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Towards an ISO-compliant *modus operandi* for the certification of microanalytical reference materials

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GEO ANALYSIS 2022

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Introduction

- International Organisation for Standardization

- Rule book for reference material production
  - **ISO 17034**

- Manual on how to technically apply the rules
  - **ISO Guide 35**

Introduction

Reference Material (RM)

“Material sufficiently **homogenous** and **stable** with respect to one or more specified properties, which has been established to be fit for its intended use in a measurement process.”

Certified Reference Material (CRM)

“Reference material **characterized** by a metrologically valid procedure for one or more specified properties accompanied by a reference material **certificate** that provides the value of the specified property, its associated **uncertainty,** and a statement of **metrological traceability**”

Metrological Traceability: Property of a measurement result which relates to a national or international standard through an unbroken chain of comparisons with stated uncertainties.

Modus operandi

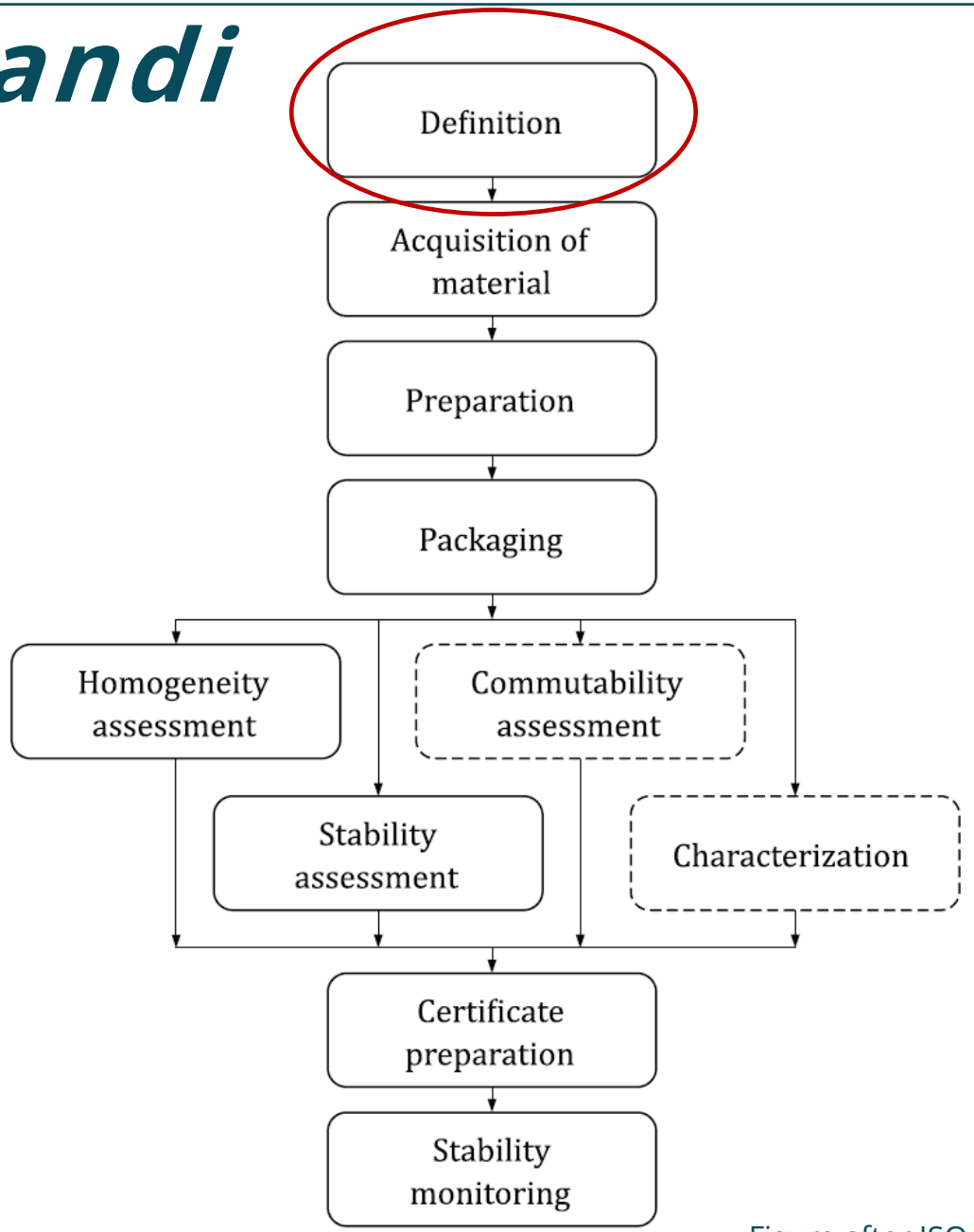


Figure after ISO Guide 35:2017

Definition

- Nano-particulate pressed pellets (Nano-Pellets) made from Apatite crystals[1]

- **Certified values** for major- and trace elements as well as $^{87/86}Sr$ and U/Pb ratios using LA-ICP-MS

- Suitable as a **RM** for techniques such as LIBS & micro-XRF.

[1] Garbe-Schönberg & Müller 2014

Modus operandi

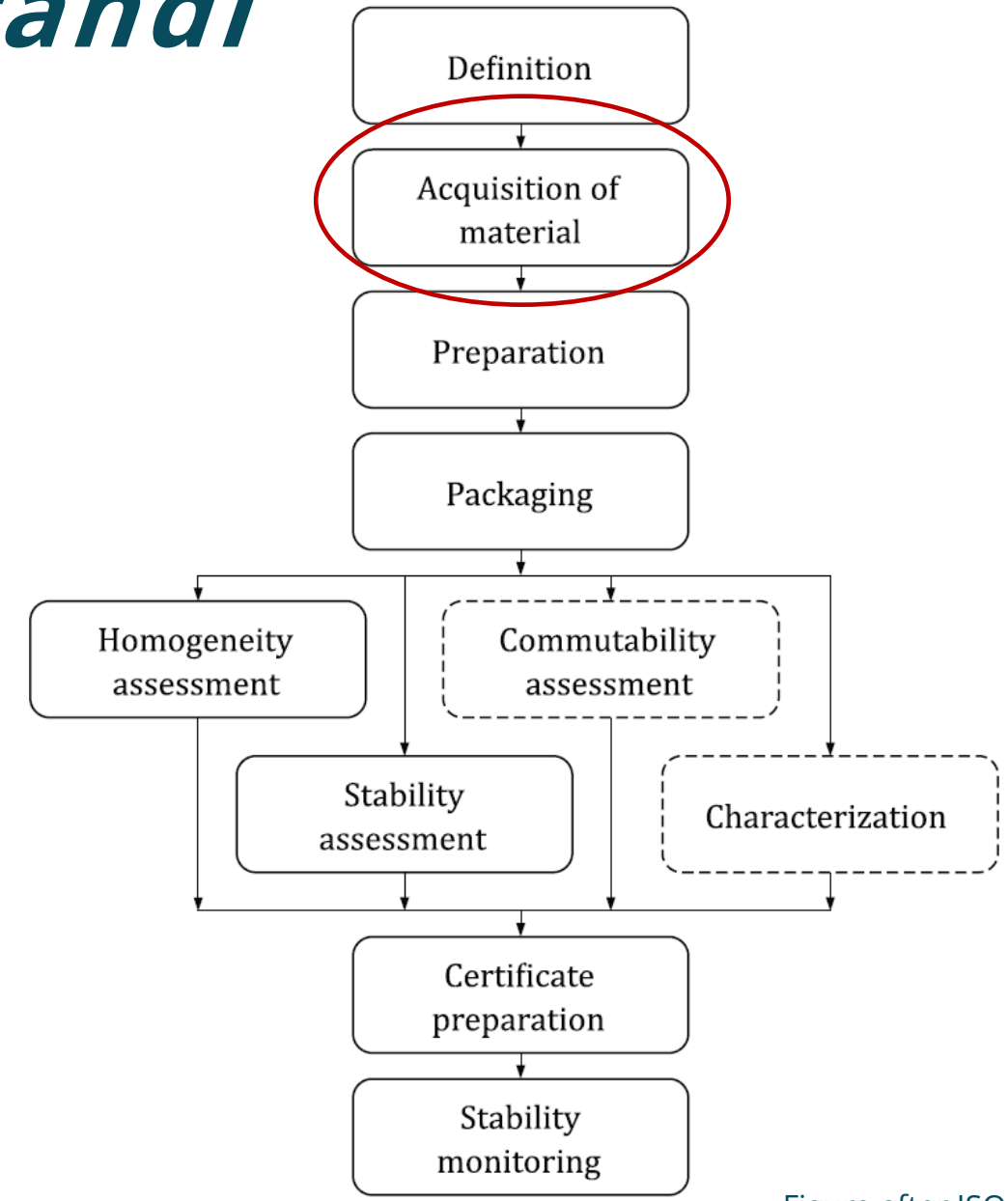


Figure after ISO Guide 35:2017

Acquisition

- **5 kg** of apatite $Ca_5(PO_4)_3$ (OH,F,Cl) crystals were purchased from a mineral dealership (Mikon Mineralienhändler GmbH)

