Bundesanstalt für Materialforschung und -prüfung (BAM)

in co-operation with the

Committee of Chemists of GDMB
Gesellschaft der Metallurgen und Bergleute e.V.

Certification Report

Certified Reference Material

BAM-S014

Li-NMC 111 Cathode Material

Certification report

March 2023

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Abstract

This report describes the preparation and certification of reference material BAM-S014, a Li-NMC powder, carried out in co-operation with the Committee of Chemists of GDMB. The certified mass fractions and additional determined data are listed below.

Element	Mass fraction [1)]in %	Uncertainty [2)]in %
Li	7.62	0.16
Ni	19.76	0.13
Mn	18.22	0.14
Co	19.80	0.12
O	34.0	1.0
	in mg/kg	**in mg/kg**
Al	14.1	1.9
C	600	50
Cr	6.3	0.8
S	1421	70
Na	512	12
Fe	26	4

1) Unweighted mean value of the means of accepted sets of data (consisting of 4 single results), each set being obtained by a different laboratory and/or a different method of measurement.

2) Estimated expanded uncertainty *U* with a coverage factor of $k = 2$, corresponding to a level of confidence of approx. 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

The mass fractions of P, Si, Ti, and V as well as the $^{6}Li/^{7}Li$ isotopic ratio and the particle size distribution and specific surface area are given for information.

Informative Values

Element	Mass fraction [1)]in mg/kg	Uncertainty [2)]in mg/kg
P	12.2	2.2
Si	< 100	
Ti	< 1	
V	< 2	

1) Values were not certified, but given for information, when the number of accepted data sets was considered to be too low (< 5) or when the uncertainty from the inter-laboratory certification was considerably larger than the expected range or in case there were hints that the material was not homogeneous enough.

2) Estimated expanded uncertainty *U* with a coverage factor of $k = 2$, corresponding to a level of confidence of approx. 95 %, as defined in the Guide to the expression of uncertainty in measurement, (GUM, ISO/IEC Guide 98-3:2008).

Property		Property value	Uncertainty*
Specific surface area (BET)[1)]		0.487 m^2/g	0,028 m^2/g
Isotopic ratio $^6Li/^7Li$		12.35	0.02
Particle size	d_{10}	6.2 µm	0.5 µm
	d_{50}	11.2 µm	0.5 µm
	d_{90}	19.1 µm	1.2 µm

*Estimated expanded uncertainty *U* with a coverage factor of *k* = 2, calculated from the standard deviation of laboratory means (BET: standard deviation within the laboratory, n = 7)

[1)] The specific surface area was determined using the gas adsorption method with krypton at 77 K to measure the adsorption branch up to p/p_0 0.5.

Contents

List of abbreviations
(if not explained elsewhere)

CSAAS	Continuum source atomic absorption spectrometry
ICP-OES	Inductively coupled plasma optical emission spectrometry
ICP-MS	Inductively coupled plasma mass spectrometry
MC-ICP-MS	Multicollector inductively coupled plasma mass spectrometry
XRF	X-ray fluorescence spectrometry
BET	Brunauer-Emmett-Teller (method)

M	mean of the laboratories' means
u_c	combined uncertainty of certified mass fraction
s_M	standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification
n	number of accepted laboratory mean values of interlaboratory comparison for certification

1 Introduction

Lithium-ion batteries (LIBs), a key technology for the development of portable electronics and electric vehicles, are nowadays one of the solutions to the challenges associated with the climate crisis and clean energy transition. The most common types are lithium nickel manganese cobalt oxide (Li-NMC) and lithium iron phosphate batteries. Knowing the exact composition of the NMC material is important on the one hand, as individual components such as cobalt are expensive, and on the other hand, undesirable impurities can have a negative impact on the performance characteristics or service life of the batteries made from the material. In order to ensure correct and precise analysis of Li-ion battery materials, standardised procedures are required as well as certified reference materials. A standardised method for the analysis of Li composite oxide cathode materials with ICP-OES is currently being developed in the ISO TC 208. After consultation with experts from battery industry BAM decided to develop a first certified reference material, BAM-S014, based on Li-NMC 111.

Certification of reference material BAM-S014 was carried out in close cooperation with the working group „Special Materials" of the Committee of Chemists of the Society of Metallurgists und Miners (GDMB).

Certification of the CRM BAM-S014 Li-NMC was performed on the basis of ISO 17034 [1] and the relevant ISO-Guides [2, 3].

2 Candidate material

25 kg of Li-NMC material, obtained from MEET - Münster Electrochemical Energy Technology (Universität Münster) was taken as candidate material. The material was mixed and filled into six containers for storage. From each of the containers three bottles à 20 g were filled and taken to test for homogeneity.

In total ca. 1000 units à 25 g will be filled in amber glass bottles.

3 Companies/laboratories involved

3.1 Preparation of the material

- The material was produced by MEET - Münster Electrochemical Energy Technology, Münster, Germany
- The material was mixed and bottled by Bundesanstalt für Materialforschung und -prüfung (BAM)

3.2 Homogeneity testing

The analytical investigations and all statistical evaluations for the homogeneity testing were carried out by BAM.

3.3 Certification analysis

14 laboratories participated in the interlaboratory comparison for certification. The participating laboratories took part in a subsequent interlaboratory comparison on a Li-NMC material within the framework of the working group „Special Materials" of GDMB.

- BMW AG, München (Germany)
- Bruker AXS GmbH, Karlsruhe (Germany)
- Bundesanstalt für Materialforschung und -prüfung (BAM), Berlin (Germany)
- Dorfner Analysenzentrum und Anlagenplanungsgesellschaft mbH (ANZAPLAN), Hirschau (Germany)
- Elementar Analysensysteme GmbH, Langenselbold (Germany)
- Forschungsinstitut für Glas - Keramik GmbH, Höhr-Grenzhausen (Germany)
- Horn & Co. Analytics GmbH, Wenden-Hünsborn, (Germany)
- Institut für Materialprüfung Glörfeld GmbH, Willich, (Germany)
- Karlsruher Institut für Technologie, Eggenstein-Leopoldshafen (Germany)

- LECO European Application and Technology Center, Berlin (Germany)
- MEET Electrochemical Energy Technology, Münster (Germany)
- revierlabor, Essen (Germany)
- SPECTRO Analytical Instruments GmbH, Kleve (Germany)
- TU Clausthal, Institut für Aufbereitung, Deponietechnik und Geomechanik, Clausthal-Zellerfeld (Germany)
- VOLKSWAGEN Aktiengesellschaft, Salzgitter (Germany)

4 Homogeneity investigation of the material

From each of the six containers three bottles à 20 g (in total 18 bottles) were filled and tested for homogeneity (Co, Ni, Mn) twice using wavelength dispersive X-ray fluorescence spectrometry (XRF, MagiX Pro, Panalytical, Almelo, Netherlands). XRF-measurements were carried out on pressed powder pellets. The test samples were pressed in Al-cups on a 200 kN-press to pellets with a thickness of 5 mm and a diameter of 32 mm (pressing-time: 10 s). One of the pellets was randomly chosen as drift control sample. This sample was measured 10 times before and five times during the whole measurement sequence.
Homogeneity measurements for the elements Li, Al, Cr, Fe, Na, S and Si were carried out using ICP-OES (Spectro Arcos, Kleve, Germany). The number of samples was the same as for XRF except of Li (n = 16).
Homogeneity measurements for carbon was performed using a C/S-analyser Elementrac CS-I (Eltra, Haan, Germany). From each of the 18 bottles two test portions were taken to determine carbon.

The estimates of inhomogeneity contributions u_{bb} potentially hidden by the measurement uncertainty and to be included into the total uncertainty budget were estimated according to ISO Guide 35 [4] as the maximum of the values obtained from Eq. (1) and (2).

$$s_{\text{bb}} = \sqrt{\frac{MS_{\text{among}} - MS_{\text{within}}}{n}} \quad (1)$$

$$u^{*}_{\text{bb}} = \sqrt{\frac{MS_{\text{within}}}{n}} \sqrt[4]{\frac{2}{N(n-1)}} \quad (2)$$

where:

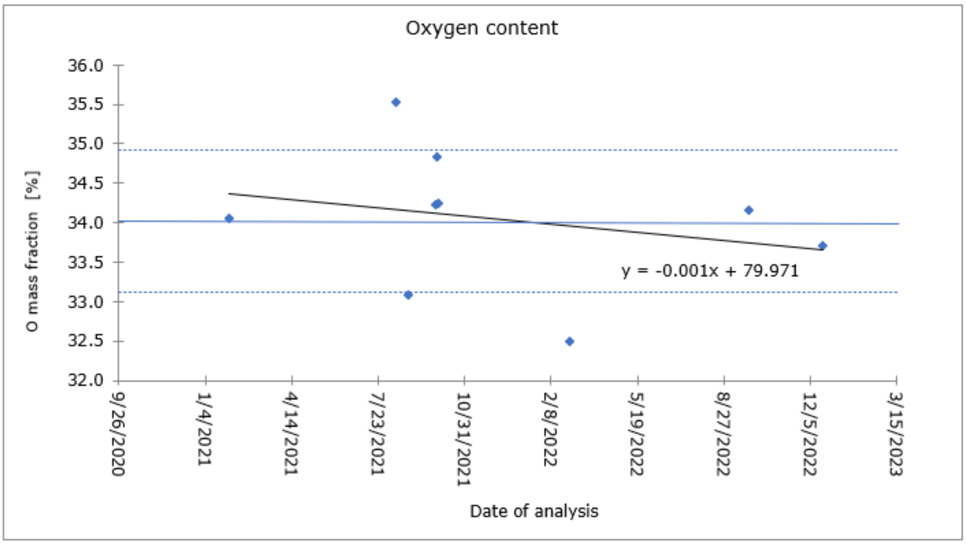
MS_{among}	mean of squared deviations between bottles (from 1-way ANOVA)
MS_{within}	mean of squared deviations within bottles (from 1-way ANOVA)
n	number of replicate sub-samples per bottle
N	number of bottles selected for homogeneity study

s_{bb} signifies the between-bottle standard deviation, whereas u^{*}_{bb} denotes the maximum heterogeneity that can potentially be hidden by an insufficient repeatability of the applied measurement method (which has to be considered as the minimum uncertainty contribution). In any case the larger of the two values was used as u_{bb}. Eq. (1) does not apply if MS_{within} is larger than MS_{among}, which was true for Cr and Na. The results of the homogeneity testing measurements as well as the ANOVA calculations can be found in the annex.

5 Stability of the material

Due to its chemical composition Li-NMC is very stable, which is an important prerequisite for use in lithium batteries. Therefore, no specific stability test was performed for BAM-S014. Possible oxidation of the material is imaginable but cannot be detected from the data obtained in the interlabioratory comparison (see Fig. 1). Nevertheless, the oxygen content of the CRM will be checked regularly.

Fig. 1: Oxygen content depending on date of analysis



6 Characterisation study

6.1 Analytical methods used for certification

16 laboratories participated in the certification interlaboratory comparison. For some elements several of the laboratories used more than one analytical method and therefore reported more than one dataset. The laboratories were asked to take six test portions for analysis. They were free to choose any suitable method for analysis. Table 1 shows the analytical methods used by the participating laboratories.
All participating laboratories were instructed to use only calibrants prepared from pure metals or stoichiometric compounds or well checked commercial calibration solutions.

