ICG-TC2

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International Commission on Glass – TC2

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The Certification of the Mass Fractions of
Arsenic (III) oxide, Barium oxide, Cadmium oxide, Cerium (IV) oxide,
Chloride, Cobalt oxide, Chromium (III) oxide, Copper (II) oxide,
Iron (III) oxide, Manganese (II) oxide, Molybdenum (VI) oxide,
Nickel (II) oxide, Lead (II) oxide, Antimony (III) oxide, Selenium,
Tin (IV) oxide, Sulfur trioxide, Strontium oxide, Titanium (IV) oxide,
Vanadium (V) oxide, Zinc oxide, and Zirconium (IV) oxide

in Soda Lime Glass

BAM-S005-A

and

BAM-S005-B

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Final certification report

Abstract

This report describes the preparation and certification of the common reference materials BAM-S005A and BAM-S005B produced by BAM and ICG. Both CRMs are soda lime glasses with certified impurity contents of 22 Elements for use with X-ray fluorescence spectrometry. The certified mass fractions and additional determined data are listed below. The expression of mass fractions of elements as mass fractions of their oxides was used in accordance with the common approach in the field of glass technology. This specification does not express that the related elements were really determined as the specified oxides. Both CRMs only differ in some quantities of the certified values. If not accentuated, all other statements in this report are valid for both CRMs.

BAM-S005A
Multielement Glass for XRF Analysis – Type A

Parameter	Mass fraction	
	Certified value [1] in mg/kg	Uncertainty [2] in mg/kg
Arsenic (III) oxide	132	8
Barium oxide	115	9
Cadmium oxide	62	4
Cerium (IV) oxide	105	6
Chloride	247	33
Cobalt oxide	49.4	2.4
Chromium (III) oxide	15.6	2.4
Copper (II) oxide	112	5
Iron (III) oxide	422	11
Manganese (II) oxide	124	5
Molybdenum (VI) oxide	343	12
Nickel (II) oxide	59.0	2
Lead (II) oxide	202	8
Antimony (III) oxide	132	7
Selenium	19.6	1.7
Tin (IV) oxide	100	7
Sulfur trioxide	1942	85
Strontium oxide	151	7
Titanium (IV) oxide	164	9
Vanadium (V) oxide	350	22
Zinc oxide	203	10
Zirconium (IV) oxide	842	125

1) The certified values are the means of 11-25 series of results (depending on the parameter) obtained by different laboratories. 3 up to 9 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of element mass fractions were calibrated by pure substances of definite stoichiometry or by solutions prepared from them, thus achieving traceability to SI unit.

2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$.

BAM-S005B
Multielement Glass for XRF Analysis – Type B

Parameter	Mass fraction	
	Certified value [3] in mg/kg	Uncertainty [4] in mg/kg
Arsenic (III) oxide	132	8
Barium oxide	115	5
Cadmium oxide	62	3
Cerium (IV) oxide	105	5
Chloride	247	24
Cobalt oxide	49.4	2.3
Chromium (III) oxide	15.2	1.2
Copper (II) oxide	112	4
Iron (III) oxide	422	10
Manganese (II) oxide	124	5
Molybdenum (VI) oxide	343	12
Nickel (II) oxide	59.0	1.9
Lead (II) oxide	202	7
Antimony (III) oxide	132	6
Selenium	19.6	1.2
Tin (IV) oxide	100	7
Sulfur trioxide	1942	57
Strontium oxide	151	7
Titanium (IV) oxide	163	7
Vanadium (V) oxide	349	22
Zinc oxide	203	6
Zirconium (IV) oxide	842	76

3) The certified values are the means of 11-25 series of results (depending on the parameter) obtained by different laboratories. 3 up to 9 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of element mass fractions were calibrated by pure substances of definite stoichiometry or by solutions prepared from them, thus achieving traceability to SI unit.

4) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$.

Sample description

The CRM consist of a disc of soda lime glass (39 mm diameter and 5 mm thick, with a weight of about 26 g to 30 g) which has been polished at one side. It is. intended to be directly used with X-ray fluorescence spectrometry (XRF) for calibration and determination of the 22 certified trace elements.

Informative values

Not certified informative values were determined by only one of the participating laboratories.

All mass fractions are given in %

Silicon (IV) oxide	71
Sodium oxide	13.7
Calcium oxide	10.5
Magnesium oxide	2.3
Aluminium oxide	1.1
Potassium oxide	0.7

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1 Introduction

1.1 Scope

Soda-lime glass is one of the world wide mostly distributed mass-produced articles and is of enormous technical and economic importance. The impurities in soda-lime glasses come from the intake by raw materials and from production process. They influence the properties of the glass and, therefore, their mass fractions must not exceed defined limit values. The analytical method of X-ray fluorescence spectrometry (XRF) is a powerful tool of effective determination of trace contents of most elements in soda-lime glass at the relevant level of mass fractions. The advantage of this method is that the samples can be measured directly without applying time consuming chemical procedures of sample digestion. The disadvantage is, as common with all direct solid sampling analytical methods, consists in the difficulty to dispose of appropriate samples for calibration. A certified reference material for the multi-element trace-determination in soda-lime glass by XRF is world-wide lacking. The aim of the certification process described here was to make such a CRM available. The CRM can be used to support the XRF-evaluation program basing on fundamental parameter approach by a definite calibration point for each of the relevant trace elements. Thus the semi-quantitative character of the evaluation procedure can be improved and changed to a quantitative one. Therefore the decisions basing on the results of trace analyses of soda lime glass can become more reliable and effective. 22 trace elements were identified to be relevant for the analytical characterization of soda-lime glass. Their mass fractions were certified in a batch of doped soda-lime glass, especially prepared for this purpose.

1.2 Certification procedure

The glass material for the CRMs was produced in a special preparation procedure from a melt of soda-lime glass doped with pure compounds of the relevant trace elements to be certified (see 4.1). The glass samples were taken at two different points of time from the melt. Samples arising from the first point of time belong to the type A whereas samples from the later point of time belong to the type B of material. In both steps caky glass plates were formed from which the final sample discs were shaped in a procedure carried out afterwards. The certification procedure was not carried out using the sample discs appropriate for XRF analysis. For this purpose samples were distributed stemming from the centre of the caky glass plates. Only samples of type B were distributed. 24 laboratories from 11 countries participated in the interlaboratory comparison for certification. For the final certification, each laboratory carried out 6 independent determinations for the investigated analytes. The statistical evaluation of the results of interlaboratory comparison included some statistical tests. Indicated outliers were discussed at the semi-annual meetings of ICG TC2. The laboratories who had delivered these values were informed. After removal of all relevant outliers the mean values of the interlaboratory comparison were taken as the certified mass fractions of the samples of type B. Homogeneity studies were separately carried out at sample discs of type A and type B. The certified uncertainties were calculated by taking into account the contributions from interlaboratory comparison and from inhomogeneity of the material. The certified mass fractions of the samples of the type A were calculated on the basis of the mass fractions of type B. The certified value of the type B material was also accepted as the mass fraction of the related analyte in the samples of type A if the mean values determined in the frame of the homogeneity studies of both materials did not differ markedly for this analyte. In case of a significant deviation a related correction factor was calculated from mean values of types A and B, determined in the frame of the homogeneity study. The uncertainty of the mass fractions in samples of type A was calculated in an analogous way as for samples of type B.

2 Participating laboratories

2.1 Allocation and preparation of the material

- The material was melted, sampled and the discs were mechanically shaped by Stazione Sperimentale del Vetro, Murano – Venice (Italy).
- The material for the certification was crushed by Stazione Sperimentale del Vetro, Murano – Venice (Italy).
- The sample discs were wrapped and packed by BAM, Federal Institute for Materials Research and Testing, Berlin (Germany).

