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

Bruker Nano Analytics, Berlin, Germany
Webinar, December 05, 2018

Presenters / Moderators

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Expanded Coating Analysis Performance
Webinar Outline

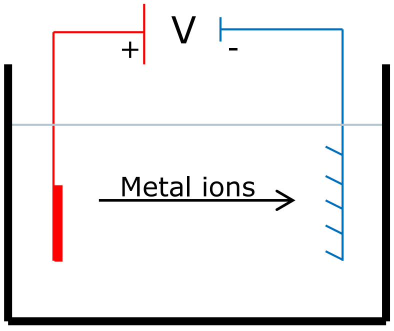
- Overview of ENP basics
- XRF Technology with M1 MISTRAL
- ENP use cases (1-3)
- Other light element applications
- Live Measurements
- Questions and Answers

Electroless Ni Plating

What is electroless (chemical) plating?
Short overview

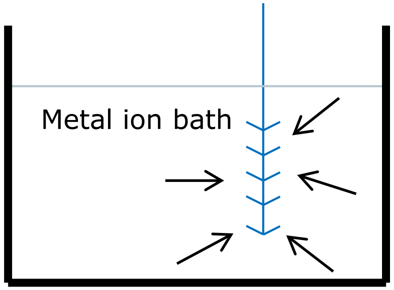
Normal galvanic plating/coating

- 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

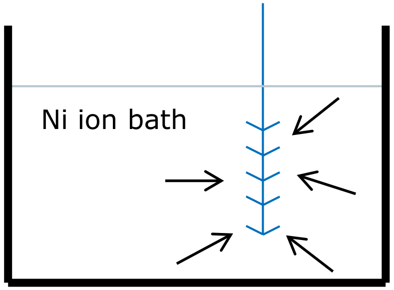
- Sample/base material must not be conductible
- Coating homogeneity increased (autocatalytic)
- No max. limit in principle
- Alternative to Cr-6 coatings
- Wear and corrosion resistance, electrical resistivity, lubricity and hardness increased, ductility decreased
- Growth parameter depends on bath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



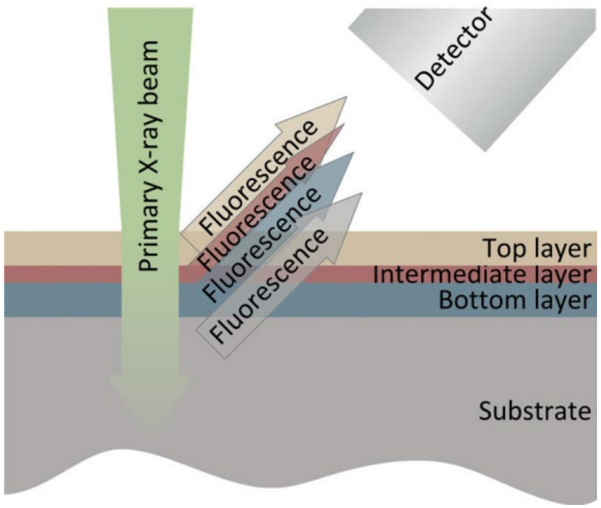
What is electroless Ni plating?
Short overview

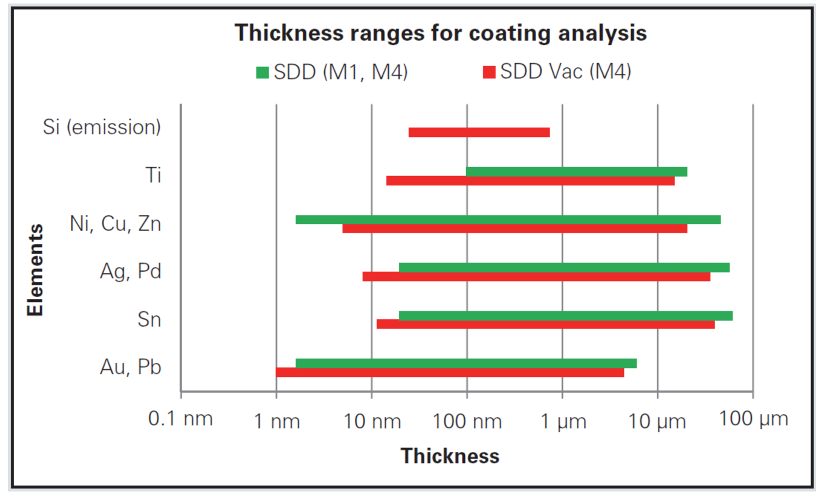
Electroless Nickel (EN) plating/coatings

