

Expanded Coating Analysis Performance for electroless Ni Plating and Bath Analysis with Micro-XRF



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Presenters / Moderators



Robert Erler

Product Manager Micro-XRF
Bruker Nano Analytics, Berlin, Germany



Falk Reinhardt

Application Scientist Micro XRF
Bruker Nano Analytics, Berlin, Germany

Expanded Coating Analysis Performance Webinar Outline



- Overview of ENP basics
- XRF Technology with M1 MISTRAL
- ENP use cases (1-3)
- Other light element applications
- Live Measurements
- Questions and Answers



Electroless Ni Plating

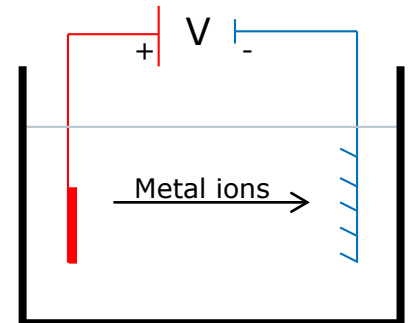
What is electroless (chemical) plating?

Short overview



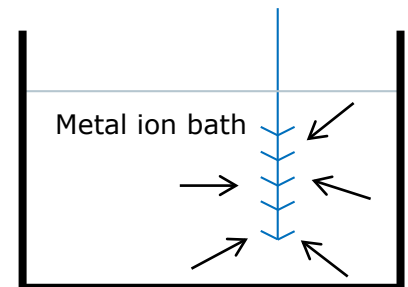
Normal galvanic plating/coating

- Sample/base material must be conductible
- Coating homogeneity depends on the current distribution on the surface
- Max. thickness is limited
- Growth parameter depends on both, bath solution properties and power settings



Electroless (chemical) coating differences

- Sample/base material must not be conductible
- Coating homogeneity increased (autocatalytic)
- No max. limit in principle
- Alternative to Cr-6 coatings
- Wear and corrosion resistance, electrical resistivity, lubricity and hardness increased, ductility decreased
- Growth parameter depends on bath solution properties



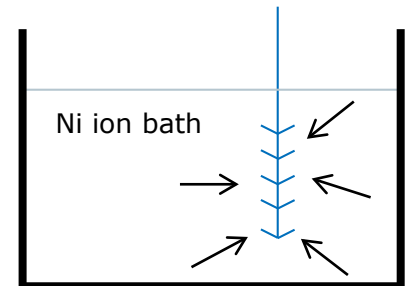
What is electroless Ni plating?

Short overview



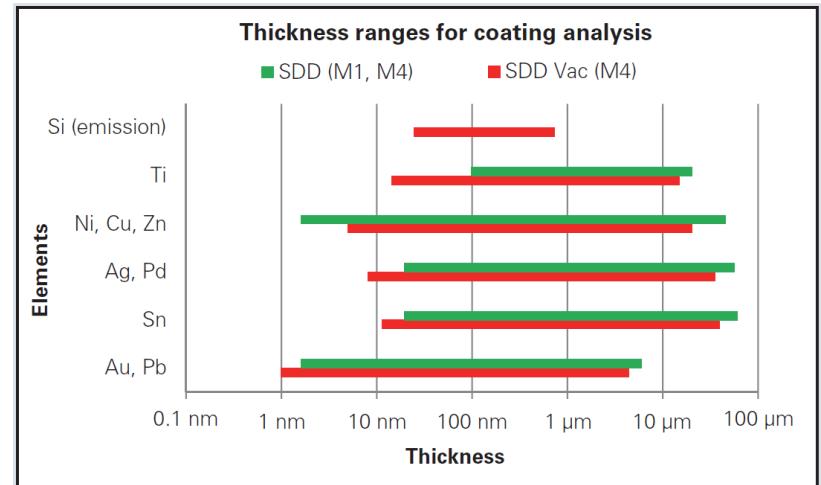
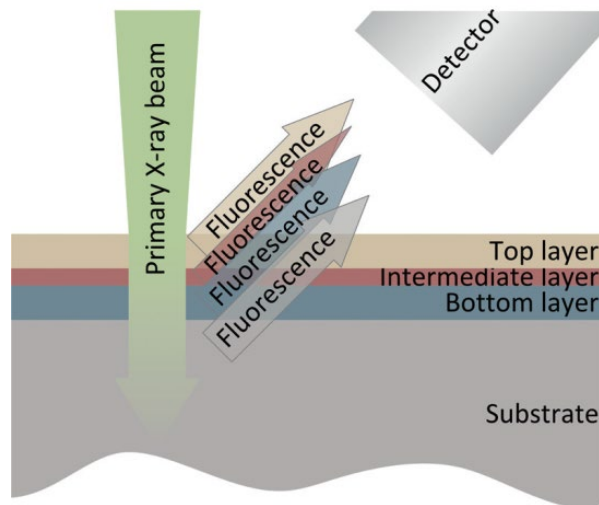
Electroless Nickel (EN) plating/coatings

