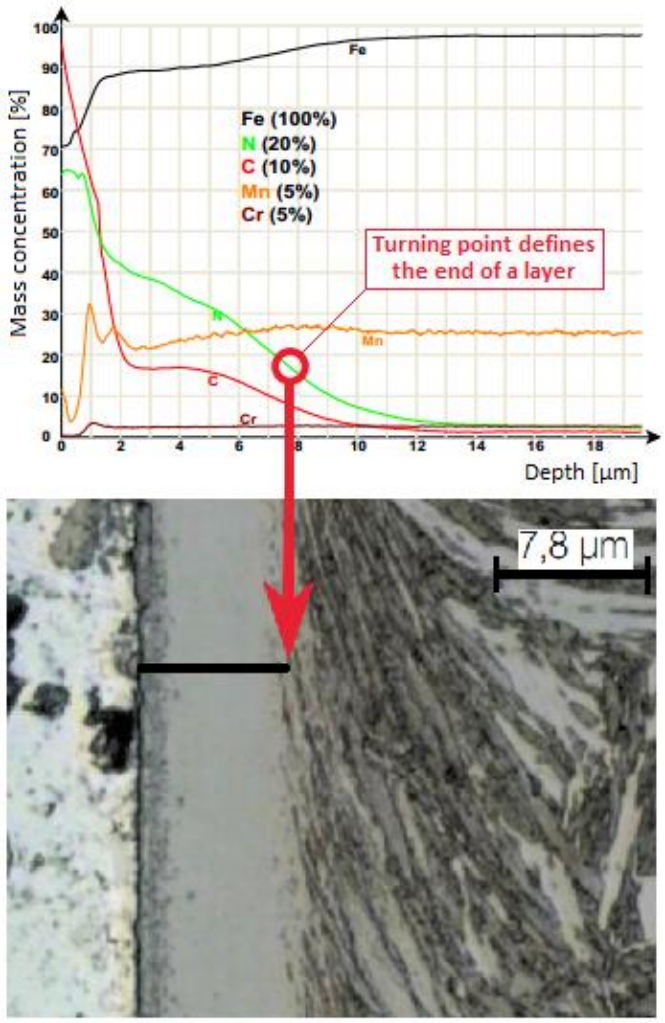


Application:
Traitements Thermiques

Le graphe montre le résultat d'une analyse en profondeur avec la GDOES d'un échantillon nitrocarburé avec une épaisseur d'azote de 7.8 µm
On discerne une fine couche de Carbone en surface

L'épaisseur de la couche peut être aussi determinée par microscopie. Il faut pour cela poncer l'échantillon, le polir et puis l'analyser par microscopie.

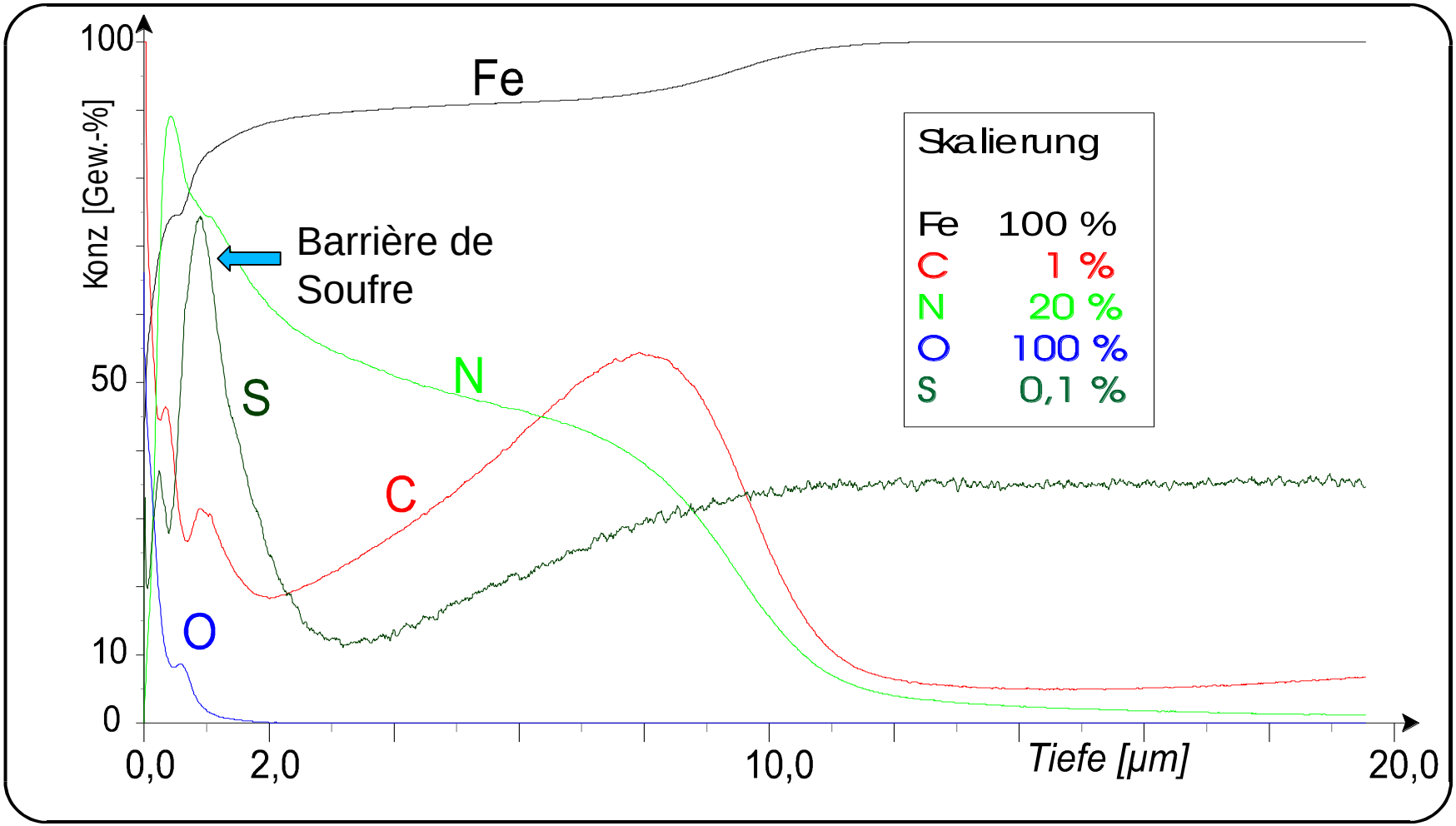
Cela prend une heure comparée aux quelques minutes avec la GDOES.



Analysis of a nitrocarburized iron sample. The result obtained by the GDA-Alpha (top) is in very good agreement with the result obtained by microscopy (bottom).

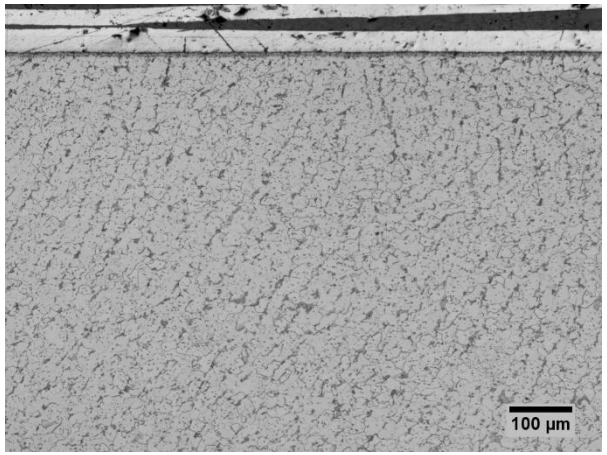
Exemple fourni par TAZ GmbH

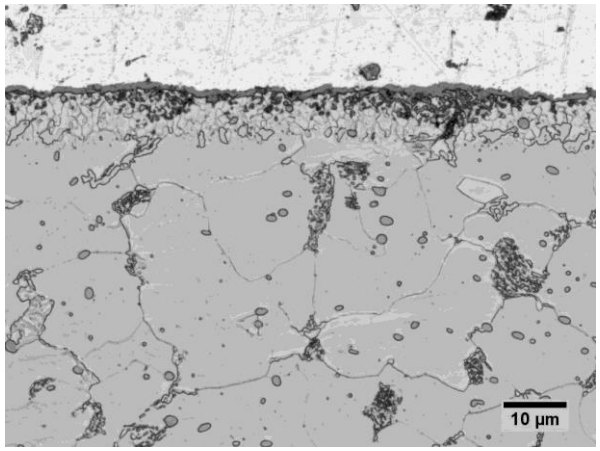
Nitruration (de mauvaise qualité) d'un Piston