- 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 = Cu; W; Mo)
- Three levels of P content in the layer:
  - Low-phosphorus ENP (< 4% P)
  - Medium-phosphorus ENP (4% - 10% P)
  - High-phosphorus ENP (10% - 14% P)
- Applications:
  - Automotive, Aerospace, Electronics, Chemical processing, Oil and Gas industry, Others



Why XRF for coating analysis?
Short overview





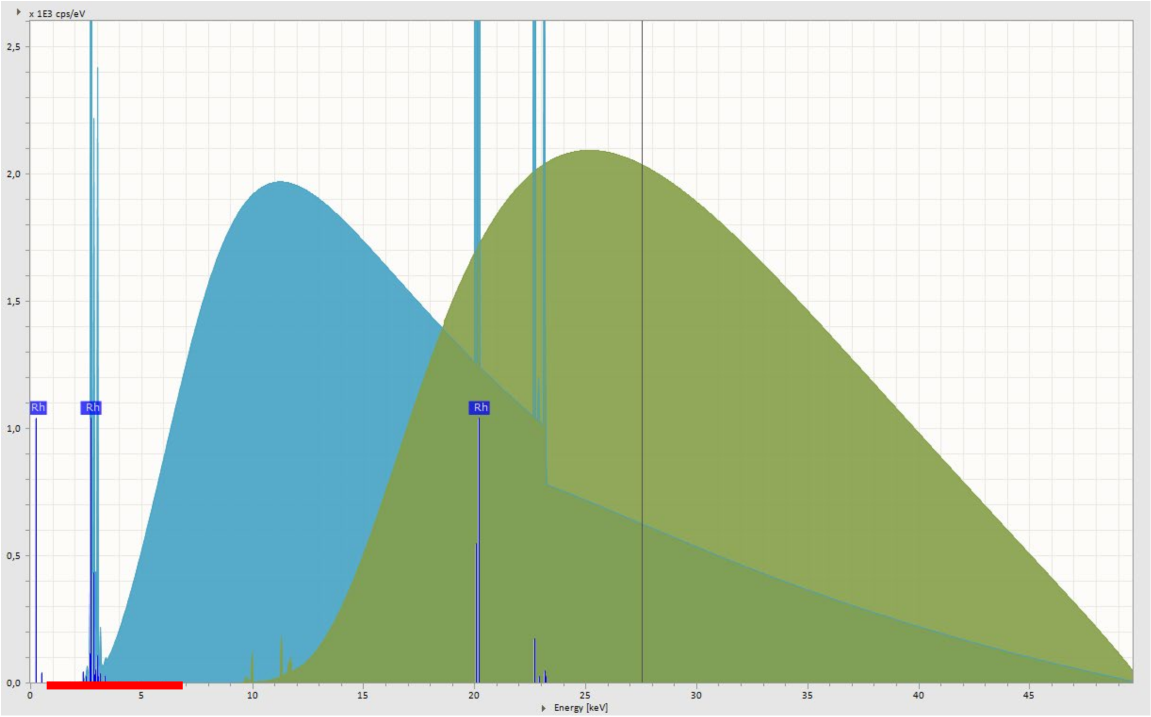
Advantages of XRF

- 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
- Programable 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