- Sample/base must be cleaned very carefully
- For autocatalytic reaction a reducing agent is needed
- This can be hypophosphite (PH_2O_2^-) or borohydride (BH_4^-) or other organic Boron compounds
- Most common available are NiP coatings (ENP)
- Possible added elements could be light compounds (teflon, silicon carbide) or heavy elements for a ternary alloy NiPX ($X = \text{Cu}; \text{W}; \text{Mo}$)
- Three levels of P content in the layer:
 - Low-phosphorus ENP ($< 4\% \text{ P}$)
 - Medium-phosphorus ENP ($4\% - 10\% \text{ P}$)
 - High-phosphorus ENP ($10\% - 14\% \text{ P}$)
- Applications:
 - Automotive, Aerospace, Electronics, Chemical processing, Oil and Gas industry, Others



Why XRF for coating analysis?

Short overview



Advantages of XRF

- Non-destructive and fast (down to 10 s)
- Multi coating thickness and composition determination (limitless coatings and elements)
- Small spot sizes for filigree structures or check of inhomogeneities (down to μm spots)
- Certain thickness range (depends on main element)
- Certain element range (depends on hardware)

Micro-XRF for coating analysis

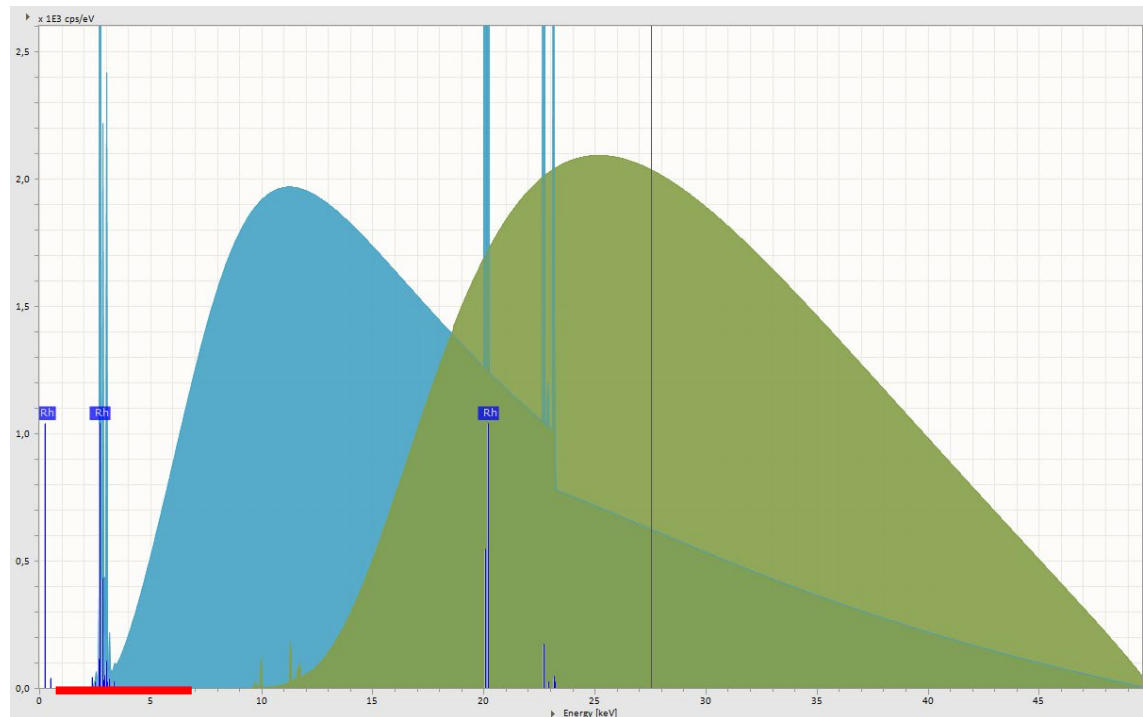
M1 MISTRAL



- State-of-the-art XFlash® SDD technology
- Measurement on air
- Programmable stage and easy to handle routine analysis software
- 50 W micro-focus tube with W or Rh target

Micro-XRF for coating analysis

M1 MISTRAL Rh vs. W Target



- State-of-the-art XFlash® SDD technology
- Measurement on air
- Programmable stage and easy to handle routine analysis software
- **50 W micro-focus tube with W or Rh target**

Micro-XRF for coating analysis

M1 MISTRAL



- Used instrument M1 MISTRAL in Bruker Nano lab, Berlin
- 50 W micro-focus Rh target X-ray tube (Be window)
- Collimator changer J01 (1.5 mm and 0.6 mm spot size), measurement times 30-120 s
