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ANALYTIK GMBH

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GDOES – An Introduction

What is GDOES?

Glow Discharge Optical Emission Spectrometry (GDOES) is a spectrometric method for the qualitative and quantitative analysis of metallic and non-metallic solid materials.

What can be examined by GDOES?

- Chemical composition
- Layer thickness and layer composition
  → layer thicknesses between < 50 nm and > 100 µm analyzable
- Coating weight (calculated)

Which materials can be analyzed?

- Metals
- Semiconductors
- Glass
- Ceramics
- Polymers

Advantages of GDOES

- Precise analytical performances:
  - (almost) all elements of the PSE analyzable
  - low detection limits
  - very good reproducibility
- Electroconductive and insulating samples analyzable
- No laborious sample preparation required
- Short analysis times → fast results
- Easy operation
- Low operating costs

Disadvantages of GDOES

- Only solid materials analyzable
- Destructive method

Samples with burning spots of different sizes beside a European 2-cent-coin (18.75 mm diameter) for size comparison

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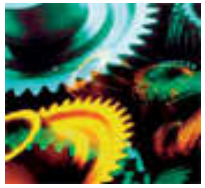
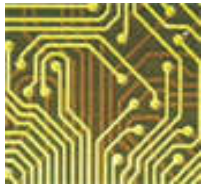
Fields of application for GDOES

Our GDOES-technology is an established method in numerous branches of industry. Some of the most important branches are:

- Automotive industry and automotive suppliers
- Metal industry
- Iron and steel industry
- Precision mechanics industry
- Aerospace sector
- Electronic industry
- Plastics industry
- Glass and ceramics industry
- Surface technology
- Galvanic industry
- Pharmaceutical industry
- Photovoltaic industry
- Research and development
- Universities and many more

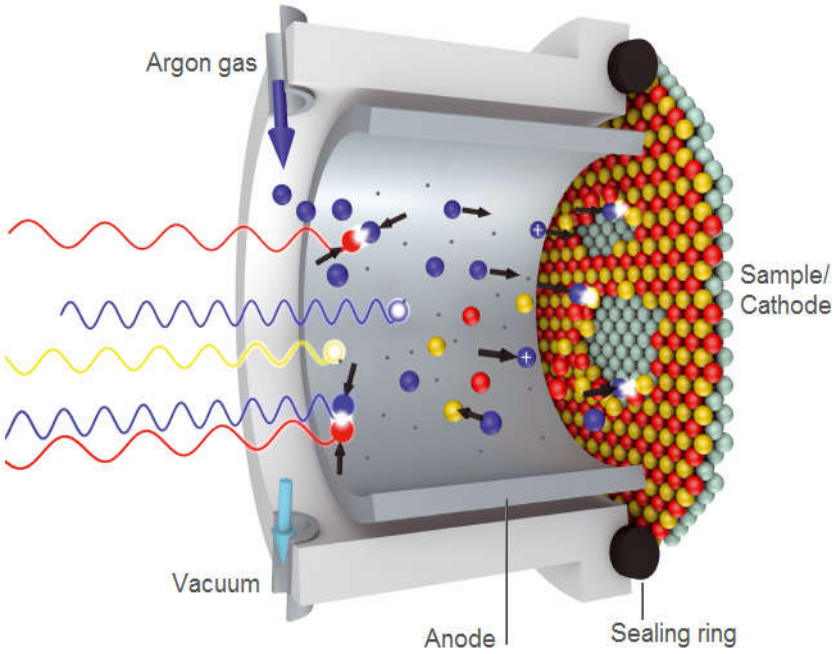




How does GDOES work?

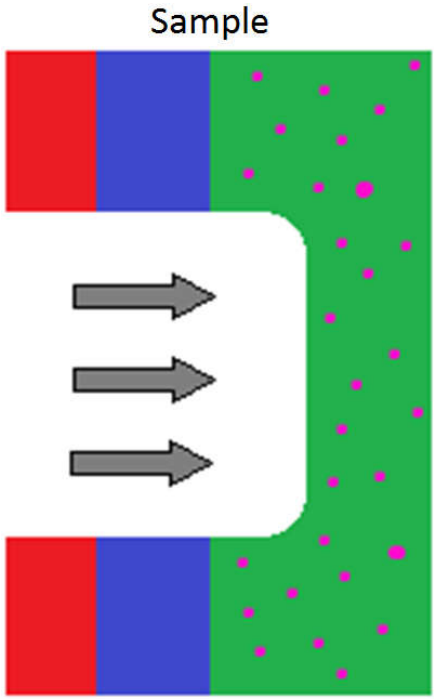
The sample is placed into the Glow Discharge Source and switched as cathode. The Glow Discharge Source is filled with argon gas under low pressure. Direct Voltage is applied between a hollow anode and the cathode (≙ sample). Due to the energy input of the DC voltage the argon atoms are ionized resulting in the formation of a plasma. Argon cations are accelerated towards the negative sample surface and knock out some sample atoms.

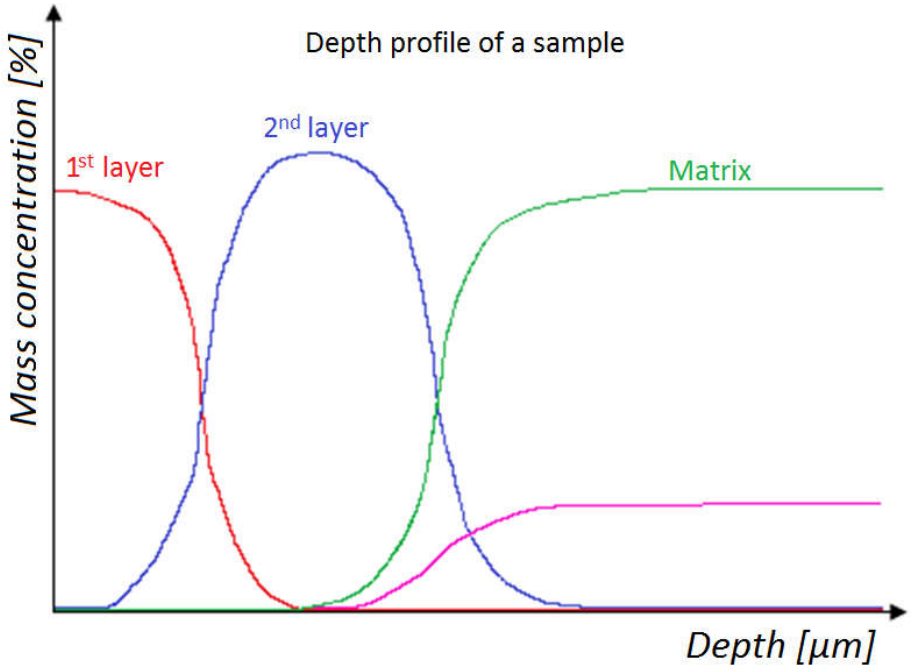
The knocked out sample atoms diffuse into the plasma where they collide with high-energy electrons. During these collisions energy is transferred to the sample atoms promoting them to excited energy states. Returning to the ground state the atoms emit light with a characteristic wavelength spectrum.
In the spectrometer the light is dispersed into its spectral components, which are registered by the detection system. The intensity of the lines is proportional to the concentration of the corresponding element in the plasma.