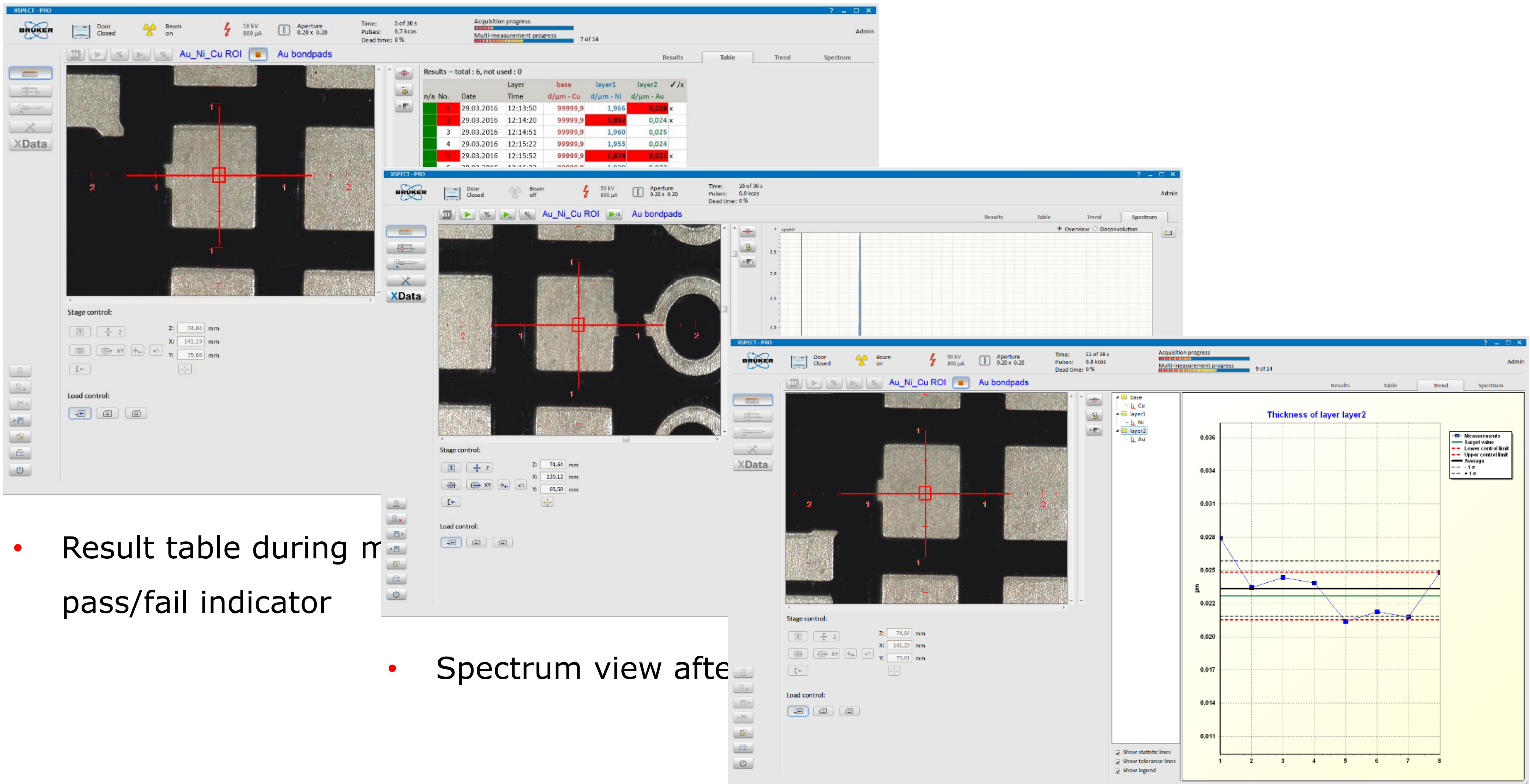


- State-of-the-art XFlash® SDD technology
- Measurement on air
- Programable stage and easy to handle routine analysis software
- **50 W micro-focus tube with W or Rh target**