Table 1: Analytical procedures used by the participating laboratories

Lab-No.	Element/ property	Sample mass	Sample pretreatment/Calibration	Analytical method
NMC-01	Li, Ni, Mn, Co	500 mg	Dissolution in HCl/H_2O_2	ICP-OES, calibration with commercial standard solutions (Merck, NIST-traceable), Sc as internal standard
	Cr, Cu, Fe, Na, P, S, Ti, V	500 mg	Dissolution in HCl/H_2O_2	ICP-MS, calibration with commercial standard solutions (Labkings, NIST-traceable), In as internal standard
	O	150 mg	Additives: Ni-capsule	Carrier gas hot extraction, calibration with SiO_2
	C, S	250 mg		Combustion/IR, calibration with steel-CRM (B.S. CSN-A)

*accredited acc. to ISO IEC 17025

Lab-No.	Element/ property	Sample mass	Sample pretreatment/Calibration	Analytical method
NMC-02	Al, Cr, Cu, Fe, Na, P, S, Si, V	1 g	Dissolution in aqua regia (acc. to Draft ISO/TC208 WG3 - Li composite oxide cathode materials – ICP-OES method using an internal standard element	ICP-OES, calibration with commercial standard solutions (Merck, certipur), internal standard, matrix matching with Li, Ni, Mn, Co
	Li, Ni, Mn, Co	20 mg	Dissolution in aqua regia (acc. to Draft ISO/TC208 WG3 - Li composite oxide cathode materials – ICP-OES method using an internal standard element	ICP-OES, calibration with commercial standard solutions (Merck, certipur), internal standard, bracketing
	Al, Cr, Na, Fe	1 g	Dissolution in aqua regia (acc. to Draft ISO/TC208 WG3 - Li composite oxide cathode materials – ICP-OES method using an internal standard element	ICP-MS, calibration with commercial standard solutions (Merck, certipur), internal standard, matrix matching with Li, Ni, Mn, Co
	C, S	100 mg	2 g W; 1 g Fe Instrument: Eltra CS 800	Combustion/IR Calibration with $BaCO_3$ (carbon) and $BaSO_4$ (sulfur)
	O	0.2 mg	Sn-capsule Instrument: Bruker Galileo G8	Carrier gas hot extraction Calibration with Fe_2O_3
	$^6Li/^7Li$	100 mg	Dissolution in aqua regia	CS-AAS, calibration with NIST SRM 8545 and IRMM-016 (JRC)
	$^6Li/^7Li$	100 mg	Dissolution in aqua regia, ion-exchange-chromatographic separation of the matrix	CS-AAS, calibration with NIST SRM 8545 and IRMM-016 (JRC)
	$^6Li/^7Li$	100 mg	Dissolution in 6 ml HCl/ 2 ml HNO_3 at 80 °C (4 h)	CS-AAS, calibration with NIST SRM 8545 and IRMM-016 (JRC)
NMC-03	Li, Ni, Mn, Co	50 mg	Dissolution in aqua regia after drying at 120 °C for 12 h	ICP-OES, calibration with commercial standard solutions (VWR), bracketing
	Al, Cr, Cu, Fe, Na, P, S, Si, Ti, V	100 mg	Dissolution in aqua regia after drying at 120 °C for 12 h	ICP-OES, calibration with commercial standard solutions (Merck)
NMC-04	C, S	100 mg	Additives: 1,5 g W/Sn (AlphaCell II) Instrument: Bruker G4 ICARUS	Combustion/IR Calibration with steel-CRM 284-2
	O	5 mg	Sn-capsule + graphite Instrument: Bruker Galileo G8	Carrier gas hot extraction Calibration with steel-CRM JK47

*accredited acc. to ISO IEC 17025

Lab-No.	Element/ property	Sample mass	Sample pretreatment/Calibration	Analytical method
NMC-05	Li, Ni, Mn, Co	115 mg	Dissolution in aqua regia	ICP-OES, calibration with commercial standard solutions (Merck)
	Al, Fe, Na, S, Si	1 g	Dissolution in aqua regia	ICP-OES, calibration with commercial standard solutions (Merck)
	C	100 mg	Additives: Fe, (Lecocell II, W/Sn)	Combustion/IR Calibration with LECO steel standards
NMC-06	O	3.5 mg	Additives: Ni-capsule, Sn	Carrier gas hot extraction Calibration with ZrO_2
	C, S	200 mg	Fe and W/Sn as additives	Combustion/IR Calibration with steel-CRM 031-3
NMC-07*	C, S	300 mg		Combustion/IR Calibration with pure substances
	O	150 mg		Carrier gas hot extraction Calibration with pure substances
	Li, Ni, Mn, Co, Al, Cr, Cu, Fe, Na, P, Si, Ti, V	0.5 g	Microwave pressure digestion	ICP-OES, calibration with pure substances
NMC-08	Li, Ni, Mn, Co	50 mg	Dissolution in HCl/HNO_3	ICP-OES, calibration with commercial standard solutions
	Al, Cr, Cu, Fe, Na, P, Ti, V	50 mg	Dissolution in $HCl/HNO_3/HF$	ICP-OES, calibration with commercial standard solutions
	O	8 mg	Ni/Sn-additive Instrument: LECO ON836	Carrier gas hot extraction Calibration with ZrO_2
	C, S		W18/Sn5-additive Instrument: Bruker G4 ICARUS	Combustion/IR Calibration with CO_2 (carbon) and K_2SO_4 (sulfur)
NMC-09	Li, Ni, Mn, Co	0.1 – 0.4 g	Dissolution in 6 ml HCl/ 2 ml HNO_3 at 80 °C (4 h)	ICP-OES, calibration with commercial standard solutions (CPAchem, Agilent), Sc as internal standard
	Al, Cr, Cu, Fe, Na, P, S, Ti, V	0.1 – 0.4 g	Dissolution in 6 ml HCl/ 2 ml HNO_3 at 80 °C (4 h)	ICP-OES, calibration with commercial standard solutions (CPAchem, Agilent, VWR, Labkings, AlphaAesar), Sc as internal standard, matrix matched with Li, Mn, Co, Ni
	C	150 mg	Additives: Lecocell II HP Instrument: LECO CS600	Combustion/IR Calibration with Steel-CRM (BAM)
NMC-09	O	2 mg	Additives: Ni-capsule, Sn, graphite Instrument: Bruker Galileo G8	Carrier gas hot extraction Calibration with TiO2, ZrO2
	Ni, Mn, Co	50 mg	Fusion with Li-tetraborate, Li-metaborate, LiBr (HRT)	Calibration with pure substances
	6Li/7Li	0.1 – 0.4 g	Dissolution in 6 ml HCl/ 2 ml HNO_3 at 80 °C (4 h)	Calibration with isotopic standard, matrix matched with Li, Mn, Co, Ni

*accredited acc. to ISO IEC 17025

Lab-No.	Element/ property	Sample mass	Sample pretreatment/Calibration	Analytical method
NMC-10	Li, Ni, Mn, Co	50 mg	Microwave-dissolution	ICP-OES, calibration with commercial standard solutions
NMC-11*	Li, Ni, Mn, Co, Al, Cr, Cu, Fe, Na, P, Ti, V	100 mg		ICP-OES, calibration with commercial standard solutions
	O	5 – 10 mg		Carrier gas hot extraction Calibration with ZrO_2
	C	300 mg		Combustion/IR Calibration with Steel-CRM
NMC-12	Li, Ni, Mn, Co	125 mg	Dissolution in aqua regia	ICP-OES, calibration with commercial standard solutions (Bernd Kraft), bracketing, Sc as internal standard
	Al, Cr, Cu, Fe, Na, P, Si, Ti, V	250 mg	Dissolution in aqua regia	ICP-OES, calibration with commercial standard solutions (Bernd Kraft), standard addition
NMC-13	Li, Ni, Mn, Co	50-100 mg	Acid pressure digestion with HCl/HNO_3 (TurboWave digestion autoclave, MWS)	ICP-OES
NMC-14	Li, Ni, Mn, Co	100 mg	Dissolution in aqua regia at 90 °C (2 h)	ICP-OES, calibration with commercial standard solutions (Merck), Y as internal standard
NMC-15	Na	0.5 g	$Li_2B_4O_7$ glass bead	XRF
	S	200 mg		Combustion/IR Calibration with Steel-CRM (Eltra)
NMC-17	O	60 mg		Carrier gas hot extraction Calibration with ZrO_2 and WO_3
	C, S	150 mg		Combustion/IR Calibration with Steel-CRM (Leco)

*accredited acc. to ISO IEC 17025

Table 2: Instrumental equipment used by the participating laboratories for particle size determination

Lab. No.	Instrument		Calculation according to
NMC-01	Beckman Coulter particle sizer LS 13 320	Laser-diffraction according to ISO 13320:2020-01 USB 0.05% TNPP-solution Sample size: 0.4 g	Fraunhofer approximation
NMC-02	Mastersizer 3000	Laser-diffraction according to ISO 13320:2020-01	Fraunhofer approximation
NMC-05	Malver Mastersizer	Laser-diffraction according to ISO 13320:2020-01 USB Water	Fraunhofer approximation
NMC-07	HELOS/KF-Magic, Fa. Sympatec GmbH	Laser-diffraction Sample size: 1 g	Fraunhofer approximation
NMC-11	Mastersizer 3000E	Laser-diffraction USB Water, detergent	Fraunhofer approximation
NMC-14		Laser-diffraction $Na_4P_2O_7$-solution	Fraunhofer approximation
NMC-15*	Mastersizer 3000	Laser-diffraction according to DIN EN 725-5	Fraunhofer approximation

*accredited acc. ISO 17025

Several participants determined the specific surface area A_{BET} of BAM-S014. But the data of only one laboratory was used to give an informative value for this property but the data from only one laboratory was used to give an informative value because that laboratory was the only one to use krypton as adsorption gas, which is necessary for the determination of a specific surface area of 0.5 m^2/g.
Prior to measurement, sample preparation was performed including outgassing in vacuum with a final pressure of below 10 Pa. The sample was then heated in vacuum with a rate of 5 K/min to 473.15 K and then held at 473.15 K for at least five hours. Afterwards, the sample was cooled slowly to ambient temperature.
To determine the specific surface area the gas adsorption method is to use with krypton at 77 K to measure the adsorption branch up to p/p0 0.5.
The supported value of specific surface area is calculated with the multipoint BET data analysis method [4] according to ISO 9277 [5] by using the linear form with a minimum of five adsorption points in a relative pressure range of $0.03 \leq p/p0 < 0.14$. The value used for cross-sectional area of krypton was 0.202 nm^2, the sample intake was 3.0 to 3.5 g.

6.2 Analytical results and statistical evaluation

The analytical results of the certification inter-laboratory comparison are shown in Tables 3 to 13. Figures 2 to 4 show the results of the particle size determination. The tables show the single results (M_i) of each laboratory, the respective laboratories' mean values (M), absolute and relative intra-laboratory standard deviation (s and s_{rel}, respectively), the standard deviation of laboratory means (s_M), and in addition the square root of mean of variances of data sets under repeatability conditions ($\bar{s}_i$). *n* is the number of accepted data sets. The continuous line in the figures marks the certified value (mean of the laboratories' means), the broken lines mark the standard deviation, calculated from the laboratories' means.
In the related figures for each laboratory its mean value and single standard deviation is given.