2.2 Homogeneity testing

- All measurements and statistical evaluations were carried out by BAM.

2.3 Certification analysis

- The samples for certification analysis were distributed by
  Stazione Sperimentale del Vetro, Murano – Venice (Italy).
- The interlaboratory comparison was organized by BAM.

To achieve high international acceptance prominent laboratories located world wide were asked to participate in the interlaboratory comparison. They were either experts in glass analysis or had well known ability to analyze difficult materials by adequate analytical methods. The 24 laboratories of the interlaboratory comparison for certification are listed alphabetically in Tab. 1.

Tab. 1: Participating laboratories (arranged alphabetically)

BAM, Federal Institute for Materials Research and Testing
- Laboratory: Activation Analysis; Gas Analysis
- Laboratory: Isotope Dilution and Nuclear Fuel Analysis
- Project group: Quality Assurance and Metrological Aspects in Production of High Tech Reference materials

Corning Europe Inc. SA CERF, Avon (France)
Corning Inc., Corning (USA)
CRITT Matériaux LNE EST, Schiltingheim Cedex (France)
Forschungsinstitut für anorganische Werkstoffe – Glas/Keramik GmbH, Höhr-Grenzhausen (Germany)
Fraunhofer-Institut für Silikatforschung, Würzburg (Germany)
Glasforskningsinstitutet (GLAFO), Växjö (Sweden)
Glass Institute, Hradec Králové (Czech Republic)
Glaverbel Mecaniver SA, Jumet (Belgium)
INISMa (L'Institut National Interuniversitaire des silicates sols et Matériaux), Charleroi (Belgium)
ISOVER Saint-Gobain CRIR, Rantigni (France)
"Jožef Stefan" Institute, Ljubljana (Slovenia)
NSG Techno-Research Company, Itami-city, Hyougo (Japan)
Pilkington European Technical Centre, Group Analytical Services, Lancashire (Great Britain)
Saint-Gobain Glass Deutschland, Forschung und Entwicklung Bauglas (FEB), Herzogenrath (Germany)
Saint-Gobain Recherche, Aubervilliers Cedex (France)
Schott Glass Technologies Inc., R&D-Technical Services, Duryea (USA)
Schott Glas, Mainz (Germany)
Stazione Sperimentale del Vetro, Murano-Venice (Italy)
TU Bergakademie Freiberg – Institut für Silikattechnik, Freiberg (Germany)
Turkiye Şişe ve Cam Fabrikalari A.Ş., Glass Research Center, Topkapi-Istanbul (Turkey)

2.4 Determination of informative values

- The informative values were determined by
  Stazione Sperimentale del Vetro, Murano – Venice (Italy).

3 Abbreviations used

Tab. 2: List of abbreviations

Comb.-IR	Combustion method with infrared detection
ET AAS	Atomic absorption spectrometry with electrothermal atomisation
F AAS	Flame atomic absorption spectrometry
FI-HG AAS	Atomic absorption spectrometry with flow injection hydride generation
GRAV	Gravimetry
HG AAS	Atomic absorption spectrometry with hydride generation
ICP OES	Inductively coupled plasma optical emission spectrometry

ICP-MS	Inductively coupled plasma mass spectrometry
ID-TIMS	Isotope dilution mass spectrometry with thermal ionisation
INAA	Instrumental neutron activation analysis
K_0-INAA	K_0- Instrumental neutron activation analysis
MAS	Molecular absorption spectrometry
POT	Titrimetry with potentiometric end point determination
TITR	Titrimetry
XRF	X-ray fluorescence spectrometry

4 Origin and homogeneity investigation of the material

4.1 Preparation of samples

The reference glass was designed to contain trace elements in a concentration range selected in order to fulfil several requirements: the glass had to be a soda-lime glass, the elements to be incorporated should:

(i) occur as natural traces in current production,
(ii) be present at a minimum concentration level corresponding to a value being about 3 times of the related limit of determination by XRF,
(iii) cause a minimum of spectral interferences that might affect the determination of mass fractions of analytes..

Weighted masses of pure chemicals were added to a typical soda-lime glass batch to obtain a glass containing the following trace elements : As, Ba, Cd, Ce, Cl, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, SO_3, Sr, Ti, V, Zn, Zr. For chloride, barium, iron, chromium, zirconium, molybdenum and titanium no addition was necessary because they are either present as contaminants of the main raw materials or derive from refractory corrosion (zirconium) or electrode corrosion (molybdenum).
The composition of the batch, which is given in Table 3, was designed to produce about 70 Kg of glass.

The batch was melted in a day tank electrically heated by molybdenum rod electrodes, under oxidising conditions. The lining tiles of the furnace were in ER 1711 refractory material having the following mass fractions (in percent) of composition: Al_2O_3 45.9, ZrO_2 40.8, SiO_2 12.8, Na_2O 0.8, Fe_2O_3 0.08, TiO_2 0.08.
Melting was performed at a temperature of 1400°C for 12 hours, followed by a conditioning period of 8 hours at 1100°C for the re-adsorption of gas bubbles.
After removing the upper glass layers, several glass portions were gathered with a cast iron spoon and poured over rectangular steel plates to obtain 34 caky glass samples (about 18x14 cm in shape, 1 cm thick).
After abrading the glass surface wich had been directly in contact with the steel plate, 4 disks of about 4 cm diameter and 0.7-0.8 cm thickness were formed from each caky glass sample using a hole saw. Finally, the surfaces of each disk were mechanically smoothed and polished with corundum. This set of samples was denoted as “type A material” (129 disks).

Because some bubbles had been identified in these glass samples, it was decided to improve the glass quality by further conditioning the remaining part of the melt for 24 hours in the melting furnace. The same procedure of sample taking and preparation was then followed to obtain 45 caky glass samples (about 14x11 cm in shape, 1 cm thick) and from them a second set of disks denoted as “type B material” (130 disks).

Tab. 3: Composition of the batch (in kg)

Silica sand	49.330
Aluminum hydroxide	1.070
Sodium carbonate	17.349
Potassium nitrate	0.901
Magnesium carbonate	3.661
Calcium carbonate	13.125
Sodium sulphate	0.248
Arsenic oxide	0.007
Antimony oxide	0.008
Red lead	0.016
Zinc oxide	0.008
Strontium carbonate	0.012
Cobalt oxide	0.004
Tin oxide	0.007
Cerium oxide	0.008
Nickel oxide	0.004
Vanadium oxide	0.025
Cadmium oxide	0.004
Manganese sulphate monohydrate	0.020
Selenium metal powder	0.003
Cupper oxide	0.008
	Total batch weight : 85.819

4.2 Homogeneity study

For details see Appendix

The homogeneity test was carried out at different samples (discs) which had been polished at one side. This side was measured for the test by XRF with the Siemens sequential spectrometer SRS303.
All samples had been produced from the same glass melt, but the melt had been casted two times as described in 4.1 (for further sample preparation see also 4.1).

A representative number of analytical samples was taken from the entire number of samples by systematic selection for using in the homogeneity study.

From the type A material the following samples were taken for the test:

3A, 7A1, 7A2, 7A3, 7A4, 11A1, 15A, 19A, 23A, 27A, 31A1, 31A2, 31A3, 31A4,

From the type B material the following samples were taken for the test:

2B, 6B1, 6B2, 6B3, 6B4, 10B, 14B, 18B, 22B, 26B, 30B, 34B, 38B1, 38B2, 38B3, 38B4, 42B.