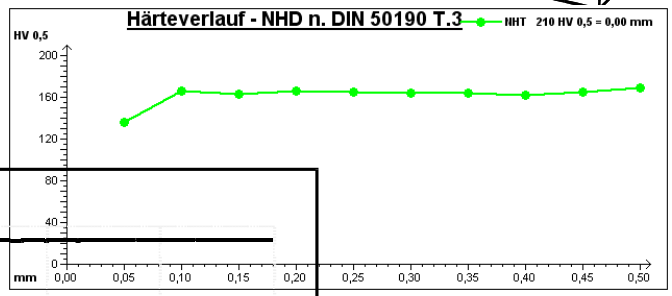


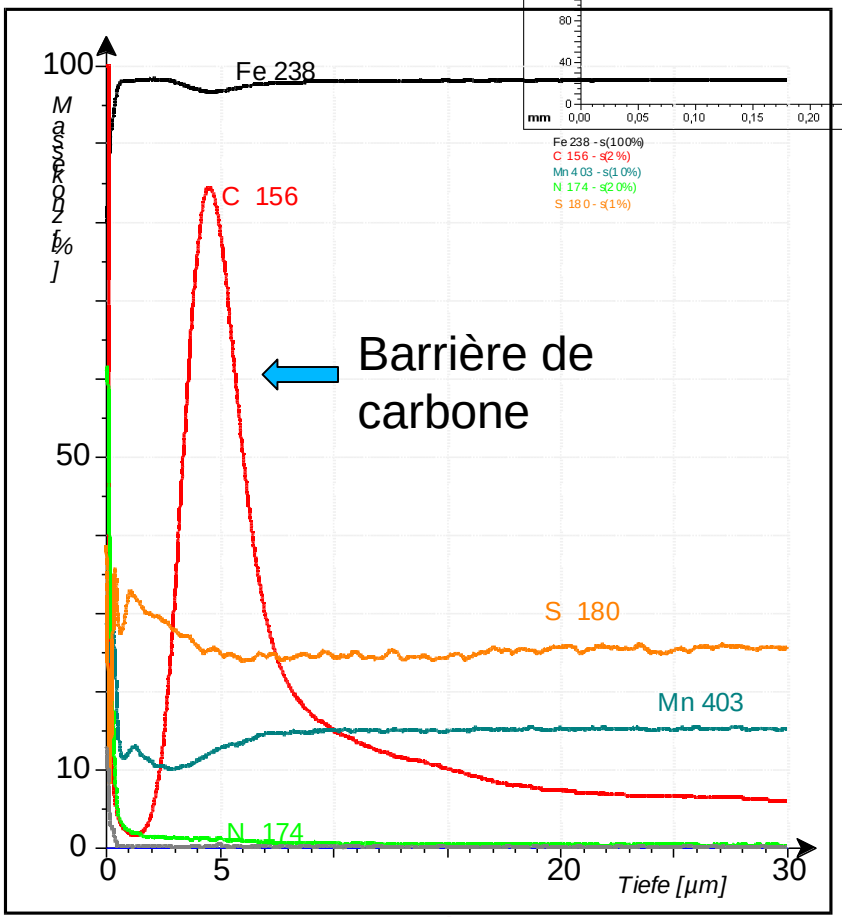
Exemple fourni par TAZ GmbH

Nitruration, Spécifications VS = 15 – 20 µm





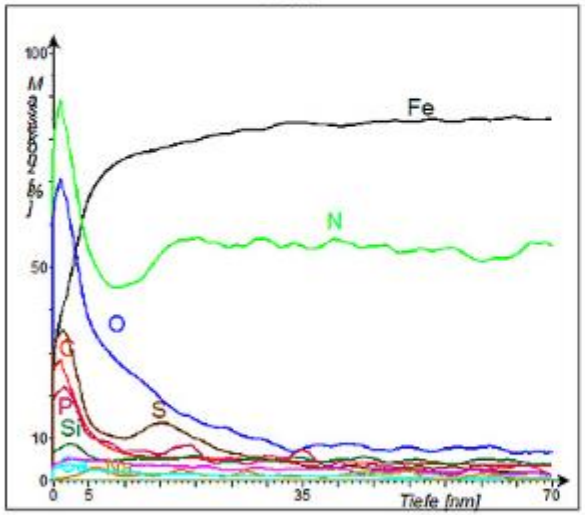




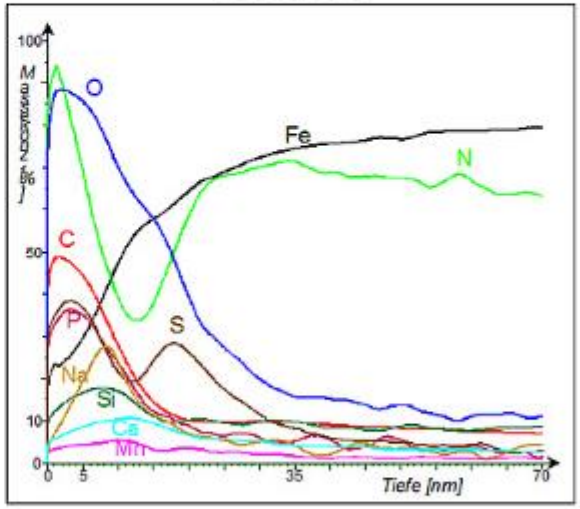
Schadensfall: Reinigungsrückstände

Exemple fourni par TAZ GmbH

Gut



Schlecht

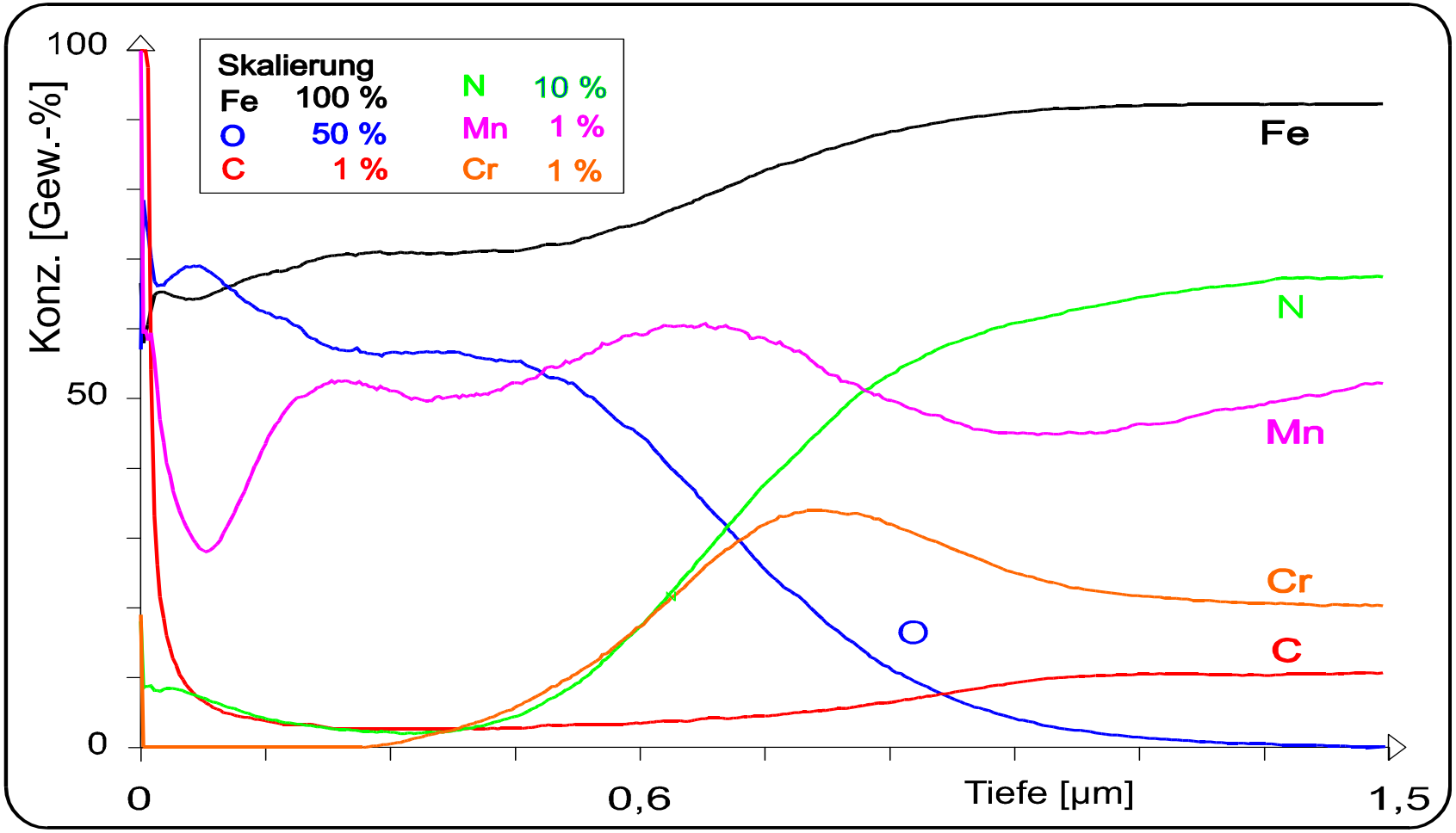


Skalierung:

- Fe: 100 %
- C: 25 %
- N: 20 %
- O: 50 %
- Si: 2 %
- P: 0,5 %
- S: 1 %
- Mn: 10 %
- Na: 2 %
- Ca: 10 %

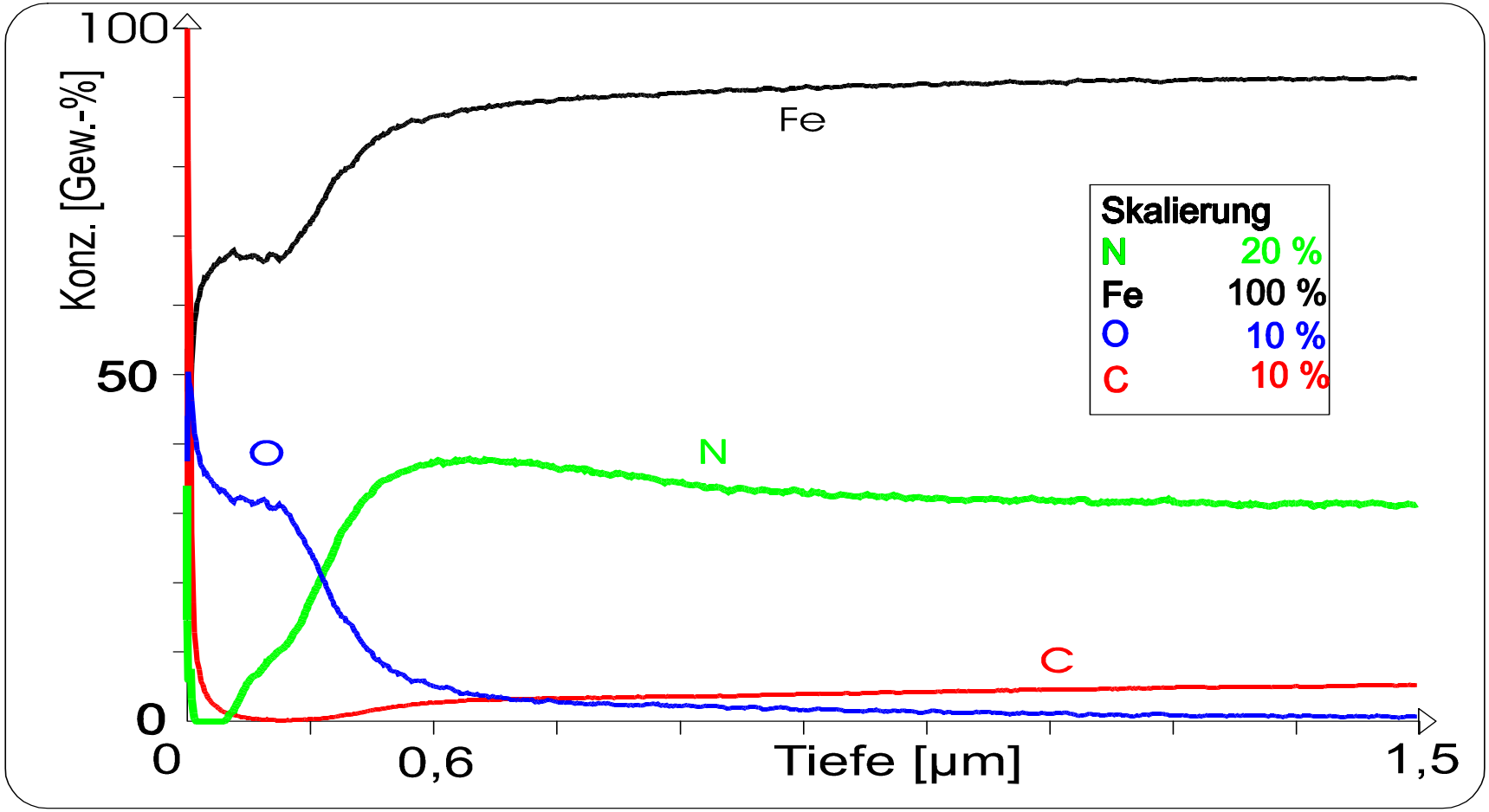
Exemple fourni par TAZ GmbH

Couche d‘Oxyde: 0,6 µm attendue



Exemple fourni par TAZ GmbH

Couche d‘Oxyde: 0,4µm obtenue



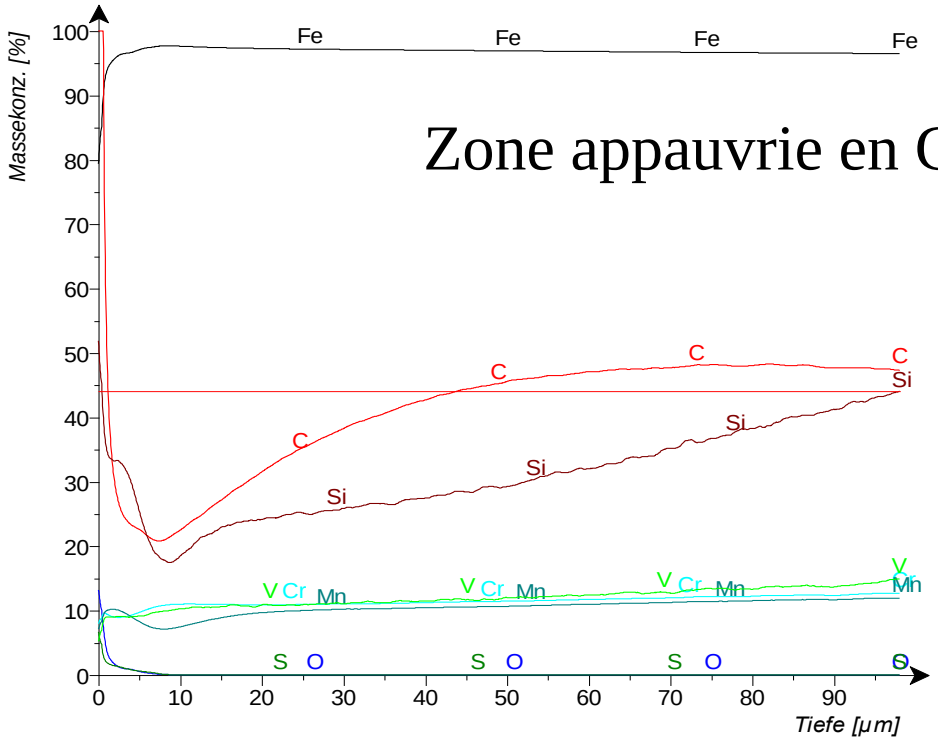
Exemple fourni par TAZ GmbH

Appauvrissement en carbone

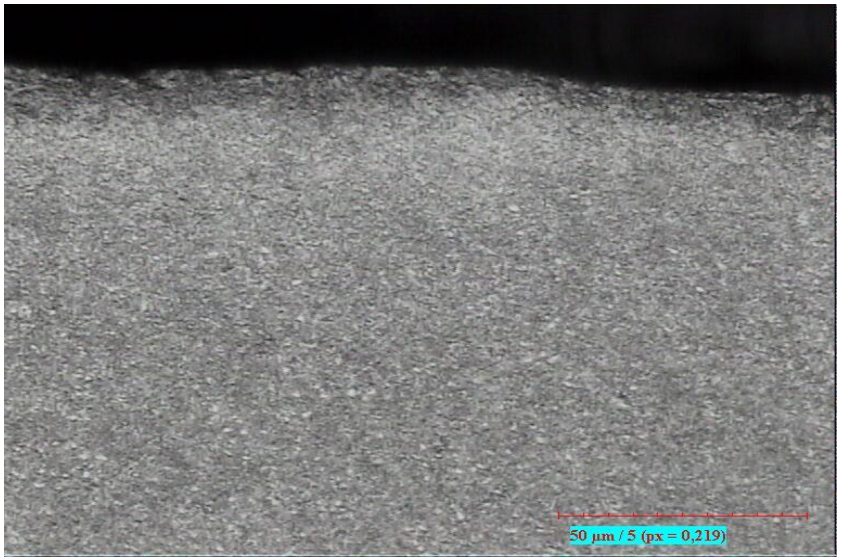
Probenbezeichnung:	GDS-Bedingungen:	Datum/Zeit:
TF15019-6964	900V,18mA / 0,0	25.01.2006 09:57:01

RAW=\\Tazsrv1\daten\Messdaten\2006\1-Januar\0810106\TF15019-6964.raw : MTH=Multi-25

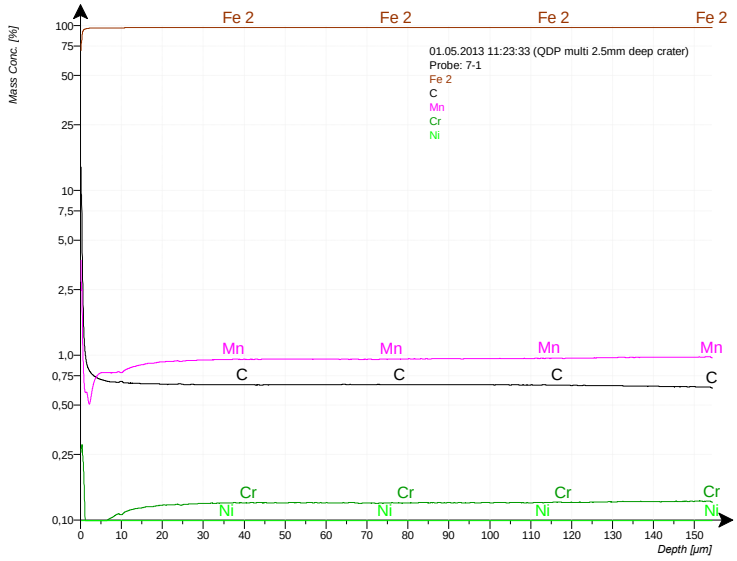
Fe - s(100%)
C - s(1%)
O - s(100%)
Cr - s(10%)
Mn - s(10%)
S - s(1%)
Si - s(1%)
V - s(1%)