- NiP analysis methods supported with standards and relative mode

Micro-XRF for coating analysis XSpect Pro GUI



The screenshot displays the XSpect Pro software interface with several key components:

- Main Control Window:** Shows a microscope image of a sample with a red crosshair. It includes stage control (Z: 74.64 mm, X: 141.19 mm, Y: 75.66 mm) and load control buttons.
- Results Table:** A table showing measurement data for different layers.

n/a	No.	Date	Time	Layer	base	layer1	layer2	✓/x
1	29.03.2016	12:13:50	99999.9	d/μm - Cu	1.960	0.024	x	
2	29.03.2016	12:14:20	99999.9	d/μm - Ni	1.959	0.023		
3	29.03.2016	12:14:51	99999.9	d/μm - Au	1.960	0.024		
4	29.03.2016	12:15:22	99999.9	d/μm - Ni	1.959	0.023		
5	29.03.2016	12:15:52	99999.9	d/μm - Cu	1.958	0.024		
6	30.03.2016	13:15:33	99999.9	d/μm - Ni	1.959	0.023		
- Spectrum View:** A window showing the X-ray spectrum with a peak at approximately 2.0 keV.
- Trendline Diagram:** A graph titled "Thickness of layer layer2" showing the thickness of layer 2 over 8 measurements. The y-axis ranges from 0.011 to 0.036. The legend includes:
 - Microconicals (blue line with circles)
 - Target value (green horizontal line)
 - Lower control limit (red dashed line)
 - Upper control limit (red dashed line)
 - Mean (black horizontal line)
 - Stdev (black horizontal line)
 - 1.0 (green horizontal line)
 - 1.0 (red horizontal line)

- Result table during measurement with pass/fail indicator
- Spectrum view after measurement

- Trendline diagram during measurement

Micro-XRF for coating analysis

XData Calibration



METHOD EDITOR
NIP-SbBi_Cu-cal rel

Structure Normation Calibration Spectrum

Method data

Description: NIP-SbBi_Cu-cal rel
Type: layer
Spectrum deconvolution: Standard spectrum deconvol