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

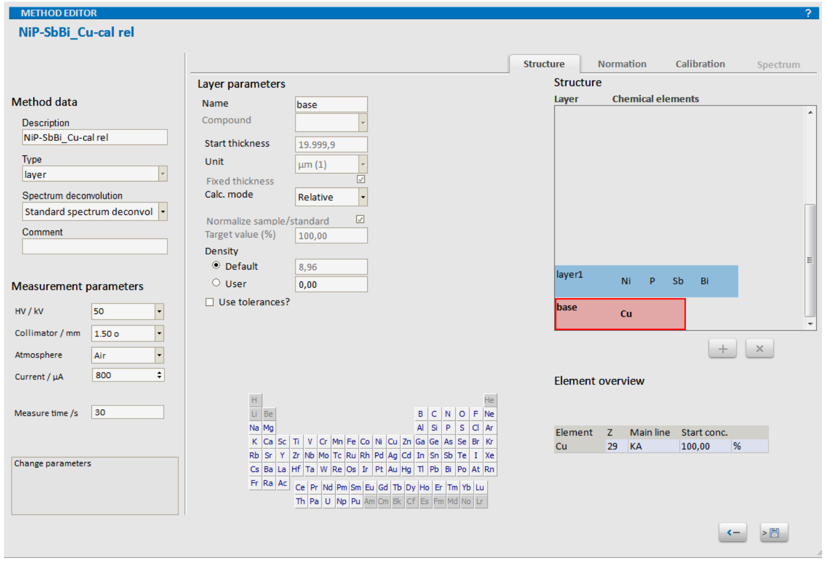


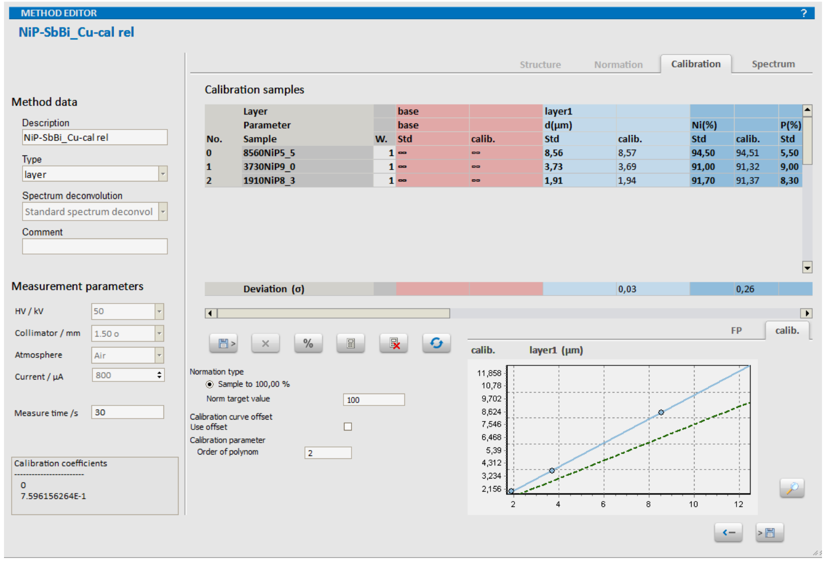
- Result table during m
  pass/fail indicator

- Spectrum view afte

- Trendline diagram during measurement

Micro-XRF for coating analysis
XData Calibration



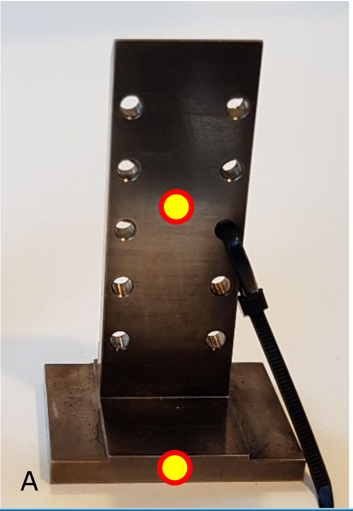


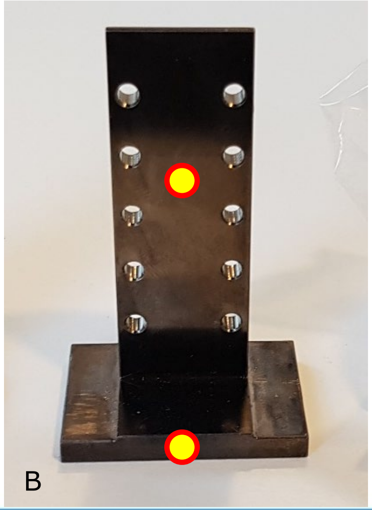
- Method calibration with XData as part of XSpect Pro
- Simple defining the coating structure and linking to pure element intensities
- Simple calibration with different settings after loading suitable and available standards