Scheme of the Glow Discharge Excitation process

The sputtering process described on the previous page is uniform so that the sample atoms are removed in a plane-parallel manner enabling the analysis of layers. The figure below illustrates the correlation between the plane-parallel ablation of a sample and the resulting depth profile.





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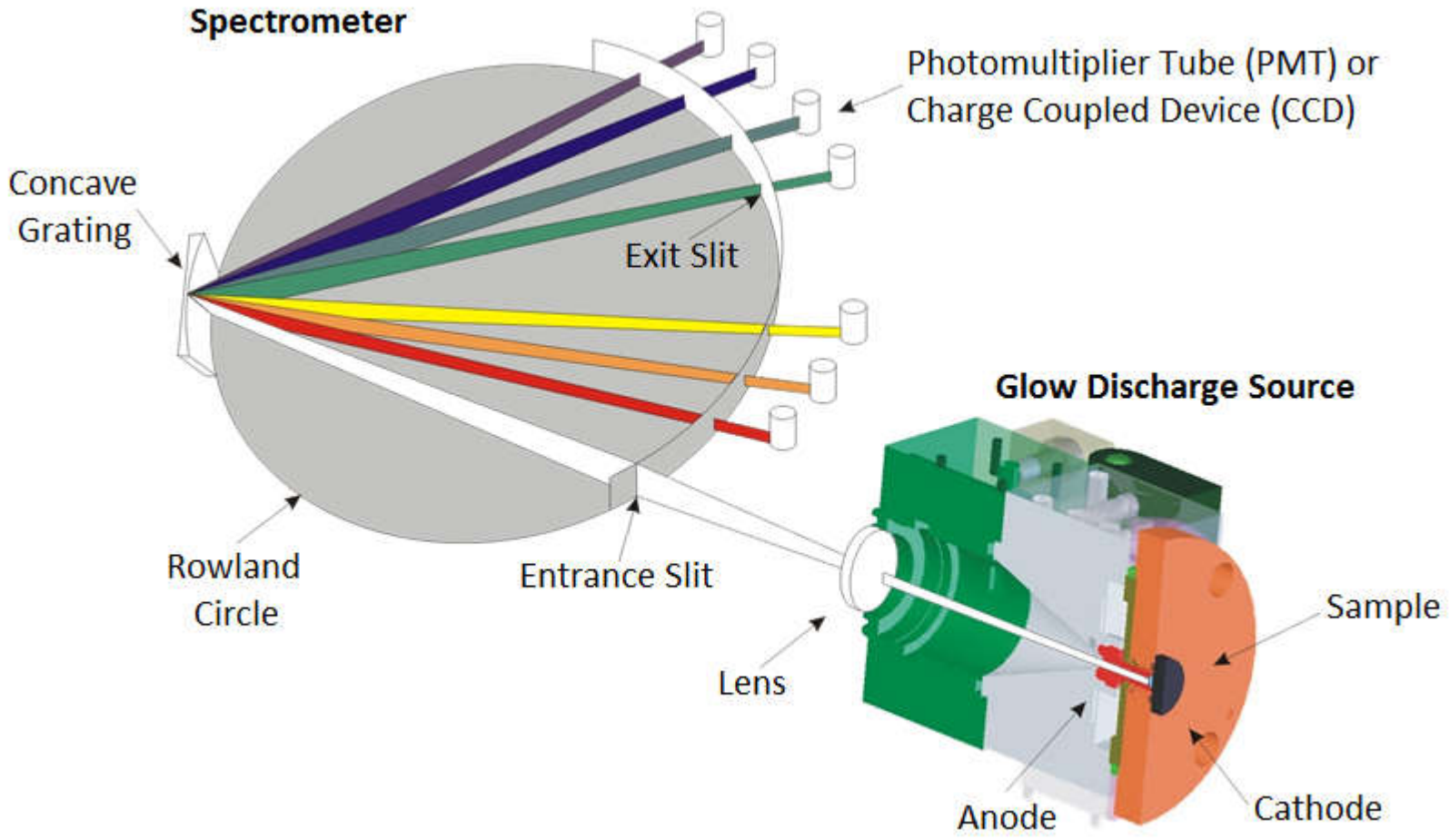
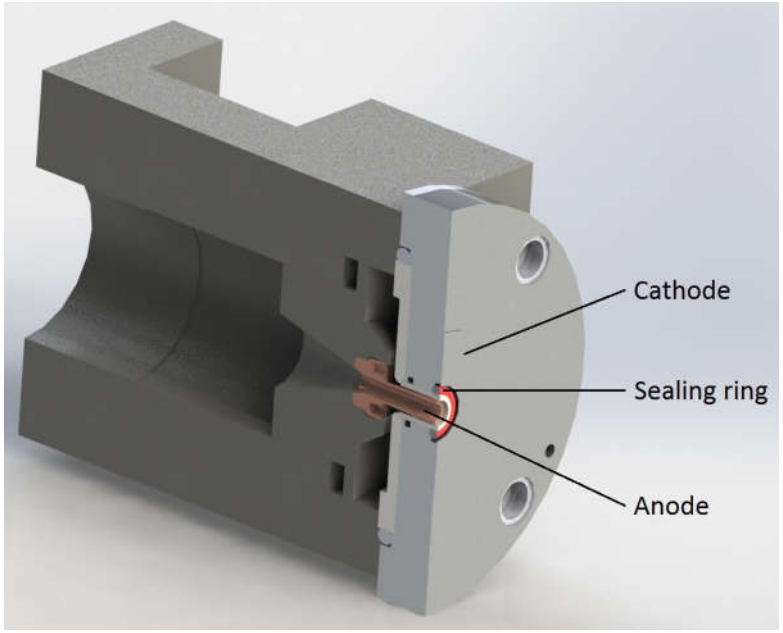
Schematic layout



Glow Discharge Source

The Glow Discharge Source is a Grimm type discharge tube characterized by a special arrangement of the electrodes: The two electrodes of the DC Current Source are set up of a cylindrical hollow anode and the sample as cathode. The sample must seal the anode tightly so a vacuum can be generated. Thus, a flat and preferably smooth sample surface is required.



