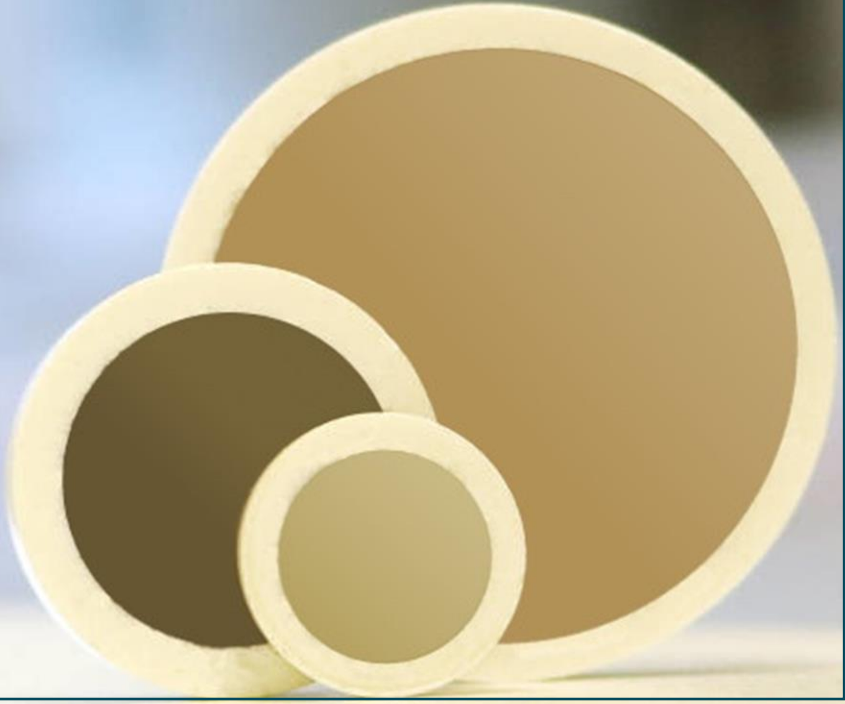
µ standards

precision.accuracy.trust.

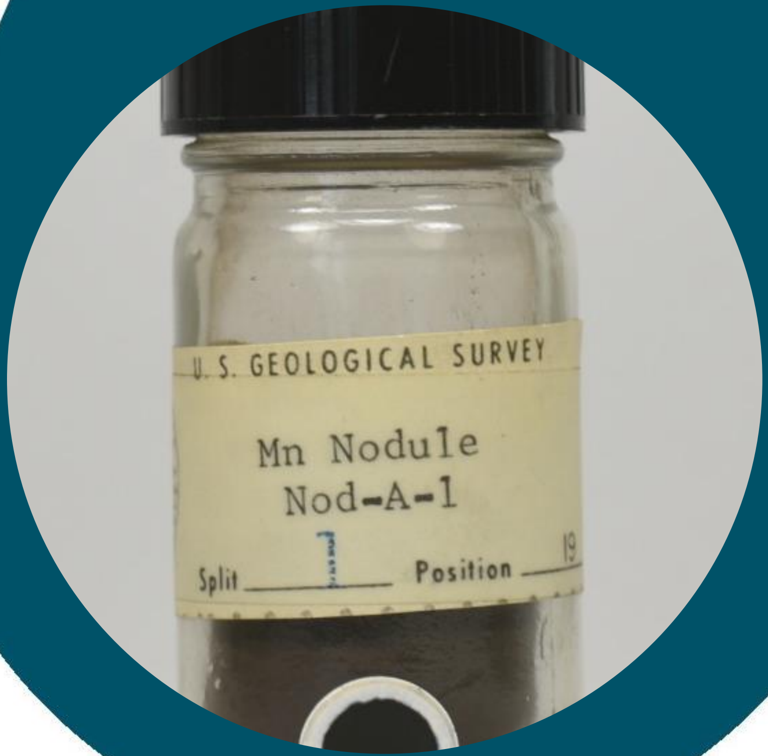
Homogeneity Test on a Candidate Microanalytical Mn-Nodule Reference Material using Micro-XRF

Simon Nordstad, Roald Tagle, Falk Reinhardt



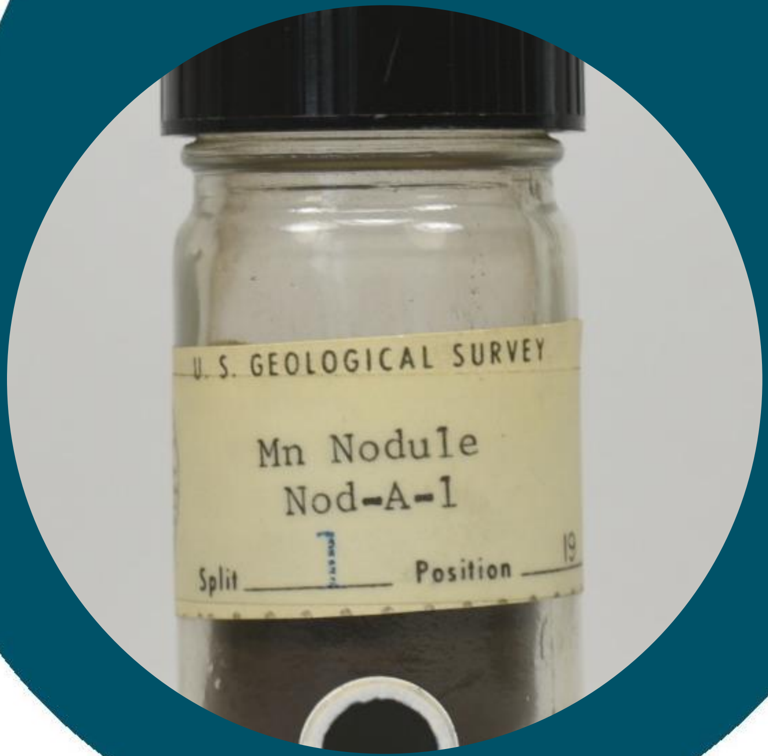
Introduction

- Mn-Nodules have been discussed as a possible resource for metals and have also sparked innovation with respect to sea floor mining
- Scientifically they are used as geochemical archives for ocean chemistry
- This project aims as at making it possible to turn a pre-existing reference material (RM) for bulk analysis into a RM usable for spatially resolved microanalysis



Introduction

- Matrix-matched microanalytical Reference Materials (RM) for microbeam techniques are scarse
- Natural materials are inherently heterogenous at the µm-scale. If not, the naturally homogenous materials are rare.
- Particle-size reduction to the nm-scale(d_{50} 200 nm, d_{90} 500 nm) rehomogenises natural heterogeneities and enables application for microanalysis



Sample Location

- **NOD-A1**: 31° 02‘N, 72° 22‘W; 788 m water depth
- **NOD-P1**: 14° 50‘N, 124° 28‘ W; 4300m water depth