Table 3 results for Li

Lab./Meth.	NMC-10	NMC-01	NMC-05	NMC-13	NMC-07	NMC-03	NMC-11	NMC-12	NMC-14	NMC-09a	NMC-02	NMC-09b	NMC-08		
M_i [%]	7.450	7.59	7.60	7.599	7.607	7.64	7.858	7.622	7.601	7.629	7.741	7.709	7.677		*n*
	7.483	7.57	7.62	7.609	7.725	7.62	7.884	7.628	7.704	7.627	7.725	7.702	7.701		13
	7.487	7.57	7.50	7.585	7.429	7.64	7.660	7.625	7.622	7.667	7.732	7.715	7.732		
	7.598	7.54	7.50	7.542	7.580	7.61	7.459	7.645	7.623	7.672	7.622	7.700	7.711		
	7.598	7.53		7.523	7.684	7.62	7.287	7.642	7.677	7.680	7.657	7.674	7.735		
	7.560	7.48		7.543	7.392	7.62		7.649	7.722	7.692	7.656	7.714	7.742		
***M* [%]**	**7.529**	**7.547**	**7.555**	**7.567**	**7.570**	**7.625**	**7.630**	**7.635**	**7.658**	**7.661**	**7.689**	**7.702**	**7.716**		**7.622**
s [%]	0.0642	0.0393	0.0640	0.0354	0.1342	0.0122	0.2570	0.0115	0.0496	0.0271	0.0501	0.0152	0.0249	s_M [%]	0.0629
														$\bar{s}_i$ [%]	0.0886
s_{rel}	0.0085	0.0052	0.0085	0.0047	0.0177	0.0016	0.0337	0.0015	0.0065	0.0035	0.0065	0.0020	0.0032		0.0083

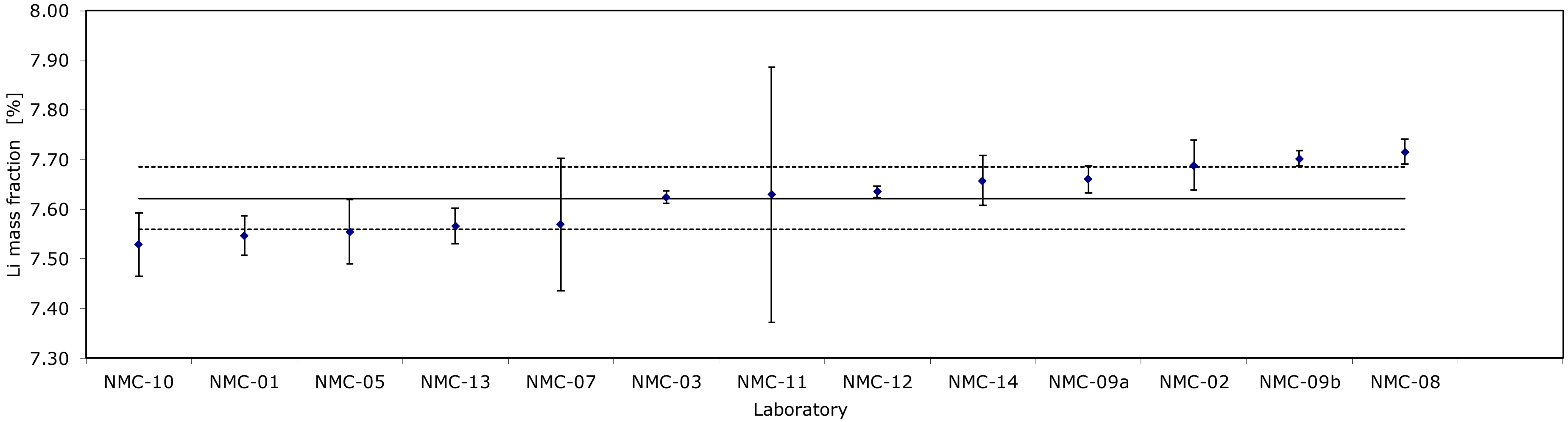


Table 4: results for Ni

Lab./Meth.	NMC-13	NMC-07	NMC-01	NMC-02	NMC-08	NMC-14	NMC-09b	NMC-12	NMC-03	NMC-10	NMC-09c	NMC-05	NMC-11		
M_i [%]	19.00	19.64	19.53	19.67	19.61	19.61	19.66	19.75	19.80	19.56	20.20	19.90	19.80		*n*
	19.01	20.55	19.51	19.66	19.61	19.76	19.70	19.76	19.80	19.89	20.15	20.00	20.42		12
	19.03	19.95	19.49	19.70	19.70	19.61	19.71	19.73	19.80	19.83	20.20	19.90	20.12		
	19.14	18.73	19.53	19.52	19.62	19.58	19.72	19.77	19.78	19.77	19.74	20.50	20.66		
	19.08	18.42	19.59	19.47	19.68	19.64	19.59	19.74	19.80	19.91	19.67		20.06		
	19.10	19.55	19.52	19.48	19.69	19.82	19.81	19.79	19.61	19.82	19.85		19.68		
***M* [%]**	**19.06**	**19.47**	**19.53**	**19.58**	**19.65**	**19.67**	**19.70**	**19.76**	**19.77**	**19.80**	**19.97**	**20.08**	**20.12**		**19.76**
s [%]	0.055	0.787	0.034	0.103	0.041	0.096	0.073	0.022	0.076	0.124	0.243	0.287	0.369	s_M [%]	0.206
														$\bar{s}_i$ [%]	0.281
s_{rel}	0.0029	0.0404	0.0017	0.0053	0.0021	0.0049	0.0037	0.0011	0.0039	0.0063	0.0122	0.0143	0.0183		0.0104

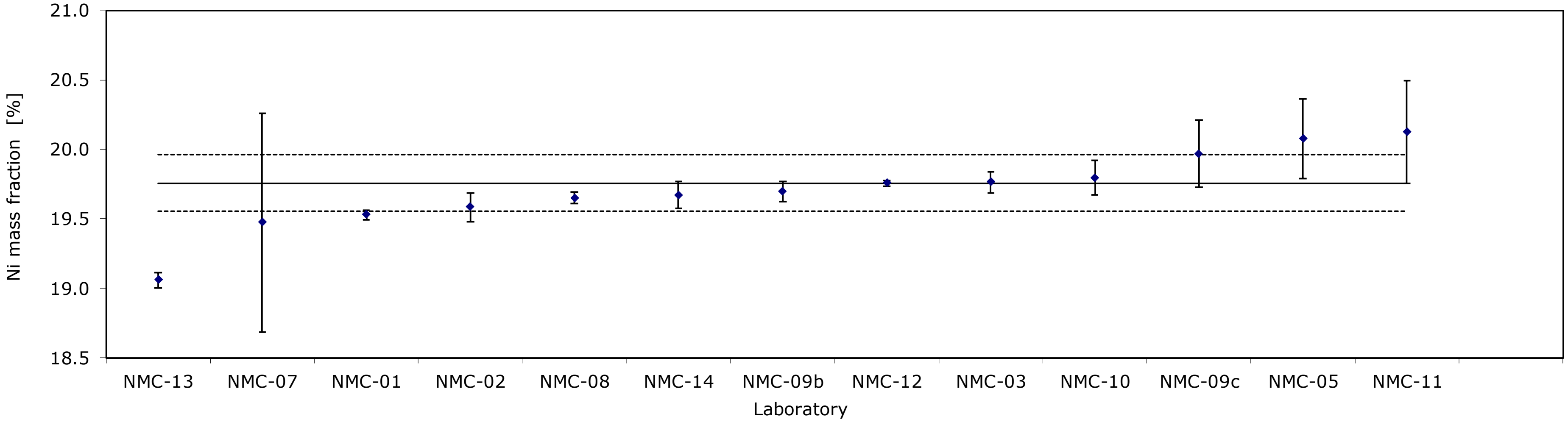


Table 5: results for Mn

Lab./Meth.	**NMC-03**	**NMC-13**	**NMC-11**	**NMC-10b**	**NMC-02b**	**NMC-01**	**NMC-05**	**NMC-08**	**NMC-12**	**NMC-14**	**NMC-09b**	**NMC-10a**	**NMC-09c**	**NMC-07**		
M_i [%]	17.78	17.80	17.54	18.05	18.25	18.21	18.40	18.23	18.29	18.21	18.32	18.21	18.52	18.39		*n*
	17.81	17.84	17.28	17.94	18.21	18.18	18.40	18.22	18.34	18.36	18.34	18.44	18.59	18.67		14
	17.82	18.02	17.59	17.97	18.23	18.18	18.20	18.33	18.27	18.29	18.34	18.43	18.61	18.46		
	17.81	17.82	18.15	17.96	18.19	18.22	18.00	18.26	18.27	18.27	18.42	18.39	18.49	19.01		
	17.76	17.96	18.68	18.04	18.10	18.20		18.31	18.21	18.40	18.33	18.40	18.42	18.71		
	17.85	18.04	18.43	17.84	18.11	18.14		18.27	18.29	18.42	18.41	18.29	18.62	18.82		
***M* [%]**	**17.81**	**17.91**	**17.95**	**17.97**	**18.18**	**18.19**	**18.25**	**18.27**	**18.28**	**18.32**	**18.36**	**18.36**	**18.54**	**18.67**		**18.22**
s [%]	0.031	0.106	0.557	0.075	0.063	0.029	0.191	0.041	0.042	0.082	0.043	0.093	0.079	0.229	s_M [%]	0.244
															$\bar{s}_i$ [%]	0.179
s_{rel}	0.0018	0.0059	0.0310	0.0042	0.0035	0.0016	0.0105	0.0023	0.0023	0.0045	0.0024	0.0051	0.0043	0.0123		0.0134

