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D7: Report describing the development of one aqueous certified reference material that is certified for the same stable isotope ratios of B, Cd, Li, Ni, Pb and U with lowest possible uncertainties

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D7: Report describing the development of one aqueous certified reference material that is certified for the same stable isotope ratios of B, Cd, Li, Ni, Pb and U with lowest possible uncertainties

Organisation name of the lead participant for the deliverable:

TÜBİTAK UME National Metrology Institute of TÜRKİYE

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Glossary

CCQM	Consultative Committee for Amount of Substance
CIPM	International Committee for Weights and Measures
CRM	Certified reference material
GUM	Guide to the expression of uncertainty in measurement
ICP-MS	(Single-collector) Inductively coupled plasma mass spectrometry
ICP-MS/MS	Inductively coupled plasma tandem mass spectrometry
MC-ICP-MS	Multi-collector inductively coupled plasma mass spectrometry
RM	Reference material
UME	TÜBİTAK National Metrology Institute of Türkiye

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1 Summary

This report is intended to be the 7th deliverable report of the project 21GRD09 MetroPOEM describing the production of UME MetroPOEM CRM, a seawater material certified for the isotope amount ratios of selected elements: B, Cd, Li, Ni, Pb and U. The certified reference material was produced in accordance with the requirements of ISO 17034:2016 standard [1]. The collection of starting material, 250 L of seawater, was conducted at the station UE67, which was located at the edge of German EEZ in the North Sea (55° 25’ N; 4° 5’ E). The sample was filtered before filling into pre-cleaned 25 L HDPE carboys and acidified using subboiled HNO_3 for the stabilisation. The carboys were sealed and individually packed in clean PE foil, and stored at 4 °C prior to transport to TÜBİTAK UME by Hereon for further processing. After preliminary analysis, the material was spiked with the elements whose mass fractions were below the target levels to obtain the material having suitable concentrations to be measured in standard analytical laboratories. After filling into pre-cleaned 250 mL polypropylene bottles, the whole batch was sterilized with 25 kGy γ-radiation by ^{60}Co source. Between-unit homogeneity and stability during dispatch and storage conditions were assessed in accordance with ISO 33405:2024 standard [2] by 21GRD09 MetroPOEM Project [3] partners in a collaborative manner. The characterisation was conducted by an interlaboratory study where, in addition to the project partners, several expert laboratories were also involved in isotope ratio measurements. Uncertainties of the characterisation measurements were estimated in compliance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4]. Certified values include uncertainties arising from possible inhomogeneity, instability and characterisation measurements. The material is intended to be used for calibration or quality control purposes in laboratories performing isotope ratio measurements.

2 Introduction

Measurement capabilities have become important as water matrices need to be evaluated for compliance with the countries’ own quality standards. It is well known that monitoring useful parameters systematically such as contaminants and keeping them under control directly affect the quality of life. Besides, the importance of air and soil quality, water quality is also quite important for Earth. Understanding the dynamics of ocean life has become crucial over the last decade as oceans cover about two-thirds of Earth (70 %), and are the main reservoir of CO_2 with a notable role in the global carbon cycle [5,6]. Countries with coastal borders have to follow well established regulations to help those mechanisms and keep most environmental pollution under control by performing routine analyses. However, as the necessity of monitoring trace elements in seawater is well established, the challenges of these measurements have raised the topic for the last few decades. There is a strong need to improve data quality for the monitoring and reporting of pollution in air, water and soil. In addition, comparability and robustness of measurements are often compromised by lack of suitable traceability chains and appropriate quality controls. Thus, laboratories performing sampling and tests in this field are regulated by respective authorities, and need matrix certified reference materials (CRMs) for appropriate quality controls as well as to ensure long term comparability of the data.

For the determination of either stable or radioactive polluting elements in the environment, fast, sensitive and inexpensive analytical procedures are needed. Many of the measurement principles in chemical analysis are on molar bases and some are isotope selective. Conversion from mass fraction to amount content requires knowledge of isotopic composition. The determination of isotope ratios is highly important in establishing traceability in quantitative elemental analysis by the method of isotope dilution which is widely considered as a primary method. As the isotopic compositions of elements do vary in nature due to several processes, including radioactive decay, biological mass fractionation, cosmic ray spallation and mass-independent fractionation, isotope ratio data plays a fundamental role in earth and environmental sciences. Despite its importance, the SI-traceability of isotope amount ratios is realised only very rarely, and its establishment remains a critical and highly demanding task in all areas concerning the pollutants mentioned above. This situation caused the CCQM to demand a ‘traceability exception related to delta scale isotope ratio measurements’ from the CIPM [7]. Such delta scale measurements in most cases are based on iRMs without SI-traceable isotopic composition, in other words artefacts. Most iRMs from artefacts containing different isotopes of the same element are inhomogeneous, are running out of stock or are hypothetical materials. Therefore, SI traceable matrix matched reference materials are needed [8].

The project aimed at the production and certification of a new seawater reference material for selected isotopes of environmentally relevant elements covering the mass range of elements while improving our understanding of mass fractionation behaviour across different atomic masses. Because these types of measurements require specific capabilities and only a limited number of institutes can provide reliable absolute isotope ratio data. Combined with constraints in available traceability sources, the range of elements and measurands selected for certification was intentionally kept limited. Seawater is one of the most challenging matrices for ICP techniques as it contains high amount of salt, which requires matrix separation for accurate and reliable measurements. The mass fraction ranges of the target elements and the measurands selected for certification in the seawater reference material are given in Table 1.

Table 1. The mass fraction range of the target elements and the measurands selected for certification in seawater reference material.

Element	*Mass fraction range, µg/kg*	*Measurand, mol/mol*
B	5000 - 6000	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$
Li	140 - 170	$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$
Cd	10 - 15	$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$ $n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$
Cr	12 - 18	$n(^{53}\mathrm{Cr})/n(^{52}\mathrm{Cr})$
Ni	10 - 16	$n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$
Pb	6 - 8	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$
Sb	5 - 10	$n(^{123}\mathrm{Sb})/n(^{121}\mathrm{Sb})$
U	3 - 5	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$

2.1 Certification of CRM

The certification of CRM was realized under WP4 by the coordination of TÜBİTAK UME in accordance with the requirements of ISO 17034. Isochronous design was used for the stability and homogeneity studies where measurements were carried out by project partners contributing to WP4. Seawater is one of the most challenging matrices due to high salt content and usually requires matrix separation before introduction to instrument. The methods developed in WP2 of this project were used by the project partners in the certification measurements. Due to difficulties encountered during matrix separation, some measurements took longer time than expected. The characterisation of the materials were conducted by an interlaboratory study with participation of external laboratories which are experienced in the field of precise isotopic measurements. The certified values and associated uncertainties are given in Table 2.

Table 2. Certified values and associated uncertainties with its uncertainty components

Parameter	**Certified Value, mol/mol**	U_{CRM}, **mol/mol**	***Coverage Factor***	$U_{CRM,rel}$ **%**	$u_{char,rel}$ **%**	$u_{bb,rel}$ **%**	$u_{lts,rel}$ **%**	$u_{sts,rel}$ **%**
$n(^{11}\text{B})/n(^{10}\text{B})$	4.2041	0.0061	2.03	0.15	0.062	0.018	0.024	0.018
$n(^{114}\text{Cd})/n(^{110}\text{Cd})$	2.30378	0.00098	2.03	0.043	0.019	0.0047	0.0059	0.0050
$n(^{114}\text{Cd})/n(^{111}\text{Cd})$	2.24559	0.00084	2.02	0.037	0.015	0.0061	0.0045	0.0079
$n(^{6}\text{Li})/n(^{7}\text{Li})$	0.07972	0.00042	2.20	0.53	0.24	0.0088	0.013	0.0084
$n(^{204}\text{Pb})/n(^{206}\text{Pb})$	0.05502	0.00019	2.13	0.35	0.034	0.060	0.082	0.12
$n(^{207}\text{Pb})/n(^{206}\text{Pb})$	0.8572	0.0025	2.10	0.29	0.016	0.059	0.079	0.095
$n(^{208}\text{Pb})/n(^{206}\text{Pb})$	2.0995	0.0050	2.13	0.23	0.022	0.044	0.056	0.080
$n(^{234}\text{U})/n(^{238}\text{U})$	0.0000626	0.0000012	2.10	1.9	0.89	0.093	0.13	0.083
$n(^{235}\text{U})/n(^{238}\text{U})$	0.007252	0.000012	2.1	0.17	0.077	0.013	0.011	0.016

In addition to the certified parameters, nickel isotope ratio measurements took part in the certification study as an informative value. According to the aforementioned standards and the RM producer quality policies, parameters with limited number of characterisation data may be provided to customers as an informative parameter. Thus, nickel isotope ratio was provided as informative value because of the limited number of characterisation measurements as well as stability and homogeneity tests. One participant managed reporting isotopic ratio values for $n(^{60}\text{Ni})/n(^{58}\text{Ni})$. Despite the inability to cross check the reported value, the value was acknowledged to be an informative parameter as very limited matrix reference materials are available for Ni isotope ratio The data are given in Table 3.

Table 3. The informative value and associated measurement uncertainty for $n(^{60}\text{Ni})/n(^{58}\text{Ni})$ reported by LGC

Measurand	**Informative Value, mol/mol**	U, **mol/mol**	U_{rel} **%**	u_{char_rel} **%**
$n(^{60}\text{Ni}/n(^{58}\text{Ni})$	0.38833	0.00060	0.16	0.076

The details of the whole certification is given in the certification report for the stable isotope ratios in seawater that is given as Annex 1 to this D7 report.

3 Conclusions

During the life time of the project, the majority of the isotope ratios of B, Cd, Li, Pb and U given in Table 1 have successfully been certified within the limits of target uncertainties aimed at the beginning of the project. A collaborative study conducted with the involvement of project partners produced the seawater CRM for isotope ratios of elements having environmental concern. The total number of units produced are 470. Approximately one third of the whole batch is used during the certification studies. The material will be useful for the reliability of the measurements related to tracing the environmental pollutants. Although in the proposed list, Cr

($n(^{53}Cr)/n(^{52}Cr)$) and Sb ($n(^{123}Sb)/n(^{121}Sb)$) could not be certified due to the difficulties encountered during high salt content of matrix separation, and the lack of traceable isotopic standards, respectively. A follow up project can be conducted in the future to certify these elements or other elements in the same material.

The certified reference material can be used as QC material for validation of the methods, including trueness, for measurements of isotope ratios in seawater matrices. The material is suitable for checking the sample preparation processes prior to stable isotopic measurements.

4 References

[1] ISO 17034:2016 General requirements for the competence of reference material producers, 2016

[2] ISO 33405 Reference Materials – Approaches for characterization and assessment of homogeneity and stability, 2024

[3] Annex 2 of the JRP 21GRD09 MetroPOEM “Metrology for the Harmonisation of Measurements of Environmental Pollutants in Europe”

[4] JCGM 100, Evaluation of measurement data — Guide to the expression of uncertainty in measurement, September 2008, BIPM

[5] P.G. Falkowski, The role of phytoplankton photosynthesis in global biogeochemical cycles, Photosynth. Res. 39 (1994) 235–258. doi:10.1007/BF00014586

[6] J.H. Martin, Glacial-Interglacial CO2 Change: The Iron Hypothesis, Paleoceanography. 5 (1990) 1–13.

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https://www.bipm.org/documents/20126/34439501/CIPM2015-I-EN.pdf/58ff6e3f-47f5-a230-4194-e2a23667e6da

[8] Willi A. Brand, Tyler B. Coplen, Jochen Vogl, Martin Rosner and Thomas Prohaska, Assessment of international reference materials for isotope-ratio analysis (IUPAC Technical Report), Pure Appl. Chem. 2014; 86(3): 425–467.

5 Appendix 1 – Certification Report for Stable Isotope Ratios in Seawater (UME MetroPOEM CRM)

Stable Elements in Seawater
UME MetroPOEM CRM

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Date
28.11.2025

Assoc. Prof. Mustafa ÇETİNTAŞ
Director

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ABBREVIATIONS

α	Significance level
ANOVA	Analysis of variance
CCQM	Consultative Committee for Amount of Substance
CIPM	International Committee for Weights and Measures
CRM	Certified reference material
GUM	Guide to the expression of uncertainty in measurement
HDPE	High density polyethylene
HR-ICP-MS	High resolution inductively coupled plasma mass spectrometer
ICP-MS	Inductively coupled plasma mass spectrometer
ICP-MS/MS	Tandem ICP-MS
ID-ICP-MS	Isotope dilution ICP-MS
iRM	Isotopic reference material
iCRM	Isotopic certified reference material
ISO	International Organization for Standardization
k	Coverage factor
LDPE	Low density polyethylene
LTS	Long-term stability
MC-ICP-MS	Multi Collector ICP-MS
$MS_{between}$	Mean square between-bottle from ANOVA
MS_{within}	Mean square within-bottle from ANOVA
n	Number of replicates per unit
PFA	Perfluoroalkoxy
PTFE	Polytetrafluoroethylene
PVDF	Polyvinylidene fluoride
QQQ-ICP-MS	Triple quadrupole ICP-MS
ρ	Mass concentration
RSD	Relative standard deviation
RSS	Random stratified sampling
s	Standard deviation

s_{bb}	Between-bottle standard deviation
SI	International System of Units
STS	Short-term stability
s_{wb}	Within-bottle standard deviation
u_{bb}	Standard uncertainty related to possible between-bottle heterogeneity
u^*_{bb}	Standard uncertainty of heterogeneity that can be hidden by method repeatability
UME	TÜBİTAK National Metrology Institute of Türkiye
u_{char}	Standard uncertainty related to characterisation
u_{lts}	Standard uncertainty related to long-term stability

The subscript "rel" is added when a variable is expressed in relative terms (e.g. as percent)

ABSTRACT

This report describes the production of UME MetroPOEM CRM, a seawater material certified for the isotope amount ratios of selected elements: B, Cd, Li, Ni, Pb and U. The certified reference material was produced following the requirements of ISO 17034 standard [1]. The collection of starting material, 250 L of seawater, was conducted at the station UE67, which was located at the edge of German EEZ in the North Sea (55° 25’ N; 4° 5’ E). The sample was filtered before filling into pre-cleaned 25 L HDPE carboys and then acidified using sub-boiled HNO_3 for the stabilisation. The carboys were sealed and individually packed in clean PE foil, and stored at +4 °C until transport to Hereon and then to TÜBİTAK UME for further processing. After preliminary analysis, the material was spiked with the elements whose mass fractions were below the target concentrations to obtain the material having suitable concentrations to be measured in standard analytical laboratories. After filling into pre-cleaned 250 mL HDPE bottles, the material was sterilized with 25 kGy γ-radiation by ^{60}Co source. Between-unit homogeneity and stability during dispatch and storage conditions were assessed in accordance with ISO 33405 standard [2] by 21GRD09 MetroPOEM Project [3] partners who are involved in the measurements. The characterisation was conducted by an interlaboratory study where, in addition to the project partners, several expert laboratories were also involved in isotope ratio measurements. Uncertainties of the characterisation measurements were estimated in accordance with the Guide to the Expression of Uncertainty in Measurement (GUM) [4]. Certified values include uncertainties arising from possible inhomogeneity, instability and characterisation measurements. The material is intended to be used for calibration or quality control purposes in laboratories performing isotope ratio measurements.

INTRODUCTION

Measurement capabilities have become important as water matrices need to be evaluated for compliance with the countries' own quality standards. It is well known that systematically monitoring useful parameters such as contaminants and keeping them under control directly affect the quality of life. Besides, the importance of air and soil quality, water quality is also quite important for Earth. Understanding the dynamics of ocean life has become crucial over the last decade as oceans covering about two-thirds of Earth (70 %) and they are the main reservoir of CO_2 and have a notable role in the global carbon cycle [5,6]. Countries with coastal borders have to follow well established regulations to help those mechanisms and keep environmental pollution under control by performing routine analyses. However, as the necessity of monitoring trace elements in seawater is well established, the challenges of these measurements have raised the topic for the last few decades. There is a strong need to improve data quality for the monitoring and reporting of pollution in air, water, and soil. In addition, comparability and robustness of measurements are often compromised by a lack of suitable traceability chains and appropriate quality control. Thus, laboratories performing sampling and tests in this field regulated by respective authorities, need matrix certified reference materials (CRMs) for appropriate quality controls as well as to ensure long term comparability of the data.

For the determination of polluting elements either stable or radioactive in the environment, fast, sensitive and inexpensive analytical procedures are needed. Many of the measurement principles in chemical analysis are on molar bases and some are isotope selective. Conversion from mass fraction to amount content requires knowledge of isotopic composition. The determination of isotope ratios is highly important in establishing traceability in quantitative elemental analysis by the method of isotope dilution which is widely considered as a primary method. As the isotopic compositions of elements do vary in nature due to several processes, including radioactive decay, biological mass fractionation, cosmic ray spallation, and mass-independent fractionation, isotope ratio data plays a fundamental role in Earth and environmental sciences. Despite its importance, the SI-traceability of isotope amount ratios is realised only very rarely, and its establishment remains a critical and highly demanding task in all areas concerning the pollutants mentioned above. This situation caused the CCQM to request a 'traceability exception related to delta scale isotope ratio measurements' from the CIPM [7]. Such delta scale measurements in most cases are based on iRMs without SI-traceable isotopic composition, in other words artefacts. Most iRMs from artefacts containing different isotopes of the same element are inhomogeneous, are running out of stock or are hypothetical materials. Therefore, SI traceable matrix matched reference materials are needed [8].

The measurement of isotope ratios underlies significant fractionation during the measurement. Most fractionation effects are mass-dependent. Therefore, calibration for such effects is a prerequisite and usually performed with solutions containing the analyte element with known isotopic composition. However, analytical protocols demand for matrix CRMs. This is especially important in fields such as tracing pollutants. In addition to the fact that single-certified reference materials for isotope measurements of different elements are still not sufficiently available, matrix CRMs that would enable the validation of analytical methods developed for measurements of different matrices are not yet available and represent a major requirement for the accurate monitoring of environmental pollution. Nevertheless, these reference materials are urgently needed to calibrate mass spectrometric measurements, due to mass bias effects occurring during the measurements in mass spectrometers.

With the developments in the sensitivities of mass spectrometric instrumentation, even very small variations in the isotopic composition of most elements can be reliably detected. Yet realising these new capabilities in full remains a significant challenge for an analyst due to a vast number of analyte/matrix combinations, concomitant matrix effects, spectral interferences and instrumental isotopic fractionation causing a measurement bias. Therefore, success in developing new and improved methods for stable and long-lived radiogenic isotope ratio measurements by mass spectrometry with uncertainties sufficient to resolve natural mass-dependent isotope fractionation is a major determinant of further progress. Several elements suitable as model systems for the development and optimisation of measurement procedures include Li, B, Cr, Cd, Ni, Sb, Pb and U.

The orientation document issued by EURAMET's Technical Committee for Ionising Radiation and the European Metrology Network (EMN) on Radiation Protection clearly describes a metrological need for a project focusing on the 'traceability of radionuclide concentration measurements in the environment'. This topic refers to the classification of the Green Deal "A zero-pollution ambition for a toxic-free environment" and is in line with Chapter VIII – Public Exposure of the Council Directive 2013/59/Euratom of 5 December 2013 laying down basic safety standards for protection against the dangers arising from exposure to ionising radiation. There is a need for increasing the use of mass spectrometric techniques for measurements of both radioactive and non-radioactive pollutants in monitoring laboratories. However, this will require increased access to certified reference materials that are traceable to the SI.

National metrology institutes and designated institutes, as well as other organizations with high level expertise in measurement capabilities are needed for the production and certification of reference materials. The joint research project 21GRD09 MetroPOEM "Metrology for the Harmonisation of Measurements of Environmental Pollutants in Europe" [3] in the frame of European Partnership in Metrology (EPM) developed capacity to produce CRMs for environmental analysis by transferring the theoretical and practical know-how between the partners and combining their skills to focus on both development of measurement methods and production of CRMs to be used for providing traceability and as quality control materials for isotope ratio measurements.

The project aimed at the production and certification of a new seawater reference material for isotopes of selected environmentally relevant elements covering as much of the periodic table as possible while improving our understanding of mass fractionation behaviour across different atomic masses. Because these types of measurements require specific capabilities and only a limited number of institutes can provide reliable absolute isotope ratio data, combined with constraints in available traceability sources, the range of elements and measurands selected for certification was intentionally kept limited. Seawater is one of the most challenging matrices for ICP techniques as it contains high amount of salt, which requires matrix separation for accurate and reliable measurements. The mass fraction ranges of the target elements and the measurands selected for certification in the seawater reference material are given in Table 1.

Table 1. The mass fraction of the target elements and the measurands selected for certification in seawater reference material.

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Sb	5 - 10	$n(^{123}\mathrm{Sb})/n(^{121}\mathrm{Sb})$
U	3 - 5	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$

This report describes the production of UME CRM MetroPOEM, a seawater material certified for the isotope amount ratios of selected elements: B, Cd, Li, Cr, Ni, Pb and U. The production and certification of reference material UME CRM MetroPOEM was performed in accordance with ISO 17034 [1] and ISO 33405 [2] using the infrastructure of TÜBİTAK UME and a collaborative study between the partners of the project and additional external participants to the characterisation study. Uncertainties of the characterisation measurements were estimated in accordance with the *Guide to the Expression of Uncertainty in Measurement* (GUM) [4]. Target concentration level of each element was decided to meet the laboratories needs and measurement capabilities. The target elements were selected among those to represent the whole range of the periodic table as well as the availability of the measurement techniques and sources of traceability issues.

PARTICIPANTS

The production plan for processing and certification of the reference material was prepared and coordinated by TÜBİTAK UME which is the leading institute for the relevant work package in the project. Sampling of seawater and the preliminary mass fraction measurements were performed by the Helmholtz Zentrum Hereon. The processing of the raw material was done at TÜBİTAK UME premises using the reference material infrastructure. The material is dispatched to the project partners or external partners involved in the measurements. The participants and their contributions to the certification are presented in Table 2. The homogeneity and stability measurements were shared by participants who have the capability of measuring isotope ratio measurements by MC-ICP-MS. The characterisation measurements were performed by an interlaboratory study between project partners as well as external partners who are experienced in high precision isotope ratio measurements.

Table 2. The laboratories/organisations and their contributions

Laboratory/Organization	**Contribution**
TÜBİTAK UME (Gebze, Türkiye)	CRM Production Project Management, Material Processing and Certification
Physikalisch-Technische Bundesanstalt (PTB) (Braunschweig, Germany)	Homogeneity, short-term stability, long-term stability and characterisation measurements
Bundesanstalt für Materialforschung und – prüfung (BAM) (Berlin, Germany)	Homogeneity, short-term stability, long-term stability and characterisation measurements
Jožef Stefan Institute (JSI) (Ljubljana, Slovenia)	Homogeneity, short-term stability, long-term stability and characterisation measurements
LGC Limited (LGC) (Teddington, UK)	Characterisation measurements
Helmholtz-Zentrum Hereon GmbH (Hereon) (Geesthacht, Germany)	Sampling, preliminary analysis, and homogeneity, short-term stability, long-term stability and characterisation measurements
Montanuniversität Leoben (MUL) (Leoben, Austria)	Homogeneity, short-term stability, long-term stability and characterisation measurements
Institutt for Energiteknikk (IFE) (Kjeller, Norway)	Characterisation measurements
Aarhus Universitet (AU) (Aarhus, Denmark) University of Gothenburg (UGOT) (Gothenburg, Sweden)	Characterisation measurements
Danmarks Tekniske Universitet (DTU) (Roskilde, Denmark)	Characterisation measurements
National Metrology Institute of China (NIM) (Beijing, PRC)	Characterisation measurements
Imperial College London (ICL) (London, UK)	Characterisation measurements
University of Warsaw (UW) (Warsaw, Poland)	Characterisation measurements
Agilent United Kingdom (AUK) (Cheshire, UK)	Characterisation measurements

SAMPLING AND PROCESSING OF SEAWATER

Preparation of the sampling material

The equipment for ultra-trace seawater analysis for trace metals was prepared in accordance with e.g. GEOTRACES procedures [9] and internally approved and validated protocols for trace analysis in seawater. All materials were prepared in advance to prevent any contamination. New 25 L HDPE carboys specified for food applications were used for the sample storage of the large seawater sample. The carboys were flushed three times with DI water before they were filled with ultrapure water from Millipore Milli-Q® purification system containing 1.0 % (V/V) sub-boiled HCl and then kept for one week to leach possible contaminants. Then, the carboys were rinsed three times with ultrapure water. This treatment with 1.0 % HCl (V/V) was repeated once more and then the carboys were rinsed three times with ultrapure water. The cleaning procedure was repeated twice with 1.0 % (V/V) HNO_3 in place of 1.0 % (V/V) HCl. Finally, they were flushed three times with ultrapure water and then dried in a cleanroom (Class 7) before sealing and packaging for shipment.

The Pall AcroPak 1500 0.8/0.2 µm filters were cleaned three times by flushing with 1.2 mol/L HCl and storing them acid filled overnight. Afterwards, they were flushed several times with ultrapure water until the typical pH of the ultrapure water was achieved. Then, they were stored in ultrapure water until their use on the ship. Prior to use, the filter was flushed with at least 2 L of seawater to remove remaining ultrapure water as well as to condition the filtration membrane.

All tubings as well as the clean seawater sampling system was operated throughout the entire sampling day continuously to ensure constant flushing the system with fresh seawater before collecting the final sample.

Sampling location

The sampling was conducted as part of the regular monitoring research cruise AT 020, starting from Bremerhaven, Germany between 15-26 May 2023 with the RV ATAIR (Figure 1) operated by the German BSH covering the entire German EEZ as shown on the map presented in Figure 2. The sampling for the larger volume water samples was conducted at station UE67, which is located at the edge of the German EEZ. The salinity map of the sampling zone at dept of 5 m is shown in Figure 3.

Figure 1. ATAIR in Bremerhaven, Germany, before the start of the sampling campaign

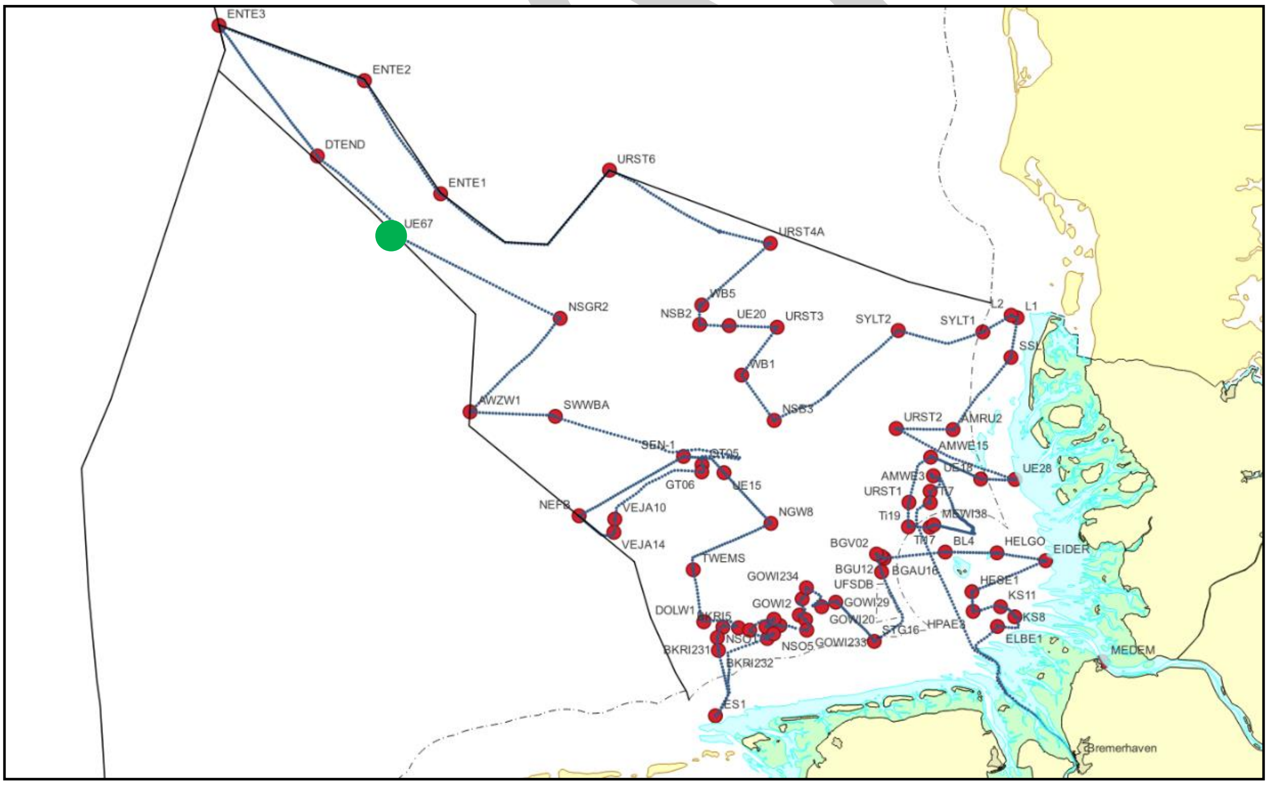

Figure 2. Route of the sampling cruise AT020. The sampling location UE67 is marked with green dot (●).

Sampling procedure

The water was sampled using the trace metal clean PVDF seawater inlet system on board of the German research vessel ATAIR. The water was pumped from a depth of 5 m below sea level directly into 25 L acid cleaned carboys through a filter to obtain the dissolved metal fraction. Pre-cleaned trace metal free filter cartridges (Pall AcroPak 1500 0.8/0.2 µm) were used for on-line filtration of the sample (Figure 3). Before collecting the sample, each pre-cleaned carboy was rinsed three times with ca. 1 L of seawater filtrate to precondition the surface of the carboy. In total two filter units were necessary to process the total volume of ca. 250 L seawater. After filling the carboys with sample, they were closed tightly, and the outside of each carboy was rinsed with ultrapure water to remove any spilled seawater from the surface. All additional handling was performed inside the trace metal analysis container of the BSH to prevent contamination.

Figure 3. Direct filtration of sampled seawater using Pall AcroPak 1500 0.8/0.2 µm filters

Material preservation and storage

The filtered raw material was acidified using 2 times sub-boiled HNO_3 to stabilize the material. The carboys were sealed and individually packed in clean PE foil and stored at +4 °C until their further transport to Hereon and subsequently to TÜBİTAK UME.