Layer parameters

Name: base
Compound: [dropdown]
Start thickness: 19.999,9
Unit: μm (1)
Fixed thickness: [checkbox]
Calc. mode: Relative
Normalize sample/standard: [checkbox]
Target value (%): 100,00
Density: Default 8,96 / User 0,00
Use tolerances?: [checkbox]

Structure

Layer Chemical elements

layer1: Ni P Sb Bi
base: Cu

Element overview

Element	Z	Main line	Start conc.
Cu	29	KA	100,00 %

METHOD EDITOR
NIP-SbBi_Cu-cal rel

Structure Normation Calibration Spectrum

Method data

Description: NIP-SbBi_Cu-cal rel
Type: layer
Spectrum deconvolution: Standard spectrum deconvol

Calibration samples

Layer No.	Sample	base W.	base Std	layer1 calib.	layer1 std	calib.	Ni(%) Std	calib.	P(%) Std
0	8560NIP5_5	1	--	--	8,56	8,57	94,50	94,51	5,50
1	3730NIP9_0	1	--	--	3,73	3,69	91,00	91,32	9,00
2	1910NIP8_3	1	--	--	1,91	1,94	91,70	91,37	8,30

Deviation (o): 0,03 / 0,26

Measurement parameters

HV / kV: 50
Collimator / mm: 1.50 o
Atmosphere: Air
Current / μA : 800
Measure time / s: 30

Calibration coefficients

0
7.596156264E-1

Graph

calib. layer1 (μm)

- Method calibration with XData as part of XSpect Pro
- Simple defining the coating structure and linking to pure element intensities
- Simple calibration with different settings after loading suitable and available standards

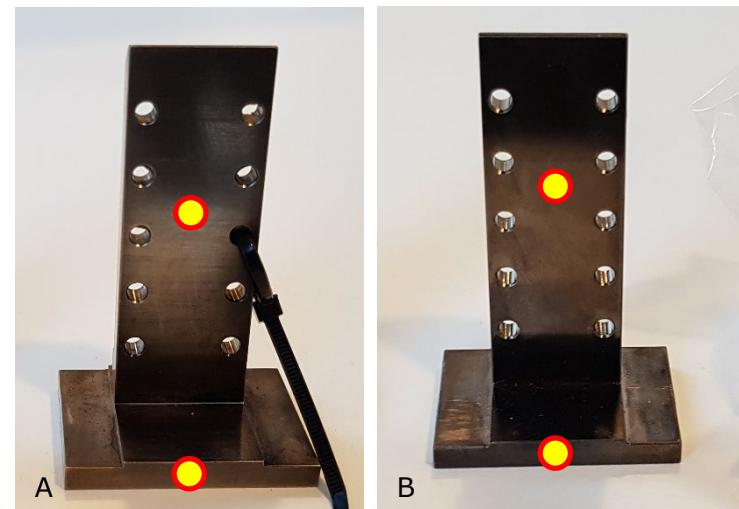
ENP use cases 1

Quality check by supplier



Start

- Same base material but different coating suppliers (A and B)
- Target coating DNC471 (high ENP, Pb and Cd free) 20 μm thickness
- Parameters to be checked for comparison:
 - Thickness, P content, impurities, homogeneity
- P is invisible for W target excitation (X-ray tubes) but can be determined e.g. with Rh target excitation
- P content can be set for the analysis based on beforehand knowledge