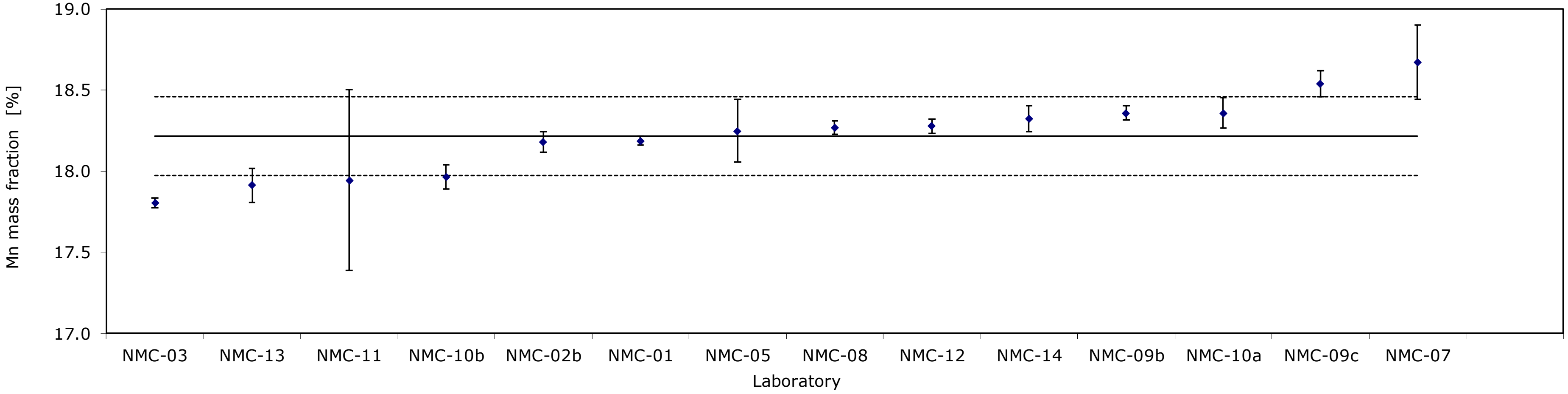


Table 6: results for Co

Lab./Meth.	NMC-13	NMC-03	NMC-12	NMC-02b	NMC-09b	NMC-10a	NMC-08	NMC-01	NMC-14	NMC-09c	NMC-05	NMC-07		
M_i [%]	19.42	19.62	19.61	19.76	19.70	19.54	19.81	19.87	19.63	20.00	19.80	19.95		*n*
	19.36	19.68	19.65	19.73	19.72	19.63	19.79	19.87	20.08	20.06	20.00	20.10		12
	19.39	19.67	19.63	19.76	19.74	19.68	19.87	19.85	19.93	20.10	19.90	19.90		
	19.55	19.56	19.64	19.65	19.75	19.75	19.81	19.85	19.79	19.95	20.40	20.34		
	19.49	19.65	19.63	19.59	19.63	19.97	19.91	19.88	20.07	19.90		20.22		
	19.62	19.56	19.66	19.61	19.81	19.80	19.88	19.82	20.01	20.09		20.20		
***M* [%]**	**19.47**	**19.62**	**19.64**	**19.68**	**19.73**	**19.73**	**19.84**	**19.86**	**19.92**	**20.02**	**20.03**	**20.12**		**19.80**
s [%]	0.101	0.053	0.018	0.077	0.060	0.148	0.048	0.022	0.177	0.081	0.263	0.168	s_M [%]	0.192
													$\bar{s}_i$ [%]	0.123
s_{rel}	0.0052	0.0027	0.0009	0.0039	0.0030	0.0075	0.0024	0.0011	0.0089	0.0040	0.0131	0.0084		0.0097

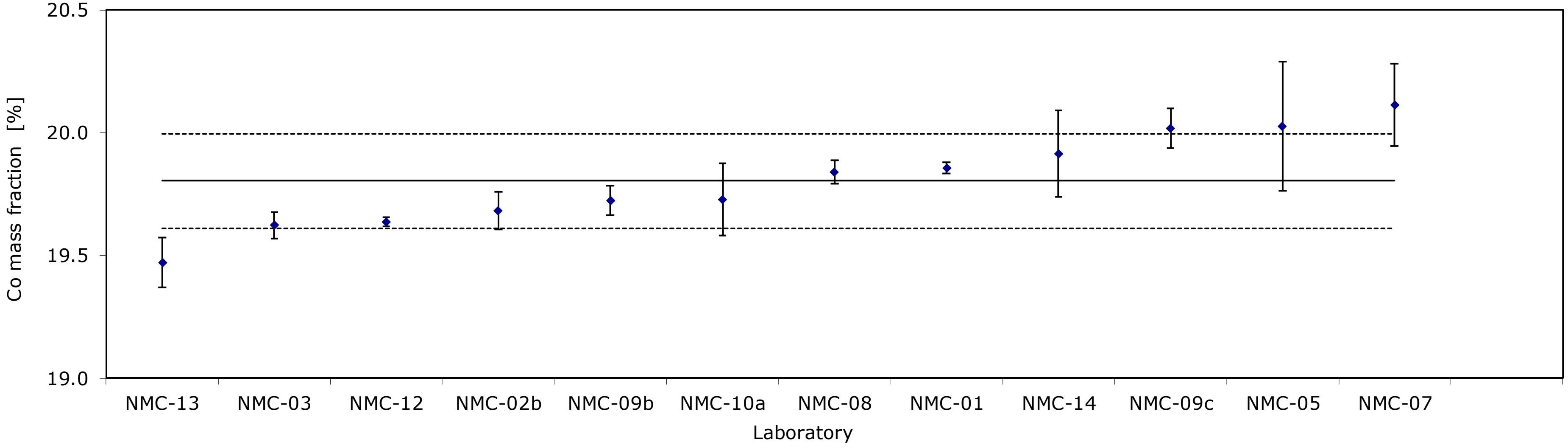


Table 7: results for O

Lab./Meth.	NMC-07	NMC-11	NMC-17	NMC-01	NMC-08	NMC-02a	NMC-06	NMC-09b	NMC-04		
M_i [%]	34.10	32.05	34.62	33.90	33.96	34.05	33.69	34.11	35.50		*n*
	31.60	33.21	33.25	34.10	34.17	34.42	33.96	34.93	35.09		9
	33.80	33.73	33.71	33.70	34.24	34.20	34.28	35.64	35.52		
	31.90	32.73	33.59	35.30	33.79	34.30	34.74	35.02	35.50		
	32.20	32.75	33.42	32.30	34.55	34.45	34.92	34.30	35.70		
	31.40	34.08	33.70	35.00	34.22	33.95	33.88	35.06	35.84		
***M* [%]**	**32.50**	**33.09**	**33.72**	**34.05**	**34.16**	**34.23**	**34.24**	**34.84**	**35.52**		**34.04**
s [%]	1.159	0.739	0.477	1.065	0.262	0.203	0.495	0.557	0.252	s_M [%]	0.888
										$\bar{s}_i$ [%]	0.665
s_{rel}	0.0357	0.0223	0.0142	0.0313	0.0077	0.0059	0.0144	0.0160	0.0071		0.0261

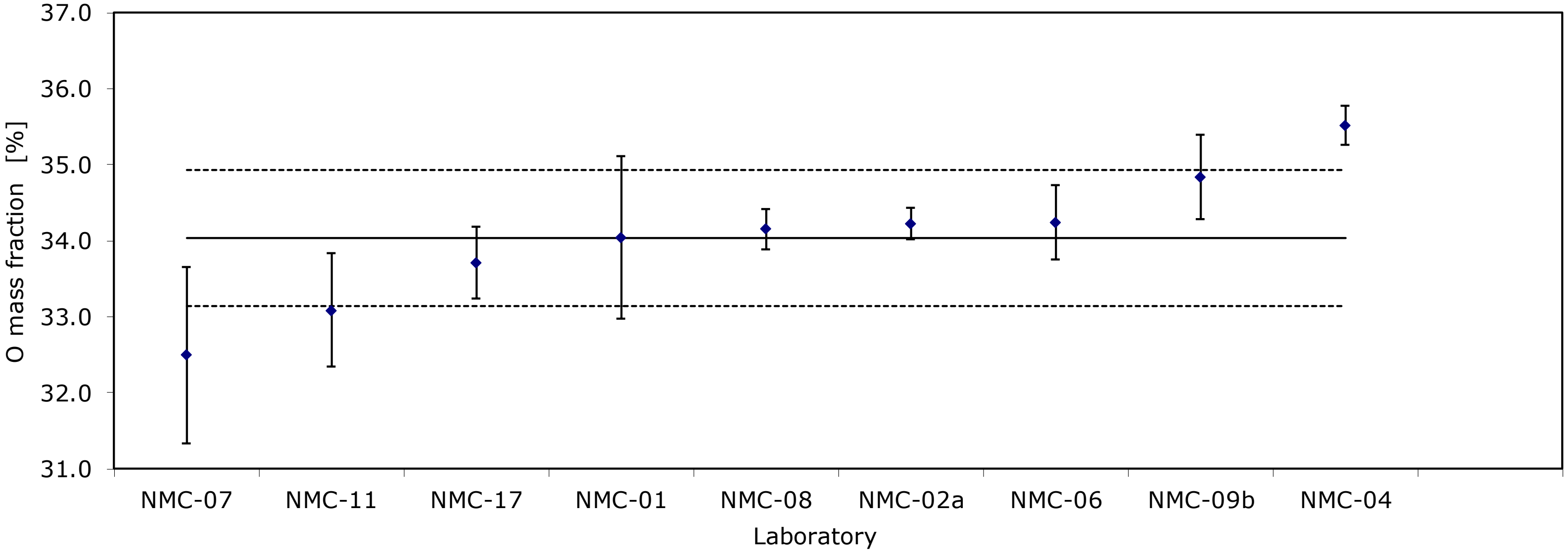


Table 8: results for Al

Lab./Meth.	NMC-02a	NMC-12	NMC-02b	NMC-03	NMC-01a	NMC-05	NMC-08	NMC-09b		
M_i [mg/kg]	10.2	11.8	11.5	11.8	14.1	15.9	18.9	17.2		n
	10.5	12.0	12.9	12.2	14.3	14.8	13.1	15.7		8
	10.2	11.5	12.3	18.1	13.7	14.8	16.5	20.9		
	11.7	11.7	12.3	14.6	16.7	15.5	19.0	16.1		
	11.4	11.9	11.2	14.1	15.9	15.2	13.4	16.6		
	11.8	11.6	11.9	16.6	13.4		14.1	18.8		
***M* [mg/kg]**	**11.0**	**11.8**	**12.0**	**14.6**	**14.7**	**15.2**	**15.8**	**17.6**		**14.1**
s [mg/kg]	0.75	0.19	0.59	2.45	1.32	0.47	2.71	1.97	s_M [mg/kg]	2.28
									$\bar{s}_i$ [mg/kg]	1.59
s_{rel}	0.0680	0.0159	0.0489	0.1684	0.0896	0.0310	0.1712	0.1120		0.1619