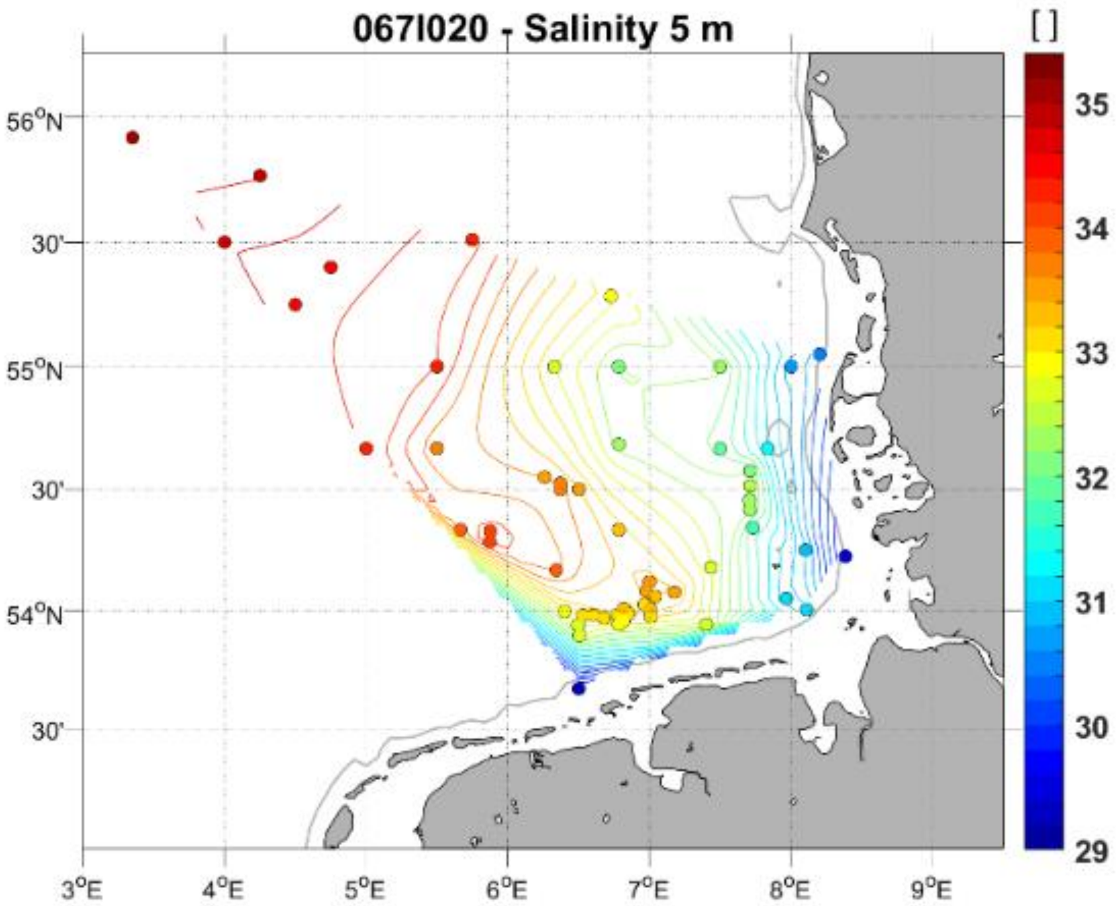

Figure 4. Salinity (g/kg) measured at a depth of 5 m at different sampling locations

Preliminary analysis

After the transport to the Hereon laboratory, 50 mL of seawater subsamples from each carboy were taken under cleanroom conditions to allow a preliminary analysis of the total dissolved trace metal content of the individual water samples. The aim was to determine the initial concentration as well as between carboy variations. The analysis has been carried out using an ESI seaFASTSP2 coupled to Agilent 8900 triple quad ICP-MS/MS using a He/H_2 mixed gas mode [10]. The results of the measurements of the raw material in individual carboys are given in Table 3. Then 125 L of collected seawater were transferred to TÜBİTAK UME for further processing including spiking, homogenisation and bottling.

Table 3. The natural mass concentrations of target elements in raw seawater material

ρ_i / (µg/L)	**B**	**Cd**	**Cr**	**Li**	**Ni**	**Pb**	**Sb**	**U**
Carboy-1	5200	0.0149	< 0.30	155	0.28	0.17	0.08	2.31
Carboy-2	5500	0.0146	< 0.30	154	0.23	0.11	0.13	2.38
Carboy-3	5600	0.0152	< 0.30	161	0.25	0.10	0.14	2.45
Carboy-4	5200	0.0150	< 0.30	151	0.25	0.11	0.17	2.28
Carboy-5	5700	0.0154	< 0.30	170	0.24	0.09	0.12	2.40
Carboy-6	5900	0.0154	< 0.30	171	0.27	0.13	0.16	2.44
Average	***5500***	***0.0151***	***< 0.30***	***160***	***0.25***	***0.12***	***0.13***	***2.38***
s	***280***	***0.003***	***-***	***9***	***0.02***	***0.03***	***0.03***	***0.07***
%RSD	***5.1***	***2.1***	***-***	***5.3***	***7.3***	***24***	***24***	***2.9***

Spiking the material

In order to assure the concentrations of the elements in the seawater is fit for purpose for the measurements by the standard laboratories, the concentrations present originally in the raw material has been determined and the results have been evaluated by the project consortium. It has been decided to spike the material for those elements having very low levels to ensure the fit for purpose of the material for being measured at standard laboratories. These elements are Cd, Cr, Ni, Pb and Sb. For spiking, NIST 3100 series single element standard calibration solutions with natural isotopic distributions were used. The spiking was done gravimetrically in order to obtain target concentration values which were agreed by the project consortium. To avoid any loss of the elements due to coprecipitation when mixing at elevated concentrations, step by step mixing was used. First, single element standards having nominal concentrations were diluted 50 times using the seawater material to ensure no precipitation occurs in the seawater at these concentrations of about 200 mg/kg. Then, these solutions were used as intermediate solution from which the needed amounts were weighed and added to one of the 25 L carboy which was shaken in a circular homogenizer. After adequate mixing time and homogenization, the contents of the 25 L carboy was transferred to mixing tank for the whole batch and mixed with the rest of the seawater to obtain predetermined target concentrations. Then the whole batch is homogenized thoroughly in a drum where a mixing is provided by using a vertical axis mixer with PFA coated propeller.

Table 4. The mass fractions of the elements in raw and certified reference materials

Element	***Mass fraction in Raw Material***[#] ***in µg/kg***	***Mass fraction after spiking in µg/kg***
B	5400	5400[#] (Natural Level)
Cd	0.015	12.5[*]
Cr	< 0.30	15.6[*]
Li	160	150[#] (Natural Level)
Ni	0.25	13.4[*]
Pb	0.11	7.3[*]
Sb	0.13	9.4[#]
U	2.3	2.3[#] (Natural level)

[*] Determined by ID-ICP-MS by single laboratory

[#] Determined by ESI seaFASTSP2 ICP-MS/MS by single laboratory

Cleaning the materials used in homogenisation and bottling

The materials used during the homogenisation of the whole batch and getting in contact with the seawater material were all subjected to acid cleaning procedure. A new 125 L HDPE drum, which was used to homogenize the whole batch, was first flushed with tap water and then filled with ultrapure water. It was subsequently filled with ~5.0 % (*V/V*) analytical grade HNO_3 and stored under this condition for two months. Afterwards, the drum was rinsed with ultrapure water several times and then filled with 1.0 % (*V/V)* sub-boiled HNO_3 and kept for one month to leach potential contaminant elements from the surfaces. At the end of this period, to ensure the effectiveness of the cleaning protocol, three subsamples of final 1.0 % (*V*/*V*) sub-boiled HNO_3 were measured by using HR-ICP-MS. Finally, the drum was rinsed again and filled with deionized water and kept for one week prior to use.

To verify the cleanliness of Nalgene Certified Low Particulate Narrow-Mouth HDPE bottles, 36 bottles were tested, representing six randomly selected samples from each batch of six boxes (72 bottles per box). To accelerate the extraction/leach of the analytes from the interior surfaces of the bottles, the bottles filled with 5.0 % (*V/V*) sub-boiled HNO_3 were subjected to at 60 °C for four weeks. HR-ICP-MS measurements of target analytes allowed for the assessment of potential contamination from the bottles. The evaluation of the measurement results confirmed the suitability of the bottles for being used as containers of samples at trace-level analysis. As a result of this systematic analysis performed on randomly selected vials, it was determined that the analytes targeted for certification were well below the target levels (< 100 ng/L). Therefore, the bottles were only rinsed with ultrapure water in an ISO 6 laboratory and dried in an ISO 4 class to be prepared for production.

Homogenisation and bottling

The entire processing of seawater reference material, including spiking, homogenisation, and filling into bottles, was conducted in the ISO 6 Clean Chemical Laboratory at TÜBİTAK UME. Approximately 125 L of raw material were transferred to a 125 L HDPE drum. Following the spiking process, the seawater underwent a four-hour homogenisation, and subsequently, the entire water content was filtered from one drum to another drum using a 0.8/0.2 µm (Pall Corp, Supor® Membrane, AcroPackTM 1000). The manual bottling was done in the clean environment and resulted in a total of 470 bottles each containing 250 mL seawater. Thereafter, all bottles were labelled and numbered according to the filling order. For the inhibition of any biological activity, the units were sterilized by 25 kGy γ-radiation by ^{60}Co source. All of the units were stored at a reference temperature of +4 °C.

HOMOGENEITY

Establishing the equivalence between the various units is a key requirement for a certified reference material according to ISO 17034 standard [1]. Both within-unit and between-unit variations contribute to the uncertainty of the certified value. For single phase liquid samples, where homogeneous mixing within the bottle is maintained easily, within unit inhomogeneity is not a critical concern. A sample intake amount which is suitable for the method used for the certification measurements can be accepted as the minimum amount to be used safely even though the smaller sample sizes would also be possible for many methods, except the extreme subsampling cases. However, the uncertainty contribution from within-unit heterogeneity becomes significant, especially in the case of solid materials which mainly depend on the amount of subsample taken for each replicate analysis, and the particle size of the material. Therefore, in this certification project, when evaluating the uncertainty arising from inhomogeneity of the material, only between-unit variations is considered and added to the calculation of the certified value.

According to the ISO 17034, the homogeneity of the reference material should be determined by a number of selected units corresponding to approximately cubic root of total number of the produced batch with a minimum limit of ten units. Therefore, ten bottles were needed for the evaluation of uncertainty arising from inhomogeneity. A different approach has been used in this project when designing the homogeneity measurements. Since the measurements were very challenging, laborious, time consuming and required matrix separation at large sample amounts, a combined design for the homogeneity measurements and stability measurements was used. In this project, four points in time (three, six, nine and twelve month) were selected as the test point for long-term stability at a single temperature, +21 °C, and at each point in time two units were tested. Additional four units were stored directly at +4 °C condition which serves as the reference condition, at which the sample is considered to be stable with the supporting evidence from previous experiences. The total number of units chosen for testing long-term stability was twelve, which were selected by using random stratified sampling (RSS) scheme generated using the TRaNS software developed by TÜBİTAK UME. All the results for each measurand from these twelve bottles served to evaluate both homogeneity and the long-term stability of seawater reference material for eah partner.

The evaluations were based on the isotopic ratio measurements and each measurand was measured by one of the project partners participating in the homogeneity-LTS measurements. The elemental concentrations of elements in seawater were also measured by Hereon to assess the stability of the elements assuming that no change in the concentration means no change in the isotopic values. However, these values are found to be not appropriate for the assessment of homogeneity of an isotopic CRM as the uncertainty of the mass fraction measurements is much higher than isotope ratio measurements. The institutes that participated in the measurement of isotope ratios are given in Table 5 together with the corresponding measurand.

Table 5. The institutes and the unit numbers used for homogeneity, long-term stability and short-term stability test measurements

Partner	***Measurand***	***Unit numbers used for homogeneity and LTS assessment***		***Units subjected to STS test temperature, +45 °C***
		Units kept at ref. conditions for both LTS and STS, +4 °C	***Units subjected to LTS test temperature, +21 °C***	
BAM	n(^{11}B)/n(^{10}B)	49, 156, 249, 395	14, 440, 105, 166, 287, 417, 207, 348	15, 304
BAM	n(^{7}Li)/n(^{6}Li)			
JSI	n(^{114}Cd)/n(^{110}Cd) n(^{114}Cd)/n(^{111}Cd) n(^{110}Cd)/n(^{111}Cd)	59, 143, 250, 360	3, 446, 83, 161, 289, 434, 205, 319	209, 399
MUL	n(^{204}Pb)/n(^{206}Pb) n(^{207}Pb)/n(^{206}Pb) n(^{208}Pb)/n(^{206}Pb)	77, 144, 239, 388	37, 445, 80, 172, 288, 406, 213, 337	229, 286
Hereon	n(^{204}Pb)/n(^{206}Pb) n(^{207}Pb)/n(^{206}Pb) n(^{208}Pb)/n(^{206}Pb) Mass fractions of Cd, Cr, Li, Ni, Pb, Sb, U	52, 152, 260, 358	7, 468, 113, 194, 309, 427, 236, 317	145, 251
PTB	n(^{234}U)/n(^{238}U) n(^{235}U)/n(^{238}U)	44, 138, 243, 393	39, 473, 108, 181, 303, 402, 232, 350	8, 282

During the measurements for obtaining each data set for assessing the between bottle homogeneity and stability of each element, the participants were asked to make three sub-samples for each unit. Multi-collector ICP-MS instruments were used for isotope ratio measurements to obtain the possible lowest uncertainty contribution from homogeneity and stability testing. During the measurements, a randomized order of introduction to the instrument was applied in order to check if there is a trend in analytical or filling order except Pb measurements by Hereon.

The data set for all parameters were evaluated statistically in the following order:

a) Regression analysis to evaluate potential trends in each analytical run at 95 % and 99 % confidence level.

   The analytical sequence is designed in such way that it is not correlated with the filling order. In that case, if a trend occurs at the confidence level of 95 % during the measurements it can be corrected according to the following Equation (1):

$$\boldsymbol{C_{Corrected} = C_{Measured} - b \cdot i} \quad (1)$$

where;

b : slope of the linear regression,

i : position of the result in the analytical sequence.

b) Regression analysis to evaluate potential trends in filling sequence order at 95 % and 99 % confidence level.
c) Datasets were checked for individual results and unit outliers at 95 % and 99 % confidence level using Grubbs outlier test.
d) As the unimodal distribution of data is a prerequisite to apply the statistical evaluation one-way analysis of variance (ANOVA), the distribution of individual results was checked for both normal distribution via a normal probability plot, Shaphiro-Wilk test and unimodality with a histogram.

Uncertainties of homogeneity between units were evaluated with one-way ANOVA.

Equation (2) is used for repeatability of method (s_{wb}) and Equation (3) is used for the calculation of standard deviation between units (s_{bb}).

$$\boldsymbol{s_{wb} = \sqrt{MS_{within}}} \quad (2)$$

where;

$\boldsymbol{MS_{within}}$: mean of square of variance within the unit,

$\boldsymbol{s_{wb}}$: $\boldsymbol{s}$ of the method as long as sub-samples represent the whole unit.

$$\boldsymbol{s_{bb} = \sqrt{\frac{MS_{between} - MS_{within}}{n}}} \quad (3)$$

where:

$\boldsymbol{MS_{between}}$: mean of square of variance between units,

$\boldsymbol{n}$: number of replicates per unit.

The occurrence of $\boldsymbol{MS_{between}} < \boldsymbol{MS_{within}}$ for some elements demonstrates that material heterogeneity is smaller than the detection limit. In these cases, since $\boldsymbol{s_{bb}}$ cannot be calculated, $\boldsymbol{u_{bb}^{*}}$ is calculated as heterogeneity contributing to uncertainty including method repeatability using Equation (4).

$$\boldsymbol{u_{bb}^{*}} = \frac{\boldsymbol{s_{wb}}}{\sqrt{\boldsymbol{n}}} \sqrt[4]{\frac{\boldsymbol{2}}{\boldsymbol{n_{MS_{within}}}}} \qquad (4)$$

where:

$\boldsymbol{n_{MS_{within}}}$: degrees of freedom for $\boldsymbol{MS_{within}}$

The data for each measurand was evaluated using the Excel template produced by TÜBİTAK UME for the distribution of data, whether normal/unimodal. Single- and double-sided Grubb's outlier tests were applied if there is a need for any data rejection. The results are summarised in Table 6. For all the measurands, at least one outlier is identified in the data sets except for $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ for which the data distribution is found to be not a normal distribution. For the other measurands where outliers are identified, the distribution of data became a normal distribution when the outliers are excluded from the data sets. The calculation of uncertainty values was done for both including and excluding outliers and the results are given in Table 6. In all cases the relative uncertainty values are below 0.1 %, except for $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$ for which the ratio value is farthest to unity meaning that one of the isotope signal is challenging. For $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ the data set contained two outliers on both ends and there appeared another outlier when the calculation was repeated when these two outliers were excluded. Since including or excluding outliers did not affect the final uncertainty, all data were retained for calculating the uncertainty arising from material inhomogeneity. For all isotopes of B and Pb, between unit standard deviation is found to be smaller than within unit standard deviation ($\boldsymbol{MS_{between}} < \boldsymbol{MS_{within}}$). In these cases, $\boldsymbol{u_{bb}^{*}}$ is used for the calculation of uncertainty due to between unit inhomogeneity of the sample. The Pb isotope ratio values determined by Hereon were obtained by only one replicate measurement from each bottle but increased number of repetitive measurements, it is used as supporting homogeneity value for Pb isotopes. As given in Table 7, these uncertainties were even lower than those determined by MUL. The plotted data used for the evaluation of homogeneity are presented in Annex 1.

Table 6. Summary of the results for statistical evaluation of homogeneity data

Isotope ratio	*Significance of the trend on a 95 % confidence level*		*Number of outliers (95 % confidence level)*		*Distribution ($\alpha = 0.05$)*	*Note*
	Analytical Sequence	*Filling Sequence*	*Individual Results*	*Unit*	*Individual results*	
$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	-	-	1	-	Normal/Unimodal	-
$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	-	-	-	-	Normal/Unimodal	1
$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$	-	-	1	-	Not Normal	-
$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$	-	-	1	-	Normal/Unimodal	1
$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$	-	-	-	-	Normal/Unimodal	2
$n(^{110}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	-	-	-	-	Not Normal	-
$n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	-	-	1	-	Not Normal	
$n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	-	-	-	-	Normal/Unimodal	1
$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	-	-	1	-	Not Normal	-
$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	-	-	-	-	Normal/Unimodal	1
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Yes	-	1	-	Not Normal	
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Yes	Yes	-	-	Not Normal	1
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	-	-	-	-	Normal/Unimodal	1, 4
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	-	-	1	-	Not Normal	
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Yes	-	-	-	Normal/Unimodal	1
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	-	-	-	-	Normal/Unimodal	1, 4
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Yes	-	2	-	Not Normal	
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Yes	-	1	-	Not Normal	2
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Yes	-	-	-	Not Normal	3
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	-	-	-	-	Normal/Unimodal	3, 4
$n(^{208}\mathrm{Pb})/n(^{204}\mathrm{Pb})$ §	Yes	Yes	-	-	Normal/Unimodal	5
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ §	Yes	Yes	-	-	Normal/Unimodal	5
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ §	-	-	-	-	Normal/Unimodal	5
$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$	-	-	1	1	Not Normal	-
$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$	-	-	-	-	Normal/Unimodal	1
$n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	-	-	-	-	Not Normal	-

[1] One outlier is excluded from the dataset.
[2] Two outliers are excluded from the dataset.
[3] Three outliers are excluded from the dataset.
[4] The analytical trend is corrected mathematically.
[5] Run order is the same as filling order and bottle averages are used (Hereon).

Table 7. Within-bottle and between-bottle standard deviation and corresponding between-bottle uncertainty contributions from homogeneity study

Isotope ratio	$s_{wb,rel}$ / %	$s_{bb,rel}$ / %	$u^*_{bb,rel}$ / %	$u_{bb,rel}$ / %	*Note* §
$n(^{11}B)/n(^{10}B)$	0.055	$MS_{between} < MS_{within}$	0.018	0.018	-
$n(^{11}B)/n(^{10}B)$	0.055	$MS_{between} < MS_{within}$	0.016	0. 016	1
$n(^{114}Cd)/n(^{110}Cd)$	0.012	0.0047	0.0036	0.0047	-
$n(^{114}Cd)/n(^{110}Cd)$	0.010	0.0048	0.0030	0.0048	1
$n(^{114}Cd)/n(^{110}Cd)$	0.0076	0.0060	0.0023	0.0060	2
$n(^{110}Cd)/n(^{111}Cd)$	0.0075	0.0031	0.0022	0.0031	-
$n(^{114}Cd)/n(^{111}Cd)$	0.0088	0.0061	0.0026	0.0061	-
$n(^{114}Cd)/n(^{111}Cd)$	0.0070	0.0056	0.0021	0.0056	1
$n(^{6}Li)/n(^{7}Li)$	0.016	0.0088	0.0049	0.0088	-
$n(^{6}Li)/n(^{7}Li)$	0.012	0.0095	0.0036	0.0095	1
$n(^{204}Pb)/n(^{206}Pb)$	0.20	$MS_{between} < MS_{within}$	0.061	0.061	-
$n(^{204}Pb)/n(^{206}Pb)$	0.14	$MS_{between} < MS_{within}$	0.045	0.045	1
$n(^{204}Pb)/n(^{206}Pb)$	0.11	0.013	0.033	0.033	1, 4
$n(^{207}Pb)/n(^{206}Pb)$	0.19	$MS_{between} < MS_{within}$	0.059	0.059	-
$n(^{207}Pb)/n(^{206}Pb)$	0.12	$MS_{between} < MS_{within}$	0.037	0.037	1
$n(^{207}Pb)/n(^{206}Pb)$	0.10	$MS_{between} < MS_{within}$	0.032	0.032	1, 4
$n(^{208}Pb)/n(^{206}Pb)$	0.14	$MS_{between} < MS_{within}$	0.044	0.044	-
$n(^{208}Pb)/n(^{206}Pb)$	0.10	$MS_{between} < MS_{within}$	0.032	0.032	2
$n(^{208}Pb)/n(^{206}Pb)$	0.088	$MS_{between} < MS_{within}$	0.028	0.028	3
$n(^{208}Pb)/n(^{206}Pb)$	0.062	$MS_{between} < MS_{within}$	0.020	0.020	3, 4
$n(^{208}Pb)/n(^{204}Pb)$*	-	-	-	0.017	5
$n(^{207}Pb)/n(^{206}Pb)$*	-	-	-	0.015	5
$n(^{208}Pb)/n(^{206}Pb)$#	-	-	-	0.0024	5
$n(^{234}U)/n(^{238}U)$	0.222	0.15	0.0712	0.28	-
$n(^{234}U)/n(^{238}U)$	0.178	0.093	0.059	0.093	1
$n(^{235}U)/n(^{238}U)$	0.017	0.013	0.0056	0.013	-

* Since one replicate measurement was performed for each bottle, ANOVA could not be applied and the Excel templates could not be used for the calculations. Uncertainty is calculated by taking the analytical/filling trend into account. It is lower (0.0046 % for $n(^{208}Pb)/n(^{204}Pb)$ and 0.0035 % for $n(^{207}Pb)/n(^{206}Pb)$) when all data is included, but the trend is not included in the calculation (by Hereon).

Since one replicate measurement were performed from each bottle, ANOVA could not be applied and the Excel templates could not be used for the calculations. The result is calculated from the standard deviation for all the bottles measured (by Hereon).

§ See footnotes in Table 6.

Establishment of within-unit homogeneity was necessary to demonstrate that the isotope ratio values of the elements of interest in each individual aliquots represent the same ratio values in whole unit. In this respect, the within-unit heterogeneity is closely correlated to the minimum sample intake which is the minimum amount of sample that is representative for the whole unit and should be taken as the amount in the analysis. The certified value within its stated uncertainty is guaranteed when the sample sizes equal to or above the minimum sample intake used for analysis. This material is not expected to have any significant within-unit heterogeneity as it is in solution form with well mixing characteristics. Furthermore, since the mass fractions of the elements are relatively low and a matrix separation and/or pre-concentration is needed, the measurement methods usually require high sample volumes. Nevertheless, even though no significant heterogeneity is expected between bottles, it is advised to use the amounts given in Table 8.

Table 8. Amounts of sample used in tests for homogeneity and stability of parameters in seawater

Isotope Ratio	***Amount used in homogeneity and stability tests / mL***
$n(^{11}\text{B})/n(^{10}\text{B})$	5
$n(^{114}\text{Cd})/n(^{110}\text{Cd})$	10
$n(^{114}\text{Cd})/n(^{111}\text{Cd})$	10
$n(^{110}\text{Cd})/n(^{111}\text{Cd})$	10
$n(^{6}\text{Li})/n(^{7}\text{Li})$	20
$n(^{204}\text{Pb})/n(^{206}\text{Pb})$	4* / 20§
$n(^{207}\text{Pb})/n(^{206}\text{Pb})$	4* / 20§
$n(^{208}\text{Pb})/n(^{206}\text{Pb})$	4* / 20§
$n(^{234}\text{U})/n(^{238}\text{U})$	60
$n(^{235}\text{U})/n(^{238}\text{U})$	60

***** Used by MUL
§ Used by Hereon

STABILITY

The stability of the units which are exposed to different environmental conditions that may occur during shipment and storage should be evaluated at predefined test conditions by reference material producers. In the production of this reference material, the experimental design of the stability studies followed an isochronous scheme as described below for short-term and long-term stabilities. The uncertainty contribution of stability of material has been calculated as described by Linsinger et al. [11]. The bottles used for stability analysis were selected using random stratified sampling using the TRaNS program developed by TÜBİTAK UME. The stability measurements for the isotopic ratio values were performed by different partners which were given in Table 5. The evaluation of stability data is based on the measurement of isotope ratio values for the parameters to be certified. The mass fractions determined by external calibration were also measured for stability measurements but as expected the calculated uncertainty values were found to be too high to be used in the certification. The short-term and long-term stability evaluation results are given separately in the following sections.

Short-Term Stability

The short-term stability (STS) testing is done for testing the stability during transport of the material from producer to end users. In this study, due to limitations in the measurements as described previously and no anticipated stability issues, only one test temperature and one test duration were selected as +45 °C and three weeks, respectively. According to the designed test temperature and time points, two units for each partner, determined by TRaNS, were placed at +45 °C. After the test period of three weeks, they were transferred to reference temperature, +4 °C. Then the STS samples were measured at the same time with the reference units, already kept at reference temperature, in the same run.

The evaluation of short-term stability measurement resuts was carried out by applying first Grubbs' test at confidence levels of 95 % and 99 % for both individual results and also for the unit averages. Additionally, the statistical evaluation was done to assess any significant trend during the test period for any indication of degredation, i.e. possible changes in the isotopic abundances of the analytes by time (*regression analysis*). The calculated slopes of the regression line were tested using two-tailed *t*-test using $t_{\alpha,df}$ as the critical *t* value at $\alpha = 0.05$ (95 % confidence level). The results obtained for STS measurements are summarized in Table 9, and graphical representations of data are shown in **Hata! Başvuru kaynağı bulunamadı.**. All the STS uncertainties in the table are for three-week period at +45 °C, assuming that the shipment period will not exceed this period and temperature.

Outlier tests showed that there is one outlier in the data sets for $n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$ (measured by BAM), $n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$, $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ and $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ (measured by MUL). In addition to MUL, one set of STS samples were also analysed by Hereon for assessing the stability of Pb isotope ratios. No outlier was observed in the second data set by Hereon for all ratios for Pb isotopes.

Uncertainty contribution resulting from STS was calculated by applying Equation (5). Uncertainties were calculated for three-week exposure period.

$$u_{sts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \qquad (5)$$

where;

RSD : relative standard deviation of the points on the regression line as described ISO 33405,

t_i : point in time for each replicate,

$\bar{t}$: mean of the all-time points,

t : maximum time suggested for the transfer (three weeks).

The calculated uncertainty values from short-term stability study are given in Table 9. Among all the uncertainty values calculated from all the data including the outliers, the highest STS uncertainty values (around 0.17 %) were calculated for $n(^{204}\text{Pb})/n(^{206}\text{Pb})$ and $n(^{207}\text{Pb})/n(^{206}\text{Pb})$ determined by MUL. In these data sets, one of the three replicates from bottle number #239 was found to be an outlier. (This unit was also identified as an outlier in LTS and homogeneity evaluation). Since this outlier is one of the three replicates of four reference units each of which were measured in three replicates, there was no reason to keep it in the data set. Therefore, the STS uncertainty is calculated by rejecting this outlier from the data set. Furthermore, the overestimation of the total uncertainty of the certified value due to these outliers can be eliminated by excluding it from the data set in the most appropriate evaluation such as short term stability where the number of reference measurements comprises the majority in the data set. Although the evaluations based on the data generated by Hereon by using an independent sample set subjected to same test conditions resulted in much lower uncertainties, the MUL results were used because of single replicates were measured in the former.

Boron and Li isotopes were measured by BAM. For B, the STS uncertainty was calculated as 0.018 % and no outlier was observed in the data set. The slope of the line was not found to be significantly different from zero, indicating no degradation. For Li there was one outlier in the data set. Like Pb, this outlier was also obtained for one of the reference points and thus excluded from tha data set. Then, STS uncertainty for $n(^{6}\text{Li})/n(^{7}\text{Li})$ decreased from 0.011 % to 0.0084 % which was used in certification.

Cadmium isotopes measured by JSI were found to be stable at +45 °C for three weeks with less than 0.01 % relative uncertainties. The data set obtained for $n(^{114}\text{Cd})/n(^{110}\text{Cd})$ had one outlier. Like Pb, this outlier was one of the replicates of reference time points; it was excluded from the data set for the calculation of STS uncertainty.

The measurements for $n(^{234}\text{U})/n(^{238}\text{U})$ and $n(^{235}\text{U})/n(^{238}\text{U})$ were carried out by PTB, and no outlier was identified for both measurands. However, $n(^{235}\text{U})/n(^{238}\text{U})$ found to be degraded as the *t* statistics calculated for the the slope of the line, test duration and the measured isotope ratio value is found to be significantly higher than the crtitical value at 95 % confidence level. Due to this observation, the STS uncertainty is calculated by taking the degradation effect into account, which was 0.016 %.

Table 9. Summary of results for short-term stability test at +45 °C.

Parameter	$u_{sts,rel}$ **/ %**	**Significance of the trend on a 95 % confidence level**	**Number of individual outlying results at 95 % confidence level**	**Note**
$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	0.018	NO	-	-
$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$	0.0067	NO	1	-
$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$	0.0050	NO	-	1
$n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	0.0079	YES	-	-
$n(^{110}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	0.0048	NO	-	-
$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	0.011	NO	1	-
$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	0.0084	NO	-	1
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.21	NO	1	-
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.12	NO	-	1
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.20	NO	1	-
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.095	NO	-	1
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.11	NO	1	-
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.080	NO	-	1
$n(^{206}\mathrm{Pb})/n(^{204}\mathrm{Pb})$	0.014	NO	-	5
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.0093	NO	-	5
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.0093	NO	-	5
$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$	0.083	NO	-	-
$n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	0.016	YES	-	-

[1] One outlier is excluded from the dataset.
[2] Run order is the same as filling order and bottle averages are used (Hereon).

Long-Term Stability

The uncertainty related to the degradation during the storage of seawater CRM at (+21 ± 3) °C has been studied by performing a long-term stability test (LTS). As mentioned previously in this report, due to difficulties in the measurements and a few number of laboratories conducting such measurements, a combined design with homogeneity and LTS testing is applied to optimize the effort on the measurements. Among the selected RM units, four units were placed at the reference point and two units for each storage time period (three, six, nine and twelve months). The temperature tested for storage conditions was selected as +21 °C. The reference temperature has been set to +4 °C. At the end of each test period, the assigned units were transferred to reference conditions. After transferring the units, which were kept for long-term, all the units were measured in three replicates.

All the data obtained in LTS study was screened for outlier values using single Grubbs test at 95 % and 99 % confidence levels. The statistical evaluation of the analytical data was carried out by using Excel spreadsheets prepared and validated for this purpose by TÜBİTAK UME in accordance with the requirements of ISO 33405. Uncertainty contribution of long-term stability, u_{lts}, is calculated using Equation (5). The shelf life of UME MetroPOEM CRM was determined as twelve months after sales date at +21 °C, and the uncertainty contribution of LTS was calculated based on this period and the results are given in **Hata! Başvuru kaynağı bulunamadı.**. Graphical representation of the data related to each analyte is given in Annex 3. To ensure the stability after the certification period, post-certification monitoring will be carried out over a specific period.

$$u_{lts,rel} = \frac{RSD}{\sqrt{\sum(t_i - \bar{t})^2}} \times t \qquad (6)$$

where:

RSD : relative standard deviation of all values obtained in the stability study,

t_i : time point for each replicate,

$\bar{t}$: mean of all time points,

t : propose shelf life at test temperature +21 °C (twelve months for this material).

For all the isotopic ratios, at least one outlier is identified in each data set except for $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$. For $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$, statistical evaluation resulted in two outliers in the original data set and yielded one extra outlier when the calculation is repeated by excluding two original outliers. All the outliers were kept in the data sets when calculating the uncertainty contribution. Since only one parallel measurement was carried out by Hereon and the run order of samples in the analytical sequence was the same as the filling order, the results obtained by MUL is used in the calculation of uncertainty for Pb isotope ratio values. The statistical evaluation of the results obtained by Hereon by using another set of units resulted in lower uncertainty values, which were used as supporting evidence for long-term stability testing of Pb.

