Certification Report of CRMS-NP-B01

Processing and certification of a microanalytical reference material including its way from coral fragments to Nano-Pellets

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Abstract

The microanalytical certified reference material (CRM) CRMS-NP-B01 is designed for use by laboratories undertaking the determination of major and trace element mass fractions in calcium carbonate and equivalent matrices with LA-ICP-MS (Laser Ablation Inductively Coupled Plasma Mass Spectrometry). Sr isotope ratios have been analysed using ID-TIMS. The original coral skeletal fragments were cleaned, crushed, and milled to a particle size of < 40 µm. This powder was subjected to a material-specific milling protocol, freeze-dried, homogenised, and split into batches, resulting in the material CRMS-NP. All batches are sufficient for approximately 900 units, which should make it available for the foreseeable future. Batch number 1 was pressed, into 10 mm diameter nanoparticulate pressed powder pellets, without any binders using a programmable hydraulic press.

This report describes the selection, production, and characterisation of the material.

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1. Introduction

CRMS-NP is the abbreviation for **C**orallium **R**ubrum **M**editerranean **S**ardinia **N**ano-**P**ellet. Corallium rubrum, also known as precious coral, has a distinct red colour caused by carotenoid pigments, the same sort of pigments which colour carrots. Due their vibrant colour, they have been used to make jewellery from North America to Europe and East Asia. Their chemical composition varies depending on where and when the corals grew. This allows archaeologist to investigate the source of coral jewellery. Depending on water temperature and other parameters coral's chemical composition changes, which allows to reconstruct past ocean conditions. The earliest corals in the geologic record date back to the Cambrian period but have since gone extinct. The corals we know today evolved in the Triassic period, 225 million years ago.

2. Starting Material

A total amount of 250 g coral powder was purchased from Petronio GmbH, a mineral dealership. The powder was made from cleaned coral skeletal fragments. Some not yet cleaned fragments can be seen in Fig. 1.

Fig. 1 Photograph of the coral skeletal fragments prior to cleaning used to prepare this material.

To verify the identity of the material in accordance with ISO 17034:2016[1] the genus was zoologically/paleontologically identified. Additionally, an X-ray diffraction (XRD) analysis was performed. The diffractogram, showing magnesian calcite as the crystal structure, confirms the identity (Fig. 2), since magnesian calcite is characteristic for this coral.

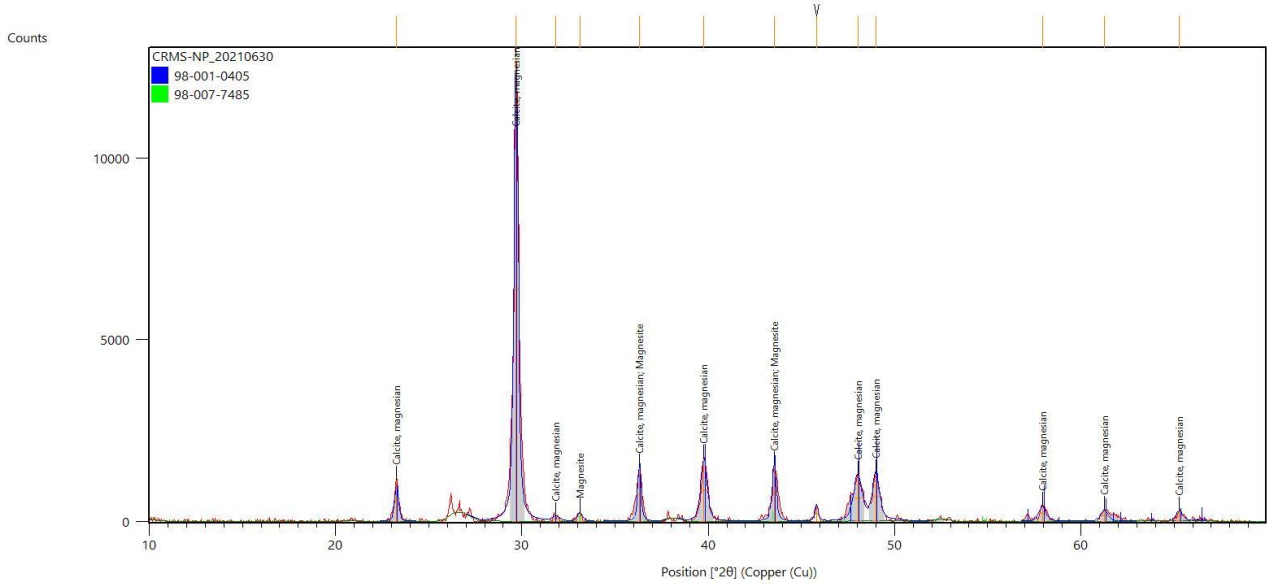

Fig. 2 X-ray diffractogram of powdered coral skeleton confirming the identity as magnesian calcite.

3. Sample Preparation

The first preparation step was removing dirt and dust using distilled water. Thereafter, the coral skeletal fragments were placed in a bath of 1 % v/v hydrogen peroxide (H_2O_2) to remove superficial organic contamination. Subsequently, they were rinsed using deionised water (18.2 MΩ resistivity) and dried in a laminar flow hood.