- The source is a mine in the Loliondo Arusha district in Tanzania, Africa

- Crystals fragments were between 0.5 to 3 cm in size

Modus operandi

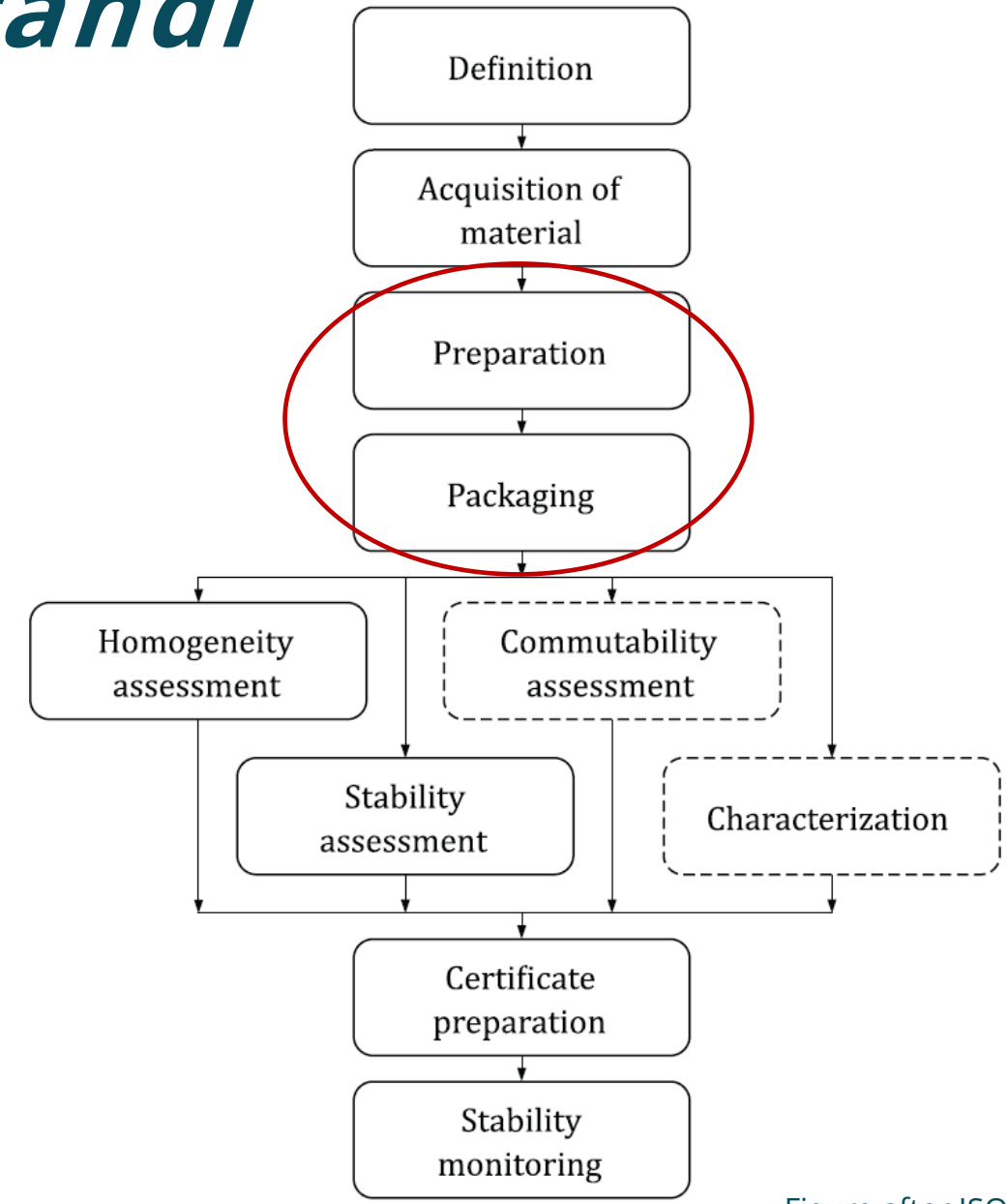
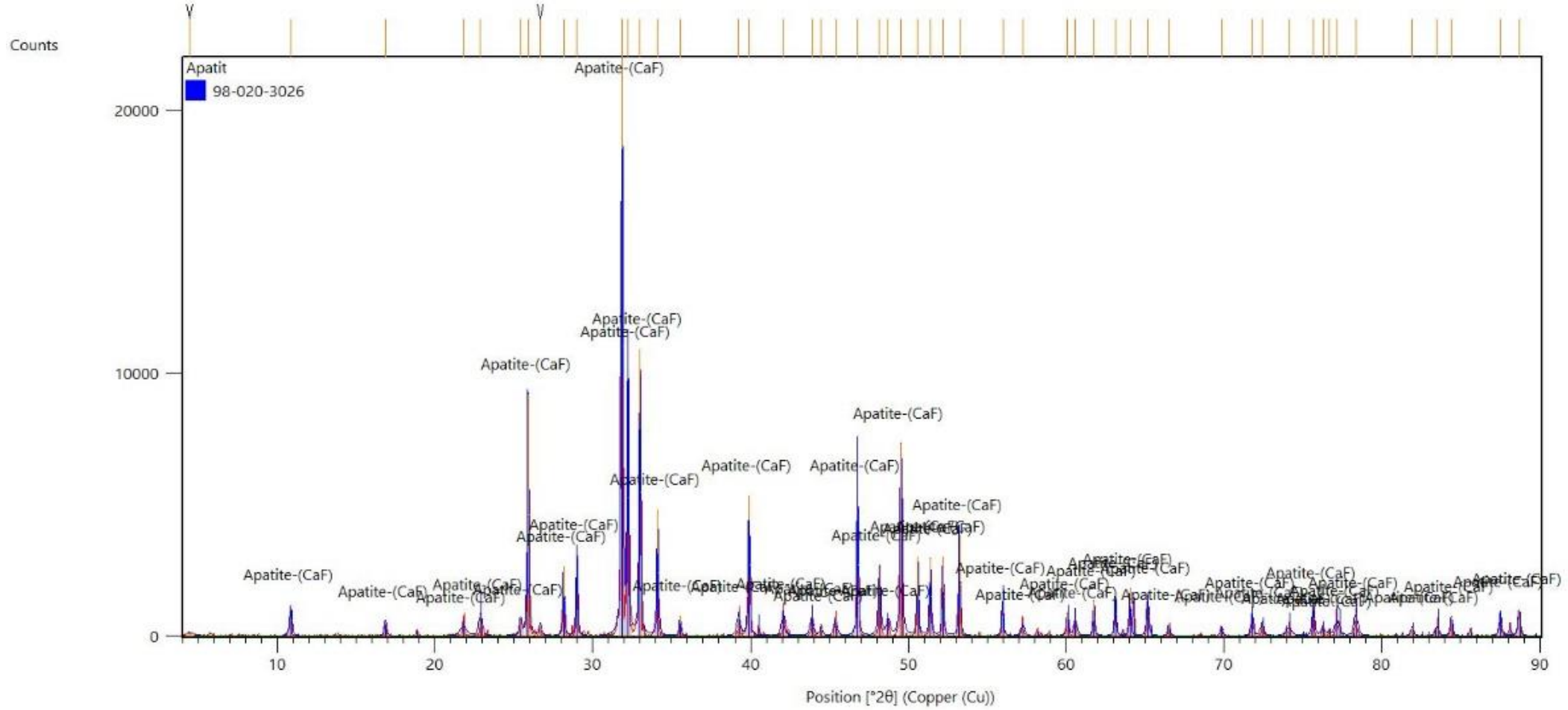


Figure after ISO Guide 35:2017

Preparation



- Qualitative analysis for verification of material type and / or identity
  - **XRD analysis of powdered crystals**

Preparation

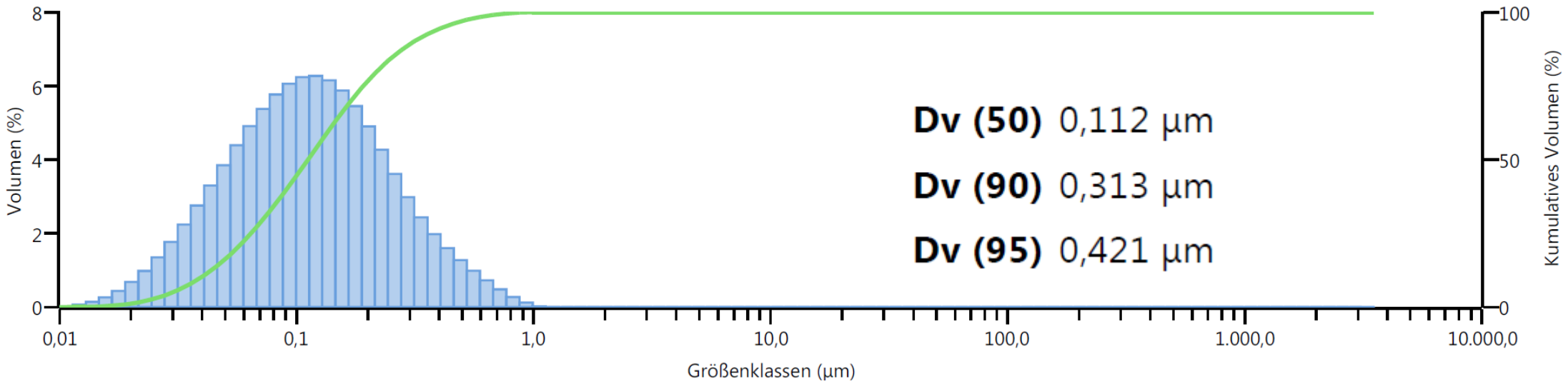
- Removal of dust and dirt using distilled water
- Removal of superficial contamination in a 1 % v/v bath of nitic acid (HNO_3)
- Rinsing using deonised water (18.2 MΩ)
- Crushing of approx. 1.5 kg of crystals in a cleaned jaw crusher to a particle size of < 1mm

Preparation

- Milling in an agate vibratory disc mill to particle size of < 63 µm
- Suspension fine-milling in agate planetary ball-mill
- Freeze-Drying
- Homogenisation in mixer-mill

[1] Garbe-Schönberg & Müller 2014

Preparation



- Measurement for control of material processing
  - ➢ Particle size distribution