The slopes of regression lines calculated on the graphs of time versus isotope ratio, were subjected to statistical evaluation to determine if any significant trend exists by using *t*-test at 95 % confidence level. For $n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$, $n(^{206}\mathrm{Pb})/n(^{204}\mathrm{Pb})$ (by Hereon) and $n(^{208}\mathrm{Pb})/n(^{204}\mathrm{Pb})$ (by Hereon), significant trends were identified observed at 95 % confidence level indicating a degradation on the measured value. However, these trends were found to be not significant at 99 % confidence level. For $n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$, where one of the individual replicates is identified as outlier at 95 % confidence level, when the outlier is excluded from the data set, the trend was not significant and the uncertainty was improved from 0.013 % to 0.0066 %. The data set generated by Hereon for Pb isotope ratios was already used as supporting data for the calculation of LTS uncertainty and was not included in the calculation of CRM uncertainty. The uncertainties for other isotope ratios were found to be below 0.1 % except for $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ with 0.13 % where one of the replicate result is identified as outlier. When the calculation was repeated with excluding the data for $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$, the uncertainty decreased below 0.1 %. No analytical trend was observed for the investigated Cd isotope ratios but two and one outliers were identified for both $n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$ and $n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$, respectively. Since there were no technical reasons identified for rejecting the outlier, the uncertainty values for LTS were calculated by keeping all the values in data sets for all isotope ratios.

Table 10. Summary of results for long-term stability study

Parameter	$u_{\mathrm{lts,rel}}$ * / %	***Significance of the trend on a 95 % confidence level***	***Number of individual outlying results at 95 % confidence level***	***Note***
$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	0.024	NO	1	-
$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	0.021	NO	-	1
$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$	0.0059	NO	2	-
$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$	0.0043	NO	-	2
$n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	0.0045	NO	1	-
$n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	0.0036	NO	-	1
$n(^{110}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	0.0037	NO	-	-
$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	0.013	YES	1	-
$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	0.0066	NO	-	1
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.082	NO	1	-
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.058	NO	-	1
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.080	NO	1	-
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.050	NO	-	1
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.056	NO	2	-
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.040	NO	1	2
$n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.036	NO	-	3
$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.025	YES	-	4
$n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	0.017	NO	-	4

Parameter	$u_{lts,rel}$ * / %	Significance of the trend on a 95 % confidence level	Number of individual outlying results at 95 % confidence level	Note
$n(^{208}Pb)/n(^{206}Pb)$	0.011	YES	-	4
$n(^{234}U)/n(^{238}U)$	0.13	NO	1	-
$n(^{234}U)/n(^{238}U)$	0.097	NO	1	1
$n(^{235}U)/n(^{238}U)$	0.011	NO	-	-

[1] One outlier is excluded from the dataset.
[2] Two outliers are excluded from the dataset.
[3] Three outliers are excluded from the dataset.
[4] Run order is the same as filling order and bottle averages are used (Hereon).

CHARACTERISATION

A collaborative interlaboratory study is one of the options for the characterisation of a candidate CRM according to ISO 17034 standard [1]. This approach was applied throughout this study. Not only the project partners but also laboratories with experience on the measurement of isotopes interested in the project were also invited to the characterisation campaign. A registration form was sent to the potential laboratories to select the isotope ratios that they would like to analyse. The laboratories registered for the characterisation study and the corresponding measurands that they reported are listed in Table 11 together with their measurement instrument.

Table 11. The laboratories that participated to the characterisation study, along with the corresponding measurands and the measurement instruments

Participating Organisation	*Measurement Instrument*	*Measurand*	*Short Description of Sample Prep Method*
Physikalisch-Technische Bundesanstalt (PTB)	MC-ICP-MS Neptune XT for Li	$n(^{6}Li)/n(^{7}Li)$	Separation by using ion exchange chromatography with DOWEX 50WX8-200 resin

Participating Organisation	***Measurement Instrument***	***Measurand***	***Short Description of Sample Prep Method***
	MC-ICP-MS Neptune Plus for U	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	Separation by using ion exchange chromatography with Triskem UTEVA resin
LGC Limited (LGC)	MC-ICP-MS Thermo Scientific Neoma	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	Matrix removal by sublimation at 100 °C
		$n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$	Three-step matrix prurification: a) Coprecipitation with $Mg(OH)_2$ using TEA, b) Anion-exchange chromotagrophic column with AG®1-X8, c) Cation exchange chromotagrophic column with Chelex 100. Coprecipitation with $Mg(OH)_2$ using TEA
Montanuniversität Leoben (MUL)	MC-ICP-MS (sample prep. As listed in column 4), ICP-MS/MS (no sample prep.)	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Matrix purification and preconcentration by using ESI seaFAST-LITER system
Institutt for Energiteknikk (IFE)	MC-ICP-MS	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	Use of ESI PrepFAST with Amberlite IRA- 743 Resin involving NH4CH$_3$COO
		$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	Matrix removal by $Fe(OH)_3$ co-precipitation of actinides followed by separation of U by UTEVA resin
Helmholtz-Zentrum Hereon GmbH (Hereon)	MC-ICP-MS	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	Matrix purification and preconcentration by using ESI seaFAST Picosystem
Jožef Stefan Institute (JSI)	MC-ICP-MS Nu Instruments II with ARIDUS II desolvation unit	$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$ $n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$ $n(^{110}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	Coprecipitation with $Mg(OH)_2$ using TEA and then separation by AG-MP-1M resin
Bundesanstalt für Materialforschung und – prüfung (BAM)	MC-ICP-MS ThermoFischer Neptune Plus	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	Separation using microsublimation
		$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	Separation using ion exchange chromatography

Participating Organisation	***Measurement Instrument***	***Measurand***	***Short Description of Sample Prep Method***
Aarhus Universitet (AU) University of Gothenburg (UG)	MC-ICP-MS	$n(^{204}\text{Pb})/n(^{206}\text{Pb})$ $n(^{207}\text{Pb})/n(^{206}\text{Pb})$ $n(^{208}\text{Pb})/n(^{206}\text{Pb})$	Pre-concentration by co-precipitation with $Fe(OH)_3$ followed by anion exchange chromatography
Danmarks Tekniske Universitet (DTU)	ICP-MS/MS	$n(^{234}\text{U})/n(^{238}\text{U})$ $n(^{235}\text{U})/n(^{238}\text{U})$	Five times dilution with 0.5 mol/L HNO_3 before measurements
National Metrology Institute of China (NIM)	MC-ICP-MS Neptune Plus	$n(^{11}\text{B})/n(^{10}\text{B})$	Separation of B by using Amberlite IRA743 boron-specific resin
Imperial College London (ICL)	MC-ICP-MS Nu Plasma II with DSN 100 desolvation system	$n(^{114}\text{Cd})/n(^{110}\text{Cd})$ $n(^{114}\text{Cd})/n(^{111}\text{Cd})$	Acidification with HCl, preconcetration by Nobias Chelate PA-1 followed by two stage column chromatography using AG-MP1 Resin
		$n(^{204}\text{Pb})/n(^{206}\text{Pb})$ $n(^{207}\text{Pb})/n(^{206}\text{Pb})$ $n(^{208}\text{Pb})/n(^{206}\text{Pb})$	Sample treatment with H2O2-NH4OAc, then separation using Nobias Chelate PA-1 resin followed by ‘on exchange chromatography using AG1X resin
University of Warsaw (UW)	MC-ICP-MS Nu Instruments Plasma 3	$n(^{204}\text{Pb})/n(^{206}\text{Pb})$ $n(^{207}\text{Pb})/n(^{206}\text{Pb})$ $n(^{208}\text{Pb})/n(^{206}\text{Pb})$	Separation of elements by using BioRAD AG 1-x8 resin
		$n(^{235}\text{U})/n(^{238}\text{U})$	
Agilent United Kingdom (AUK)	ICP-MS/MS	$n(^{11}\text{B})/n(^{10}\text{B})$ $n(^{6}\text{Li})/n(^{7}\text{Li})$ $n(^{204}\text{Pb})/n(^{206}\text{Pb})$ $n(^{207}\text{Pb})/n(^{206}\text{Pb})$ $n(^{208}\text{Pb})/n(^{206}\text{Pb})$	Dilution with 1 % (V/V) HNO_3 before measurements as follows; For B : 1000 fold For Li: 100 fold For Pb: 20 fold

The results reported by the participating laboratories were evaluated statistically. The results, the number of data included in the calculation of average isotope ratio and corresponding characterisation uncertainty for each measurand are given in Table 12.

Table 12. Summary of characterisation measurements

Parameter	*Number of results**	*Isotope ratio / mol/mol*	*u_{char} / mol/mol*	*$u_{char, rel}$ / %*
$n(^{11}\text{B})/n(^{10}\text{B})$	4	4.20408	0.0026	0.062
$n(^{114}\text{Cd})/n(^{110}\text{Cd})$	2	2.30378	0.0046	0.20
$n(^{114}\text{Cd})/n(^{111}\text{Cd})$	2	2.24559	0.0067	0.30
$n(^{6}\text{Li})/n(^{7}\text{Li})$	2	0.079717	0.00019	0.24
$n(^{204}\text{Pb})/n(^{206}\text{Pb})$	5	0.055027	0.000019	0.035
$n(^{207}\text{Pb})/n(^{206}\text{Pb})$	5	0.857186	0.000165	0.019
$n(^{208}\text{Pb})/n(^{206}\text{Pb})$	5	2.099277	0.00043	0.021
$n(^{234}\text{U})/n(^{238}\text{U})$	3	0.000062618	0.00000056	0.89
$n(^{235}\text{U})/n(^{238}\text{U})$	3	0.007251965	0.0000056	0.077

PROPERTY VALUE AND UNCERTAINTY ASSIGNMENT

The uncertainty component of the certified value is composed of the uncertainty contributions from the characterisation study (u_{char}), the between units homogeneity study (u_{bb}), the short-term stability study (u_{sts}) and the long-term stability study (u_{lts}). The uncertainty of the CRM was determined by combining the components affecting value of the assigned uncertainty and calculated using the following equation:

$$U_{CRM} = k\sqrt{u_{char}^2 + u_{bb}^2 + u_{sts}^2 + u_{lts}^2} \tag{7}$$

The uncertainty of the certified value was expanded by a coverage factor corresponding to a confidence level of 95 %. The coverage factors for each parameter were calculated from effective degrees of freedom according to GUM [4]. Certified values and associated uncertainties are stated in Table 13 and the relative uncertainty contributions to the combined uncertainty are reported in Table 14.

Table 13. Certified values and associated uncertainties with its uncertainty components

Parameter	*Certified Value / mol/mol*	*U_{CRM} / mol/mol*	*Coverage Factor*	*$U_{CRM,rel}$ / %*	*$u_{char,rel}$ / %*	*$u_{bb,rel}$ / %*	*$u_{lts,rel}$ / %*	*$u_{sts,rel}$ / %*
$n(^{11}\text{B})/n(^{10}\text{B})$	4.2041	0.0061	2.03	0.15	0.062	0.018	0.024	0.018

$n(^{114}Cd)/n(^{110}Cd)$*	2.30378	0.00098	2.07	0.043	0.20	0.0047	0.0059	0.0050
$n(^{114}Cd)/n(^{111}Cd)$*	2.24559	0.00083	2.07	0.037	0.30	0.0061	0.0045	0.0079
$n(^{6}Li)/n(^{7}Li)$	0.07972	0.00042	2.20	0.54	0.24	0.0088	0.013	0.0084
$n(^{204}Pb)/n(^{206}Pb)$*	0.05503	0.00019	2.13	0.34	0.035	0.060	0.082	0.12
$n(^{207}Pb)/n(^{206}Pb)$*	0.8572	0.0025	2.09	0.29	0.019	0.059	0.079	0.095
$n(^{208}Pb)/n(^{206}Pb)$*	2.0993	0.0049	2.13	0.23	0.021	0.044	0.056	0.080
$n(^{234}U)/n(^{238}U)$	0.0000626	0.0000012	2.10	2.0	0.89	0.093	0.13	0.083
$n(^{235}U)/n(^{238}U)$	0.007252	0.000012	2.09	0.17	0.077	0.013	0.011	0.016

*Uncertainties from characterization study (u_{char}) and thus those on the certified values will be revised.

Table 14. Percent contribution of each uncertainty component to U_{CRM}

Parameter	u_{char} **/ %**	u_{bb} **/ %**	u_{lts} **/ %**	u_{sts} **/ %**
$n(^{11}B)/n(^{10}B)$	0.76	0.06	0.11	0.07
$n(^{114}Cd)/n(^{110}Cd)$*	1.00	0.01	0.01	0.01
$n(^{114}Cd)/n(^{111}Cd)$*	1.00	0.01	0.01	0.01
$n(^{6}Li)/n(^{7}Li)$	0.99	0.001	0.003	0.001
$n(^{204}Pb)/n(^{206}Pb)$*	0.05	0.14	0.26	0.56
$n(^{207}Pb)/n(^{206}Pb)$*	0.02	0.18	0.32	0.48
$n(^{208}Pb)/n(^{206}Pb)$*	0.04	0.16	0.27	0.54
$n(^{234}U)/n(^{238}U)$	0.96	0.01	0.02	0.01
$n(^{235}U)/n(^{238}U)$	0.92	0.03	0.02	0.04

*The contributions will be revised accordingly after revisions of u_{char} values in Table 13.

Informative value

The target elements whose isotopic ratio values to be certified were decided according to the needs in environmental monitoring for the pollutants. Considering the environmental importance of the elements, the stable isotopes were chosen as B, Cd, Cr, Li, Ni, Pb, Sb and U, whose molar masses are distributed along the whole mass range in the periodic table. The isotopic ratios $n(^{53}\mathrm{Cr})/n(^{52}\mathrm{Cr})$ and $n(^{123}\mathrm{Sb})/n(^{121}\mathrm{Sb})$ could not be certified in the seawater standard reference material, because of difficulties related to sample matrix separation techniques (in case of Cr) and a lack of traceable isotopic calibration standards (in case of Sb). Furthermore, Ni is another element whose homogeneity and stability could not be assessed by using the isotope ratio measurements. Instead, the concetration values were measured in the test samples showing that no significant inhomogeneity and instability is observed 95 % confidence interval. Furthermore, only one participant, LGC limited, registered and reported isotopic ratio values for $n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$. Considering that very limited matrix reference materials are available for metals, particularly in seawater, the Ni isotope ratio was decided to be included in the certificate as informative value with the measurement uncertainty given in Table 15. The uncertainty contributions from homogeneity and stability measurements based on the Ni mass concetration values were not included in the uncertainty of informative $n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$ ratio.

Table 15. The informative value and associated measurement uncertainty for $n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$ reported by LGC

Measurand	*Informative Value / mol/mol*	U^* / mol/mol	U^*_{rel} / %	u_{char_rel} / %
$n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$	0.38833	0.00060	0.16	0.076

* The uncertainty on the informative value includes only characterisation measurement uncertainty.

COMMUTABILITY

No commutability studies have been performed for seawater reference material. The material is natural sea water. Since the natural concentration level of the target elements are very low, the material is spiked with the standards having natural isotopical distribution. Therefore, the isotope ratio in the material is close to the natural isotopic ratios. Therefore, the material is suitable for the laboratories performing isotope ratio measurements of the certified elements in natural seawater samples.

TRACEABILITY

In this study, all measurements including the homogeneity and stability studies were performed by validated methods as reported by the participants. Metrological traceability of measurements was ensured by using the isotopic standards traceable to the SI, International System of Units. The source of traceability of standards used in the measurements are listed in Table 6.

Table 16. The standards used in the characterisation measurements for metrological traceability of the certified values

Participating Institute	*Parameter*	*Name of the Standard*	*Source of Traceability*
LGC	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	NIST SRM 951a	NIST

Participating Institute	***Parameter***	***Name of the Standard***	***Source of Traceability***
	$n(^{60}\mathrm{Ni})/n(^{58}\mathrm{Ni})$	HINI-1	NRC
MUL	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	NIST SRM 981	NIST
IFE	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	NIST SRM 951a	NIST
	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	NBS U-010 NBS U-020 NBS U-030	
Hereon	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	NIST SRM 981	NIST
JSI	$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$ $n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	BAM-I012	BAM
BAM	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$ $n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	NIST SRM 951a NIST RM 8545 (LSVEC)	NIST
AU & UGOT	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	NIST SRM 981	NIST
PTB	$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	LSVEC (NIST RM 8545)	IAEA
	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	IRMM-184	European Commission's JRC
UW	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	NIST SRM 997 (Tl) NIST SRM 987 (Pb)	NIST
	$n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	NBL C112A	Original Material NIST Re-certified by NBL
NIM China	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	NIST SRM 951a	NIST

Participating Institute	***Parameter***	***Name of the Standard***	***Source of Traceability***
ICL	$n(^{114}\mathrm{Cd})/n(^{110}\mathrm{Cd})$ $n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$	NIST SRM 3108	NIST
	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	NIST SRM 981	
DTU	$n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$ $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$	No mass bias correction was made	-
Agilent UK	$n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$	-	-
	$n(^{6}\mathrm{Li})/n(^{7}\mathrm{Li})$	-	-
	$n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$ $n(^{208}\mathrm{Pb})/n(^{206}\mathrm{Pb})$	NIST SRM 981/VHG-LISPB1-50	NIST / VGH Labs

INSTRUCTIONS FOR USE

Before the use, the CRM bottle should be kept in the laboratory environment and should be shaken before opening the cap to avoid a potential bias due to condensed water at the inner surfaces of bottleneck. To avoid contamination, it is highly recommended that the bottle should be kept and opened in a clean environment. It is not advised to insert pipette or any other tip for sampling form the bottle. After use, the bottle should be immediately and tightly recapped.

This material can be safely dispatched under conditions where the temperature do not exceed +45 °C for up to three weeks without applying any cooling elements.

Storage conditions

This material should be stored at (+21 ± 3) °C in a dark and clean environment as well as additionally packed (e.g. sealed bottle or sealed plastic bag) to minimize evaporation during storage.

TÜBİTAK UME cannot be held responsible for changes that might happen to the material at customer’s premises due to noncompliance with the instructions for use, and the storage conditions given in the certificate.

Safety precautions

The material contains 2 % (v/v) nitric acid and some of the target elements were spiked into solution. Therefore, the usual laboratory safety measures apply as in the case of similar solutions. The usual laboratory safety measures apply as in the case of similar acidified solutions. It is strongly recommended that the material must be handled and disposed according to the safety guidelines where applicable. Please refer to the Safety datasheet (SDS) before any use of the material.

Minimum sample intake

No study was conducted for the determination of minimum intake which will not result in any within-unit inhomogeneity because the material is in the liquid form, mix well and experiences from previous seawater certification showed no inhomogeneity when 1 mL - 5 mL of sample is used in the analysis. Furthermore, the levels are low and usually larger sample volumes are needed to conduct measurements. Nevertheless, even though no significant inhomogeneity is expected, use of the amounts given for each isotope pair in Table 8 in this report may be advised to the end user as these amounts were used during the certification measurements.

Use of Certified Value

The certified values can be used as quality control material for validation of the methods, including trueness, for measurements of isotope ratios in seawater matrices. The material is also suitable for checking the sample preparation processes prior to stable isotopic ratio measurements.

ACKNOWLEDGEMENTS

This material is produced by a collaborative study under the project 21GRD09 MetroPOEM. The project 21GRD09 MetroPOEM has received funding from the EURAMET European Partnership on Metrology, co-financed from the European Union’s Horizon Europe Research and Innovation Programme and by the Participating States.

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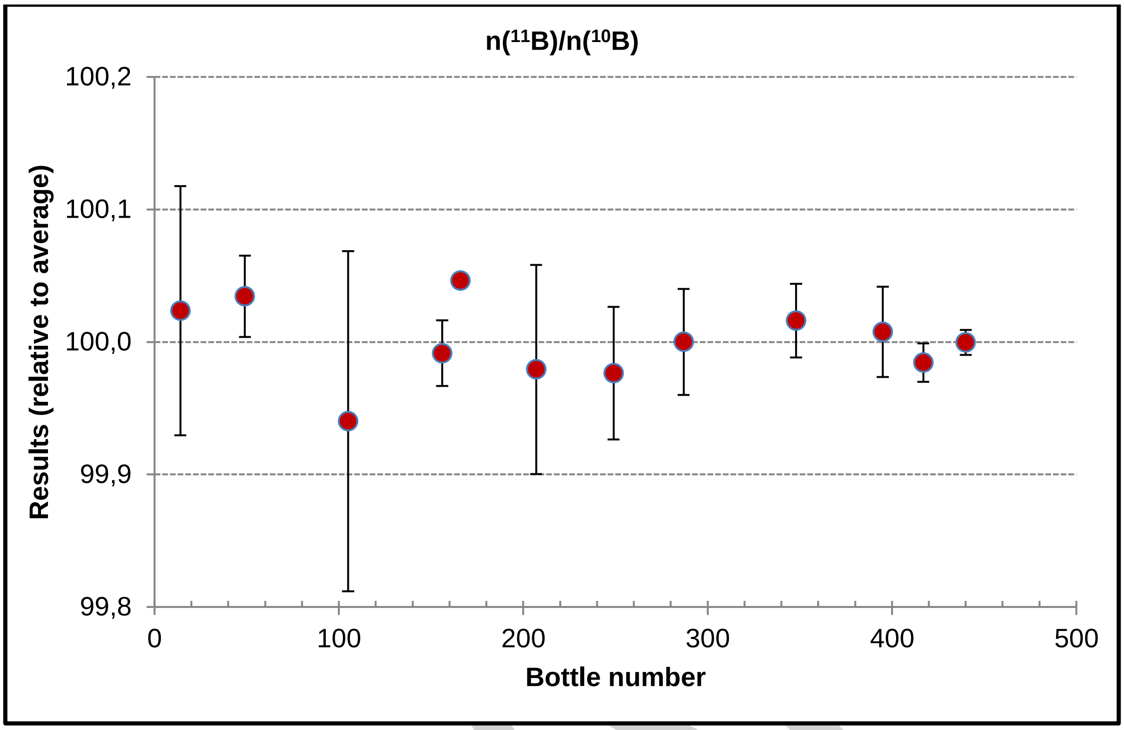
REVISION HISTORY

Date	Remarks
30.09.2025	First Issue

ANNEXES

Annex 1. Graphs of homogeneity study



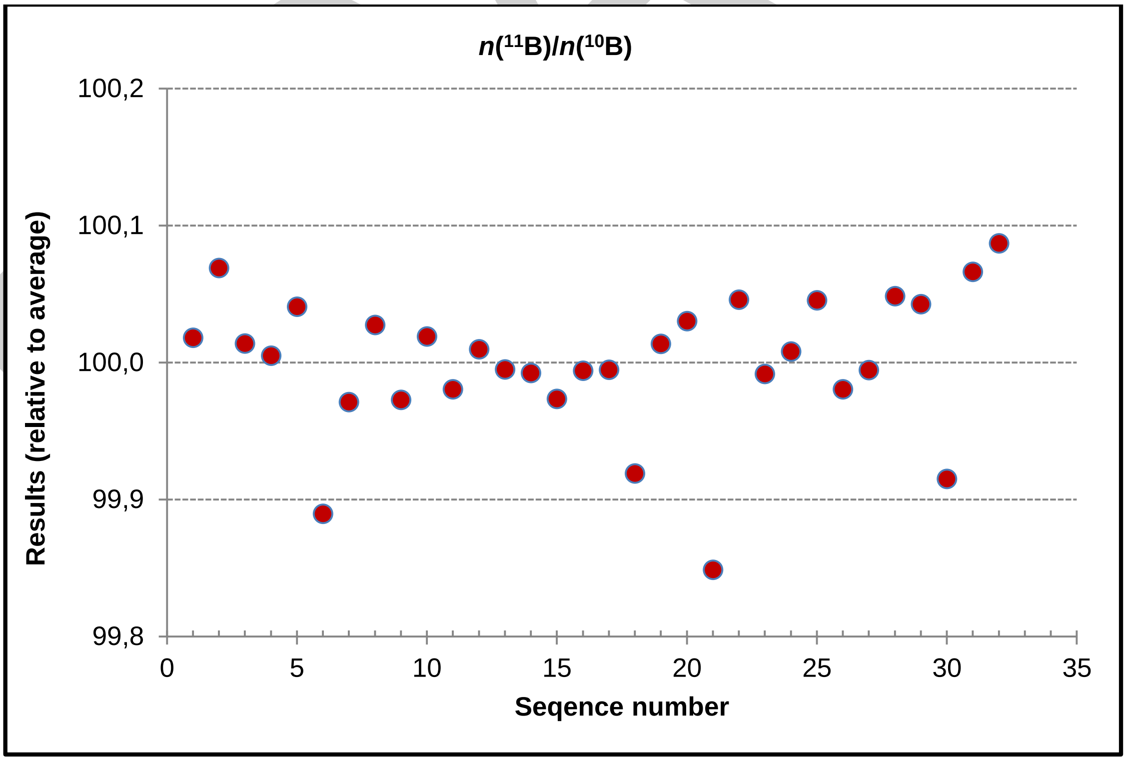
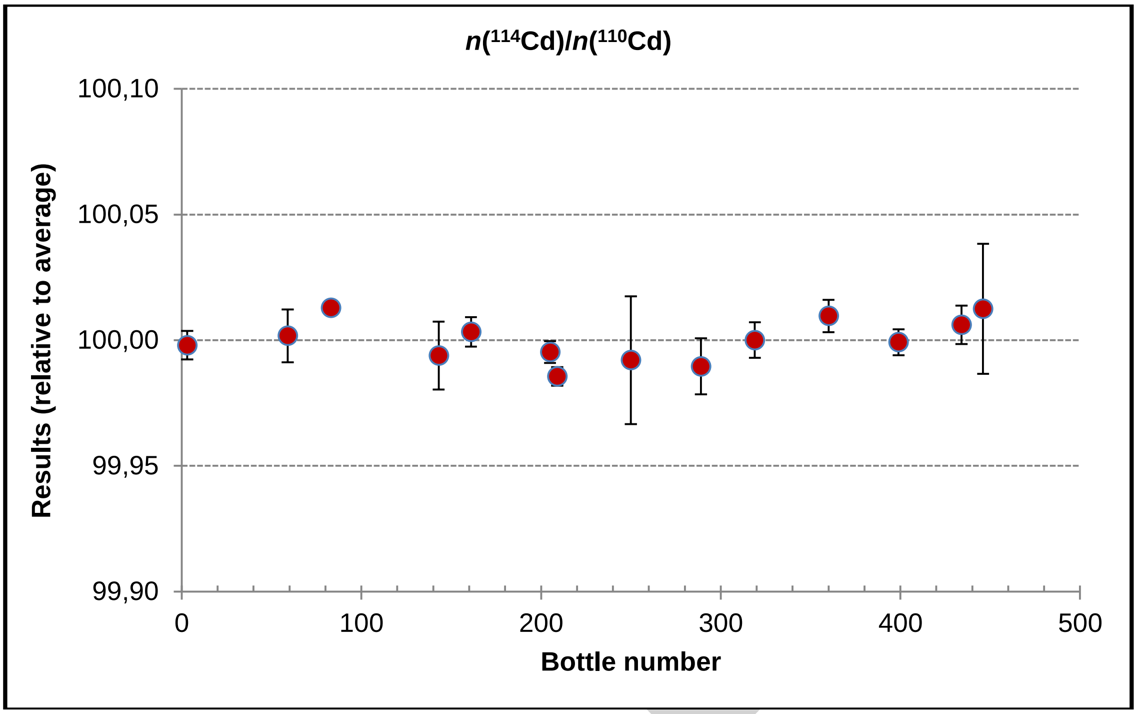


Figure A1.1. Homogeneity graphs for $n(^{11}B)/n(^{10}B)$



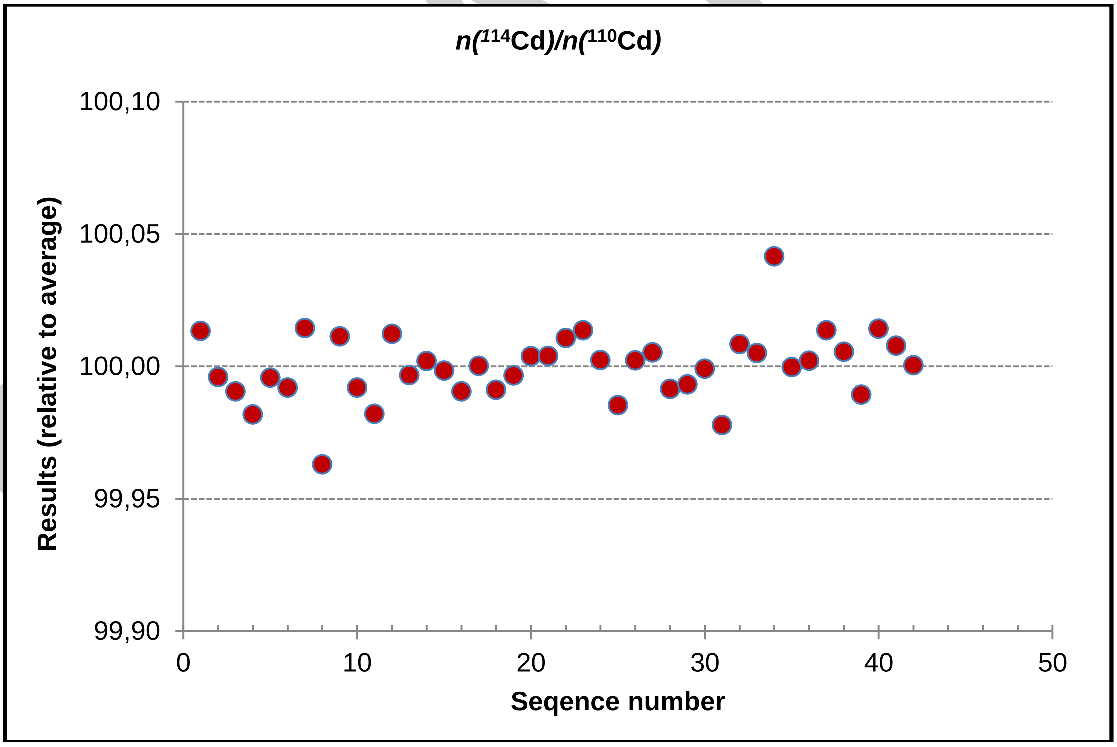


Figure A2.2. Homogeneity graphs for *n(*^{114}Cd*)/n(*^{110}Cd*)*

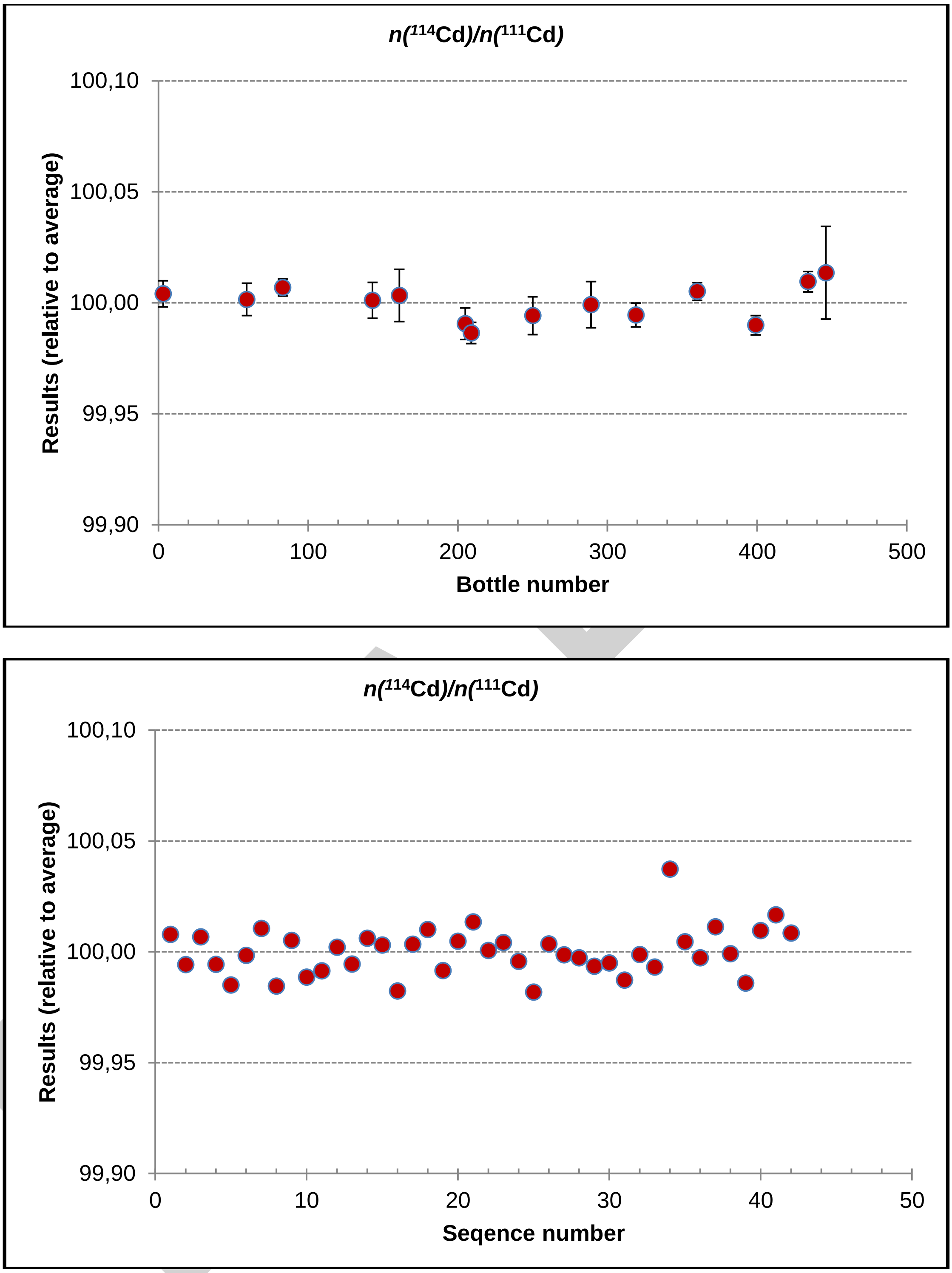
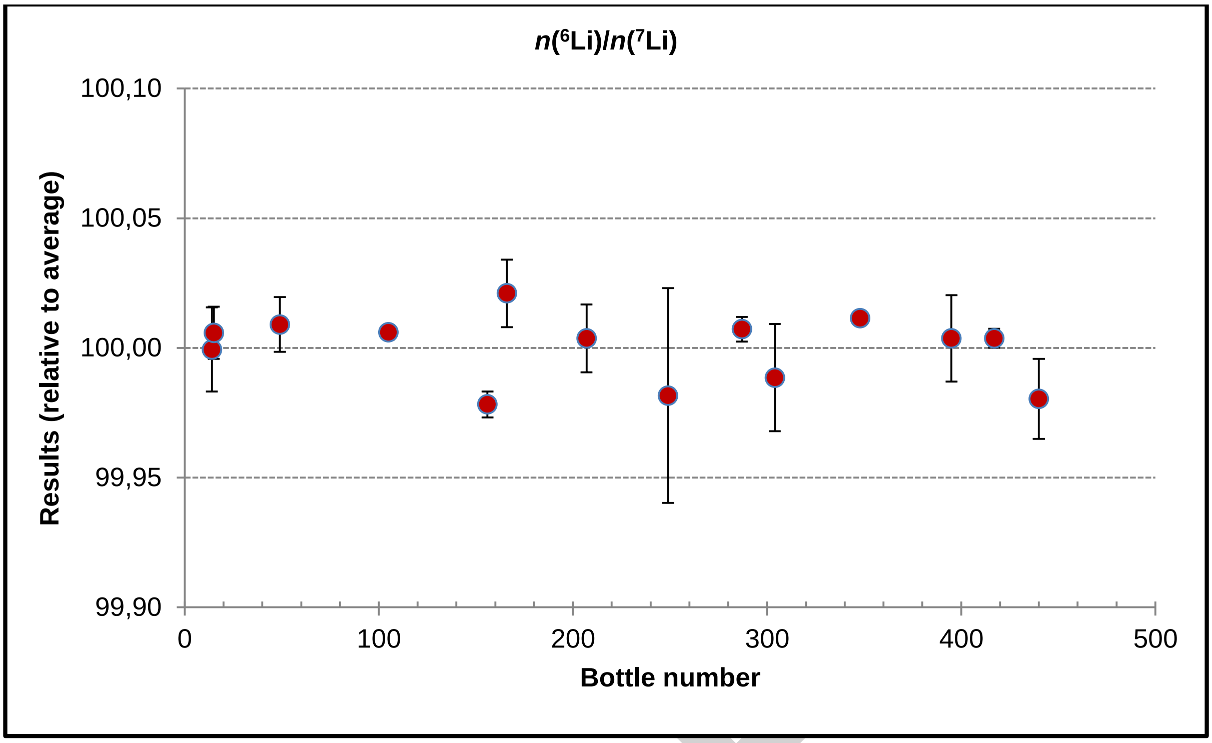