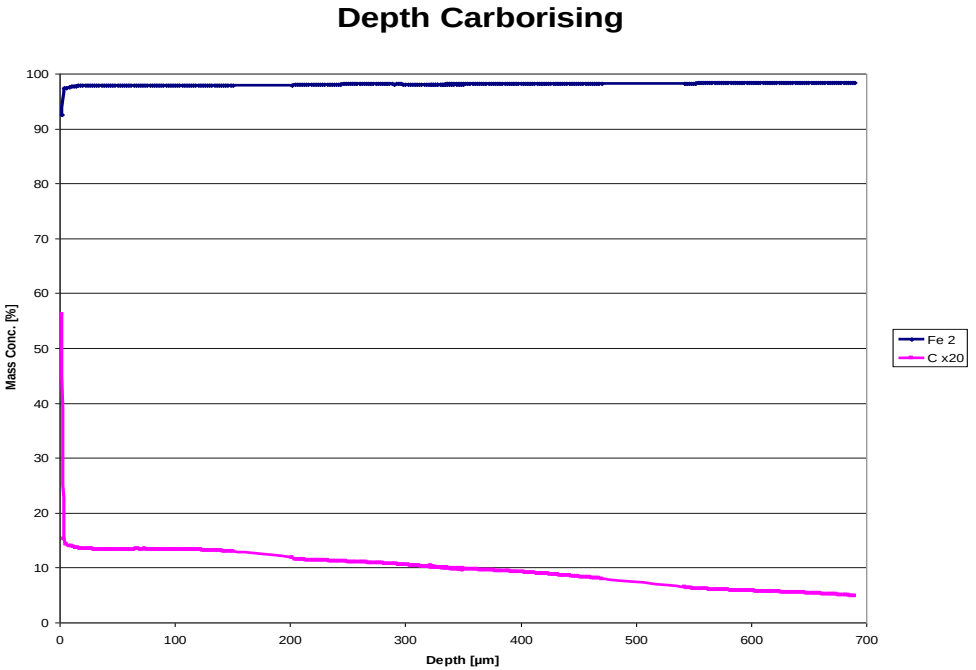


Zone appauvrie en Carbone: 44µm



Application:
échantillons cementés, analyse de couches épaisse

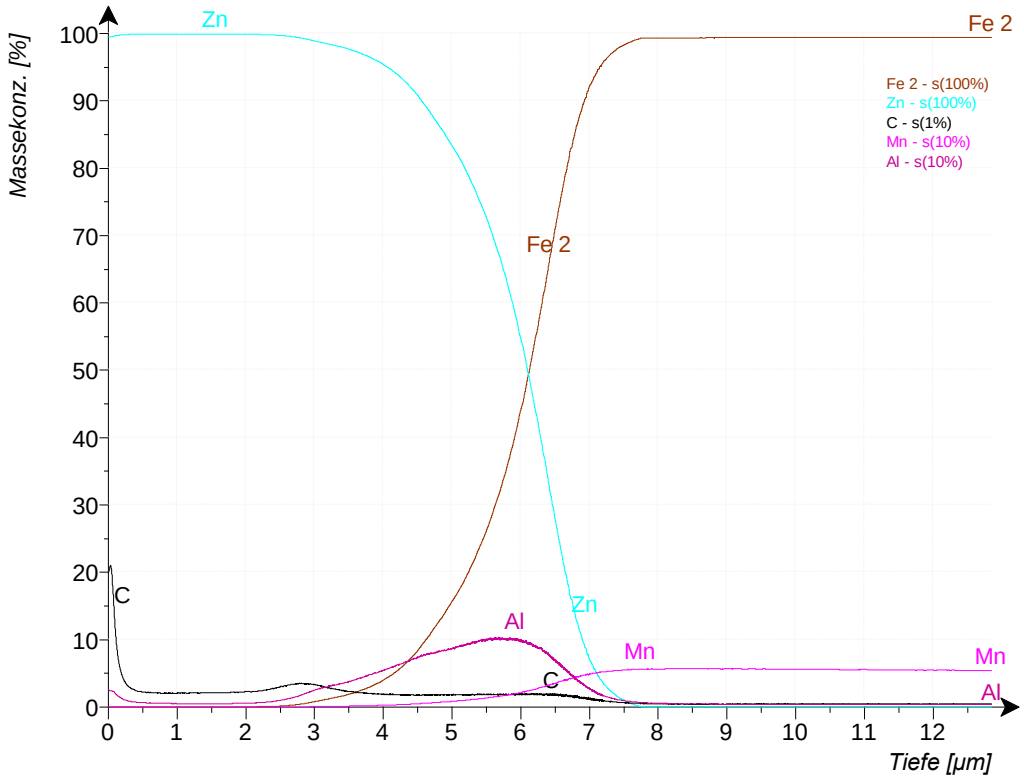




Carbon is diffused into the surface of the material to **increase its wear resistance**. The resultant diffusion layers are commonly much thicker then those obtained in the nitriding process. The layer thickness is typically **several hundred microns** to more than a millimetre.
The maximum sputtering depth of the GDOES technology for conducting material is of **200 µm**. The technique however can still be used to analyze carbon profiles. This is achieved by a **step grinding procedure**, simply by taking the first measurement, removing the outer layer mechanically (with a swing grinder for example) and repeating the process. **Adding these graphs** together then produces a clear picture.

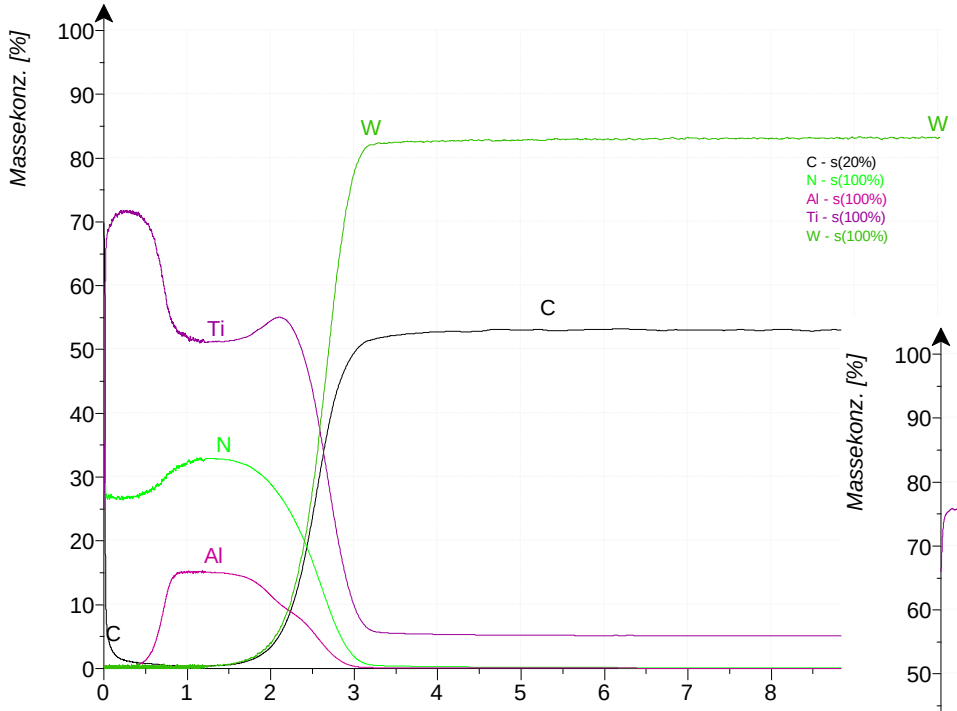
These figures show the analysis of a case-hardened cube. At the beginning there is a higher amount of carbon (about 10 % by weight), in the analyzed material there is an amount up to 0.7 % by weight. But only with additional measurements a clear concentration gradient for carbon over 700 µm can be obtained.

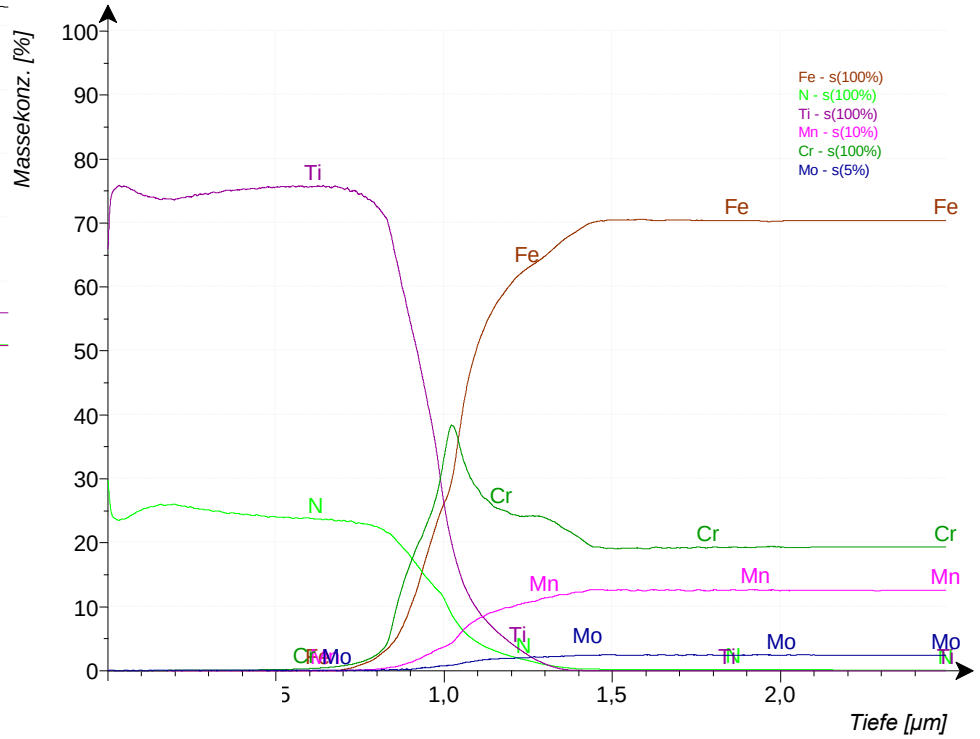
GDA-Alpha
applications typiques: Galvanisation



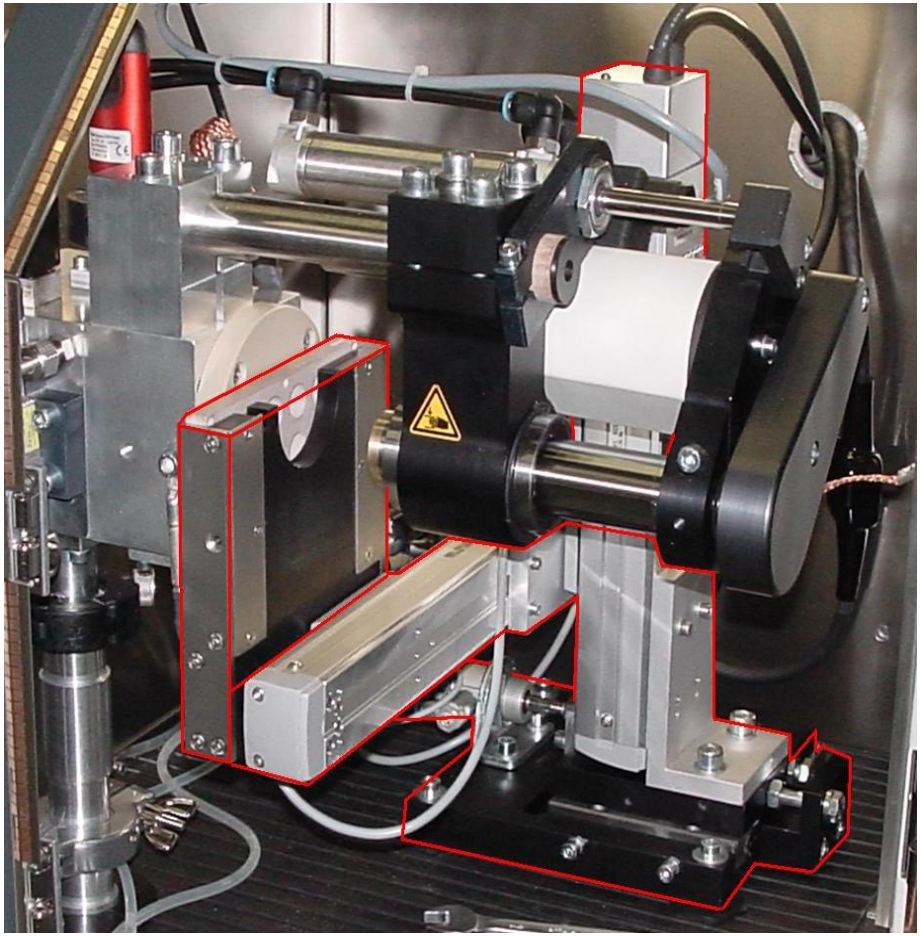
GDA-Alpha

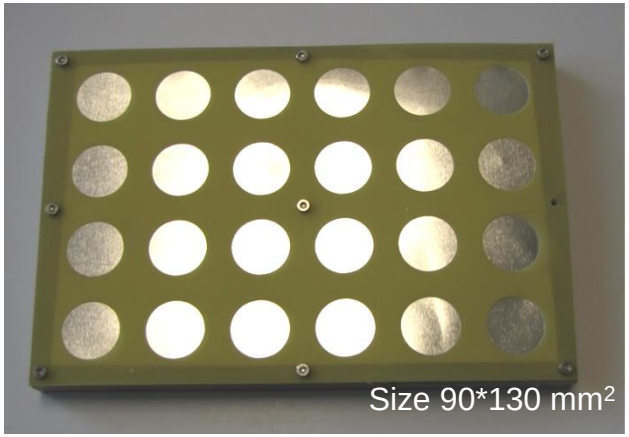
Applications typiques: TiN sur des métaux durs ou aciers





Passeur d‘échantillons





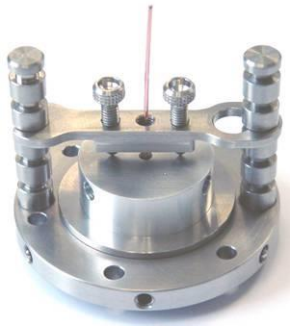
-24 échantillons différents peuvent être placés sur le portoir et être analyses en plusieurs points.