Procedure

- Milling NOD-A1 & NOD-P1 powder (USGS) in a high-power planetary ball mill

- 10 binder-free Pellets of each respective material were made

- One pellet of each original powder for comparsion

- Subsequent µXRF Analysis – Mapping and Spots

Micro-XRF Instrumentation

Bruker M4 Tornado

- **30 W micro-focus Rh-tube** with polycapillary lens for excitation spot sizes < 20 µm for Mo-Ka)

- **Optional 40 W micro-focus W-tube** with collimator for exciation of „heavy“ elements embedded in lighter matrices

- **Two Silicon Drift Detectors (SDD)** with 60 mm2 active area. Each having an energy resolution of < 145 eV (for Mn-Ka at 130 kcps throughput

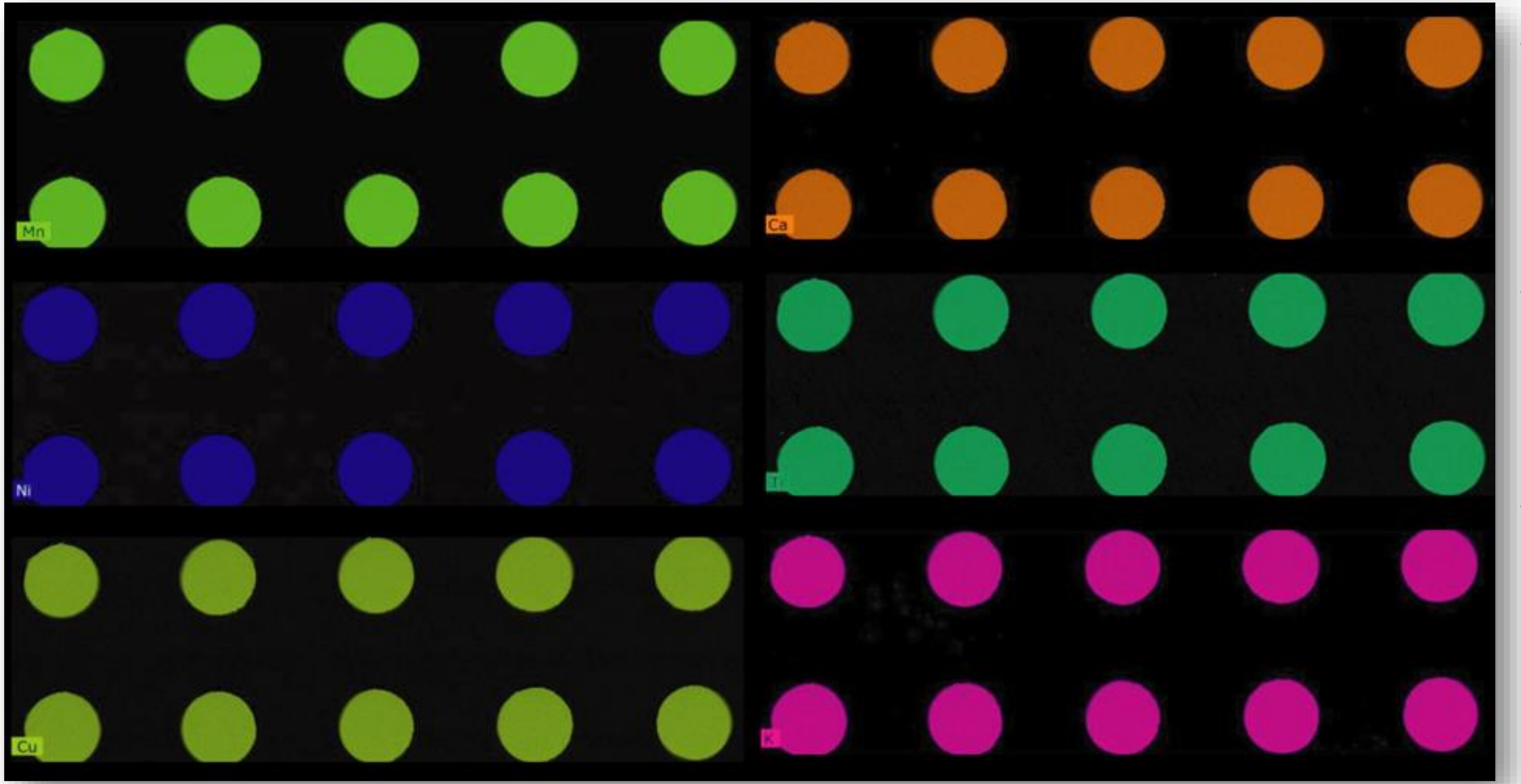
- **Sealed sample chamber** with adjustable pressure between atmospheric and 2 mbar. Elemental detection down to Na

Measurement Setup

Acquisition parameters	
Acceleration voltage	50 kV
Anode current	600 µA
Anode material	Rh
Spot size	20 µm
Chamber pressure	20.1 mbar
Number of Silicon Drift Detectors	2
Max. pulse throughput	275000 cps
Stage speed	833 µm/s
Pixel time	60 ms/pixel
Frame count	1

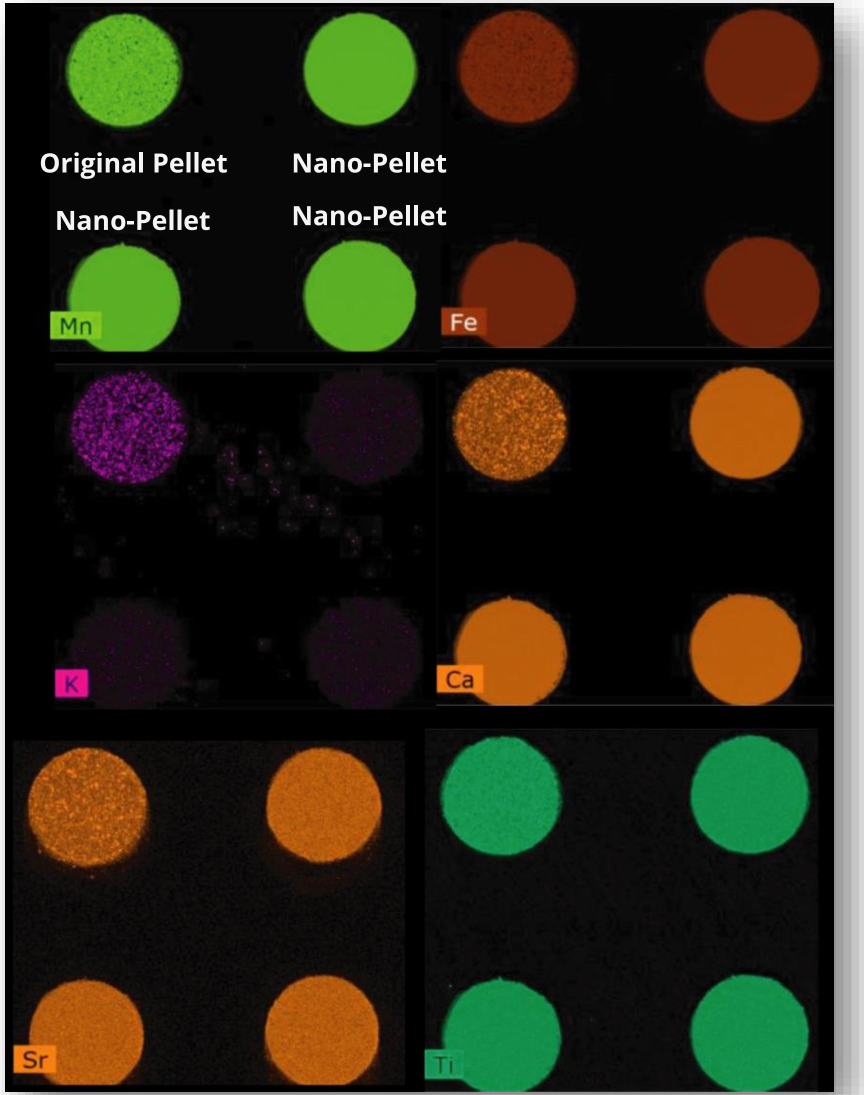
Measurement Setup inside M4 Tornado similar.
Pellets inside CNC-milled aluminium Mount