Approximately 250 g of the cleaned coral skeletal fragments were milled an agate planetary ball mill to a particle size of < 40 µm.

The final grinding step was performed using our patented milling technique. The resulting slurry was freeze-dried, homogenised in a mixer-mill, and split into batches of 5 g using a rotary sample splitter and filled into hydrolytic class 1 glass vials for storage. A total of 38 batches were prepared, 19 of which were used for the analyses.

Finally, batch number 1 (B01) was pressed into Nano-Pellets (10 mm diameter) resulting in a total of 44 units.

4. Homogeneity & Stability Testing

The homogeneity test was performed on the pellets (final packaged form). For this purpose, the samples were taken according to a random stratified sampling strategy. The number of units recommended to perform a homogeneity study are outlined in ISO Guide 35:2017[2]. For batches < 100 units it is suggested to test 10 % of the batch for homogeneity. In this case 10 % of 44 units is 4.4, which is rounded up to 5 units.

Homogeneity testing was performed adapting a procedure from the ASTM Guide E-826-14[3]. To transfer this procedure to LA-ICP-MS, the pellet surface was divided into seven analytical zones (Fig. 3). However, instead of making three repeated measurements on the same spot, three repeated measurements in close proximity were made (n=21). In total the homogeneity test is comprised of 105 spot measurements. The three results (a, b, c) in each analytical zone are then averaged, so each pellet contributes 7 results for the calculation of the uncertainty component pertaining to homogeneity. The resulting data were reduced using the software LADR (Norris Scientific Pty. Ltd.). The uncertainty component resulting from homogeneity was calculated following Annex C.1 in ISO Guide 35:2017.

Stability and its uncertainty component were assessed and calculated following Annex E.2 in ISO Guide 13528:2015[4]. Therefore, two randomly chosen pellets were placed in an oven at 60 °C for 8 h to simulate shipping in the back of a warm delivery vehicle. This assesses short-term stability. Long-term stability will be assessed in intervals of 4, 8 and 12 months. After successful assessment the stability will be monitored annually.

Ultimately, the usability of an uncertainty is determined by the manufacturer and the reference materials' intended use. Therefore, the Horwitz equation[5] and Horwitz Ratio (HORRAT) (eq. 1 & 2) was used to provide a mathematical basis for determining the usability of an uncertainty.

$$RSD_{Horwitz} = 2 \times Concentration^{(-0{,}1505)} \quad (1)$$

$$HORRAT = \frac{RSD_{Meausured}}{RSD_{Horwitz}} \quad (2)$$

A HORRAT of ≤ 1 is ideal, between 1 and 2 acceptable and > 2 unacceptable.

A working example of such evaluations can be found here:

Example of our Data Evaluation for Certified Values

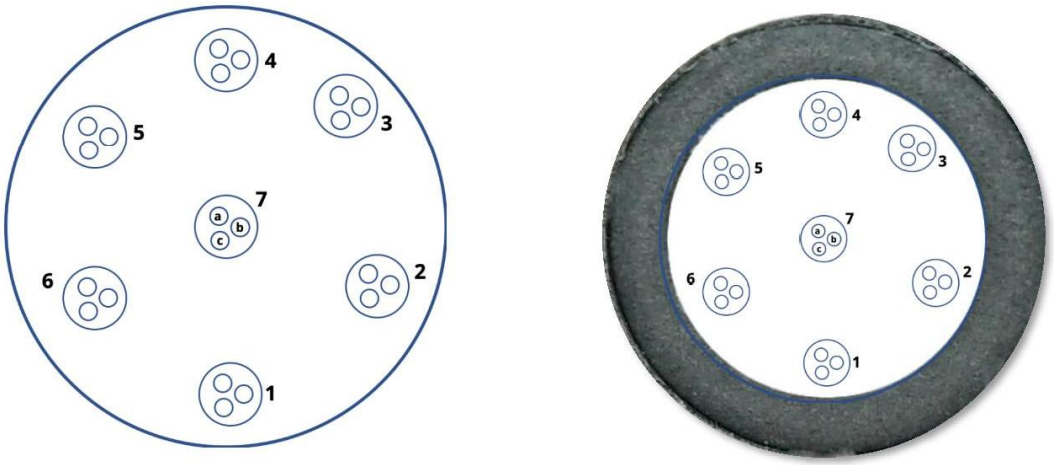

Fig. 3 Ablation pattern adapted from ASTM Guide E826-14.

5. Characterisation & Value Assignment

The characterisation approach applied was:

"Characterisation of a non-operationally defined measurand using two or more methods of demonstrable accuracy in one or more competent laboratories"

For characterisation of major and trace elements 19 aliquots of the CRMS-NP powder were analysed in two accredited (ISO 17025:2017) laboratories as well as in a competent research institute using a variety of digestions and analytical techniques. These include 4-acid digestion (hydrochloric acid HCl, nitric acid HNO_3, hydrofluoric acid HF and perchloric acid $HClO_4$) and lithium borate fusion followed by ICP-MS, ICP-AES and XRF analyses. Boron was characterized using Solution-SF-ICP-MS as a single reference measurement procedure (as defined in ISO/IEC Guide 99[6]) in a single laboratory. The Sr isotope ratios were determined by ID-TIMS analysis at IsoAnalysis UG measuring 3 aliquots.