-Balayage de surface

le Kit Universel

The glow discharge source is constructed by the so called Grimm type design with the sample acting as electrode (cathode). The instrument can be equipped with anodes of 2.5 mm, 4 mm, and 8 mm inner diameter defining the size of the measuring spot. Usually, the sample seals the glow discharge source, so a vacuum can be generated. But when a sample is too small or has no flat surface, no vacuum can be built up. In this case, the analysis is performed using the so-called Universal Sample Unit (USU) with suitable adaptors, as shown on the bottom right.

Standard USU for curved samples; DC source

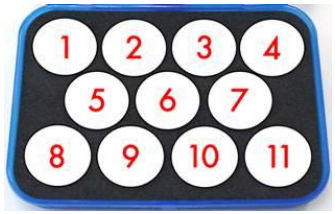


USU for wires < 2.5 mm

Standard USU for curved samples; RF source

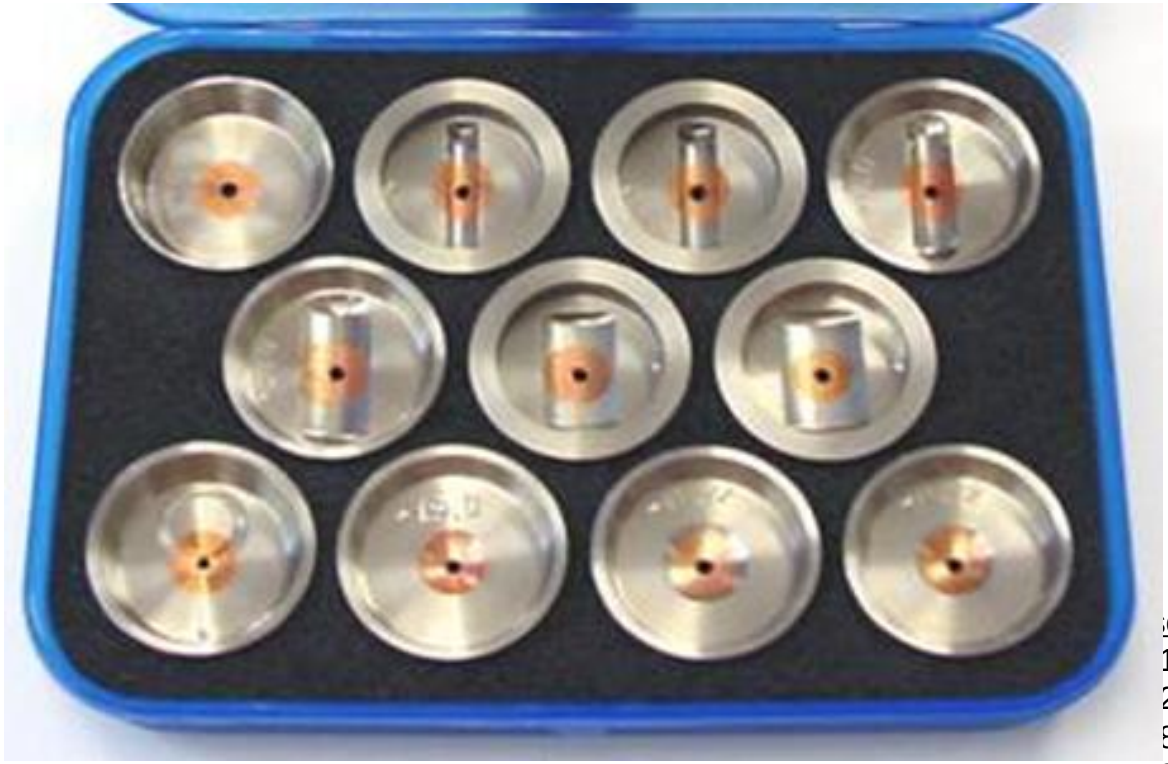
Description of the shown adaptors:

No.1: for flat samples or recalibration
No.2-7: various sizes for cylindrical samples
No.8: for grommets
No.9-11: balls for various sizes (e.g. of bearings)



Also special geometries are possible.

le Kit Universel



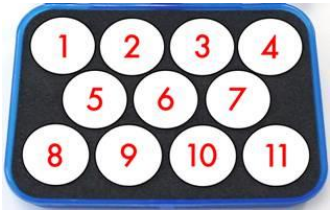
<u>cription of the shown adaptors</u>:

1: for flat samples or recalibration

2-7: various sizes for cylindrical samples

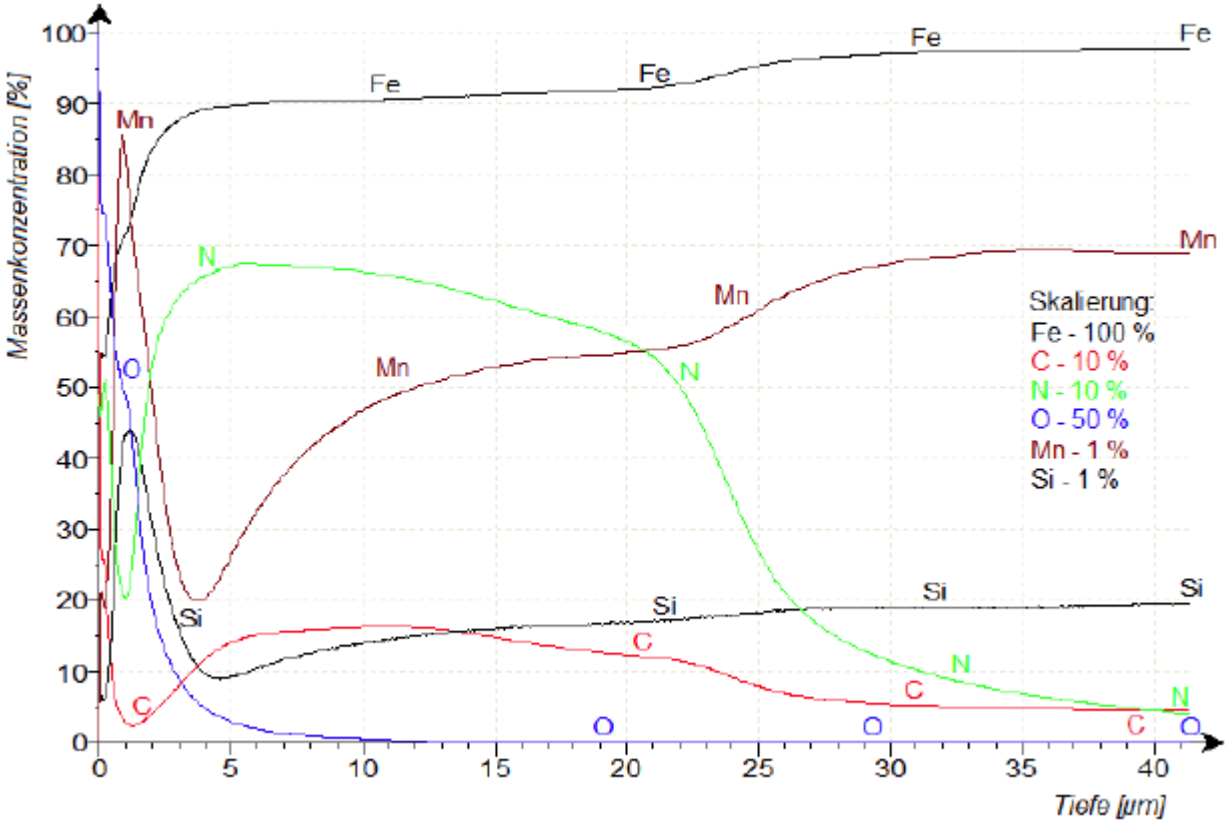
8: for grommets

No.9-11: balls for various sizes (e.g. of bearings)



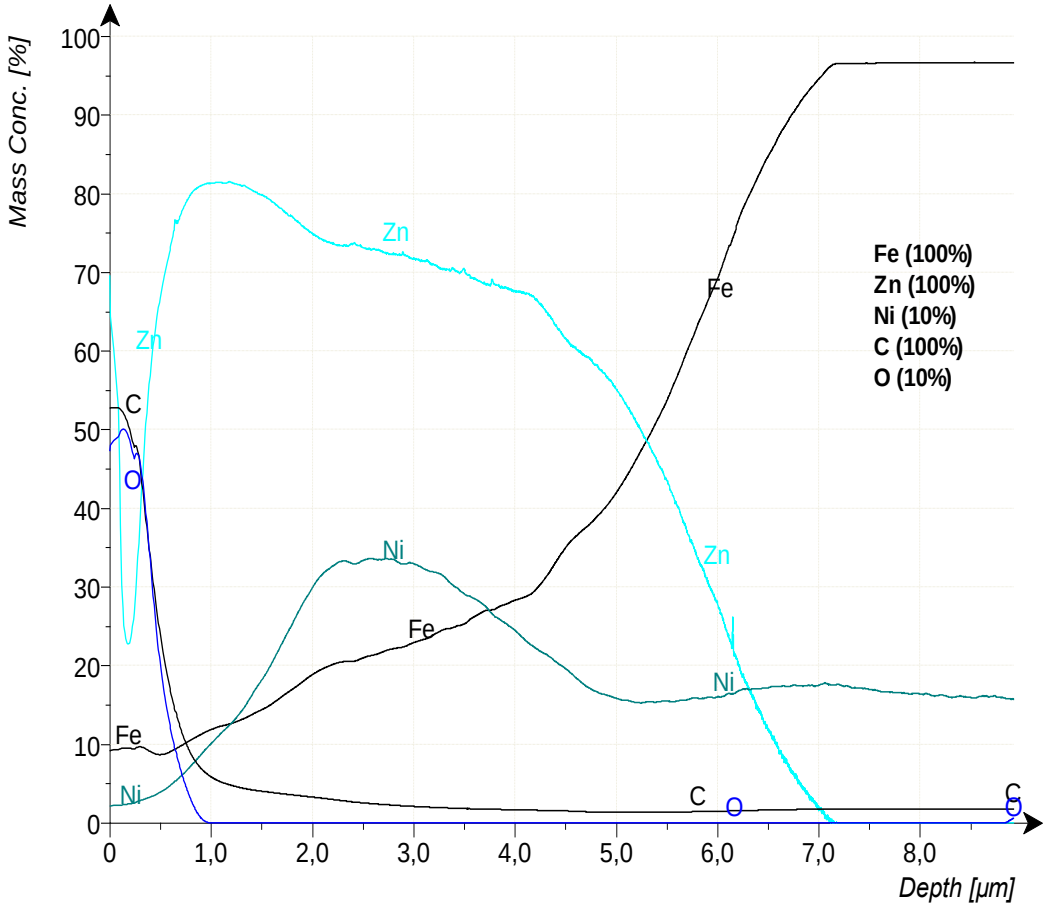
Also special geometries are possible.

Applications of the Universal Sample Unit



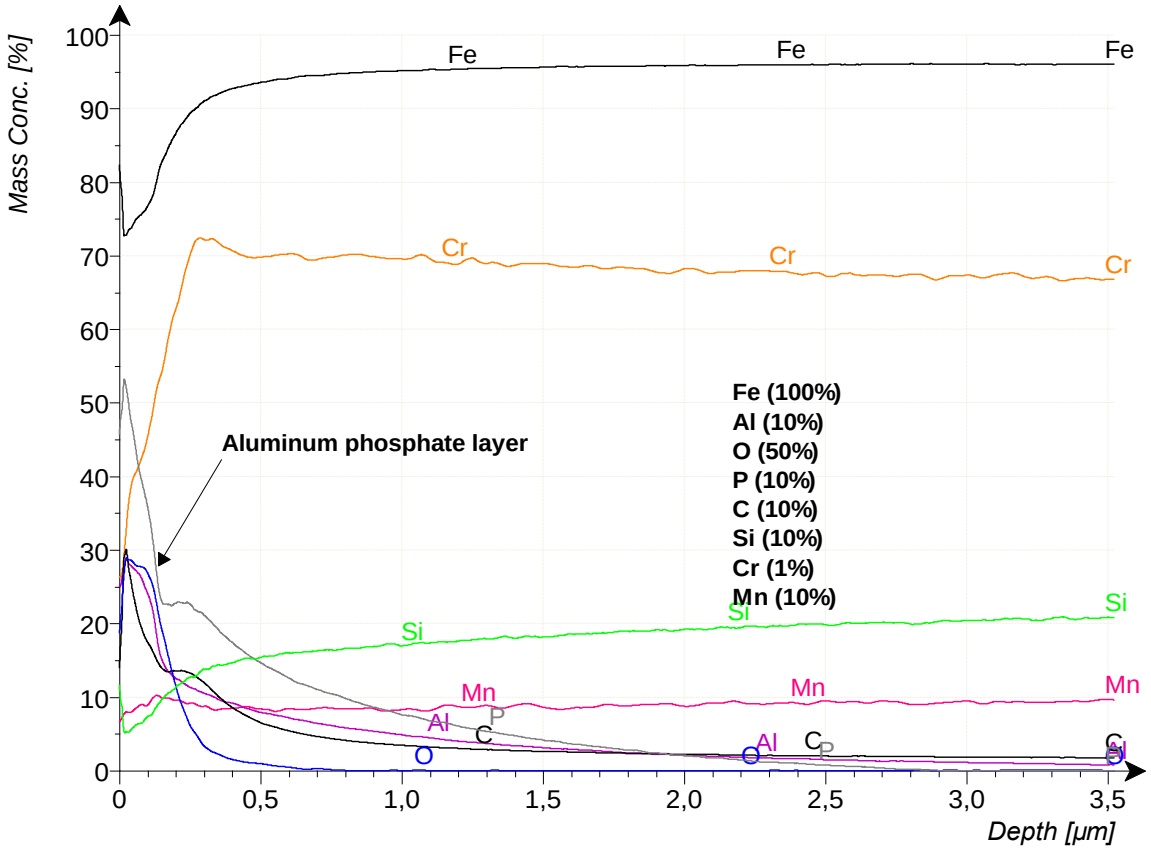
Applications of the Universal Sample Unit