Mapping – Visualised homogeneity



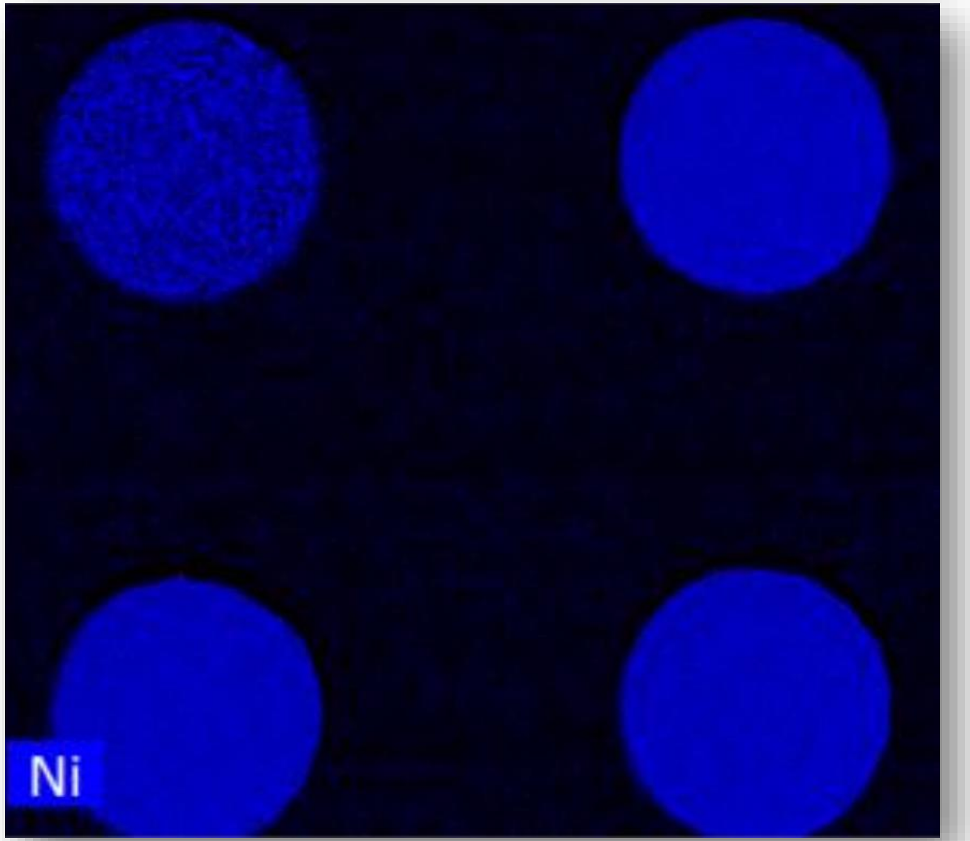
- Colour-coded distribution of a selection of elements in NOD-A1-NP (Nano-Pellet)
- Even colours represent even distribution – good homogeneity
- Pellets have a Ø of approx. 10 mm

Mapping – Visualised homogeneity



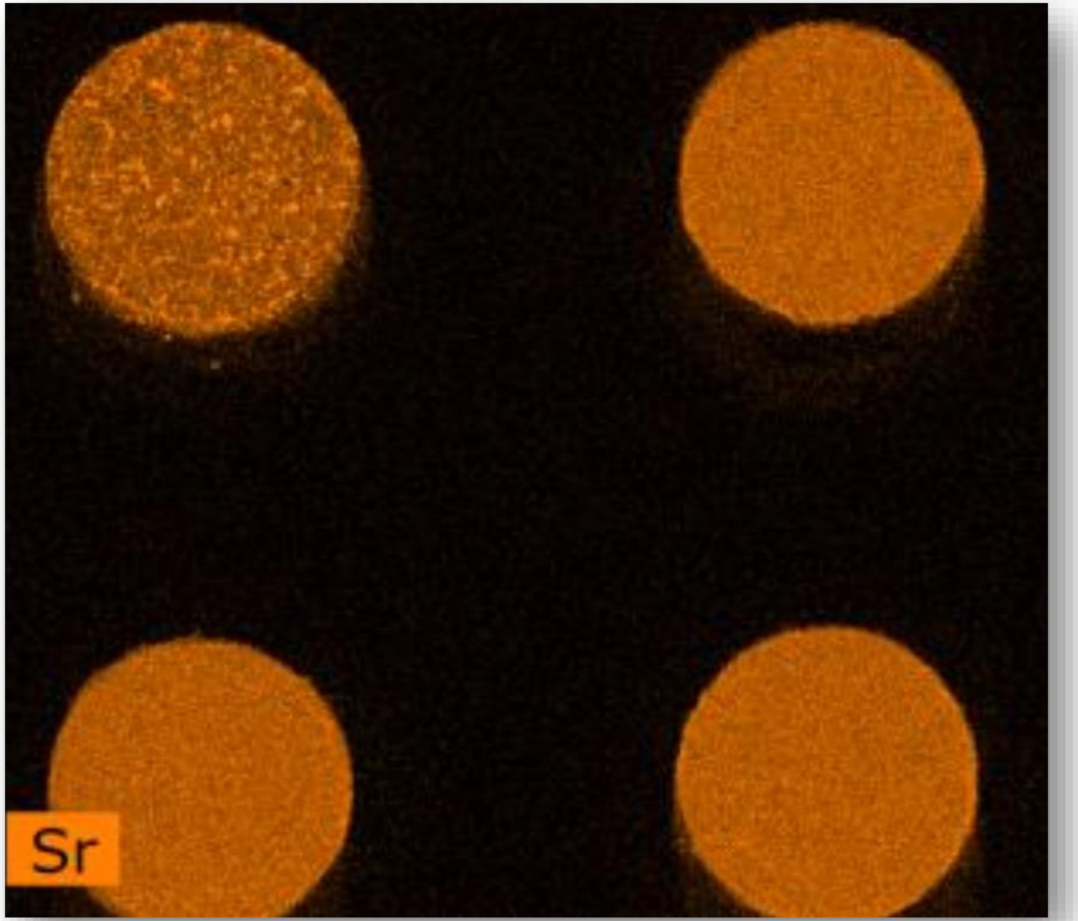
- Colour-coded distribution of a selection of elements in NOD-A1-NP (Nano-Pellet)
- Even colours represent even distribution – good homogeneity
- Top left pellet shows the elemental distribution in the original powder.
- The remaining three pellets represent the corresponding Nano-Pellets.
  - Nano-Pellets clearly exhibit more even elemental distribution – better homogeneity
  - Even variability of major elements Fe & Mn is evident in original pellet