Figure A3.3. Homogeneity graphs for *n*(^{114}Cd)/*n*(^{111}Cd)



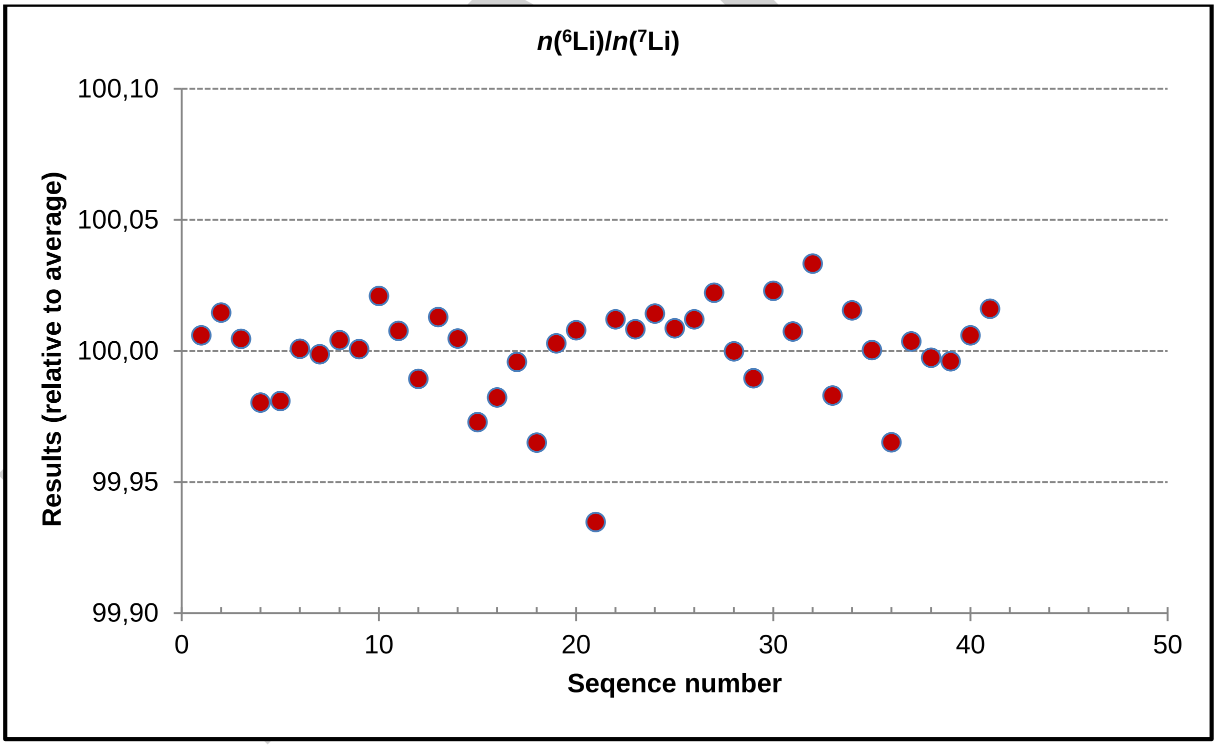
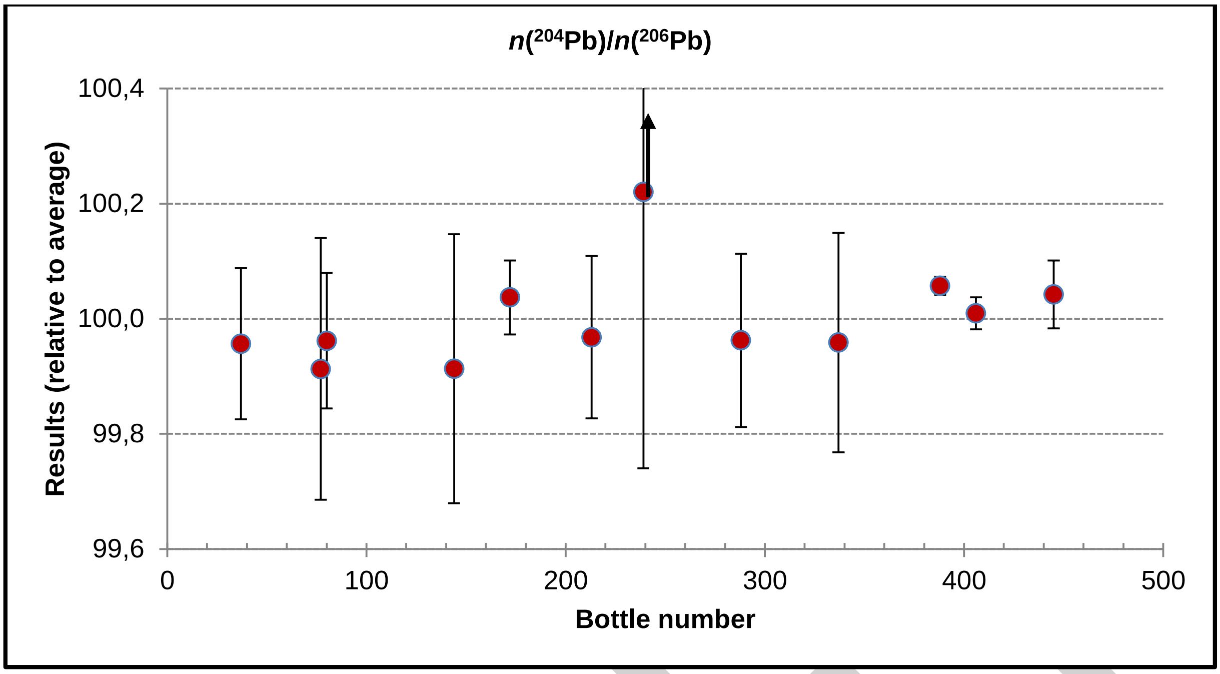


Figure A4.4. Homogeneity graphs for $n(^7\text{Li})/n(^6\text{Li})$.



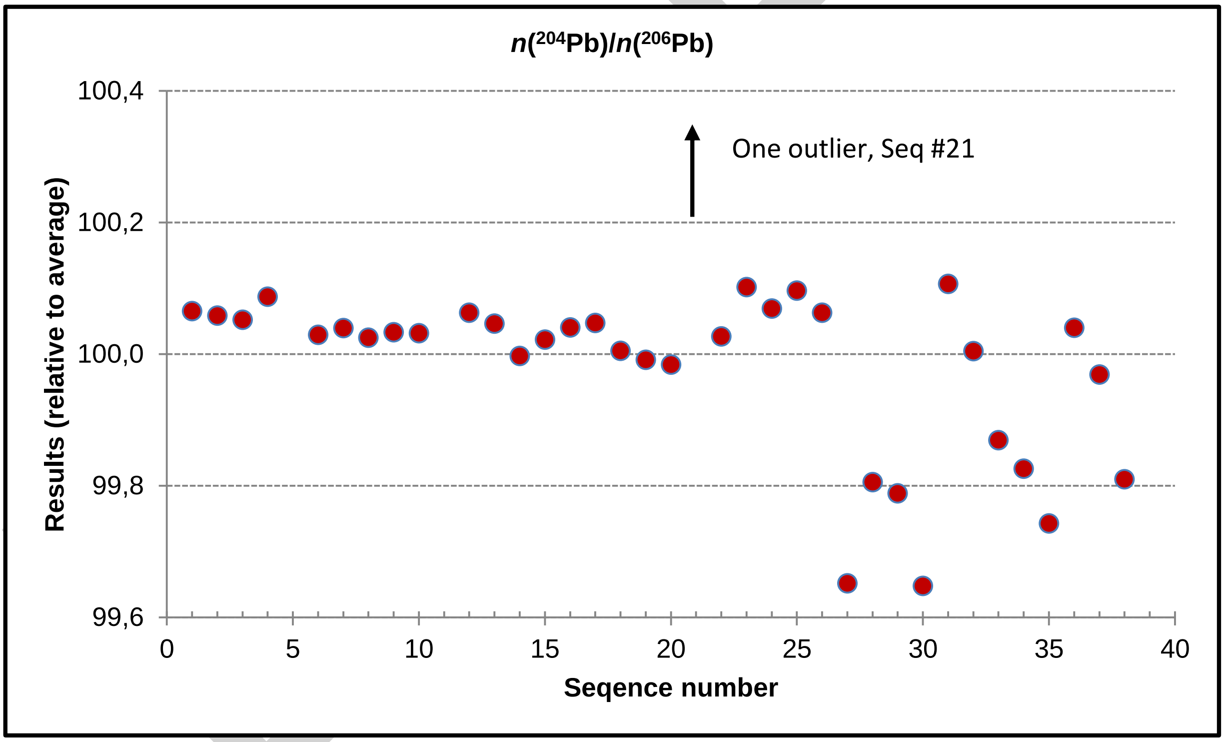
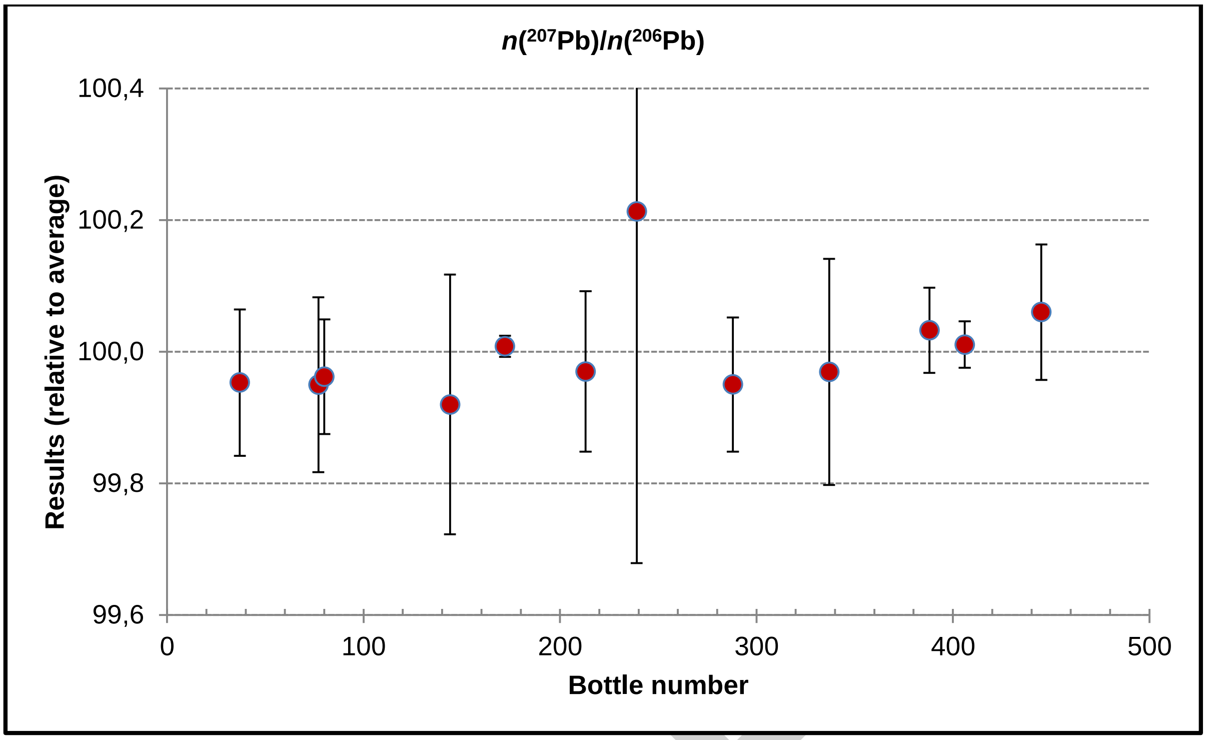


Figure A5.5. Homogeneity graphs for $n(^{204}\text{Pb})/n(^{206}\text{Pb})$



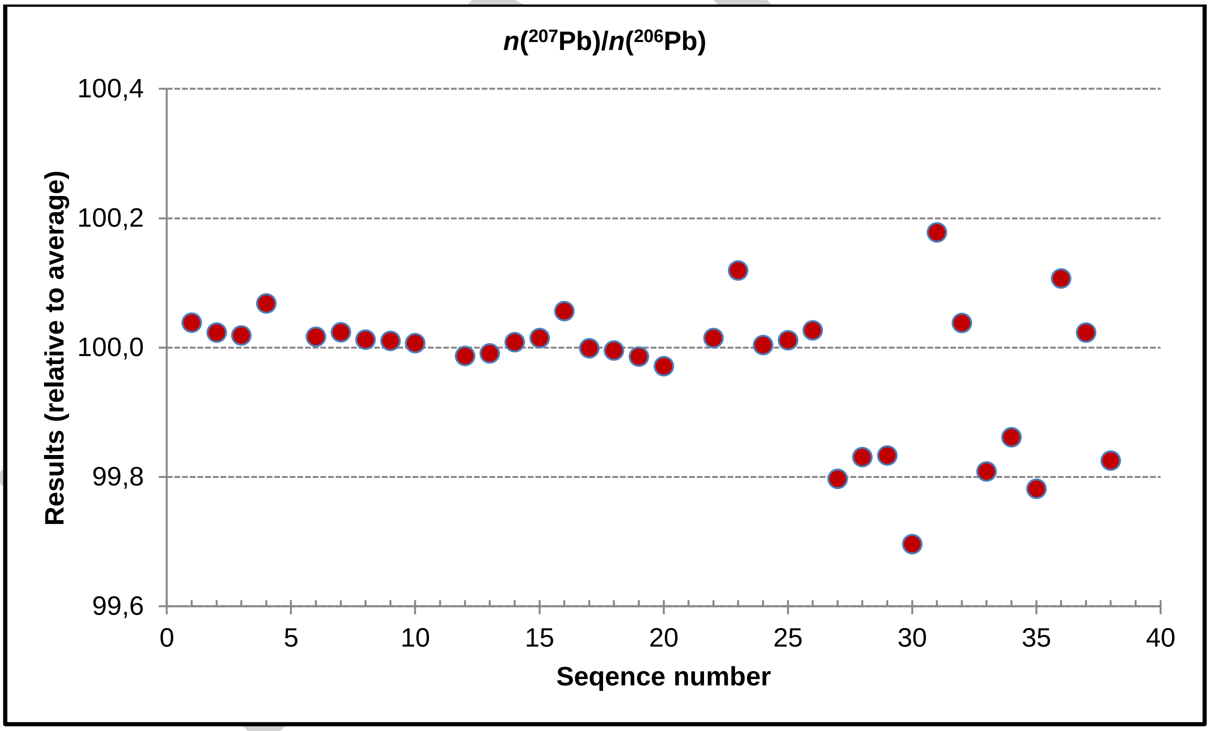
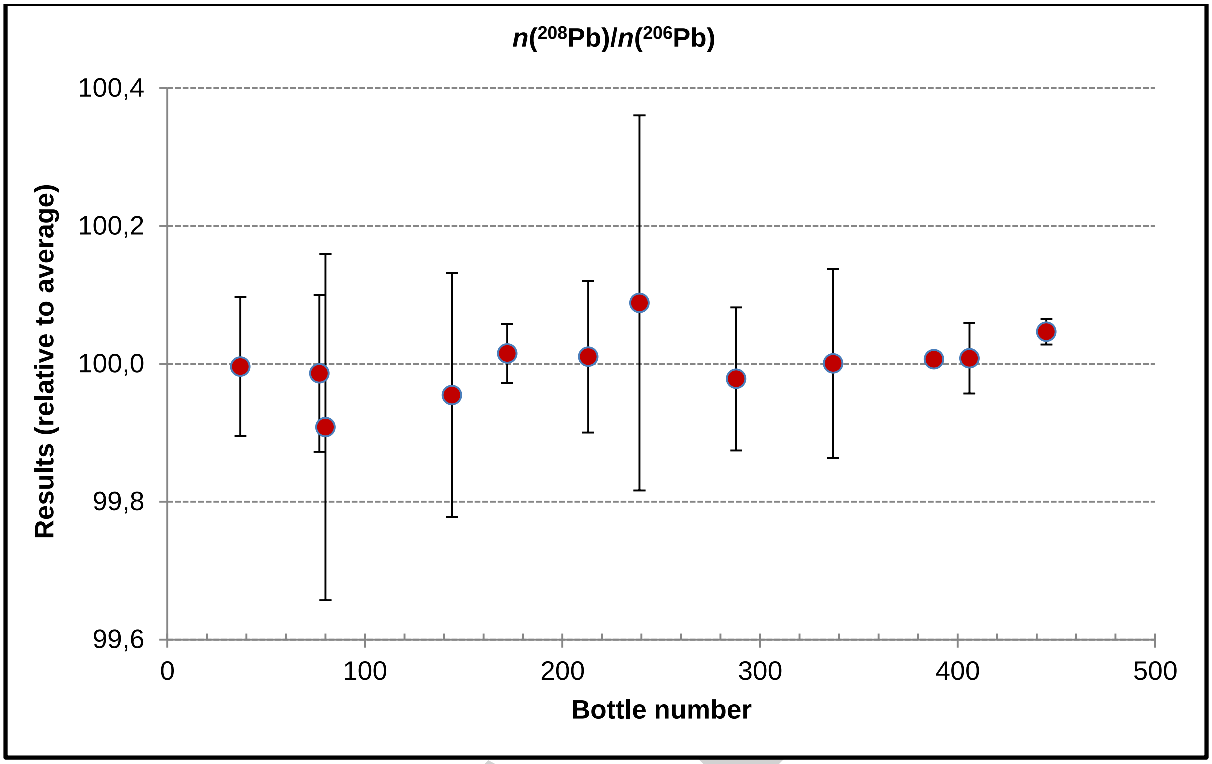


Figure A6.6. Homogeneity graphs for $n(^{207}\text{Pb})/n(^{206}\text{Pb})$



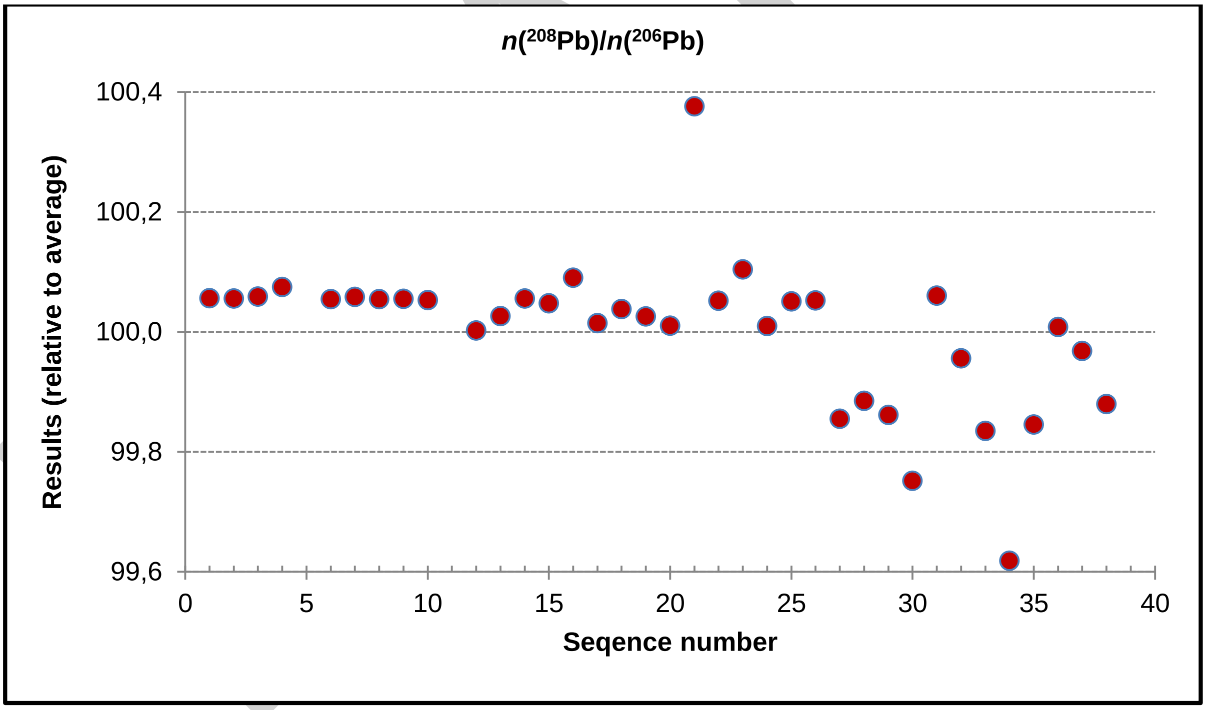
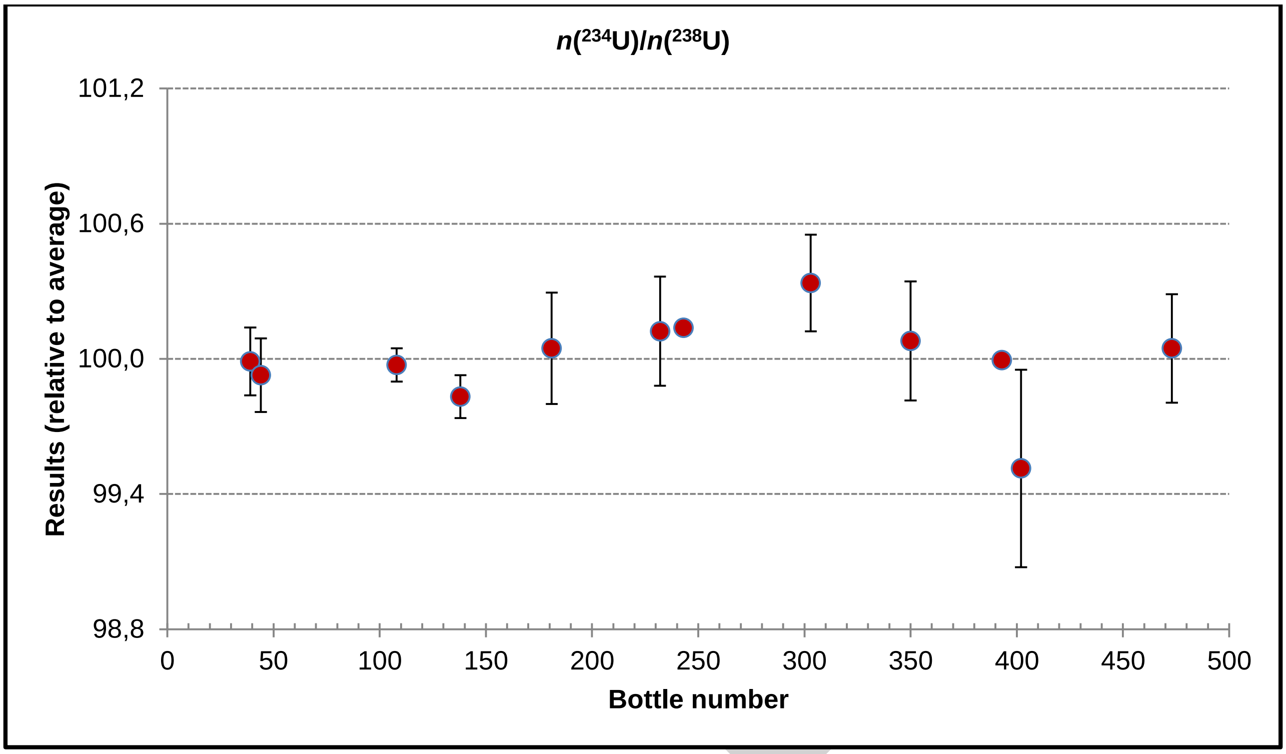