Preparation & Packaging

- Splitting of approx. 1.5 kg in a rotary sample splitter into batches of 15 g of nano-powder

- Manufacturing of 118 Nano-Pellets pressed from Batch-01
  - ➢ Every **CRM** must be in its **final form** when tested for homogeneity and stability

Modus operandi

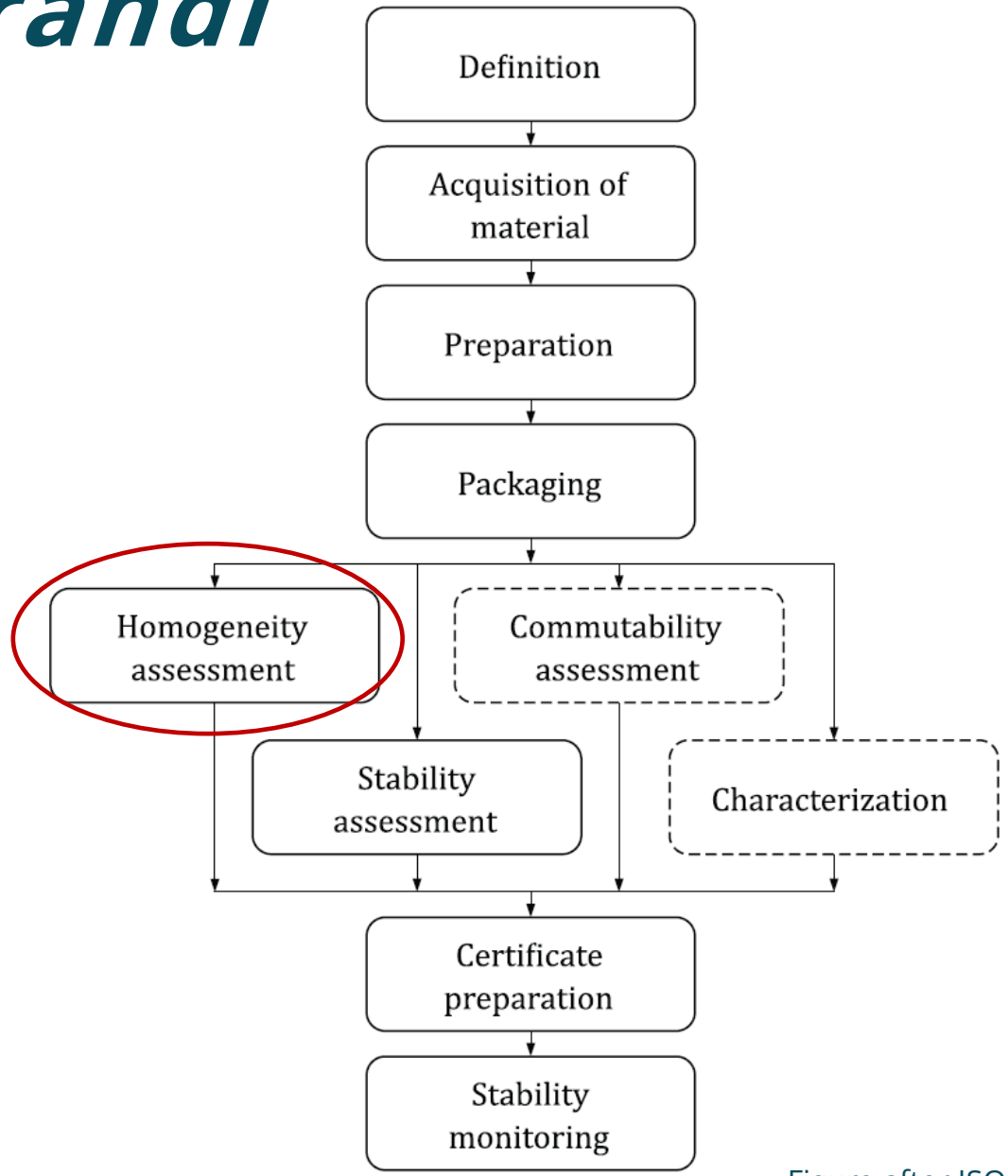
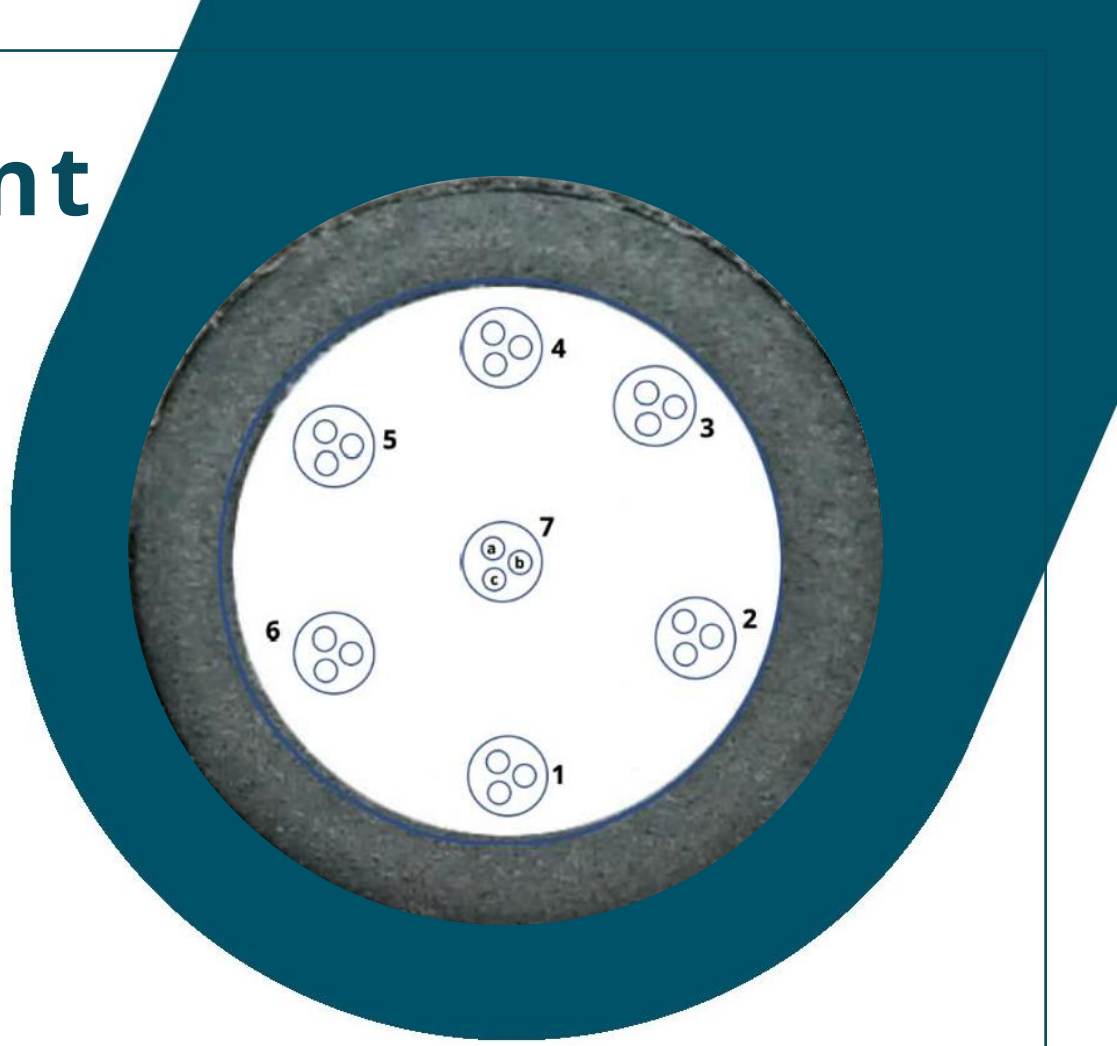


Figure after ISO Guide 35:2017

Homogeneity Assessment

- Number of units from batches > 100 units necessary for homogeneity test determined by:

$$N_{min} = \max(10, \sqrt[3]{Units_{produced}})$$



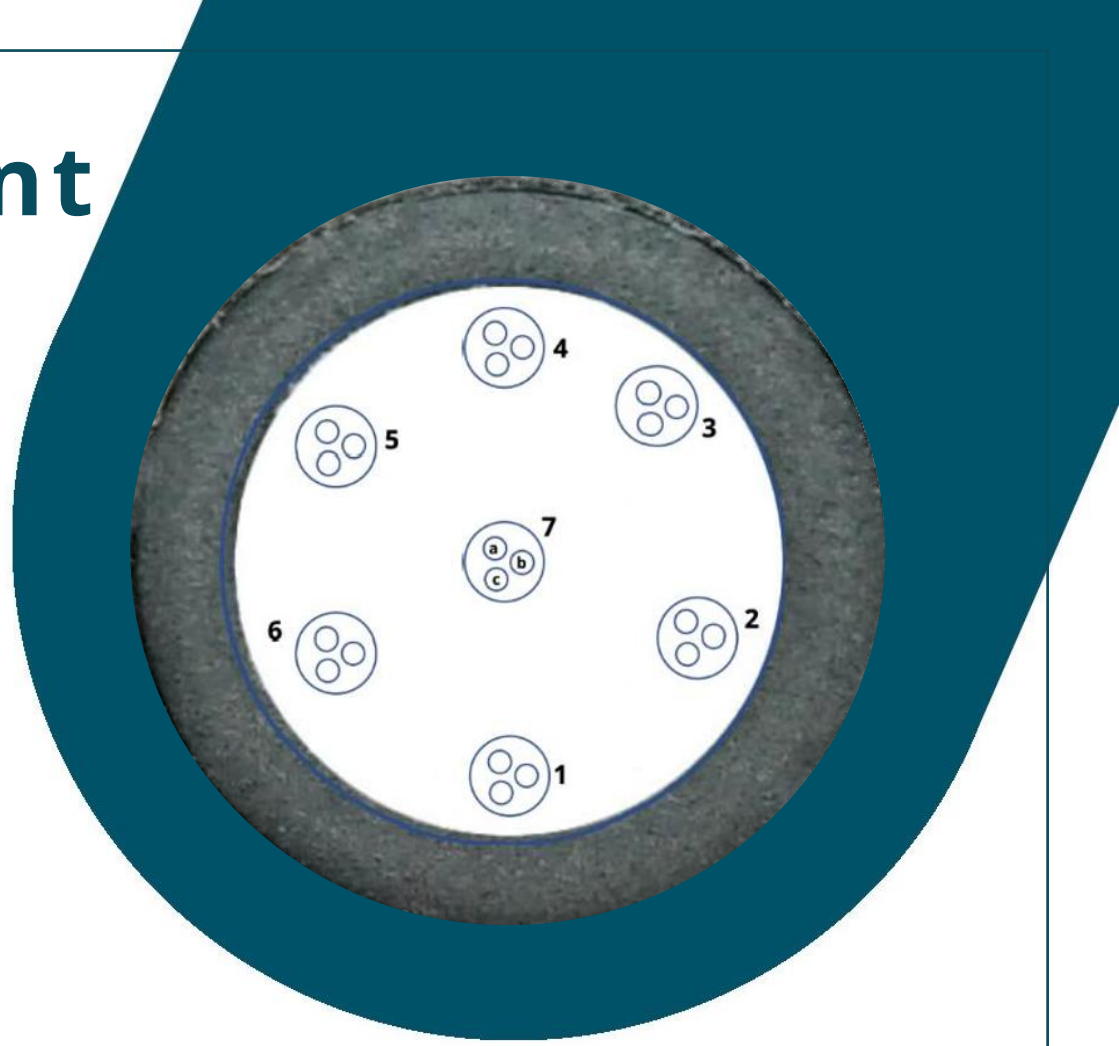
- Cube root of 118 is 4.9 i.e. 5 units
- 5 units < 10, therefore 10 units are necessary
- Batches < 100 units 10 % of units produced necessary

Homogeneity Assessment

- Subdivision of Nano-Pellet surface into 7 analytical zones

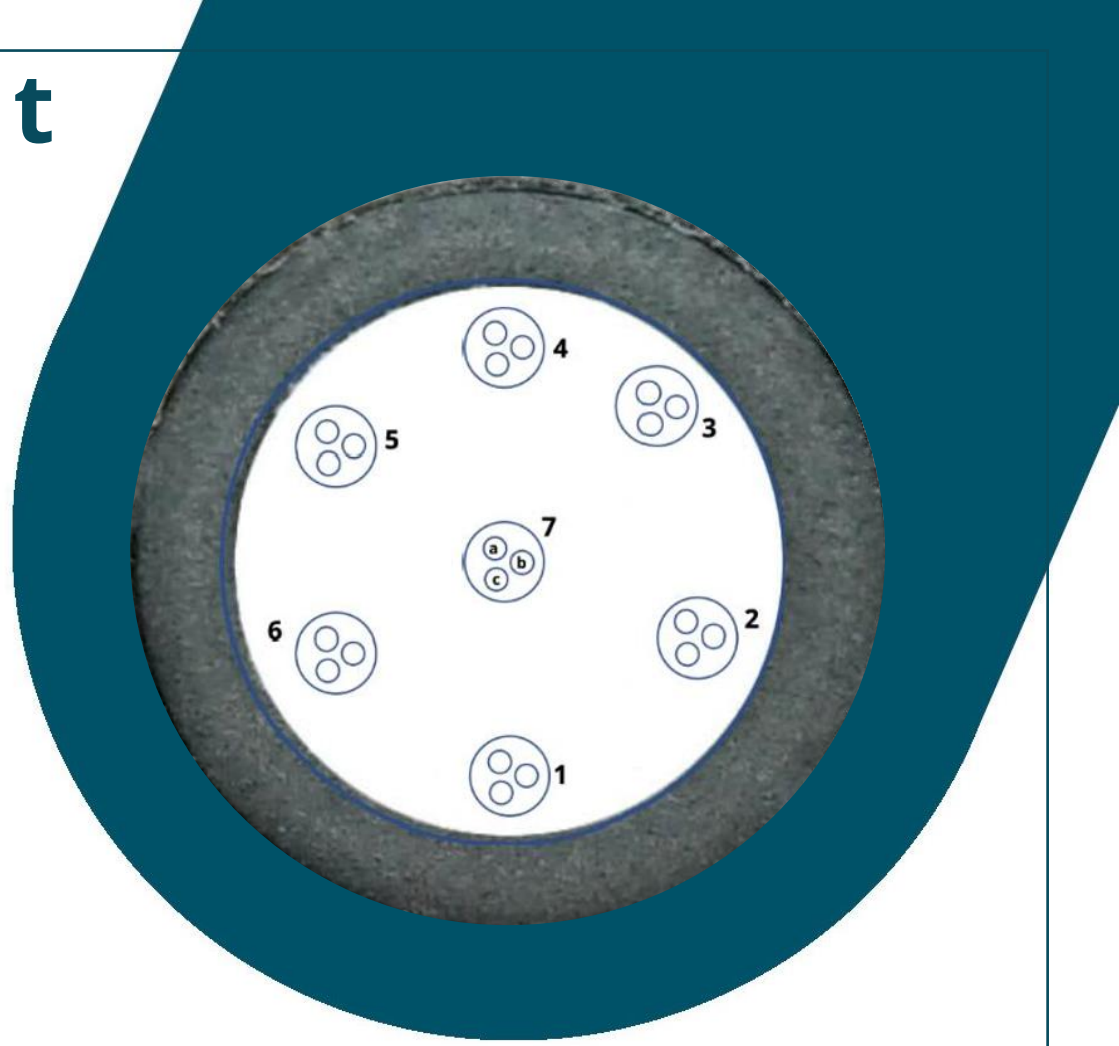
- Each zone consists of three LA-ICP-MS measurements performed in a randomised order @ 50 µm spot size – minimal sampling size

- Data quantified using NIST 610 and ^{43}Ca as internal standard



Homogeneity Assessment

Analyte		Sr
[µg/g]		
Apatite-NP-2020-07-B01-80 1a	1a	2103
Apatite-NP-2020-07-B01-80 6a	6a	2108
Apatite-NP-2020-07-B01-80 7a	7a	2100
Apatite-NP-2020-07-B01-80 2a	2a	2120
Apatite-NP-2020-07-B01-80 5a	5a	2107
Apatite-NP-2020-07-B01-80 3a	3a	2097
Apatite-NP-2020-07-B01-80 4a	4a	2146
NIST610-		518
NIST610-		514
NIST610-		513
Apatite-NP-2020-07-B01-80 3b	3b	2084
Apatite-NP-2020-07-B01-80 7b	7b	2114
Apatite-NP-2020-07-B01-80 2b	2b	2092
Apatite-NP-2020-07-B01-80 5b	5b	2111
Apatite-NP-2020-07-B01-80 6b	6b	2083
Apatite-NP-2020-07-B01-80 1b	1b	2088
Apatite-NP-2020-07-B01-80 4b	4b	2105
NIST610-		519
NIST610-		512
NIST610-		515
Apatite-NP-2020-07-B01-80 5c	5c	2069
Apatite-NP-2020-07-B01-80 7c	7c	2117
Apatite-NP-2020-07-B01-80 2c	2c	2127
Apatite-NP-2020-07-B01-80 3c	3c	2068
Apatite-NP-2020-07-B01-80 6c	6c	2118
Apatite-NP-2020-07-B01-80 1c	1c	2140
Apatite-NP-2020-07-B01-80 4c	4c	2145
NIST610-		511
NIST610-		520
NIST610-		514



Homogeneity Assessment

Apatite-NP 2020-07 B01-80

[µg/g]

	Zone 1	Zone 2	Zone 3	Zone 4	Zone 5	Zone 6	Zone 7	Average	SD	*RSD [%]*
Result 1 (a)	2103	2120	2097	2146	2107	2108	2100	**2111**	17	*0,8*
Result 2 (b)	2088	2092	2084	2105	2111	2083	2114	**2097**	13	*0,6*
Result 3 (c)	2140	2127	2068	2145	2069	2118	2117	**2112**	31	*1,5*
Average	**2110**	**2113**	**2083**	**2132**	**2096**	**2103**	**2110**			
SD	27	18	14	23	23	18	9			
RSD [%]	*1,3*	*0,9*	*0,7*	*1,1*	*1,1*	*0,9*	*0,4*			

- Results and averages of all 21 analyses performed on a single Nano-Pellet including rudimentary statistical evaluation

Homogeneity Assessment

Analyte [µg/g]	Sr						
	Result 1	Result 2	Result 3	Result 4	Result 5	Result 6	Result 7
Apatite-NP-2020-07-B01-80	2110	2113	2083	2132	2096	2103	2110
Apatite-NP-2020-07-B01-22	2118	2118	2113	2091	2121	2145	2114
Apatite-NP-2020-07-B01-97	2119	2092	2136	2125	2143	2122	2105
Apatite-NP-2020-07-B01-37	2110	2100	2113	2115	2134	2122	2108
Apatite-NP-2020-07-B01-117	2125	2129	2119	2134	2117	2111	2120
Apatite-NP-2020-07-B01-68	2122	2103	2131	2117	2103	2133	2104
Apatite-NP-2020-07-B01-49	2145	2148	2150	2149	2144	2142	2137
Apatite-NP-2020-07-B01-11	2135	2131	2153	2128	2143	2123	2134
Apatite-NP-2020-07-B01-89	2130	2157	2138	2124	2139	2147	2139
Apatite-NP-2020-07-B01-10	2110	2127	2129	2148	2137	2159	2141