Mapping – Visualised homogeneity



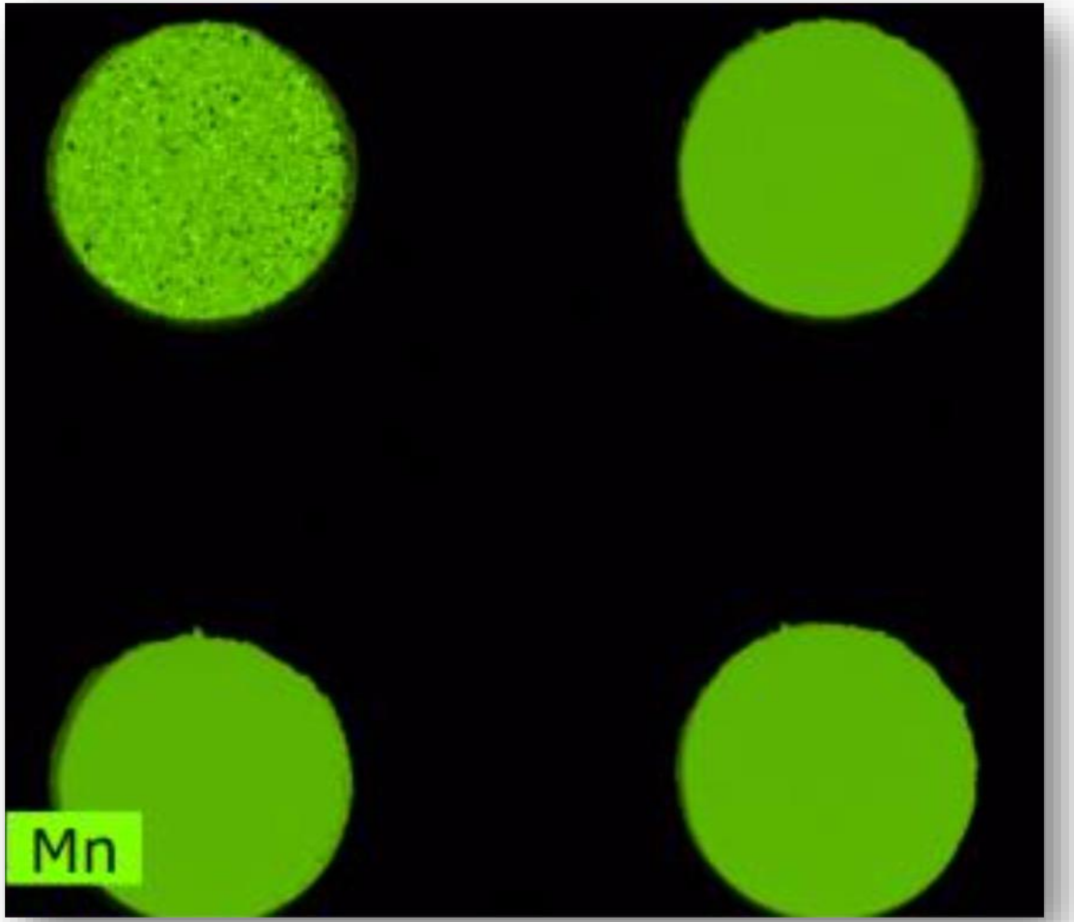
- Colour-coded distribution of **Nickel** in NOD-A1-NP (Nano-Pellets) & Original Pellet
- Even colours represent even distribution – good homogeneity
- Close-up view of pellet comparison

Mapping – Visualised homogeneity



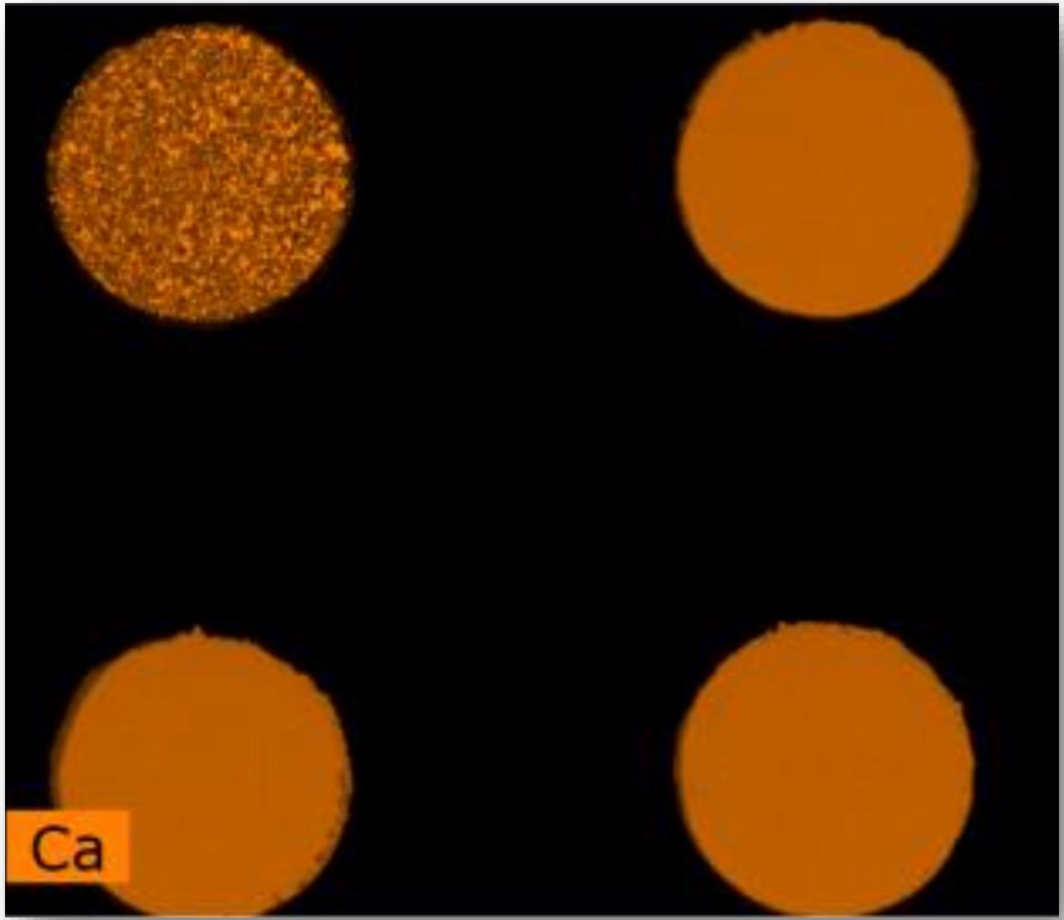
- Colour-coded distribution of **Strontium** in NOD-A1-NP (Nano-Pellets) & Original Pellet
- Even colours represent even distribution – good homogeneity
- Close-up view of pellet comparison