Figure A7.7. Homogeneity graphs for $n(^{208}\text{Pb})/n(^{206}\text{Pb})$



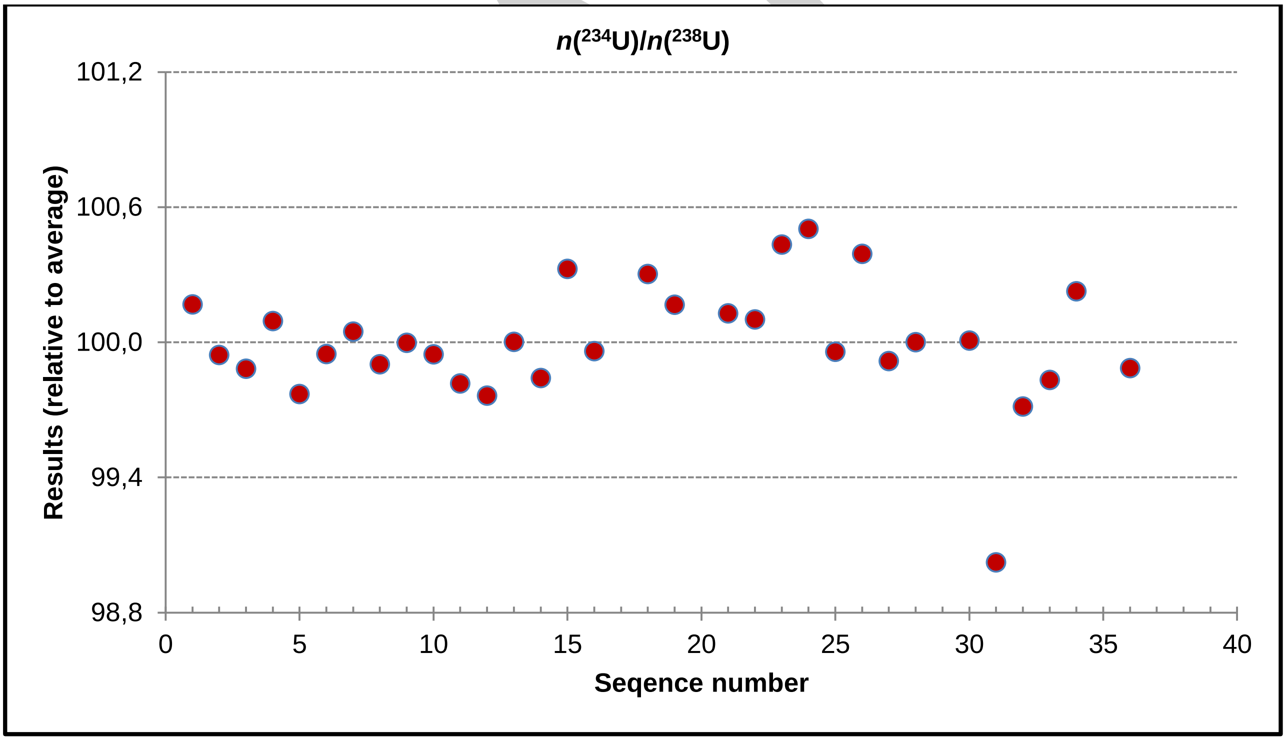


Figure A8.8. Homogeneity graphs for $n(^{234}U)/n(^{238}U)$

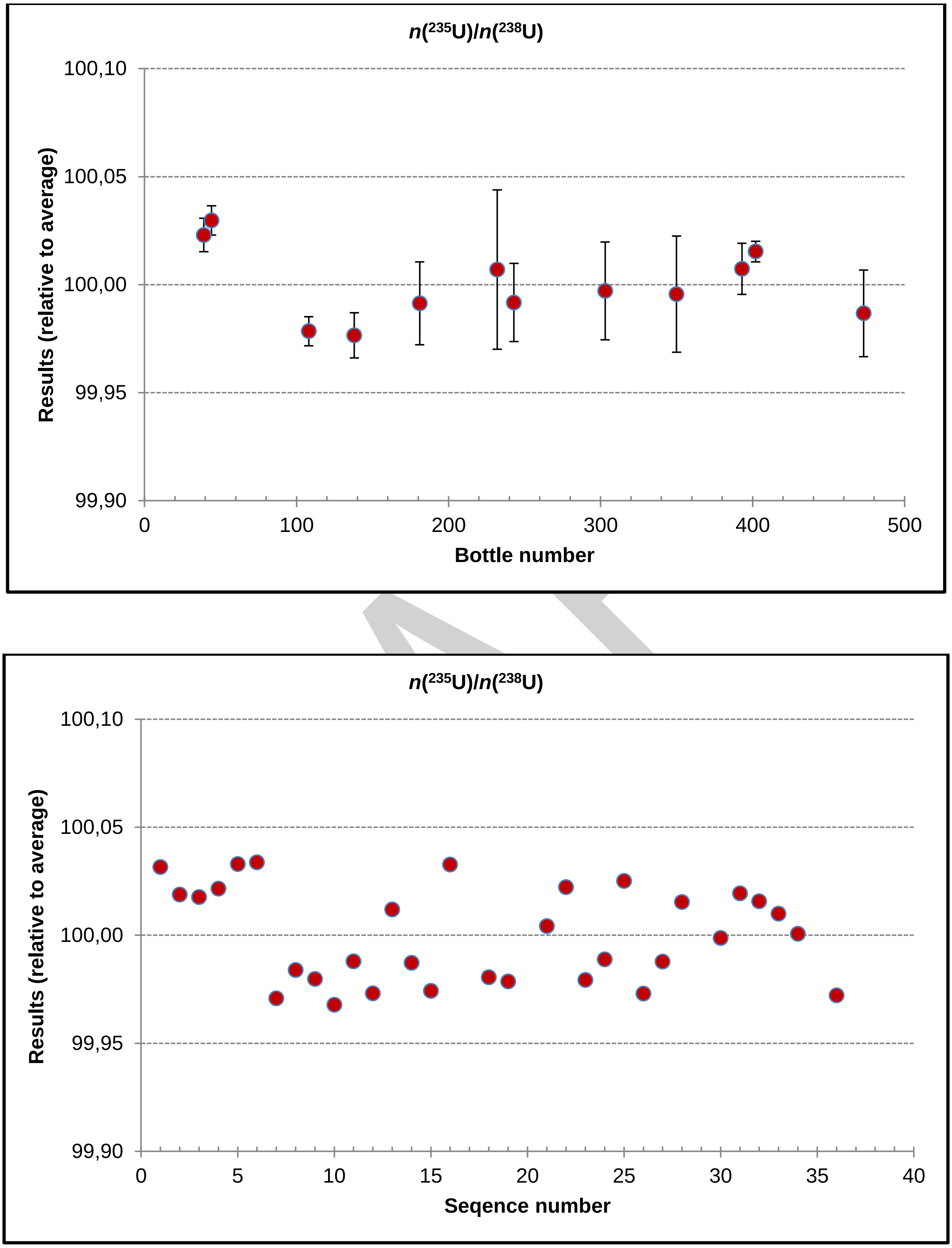
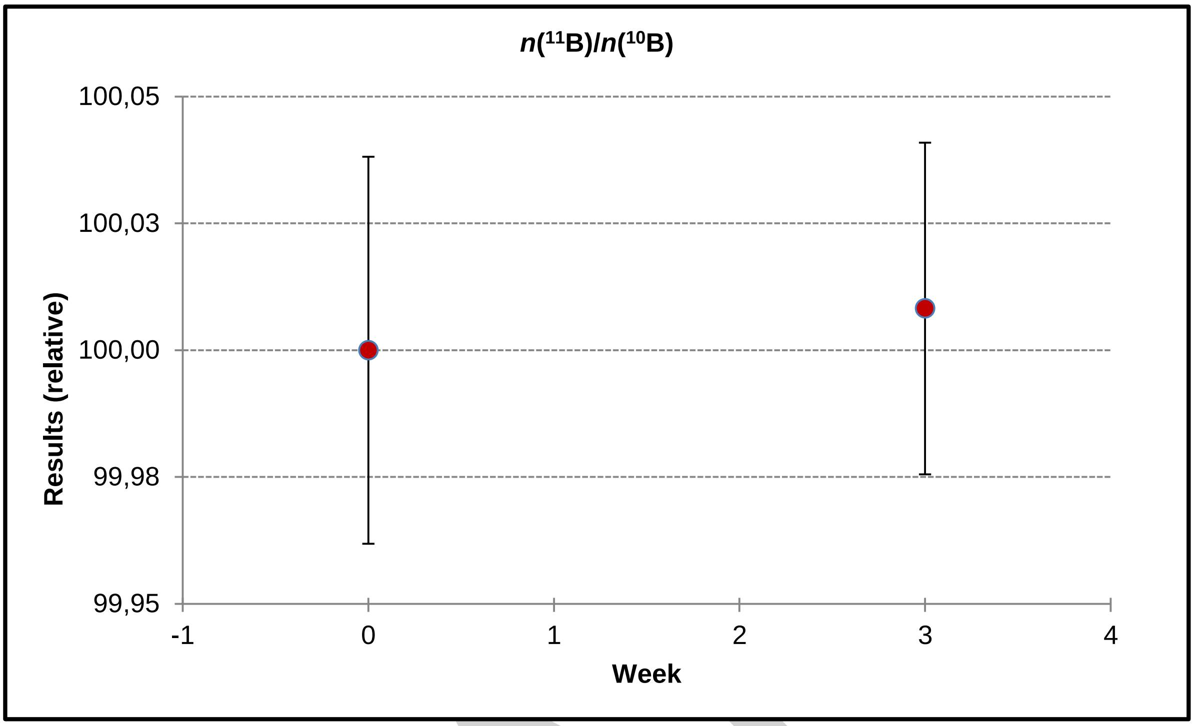


Figure A9.9. Homogeneity graphs for $n(^{235}U)/n(^{238}U)$

Annex 2. Graphs of Short-Term Stability Study



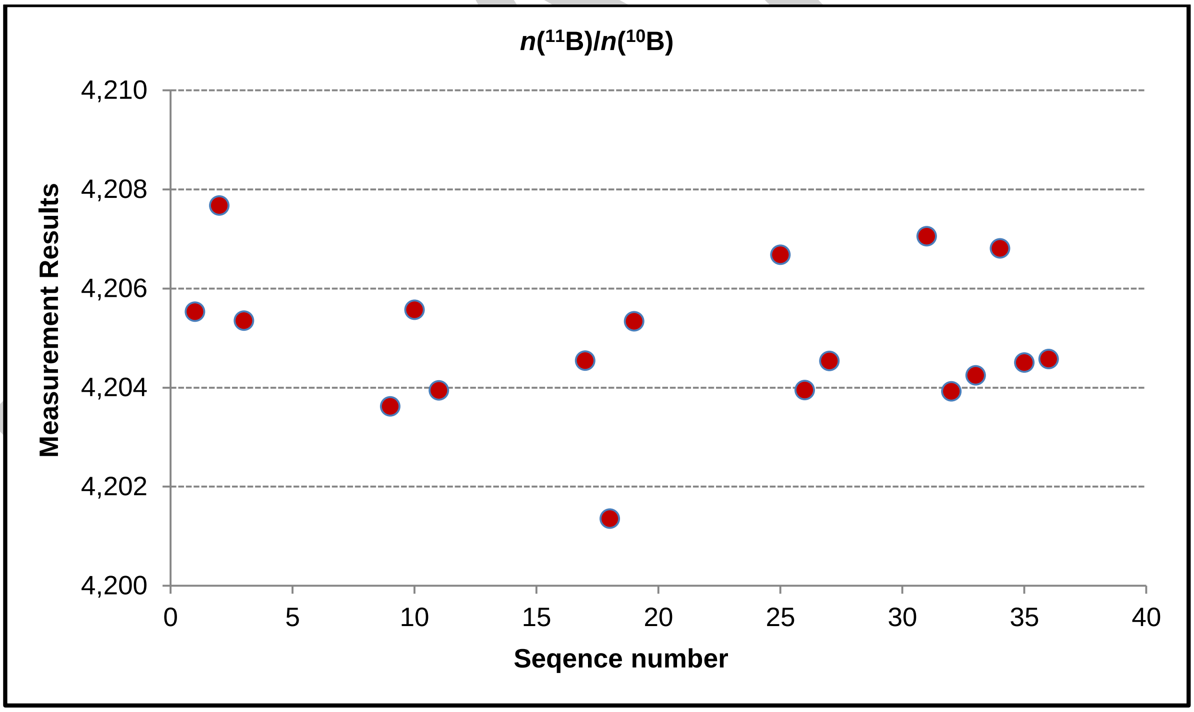
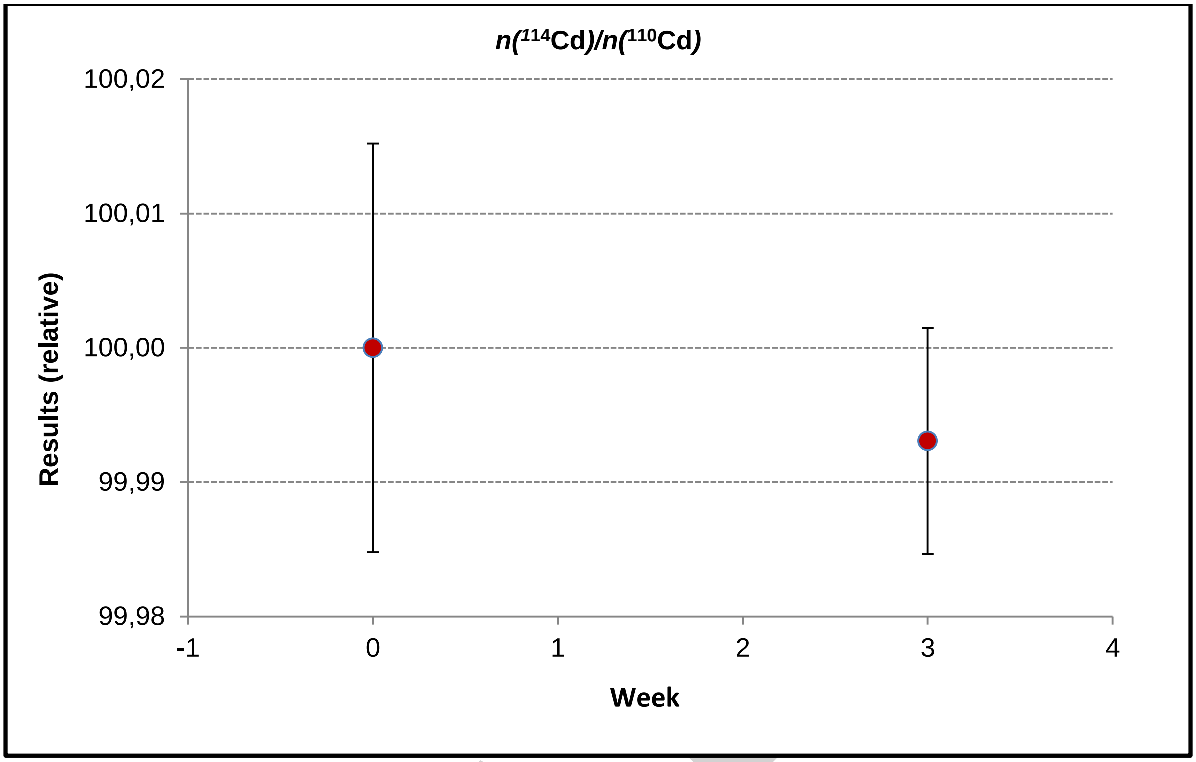


Figure A2.1. Short-term stability at +45 °C for $n(^{11}B)/n(^{10}B)$



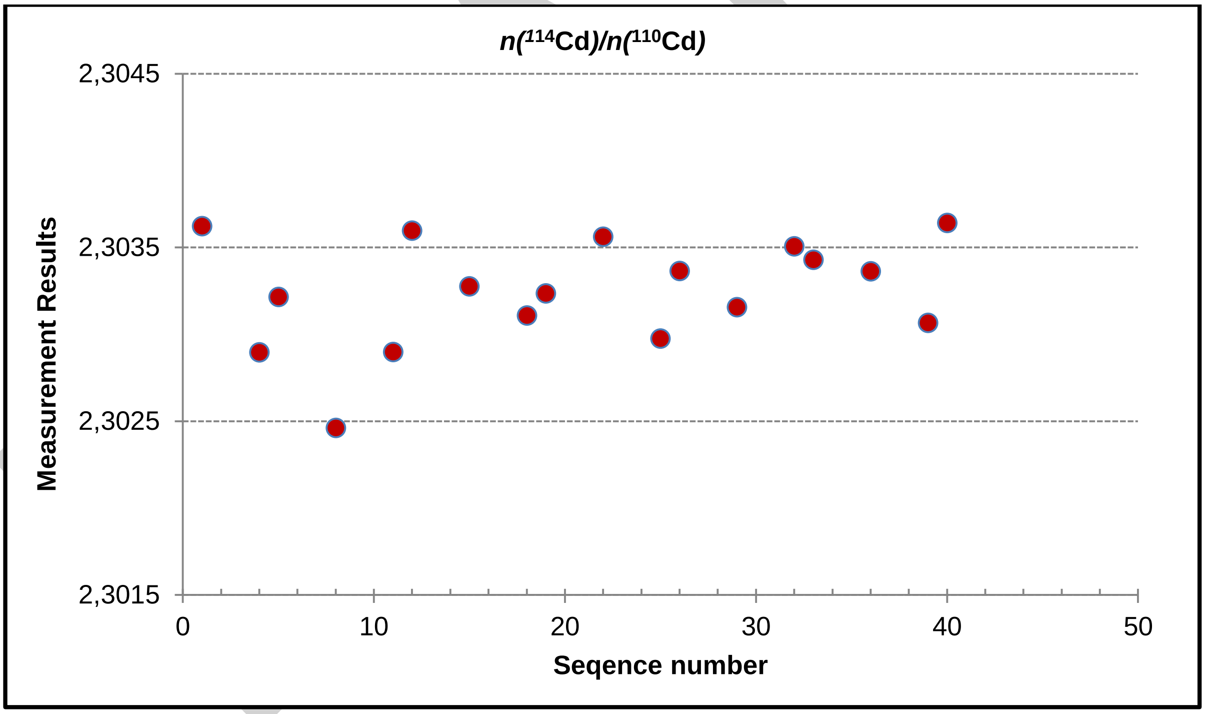
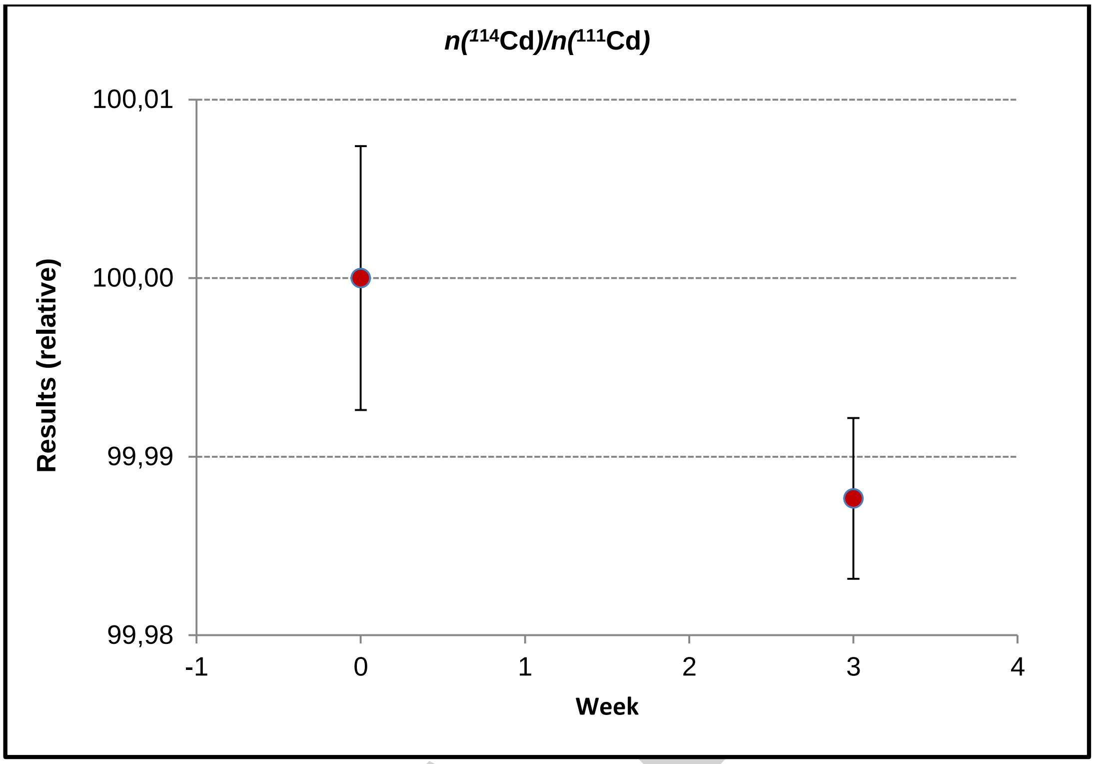


Figure A2.2. Short-term stability at +45 °C for $n(^{114}\text{Cd})/n(^{110}\text{Cd})$



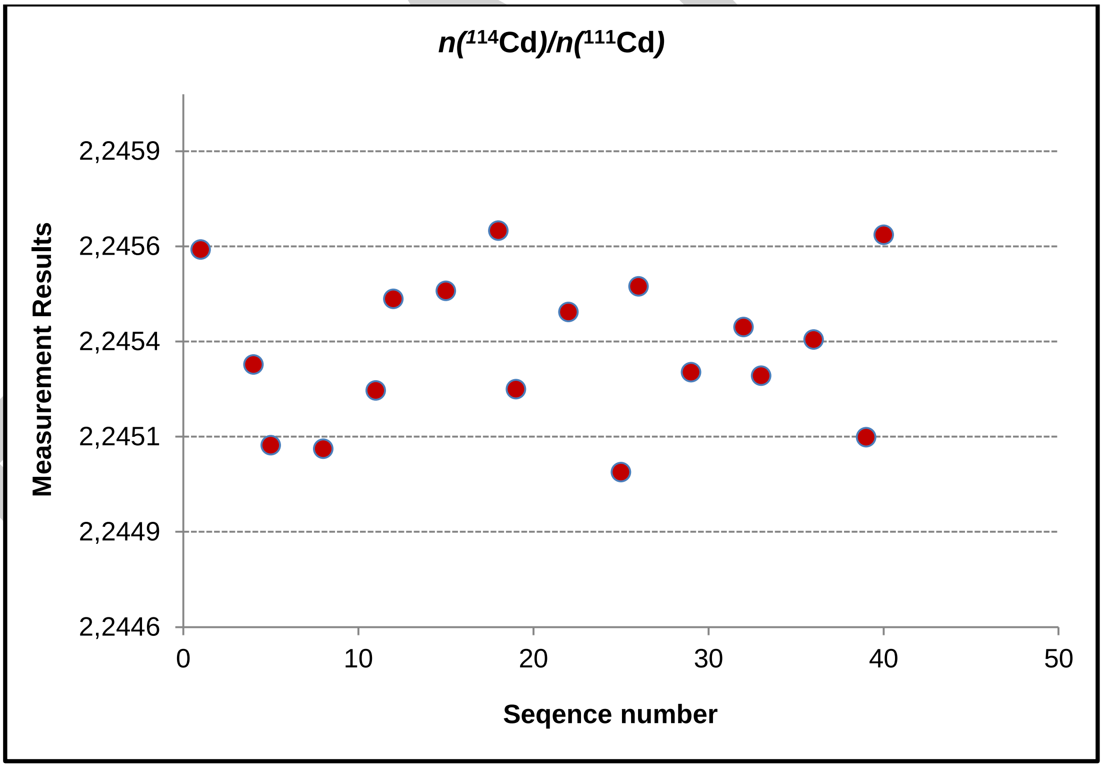
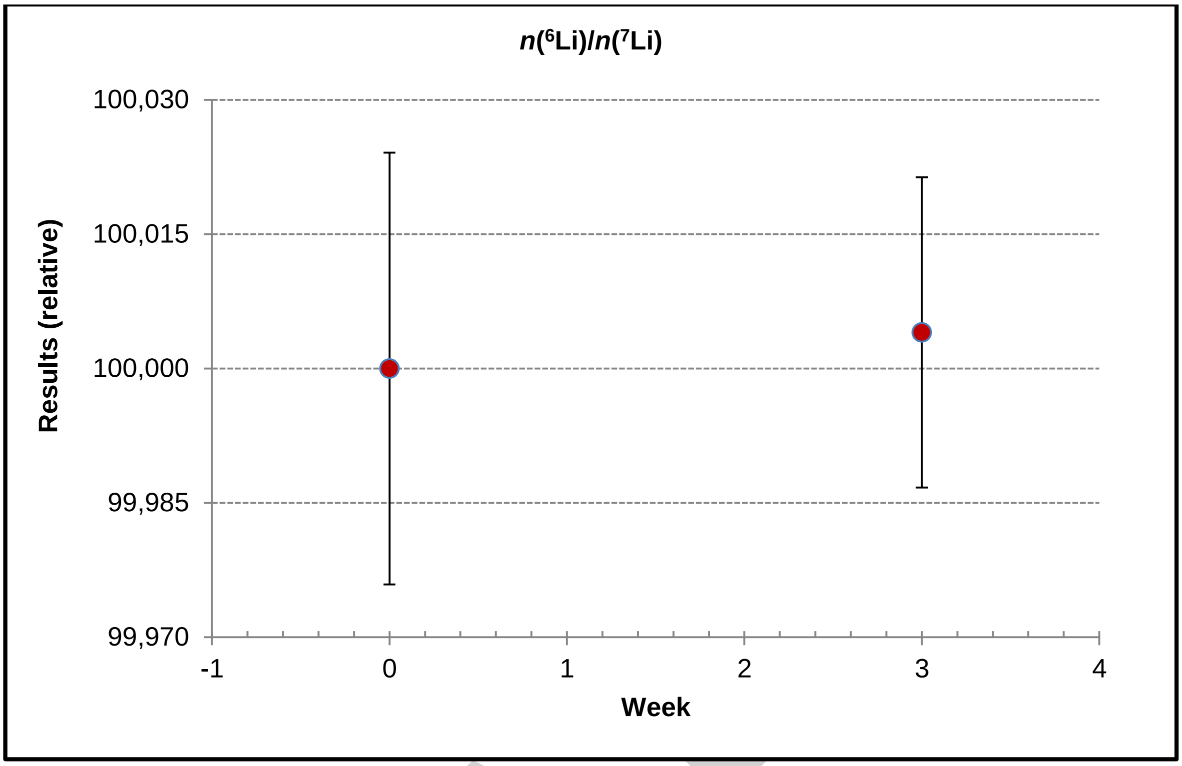


Figure A2.3. Short-term stability at +45 °C for $n(^{114}\mathrm{Cd})/n(^{111}\mathrm{Cd})$



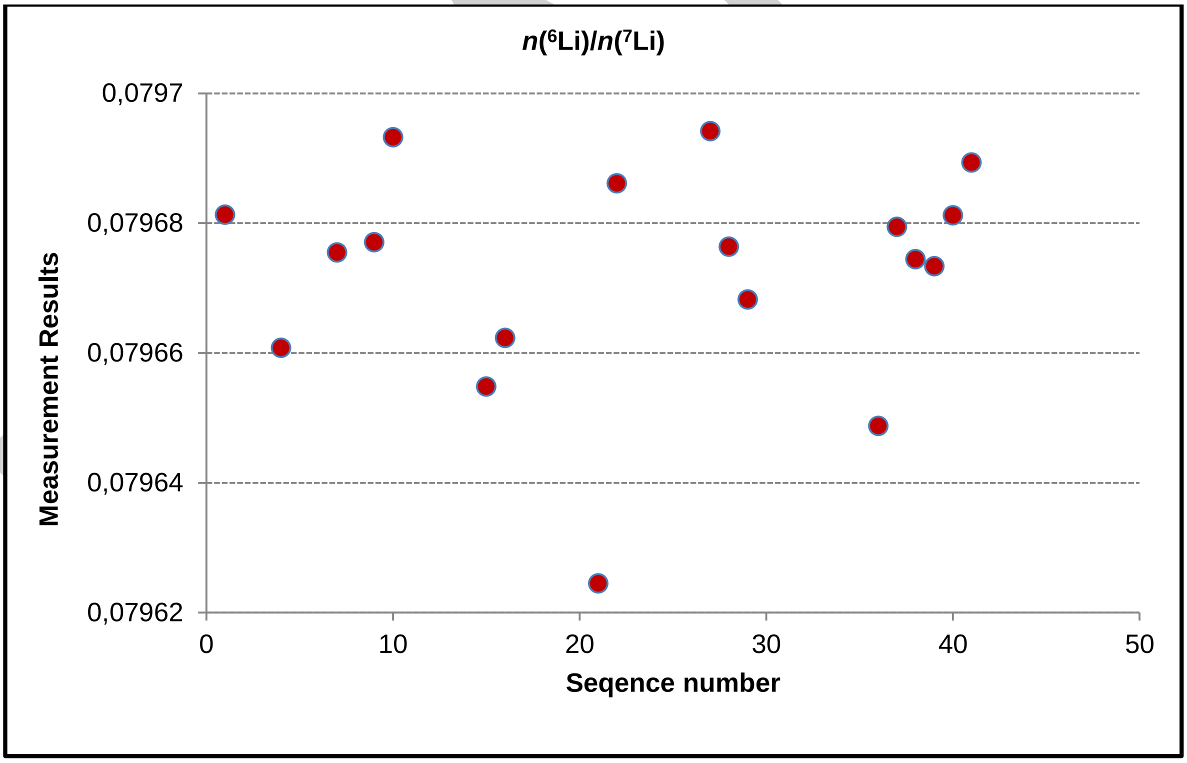
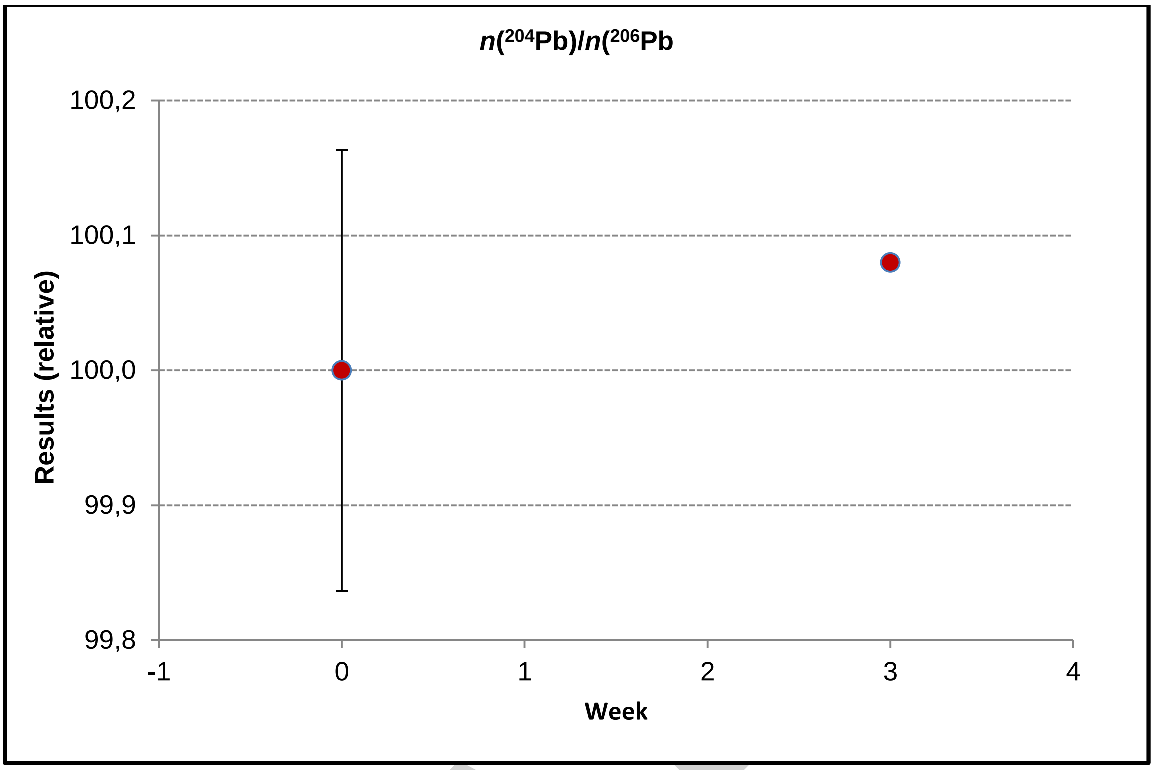


Figure A2.4. Short-term stability at +45 °C for $n(^6\text{Li})/n(^7\text{Li})$



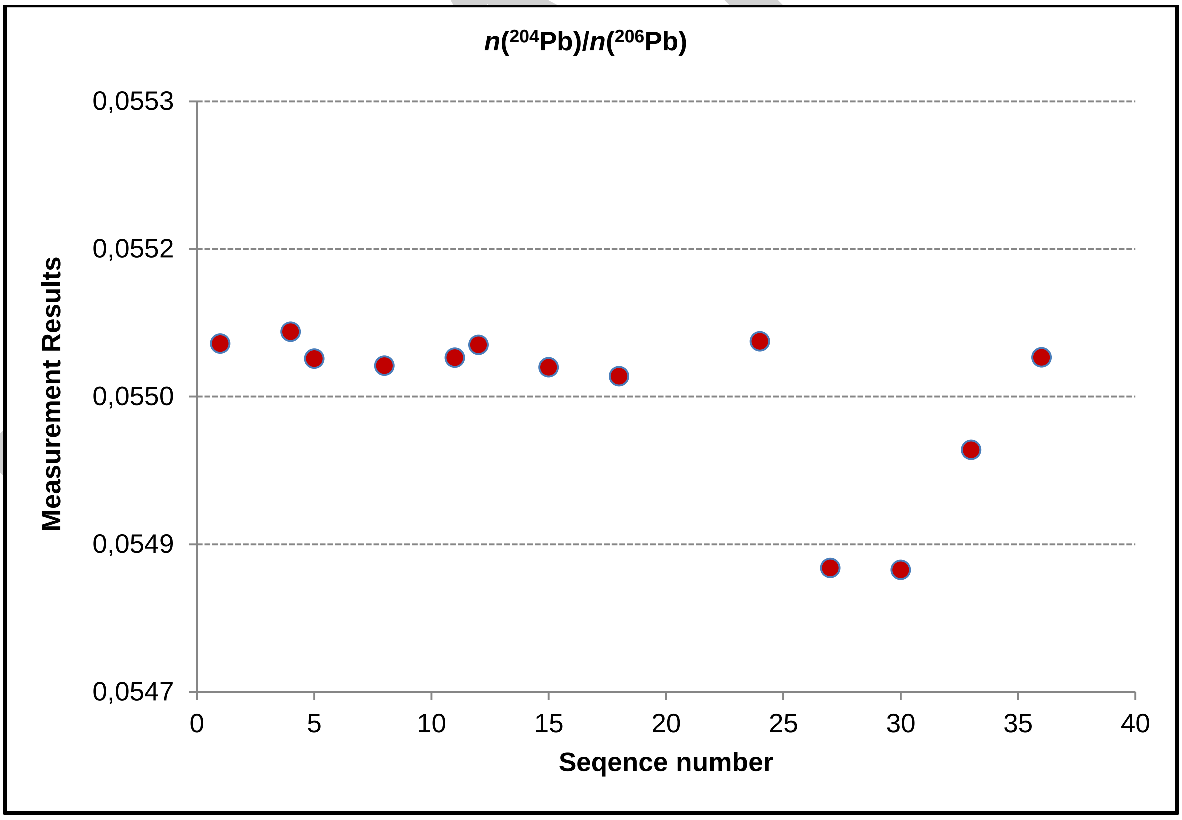
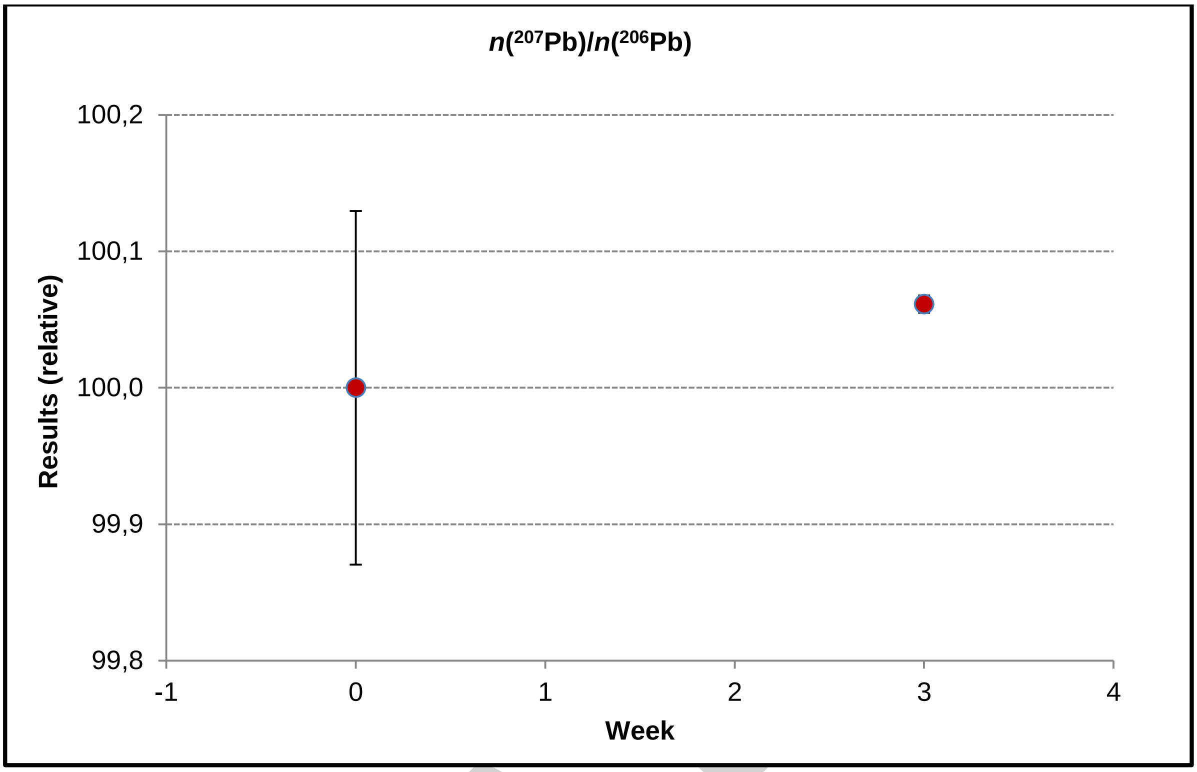