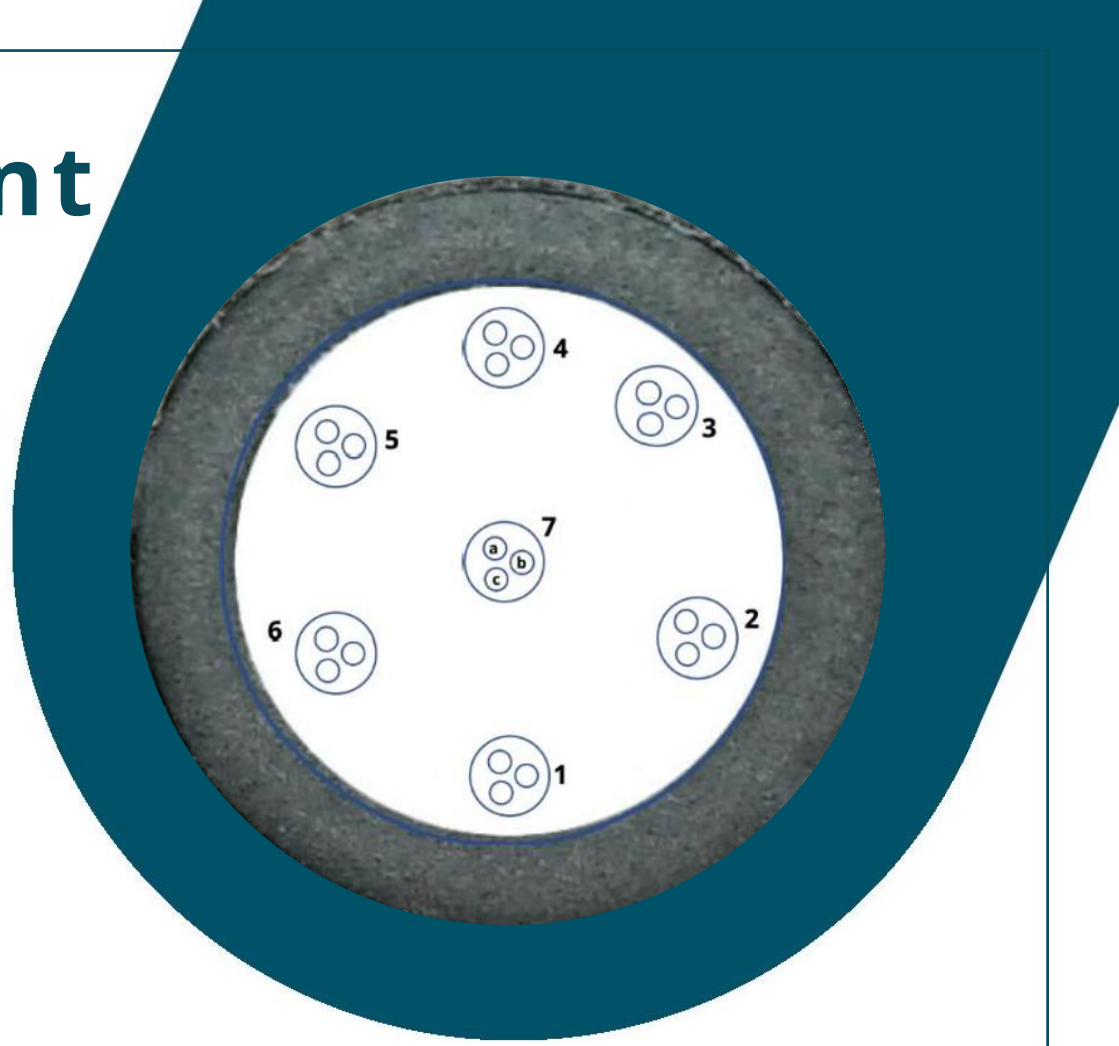
- Results from all tested Nano-Pellets presented as averaged results from each of the 7 analytical zones

Homogeneity Assessment

- Calculating uncertainty component pertaining to homogeneity following **ISO Guide 35:2017 Annex C1**

- One-way analysis of Variance (ANOVA MS Excel) using the 70 results from 10 Nano-Pellets

- Addition of **homogeneity factor** resulting from the relative contribution of the combined components of within- and between pellet standard deviations



Homogeneity Assessment

$$between\ unit\ SD = \sqrt{138} = 12\ \mu g/g$$

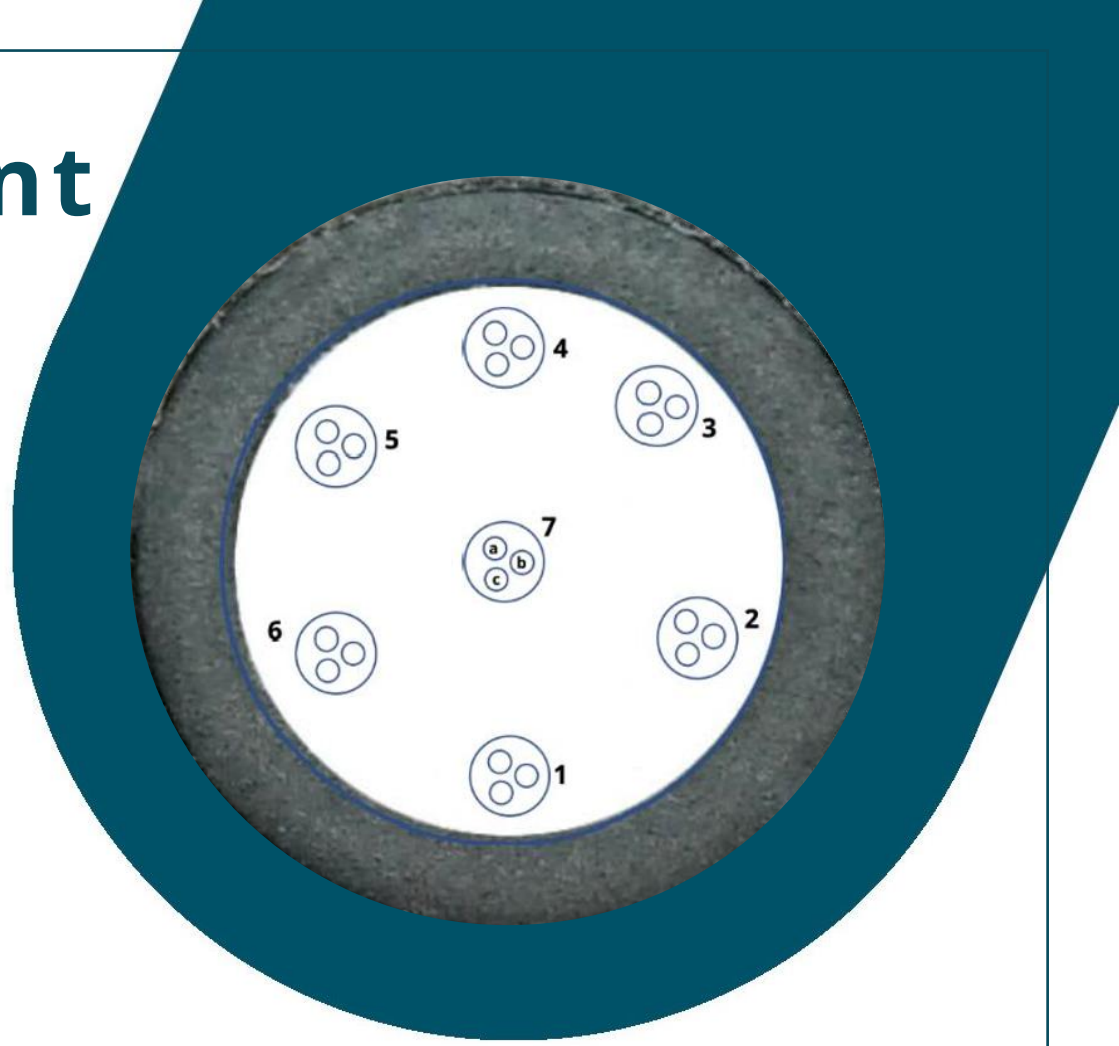
$$within\ unit\ SD = \sqrt{162} = 13\ \mu g/g$$

$$unc.\ contribution\ homogeneity = \sqrt{12^2 + 13^2} = 17\ \mu g/g$$

Homogeneity Assessment

- The overall average from 70 results in the homogeneity study is **2125 µg/g**

- The combined uncertainty contribution pertaining to homogeneity is **17 µg/g**
  - Relative contribution of 0.81 %
  - **Homogeneity factor** of **0.0081**