Mapping – Visualised homogeneity



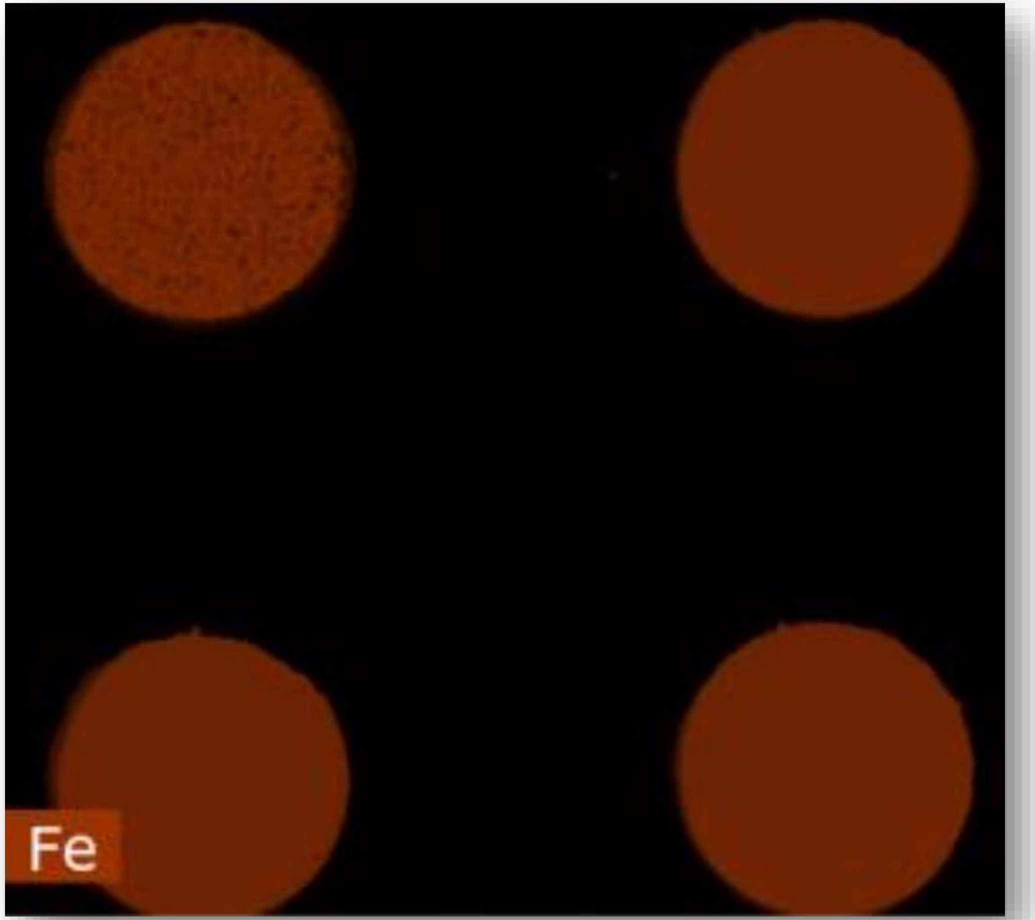
- Colour-coded distribution of **Manganese** in NOD-A1-NP (Nano-Pellets) & Original Pellet
- Even colours represent even distribution – good homogeneity
- Close-up view of pellet comparison

Mapping – Visualised homogeneity



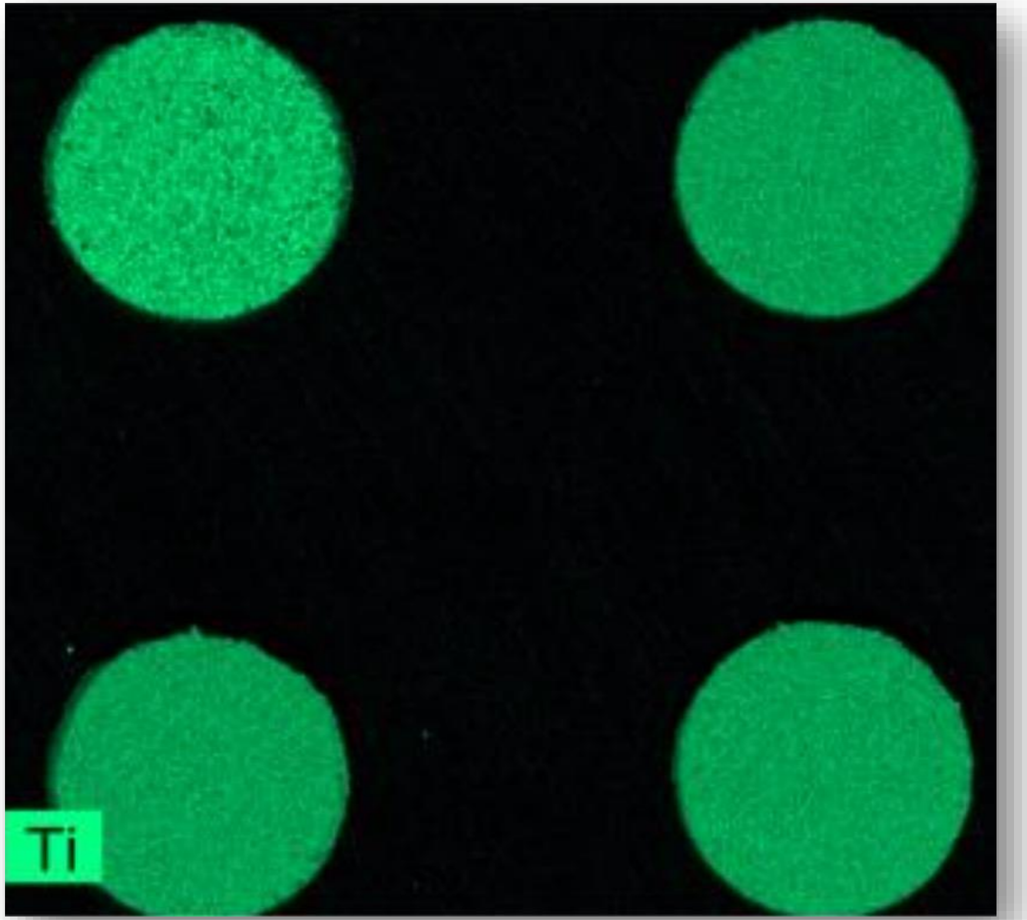
- Colour-coded distribution of **Calcium** in NOD-A1-NP (Nano-Pellets) & Original Pellet
- Even colours represent even distribution – good homogeneity
- Close-up view of pellet comparison