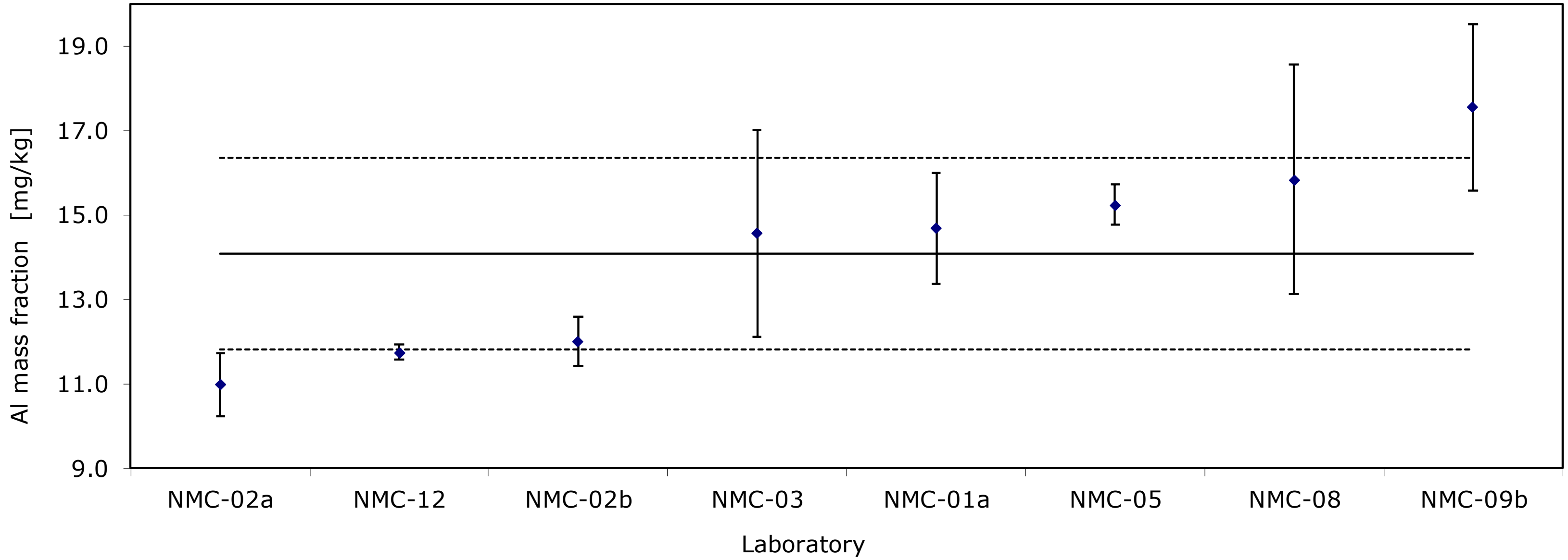


Table 9: results for C

Lab./Meth.	NMC-05	NMC-06	NMC-07	NMC-08	NMC-04	NMC-02a	NMC-17	NMC-09b	NMC-01a		
M_i [mg/kg]	512	512.3	542	594.9	560.3	608.9	617	692.0	716		*n*
	482	535.3	588	587.6	559.5	605.5	613	693.1	713		9
	536	519.3	605	585.1	558.7	602.4	622	679.8	732		
	483	517.2	583	575.3	621.1	603.3	618	644.7	746		
	496	518.1	601	578.6	616.5	598.7	614	656.9	732		
	496	518.2	586	590.6	621.4	602.4	611	665.4	734		
***M* [mg/kg]**	**500.8**	**520.1**	**584.2**	**585.4**	**589.6**	**603.5**	**615.8**	**672.0**	**728.8**		**600.0**
s [mg/kg]	20.40	7.86	22.43	7.35	33.00	3.40	3.97	19.61	12.30	s_M [mg/kg]	69.68
										$\bar{s}_i$ [mg/kg]	17.28
s_{rel}	0.0407	0.0151	0.0384	0.0126	0.0560	0.0056	0.0064	0.0292	0.0169		0.1161

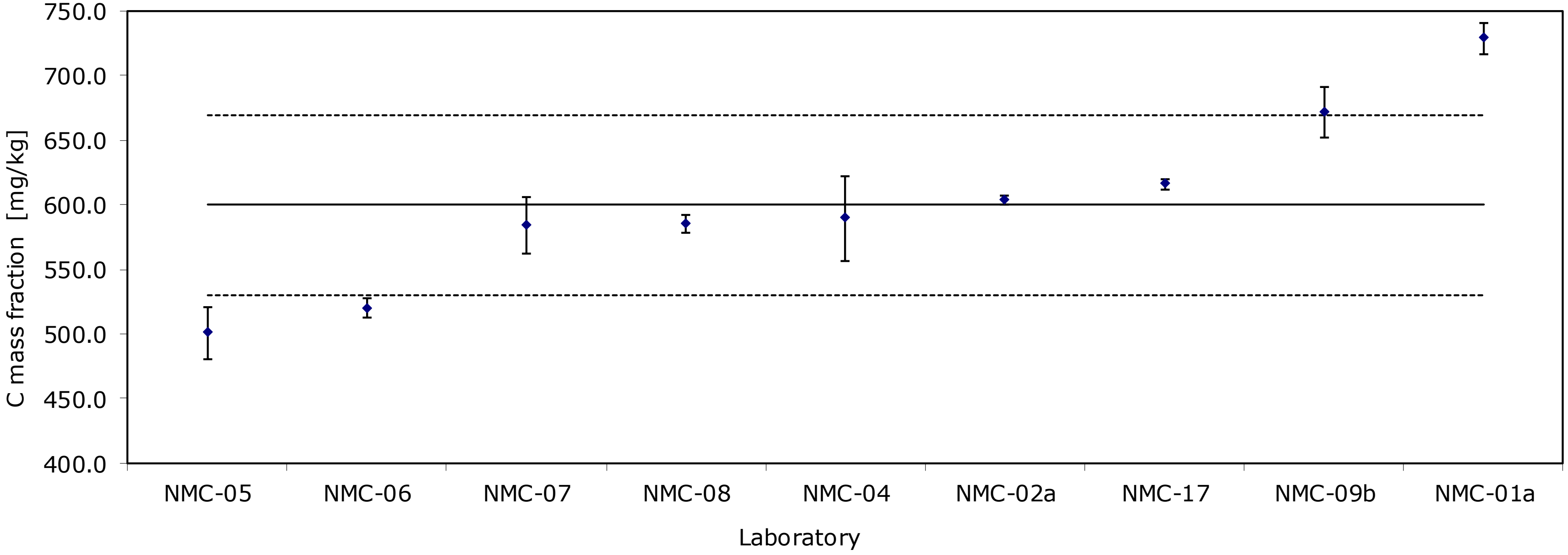


Table 10: results for Cr

Lab./Meth.	NMC-02b	NMC-09b	NMC-02a	NMC-12	NMC-01a		
M_i [mg/kg]	5.40	5.9	6.16	6.8	7.51		*n*
	5.44	6.0	6.05	6.7	7.38		5
	5.40	6.1	6.07	6.5	7.21		
	5.33	5.6	6.16	6.4	7.84		
	5.39	5.5	6.18	6.6	7.95		
	5.33	6.4	6.12	6.7	7.73		
***M* [mg/kg]**	**5.38**	**5.92**	**6.12**	**6.62**	**7.60**		**6.33**
s [mg/kg]	0.04	0.33	0.05	0.15	0.28	s_M [mg/kg]	0.84
						$\bar{s}_i$ [mg/kg]	0.21
s_{rel}	0.0081	0.0560	0.0085	0.0222	0.0375		0.1325

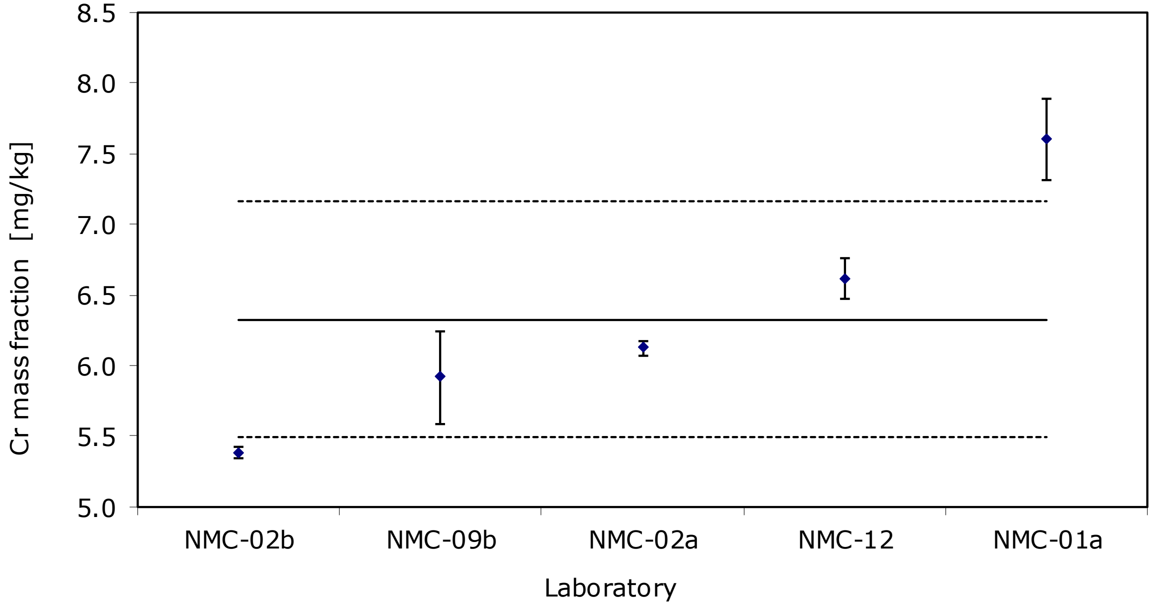


Table 11: results for Fe

Lab./Meth.	NMC-03	NMC-05	NMC-02b	NMC-02a	NMC-09b	NMC-08	NMC-01a		
M_i [mg/kg]	20.8	23.7	24.9	28.7	29.0	29.9	32.0		*n*
	18.3	24.4	25.1	27.3	28.1	29.6	32.4		7
		24.7	24.1	26.8	27.3	28.8	32.1		
		22.7	24.3	26.9	27.2	32.6	32.0		
		23.0	24.9	27.4	29.7	29.0	32.5		
		22.8	25.8	26.6	29.3	27.4	31.6		
***M* [mg/kg]**	**19.5**	**23.6**	**24.9**	**27.3**	**28.4**	**29.5**	**32.1**		**26.5**
s [mg/kg]	1.80	0.85	0.59	0.75	1.06	1.73	0.32	s_M [mg/kg]	4.18
								$\bar{s}_i$ [mg/kg]	1.14
s_{rel}	0.0923	0.0363	0.0239	0.0274	0.0372	0.0587	0.0100		0.1580