Lattices

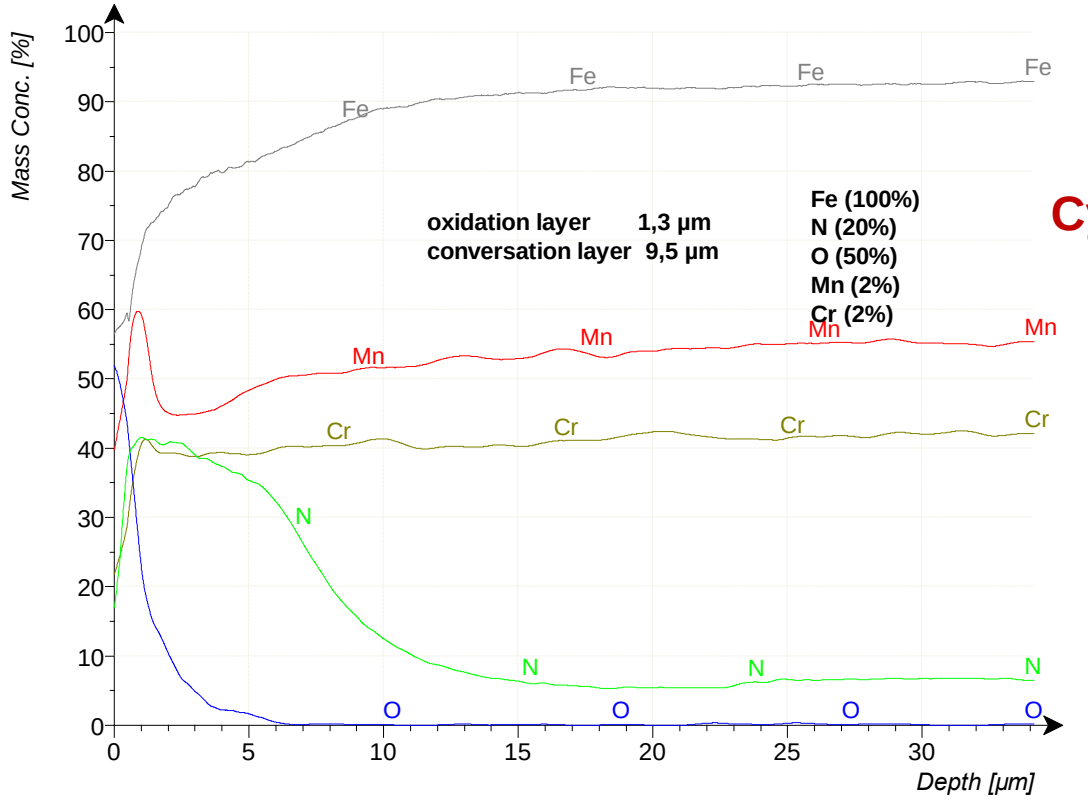


Applications of the Universal Sample Unit

Tubes



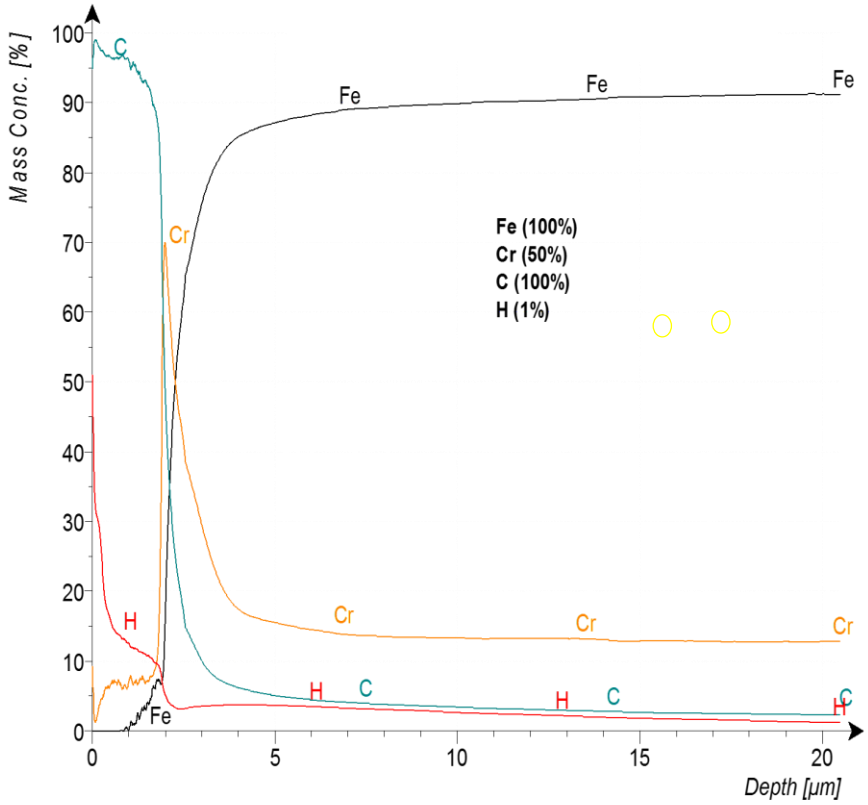
Applications of the Universal Sample Unit



Cylindrical samples

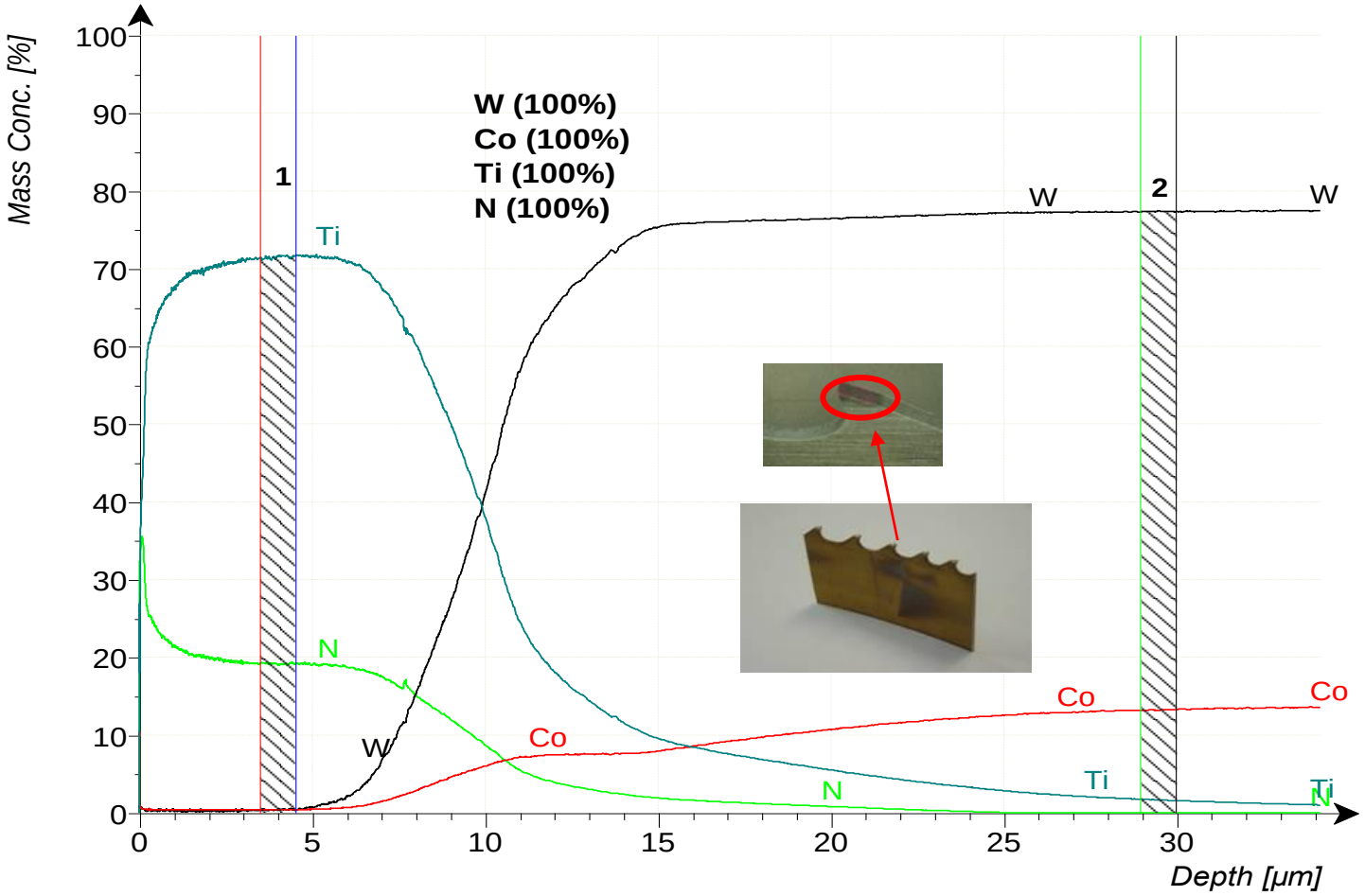
Applications of the Universal Sample Unit

Pins < 3 mm



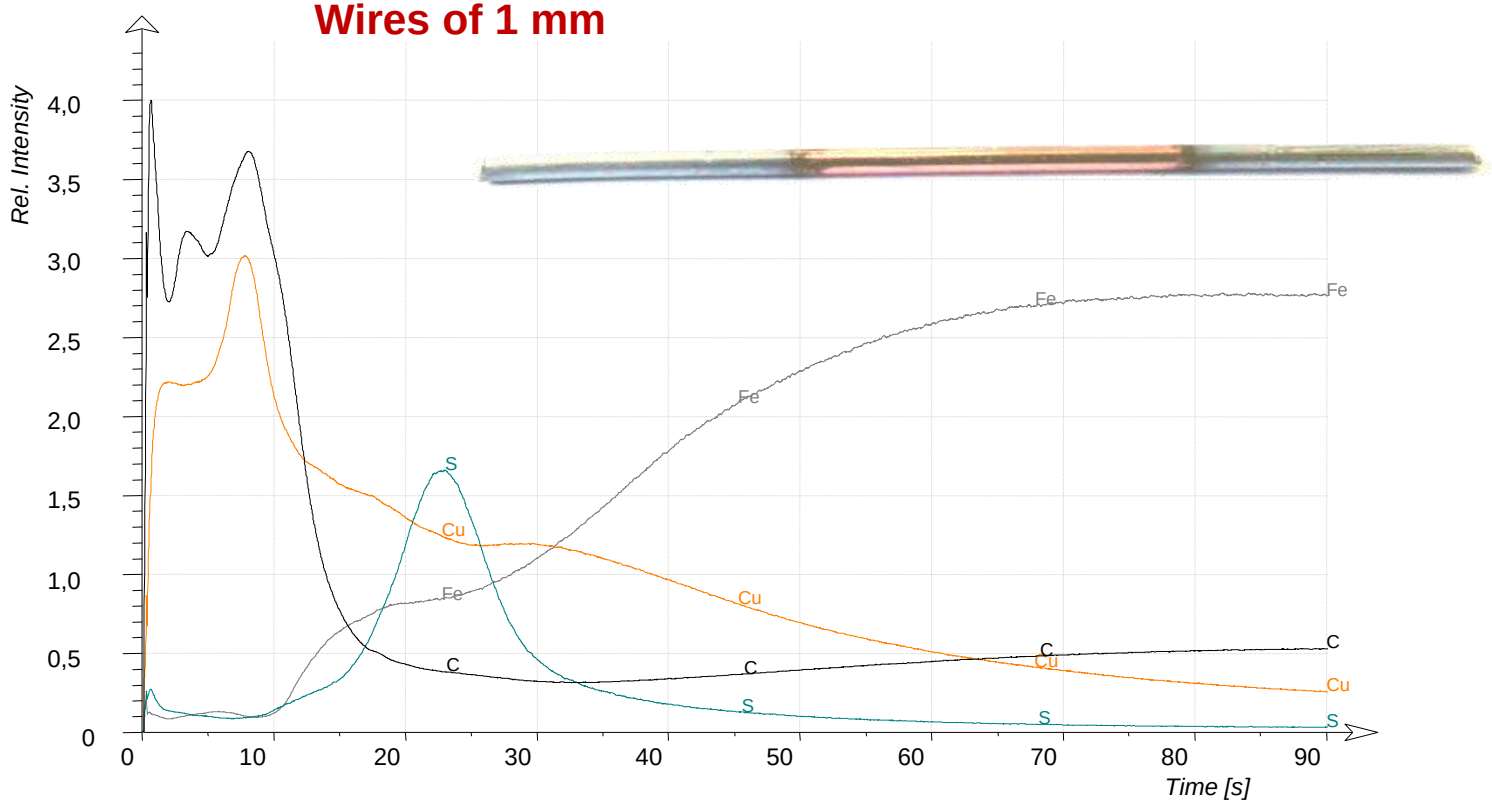
Applications of the Universal Sample Unit

Hard metals



Applications of the Universal Sample Unit

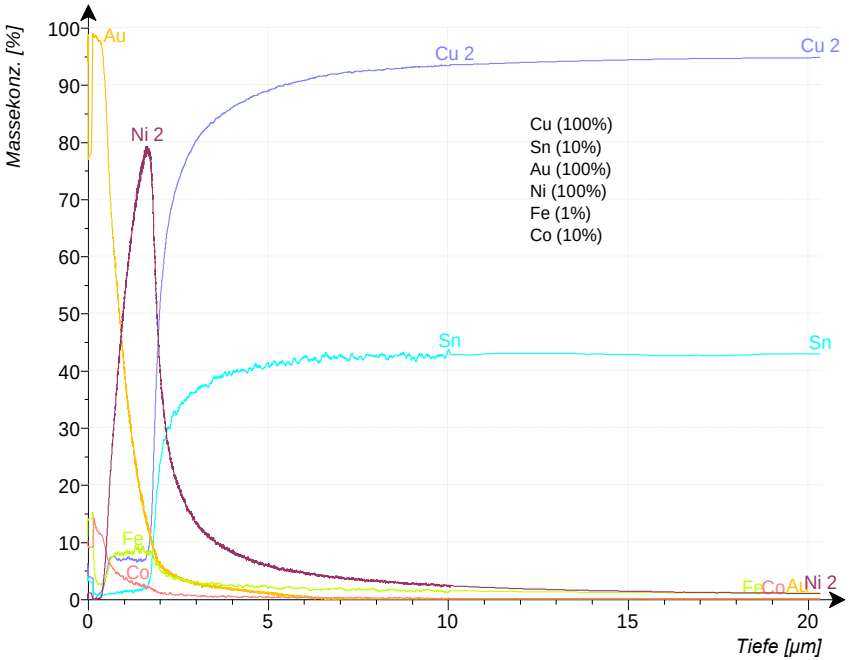
Wires of 1 mm

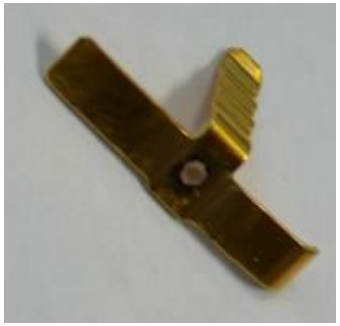


For samples smaller than 2.7 mm diameter the 1 mm anode is used.