Cross section of the Glow Discharge Source

The Glow Discharge Analyzers (GDA) can be equipped with anodes having inner diameters of 2.5 mm, 4 mm or 8 mm. The inner diameter defines the size of the measuring spot (“sputter crater”). The sample must be at least few millimeters larger than the sealing ring of the corresponding anode. For instance, using the 2.5-mm-anode requires a sample surface area of at least 6 mm.

Sample preparation

In contrast to microscopic methods GDOES does not require a laborious and time consuming sample preparation. Samples must meet only four criteria:

Criteria	Reason
1.) Under standard conditions: flat sample surface required. Alternatively, the Universal Sample Unit is applied.	1. + 2.) The sample surface must seal the glow discharge source tightly. So a proper vacuum can be generated and no contaminations from the atmosphere can get into the sample chamber.
2.) Minimum sample size: 20 mm for the 8-mm-anode, 15 mm for the 4-mm-anode and 6 mm for the 2.5-mm-anode.	
3.) Surface must be dry und free of oil and dirt.	3.) Even small traces of oil and dirt are detected and can falsify the analytical results.
4.) The distance between the anode and the reamer is 45 mm. Samples exceeding this size must be cut.	4.) Otherwise samples do not fit into the sample compartment

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Universal Sample Unit

Small as well as curved samples can be analyzed by using the so-called Universal Sample Unit (USU).

- The sample is placed into the fitting adaptor
  → Many adaptors for different sample geometries
- The generation of a vacuum is provided by the use of special plastic caps
- There is a Universal Sample Unit specially for wires

Standard USU with cap;
DC source

USU for wires
< 2,5 mm

No. 1:	for flat samples
No. 2 - 7:	for cylindrical samples of different sizes
No. 8 -11:	for spheres of different sizes
No. 12:	customized construction for a special geometry

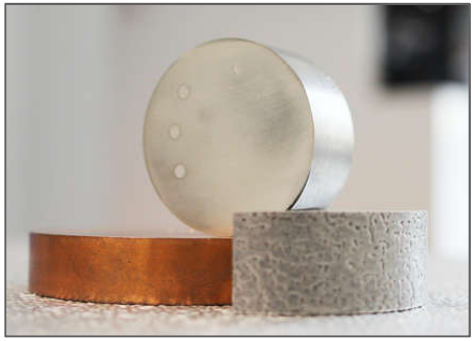
Calibration

Since GDOES is a relative investigation method based on external standards, every measured value must be compared to values of certified standard samples with known concentrations and erosion rates. Only after a proper calibration the program is able to convert the detected signals into concentrations or depths, respectively.
Glow Discharge Analyzers (GDA) are factory calibrated using certified reference materials according to the customer's analytical requirements. One of the advantages of GDOES is the linearity of the calibration functions.

Recalibration

Using the GDA continuously, the measured intensities decrease over time. They are subjected to changes by external factors (e.g. room temperature) and by contamination of the lens due to deposition of the analyzed material. To compensate the changes in the intensity the GDA needs to be recalibrated at regular intervals.

For every analytical method ordered with a GDA the corresponding samples for the recalibration and adaption to other excitation parameters are provided.



Recalibration-sample with measuring spots

Results

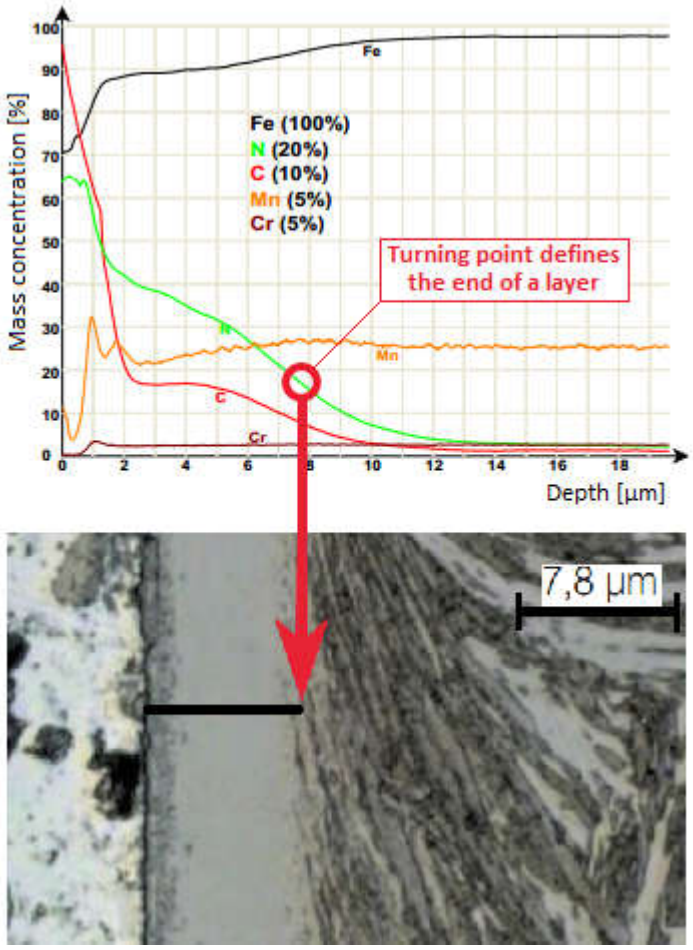
The results of bulk analyses are presented in a table as shown below, while the results of depth profile analyses are displayed in a graphic and in a tabular form. All results can be saved in an internal database for statistical purpose or be printed in a customer defined layout.
A material quality data base is included in the software enabling the direct comparison with a given quality or the search for matching data directly after the measurement. Data are easily exported to standard office applications or LIM systems.

Method:		NiCoCr-2,5mm												
Sample:	IARM 64B													
Elements:	Co 345 [%]	Cr 267 [%]	Fe 371 [%]	Mn 279 [%]	Mo 386 [%]	Ni 341 [%]	W 429 [%]	Al 396 [%]	C 165 [%]	Be 313 [%]	S 180 [%]	Si 288 [%]	P 178 [%]	Pb 220 [%]
	53,761	25,629	3,160	0,722	4,873	8,981	2,383	0,095	0,070	0,003	0,001	0,276	0,009	0,011
	53,850	25,589	3,153	0,721	4,862	8,982	2,362	0,093	0,069	0,003	0,001	0,275	0,009	0,012
	53,787	25,635	3,152	0,720	4,856	8,996	2,378	0,094	0,069	0,003	0,001	0,274	0,009	0,012
	53,885	25,535	3,150	0,717	4,849	9,022	2,354	0,095	0,069	0,003	0,001	0,274	0,009	0,012
Mean	53,821	25,597	3,154	0,720	4,860	8,995	2,369	0,094	0,069	0,003	0,001	0,275	0,009	0,012
Std. Dev.	0,049	0,040	0,004	0,002	0,009	0,017	0,012	0,001	0,000	0,000	0,000	0,001	0,000	0,000
Rel. Std. Dev. [%]	0,091	0,156	0,119	0,260	0,181	0,184	0,495	0,880	0,625	0,000	0,000	0,302	0,000	3,685

Extract from a table of a bulk analysis

Applications

Heat treatment: Nitrocarburizing



Note: The scaling of the elements is linear with a magnification factor. E.g. *N - (20 %)* means the display range of the y-axis of nitrogen is between 0 and 20 %.