ENP use cases 1

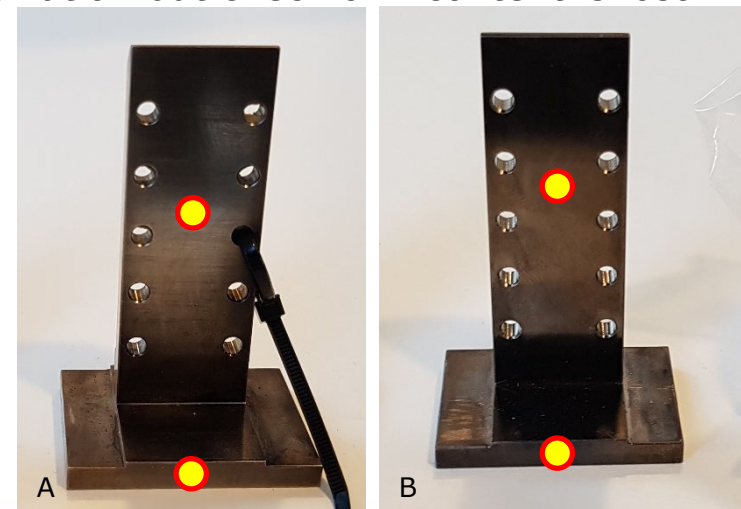
Quality check by supplier



Result

- Coating from supplier A is significant thinner than 20 μm
- Coating from supplier B has Sb impurities – effect on coating properties unknown
- Both are Pb and Cd free
- Both have same results at both points – homogeneity ok
- P content differs and is less than 10 % for both
- Deviation of P determination influences deviation of coating thickness
- Setting P to a certain value decreases thickness deviation but check of P content is lost

1.5 mm, 30 s	Supplier A	Supplier B
Thickness NiP	(8.56 +/- 0.10) μm	(20.46 +/- 0.26) μm
P content	(6.61 +/- 0.28) %	(7.87 +/- 0.29) %
Sb content	n.a.	(1.71 +/- 0.05) %
Thickness (P set to 8.22 %)	(6.99 +/- 0.01) μm	(20.44 +/- 0.01) μm



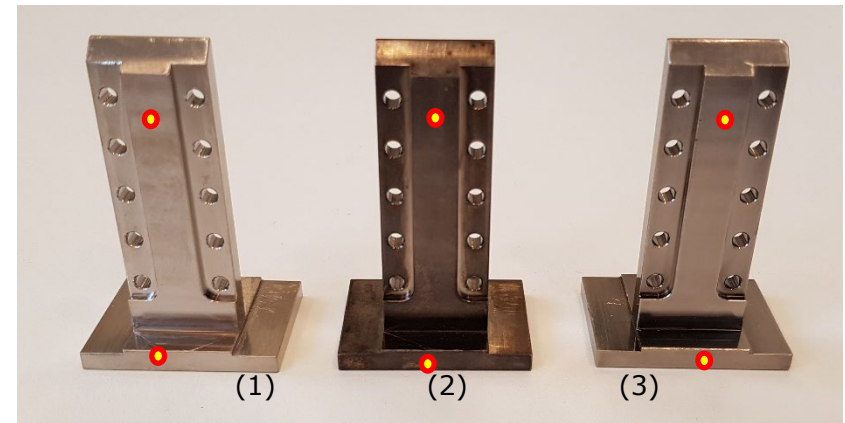
ENP use cases 2

Quality check of cleaning process



Start

- One batch of supplier B (use case 1)
- Target coating DNC471 (high ENP, Pb and Cd free) 20 μm thickness
- Cleaning process:
 - Incoming material (1) \rightarrow cleaning with acids and base (2) \rightarrow polishing with paste (3)
- Parameters to be checked for changes:
 - Thickness, P content, impurities, homogeneity