Applications of the Universal Sample Unit

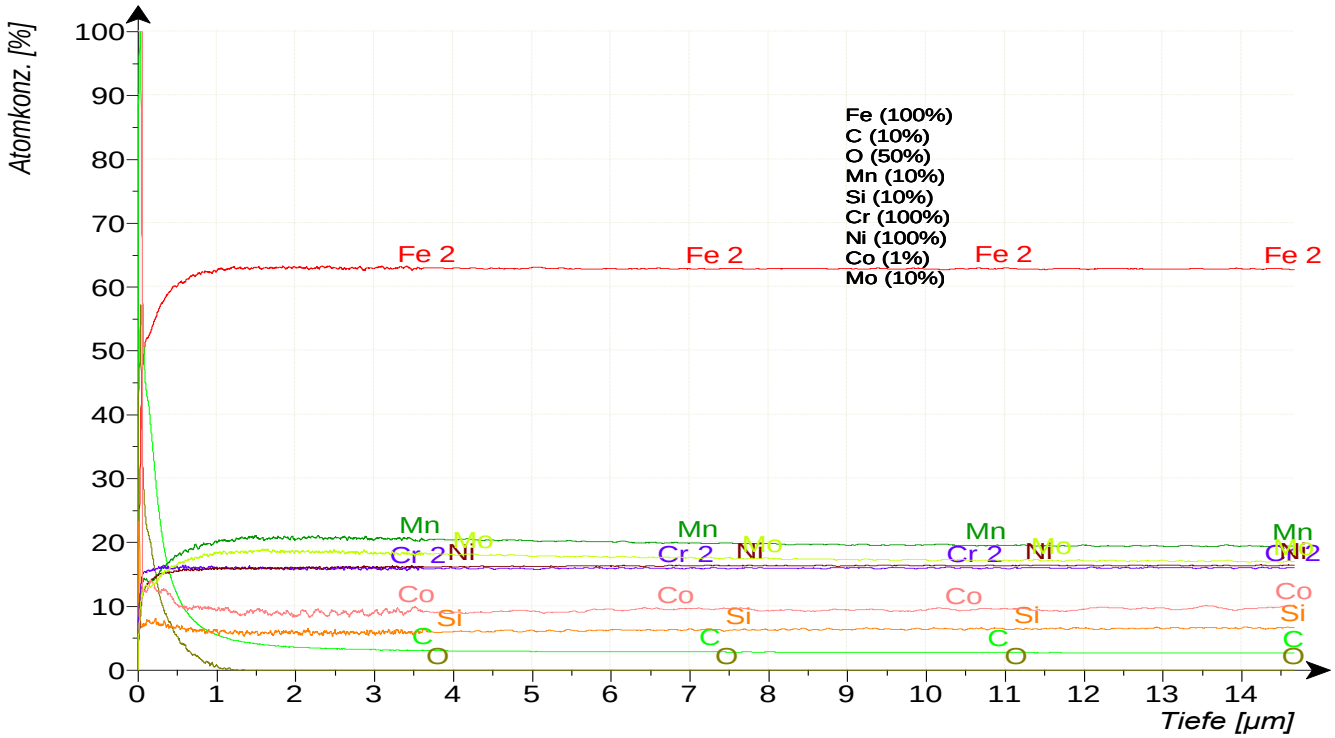
Electronic contacts





Applications of the Universal Sample Unit

Contamination of small samples

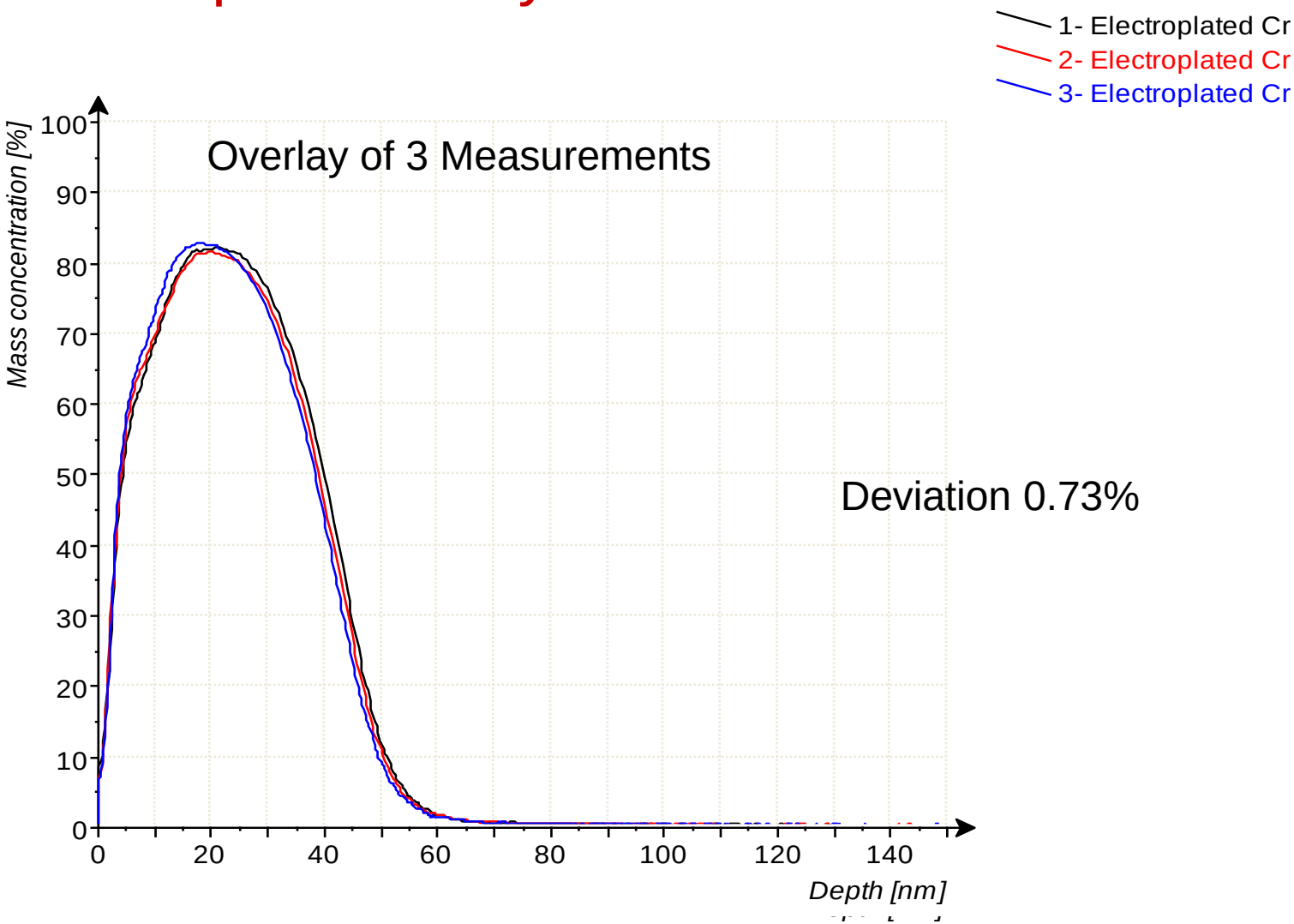


Applications of the Universal Sample Unit

Bulk analysis

Probe:	10mm								
	Fe [%]	C [%]	Mn[%]	Si [%]	P [%]	S [%]	Cr [%]	Ni [%]	Cu[%]
Mittelwert	96,63	0,993	0,353	0,221	< 0,001	0,			
Probe:	20mm								
	Fe [%]	C [%]	Mn[%]	Si [%]	P [%]	S [%			
Mittelwert	96,98	0,968	0,276	0,272	0,001	0,			

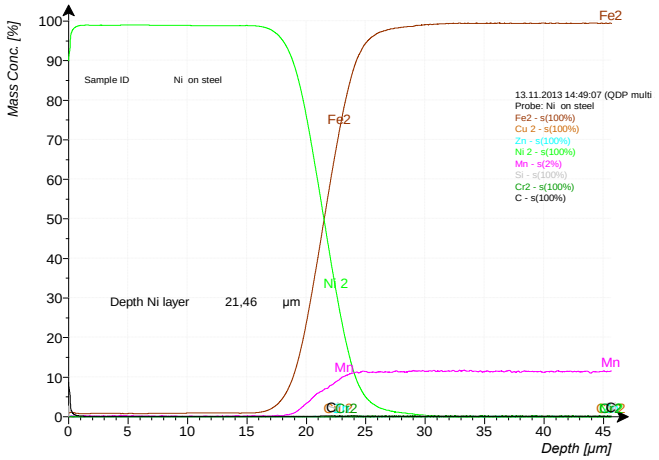
Application:
Good reproducibility



Deviation 0.73%

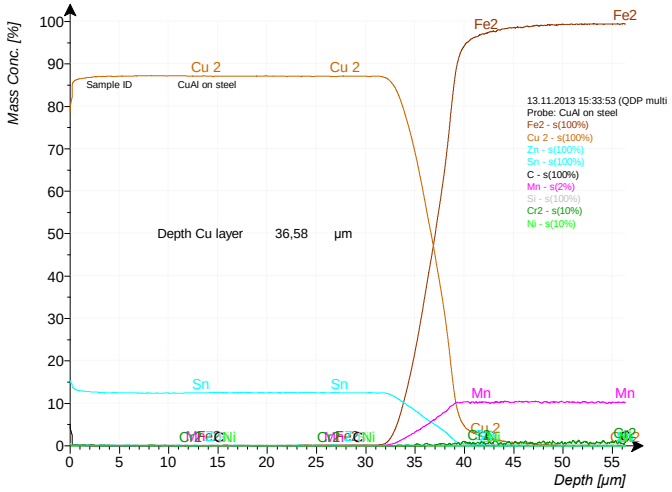
Application:
Analysis of coins

Nickel on steel, coin of Thailand

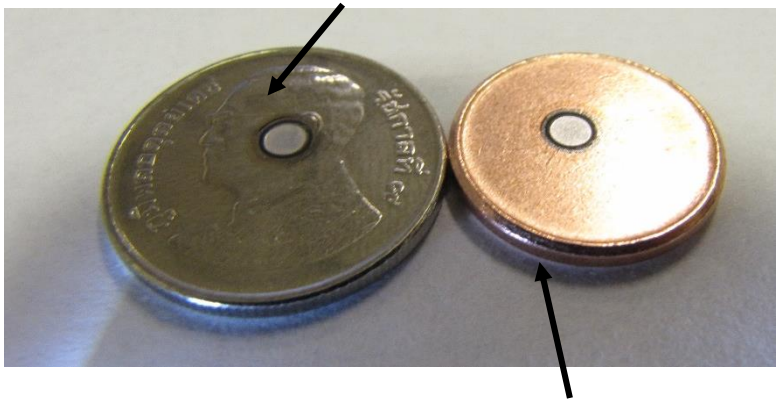


Coins can be analyzed directly. With an optional adaptor for the standard cathode plate the uneven surfaces of the coins are compensated. So no additional sample preparation is necessary.