✓Homogeneity Assessment complete

Modus operandi

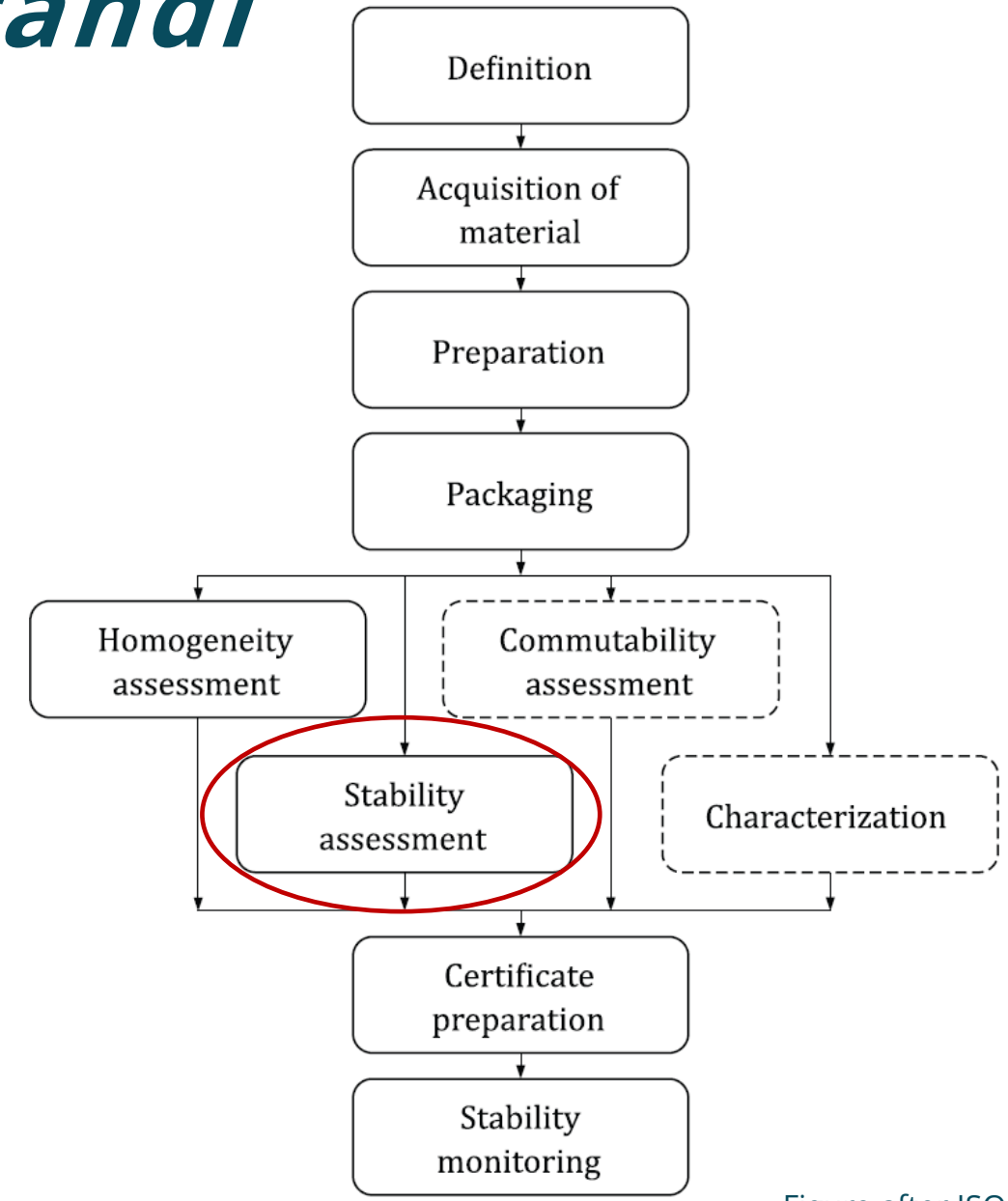


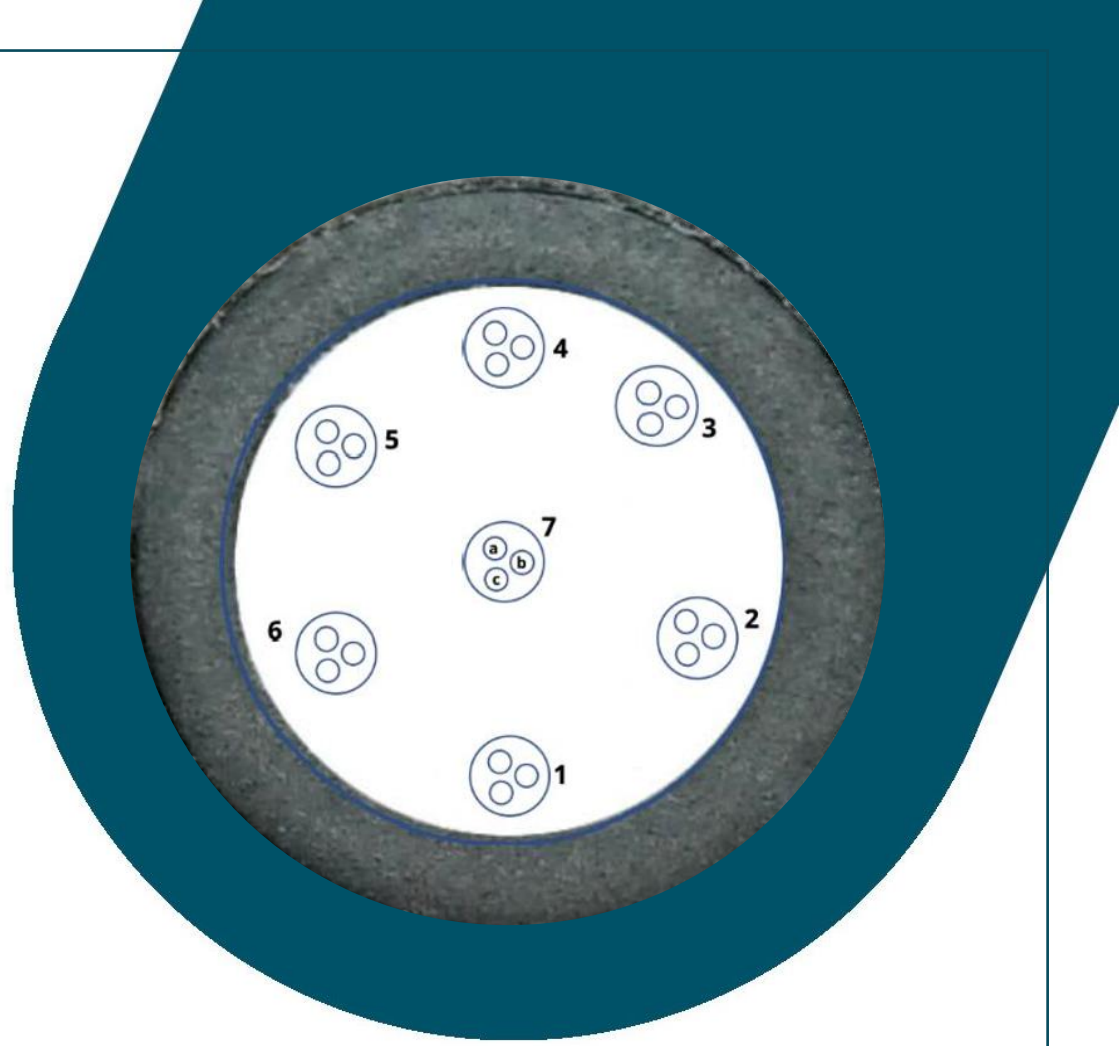
Figure after ISO Guide 35:2017

Stability Assessment

- Following **ISO 13528:2015 Annex E2**

- Two additional Nano-Pellets placed in oven at 60 °C for 8 h
  - Simulation of hot delivery conditions
  - Short-term stability assessment
  - Calculation of **stability factor**

- Long-term stability assessed on a quarterly basis within first 12 months, if stable, annual basis



Stability Assessment

Analyte [µg/g]	Sr						
	Result 1	Result 2	Result 3	Result 4	Result 5	Result 6	Result 7
Apatite-NP-2020-07-B01-40	2161	2156	2127	2138	2170	2159	2145
Apatite-NP-2020-07-B01-96	2164	2146	2117	2144	2152	2122	2104

Stability Average	**2143**	
Homogeneity Average	**2125**	
Absolute Difference	**18**	
Check value stability	**32**	
relative contribution Stability	**0,85**	[%]
Stability contribution factor	0,0085	[-]

- Stability test passes as long as check value > absolute difference
- In case stability test should fail data need not be discarded as long as final uncertainty deemed usable