ENP use cases 2

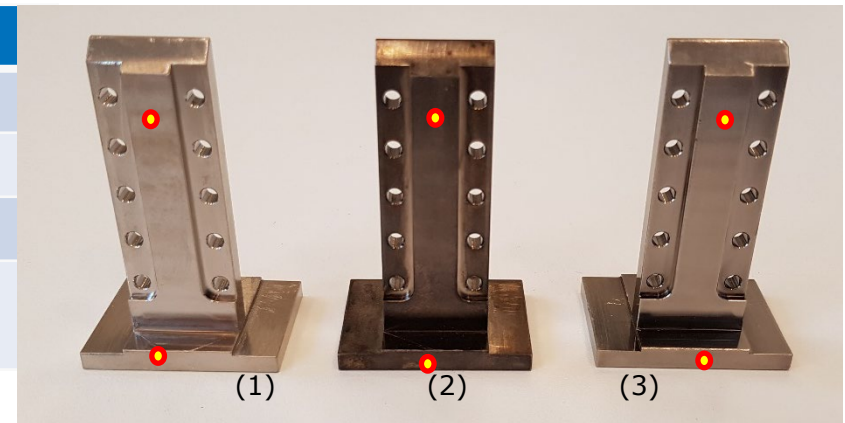
Quality check of cleaning process



Result

- Homogeneity ok
- Polish step does increase P and also the total thickness
 - Surface contamination (organics or oxides invisible for XRF) can reduce P signal, polish step eliminates this → more P signal and therefore higher content.
 - Total thickness depends on density → depends on P content
 - Increased P calculation based on detected intensity reduces the calculated density → increase of calculated thickness
- Only minor changes within supplier tolerances

1.5 mm, 30 s	(1)	(2)	(3)
Thickness NiP	20.42 μm	20.46 μm	21.06 μm
P content	8.06 %	7.87 %	8.65 %
Sb content	1.24 %	1.71 %	1.60 %
Thickness (P set to 8.22 %)	20.28 μm	20.44 μm	20.38 μm



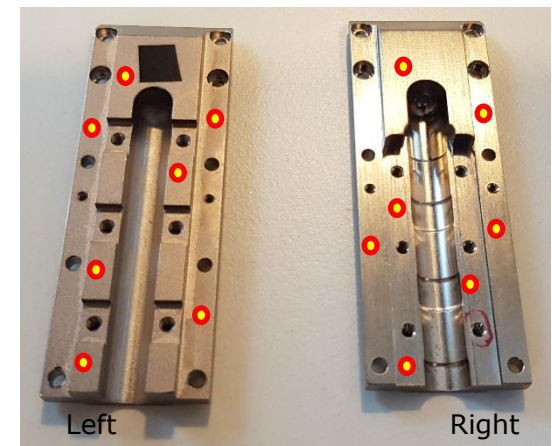
ENP use cases 3

Quality check of properties



Start

- Different parts and coatings from supplier A
- Target coating DNC471 (high ENP, Pb and Cd free) unknown thickness
- Surface appearance difference:
 - Left: dull, rough
 - Right: shiny, smooth
- Parameters to be checked for changes:
 - Thickness, P content, impurities, homogeneity



ENP use cases 3

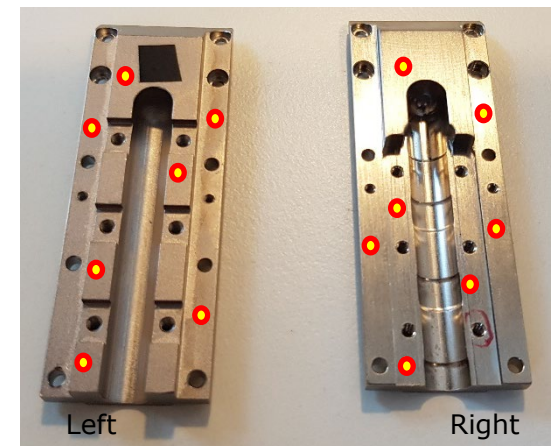
Quality check of properties



Result

- Homogeneity ok
- Surface appearance difference caused by:
 - Thicker coating, less P and Sb content (left to right)
- Choosing a wrong P content as set value leads to wrong thickness values

1.5 mm, 30 s	Left (dull)	Right (shiny)
Thickness NiP	9.63 μm	13.01 μm
P content	9.48 %	6.12 %
Sb content	1.63 %	n.a.
Thickness (P set to 8.22 %)	9.13 μm	13.92 μm