Bronze on steel



Coin of Thailand with engraving



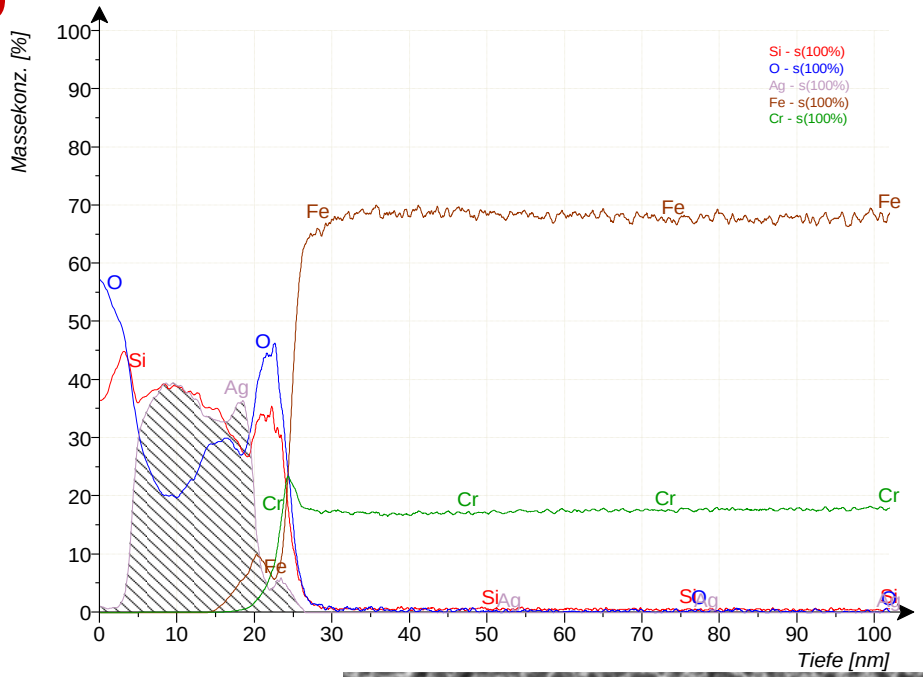
Condition as delivered with higher edge

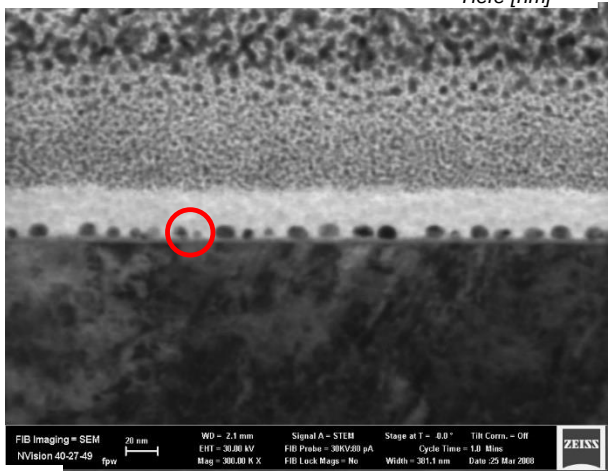
Application:
Medical science sector

- With the pulse mode thin layers can be detected

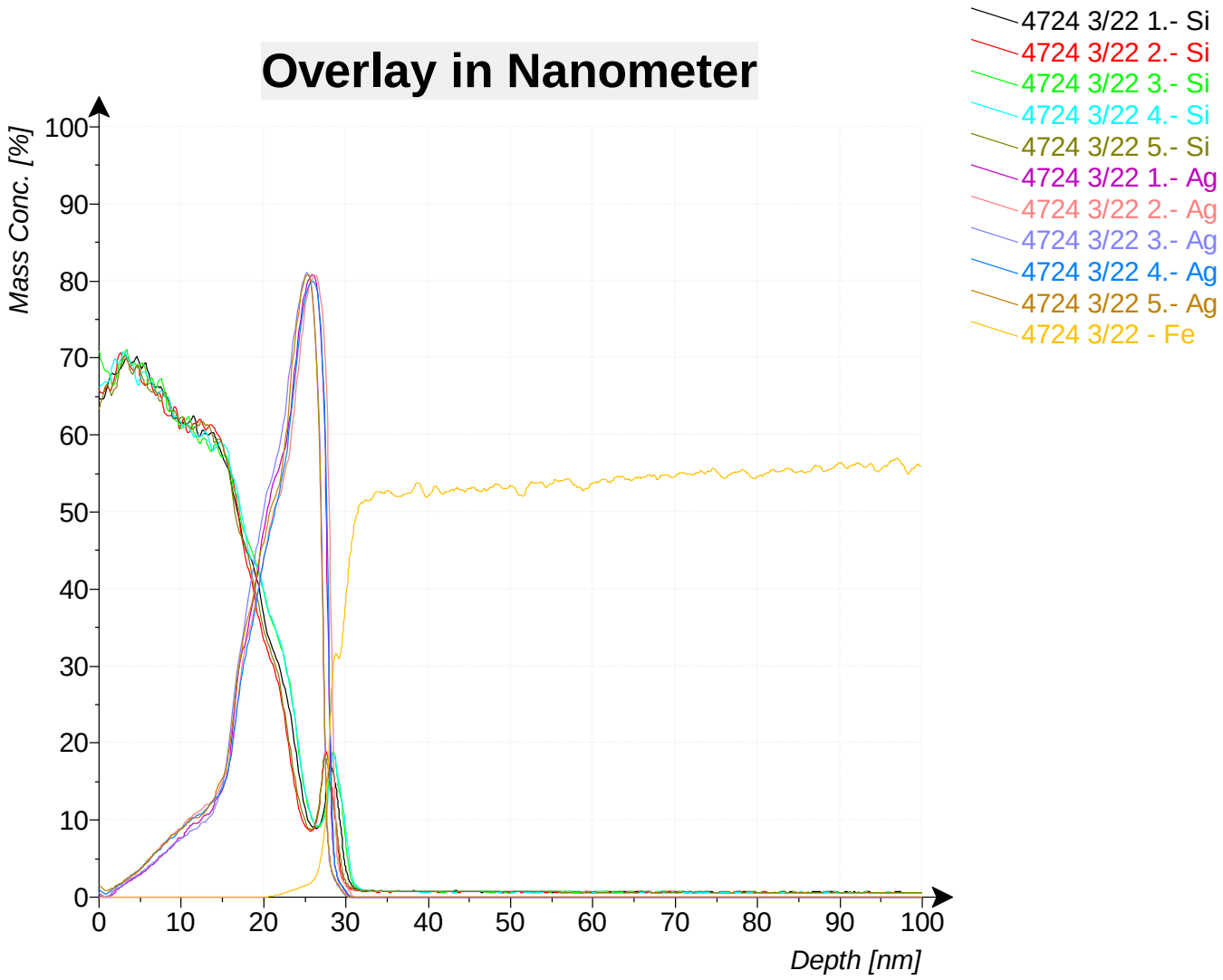
- On the **picture** of the TEM the small spheres of silver can be seen. They are located in a matrix of siloxane on metals or foils.

- With GDOES layer thickness, coating weight, oxidation level, roughness of base material and many more can be read out.



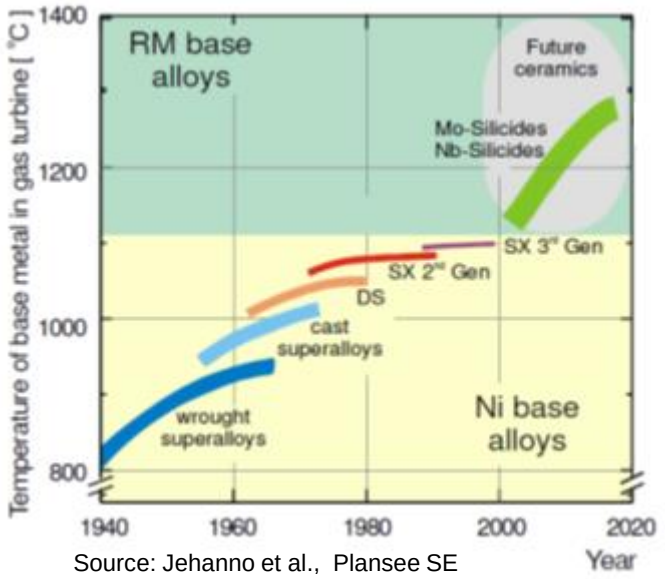


Application:
Good reproducibility

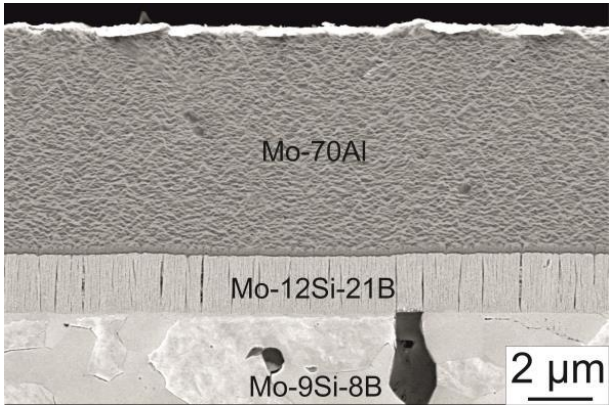


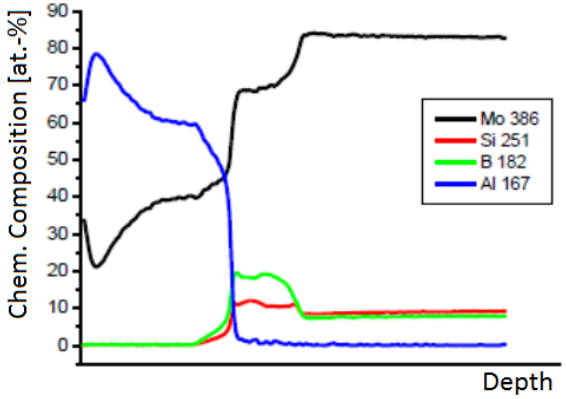
Application:
GDOES in Aerospace

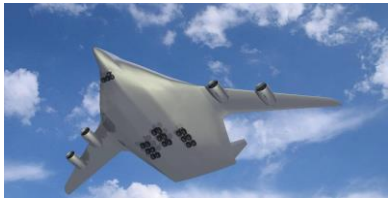
- In the field of aerospace GDOES can help to determine layers and interfaces accurately. Other techniques like microscope will not help enough to evaluate / determine the development.
- The development of heat-resistant materials has been one of the important research topics for the last years. A lot of experiments were conducted with so-called Mo-Si-B-alloys, which can perfectly be analyzed by GDOES (see graph).



Source: Jehanno et al., Plansee SE







Source: DLR

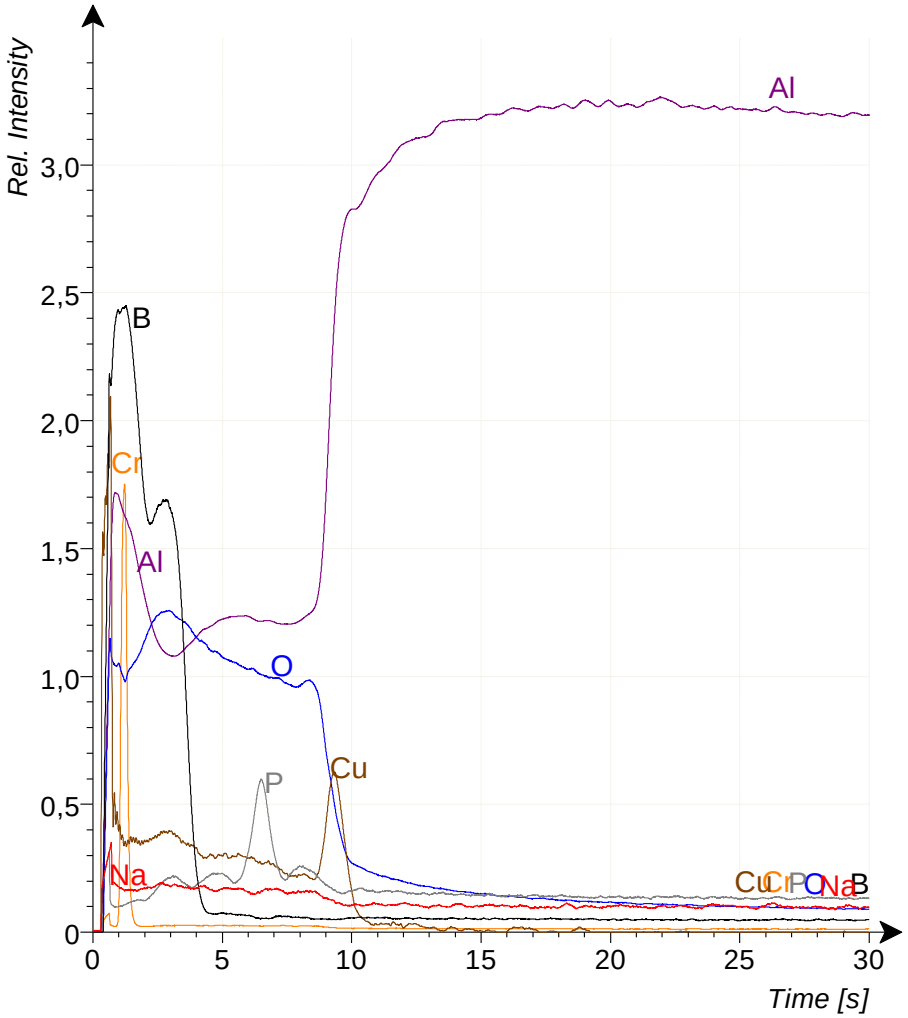
Source: A. Lange, R. Braun, M. Heilmaier, Intermetallics, to be published

Application:
Thin anodic alumina films

- Ultra-thin alumina films with self-ordered cylindrical vertical pores were fabricated by anodization of Al films with thickness in the range of 30 – 500 nm in aqueous solutions of sulfuric or oxalic acid.

- They are used as a dielectric layer of electronic devices.

- With GDOES it is possible to determine the thickness and to find out which solution was applied. In this case, a 0.1 M Na_2CrO_4 solution was used. Small quantities of Na and Cr were detectable.

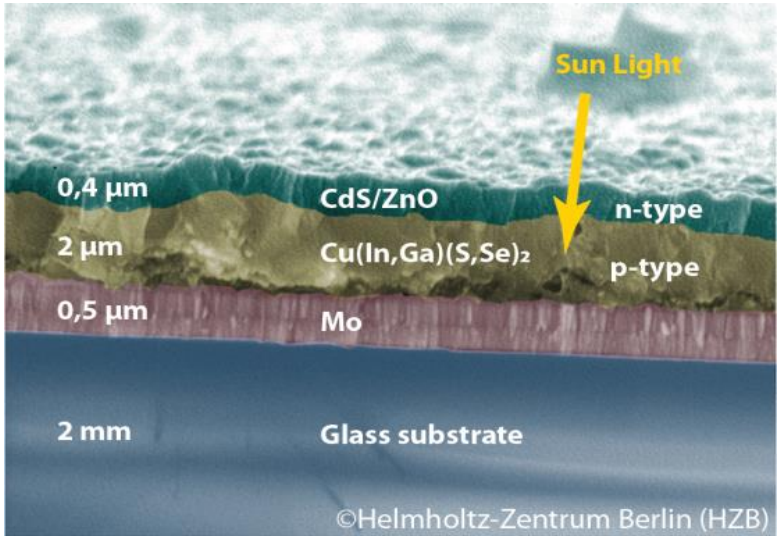


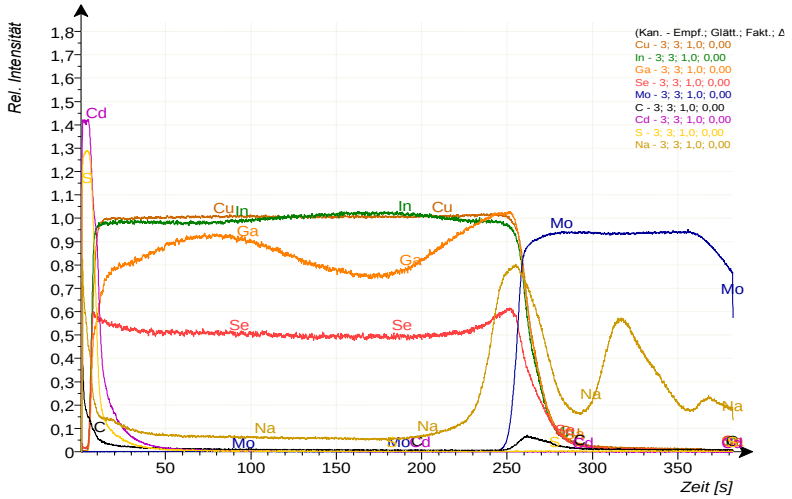
Application:
Solar cells industry

- In the semiconductor industry copper-indium-gallium(di)selenide (CIGS) is coated on a substrate (e.g. glass, Si wafer or steel).