Figure A2.5. Short-term stability at +45 °C for $n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$



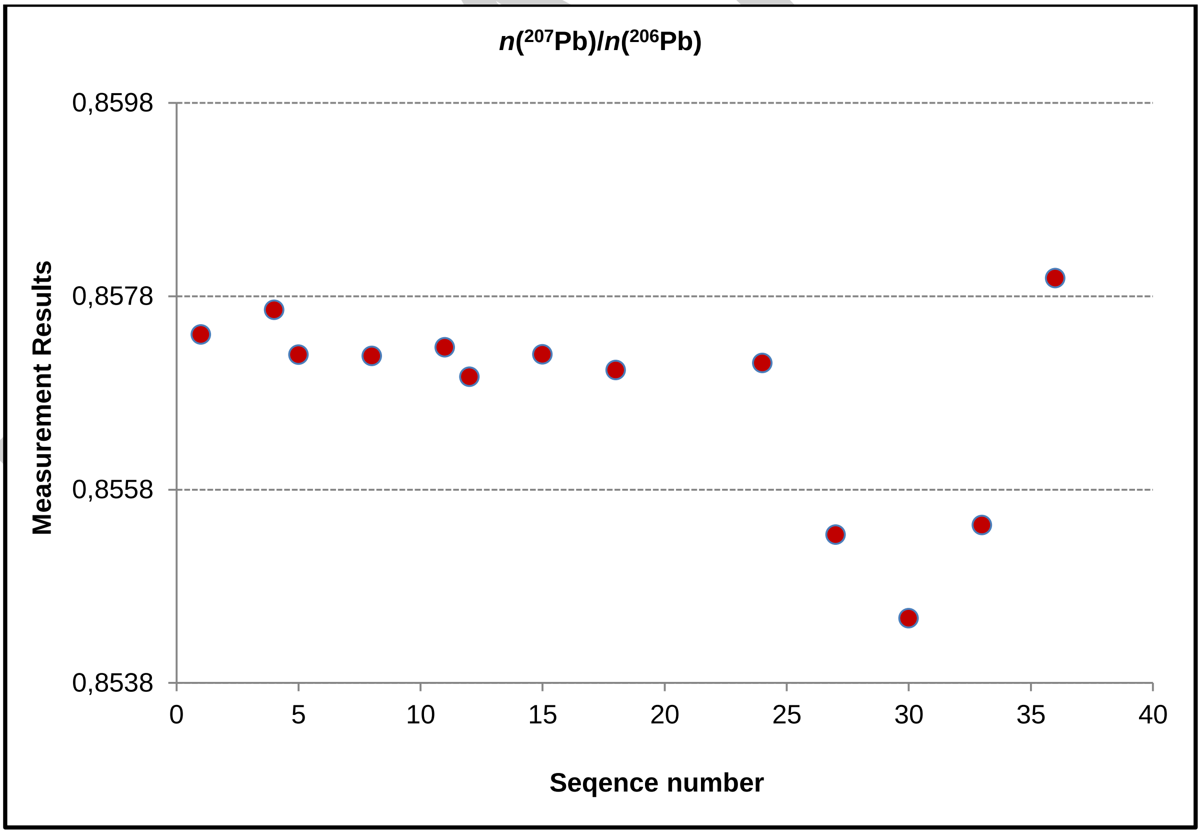
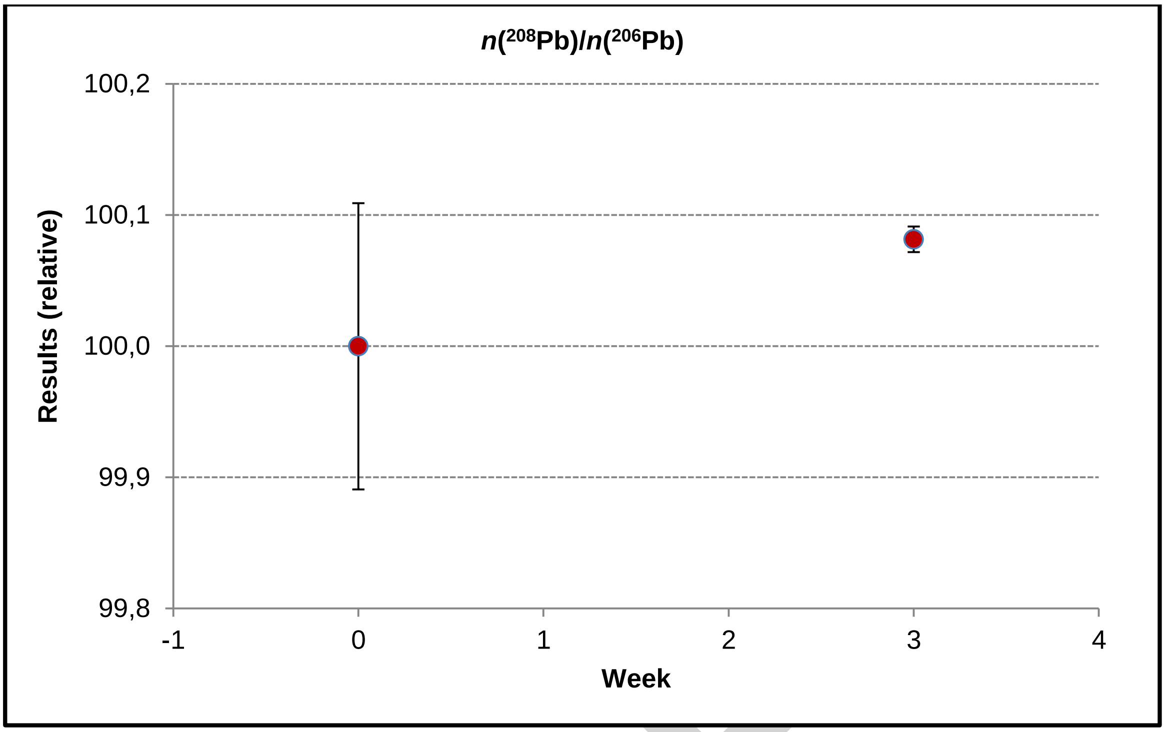


Figure A2.6. Short-term stability at +45 °C for $n(^{207}\text{Pb})/n(^{206}\text{Pb})$



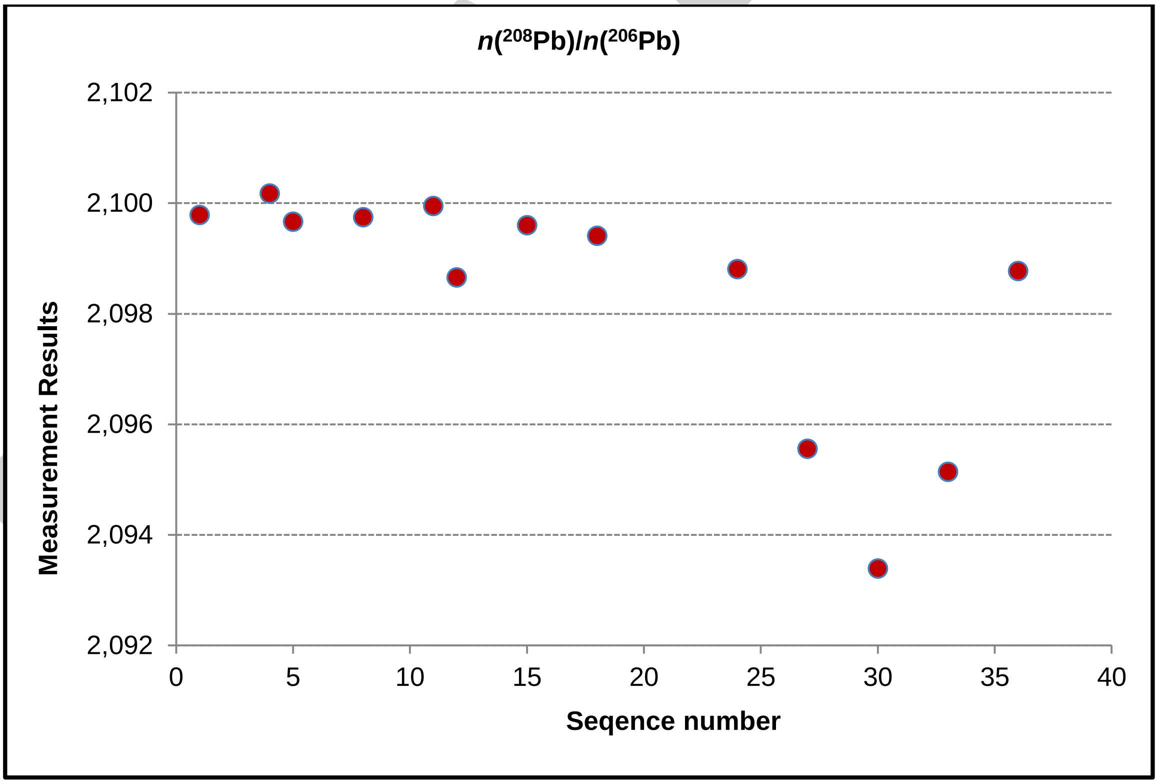
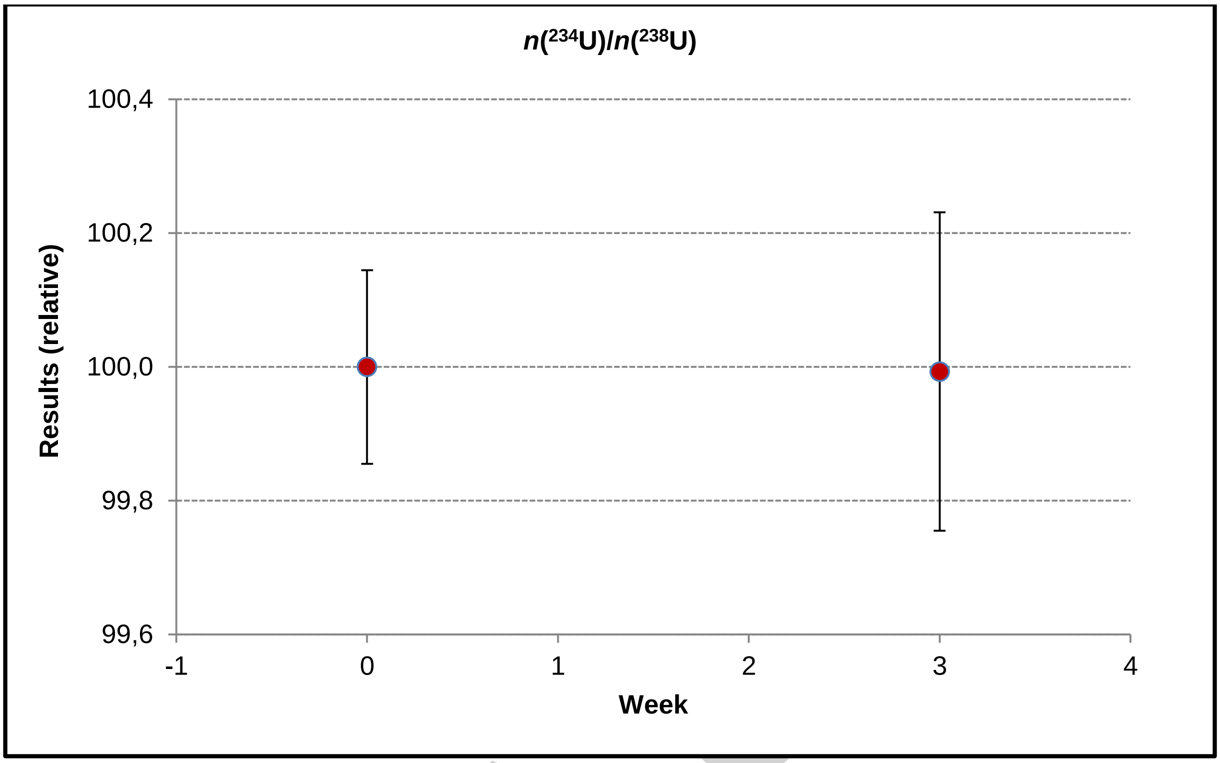


Figure A2.7. Short-term stability at +45 °C for $n(^{208}\text{Pb})/n(^{206}\text{Pb})$



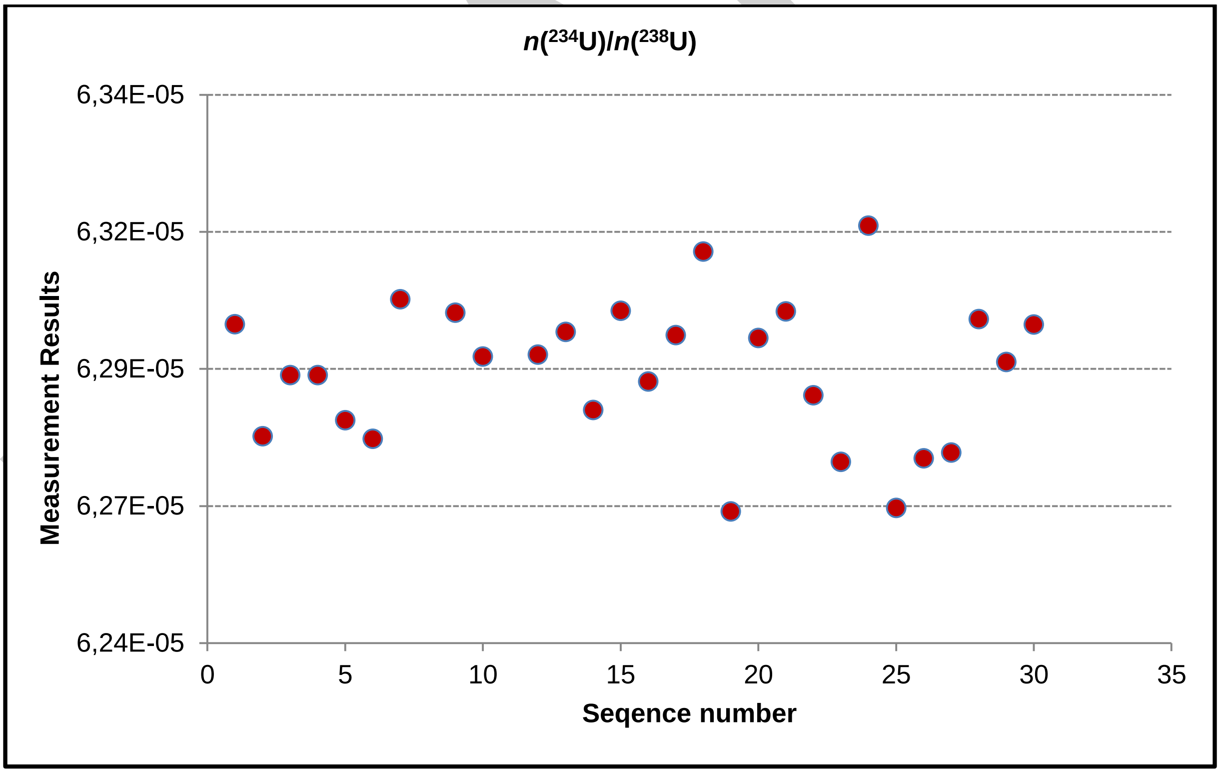
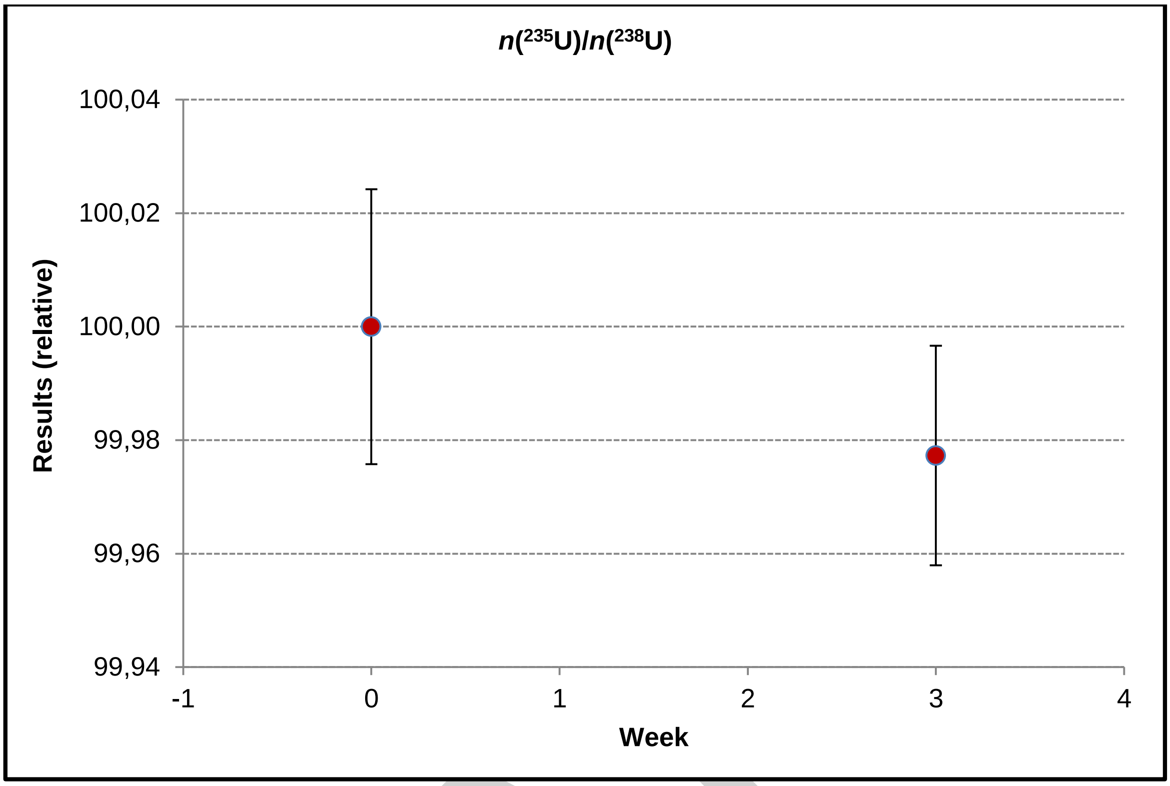


Figure A2.8. Short-term stability at +45 °C for $n(^{234}U)/n(^{238}U)$



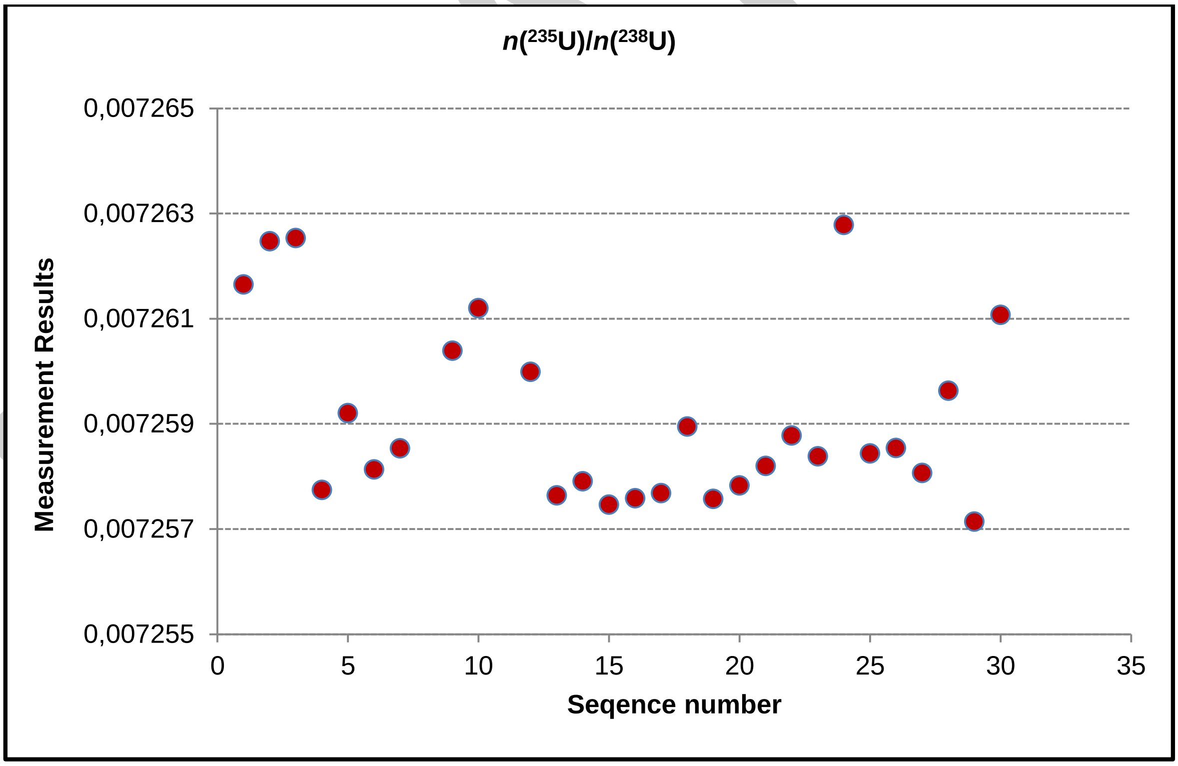
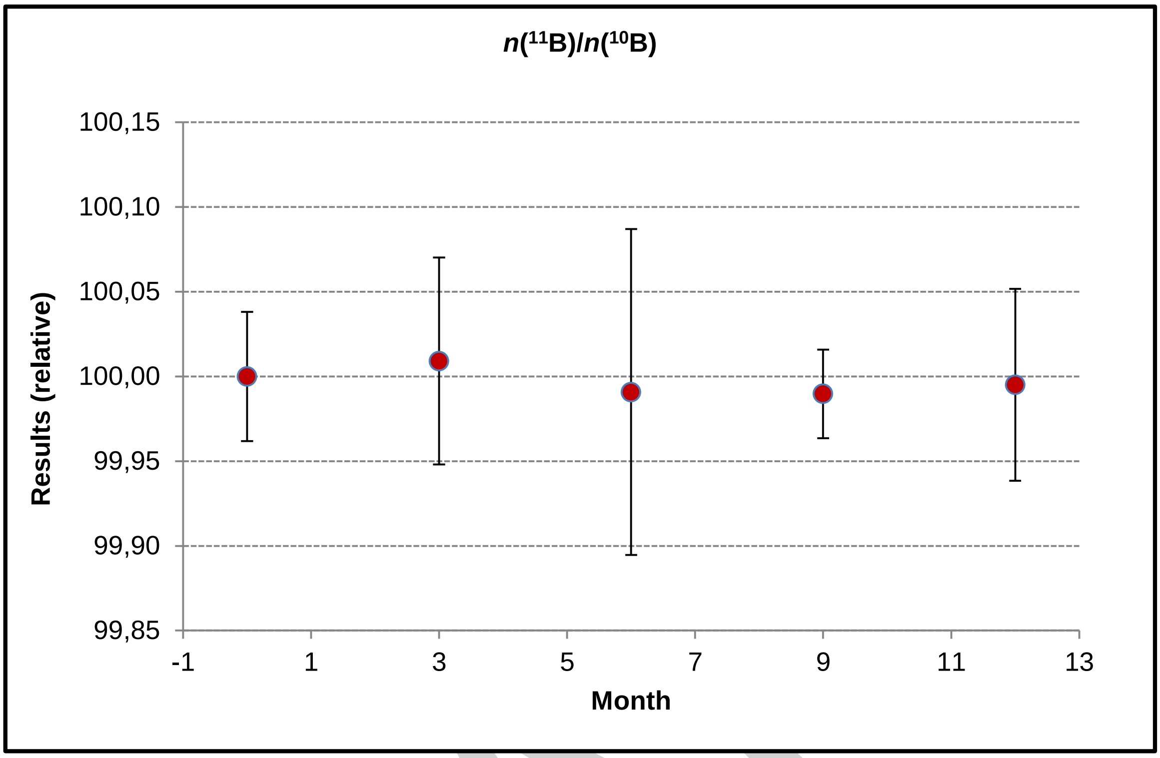


Figure A2.9. Short-term stability at +45 °C for $n(^{235}U)/n(^{238}U)$

Annex 3. Graphs of Long-Term Stability Study



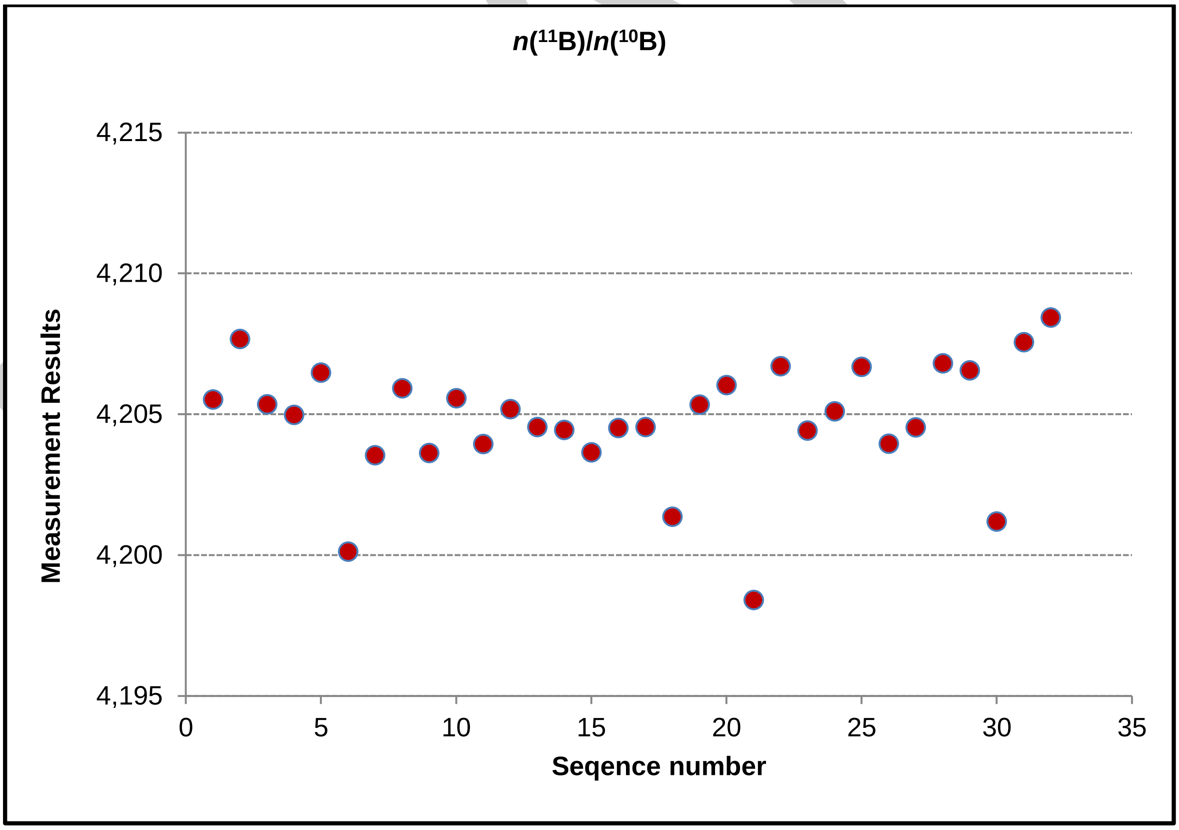


Figure A3.1. Long-term stability at +21 °C for $n(^{11}\mathrm{B})/n(^{10}\mathrm{B})$

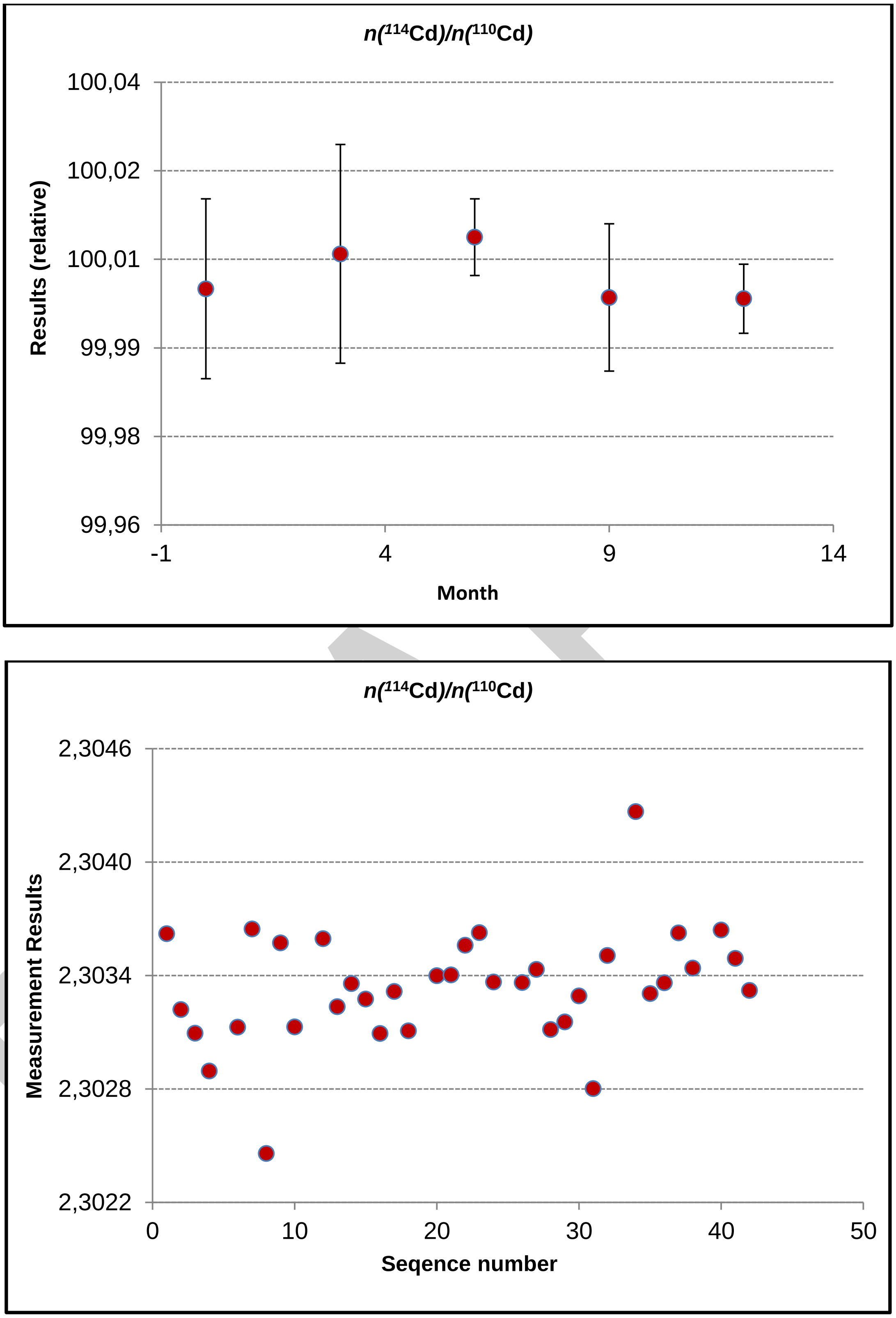


Figure A3.2. Long-term stability at +21 °C for $n(^{114}\text{Cd})/n(^{110}\text{Cd})$