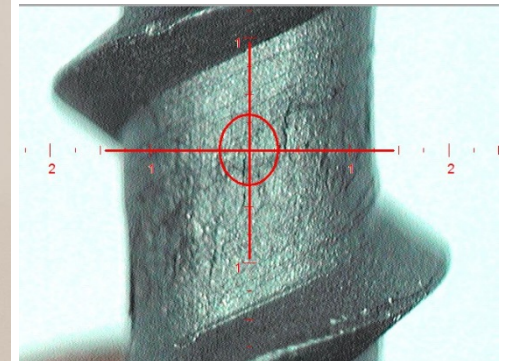
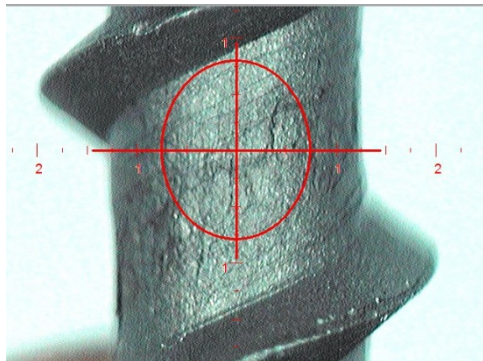
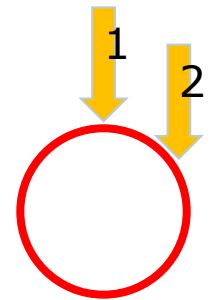
Other Light Element Analysis

Light element coatings

Phosphatized Screws



- Samples are black and dull screws
- Unknown coating structure
- Elements present for sure: P, Zn, Fe
- Correct spot size and position must be chosen because of side effects for detection (here: 0.6 mm spot in position 1)
- Assumed coating structure: P on Zn on Fe (P/Zn/Fe or P_Zn_Fe)
- Larger measurement times recommended (> 120 s)
- Calibration similar to ENP possible
- Result: P layer with 0.44 μm ; Zn layer with 0.35 μm ; Fe base without detectable traces

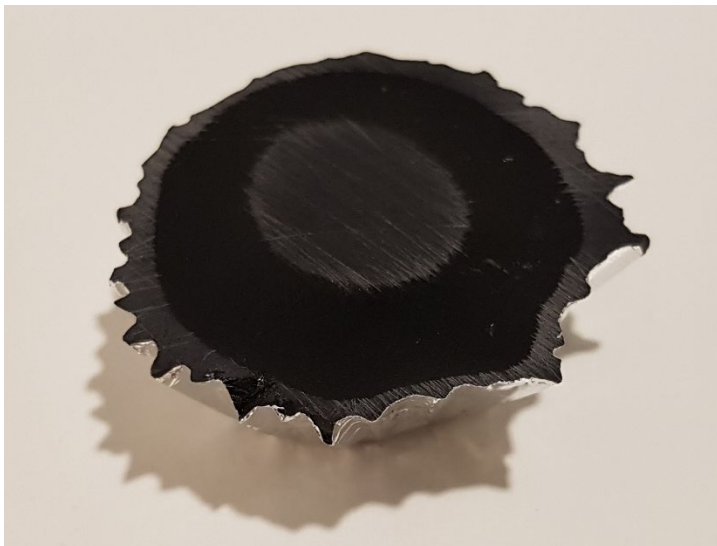


Light element bulks

Resins check



- Sample is a raw material made of resin
- Detectable elements: S
- Largest spot and larger measurement times recommended (> 120 s)
- Calibration similar to ENP possible
- Result: 0.13 % S in light matrix (invisible for XRF)





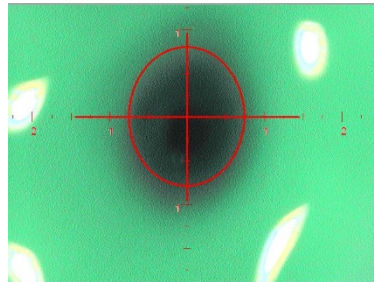
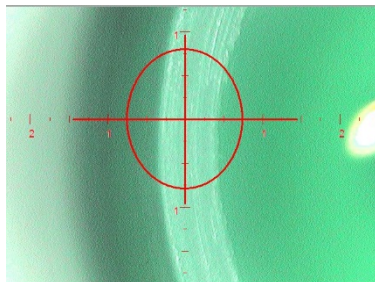
Bath Analysis (Light Matrices)