- The **picture** shows an example of such a layer system.

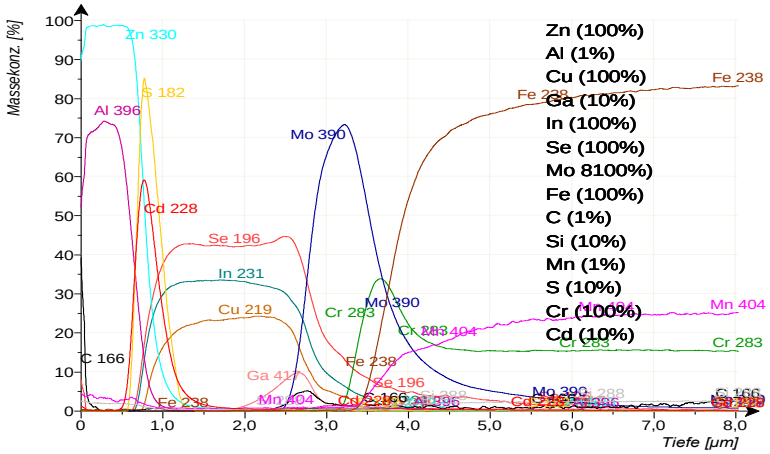
- With GDOES development and/or production control can be fulfilled.



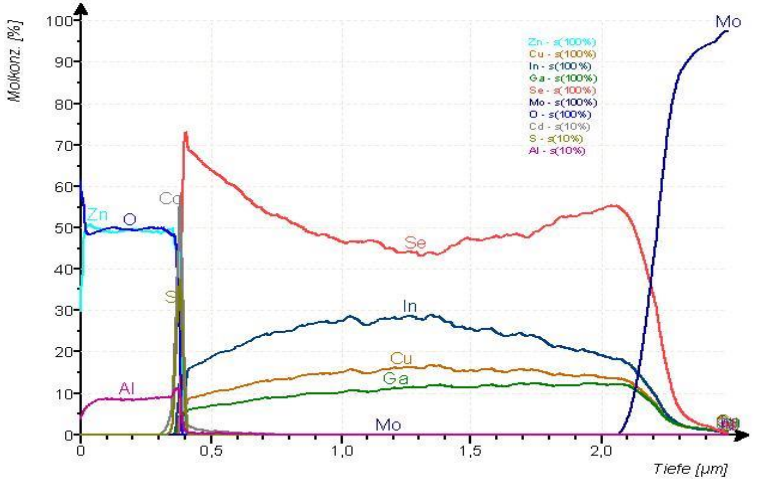


CdS on CIGS on glas

Solar cells industry
Further examples



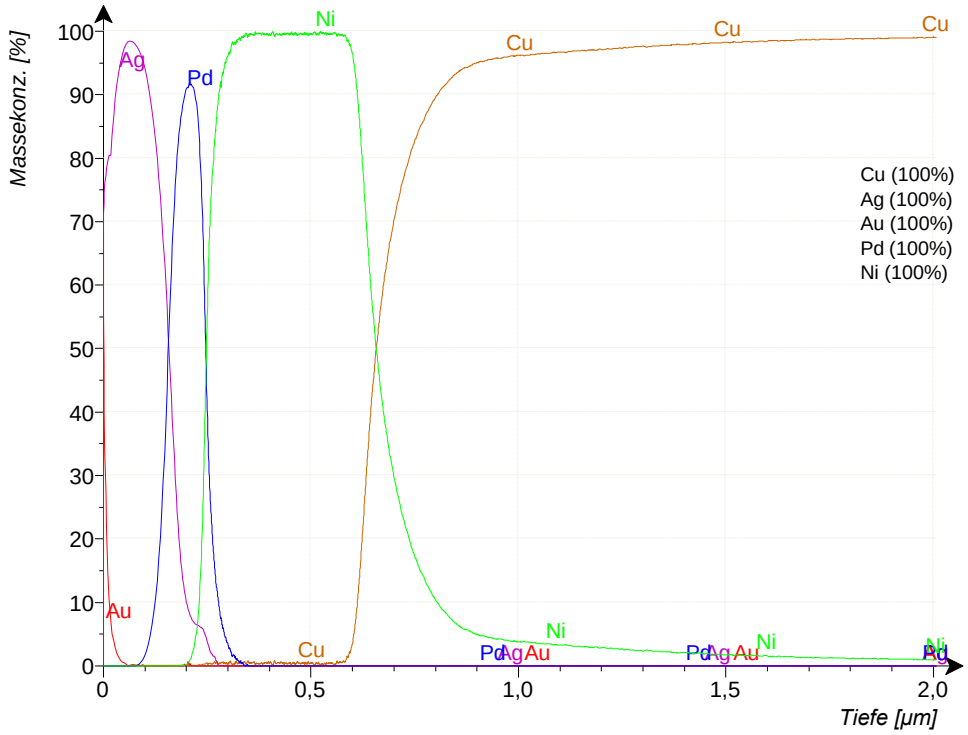
ZnO:Al on CdS on CIGS on steel



ZnO:Al on CdS on CIGS on glas

Application:
CCD - thin layers diffusion of Au in the Ag layer

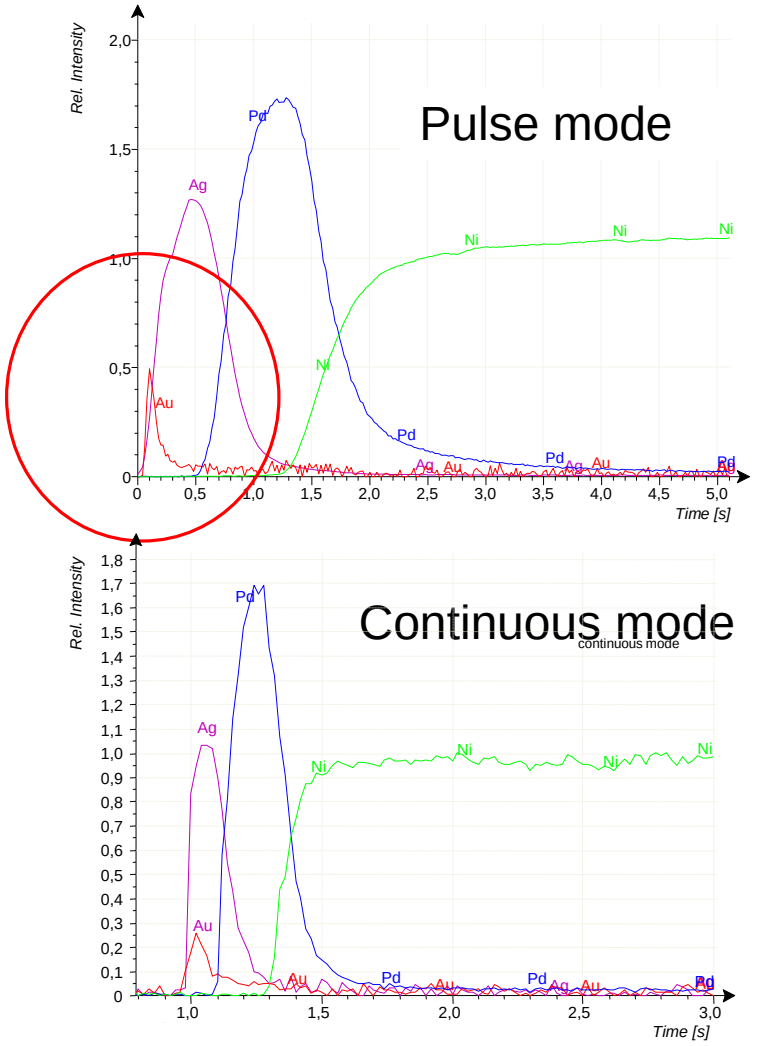
- Layer thickness Au 10 nm, Ag 120 nm on nickel on copper (electronic device).
- For applications with layers thinner than 50 nm the radiofrequency with **pulse mode** can be used.
- **Pulse mode**: In the plasma there are the same conditions, but the sputtering takes only fractions of seconds.
- Measurements are performed within seconds (here: 20 seconds).



Application:

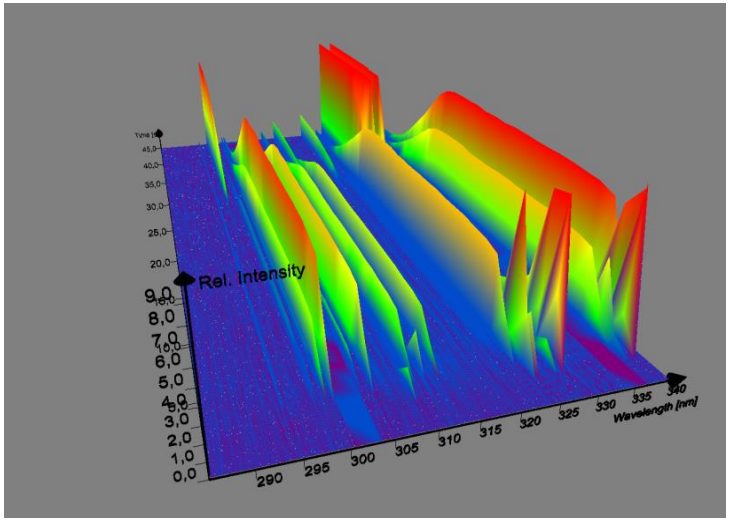
CCD - thin layers diffusion of Au in the Ag layer

For pulse mode Au signal raises before Ag signal → separating of the 2 layers

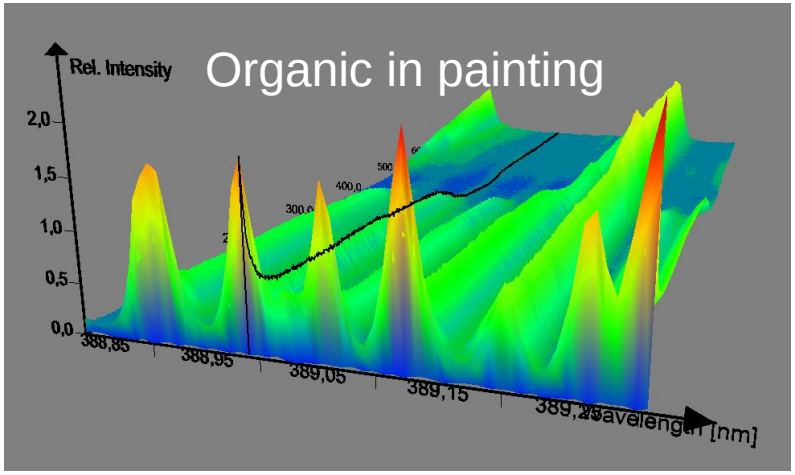


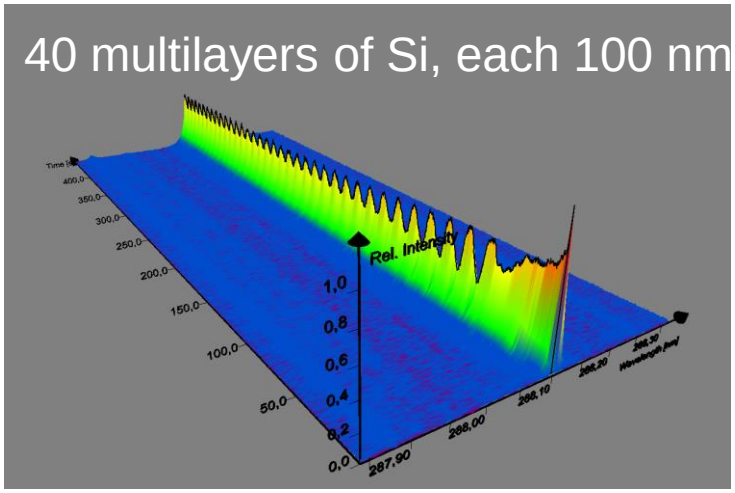
Example for CCD measurements

With the CCD, spectra over a wide wavelength range can be recorded. Between **120 and 700 nm** all important wavelengths of the PTE can be found.
The courses can be output as a depth profile from this analysis or can be defined as a channel for further measurements.



*** demonstrative 3D display over**





Résumé

Avec la GDOEs on peut:

- déterminer la concentration dans des échantillons solides de presque tous les éléments de quelques 0,0001% à 100 %

- déterminer la composition et l'épaisseur de plusieurs couches succesives de quelques nm jusqu'á plusieurs centaines de µm

- représenter des gradients de concentration en profondeur

Le Prix ???

La GD Alpha coûte ~ 55.000 CHF

Calibrée pour quelques matrices bulk

Calibrée pour une application d'analyse en Profondeur