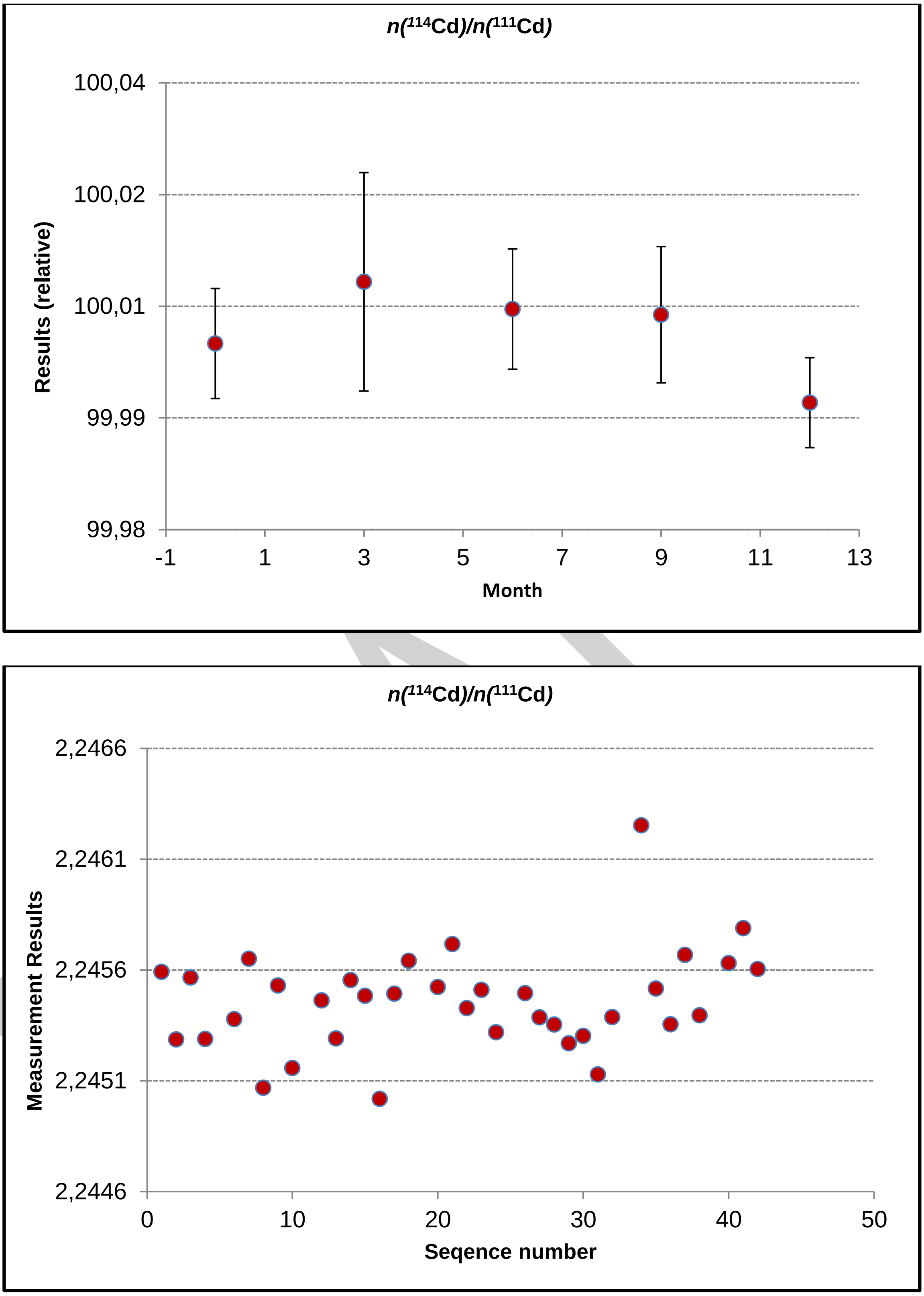
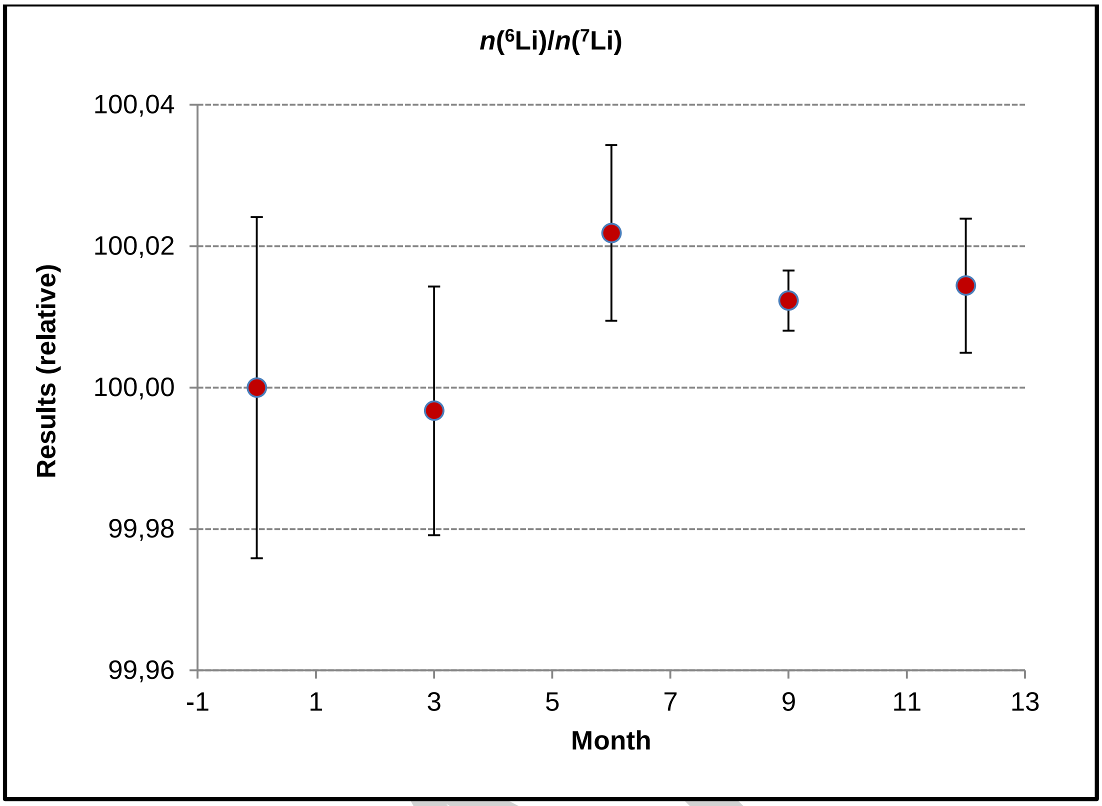


Figure A3.3. Long-term stability at +21 °C for *n*(^{114}Cd)/*n*(^{111}Cd)



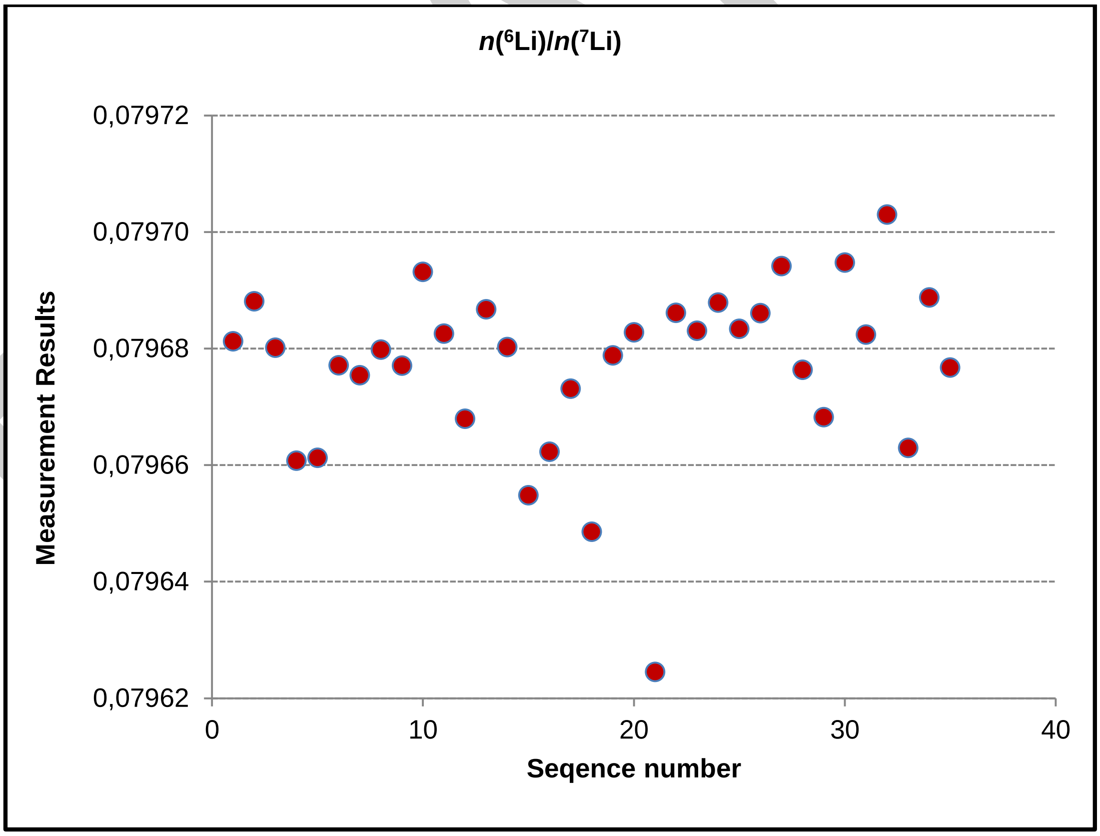


Figure A3.4. Long-term stability at +21 °C for $n(^{6}\text{Li})/n(^{7}\text{Li})$

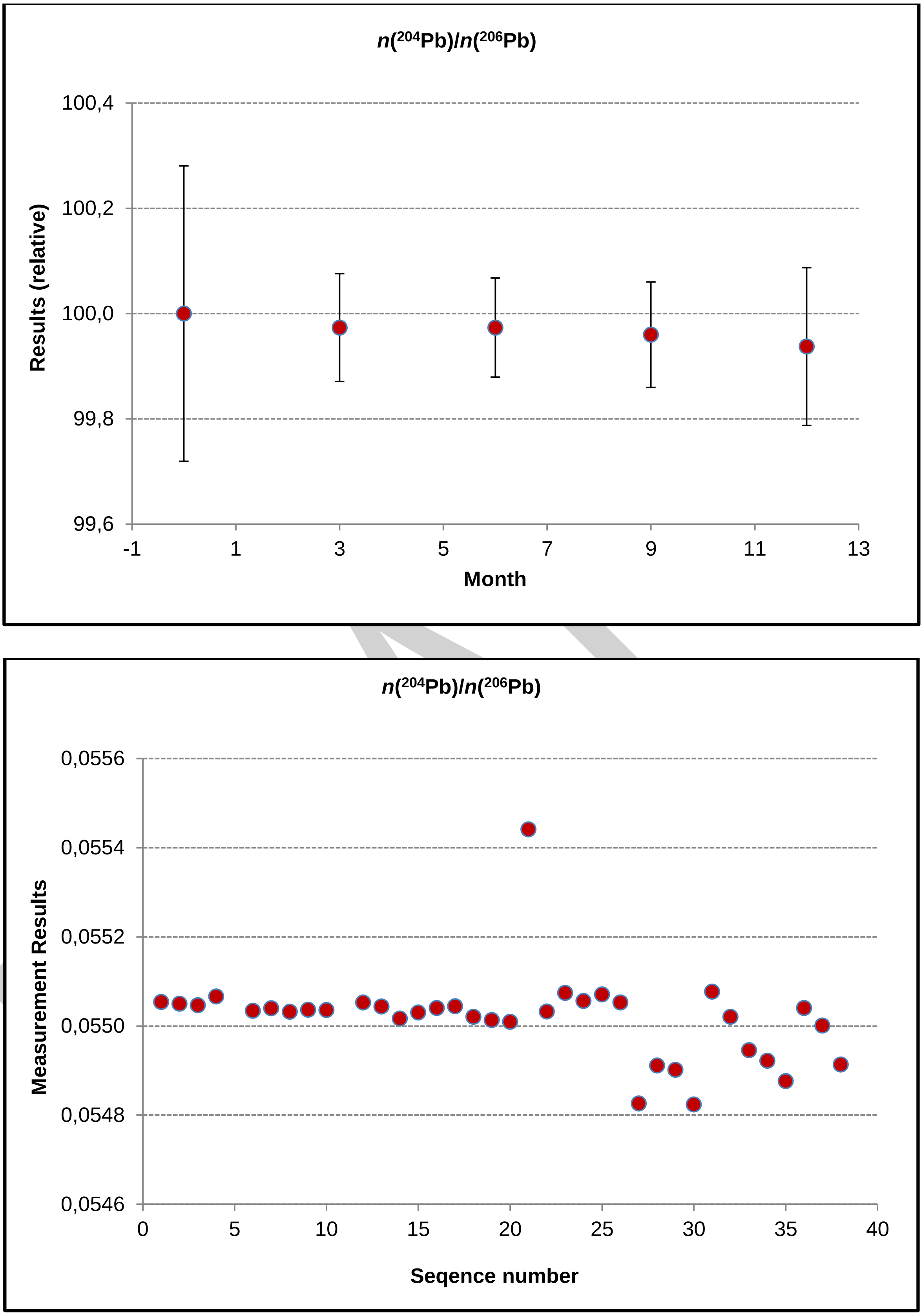
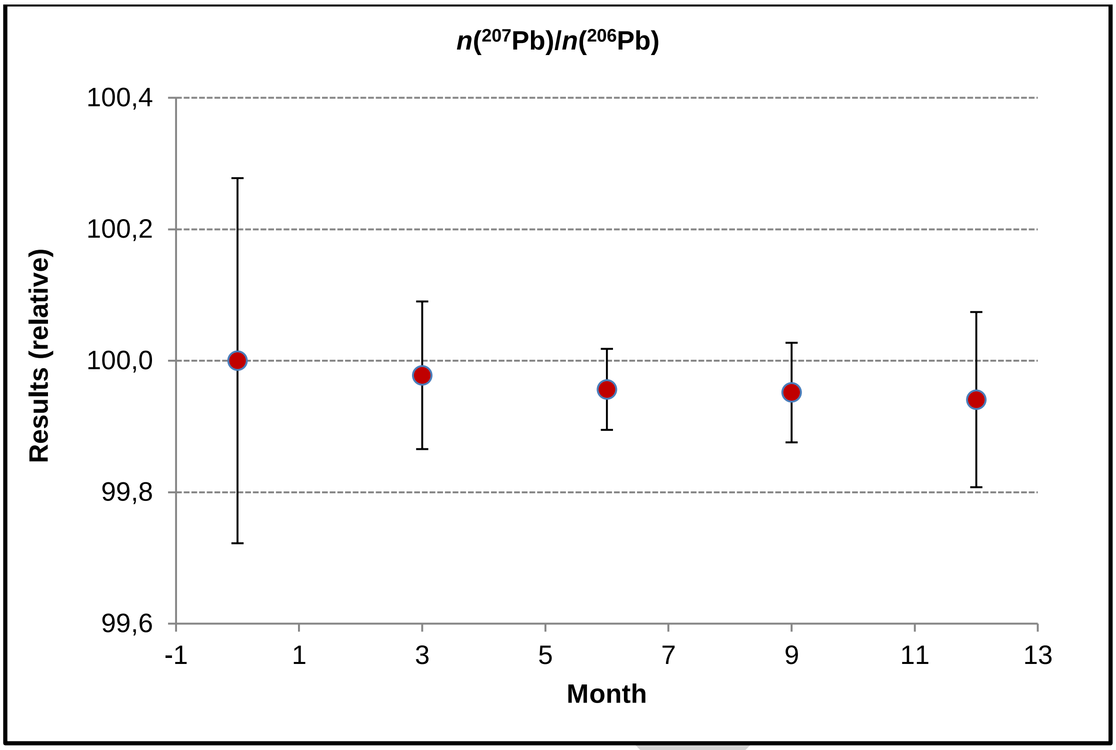
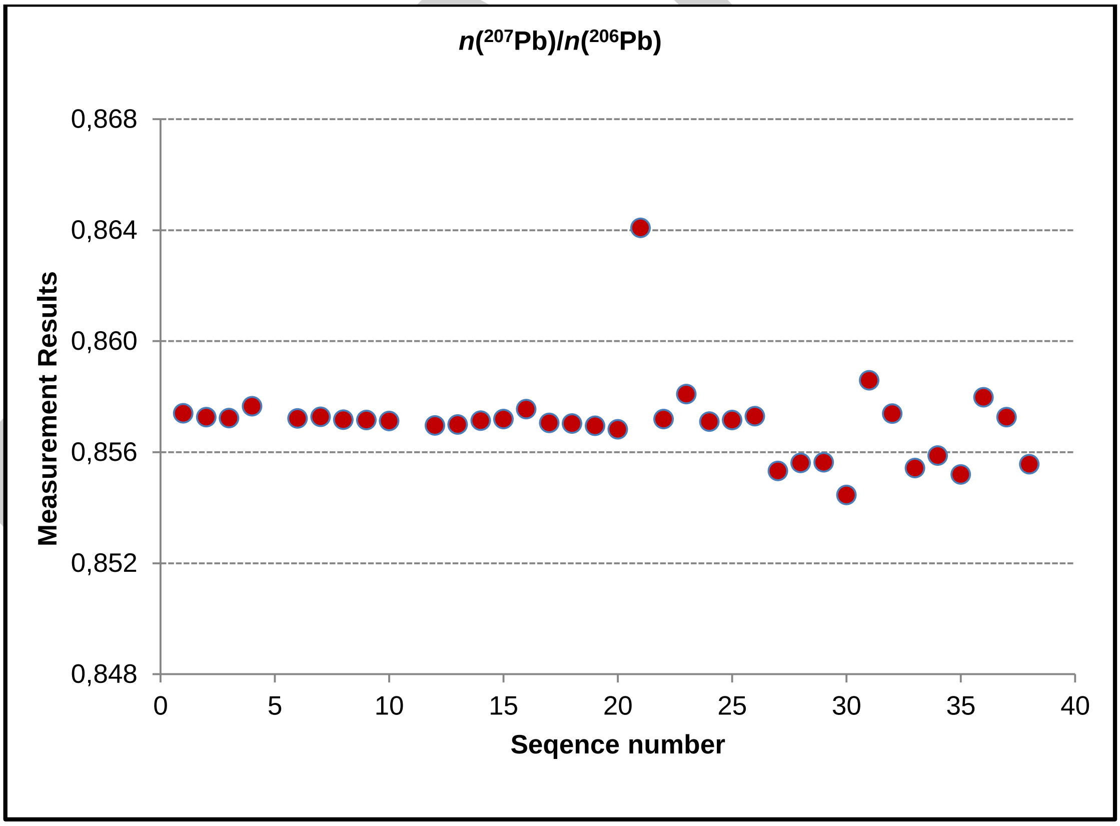


Figure A3.5. Long-term stability at +21 °C for $n(^{204}\text{Pb})/n(^{206}\text{Pb})$





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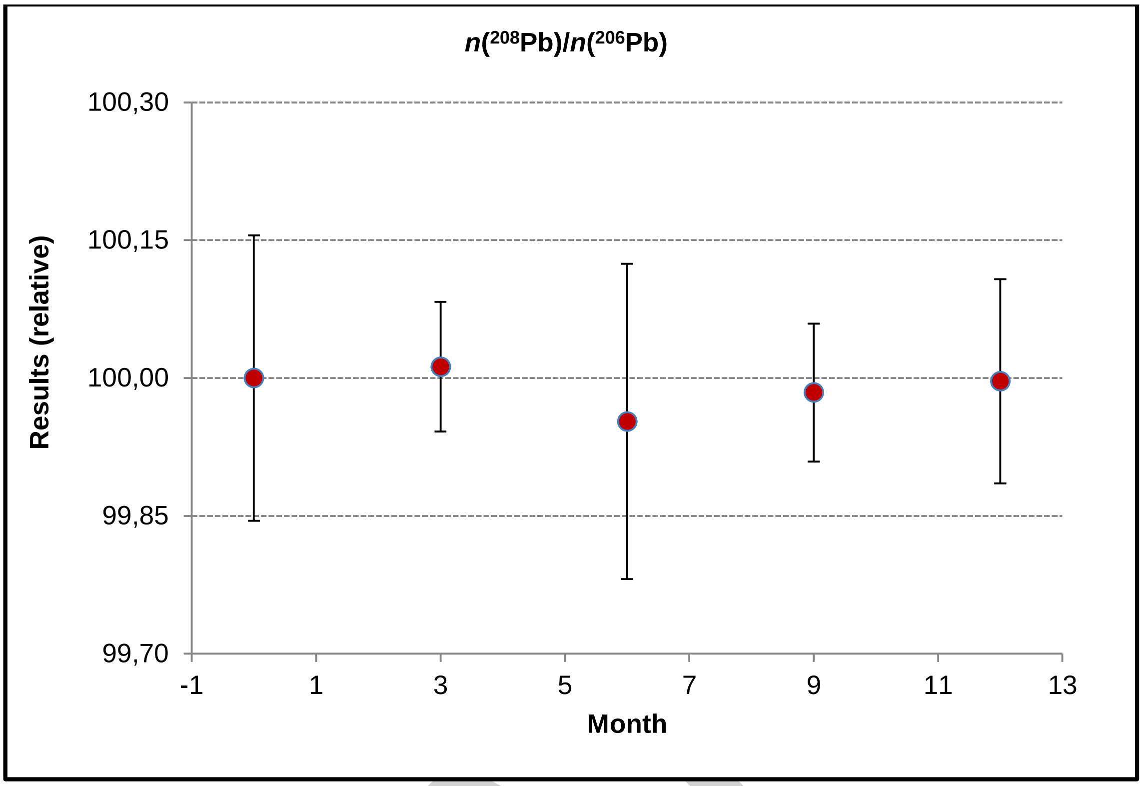


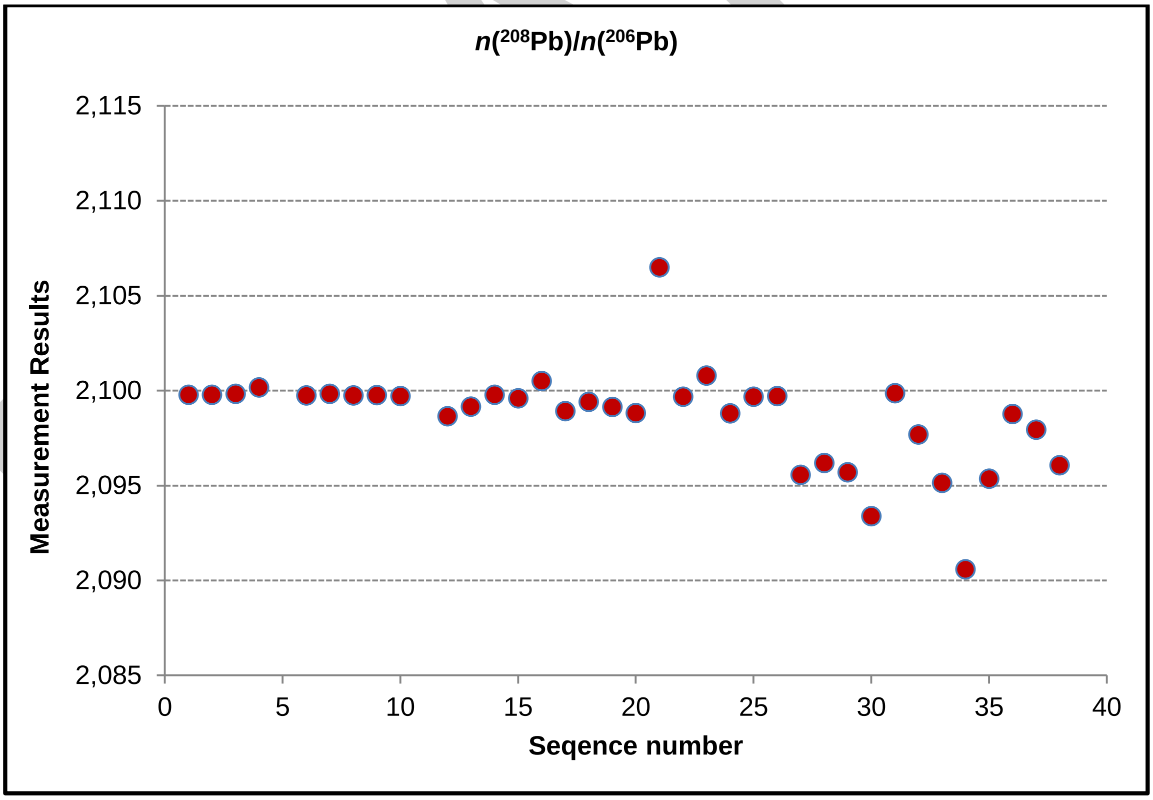
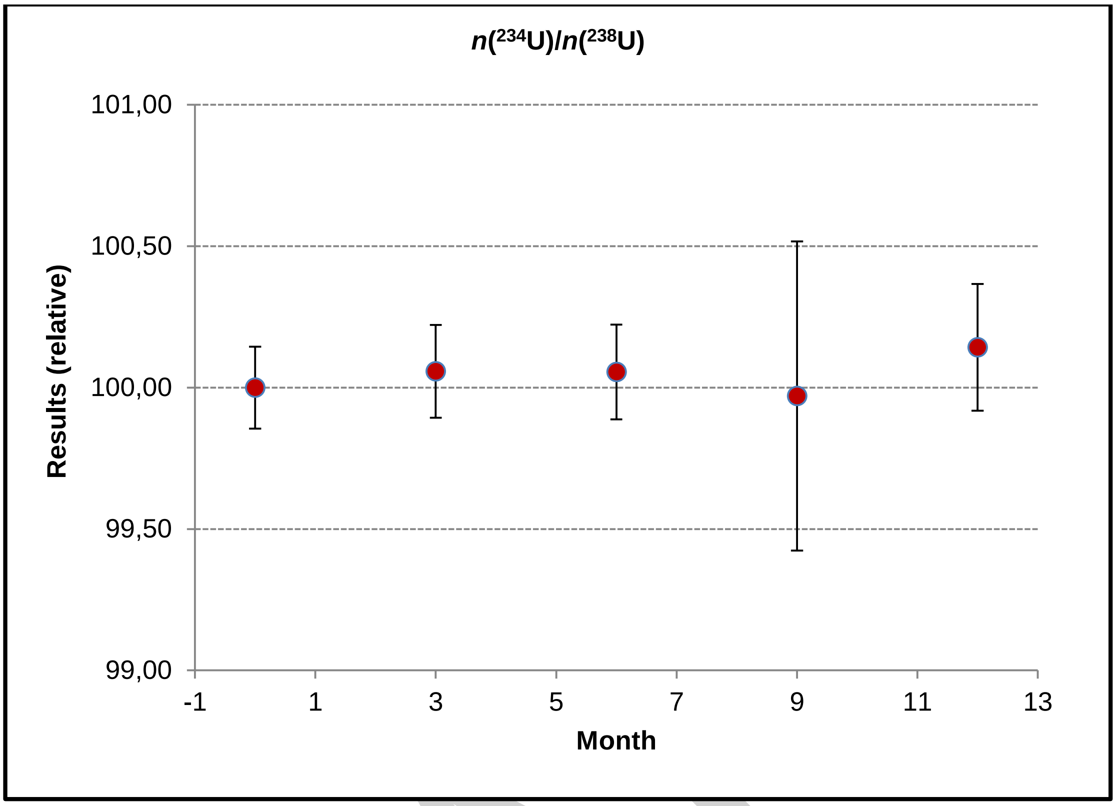


Figure A3.7. Long-term stability at +21 °C for $n(^{208}\text{Pb})/n(^{206}\text{Pb})$



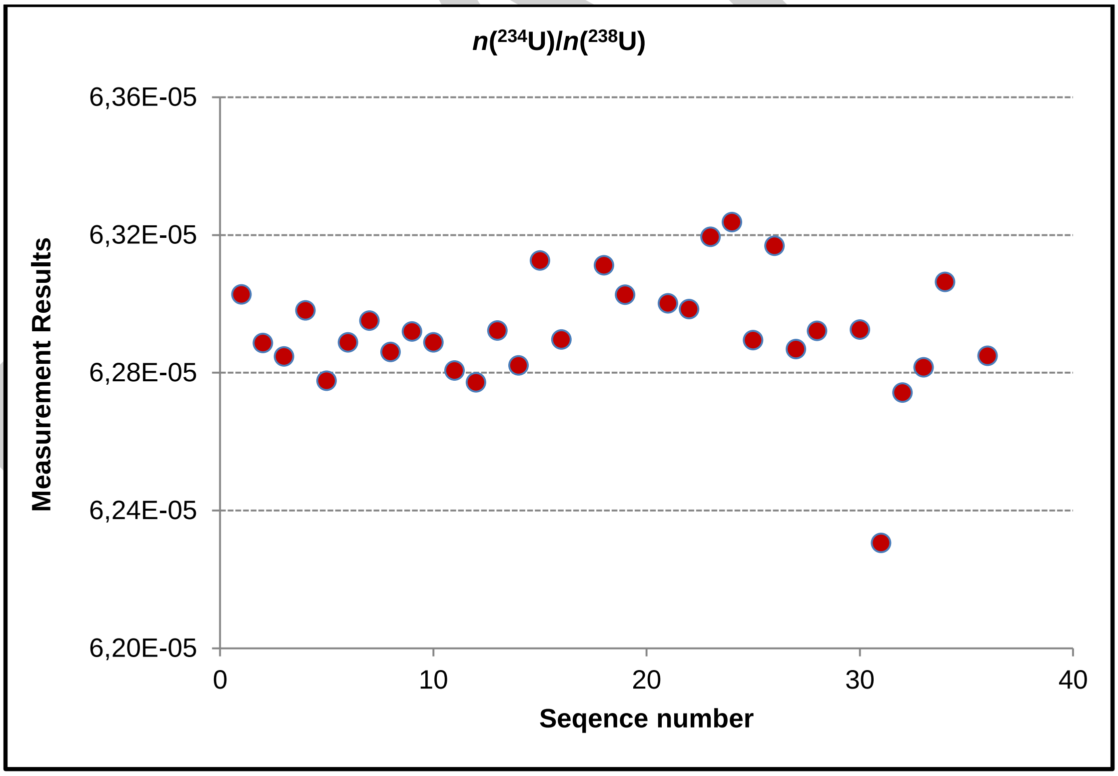
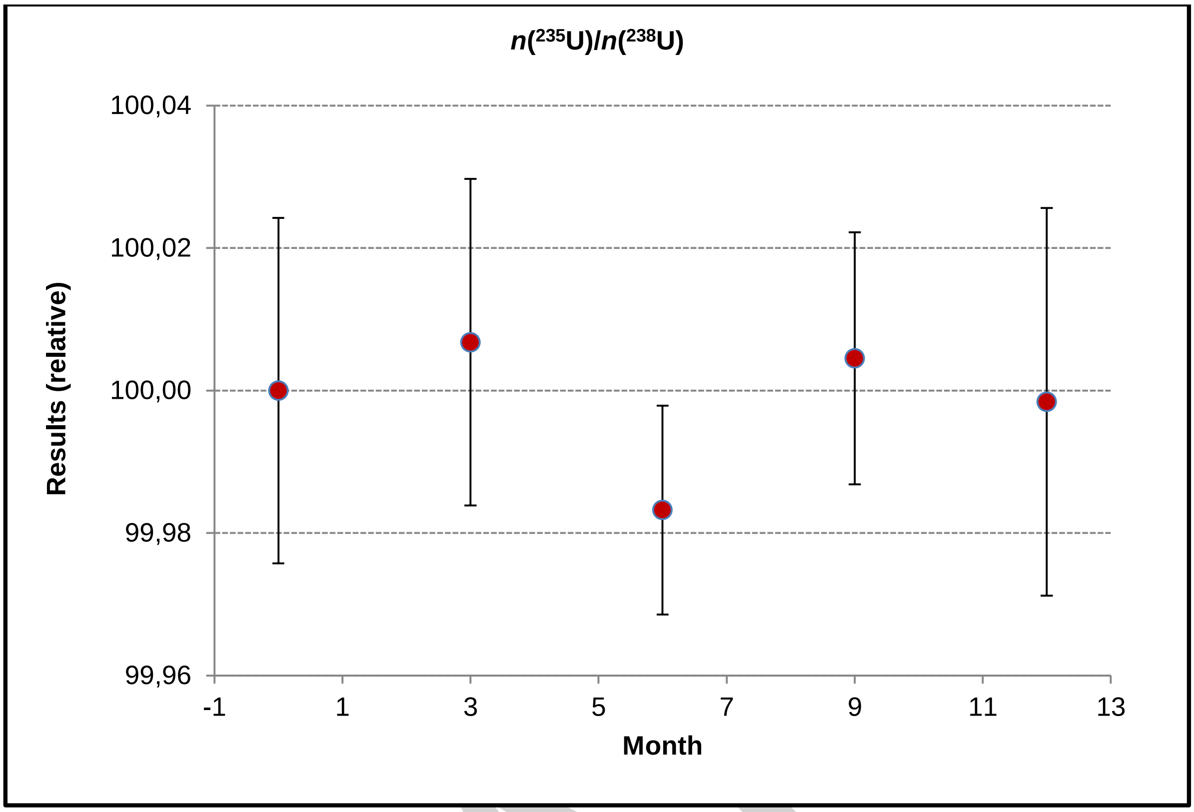