Modus operandi

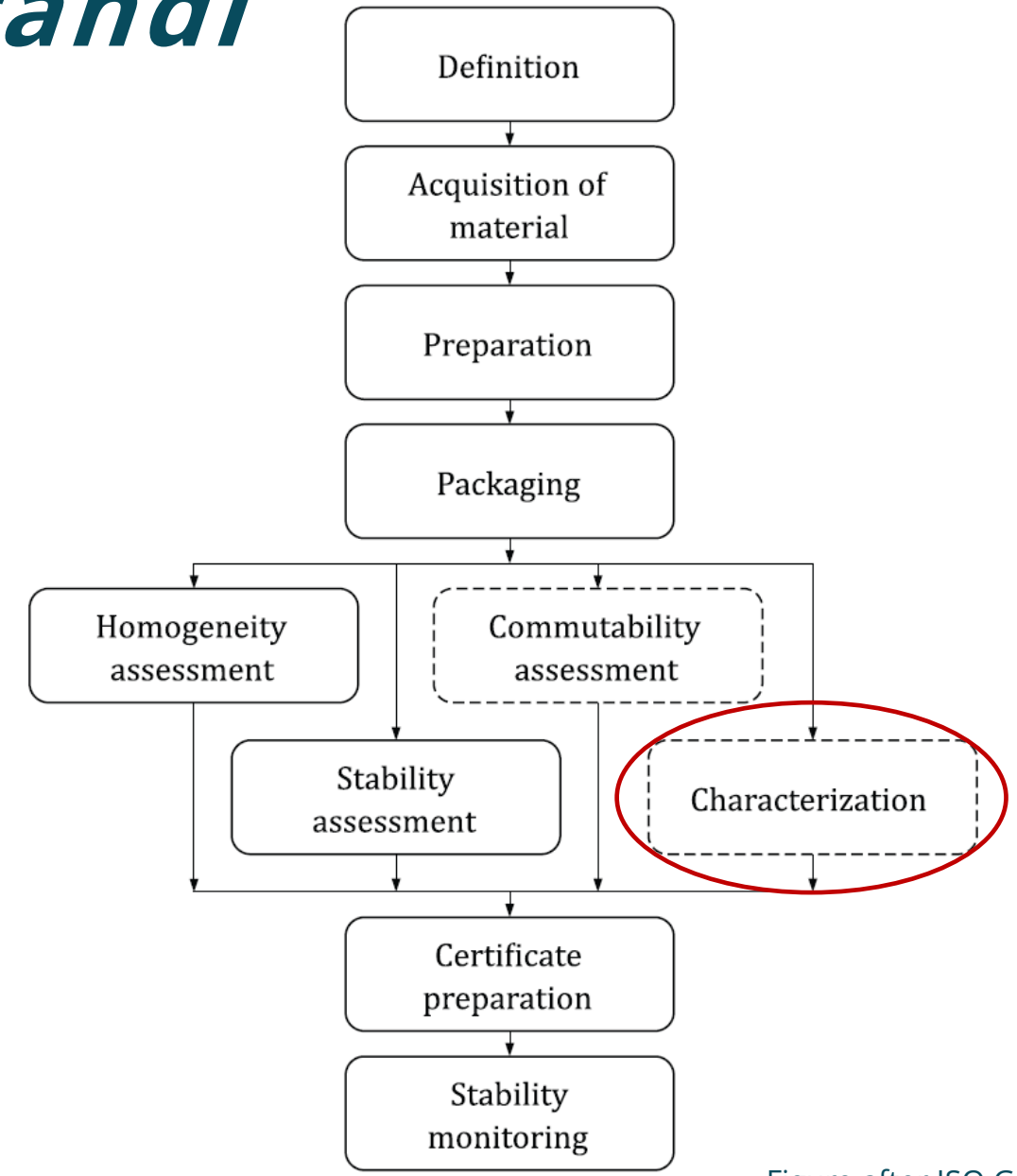
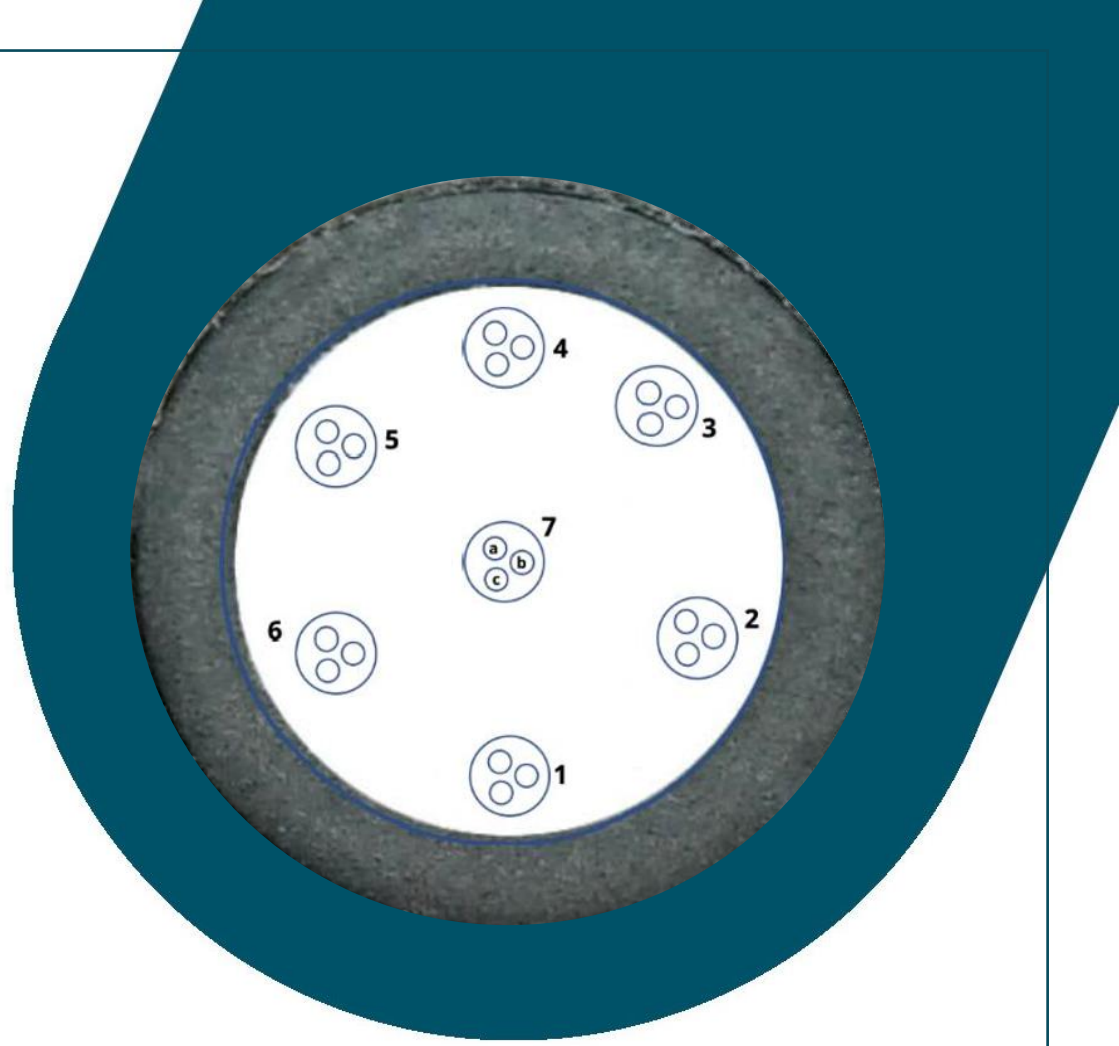


Figure after ISO Guide 35:2017

Characterisation

- Following **ISO 17034** recommendation
  - **“characterisation of a non-operationally defined measurand using two or more methods of demonstrable accuracy in one or more competent laboratories”**

- Laboratory competence is either shown by ISO 17025 accreditation and/or precise and accurate measurements of certified reference materials



Characterisation

$$Certified\ Value = \frac{\sum Data\ Set\ Means}{Number\ of\ Data\ Set\ Means}$$

$$Uncertainty\ component_{Char.} = \frac{Std.Dev\ of\ Data\ Set\ Means}{\sqrt{Number\ of\ Data\ Set\ Means}}$$

Analyte **Strontium - Sr µg/g**

	4-acid ICP-MS	Li-Borate ICP-MS	Li-Borate ICP-OES	Li-Borate XRF
Data Set Mean 1	2600	2795	2706	2621
Data Set Mean 2	2690	2685	2664	2664
Data Set Mean 3	2600	2685	2621	2664
Data Set Mean 4	2780	2750	2706	2664
Data Set Mean 5	2615	2840	2706	2664
Data Set Mean 6	2745	2830	2664	2664
Data Set Mean 7	2680	2840	2664	2706
Data Set Mean 8	2810	2790	2664	2790

Certified Value	**2705**	µg/g
Uncertainty component Characterisation	*13*	µg/g

Final Value & Uncertainty

$$Certified\ Value: 2705\ \mu g/g$$

$$Uncertainty\ factor_{Homogeneity}: 0.0081$$
$$Uncertainty\ factor_{Stability}: 0.0085$$

$$Uncertainty_{Characterisation}: 13\ \mu g/g$$
$$Uncertainty_{Homogeneity}: 22\ \mu g/g$$
$$Uncertainty_{Stability}: 23\ \mu g/g$$