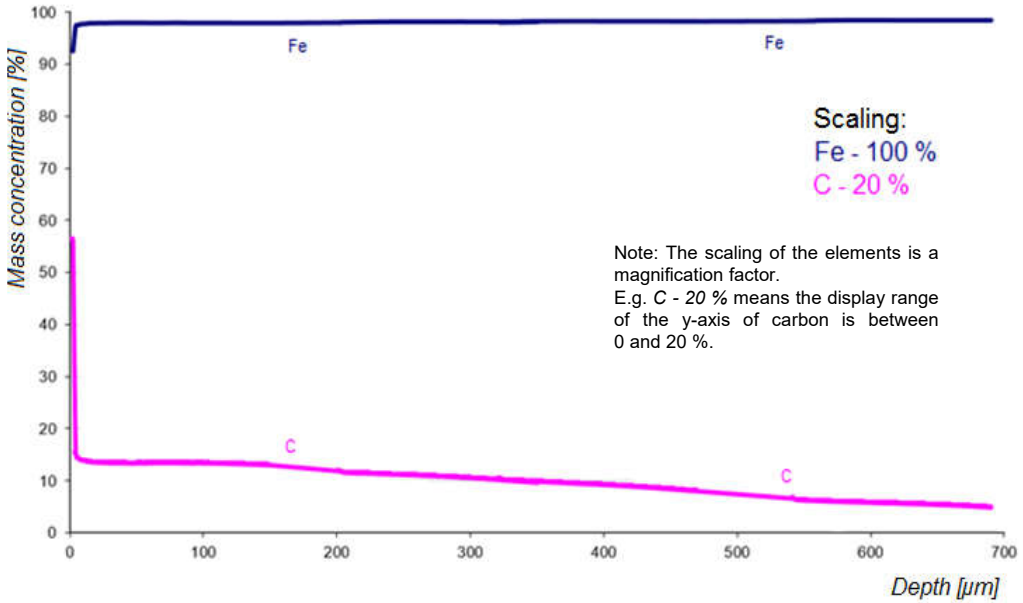
The graph on the top displays the result of a depth profile analysis of a nitrocarburized sample via GDOES. The thickness of the nitrogen layer amounts to 7.8 µm. Moreover, a carbon layer is discernible.

Alternatively, the layer thickness can be determined by a metallographic analysis. Usually, such analyses comprise the following steps:

- Grinding the sample
- Polishing the sample
- Microscopic analysis

The picture on the bottom shows a microscope image of the same sample as above. The layer thickness of 7.8 µm is in accordance with the result of the GDOES analysis. While the sample preparation for the microscope takes approximately an hour for each sample, GDOES measurements do not require sample preparations. The measurement period is only a few minutes.

Heat treatment: Carburizing

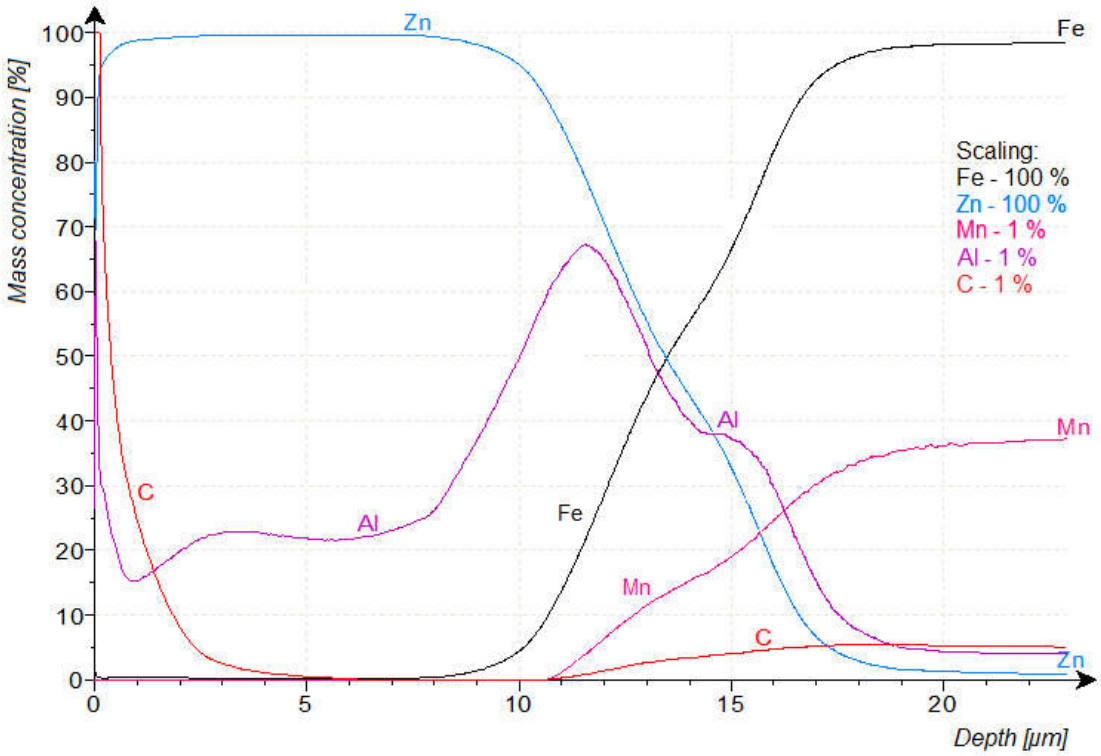


To increase the wear protection, carbon is introduced into steel. The layer thicknesses of such carbon layers may be up to 1 mm. Since the maximum layer thickness detectable by GDOES amounts to approx. 200 µm, these layers cannot be measured in a single step. Instead, several measurements are performed on the same sample.

After the first measurement the sample is grinded a little bit in such a way, that the first burning spot is still visible. The next measurement is performed on the grinded area as near as possible to the old spot. The recorded spectra are stringed together to a single profile. This procedure can be repeated until the desired depth is reached.
The figure shows a depth profile combined of several measurements. Only the elements iron and carbon are displayed.