Bath Analysis

Ni and Au bath solution



- Sample is liquid, solution containing Ni and Au
- Detected elements: Ni, Au, K, Ti
- XRF suitable sample holder needed:
 - Surface must be large enough (micro-XRF, 1.5 mm spot, surface diameter 10 mm)
 - Holder material must be invisible (for XRF, e.g. polymers)
 - Sample volume must be deep enough (> 20 mm)
- Largest spot and larger measurement times recommended (> 60 s)
- Comparison of different sample holder types, focus on holder
- Calibration similar to ENP possible
- Result: Ni 2.0 g/l; Au 3.2 g/l; K 64.9 g/l; Ti 0.3 g/l for both sample holder



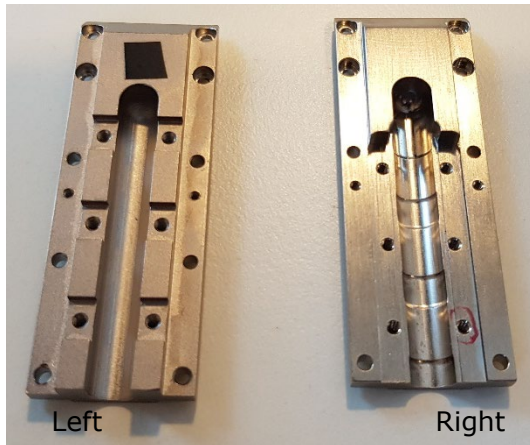


Measurement Examples

Live Measurements Examples



- Samples: ENP curved piece, phosphatized screw and bath solution
- Method selection, measurement series and stage program
- Method creation and calibration process





Q & A Time



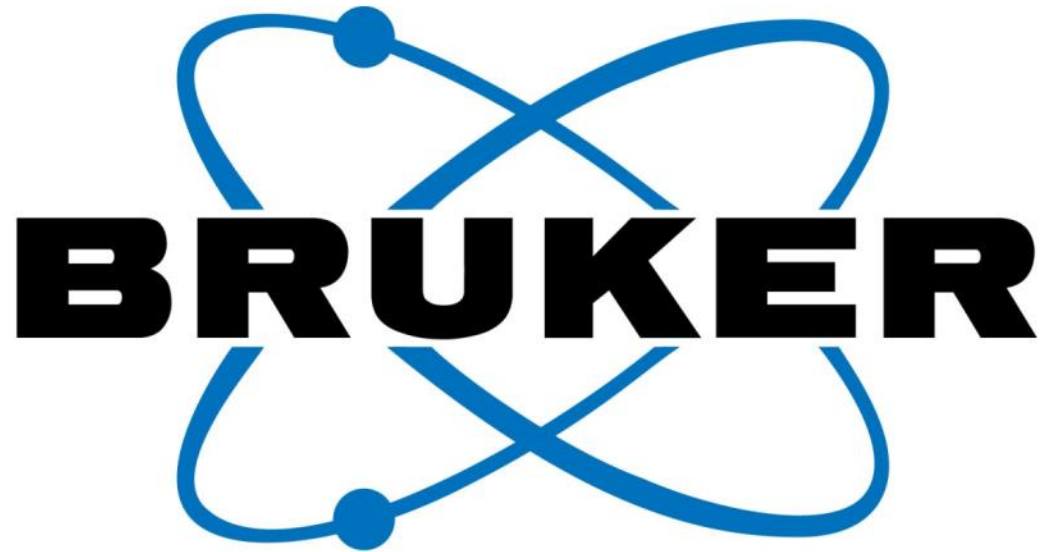
For more information, please contact us:

robert.erler@bruker.com

falk.reinhardt@bruker.com

info.bna@bruker.com

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