The numbering of the samples is explained by two examples:

- No. “38B1” stands for: “1st of the four prepared sample discs coming from the 38th raw sample (caky glass plate) of B series”
- No. “15A” stands for: “one of the four prepared sample discs coming from the 15th raw sample (caky glass plate) of A series”.

All samples without a final digit and those samples with the final digit “1” were taken for the determination of standard deviations occurring between the samples of different raw sample plates (“between the samples”), whereas the standard deviations within the samples from the same raw sample plates (“within the samples”) were determined using the samples 7A1-7A4, 31A1-31A4; 6B1-6B4 and 38B1-38B4.

The measurements were carried out at the cleaned samples, polished sides.

The trueness of results was for this study not of high interest, but the precision was very important. Therefore semi-quantitative calibration could be used.

The drift over the entire time of measurement was checked using sample 3A. The standard deviations of these measurements were treated like results from a homogeneous sample and were used for comparison.

For each analyte (all certified and informative ones, except Ni) there are at least two tables of homogeneity evaluation, one for the homogeneity test “between the samples” (A and B samples together) and one for the test “within the (raw) samples” (A and B samples together). In case of significant t- test results for the mean values between A- and B-groups of samples, two tables were calculated additionally for the homogeneity test “between the samples”, related to A- and to B- samples, separately.
The following results were achieved:

- Most test results do not indicate significant inhomogeneities.

Exceptions are following :
- Significant strong inhomogeneities “within” for Cl, CuO, MoO_3, ZrO_2 ;
- significant inhomogeneities “within” for K_2O, ZnO and Se ;
- significant weak inhomogeneities “within” for Al_2O_3, PbO.

Almost no significant inhomogeneities were found between the samples, - exceptions are weak inhomogeneities in type A material for Ba and Zn and in A+B Material for Cr.
This can be interpreted that way that most contents in the sample discs coming from different raw sample plates differ in the similar extent as those, coming from the same raw sample plate.

The contributions of the inhomogeneity (detected or maybe as a not detected, “masked” contributions) of certified analytes were included in a later stadium of evaluation into the total uncertainty of the certified values (see 8.2).

5 Time stability of the material

The total trace element content is not apt to change with time, as long as the material is not debased by contamination. It is widely assumed that the chemical composition of glass is stable over long-term periods [1, 2]. Repeated analyses carried out by INAA in 1997 and 1998 within the frame of the certification of BCR CRM 664 showed that the variation of trace element mass fractions was essentially negligible over one year [3].
The trace element content in the bulk material cannot be changed because of the chemically inert position of the molecules in the material. The concentration of trace elements is “frozen” in the glass structure and not subject to changes due to migration phenomena that may occur under normal storing conditions. Possible absorption of moisture from a compact glass due to weathering can be estimated to be so low that the date of expiry of certification was set to ten years under the storing conditions in BAM (normal humidity conditions). Moreover, it is considered that this glass contains a high amount of alumina that makes it hydrolytically stable and strongly prevents water adsorption. A proper storage under dry environment is nevertheless recommended (see 9.3) as well as a surface preparation periodically carried out as described in 9.2.

6 Analytical methods

This chapter describes the analytical procedures and specific parameters used in the certification campaign.

- The method used for homogeneity investigations (XRF) was described above (see chapter 4).

- The method used for the additional certification of type A material – in terms of a correction of values certified for the B material was the same as the method used for the homogeneity study because the same data were used for both purposes.

- XRF was also used as method for the determination of the informative values. It was carried out by direct measurement of the glass sample after appropriate polishing of the measuring surface. A PHILIPS PW 2400 X-ray spectrometer was used, the analytical programme was the SuperQ version 2.1D developed by Philips. For the calibration, the following certified reference materials were used: NBS 620, NBS 621 and NBS 1830. Accuracy was checked using in-house standards, analysed by both, X-ray fluorescence and wet chemical methods.

6.1 Analytical methods used for certification (of type B material)

In Tab. 4 the certified elements (mostly as their oxides) with certified values are listed together with the methods used for their certification (in type B material) by the participants of the interlaboratory comparison.

Note: In Tab. 4 and 5 the designation "element" also stands for its oxide.

In the first column the elements or element oxides are specified. In the following column "line numbers" are given. These line numbers correspond with the related line numbers in Tab. 6 and should not to be confused with the laboratory code numbers. They indicate at which position the related result stands in an arrangement of results for the related element arranged by increasing values (e.g. line number 1 always stands for the lowest value). In the last column the analytical methods used (abbreviations see Tab. 2 in chapter 3) are indicated belonging to the related line numbers in Tab. 6. Thus it is possible to identify which result in Tab. 6 is based on which analytical method.

Tab. 4: Analytical methods used for final determination of certified values

Element	Line number	Analytical method used
As_2O_3	3	F AAS
	7	FI-HG AAS
	5, 9, 16	HG AAS
	12	ICP-MS
	(1), (2),4, 6, 8, 13, 15, (17)	ICP OES
	10	INAA
	11	K_0-INAA
	14	MAS
BaO	17	ET AAS
	(18), (19)	F AAS
	2	K_0-INAA
	14	ICP-MS
	(1), 3, 4, 5, 6, 7, 8, 9, 10, 12, 13, 15, 16	ICP OES
	11	XRF
CdO	3, 13	ET AAS
	2, 8, 10, 15, 18, 20	F AAS
	19	K_0-INAA
	17, 21	ICP-MS
	1, 4, 5, 6, 7, 9, 11, 12, 14, 16, 22	ICP OES
CeO_2	6	K_0-INAA
	12	ICP-MS
	1, 2, 3, 4, 5, 7, 8, 9, 10, 11, 13, 14, (15)	ICP OES
Cl	9	K_0-INAA
	8	MAS
	1, 2, 3, 4, 5, 6, 7, 10, 11,	POT

CoO	10, 20	ET AAS
	5, 8, 15, 16, 23	F AAS
	19	INAA
	13	K_0-INAA
	21, 22	ICP-MS
	1, 2, 3, 4, 6, 7, 9, 11, 12, 17, 18	ICP OES
	14	MAS
Cr_2O_3	12, 19	ET AAS
	3, 4, 6	F AAS
	15	INAA
	9	K_0-INAA
	11	ICP-MS
	1, 2, 5, 7, 8, 10, 13, 14, 16, 20, 21, (22)	ICP OES
	17	ID-TIMS
	18	MAS
CuO	6, 11	ET AAS
	4, 14, 17, 18, 19, 22	F AAS
	20	ICP-MS
	1, 2, 3, 5, 7, 8, 9, 10, 12, 13, 15, 16, 23, 25	ICP OES
	21	ID-TIMS
	24	MAS
Fe_2O_3	16	ET AAS
	9, 11, 13, 15, 17, 19	F AAS
	6	K_0-INAA
	1, 2, 3, 4, 10, 12, 14, 18, 20, 21, 22, 23, (24)	ICP OES
	5, 7, 8	MAS
MnO	10	ET AAS
	2, 9, 16, 20, 21, 23, 25	F AAS
	17	K_0-INAA
	22	ICP-MS
	1, 3, 4, 5, 7, 8, 11, 12, 13, 14, 18, 19, 24	ICP OES
	6	MAS
	15	XRF
MoO_3	7	F AAS
	5	K_0-INAA
	11, 14	ICP-MS
	1, 2, 3, 4, 6, 8, 9, 10, 12, 13	ICP OES
NiO	11, 21	ET AAS
	1, 9, 12, 15, 18, 22	F AAS
	14	ICP-MS
	2, 3, 5, 6, 7, 8, 10, 13, 16, 17, 19, 20, (23)	ICP OES
	4	MAS
PbO	11, 21	ET AAS
	6, 8, 12, 14, 20, 22, 24	F AAS
	18	ICP-MS
	1, 2, 3, 4, 5, 7, 9, 10, 13, 15, 16, 23	ICP OES
	17	ID-TIMS
	19	XRF
Sb_2O_3	12	ET AAS
	1, 4, 7	F AAS
	17, 15	FI-HG AAS
	14, 16	HG AAS
	11	INAA
	9	K_0-INAA
	18	ICP-MS
	2, 3, 5, 6, 8, 10, 13, 19	ICP OES