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



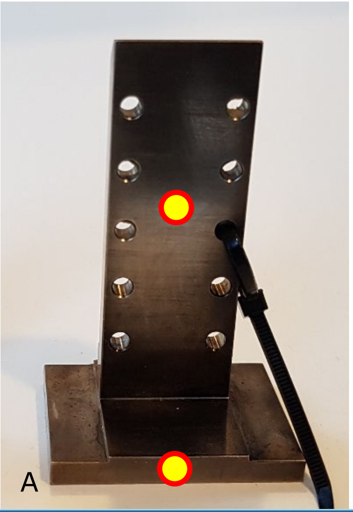


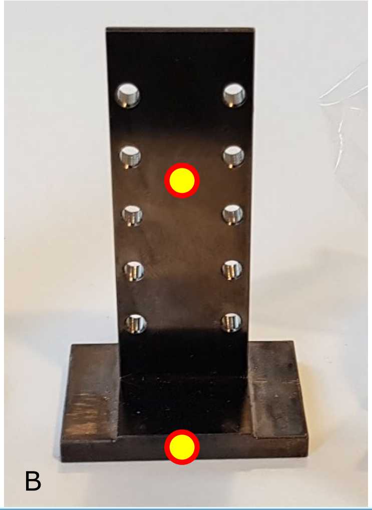
ENP use cases 1
Quality check by supplier

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

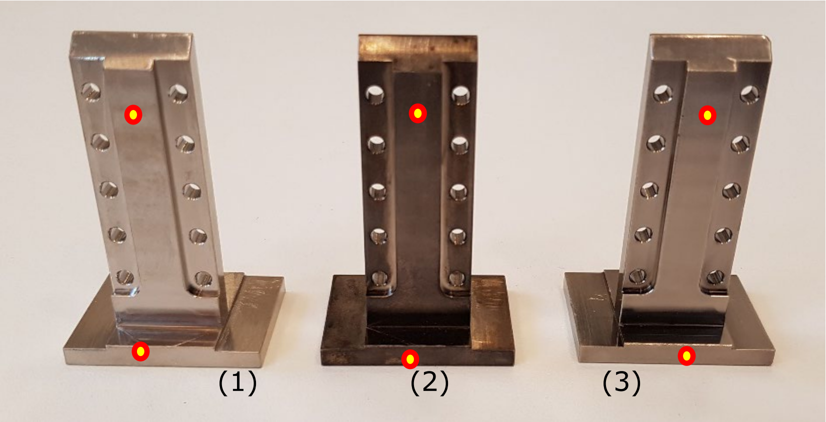




ENP use cases 2
Quality check of cleaning process

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) ➔ cleaning with acids and base (2) ➔ polishing with paste (3)
- Parameters to be checked for changes:
  - Thickness, P content, impurities, homogeneity