Mapping – Visualised homogeneity



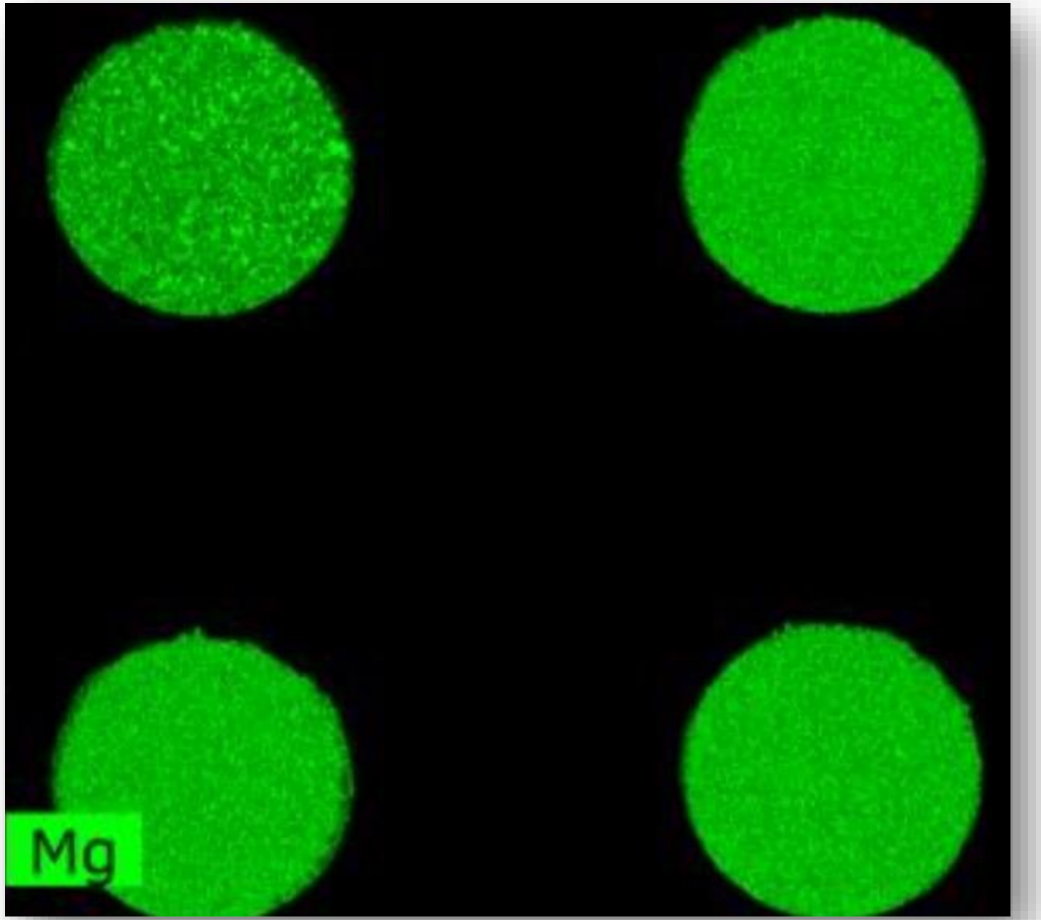
- Colour-coded distribution of **Iron** in NOD-A1-NP (Nano-Pellets) & Original Pellet
- Even colours represent even distribution – good homogeneity
- Close-up view of pellet comparison

Mapping – Visualised homogeneity



- Colour-coded distribution of **Titanium** in NOD-A1-NP (Nano-Pellets) & Original Pellet
- Even colours represent even distribution – good homogeneity
- Close-up view of pellet comparison

Mapping – Visualised homogeneity



- Colour-coded distribution of **Magnesium** in NOD-A1-NP (Nano-Pellets) & Original Pellet
- Even colours represent even distribution – good homogeneity
- Close-up view of pellet comparison

Within – and between unit Homogeneity…

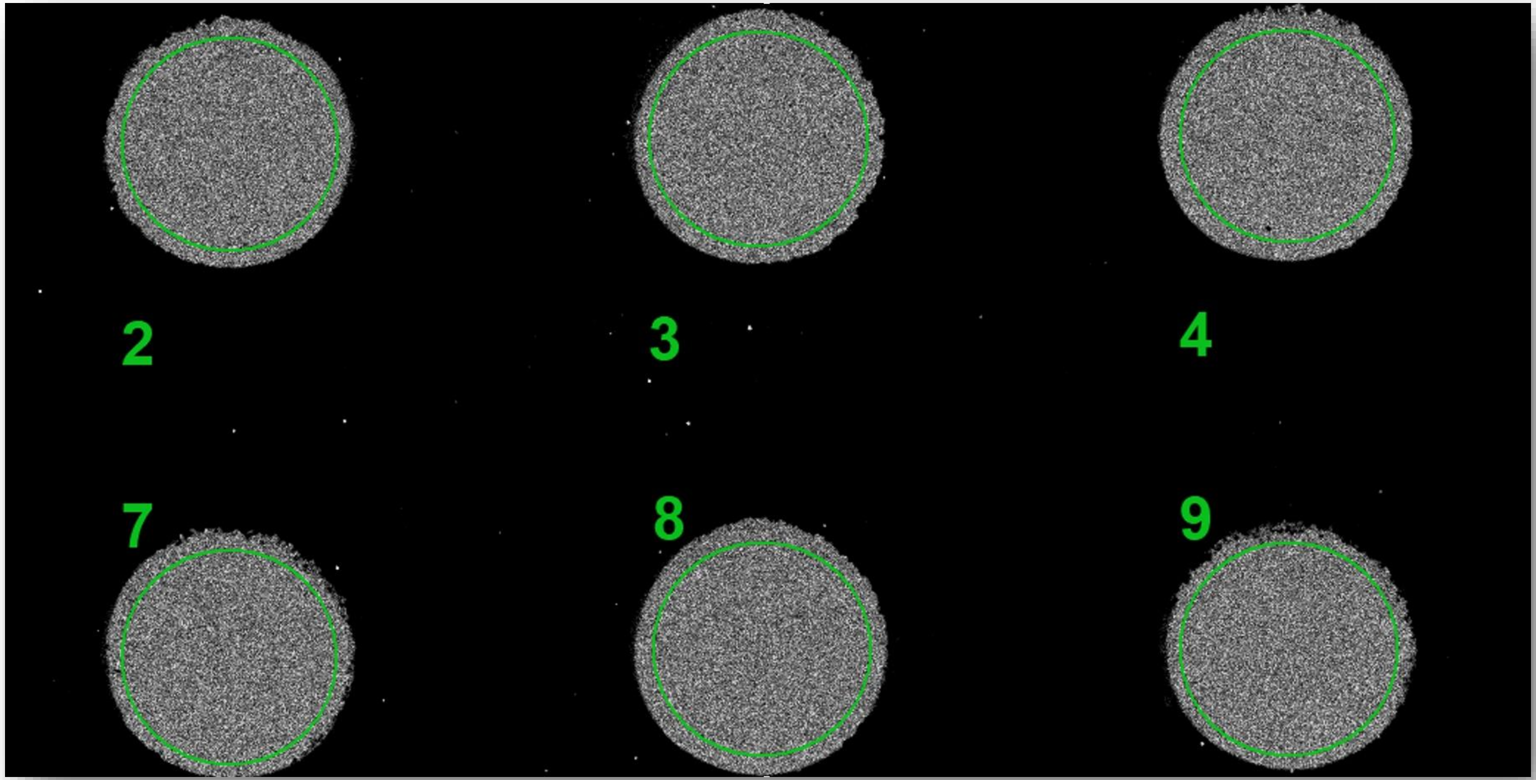
- … is a prerequisite of any reference material