Certified and information values can be found in the Certificate of Analysis here:

Certificate of Analysis

The assigned values and the uncertainty component resulting from the characterisation were calculated using equation 3 and 4.

$$Assigned\ Value = \frac{\sum accepted\ data\ set\ means}{number\ of\ data\ sets} \quad (3)$$

$$Uncertainty_{Characterisation} = \frac{Std.\,Dev.\,of\ data\ set\ means}{\sqrt{number\ of\ data\ sets}} \quad (4)$$

To use equations 3 & 4 the data set means must show an approximately normal distribution. This prerequisite was tested using the software XLSTAT.

Finally, each certified value needs to be accompanied by a combined expanded uncertainty at the 95 % CL. The uncertainty is calculated (eq. 5) by combining the uncertainty components from characterisation as well as homogeneity- and stability testing.

$$Unc._{Final} = k \times \sqrt{Unc._{Homog.}^2 + Unc._{Char.}^2 + Unc._{Stabil.}^2} \quad (5)$$

The expansion factor k is determined by the effective degrees of freedom and their corresponding value in Student's t-distribution. The coverage factor was applied to reach a confidence level of 95 %, as defined in the Guide to the Expression of Uncertainty in Measurement (GUM)[7]. According to ISO Guide 35:2017 it is permissible to use an expansion factor of 2 if there are ≥ 10 degrees of freedom. If there are < 10 degrees of freedom the appropriate factor should be taken from a Student's-t table, i.e., the distribution at the desired confidence level.

Here (eq. 6 & Tab. 1) is an example on how the final uncertainty is calculated:

Tab. 1 Calculation of the final combined and expanded uncertainty, using the analyte Uranium as an example.

	Certified Value	**Unit**
Uranium (U)	31.9	µg/g
$Uncertainty_{Chacaterisation}$	0.2	µg/g
$Uncertainty_{Homogeneity}$	0.9	µg/g
$Uncertainty_{Stability}$	0.6	µg/g
Expansion factor (k)	2	[-]

$$Unc._{Final} = 2 \times \sqrt{0.2^2 + 0.9^2 + 0.6^2} = 2.2 \quad (6)$$

Analyte [µg/g]	**Certified Value**	**Expanded Uncertainty @ 95 % CL**
Uranium (U)	31.9	2.2

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6. Minimal Sample Size

Every CRM must have a statement of its minimal sample size. Minimal sample size for powdered certified reference materials is typically given in milligrams (mg). LA-ICP-MS analyses only take subsamples of e.g. a pressed powder pellet, meaning, that the mass of the powder used to make the pellet becomes irrelevant.

Therefore, the minimal sample size was determined by the spot-size used during the homogeneity- and stability test, which in the case of CRMS-NP-B01 was 80 µm. Further ablation conditions and signal acquisition parameters are shown in Tab. 2.

Tab. 2 Ablation and signal acquisition parameters during homogeneity- and stability-testing.

Laser fluence	7 J/cm^2
Repetition rate	10 Hz
Background	10 s
Signal acquisition	40 s

7. Acknowledgements

We would like to thank Dr. Axel Sjöqvist of Axray Scientific AB and Thomas Zack of the University of Gothenburg for their tireless efforts during the LA-ICP-MS analyses and providing high-quality data sets. We are also greatly thankful to Wim Boer of NIOZ for providing a high-quality solution ICP-MS data set. Finally, we would like to thank Dr. Martin Rosner from IsoAnalysis UG for providing exceptional Sr isotope ratio data.

8. References

[1] EN ISO 17034:2016 (D/E), *General requirements for the competence of reference material producers*

[2] ISO Guide 35:2017 (E), *Reference materials – Guidance for characterization and assessment of homogeneity and stability*

[3] ASTM E826-14, *Standard Practice for Testing Homogeneity of a Metal Lot or Batch in Solid Form by Spark Atomic Emission Spectroscopy.* ASTM International, West Conshohocken, PA, 2014. www.astm.org

[4] ISO 13528:2015 (E), *Statistical methods for use in proficiency testing by interlaboratory comparison*

[5] Horwitz, W., Albert, R. (1995), *Precision in analytical measurements: Expected values and consequences in geochemical analyses.* Fresenius Journal of Analytical Chemistry. 351:507-513

[6] ISO/IEC Guide 99:2007, *International vocabulary of metrology – Basic and general concepts and associated terms (VIM)*

[7] ISO/IEC Guide 98-3:2008, *Uncertainty of measurement - Part 3: Guide to the expression of uncertainty in measurement (GUM:1995)*

9. Document History

Version	*Date*	*Changes applied*
1.0	28.03.2022	First publication
1.1	21.07.2022	Links adapted to the new website