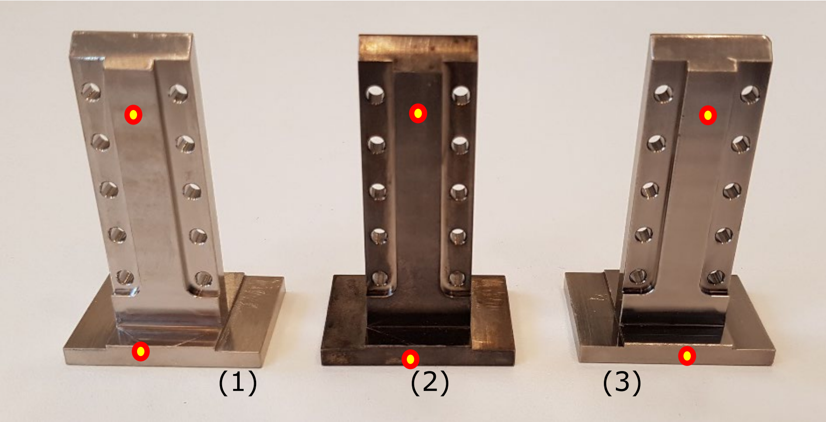


ENP use cases 2
Quality check of cleaning process

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

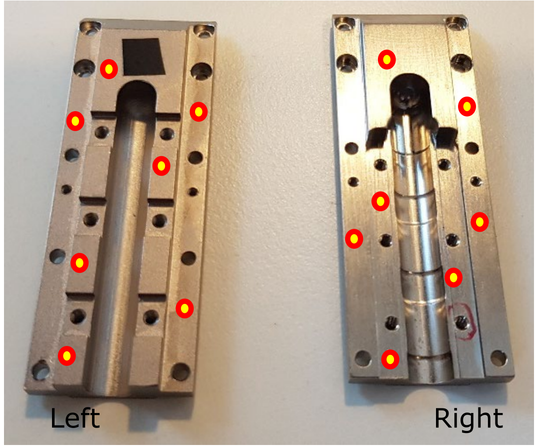
1.5 mm, 30 s	(1)	(2)	(3)
Thickness NiP	**20.42** µm	20.46 µm	**21.06** µm
P content	**8.06** %	7.87 %	**8.65** %
Sb content	1.24 %	1.71 %	1.60 %
Thickness (P set to 8.22 %)	20.28 µm	20.44 µm	20.38 µm



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

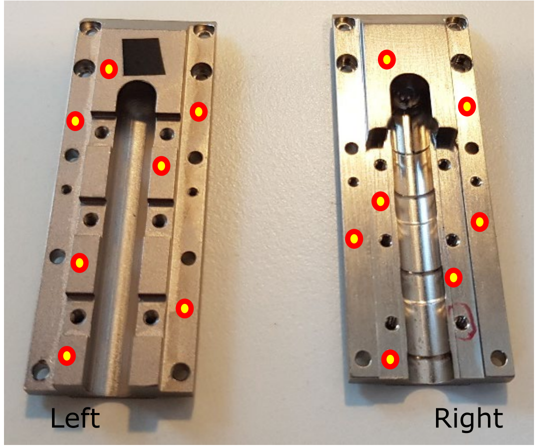


ENP use cases 3
Quality check of properties

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

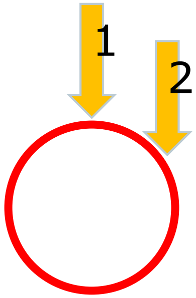
1.5 mm, 30 s	Left (dull)	Right (shiny)
Thickness NiP	9.63 µm	13.01 µm
P content	9.48 %	6.12 %
Sb content	1.63 %	n.a.
Thickness (P set to 8.22 %)	9.13 µm	13.92 µm