- Within-unit homogeneity was investigated by meausuring 50 spots @ 20 µm on Nano-Pellets and Original Pellet.

- Between-unit homogeneity was investigated by cutting „objects" using Bruker M4 Tornado's ESPRIT-Software

  - ➢ Objects in this case are circular cut-outs of approx. 7 mm diamter of the pellet averaging all data-points within (image on next slide)

Within –and between unit Homogeneity



- Software view of so-called objects
- The average counts per second (cps) for each element within each object is compared between 10 Nano-Pellets

Between-unit homogeneity

Element	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Mn	Fe	Co	Ni	Cu	Zn
RSD-%	1.71	1.86	1.60	1.73	1.85	2.10	1.54	1.59	1.60	1.54	1.54	1.52	1.54	1.52	1.43

- Table above shows relative standard deviations (RSD-%) between objects of NOD-A1-NP for a variety of elements
- On average the RSD-% is ~1.5
- Chlorine exhibits slightly higher RSD-% due to Rh-L (anode material) signal overlap not compositional variation of the sample
- Due to Coronavirus lockdown, data for NOD-P1-NP was no longer accessible in time for this conference

Within-unit homogeneity

Sample	Mg	Al	Si	P	S	K	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Ba
NOD-A1- Original	5.77	6.18	24.5	16.4	6.97	16.4	37.1	13.8	14.0	13.9	13.9	22.4	13.5	14.8
NOD-A1-NP	3.01	1.92	1.74	1.60	4.88	1.08	0.43	1.16	1.16	0.29	0.43	1.05	1.80	1.68
NOD-P1-Original	5.73	6.84	6.61	58.9	5.95	4.95	33.2	10.5	6.71	11.1	8.95	8.96	16.1	7.32
NOD-P1-NP	1.79	2.10	1.19	3.73	3.78	1.06	0.77	1.31	0.35	0.38	0.57	0.63	1.42	1.63

- Table above shows relative standard deviations (RSD-%) between 50 randomly distributed spot measurements on Original and Nano-Pellet @ 20 µm

- Evidently, RSD-% are significantly lower in Nano-Pellets compared to Original Pellet - sulfur exhibits the least significant degree of RSD% reduction

- Most significant differences can be observed for **Ca, Cu, P & Si**

Within-unit homogeneity

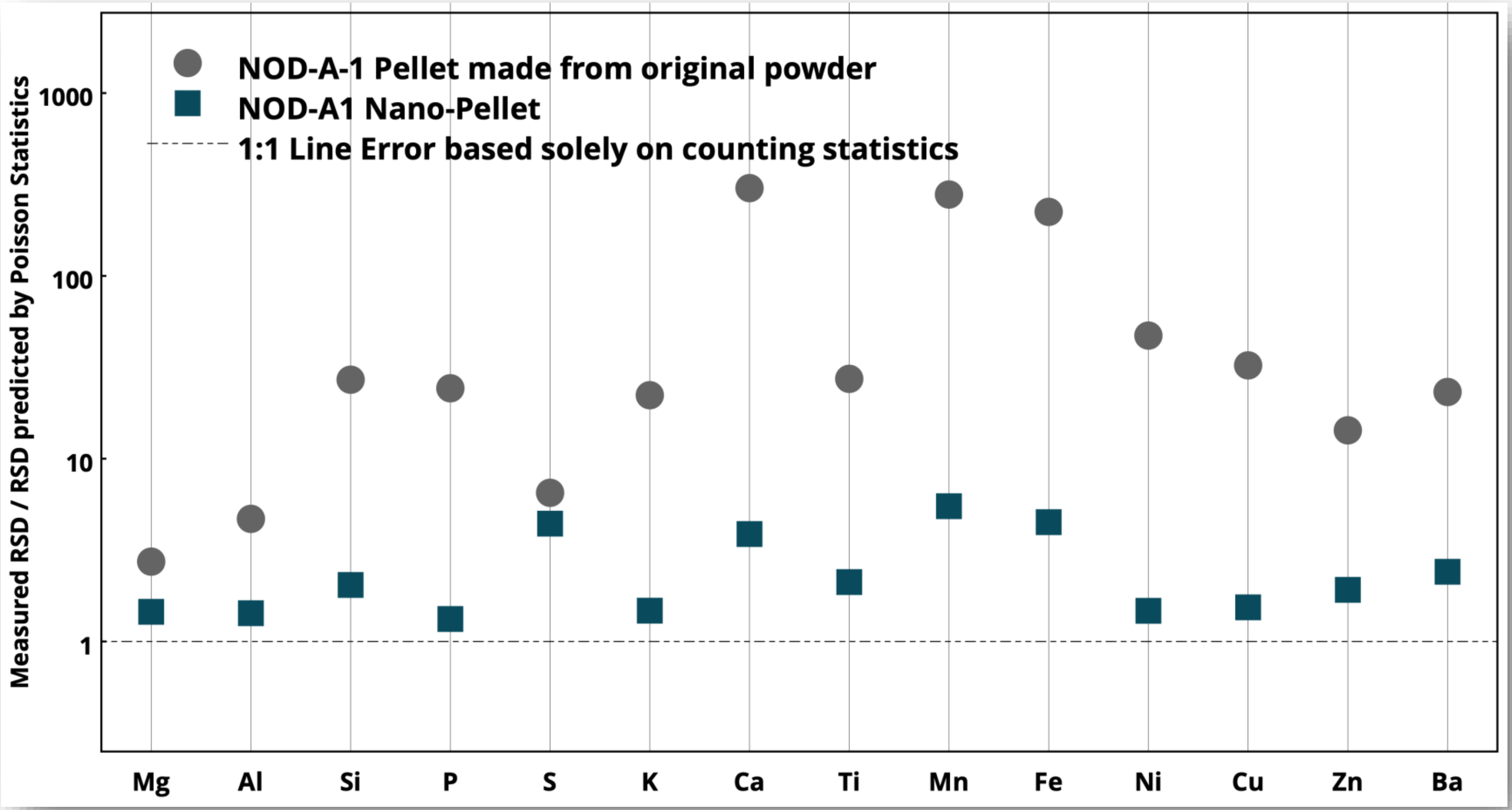
- The RSD-% from the table on the previous slide are calculated based on variations of counts per second (CPS) from the detector