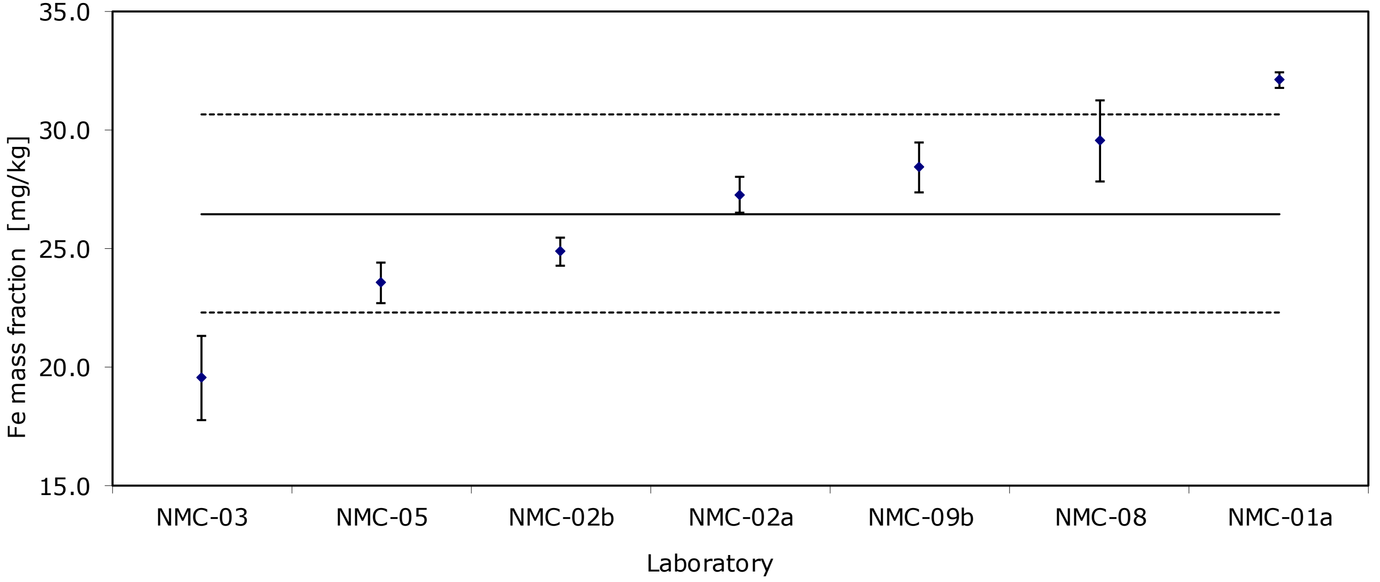


Table 12: results for Na

Lab./Meth.	NMC-03	NMC-07	NMC-01a	NMC-11	NMC-02a	NMC-02b	NMC-15	NMC-09b	NMC-05		
M_i [mg/kg]	39.9	271.0	470.0	489.0	511.8	514.5	437.7	509.0	555.0		*n*
	40.6	270.0	489.0	496.0	507.5	512.2	638.0	515.0	554.0		9
	40.2	257.0	483.0	491.0	506.1	511.1	474.8	502.0	556.0		
	40.5	271.0	499.0	508.0	511.5	510.7	549.0	524.0	520.0		
	40.9	261.0	507.0	496.0	503.9	515.0	549.0	524.0	520.0		
	40.2	257.0	502.0	523.0	502.9	510.6	445.1	524.0	522.0		
***M* [mg/kg]**	**40.4**	**264.5**	**491.7**	**500.5**	**507.3**	**512.3**	**515.6**	**516.3**	**537.8**		**511.7**
s [mg/kg]	0.35	6.92	13.76	12.85	3.74	1.96	77.35	9.35	18.83	s_M [mg/kg]	14.53
										$\bar{s}_i$ [mg/kg]	31.16
s_{rel}	0.0088	0.0262	0.0280	0.0257	0.0074	0.0038	0.1500	0.0181	0.0350		0.0284

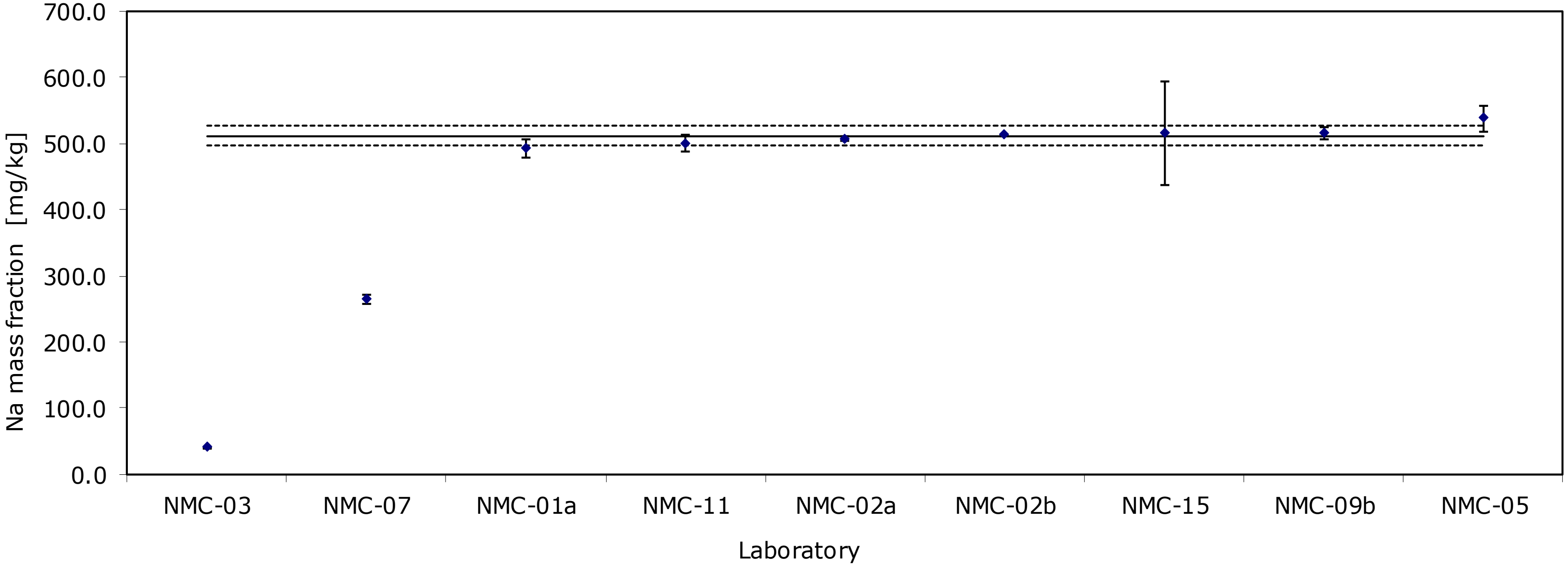
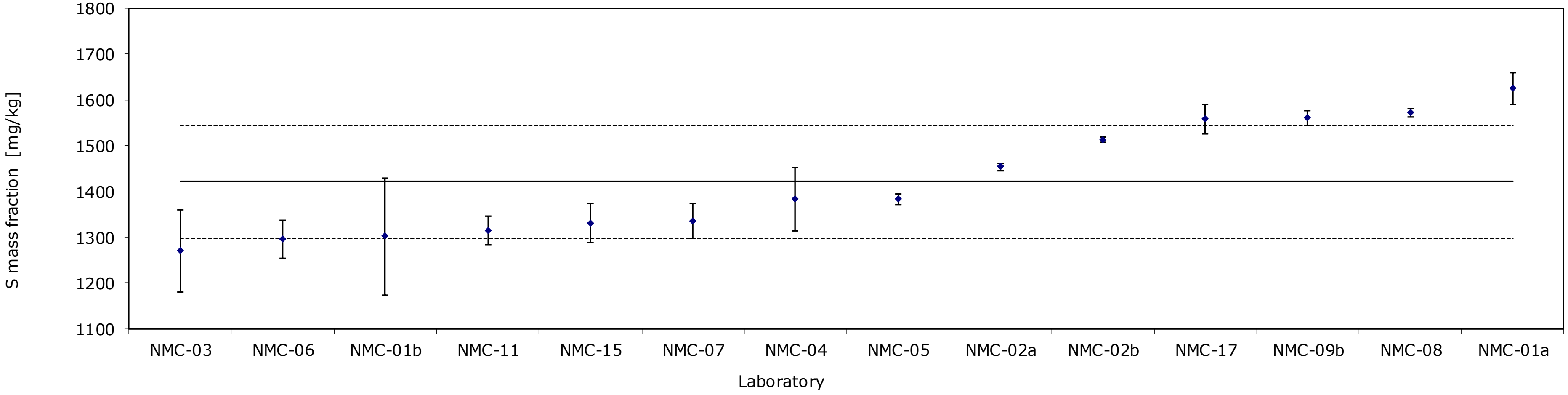


Table 13: results for S

Lab./Meth.	NMC-03	NMC-06	NMC-01b	NMC-11	NMC-15	NMC-07	NMC-04	NMC-05	NMC-02a	NMC-02b	NMC-17	NMC-09b	NMC-08	NMC-01a		
M_i [mg/kg]	1334	1335	1192	1357	1388	1328	1411	1390	1457	1517	1588	1570	1558	1562		*n*
	1206	1232	1153	1271	1344	1298	1307	1390	1462	1507	1520	1580	1588	1630		14
		1328	1234	1330	1341	1328	1309	1370	1439	1513	1582	1540	1569	1615		
		1263	1476	1301	1290	1388	1369		1456	1517	1587	1550	1570	1657		
		1324	1390	1331	1349	1298	1483		1455	1518	1543	1560	1575	1643		
		1296	1366	1296	1274	1373	1417		1454	1506	1527		1570	1649		
***M* [mg/kg]**	**1270.0**	**1296.3**	**1301.8**	**1314.3**	**1331.0**	**1335.5**	**1382.7**	**1383.3**	**1453.6**	**1512.8**	**1557.8**	**1560.0**	**1571.7**	**1626.0**		**1421.2**
s [mg/kg]	90.51	41.26	127.31	30.77	41.89	37.65	68.39	11.55	7.86	5.32	31.45	15.81	9.77	34.68	s_M [mg/kg]	122.31
															$\bar{s}_i$ [mg/kg]	51.87
s_{rel}	0.0713	0.0318	0.0978	0.0234	0.0315	0.0282	0.0495	0.0083	0.0054	0.0035	0.0202	0.0101	0.0062	0.0213		0.0861