GDOES analyses are as precisely possible for other kinds of heat treatment, like e.g. decarburizing, carbonitriding or boriding.

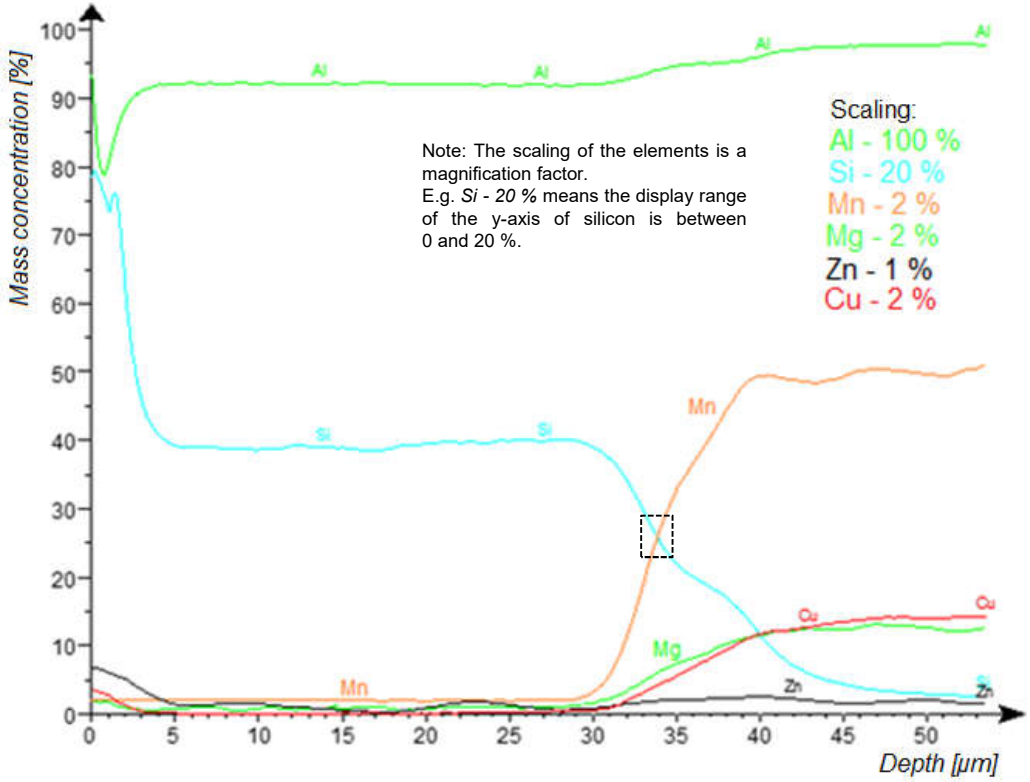
Galvanizing



Note: The scaling of the elements is a magnification factor.
E.g. *Mn - 1 %* means the display range of the y-axis of manganese is between 0 and 5 %.

Zinc coatings are applied in industry to increase the corrosion resistance of materials. The thickness of the zinc layer in the depicted example amounts to 13.5 µm.

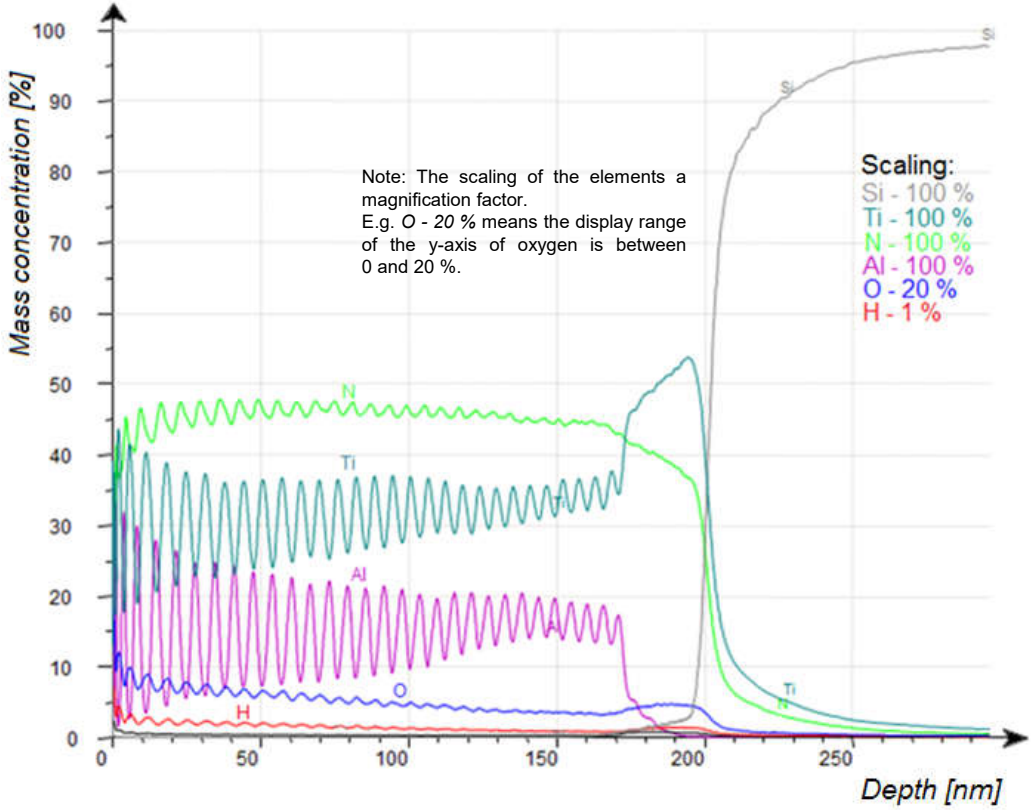
Aluminum cladding



Aluminum cladded materials are used in the automotive industry for cooling fins and radiators etc. They consist of two different aluminum alloys glued by heat and pressure.
The control over the thickness of the cladding as well as the purity of the layers and the surface is of great importance.

As can be seen in the figure above, the alloy on the surface contains silicon while the alloy beneath contains manganese, magnesium and copper. The turning point of a curve (black framed area in the diagram) defines the end of a layer. In this case, the layer thickness of the Si-containing alloy amounts to 34 µm.