Se	7	ET AAS
	2, 4, 5	FI-HG AAS
	8, 10	HG AAS
	9	INAA
	12	K_0-INAA
	3	ICP-MS
	1, 6, 11, 13, (14)	ICP OES
SnO_2	9, 10	ET AAS
	11	F AAS
	8	K_0-INAA
	12, 13	ICP-MS
	(1), 2, 3, 4, 5, 6, 7, 14, 15	ICP OES
SO_3	1, 3, 5, 11	Comb.-IR
	10	GRAV
	2, 4, 6, 7, 9	ICP OES
	8	TITR
SrO	22	ET AAS
	2, 3, 8, 17, 18, 23	F AAS
	19	K_0-INAA
	7	ICP-MS
	1, 4, 5, 6, 9, 10, 11, 12, 13, 14, 15, 20, 21	ICP OES
	16	XRF
TiO_2	1, 4, 7, 8, 9, 10, 11, 12, 13, 16, 18, 19, (20)	ICP OES
	2, 3, 5, 6, 15, 17	MAS
	14	XRF
V_2O_5	16	F AAS
	14	K_0-INAA
	10	ICP-MS
	1, 2, 3, 4, 5, 6, 7, 8, 9, 11, 12, 15, 17, 18	ICP OES
	13	XRF
ZnO	(1), 11, 15, 17, 18, 19	F AAS
	12	INAA
	8	K_0-INAA
	5	ICP-MS
	2, 3, 4, 6, 7, 9, 10, 13, 14, 16, 20, 21	ICP OES
	22	XRF
ZrO_2	8	INAA
	10	K_0-INAA
	20	ICP-MS
	(1), (2), 3, 4, 5, 7, 9, 11, 12, 13, 15, 16, 19, 21	ICP OES
	6, 14, 18	MAS
	17	XRF

Note: Line numbers in parenthesis refer to values not used in the calculation of the certified value.

For the analysis of almost all analytes a variety of different methods was used for final determination by the different participating laboratoratories. In most cases 5 or more (up to 8) different methods were applied, - exceptions are CeO_2, Cl and TiO_2 (with 3 different methods each) and MoO_3 or SO_3 (with 4 different methods each).

Another important question is the sample preparation and the way of calibration of the method of final determination used by the different participants. In Tab. 5 these information is listed. The table is structured alphabetically by the symbols of elements or oxides. For each element the information is arranged by increasing laboratory code numbers in column 1 (“Lab code”).

Note: The allocation between “line number” and “laboratory code number” can be concluded from Tab. 7, run1, of each element. The entries in the first column (“Current Lab. number”) of run 1 stand for the “line numbers” in Tab. 4 and Tab. 6 and the numbers in the second column (“Lab”) in Tab. 7 stand for the laboratory code numbers.

In the second column of Tab. 5 information on sample preparation is listed. In the third column information to the calibration of the final method of determination is given. The final method is specified in the last column of Tab. 5.

From this table it can be concluded that different procedures of sample digestion were applied by the participating laboratories, thus reducing the probability that all systematic aberrations of results caused by sample preparation tend into the same direction. Concerning the calibration it can be stated, that in all cases some different substances or solutions were used by the different participants. This minimizes a systematic influence on the final result, as well. Another advantage is that almost all calibrations were not carried out by using matrix reference materials, in other words, only pure solutions or compounds were used. Thus an essential prerequisite to guarantee metrological traceability to the SI unit was established.

Note: Only following calibrations were made by using a matrix glass reference material and were therefore not accepted and therefore excluded from all other tables: Lab. No.5 (for BaO, Fe_2O_3, SO_3, TiO_2) and Lab. No. 4 (for SO_3).

On the other hand the traceability of the used commercial solutions is not so clear and the demand of the organizer of the interlaboratory comparison, to use at least two different commercial calibration solutions was not always followed. But in view of the variety of different calibration solutions used for one element by the different participants it was decided also to accept those results which are based on the application of one commercial calibration solution, only.

Tab. 5 Interlaboratory comparison for certification of XRF glass: Compilation of sample preparation procedures, calibration procedures and methods used for final determination,
(Directly transferred from information of the participants)

Element As_2O_3

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-3) M: 0.1 g → 100 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 0.1 – 0.2 g Decomposition with HF-$HClO_4$-HNO_3-$KMnO_4$ mixture in Pt-dishes on hot plate, then dissolved with hydrochloric + tartaric acid; pre-reduced with KI, ascorbic and hydrochloric acid, reduction with $NaBH_4$	Merck, Perkin-Elmer 1000 mg/L As calibration solutions: 0-5-10-15-20-25-30 µg/L	FI-HG AAS
3	M: 0.1 g,; Decomposition with HF-$HClO_4$-HNO_3 (5/3/3) + 2 mL $KMnO_4$ (0.1N); evaporated to about 2 mL + 2mL $HClO_4$ fume again; dissolved in 5 mL HCl+H_2O → 50mL vol. flask. Aliquot of 4 mL in 100 mL vol. flask + 10 mL HCl 5 mL KI (10%); heating 10 min in boiling water..	Spex Certiprep 1 g/L As Dilution 1/1000 – (1 mg/L) 0-125-250 ppm weight (0-0.0125-0.0250 %) As in glass	HG AAS
	M: 0.5 g; Decomposition with HF-$HClO_4$-HNO_3 (5/3/3) + 2 mL $KMnO_4$ (0.1N); evaporated to about 2 mL + 2mL $HClO_4$ fume again; dissolved in 10 mL HCl+H_2O → 100 mL vol. flask.	Spex Certiprep 1 g/L As Dilution 5/100 – (50 mg/L) 0-100-200 ppm weight (0-0.0100-0.0200 %) As in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
4	M: 0.1 g; The sample is treated with HF-$HClO_4$-HNO_3 and $KMnO_4$ solution. It is evaporated to a small volume. The residue is taken into solution with HCl → dilute to 100 mL. Pre-reduction with 10% KJ and 1% ascorbic acid in 3% HCl; Hydride generation by $NaBH_4$ and NaOH.	1000 mg/L As in 5% HNO_3 certified by the supplier; traceable to SRM from NIST external calibration: 10-20-50 ng As As content checked with glass reference material CRM 664. it was found 6.2 mg/kg (certified value 5.9 mg/kg)	FI-HG AAS
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask.	Merck 1 g/L As calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
7a	M: 0.25 g; pressure digestion acid with 10 mL HF, 3 mL HNO_3 at 140°C for 2 h; neutralisation with 5 g H_3BO_3 → with H_2O to 100 mL	1000 mg/L As from As – metal in HNO_3 CPI P/N 4400-100031 calibration solution: 0-0.10-0.20-0.30-0.40 mg/L As with 10 mL HF, 3 mL HNO_3, 5 g H_3BO_3 in 100 mL as matrix matching	ICP OES
9	no sample preparation		K_0-INAA
10	M: 0.5 g; Dissolution with HF-$KMnO_4$-H_2SO_4 → 50 mL Photometric determination with molybdenum-blue	Alfa product 1000 mg/L As stock solution standard. solution. I: 1 mL = 13.2 ng As_2O_3; standard solution. II: 1 mL = 1.32 ng As_2O_3 aliquot standard solution: 0-1-2-3-4-5 mL	MAS
	M: 0.5 g; Dissolution with HF-$KMnO_4$-HCl → 50 mL	Alfa product 1000 mg/L As stock solution calibration solution: 1-5-10 mg/l matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF ($KMnO_4$)-$HClO_4$ → 100 mL	Merck 1 g/L As → 10.5624 mg / 250 mL As_2O_3 calibration solutions: 0-0.660-1.320-2.640-5.281	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL; isotope ^{75}As used	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 0.5 g; Decomposition with HF-$HClO_4$-HNO_3-$KMnO_4$ Temp. < 140°C; Residue taken up with 10% HCl → 100 mL, Aliquot taken to reduction with KI in 10% HCl at 60°C for 10 min	1000 mg/L As BDH 1000 mg/L As Merck external calibration solutions: 0.005-0.010-0.015 mg/L (Reduction with 10% KI)	HG AAS
14	M: 1 g; sample 1 – 5 open Decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6 Decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L As ChemLab 1000 mg/L As Baker calibration solutions: addition method, 3 solutions in the expected range of concentration.	ICP OES
15	M: 0.140 – 0.214 g weight in quartz ampoules; no sample digestion crushing of glass lump with a vice	1.9072 mg/g As self made from elemental As	INAA
19	M: 0.1 g; pressure digestion in Parr bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L As	ICP OES
21	M: 1.29-1.46g; open digestion in PTFE dish with HF-HNO_3-$KMnO_4$ (13-10-2 (0.1 N)) Method as recommended by TC 2	1000 mg/L As solution supplied by BDH and Fisher calibration solutions: 1.0-2.0-5.0 mg/L	F AAS