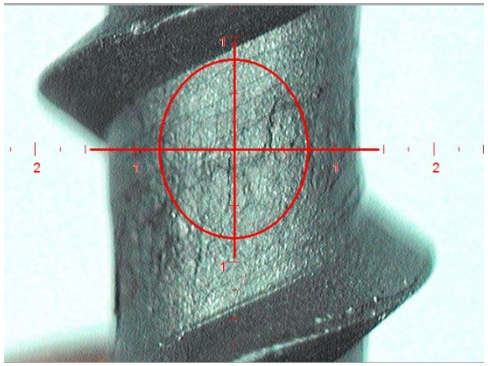


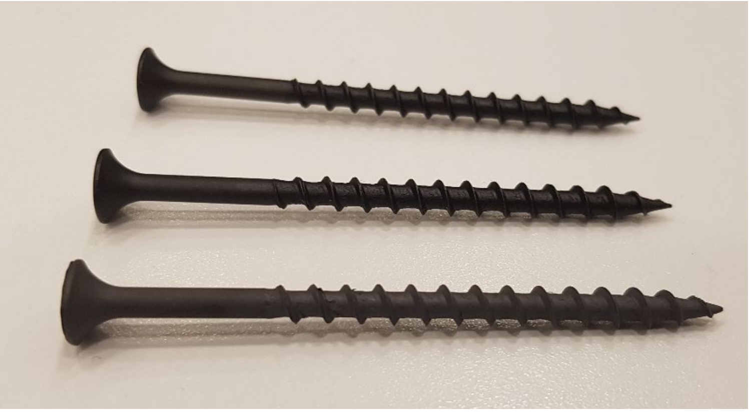
Other Light Element Analysis

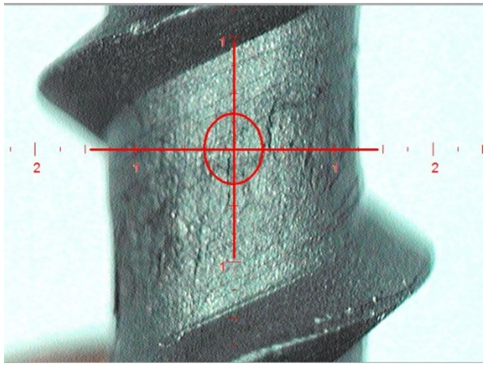
Light element coatings
Phosphatized Screws

- 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









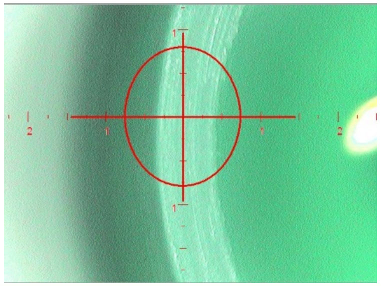
Light element bulks
Resins check

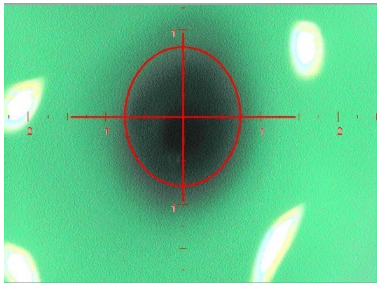
- Sample is a raw material made of resin
- Detectable elements: S
- Largest spot and larger measurement times recommended (> 120 s)
- Calibration similar to ENP possible
- Result: 0.13 % S in light matrix (invisible for XRF)

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

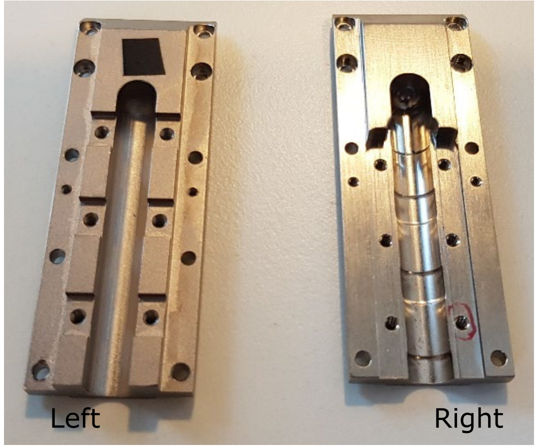


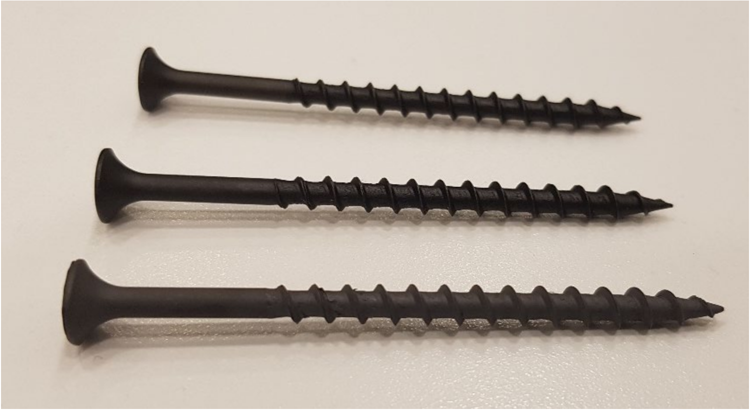


Measurement Examples

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

More Information

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