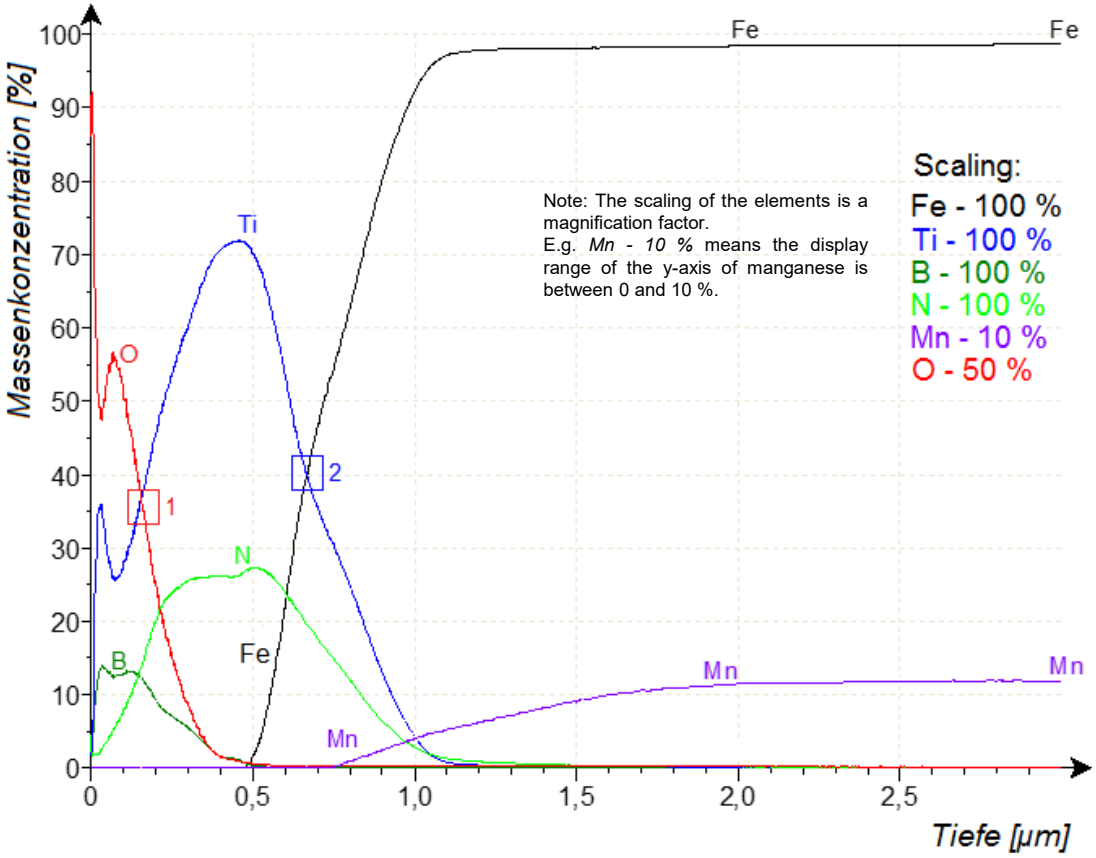
Thin film analysis



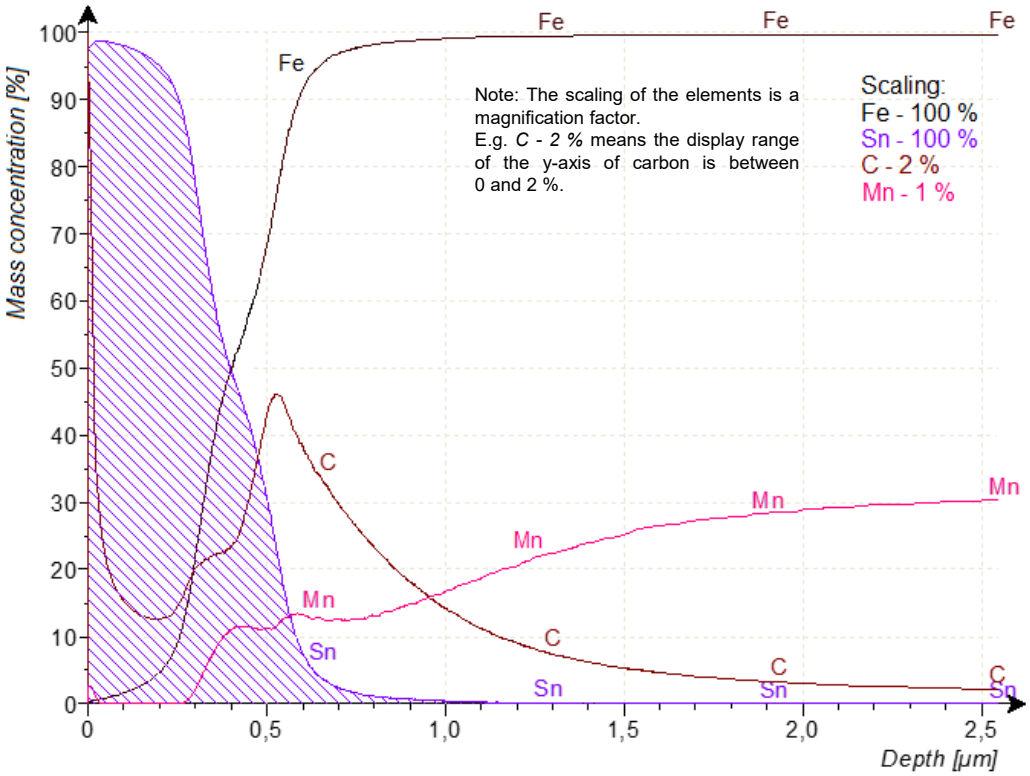
Titanium Nitride on Silicon

60 layers of TiN/TiAlN were applied on a silicon wafer. Each layer exhibits a layer thickness of about 3 nm.
Even such ultrathin layers can be analyzed by the use of the radiofrequency excitation source developed by Spectruma Analytik. The graph shows the results.

Titanium boron nitride



TiBN layers confer extreme hardness and a high temperature resistance to materials.
The graph displays the analysis of a TiBN/TiN layer on steel. The areas labelled with *1* and *2* highlight the turning points of the oxygen and titanium curves and define the end of these layers. The first layer ends at 0.15 µm. Apparently, boron migrates into the next layer. The second layer ends at 0.65 µm.