Element BaO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Ba calibration solutions: 0-0.5-1.0-1.5-2.0-2.5 mg Ba / L	F AAS
	M: 0.1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Ba calibration solutions: 0-50-100-150-200-250 µg Ba / L	ET AAS
3	M: 0.5 g; Decomposition with HF-$HClO_4$-HNO_3 (5/3/3) + 2 mL $KMnO_4$ (0.1N); evaporated to about 2 mL + 2mL $HClO_4$ fume again; dissolved in 10 mL HCl+H_2O → 100 mL vol. flask.	Spex Certiprep 1 g/L Ba Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Ba in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5). Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL +2 mL HNO_3 spike with isotope 135	Spex Certiprep 1 g/L Ba Dilution to 10 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Ba in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	$Ba(NO_3)_2$ in HNO_3 (5%) 1000 mg/L Ba It has certificate of analysis; traceable to SRM from NIST external calibration, addition method Ba content checked with glass reference material CRM 664, it were found 29.4 mg/kg (certified value 29.1 mg/kg)	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 – 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	0.2 g / 100 mL HF-$HClO_4$ digestion of matrix reference material BCR 126 **No traceability!**	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O- and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Ba from $BaCO_3$ in 2% HNO3, CPI P/N 4400-100041 calibration solution: 0-0.10-0.20-0.50-0.60 mg/L Ba in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O- and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Ba from $BaCO_3$ in 2% HNO3, CPI P/N 4400-100041 calibration solution: 0-0.10-0.20-0.50-0.60 mg/L Ba in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g Dissolution with HF-$HClO_4$-HCl → 50 mL (1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (4-6)	Alfa product Ba stock solution 1000 mg/L Ba calibration solutions: 0.5-1-5-10 mg/L matrix matching	ICP OES
	M: 1 g Dissolution with HF-$HClO_4$-HCl → 50 mL (1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (4-6)	Alfa product Ba stock solution 1000 mg/L Ba calibration solutions: 0.5-1-5-10 mg/L matrix matching MM1: CsCl (Varian), N_2O/C_2H_2-flame MM2: CsCl/Butanol (Perkin-Elmer), N_2O/C_2H_2-flame	F AAS
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Ba → 8.923mg / 250 mL BaO calibration solutions: 0-0.447-0.893-2.233-4.466	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solution: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$;until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5 Decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6 Decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: addition method, 3 solutions in the expected range of concentration.	ICP OES
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	$BaCO_3$ 99.99% from Merck calibration samples: 102-108-122-132 mg/kg	XRF (after digestion by fusion)
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Ba	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	999 ± 2 mg/L Ba Merck mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
23	M: 0.50-0.59 g; decomposition in a microwave with HF-HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix	ICP OES

	min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	matching	

Element CdO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	M: 1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Cd calibration solutions: 0-1 mg Cd / L	F AAS
	M: 0.1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Cd calibration solutions: 0-5 µg Cd / L	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5). Residue dissolved in HNO_3 (5 mL)+H_2O in 50 mL vol. flask.	Spex Certiprep 1 g/L Cd Dilution to 50 ppm, 0-100-200 ppm weight (0-0.01-0.02 %) Cd in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	F AAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5). Residue dissolved in HNO_3(5 mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL +2 mL HNO_3 spike with isotope 113	Spex Certiprep 1 g/L Cd Dilution to 10 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Cd in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The sample is decomposed with HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 → 100 mL flask	1000 mg/L Cd / $Cd(NO_3)_2$ in 2-3% HNO_3 It has certificate analysis; traceable to SRM from NIST external calibration, addition method, Cd content checked with glass reference material CRM 664, it were found 5.9 mg/kg (certified value 5.7 mg/kg)	ICP OES
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 – 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask	1 g/L CdO from $CdSO_4$ x 8 H_2O Calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Cd from Cd – metal in 2% HNO_3 CPI P/N 4400-100081 calibration solution: 0-0.10-0.20-0.30-0.40 mg/L Cd in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Cd from Cd – metal in 2% HNO_3 CPI P/N 4400-100081 calibration solution: 0-0.10-0.20-0.30-0.40 mg/L Cd in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g Dissolution with HF-$HClO_4$-HCl → 50 mL (1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (4-6)	Alfa product 1000 mg/L Cd stock solution calibration solutions: 0.2-0.5-1mg/L matrix matching MM1: La(Varian), Air/C_2H_2-flame MM2: La/Butanol (Perkin-Elmer), Air/C_2H_2-flame	F AAS
	M: 1 g Dissolution with HF-$HClO_4$-HCl → 50 mL (1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (4-6)	Alfa product 1000 mg/L Cd stock solution calibration solutions: 0.5-1-5-10 mg/L matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Cd → 11.423 mg / 250 mL CdO calibration solutions: 0-0.571-1.142-2.856-5.712	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL. Isotope ^{111}Cd used.	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution:: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness, Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab 1000 mg/L Baker calibration solutions: standard addition method (SAM), 3 solutions in the expected range of concentration.	ICP OES
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL	6541.9 mg/L Cd in 10% HCl, self made from Alfa Johnson Matthey 6N Cd calibration solutions: 0.4-0.8-1.2-1.6-2.0 µg/L Cd addition calibration technique using a glass digestion solution	ET AAS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Cd	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	999 ± 2 mg/L Cd Merck mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
21	M: 0.50-0.58 g; open digestion in Pt vessel with HF-HNO_3-$HClO_4$ (10-1-5) Method as described and recommended by ICG-TC 2	1000 mg/L Cd solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
22	M: 2 g; sample digestion with 2 times HF-HNO_3 (15-5); Residue dissolved in 10 mL HCl and diluted to 100 mL	100 mg/L Cd solution ready made from BDH and Reagecon calibration solutions: 0.5.-1.0-1.5 mg/L calibration checked by standard addition	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix	ICP OES

	residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	matching	
24	M: 5g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: 1 g/L Titrisol calibration solutions: 0.1-0.2-0.5 mg/100 mL	F AAS