$$expanded\ and\ combined\ Uncertainty = 2\ x\ \sqrt{13^2 + 22^2 + 23^2} = 68$$

Expansion factor k – Student's t-distribution

Certified Value for Sr: 2705 ± 68 µg/g @ 95 % CL

Modus operandi

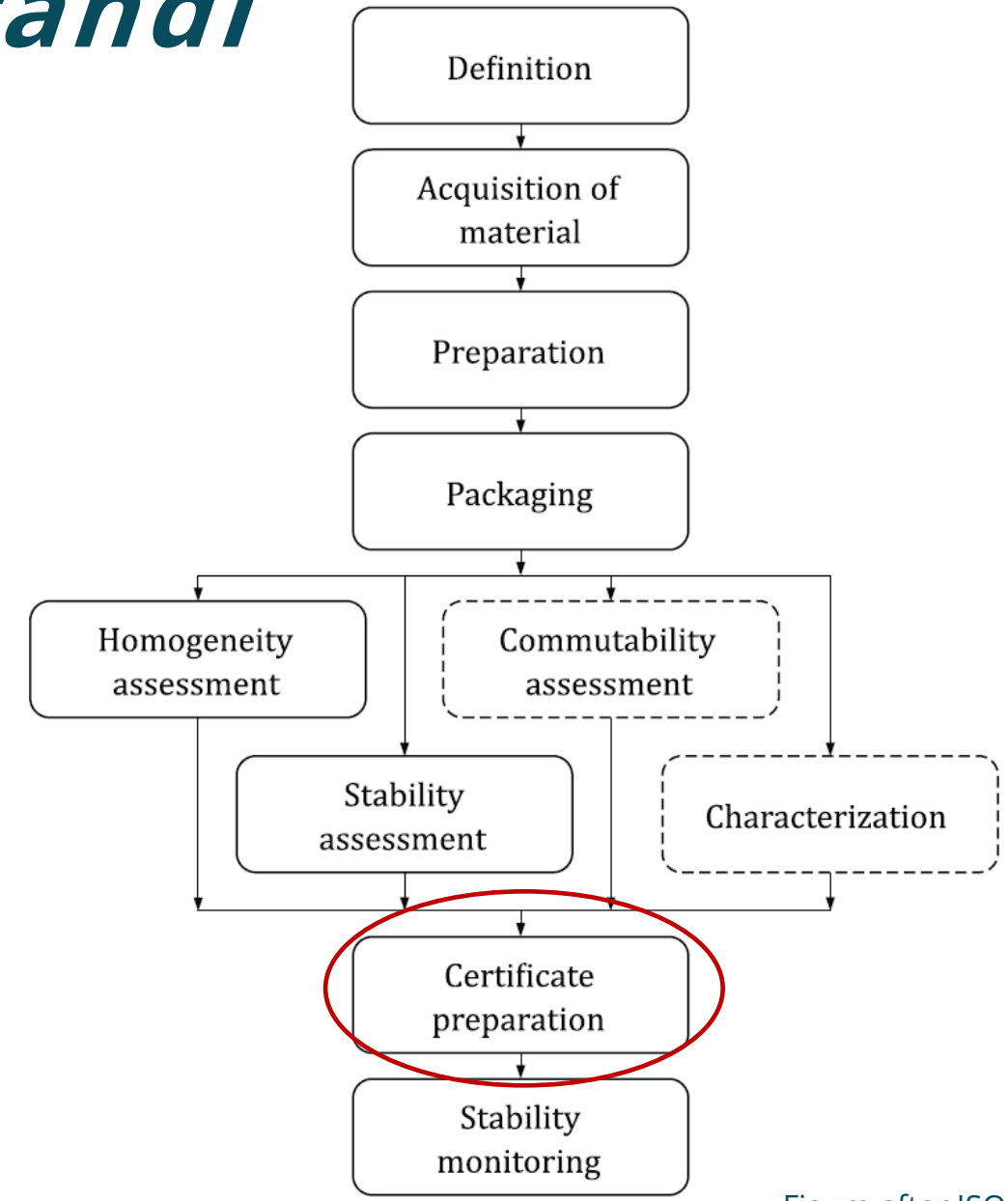


Figure after ISO Guide 35:2017

Certificate preparation

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Preliminary

Certificate

Microanalytical Reference Material

Apatite-NP-B01

Nano-particulate pressed powder pellet

Certified Values

Analyte	Value	Uncertainty (95% CL)	Unit
Ca	38.8	0.5	g/100g
P	17.7	0.6	g/100g
Na	756	42	µg/g
Mg	221	15	µg/g
Al	246	44	µg/g
Si	5700	354	µg/g
S	1169	194	µg/g
V	16.1	1.8	µg/g
Mn	451	18	µg/g
Cu	5.7	1.2	µg/g
Ga	7.9	0.5	µg/g
As	52.3	2.4	µg/g
Sr	2705	68	µg/g
Y	243	7	µg/g
Nb	0.4	0.1	µg/g
Mo	0.3	0.1	µg/g
Cd	0.47	0.13	µg/g
Ba	23.8	1.8	µg/g

Certified Values

Analyte	Value	Uncertainty (95% CL)
La	552	40
Ce	1468	44
Pr	187	8
Nd	716	23
Sm	112	4
Eu	21.2	0.9
Gd	72.0	3.5
Tb	8.69	0.36
Dy	44.9	1.5
Ho	8.40	0.37
Er	21.8	0.9
Tm	2.99	0.16
Yb	17.6	0.9
Lu	2.52	0.14
Pb	14.3	0.9
Bi	0.35	0.04
Th	101	6
U	31.9	2.2

Information Values

Analyte	Value	Uncertainty (95% CL)	Unit
Li	1.1		µg/g
Sc	0.3		µg/g
Cr	7		µg/g
Fe	477	108	µg/g
Co	1.4		µg/g
Ni	1.7	1.1	µg/g
Ge	1.5		µg/g
Se	1.4		µg/g

Information Values

Analyte	Value	Uncertainty (95% CL)
Rb	0.2	
Zr	10.7	5.5
Ag	0.043	
In	0.007	
Sb	0.11	
Hf	0.1	
W	1.1	
Re	0.004	

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The assigned values represent the mean of laboratory means. The reference values were obtained through measurements performed on the nano-powder using two or more methods (ICP-MS, ICP-OES, XRF) in two competent laboratories (ISO 17025[1] accredited). Further, each Laboratory's performance was statistically evaluated following recommendations from ISO Guide 35[2].
Homogeneity and stability tests were performed on the nano-pellets using LA-ICP-MS and in accordance with ASTM E826-14[3], ISO 13528[4], and ISO Guide 35.

The expanded uncertainty is composed of the uncertainty components from characterisation, as well as from the homogeneity, and stability. Unless stated otherwise a coverage factor $k = 2$ was applied to reach a confidence level of 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM)[5].

Information values did not fulfil all necessary statistical criteria of a reference value and should neither be considered for calibration nor validation. For most information values a homogeneity and stability test using LA-ICP-MS was not possible, due to concentrations being ≤ limit of detection. The information values, which have an uncertainty were demoted due to the calculated combined expanded uncertainty not being usable.

Preliminary Uranium–Lead Isotope Measurement Information Values (ID-TIMS)

Analyte	Value	Uncertainty (2SD)
$^{206}Pb/^{204}Pb$	36.02	0.41
$^{206}Pb/^{238}U$	0.09198	0.00103
$^{207}Pb/^{235}U$	0.7721	0.0383
$^{207}Pb/^{206}Pb$	0.06090	0.00263
Th/U	2.78	0.02
$Pb_{radiogenic}/Pb_{common}$	0.49	0.01
$^{206}Pb/^{238}U$ Date	567.2 Ma	3.4 Ma (MSWD = 0.32; n = 10)

U-Pb date is calculated assuming an initial Pb isotopic composition equivalent to the Stacey and Kramers (1975)[6] two-stage Pb evolution model (at 550 Ma) for the remainder of the common Pb, assigning an uncertainty component of 1 % to the model isotopic ratio.

Preliminary Strontium Isotope Measurement Information Values (ID-TIMS)

Analyte	Value	Uncertainty (2SD)	Uncertainty (95% CL)
$^{87}Sr/^{86}Sr$	0.704280	0.000026	0.000040

The isotope measurement information values are preliminary. The final values will be given as soon as the homogeneity and stability tests are completed.

Pellet serial number:

Date of dispatch:

This certificate was approved by the myStandards GmbH, Kiel, 11.02.2022
Signed:

Simon Nordstad CEO & Founder Method Development & Production	Christina Wittke CEO & Founder Management & Marketing

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Intended Use
This microanalytical certified reference material (CRM) is designed for use by laboratories undertaking the determination of major and trace element mass fractions in apatite and equivalent matrices with LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry). It is suitable for calibration and as a secondary reference material for the assessment of a measurement procedure and quality control. Note that the material may only be used for a single purpose in the same measurement process. For example, it must not be used for calibration and method validation at the same time.

Description of the CRM
This CRM is a nanoparticular pressed powder pellet of the apatite powder "Apatite-NP-B01". The original apatite crystals, originate from the Arusha Loliondo district in Tanzania, Africa. The crystals were crushed to a particle size of 63 µm. The resulting powder was subjected to our own material-specific milling protocol, freeze-dried, homogenised, and split into batches. Batch number 1 was pressed, into 10 mm diameter pellets, without any binders using a programmable hydraulic press. The fortification of contrasting colour surrounding the reference material is, according to the manufacturer, an "organic compound". The exact composition is not specified any closer. The certificate of analysis is available on demand.

Handling advice and Storage information
Avoid touching the pellet's surface directly in order to prevent contamination. Also, do not clean the surface with any liquids as it may compromise the pellet's integrity.
Please note the label marks the bottom of the pellet.
Store the CRM in a desiccator and or in a dark and dry environment.

The myStandards GmbH cannot be held responsible for changes that happen during storage of the material at the customer's premises, especially with respect to opened samples.

Period of Validity
Provided the storage and handling conditions are met, no chemical alteration is known to exist, and the assigned values will remain stable. Therefore, the product information and assigned values for this CRM are valid for one year, pending stability monitoring, from the date of dispatch. This validity may be extended as further evidence of stability becomes available. The manufacturer will inform the customer if any alterations occur.

Safety instructions
Nano-particulate powders can cause harm if ingested, inhaled or in contact with skin. In their pressed form however, they do not exhibit any dusting. If a pellet should accidently break, we advise wearing a dust mask during clean up.

Minimal sample size
The minimal sample size corresponds to a spot size of 50 µm.
Further ablation conditions and signal acquisition parameters during homogeneity- and stability-testing were:

Laser fluence	*6 J/cm²*
Repetition rate	*10 Hz*
Background	*20 s*
Signal acquisition	*30 s*

Metrological Traceability
This CRM has been produced in accordance with the recommendations specified in ISO 17034[7] and ISO Guide 35 and are traceable to the base units of SI via calibrated measurements in accredited laboratories (ISO 17025). The preliminary values for uranium–lead isotope measurements are traceable to the units of SI via calibrated measurements using a single reference measurement procedure in a single laboratory[8][9]. The preliminary value for strontium isotope measurements is also traceable to the units of SI via calibrated measurements using a single reference measurement procedure in an accredited laboratory (ISO 17025).

Summary

- Certified values traceable to SI through characterisation in competent laboratories and use of homogeneity- and stability factors
- Assessment and inclusion of all necessary contributors to uncertainty budget
- General methodology not only applicable to LA-ICP-MS but other techniques e.g. SIMS, LIBS, µXRF, GD-OES, Spark Emission OES as well
- Informal validation by adjudicator of the DAkkS in an advisory capacity
- 10 further materials currently underway following this procedure

Thank You
for Your attention