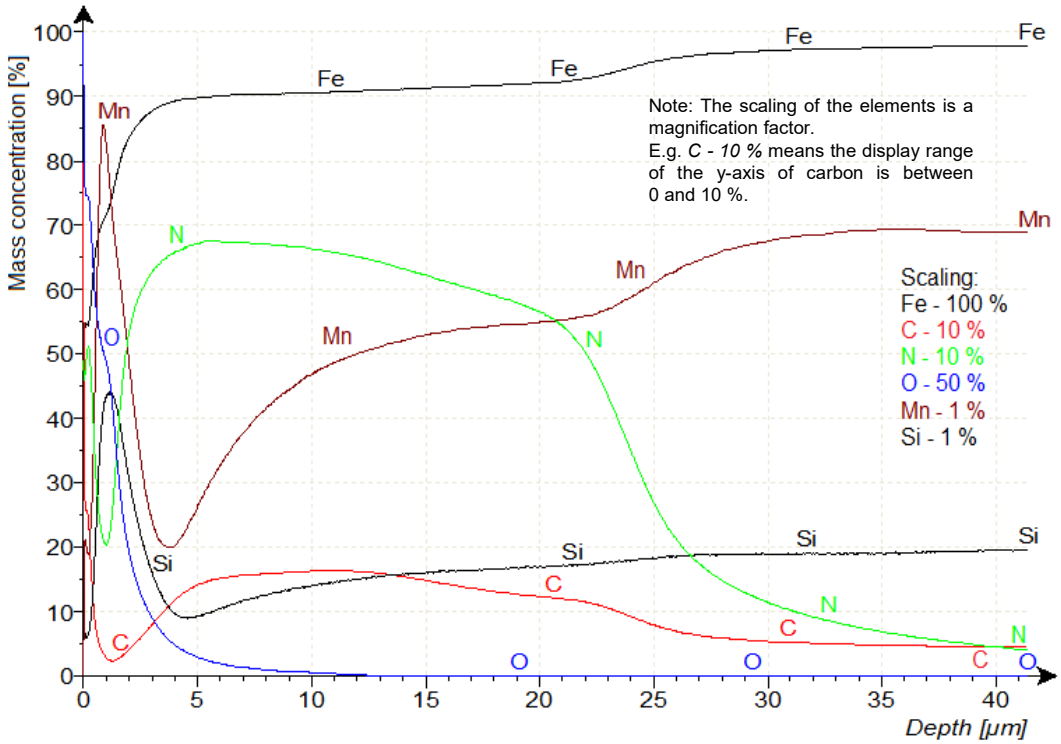


Tin layers

Although tin coatings exhibit a relatively high corrosion resistance as well, the main reasons to apply tin coatings are usually their compatibility with food stuffs and their solderability.

The tin layer in the graph has a thickness of 0.42 µm. Moreover, the software WinGDOES developed by Spectruma Analytik can easily calculate coating weights by forming the integral over the curve of an element (cross-hatched area in the diagram). The tin layer in this example has a coating weight of 3 g/m^2.

Analysis of curved samples

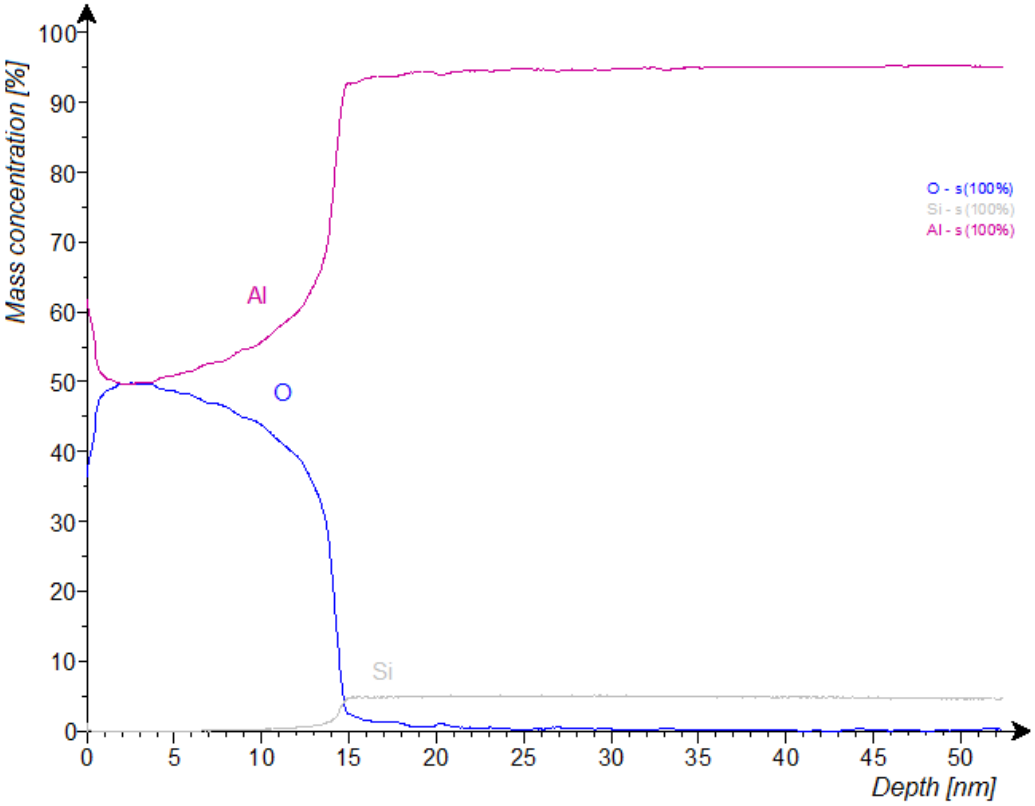


The graph displays the depth profile of a curved nitrocarburized sample (see right picture) with an oxide layer on the surface.

By using the Universal Sample Unit (see page 6) and a suitable adaptor it is possible to analyze curved and/or small samples.
Measurements with the Universal Sample Unit provide as precise results as standard measurements.

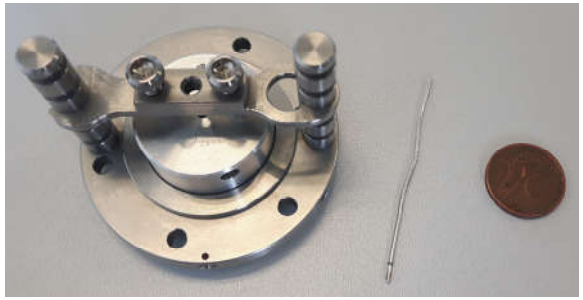
Curved sample with measuring spots beside a 2-cent-coin for a size comparison