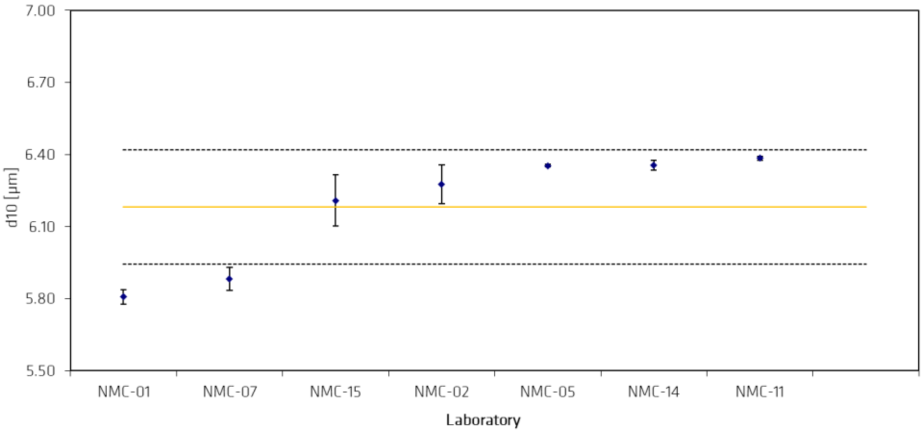


Figure 2: results for d10

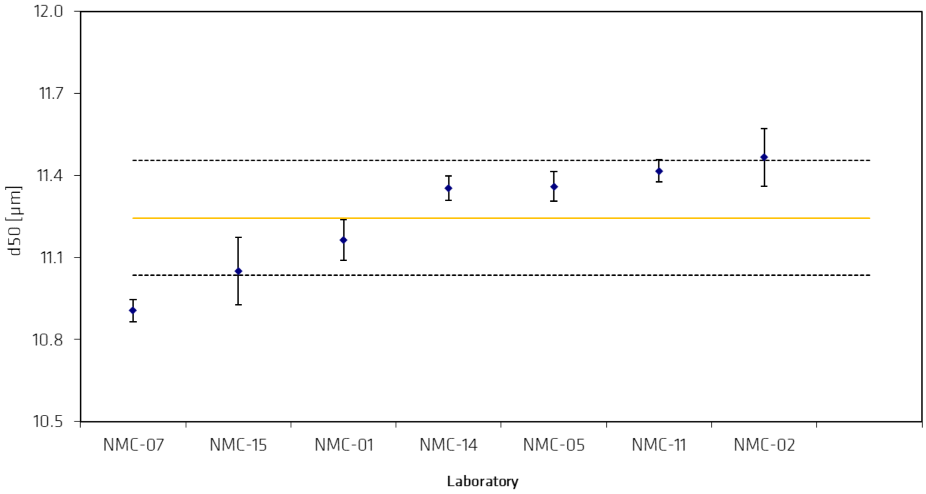


Figure 3: results for d50

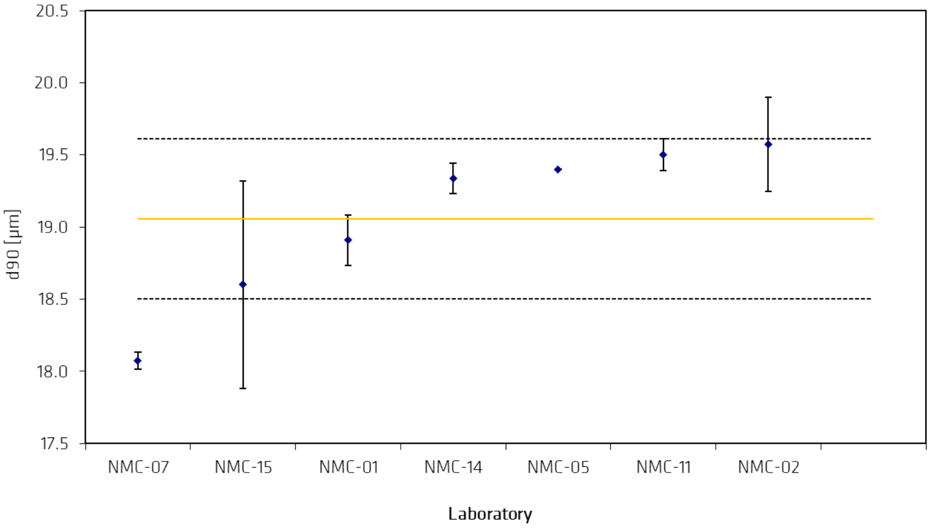


Figure 4: results for d90

The statistical evaluation of the data was performed using the software program eCerto [6]. The following results were obtained:

Tab. 14: Outcome of statistical tests on the results obtained for Li and Co

	Li	Co
Number of data sets	13	12
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Lab. NMC-11	Lab. NMC-05
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

Tab. 15: Outcome of statistical tests on the results obtained for Ni

	1st run	2nd run
Number of data sets	13	12
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. NMC-13	---
Nalimov (α = 0.01)	Lab. NMC-13	---
Grubbs (α = 0.05)	Lab. NMC-13	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Lab. NMC-07	Lab. NMC-07
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying result (Lab. NMC-13) was removed.

Tab. 16: Outcome of statistical tests on the results obtained for Mn and O

	Mn	O
Number of data sets	14	9
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. NMC-07	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	Lab. NMC-11	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

Tab. 17: Outcome of statistical tests on the results obtained for Al and C

	Al	C
Number of data sets	8	9
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	Lab. NMC-05
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

Tab. 18: Outcome of statistical tests on the results obtained for Cr and S

	Cr	S
Number of data sets	5	14
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	---	---
Nalimov (α = 0.01)	---	---
Grubbs (α = 0.05)	---	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	---	---
Grubbs Pair (α = 0.01)	---	---
Cochran	---	Lab. NMC-01b
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying result (Lab. NMC-01b) was not removed.

Tab. 19: Outcome of statistical tests on the results obtained for Na

	1st run	2nd run
Number of data sets	9	7
Scheffe's test (data compatible?)	yes	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed	Pooling not allowed
Dixon (α = 0.05)	---	---
Dixon (α = 0.01)	---	---
Nalimov (α = 0.05)	Lab. NMC-03	---
Nalimov (α = 0.01)	Lab. NMC-03	---
Grubbs (α = 0.05)	Lab. NMC-03	---
Grubbs (α = 0.01)	---	---
Grubbs Pair (α = 0.05)	Labs. NMC-03 and NMC-07	---
Grubbs Pair (α = 0.01)	Labs. NMC-03 and NMC-07	---
Cochran	Lab. NMC-05	Lab. NMC-15
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal	Distribution: normal

The outlying results (Labs. NMC-03, and NMC-07) were removed.

Tab. 20: Outcome of statistical tests on the results obtained for Fe

	1st run
Number of data sets	7
Scheffe's test (data compatible?)	yes
Snedecor-F-Test and Bartlett-Test	Pooling not allowed
Dixon (α = 0.05)	---
Dixon (α = 0.01)	---
Nalimov (α = 0.05)	---
Nalimov (α = 0.01)	---
Grubbs (α = 0.05)	---
Grubbs (α = 0.01)	---
Grubbs Pair (α = 0.05)	---
Grubbs Pair (α = 0.01)	
Cochran	---
Kolmogorov-Smirnov-Lilliefors Test (α = 0.05)	Distribution: normal

The certified mass fractions of all elements were calculated as mean of the accepted data sets. These values are given in Table 21.
The respective combined uncertainties were calculated from the spread resulting from the certification inter-laboratory comparison (u_{ilc}) and the uncertainty contributions from possible inhomogeneity (u_{bb}) of the material using Equation 3.

$$u_c = \sqrt{u_{ilc}^2 + u_{bb}^2} \quad (3)$$

with

$u_{ilc} = \sqrt{\frac{s_M^2}{n}}$: uncertainty contribution resulting from inter-laboratory comparison

n : number of data sets used for calculating the certified mass fraction of each element

Table 21: Uncertainty calculation

	uncertainty contribution from								
	M	n	s_M	u_{ilc}	u_{bb}**	$u_{combined}$	U		u_{bb} (rel)
	%		%	%	%	%	%		
Li	7.62	13	0.0629	0.0174	0.0733	0.0754	0.1507		0.9621
Ni	19.8	12	0.2058	0.0594	0.0163	0.0616	0.1232		0.0825
Mn	18.2	14	0.2443	0.0653	0.0122	0.0664	0.1329		0.0672
Co	19.8	12	0.1922	0.0555	0.0143	0.0573	0.1146		0.0724
O	34.0	9	0.8883	0.2961	0.3404	0.4512	0.9023		1.0000 *
	mg/kg		mg/kg	mg/kg	mg/kg	mg/kg	mg/kg		
Al	14.1	8	2.28	0.806	0.468	0.9323	1.8645		3.3264
C	600	9	69.7	23.227	8.546	24.7491	49.4982		1.4244
Fe	26.5	7	4.2	1.580	0.197	1.5921	3.1842		0.7441
Na	512	7	14.5	5.492	2.378	5.9845	11.9689		0.4647
Cr	6.3	5	0.8	0.375	0.054	0.3790	0.7580		0.8553
P	12.2	3	1.9	1.090	0.122	1.0967	2.1934		1.0000 *
S	1421	14	122.3	32.690	12.499	34.9974	69.9949		0.8794
	**calculated from u_{bb}(rel):			$u_{bb} = \frac{M \cdot u_{bb}(rel)}{100}$			*estimated from other elements		

The expanded uncertainties U are calculated by multiplication of u_c with a coverage factor of k = 2 using Equation 4.

$$U = k \cdot u_c \quad (4)$$

The calculated mass fractions and their resp. expanded uncertainties are given on Page 2 of this report. Rounding was done according to DIN 1333 [7].

7 Instructions for use

7.1 Area of application

The main area of application is to check the trueness of results when one or more of the certified parameters in Li-NMC materials are determined by a laboratory. Based on own results and on certified values the uncertainty of own measurements can be calculated.

7.2 Recommendations for correct sampling and sample preparation

To ensure a representative sub-sampling for the analysis the bottle containing the CRM should be shaken in different directions for about two minutes before taking the sub-sample. Each sub-sample has to be taken separately.

7.3 Recommendations for correct storage

The sample should be stored in a dust-free and dry environment avoiding contamination and moisture.

7.4 Safety guidelines

Lithium Nickel Manganese Cobalt Oxide may cause an allergic skin reaction and is suspected of causing cancer. Therefore, specific safety precautions have to be taken.

8 Metrological Traceability

To ensure traceability of the certified mass fractions to the SI (Système International d'Unités) calibration was performed using standard solutions prepared from pure metals or stoichiometric compounds or traceable commercial calibration solutions.

9 References

[1] DIN EN ISO 17034, General requirements for the competence of reference material producers, 2017

[2] ISO Guide 31, Reference materials - Contents of certificates, labels and accompanying documentation, 2015

[3] ISO Guide 35, Reference materials - Guidance for characterization and assessment of homogeneity and stability, 2017

[4] ISO 9277 Determination of the specific surface area of solids by gas adsorption – BET method. International Organization for Standardization, Geneva (2022)

[5] Brunauer, S., Emmet, P. H., Teller, E. Adsorption of Gases in Multimolecular Layers. J. Amer. Chem. Soc., 60 (1938) 309 – 319

[6] J. Lisec, eCerto Software, BAM 2021

[7] DIN 1333:1992-02 Zahlenangaben

10 Information on and purchase of the CRM

Certified reference material BAM-S014 is supplied by

Bundesanstalt für Materialforschung und -prüfung (BAM)
Fachbereich 1.6: Anorganische Referenzmaterialien
Richard-Willstätter-Str. 11, D-12489 Berlin, Germany
Phone +49 (0)30 - 8104 2061
Fax: +49 (0)30 - 8104 72061
Email: sales.crm@bam.de
https://www.webshop.bam.de

Each unit will be distributed together with a detailed certificate containing the certified values and their uncertainties, the mean values and standard deviations of all accepted data sets and information on the analytical methods used and the names of the participating laboratories.
Information on certified reference materials can be obtained from BAM, https://www.bam.de.