Figure A3.8. Long-term stability at +21 °C for °C for $n(^{234}\mathrm{U})/n(^{238}\mathrm{U})$



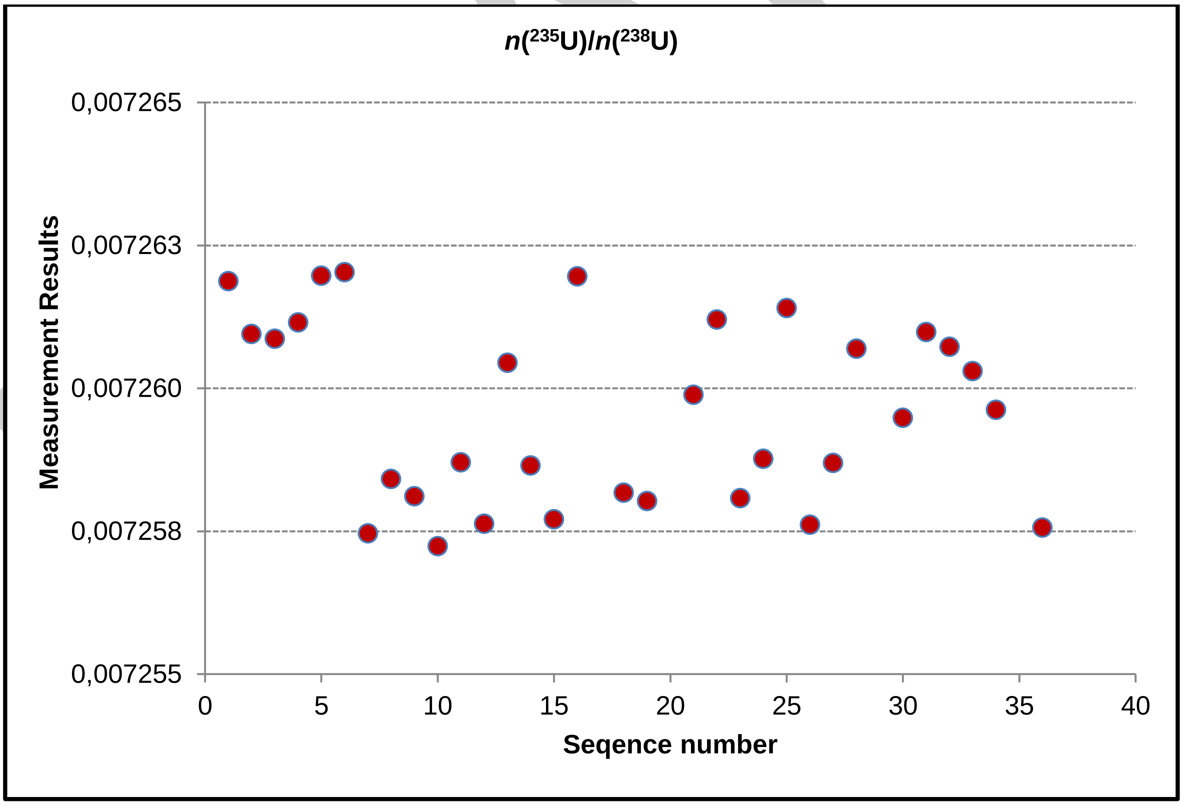


Figure A3.9. Long-term stability at +21 °C for °C for $n(^{235}\mathrm{U})/n(^{238}\mathrm{U})$

Annex 4. Graphs of Interlaboratory Study for Characterisation

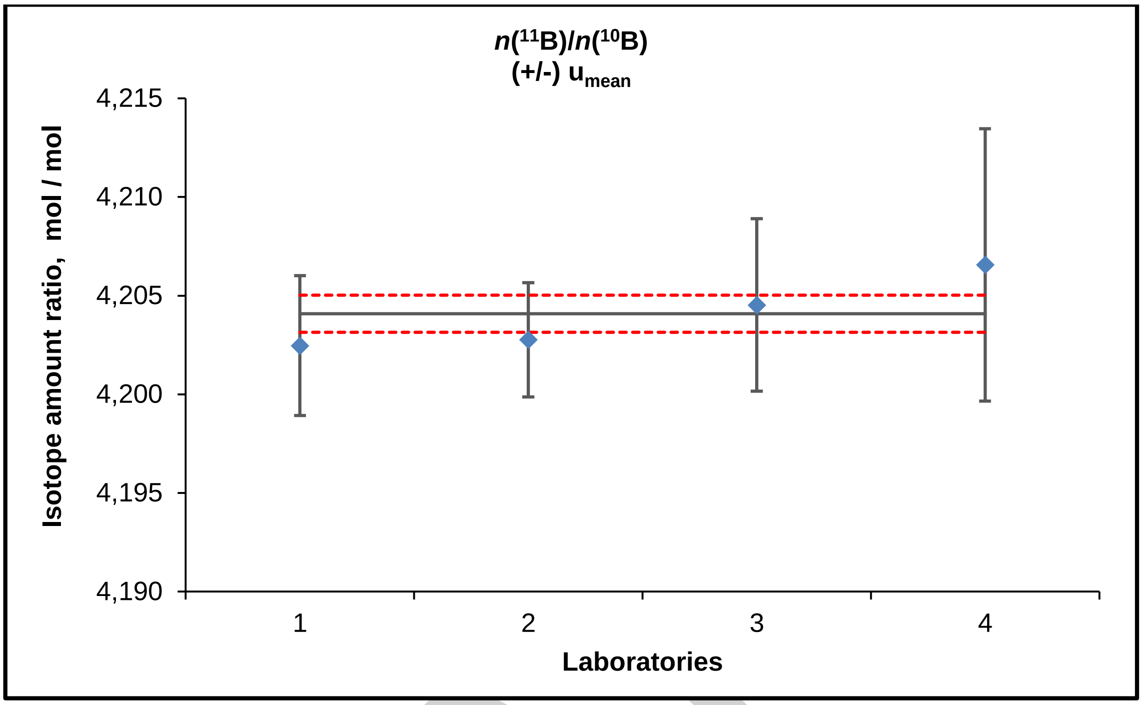


Figure A4.1. Interlaboratory study results for characterisation of $n(^{11}\text{B})/n(^{10}\text{B})$

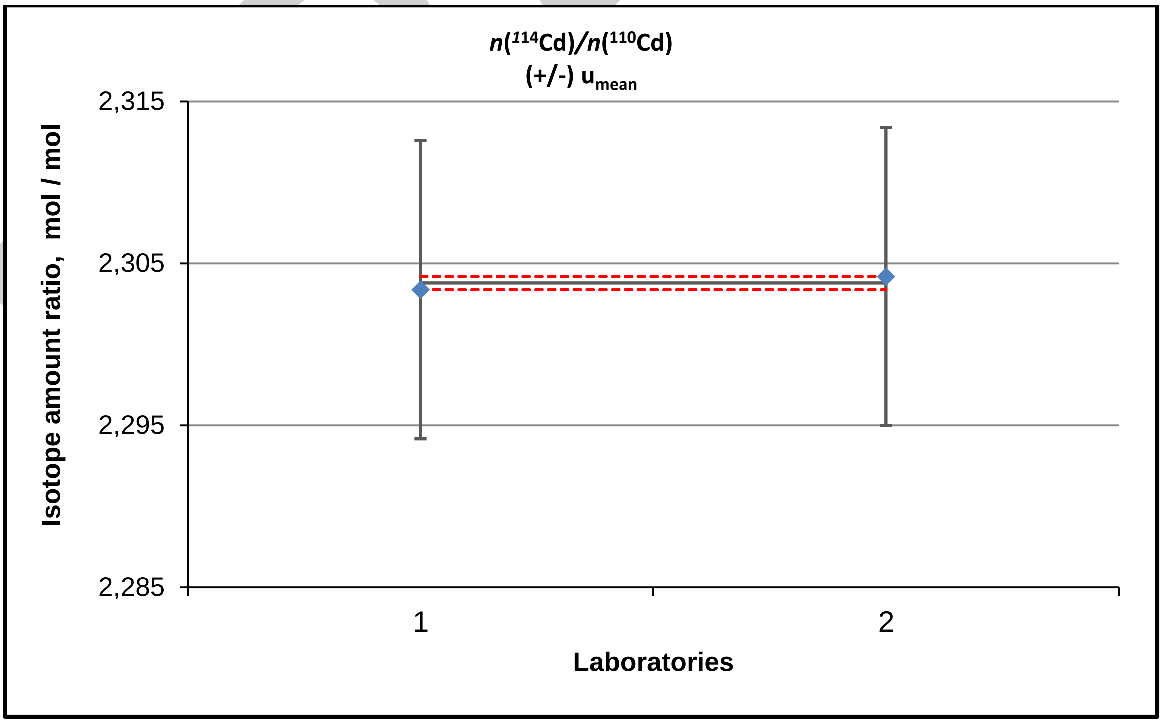


Figure A4.2. Interlaboratory study results for characterisation of $n(^{114}\text{Cd})/n(^{110}\text{Cd})$

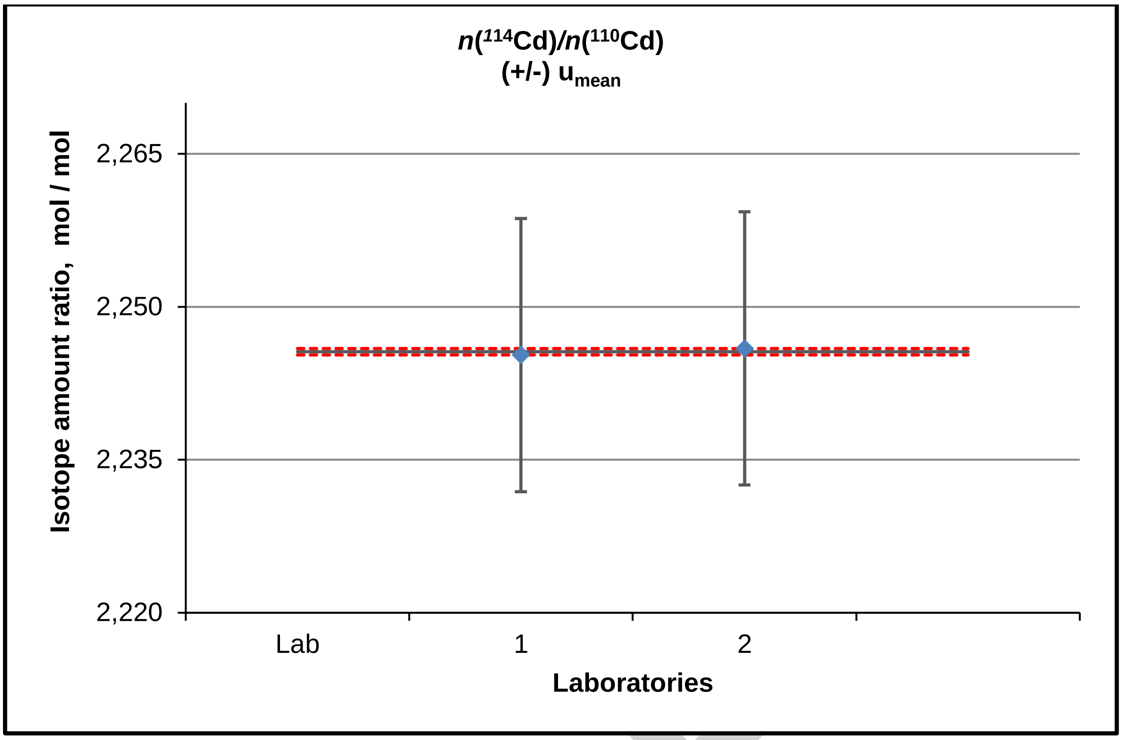


Figure A4.3. Interlaboratory study results for characterisation of $n(^{114}Cd)/n(^{111}Cd)$

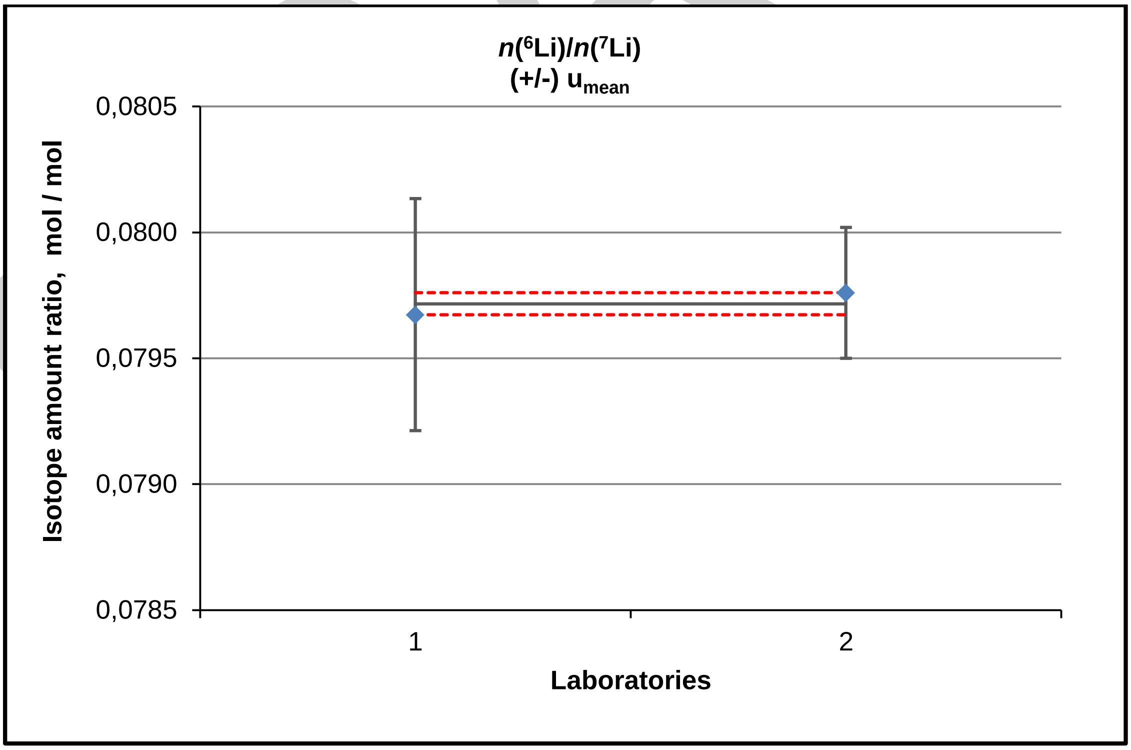


Figure A4.4. Interlaboratory study results for characterisation of $n(^{6}Li)/n(^{7}Li)$

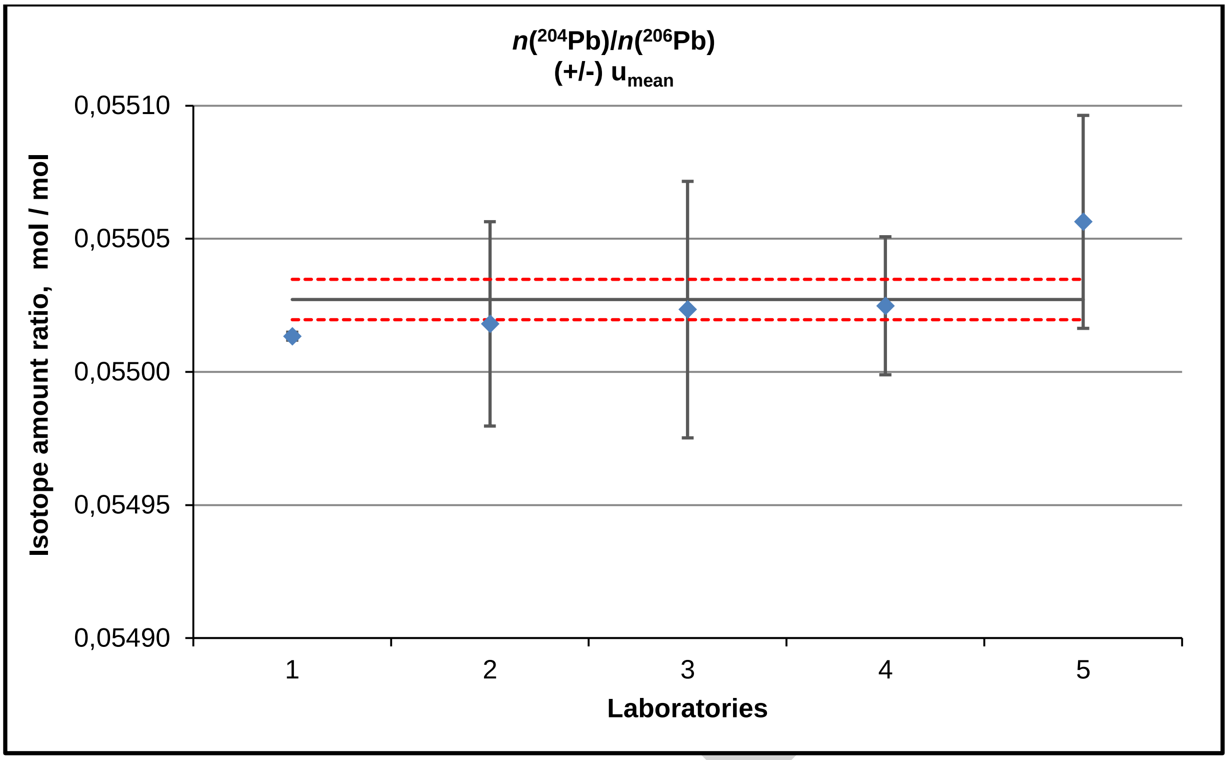


Figure A4.5. Interlaboratory study results for characterisation of $n(^{204}\mathrm{Pb})/n(^{206}\mathrm{Pb})$

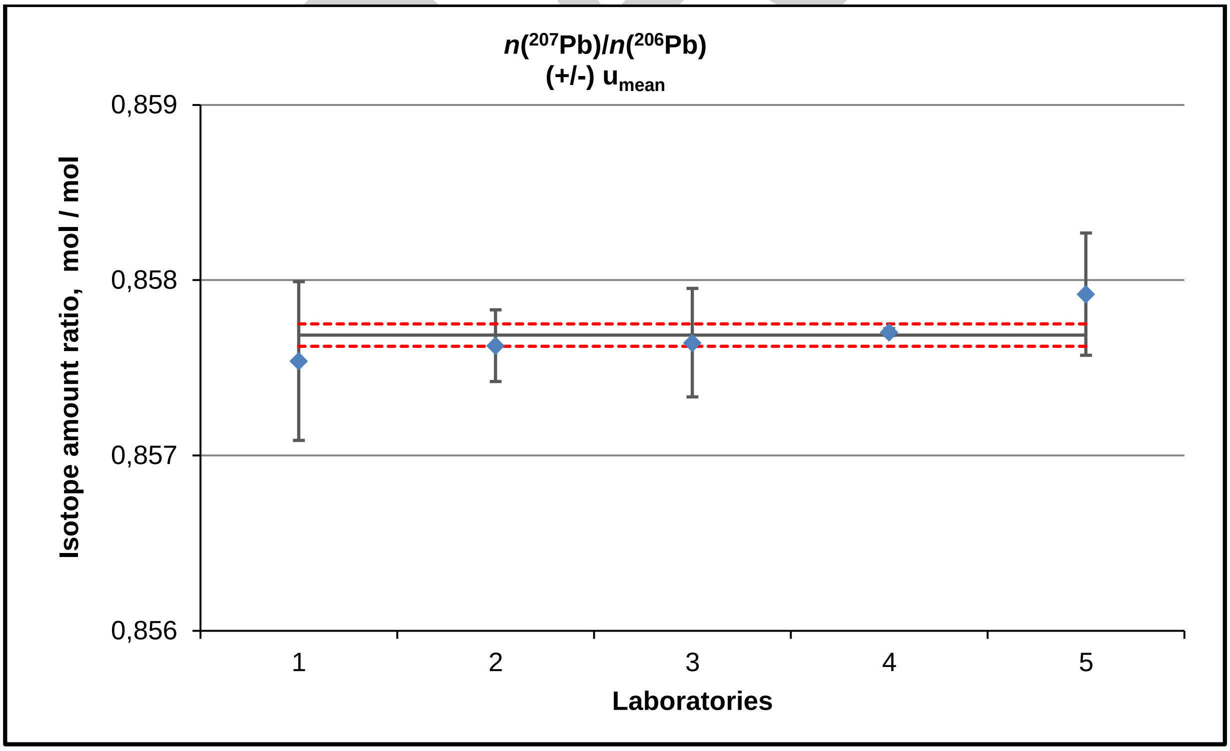


Figure A4.6. Interlaboratory study results for characterisation of $n(^{207}\mathrm{Pb})/n(^{206}\mathrm{Pb})$

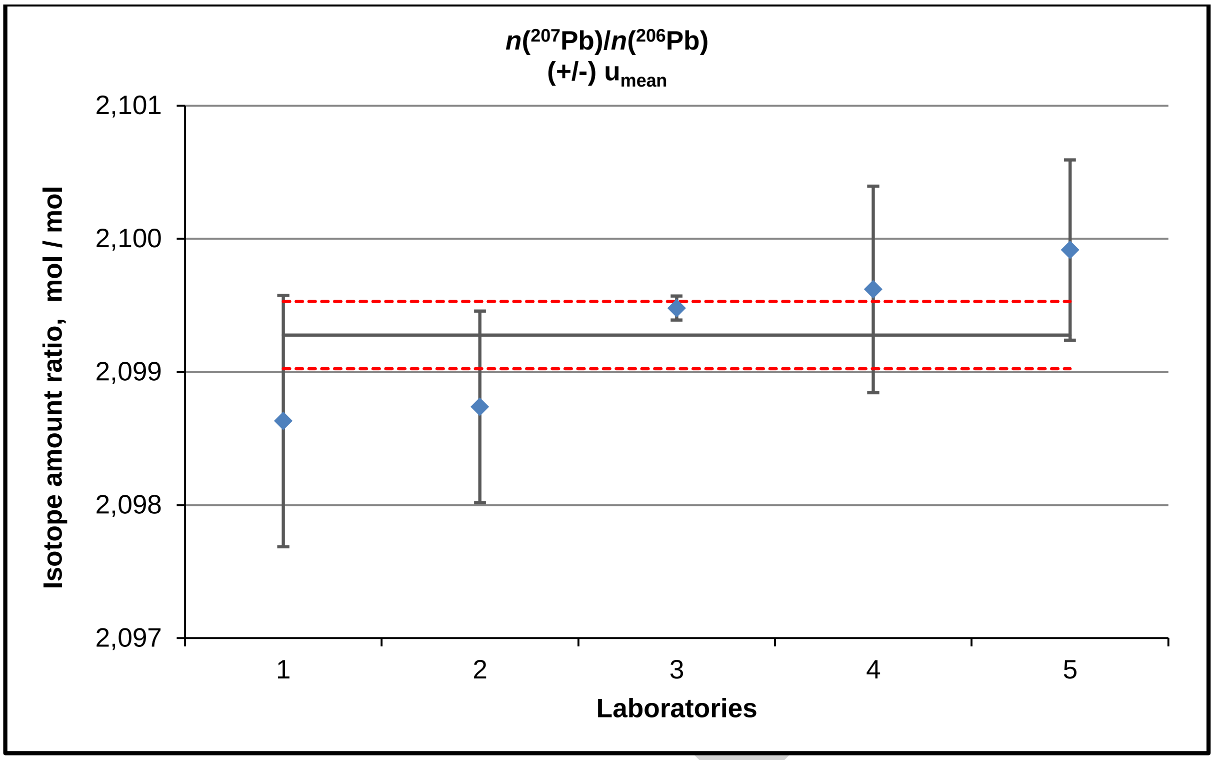


Figure A4.7. Interlaboratory study results for characterisation of $n(^{208}Pb)/n(^{206}Pb)$

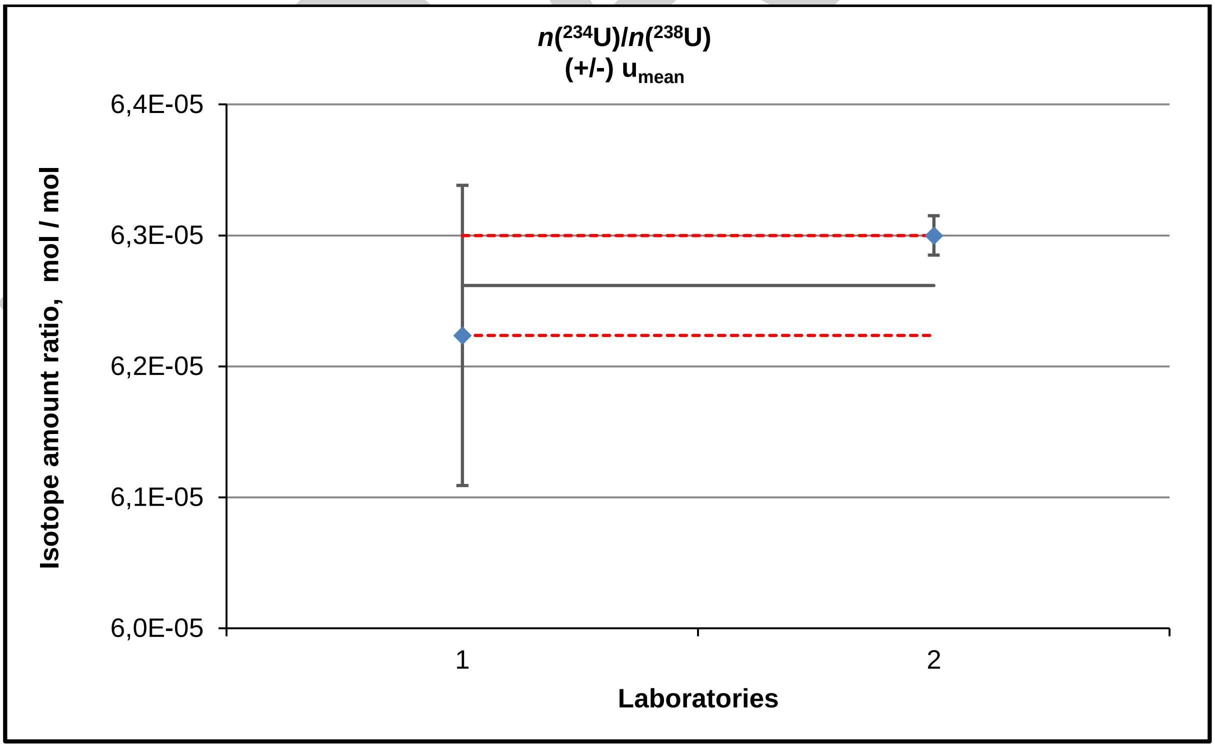


Figure A4.8. Interlaboratory study results for characterisation of $n(^{234}U)/n(^{238}U)$

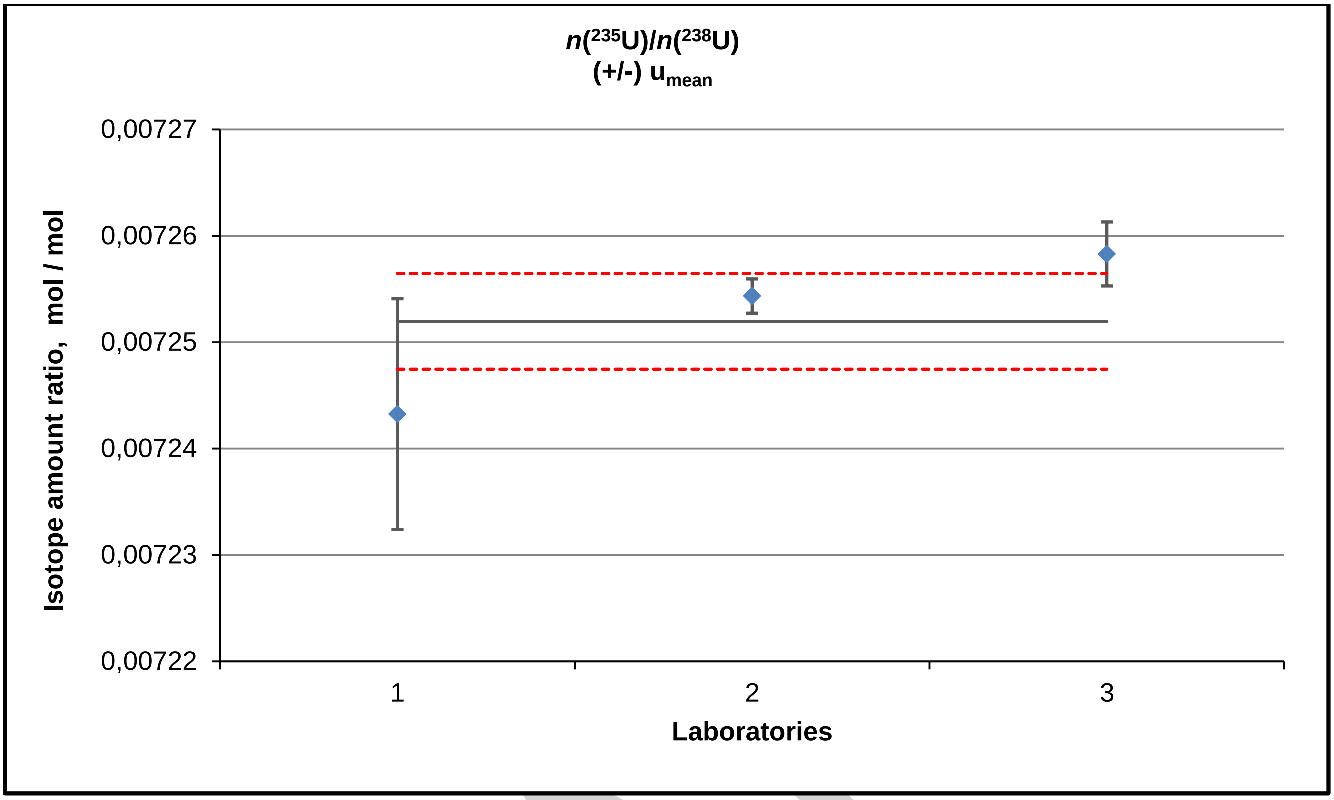


Figure A4.9. Interlaboratory study results for characterisation of $n(^{235}U)/n(^{238}U)$