Element CeO_2

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.1 g → 100 mL Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	VHG Labs, Stock Multielement Standard 60,100 mg/L Lot # : SM 6021/01 calibration solutions: 0.50-1.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Ce Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Ce in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL +2 mL HNO_3 spike with isotope 140	Spex Certiprep 1 g/L Ce Dilution to 10 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Ce in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Ce from CeO_2 in HNO_3 It has certificate analysis; traceable to SRM from NIST external calibration, standard addition method	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	1 g/L CeO_2 from $(NH_4)_2Ce(NO_3)_6$ Calibration solution: 1 mg/L (CeO_2, CdO, CoO, CuO, MoO_3, V_2O_5)	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L CeO_2 in 2% HNO3, CPI PIN 4400-1000101 calibration solution: 0-0.10-0.20-0.60-0.70 mg/L Ce in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L CeO_2 in 2% HNO3, CPI PIN 4400-1000101 calibration solution: 0-0.10-0.20-0.60-0.70 mg/L Ce in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (4-6)	Alfa product 1000 mg/L Ce stock solution calibration solutions: 0.5-1-5-10 mg/L matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Ce → 49.138 mg / 250 mL CeO_2 calibration solutions: 0-2.457-4.914-12.285-24.569	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF. evaporate to dryness. add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	1000 mg/L Single Element High Purity Standard calibration solution: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement CPI 1000 mg/L Ce CPI calibration solutions: 0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method (SAM) 3 solutions in the expected range of concentration.	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1025 mg/L Ce Aldrich pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L, checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
23	M: 0.50-0.59 g; decomposition in a microwave with HF-HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES

Element Cl

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	M: 0.2-0.9 g; cold decomposition with HF-HNO_3-H_3BO_3	no stock and calibration solutions: back titration of equivalent point with potentiometric indication (a silver electrode) Instrument: ion activity meter, silver electrode – SCE (with salt bridge)	Potentiometry
3	M: 1 - 2 g; cold decomposition with HF-HNO_3 (10/5); Addition of know amount standard Cl solution (0.01 N)	$AgNO_3$ solution (0.005N) Titrated against standard HCl solution (0.01N) prepared by dilution of a standard N solution (PROLABO)	Potentiometry
4	M: 1 g; The sample is treated with a mixture of HNO_3-HF at room temperature. EDTA, ethanol, H_3BO_3 and an excess of $AgNO_3$ were added.	calibrant: solid, dried $AgNO_3$ + NaCl, purity > 99.9% Cl content checked with glass reference material CRM 664 and were found as 70 mg/kg Cl (certified value is 68.4 mg/kg Cl)	Potentiometry
9	no sample preparation		K_0-INAA
10	M: 0.5 g; Alkaline dissolution with Na_2CO_3 → 50 mL Photlmetric determination with Iron(III)-Mercury-Thiocyanate	NaCl, dried at 150°C for 2 h standard solution I c(Cl^-) = 0.001 mol/L in Na_2CO_3 standard solution II c(Cl^-) = 0.0001 mol/L in Na_2CO_3 aliquot standard solution: 0-1-2-3-4-5 mL	MAS
12	M: 2.5 g; Dissolution with 5 mL H_2O - 2 mL HNO_3 (16M) – 30 mL HF (29M) Samples are stirred for 2 h. After 2 h sample is diluted to 150 mL with H_2O. Solution is chilled in a chem. refrigerator	stock solution is prepared from "Baker Analyzed" $AgNO_3$ Titrate with 0.01N $AgNO_3$, standardized against NIST 2201 NaCl	Potentiometry
13	M: 1 g; cold decomposition with HNO_3-HF (ICG method)	stock solution $AgNO_3$ 0.1 N BDH calibration solution: $AgNO_3$ 0.01 M (3mL) vs KCl 0.01 M	Potentiometry
21	M. 0.5 g; Potentiometric determination of chloride in glass and glass making raw materials, report of ICG/TC2	Prepared from BDH and Alfa Aesar $AgNO_3$ and NaCl crystals calibration solution: 0.01 N AgNO3 + 0.01 N NaCl	Potentiometry
22	Cold decomposition with HF-H_3BO_3 (as ICG published procedure)	solid KCl Suprapur from Merck	Potentiometry
23	M:0.46-0.56 g; cold decomposition with HF- HNO_3 (20/10) for 30 min, add 50 mL ethanol, titration with 0.01 mol $AgNO_3$	0.01 mol $AgNO_3$	Potentiometry
24	M: 2.5 g; decomposition with HF-H_2SO_4	stock solution $AgNO_3$ 0.1 N calibration solution: $AgNO_3$ 0.1 N instrument: Ag electrode; reference electrode Hg_2SO_4 (with K_2SO_4)	Potentiometry

Element CoO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.1 g → 100 mL (1-3) M: 0.25 g → 50 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Co calibration solutions: 0-0.5 mg Co / L	F AAS
	M: 0.1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Co calibration solutions: 0-50 µg Co / L	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5). Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Co; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Co in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	F AAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5). Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL +2 mL HNO_3 spike with isotope 59	Spex Certiprep 1 g/L Co; Dilution to 10 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Co in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Co from $Co(NO_3)_2$ in 2-3% HNO_3 It has certificate analysis; traceable to SRM from NIST external calibration, addition method Co content checked with glass reference material CRM 664 and were found as 3.4 mg/kg Co (certified value is 2.77 mg/kg)	ICP OES
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask.	1 g/L CoO from $CoSO_4$ x 7 H_2O calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HCl and put in a 50 mL flask.	1 g/L Co standard solution from Merck control is made with another standard from Fisher calibration solutions: 1-2-5-mg/L Co, addition method for one measurement	F AAS
7b	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Co from Co-metal in 2% HNO_3 CPI P/N 4400-1000131 calibration solution: 0-0.10-0.20-0.30-0.40 mg/L Co in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water	1000 mg/L Co from Co-metal in 2% HNO_3 CPI P/N 4400-1000131 calibration solution: 0-0.10-0.20-0.30-0.40 mg/L Co in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 2 g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination with nitrosonaphthol	Alfa product Co stock solution 1000 mg/L Co standard solution I: 1 mL = 12.71 µg CoO Co standard solution II: 1 mL = 1.27 µg CoO Aliquot standard solution: 0-1-3-5-mL	MAS
10	M: 2 g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL	Alfa product Co stock solution 1000 mg/L calibration solutions: 1-10 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Co → 10.172 mg / 250 mL CoO calibration solutions: 0-0.509-1.017-2.543-5.086	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL. ^{59}Co used	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck; 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab; 1000 mg/L Baker calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
15	M: 0.140 – 0.214 g; weight in quartz ampoules; no sample digestion crushing of glass lump with a vice	1.0086 mg/g Co self made from elemental Co	INAA
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL.	6014.7 mg/L Co in 5 % HNO_3, self made from Alfa Johnson Matthey m4N85 Co calibration solutions: 5-10-15-20 µg/L Co addition calibration technique using a glass digestion solution	ET AAS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solutions: 1.0 mg/L Co	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1000 ± 2 mg/L Co Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L)with and without matrix matching	ICP OES
21	M: 1.46-1.55 g; open digestion in Pt vessel with HF-HNO_3; Residue dissolved in 5% HCl	1000 mg/L Co solution supplied by BDH and Fisher calibration solutions: 0.25.-0.5.-1.0-2.0-5.0 mg/L	F AAS
22	M: 2 g; sample digestion with 2 times HF-HNO_3 (15-5); Residue dissolved in 10 mL HCl and diluted to 100 mL	100 mg/L Co solution ready made from BDH and Reagecon calibration solutions: 0.5-1.0-1.5 mg/L calibration checked by standard addition	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 5g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%)	standard solution: 1 g/L Titrisol	F AAS