Appendix: Homogeneity testing

Co (XRF; mass fraction in %)

	1	2
Bottle 1	19.68	19.68
Bottle 2	19.72	19.71
Bottle 3	19.68	19.72
Bottle 4	19.67	19.69
Bottle 5	19.75	19.73
Bottle 6	19.70	19.71
Bottle 7	19.65	19.71
Bottle 8	19.70	19.67
Bottle 9	19.68	19.65
Bottle 10	19.73	19.71
Bottle 11	19.71	19.70
Bottle 12	19.71	19.70
Bottle 13	19.64	19.70
Bottle 14	19.67	19.69
Bottle 15	19.66	19.70
Bottle 16	19.72	19.72
Bottle 17	19.73	19.69
Bottle 18	19.69	19.66

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.014694257	17	0.000864368	1.890586065	0.095017806	2.23254567
Within groups	0.008229525	18	0.000457196			
Total	0.022923783	35				
within-sd	0.02138214			status:	homogeneous	
n	2.00					
s_{bb}	0.01426836					
u^*_{bb}	0.00872922					
u_{bb}	0.01426836					
u_{bb}(rel.)	0.07244547					

Mn (XRF; mass fraction in %)

	1	2
Bottle 1	18.33	18.32
Bottle 2	18.35	18.35
Bottle 3	18.33	18.36
Bottle 4	18.33	18.34
Bottle 5	18.39	18.38
Bottle 6	18.35	18.36
Bottle 7	18.30	18.36
Bottle 8	18.36	18.32
Bottle 9	18.33	18.31
Bottle 10	18.37	18.36
Bottle 11	18.36	18.35
Bottle 12	18.35	18.34
Bottle 13	18.29	18.35
Bottle 14	18.32	18.34
Bottle 15	18.31	18.34
Bottle 16	18.36	18.36
Bottle 17	18.38	18.33
Bottle 18	18.33	18.32

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.011646951	17	0.000685115	1.798140325	0.11335559	2.23254567
Within groups	0.006858234	18	0.000381013			
Total	0.018505185	35				
within-sd	0.01951955			status:	homogeneous	
n	2.00					
s_{bb}	0.01233089					
u^*_{bb}	0.00796882					
u_{bb}	0.01233089					
u_{bb}(rel.)	0.06722614					

Ni (XRF; mass fraction in %)

	1	2
Bottle 1	19.60	19.58
Bottle 2	19.60	19.61
Bottle 3	19.61	19.63
Bottle 4	19.60	19.61
Bottle 5	19.67	19.64
Bottle 6	19.63	19.62
Bottle 7	19.55	19.61
Bottle 8	19.62	19.55
Bottle 9	19.59	19.58
Bottle 10	19.65	19.64
Bottle 11	19.63	19.63
Bottle 12	19.63	19.62
Bottle 13	19.56	19.62
Bottle 14	19.59	19.60
Bottle 15	19.59	19.64
Bottle 16	19.64	19.65
Bottle 17	19.66	19.62
Bottle 18	19.60	19.60

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.017861965	17	0.001050704	1.99553129	0.077865166	2.23254567
Within groups	0.009477511	18	0.000526528			
Total	0.027339476	35				
within-sd	0.02294621			status:	homogeneous	
n	2.00					
s_{bb}	0.01618912					
u^*_{bb}	0.00936775					
u_{bb}	0.01618912					
u_{bb}(rel.)	0.08254207					

Li (ICP-OES; mass fraction in %)

	1	2
Bottle 1	7.765	7.800
Bottle 2	7.704	7.643
Bottle 3	7.657	7.844
Bottle 4	7.601	7.623
Bottle 5	7.637	7.664
Bottle 6	7.664	7.641
Bottle 7	7.778	7.721
Bottle 8	7.683	7.604
Bottle 9	7.640	7.713
Bottle 10	7.635	7.609
Bottle 11	7.494	7.434
Bottle 12	7.670	7.773
Bottle 13	7.918	7.730
Bottle 14	7.653	7.619
Bottle 15	7.707	7.612
Bottle 16	7.638	7.478

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.2301456	15	0.01534304	3.4395448	0.00957954	2.35222276
Within groups	0.07137242	16	0.00446078			
Total	0.30151803	31				
within-sd	0.066789					
n	2.00					
s_{bb}	0.073764					
u^*_{bb}	0.0280813					
u_{bb}	0.073764					
u_{bb}(rel.)	0.9620585					

Al (ICP-OES; mass fraction in mg/kg)

	1	2
Bottle 1	12.72	12.38
Bottle 2	13.25	13.08
Bottle 3	12.59	14.32
Bottle 4	13.26	11.84
Bottle 5	12.65	11.68
Bottle 6	12.64	12.75
Bottle 7	14.12	11.67
Bottle 8	12.28	12.54
Bottle 9	12.72	13.72
Bottle 10	11.57	12.47
Bottle 11	11.91	11.47
Bottle 12	12.56	12.19
Bottle 13	11.06	13.74
Bottle 14	12.48	12.86
Bottle 15	12.41	14.47
Bottle 16	13.17	11.27
Bottle 17	13.83	10.96
Bottle 18	11.81	11.96

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	8.824101	17	0.51906476	0.4950769	0.92300208	2.23254567
Within groups	18.8721503	18	1.0484528			
Total	27.6962513	35				
within-sd	1.0239398			status:	homogeneous	
n	2.00					
s_{bb}	0					
u^*_{bb}	0.4180217					
u_{bb}	0.4180217					
u_{bb}(rel.)	3.3264178					

Cr (ICP-OES; mass fraction in mg/kg)

	1	2
Bottle 1	5.297	5.393
Bottle 2	5.448	5.289
Bottle 3	5.287	5.244
Bottle 4	5.644	5.251
Bottle 5	5.317	5.321
Bottle 6	5.518	5.518
Bottle 7	5.330	5.184
Bottle 8	5.321	5.296
Bottle 9	5.224	5.365
Bottle 10	5.408	5.271
Bottle 11	5.311	5.257
Bottle 12	5.304	5.446
Bottle 13	5.249	5.625
Bottle 14	5.333	5.223
Bottle 15	5.272	5.325
Bottle 16	5.324	5.287
Bottle 17	5.479	5.379
Bottle 18	5.364	5.272

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	0.177462	17	0.01043894	0.83282951	0.64500257	2.23254567
Within groups	0.22561754	18	0.01253431			
Total	0.40307954	35				
within-sd	0.1119567			status:	homogeneous	
n	2.00					
s_{bb}	0					
u^*_{bb}	0.0457061					
u_{bb}	0.0457061					
u_{bb}(rel.)	0.8553164					

Fe (ICP-OES; mass fraction in mg/kg)

	1	2
Bottle 1	24.43	24.20
Bottle 2	25.25	24.59
Bottle 3	24.96	24.78
Bottle 4	26.11	24.14
Bottle 5	24.59	24.98
Bottle 6	25.20	25.04
Bottle 7	24.56	24.07
Bottle 8	24.82	24.79
Bottle 9	24.89	25.65
Bottle 10	24.53	24.29
Bottle 11	24.61	23.91
Bottle 12	24.50	25.24
Bottle 13	24.14	24.58
Bottle 14	24.73	24.42
Bottle 15	24.66	24.96
Bottle 16	24.51	24.07
Bottle 17	24.86	24.64
Bottle 18	24.70	24.33

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	3.46447191	17	0.20379247	1.00661788	0.49274475	2.23254567
Within groups	3.64414786	18	0.20245266			
Total	7.10861977	35				
within-sd	0.4499474			status:	homogeneous	
n	2.00					
s_{bb}	0.0258825					
u^*_{bb}	0.1836903					
u_{bb}	0.1836903					
u_{bb}(rel.)	0.7440942					

Na (ICP-OES; mass fraction in mg/kg)

	1	2
Bottle 1	368.3	367.9
Bottle 2	371.5	366.1
Bottle 3	378.0	372.6
Bottle 4	364.4	367.9
Bottle 5	372.6	364.7
Bottle 6	369.8	373.0
Bottle 7	371.8	372.0
Bottle 8	372.7	371.3
Bottle 9	369.5	367.2
Bottle 10	371.1	377.5
Bottle 11	368.7	366.8
Bottle 12	371.8	372.9
Bottle 13	368.6	373.2
Bottle 14	368.5	370.1
Bottle 15	364.5	362.8
Bottle 16	372.0	369.4
Bottle 17	376.5	365.1
Bottle 18	370.6	371.9

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	270.884107	17	15.93435925	1.59035896	0.16883553	2.23254567
Within groups	180.348257	18	10.01934761			
Total	451.232364	35				
within-sd	3.1653353			status:	homogeneous	
n	2.00					
s_{bb}	1.71974					
u^*_{bb}	1.2922427					
u_{bb}	1.71974					
u_{bb}(rel.)	0.4646706					

S (ICP-OES; mass fraction in mg/kg)

	1	2
Bottle 1	1568.3	1547.5
Bottle 2	1534.3	1534.0
Bottle 3	1582.0	1566.3
Bottle 4	1560.5	1566.3
Bottle 5	1560.4	1562.9
Bottle 6	1584.6	1578.6
Bottle 7	1565.4	1560.9
Bottle 8	1547.4	1532.9
Bottle 9	1563.6	1549.9
Bottle 10	1568.5	1589.1
Bottle 11	1584.6	1574.5
Bottle 12	1579.2	1584.4
Bottle 13	1533.4	1557.1
Bottle 14	1540.3	1527.3
Bottle 15	1559.1	1534.0
Bottle 16	1567.3	1553.2
Bottle 17	1595.1	1552.1
Bottle 18	1580.0	1570.4

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	8877.051681	17	522.1795106	3.600983659	0.004967504	2.23254567
Within groups	2610.18435	18	145.0102417			
Total	11487.23603	35				
within-sd	12.04202					
n	2.00					
s_{bb}	13.732612					
u^*_{bb}	4.916134					
u_{bb}	13.732612					
u_{bb}(rel.)	0.8794311					

Si (ICP-OES; mass fraction in mg/kg)

	1	2
Bottle 1	53.2	47.4
Bottle 2	46.7	46.1
Bottle 3	45.6	
Bottle 4	44.5	43.9
Bottle 5	46.2	45.0
Bottle 6	44.7	45.5
Bottle 7	46.5	48.3
Bottle 8	47.2	46.1
Bottle 9	45.7	44.4
Bottle 10		43.6
Bottle 11	45.1	45.9
Bottle 12	45.0	45.1
Bottle 13	47.0	52.2
Bottle 14	46.3	48.2
Bottle 15	45.1	44.4
Bottle 16	44.9	44.0
Bottle 17	45.6	44.9
Bottle 18	44.8	43.8

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	103.039175	17	6.06112795	2.52304136	0.035421541	2.31672184
Within groups	38.4369629	16	2.40231018			
Total	141.476138	33				
within-sd	1.5499388			status:	inhomogeneous	
n	2.00					
s_{bb}	1.3525564					
u^*_{bb}	0.651669					
u_{bb}	1.3525564					
u_{bb}(rel.)	2.9467735					

C (combustion/IR; mass fraction in %)

	1	2
Bottle 1	0.108	0.107
Bottle 2	0.108	0.107
Bottle 3	0.108	0.108
Bottle 4	0.105	0.105
Bottle 5	0.106	0.108
Bottle 6	0.108	0.108
Bottle 7	0.103	0.104
Bottle 8	0.107	0.106
Bottle 9	0.105	0.106
Bottle 10	0.106	0.104
Bottle 11	0.105	0.105
Bottle 12	0.106	0.108
Bottle 13	0.105	0.104
Bottle 14	0.103	0.101
Bottle 15	0.107	0.106
Bottle 16	0.106	0.105
Bottle 17	0.105	0.105
Bottle 18	0.106	0.104

Source of variation	*sums of squares (SS)*	*degrees of freedom (df)*	*Mean squares (MS)*	*F-value*	*P-value*	*critical F-value*
Between groups	8.59E-05	17	5.053E-06	9.82310977	6.6261E-06	2.23254567
Within groups	9.2591E-06	18	5.144E-07			
Total	9.516E-05	35				
within-sd	0.0007172					
n	2.00					
s_{bb}	0.0015064					
u^*_{bb}	0.0002928					
u_{bb}	0.0015064					
u_{bb}(rel.)	1.4243924					