- Detector CPS can be described by Poisson Statistics
  - Therefore a standard deviation for any given amount of CPS can be mathematically estimated (eq. 1)

$$SD_{Poisson} = \sqrt{Average\ CPS_{50\ measurements}} \qquad \text{(eq .1)}$$

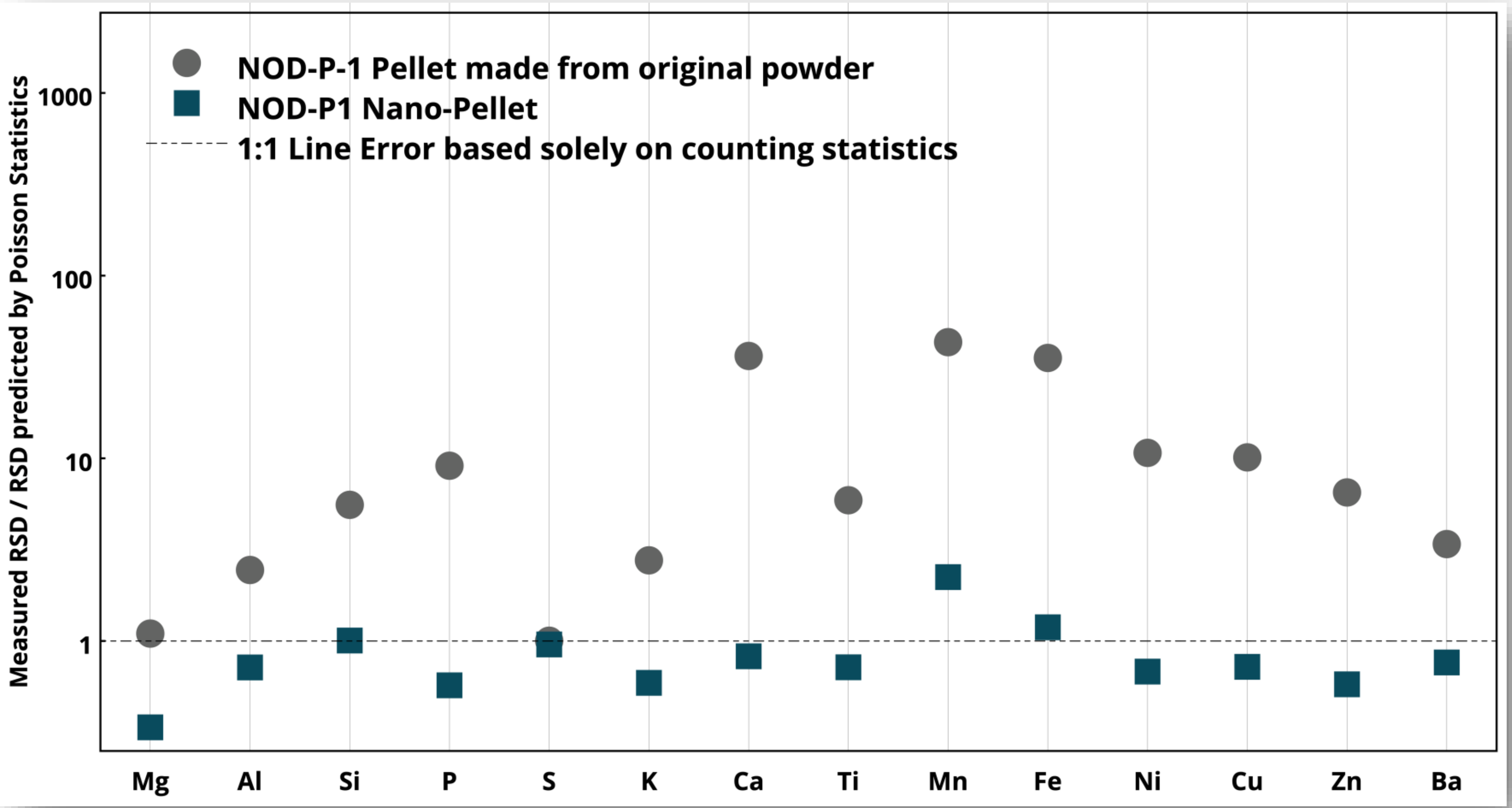
- Using eq. 1 a visual comparison of RSD-% between Original and Nano-Pellet could be created

Within-unit homogeneity – NOD-A1



- Comparison of the ratio between the measured RSD-% and the RSD-% predicted by Poisson statistics
- The ratio of measured / predicted RSD-% is closer to the the 1:1 line for all elements in the Nano-Pellet
- Please note log-scale!

Within-unit homogeneity – NOD-P1



- Comparison of the ratio between the measured RSD-% and the RSD-% predicted by Poisson statistics
- The ratio of measured / predicted RSD-% is closer to or even below the the 1:1 line for all elements in the Nano-Pellet
- Please note log-scale!

Summary

- Particle size reduction has significant effect on within-unit homogeneity.
- Between-unit homogeneity could also be demonstrated – albeit for only one of the materials
- Binder-free powder pellets are stable under vacuum (21 mbar)
- Proof of concept for applicability of Nano-Pellets as reference materials for µXRF achieved
- Disclaimer: This work is not intented to discredit NOD-A1 & NOD-P1 as reference materials. They were never intended to serve as microanalytical RMs.

Acknowledgements

We would like to thank Dr. Roald Tagle and Falk Reinhardt from Bruker Nano GmbH in Berlin for their continued support and effort in providing the data for this study!

If you would like to get more information, don´t hesitate to get in touch!

myStandards GmbH

info@my-standards.com

www.my-standards.com