Analysis of wires



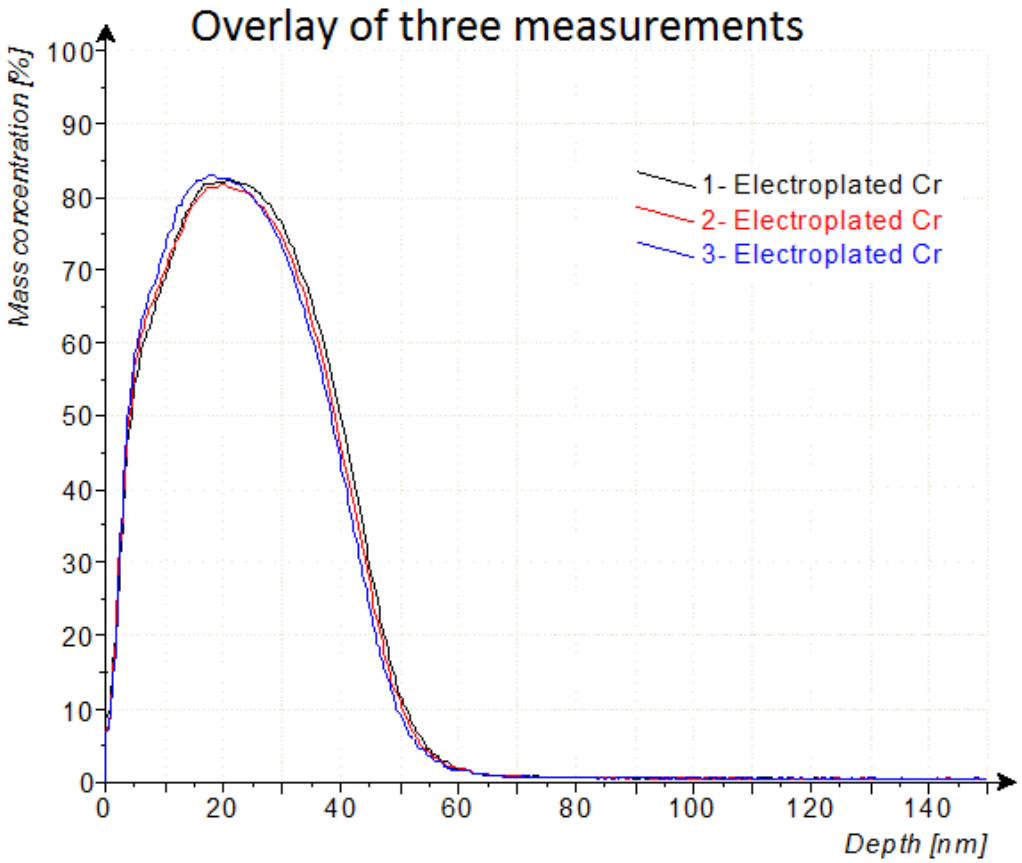
The graph displays the results of the analysis of an aluminum wire of 1 mm diameter. To analyze samples of such sizes and geometries the Universal Sample Unit for wires is used (see picture below + page 6).

In the diagram, an aluminum oxide layer of about 13 nm thickness is clearly discernible on the surface. The wire contains 5 % silicon.



Aluminum wire beside the Universal Sample Unit for wires and a 2-cent-coin for a size comparison

Reproducibility



A good reproducibility of the results is a basic requirement for every analytical method.
In the GDOES, the reproducibility is about 99 %.
The graph displays the overlay of three measurements of a sample. The deviations are negligibly small.

Generally, slight deviations can also stem from inhomogeneities of the samples.

Bulk Analysis

Sample:	NBS 1761								
Elements:	Fe [%]	C [%]	Mn [%]	Si [%]	P [%]	S [%]	Cr [%]	Ni [%]	Ti [%]
	95,159	1,028	0,672	0,178	0,038	0,033	0,225	1,957	0,160
	95,086	1,031	0,676	0,178	0,038	0,036	0,228	1,976	0,194
	95,056	1,028	0,667	0,177	0,040	0,032	0,227	1,973	0,159
	95,016	1,033	0,682	0,181	0,039	0,035	0,230	1,993	0,185
	95,026	1,026	0,681	0,180	0,041	0,033	0,230	1,984	0,186
Mean	95,068	1,029	0,676	0,179	0,039	0,034	0,228	1,977	0,177
Std. Dev.	0,051	0,002	0,006	0,002	0,001	0,001	0,002	0,012	0,014
Rel. Std. Dev. [%]	0,05	0,24	0,82	0,84	2,40	3,60	0,85	0,60	8,08

Al [%]	Cu [%]	Co [%]	Mo [%]	V [%]	W [%]	B [%]	Nb [%]	Zr [%]
0,054	0,286	0,043	0,103	0,047	0,016	0,002	0,029	0,001
0,054	0,294	0,040	0,104	0,048	0,014	0,003	0,029	0,011
0,053	0,295	0,041	0,101	0,049	0,005	0,002	0,031	0,011
0,055	0,301	0,040	0,105	0,053	0,007	0,002	0,028	0,011
0,054	0,298	0,043	0,105	0,053	0,011	0,002	0,028	0,018
0,054	0,295	0,041	0,104	0,050	0,011	0,002	0,029	0,010
0,001	0,005	0,001	0,001	0,002	0,004	0,000	0,001	0,005
1,11	1,69	3,31	1,39	4,36	37,70	7,77	4,16	52,63

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Product line

GDA 750 HR
GDA 550 HR

PMT-Spectrometer
2,5-mm-, 4-mm-, 8-mm-anodes
Radiofrequency excitation for the analysis of non-conductive materials (GDA 750 HR)
Fast analysis of thin layers (< 50 nm)
LoD 0,1 - 10 ppm

GDA 650 HR
GDA 150 HR

CCD-Spectrometer
2,5-mm-, 4-mm-, 8-mm-anodes
Radiofrequency excitation for the Analysis of nonconductors (GDA 650 HR)
Precise bulk and depth profile analyses
LoD 0,1 - 10 ppm

GDA-Alpha

CCD-Spectrometer
2,5-mm-, 4-mm-, 8-mm-anodes
Precise bulk and depth profile analyses
Compact and space-saving design
LoD 0,1 – 10 ppm

Profitability

Instrument	Acquisition costs	Costs for consumables per month	Manpower
GDOES	150.000,-€ (start at about 50.000,-€)	approx.150,-€	Laborant / Ingenieur
REM	250.000,-€	approx. 250,-€	Laborant / Ingenieur
Auger	500.000,-€	approx. 3.000,-€	Ingenieur / Doktor
SIMS	500.000,-€	approx. 3.000,-€	Ingenieur / Doktor
ESCA	500.000,-€	approx. 3.000,-€	Ingenieur / Doktor
GD-MS	750.000,-€	approx. 250,-€	Laborant / Ingenieur

All specifications are based on customer information

Additional service costs are not included. A contract for an AUGER spectrometer costs 15.000 € per year.

Summary

The GDOES allows for the precise performance of Depth profile analyses and bulk analyses. All elements of the Periodic Table can sensitively be detected.

No laborious sample preparation is required, the samples usually can be measured as received from production. The measuring period amounts to a few minutes. The analysis of curved and/or small samples is easily possible by the use of the Universal Sample Unit.

There are various fields of application. Nearly every solid material can be analyzed by GDOES.

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