	to 100 mL	calibration solutions: 0.127-0.254-0.636 mg/100 mL	

Element Cr_2O_3

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-3), M: 0.1 g → 100 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 0.1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elme; 1000 mg/L Cr calibration solutions: 0-20 µg Cr / L	ET AAS
3	M: 0.1 g; Decomposition with HF-HNO_3 (5-2); Residue dissolved in H_2O and 5 mL HNO_3 transferred into 100 mL vol. flask	Spex, Certiprep 1 g/L Cr Dilution of 10 ppm Cr calibration solutions: 0-10-20 mg/kg weight (0-0.001-0.002 %) Cr in glass in HNO_3 + matrix matching	ET AAS
4	M: 1 g; The glass sample is decomposed with a mixture of HF- HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Cr from Cr in 5% HCl it has certificate analysis; traceable to SRM from NIST external calibration, standard addition method Cr content checked with glass reference material CRM 664 and were found as 2.48 mg/kg Cr (certified value is 2.65 mg/kg)	ICP OES
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask.	1 g/L Cr_2O_3 from K_2 Cr_2 O_7 Calibration solution: 5mg/L (Cr_2O_3, MnO, P_2O_5, SrO, ZrO_2)	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HNO_3 and put in a 100 mL flask.	1 g/L Cr standard solution from Merck control is made with another standard from Fisher calibration solutions: 0-1-2-5-mg/L Cr, addition method for one measurement	F AAS
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Cr from Cr-metal in 2% HNO_3 CPI P/N 4400-1000121 calibration solution: 0-0.5 mg/L Cr in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Cr from Cr-metal in 2% HNO_3 CPI P/N 4400-1000121 calibration solution: 0-0.5 mg/L Cr in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 2g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination with diphenylcarbazide	Cr III stock solution: c(1/2 Cr_2O_3) = 0.01 mol/L from $KCr(SO_4)_2$ in H_2SO_4 Cr (III) standard solution I: c(1/2 Cr_2O_3) = 0.0001 mol/L Cr standard solution II: c(1/2 Cr_2O_3) = 0.00001 mol/L	MAS
	M: 2 g; (sample 1-3) Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL M: 1 g; (sample 4-6) Dissolution with HF-HNO_3- → 25 mL	Alfa product Cr stock solution 1000 mg/L calibration solution: 1-10 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Cr → 11.693 mg / 250 mL Cr_2O_3 calibration solutions: 0-0.585-1.169-2.923-5.846	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL. ^{52}Cr used	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 1 g; Decomposition with HF-HNO_3; Residue taken up with HNO_3-$HClO_4$-HF evaporate to dryness again. Residue taken up with HCl → 100 mL	1000 mg/L multielement Merck 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-HNO_3; in Pt-crucible. Sample 6: decomposition with HF--HNO_3; in close Teflon bomb	1000 mg/L ChemLab 1000 mg/L Baker calibration solutions: standard addition method; 3 solutions in the expected range of concentration.	ICP OES
15	M: 0.140 – 0.214 g;weight in quartz ampoules; no sample digestion crushing of glass lump with a vice	0.9994 mg/g Cr self made from elemental Cr	INAA
16	M: 1g of sample and 0.6 g of ^{53}Cr-spike sol. were decomposed with 8 mL HF and 4 mL HNO_3 using a microwave oven for 33 min. at 220°C. The solution was transferred into a Pt dish and evaporated to dryness. The residue was dissolved twice with 10 mL water and 2 mL HNO_3 and evaporated to dryness. Then the residue was taken up with 10 mL water and 1 mL HNO_3 in order to get a clear solution. The fluorides were precipitated by 1.5 mL HF and separated from the solution by centrifugation. After washing twice the precipitate it was rejected. 0.5 mL of H_2SO_4 were added to the solution and then the solution was evaporated until white fumes were observed. 10 mL water and 1 mL ethanol were added to the cold solution and the solution was heated to 60°C. The solution was transferred into a quartz-beaker, ammonium peroxodisulphate added and a pH value between 8 and 9 adjusted using ammonia solution. The MnO_2 precipitate was separated by centrifugation and the separation of the analyte was carried out using an ion exchange procedure.	Cr-53 spike solution (146,208 µg/g), back spike solution by using chromium metal of highest purity, all solutions were prepared by weighing concentration: 15,5828 µg Cr-53/g (diluted by weighing), spiking was carried out before starting sample decomposition, the spiked analyte was separated from the matrix chromatographically by using strong basic ionic exchanger AG1 X8 only isotope ratios were measured (spiked samples, unspiked sample, 4 blanks, back-spike, spike)	ID-TIMS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	999 ± 5 mg/L Cr Merck mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L)with and without matrix matching	ICP OES
21	M: 1.46-1.56 g; open digestion in Pt vessel with HF-HNO_3; Residue dissolved in 5% HCl	1000 mg/L Cr solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
22	M: 2 g; sample digestion with 2 times HF-HNO_3 (15-5); Residue dissolved in 10 mL HCl and diluted to 100 mL	100 mg/L Cr solution ready made from BDH and Accu Standard Inc. calibration solutions: 0.1-0.2-0.4 mg/L calibration checked by standard addition	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES

Element CuO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g, Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Cu calibration solutions: 0-2.5mg Cu / L	F AAS
	M: 0.1 g Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Cu calibration solutions: 0-20 µg Cu / L	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 /5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Cu; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Cu in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	F AAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 /5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Cu; Dilution to 50 ppm 0-100-200 ppm (weight (0-0.01-0.02 %) Cu in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 /5 mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL and 2 mL HNO_3. spike with isotope 65	Spex Certiprep 1 g/L Cu; Dilution to 10 ppm 0-100-200 ppm (weight (0-0.01-0.02 %) Cu in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Cu from $Cu(NO_3)_2$ in 2-3% HNO_3 It has certificate of analysis; traceable to SRM from NIST standard addition method Cu content checked with glass reference material NBS 610, and were found 448 mg/kg Cu (certified is 444 mg/kg Cu)	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	1 g/L CuO from CuO Calibration solutions: 1 mg/L (CdO, CoO, CuO, CeO_2, MoO_3, V_2O_5)	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HCl and put in a 50 mL flask.	1 g/L Cu standard solution from Merck control is made with another standard from Fisher calibration solutions: 0-1-2-5-mg/L Cu addition method for one measurement	F AAS
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Cu from Cu – metal in 2% HNO_3 CPI P/N 4400-1000141 calibration solution: 0-0.10-0.20-0.50-0.60 mg/L Cu in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Cu from Cu – metal in 2% HNO_3 CPI P/N 4400-1000141 calibration solution: 0-0.10-0.20-0.50-0.60 mg/L Cu in 6% HNO_3	ICP OES
10	M: 2 g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination with Bichinolin	Alfa product Cu stock solution 1000 mg/L; Cu standard solution I: 1 mL = 12.52 µg CuO Cu standard solution II: 1 mL = 1.25 µg CuO; Aliquot standard solution: 0-1-2-3-4-5-mL	MAS
10	M: 2 g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL	Alfa product Cu stock solution 1000 mg/L calibration solutions: 1-10 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Cu → 10.0144 mg / 250 mL CuO calibration solutions: 0-0.501-1.001-2.504-5.007	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solutions: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness; Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck ¸1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible; sample 6: Decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions:: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
16	M: 0.5 g of sample and 0.5 g of Cu^{65}-spike solution were decomposed with 12 mL HF-HNO_3 (10/2) using a micro-wave oven for 33 minutes at 220°C. The solution was transferred into a Pt dish and evaporated to dryness. The residue was dissolved twice with 10 mL water and 1 mL HNO_3 and evaporated to dryness. Then the residue was taken up with 10 mL water and 1 mL HNO_3 in order to get a nearly clear solution. 0.5 mL of $HClO_4$ were added to the solution and then the solution was evaporated until white fumes were observed. The residue was dissolved twice with 2 mL conc. HCl and 5 mL water and evaporated to dryness. Then the residue was taken up with 10 mL 0.2 mol/L HCl and the solution was transferred into a quartz-beaker. The analyte/matrix separation was carried out by an electrodeposition procedure.	Cu-65 spike solution (177.485 µg/g), back spike solution by using BAM "A-Primary-Cu-1", all solutions were prepared by weighing stock solution was used, spiking was carried out before starting sample decomposition, the spiked analyte was separated from the matrix using an electrodeposition procedure only isotope ratios were measured (spiked samples, unspiked sample, 4 blanks, back-spike, spike)	ID-TIMS
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL.	10044 mg/L Cu in 4% HNO_3, self made from Alfa Johnson Matthey 6N Cu calibration solutions: 10-20-30-40 µg/L Cu addition calibration technique using a glass digestion solution	ET AAS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solutions: 1.0 mg/L Cu	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1001 ± 2 mg/L Cu Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L)with and without matrix matching	ICP OES
21	M: 1.46-1.56 g; open digestion in Pt vessel with HF-HNO_3 ; Residue dissolved in 5% HCl	1000 mg/L Cu solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
22	M: 2 g; sample digestion with 2 times HF-HNO_3 (15-5); Residue dissolved in 10 mL HCl and diluted to 100 mL	100 mg/L Cu solution ready made from BDH and AccuStandard Inc. calibration solutions: 1-2-3 mg/L	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 5g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: 1 g/L Titrisol calibration solutions: 0.125-0.250-0.626 mg CuO / 100 mL	F AAS

Element Fe_2O_3

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: sample 1-3: 0.25 g → 50 mL M: sample 4-6: 0.1 g → 100 mL Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Fe calibration solutions: 0-5 mg Fe / L	F AAS
	M: 0.1g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Fe calibration solutions: 0-50 µg Fe / L	ET AAS
	M: 0.4-0.5 g; Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Fe calibration solution: 0-1 mg Fe / L	MAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Fe 0-200-400 ppm, weight (0-0.02-0.04 %) Fe in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	F AAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Fe Dilution to 50 mg/L, 0-100-200 ppm weight (0-0.01-0.02 %) Fe in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Fe from $Fe(NO_3)_3$ in 2-3% HNO_3 It has certificate of analysis; traceable to SRM from NIST external calibration, standard addition method The analytical findings were checked with standard glass No. 5 (Soc. of glass Technol.) and were found 293 mg/kg, certified value is 300 mg/kg.	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	0.2 g / 100 mL HF-$HClO_4$ digestion of matrix reference material DGGI standard glass, **No traceability**	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HCl and put in a 50 mL flask.	1 g/L Fe standard solution from Merck control is made with another standard from Fisher calibration solutions: 0-1-2-5-mg/L Fe, addition method for one measurement	F AAS
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Fe from Fe-metal in 2% HNO_3 CPI P/N 4400-1000261 calibration solution: 0.40-0.50-1.80-2.00 mg/L Fe in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Fe from Fe-metal in 2% HNO_3 CPI P/N 4400-1000261 calibration solution: 0.40-0.50-1.80-2.00 mg/L Fe in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 2g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination with o-phenanthroline	Alfa product Fe stock solution 1000 µg/L Fe standard solution I: 1 mL = 7.15 µg Fe_2O_3 Aliquot standard solution: 0-10-20-30-mL	MAS
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL	Alfa product Fe stock solution 1000 µg/L calibration solution: 1-2-3-5 mg/L, MM: Lanthanum	F AAS
10	M: 2g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL	Alfa product Fe stock solution 1000 µg/L calibration solutions: 1-10 mg/L matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Fe → 11.4376 mg / 250 mL Fe_2O_3 calibration solutions: 0-0.572-1.144-2.859-5.719	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solutions: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck; 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: Decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab; 1000 mg/L Baker calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL	21442 mg/L Fe in 10% HNO_3 / 2% HCl, self made from Alfa Johnson Matthey m3N Fe calibration solutions: 0.4-0.8-1.2-1.6 mg/L Fe addition calibration technique using a glass digestion solution	F AAS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solutions: 1.0 mg/L Fe	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1001 ± 2 mg/L Fe Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L)with and without matrix matching	ICP OES
21	M: 0.5 g; open digestion in Pt-vessel with HF-$HClO_4$; Residue dissolved in 5% HCl	1000 mg/L Fe solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 0.625 g: decomposition with HF-$H2SO_4$, then fusion with $KHSO_4$ dilution to 100 mL complex: Fe-II-o-phenanthroline	standard solution: **no information** calibration solutions: 0-0.1-0.2-0.5 mg Fe_2O_3 / 100 mL	MAS

Element MnO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-3) M: 0.1 g → 100 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g, Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Mn calibration solutions: 0-2.5 mg Mn / L	F AAS
	M: 0.1 g, Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Mn calibration solutions: 0-20 µg Mn / L	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Mn 2) Dilution to 50 mg/L, 0-100-200 ppm weight (0-0.01-0.02 %) Mn in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	F AAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL and 2 mL HNO_3 spike with isotope 55	Spex Certiprep 1 g/L Mn 2) Dilution to 10 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Mn in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Mn from Mn in 5% HNO_3 It has certificate of analysis; traceable to SRM from NIST external calibration, standard addition method The analytical findings were checked with glass reference material NBS 610 and were found 435 mg/kg (certified value is 485 mg/kg)	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	1 g/L MnO from $MnSO_4$ x H_2O calibration solution: 5 mg/L (Cr_2O_3, MnO, P_2O_5, SrO, ZrO_2)	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HCl and put in a 50 mL flask.	1 g/L Mn standard solution from Merck control is made with another standard from Fisher calibration solutions: 0-0.5-1-2 mg/L Mn addition method for one measurement	F AAS
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Mn from Mn metal in 2% HNO_3 calibration solution 0-0.10-0.20-0.60-0.70 mg/L Mn in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Mn from Mn metal in 2% HNO_3 calibration solution 0-0.10-0.20-0.60-0.70 mg/L Mn in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 2g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination as permanganate	Alfa product Mn stock solution 1000 mg/L; Mn standard solution I: 1 mL = 64.6 µg MnO Mn standard solution II: 1 mL = 6.46 µg MnO; Aliquot standard solution 0-1-2-3-5-mL	MAS
10	M: 2g;Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL (sample 1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 4-6)	Alfa product Mn stock solution 1000 mg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	ICP OES
	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 1-3) Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 4-6)	Alfa product Mn stock solution 1000 mg/L calibration solutions: 0.5-1-1.5-2 mg/L MM: Lanthanum, matrix matching	F AAS
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Mn → 10.3296 mg / 250 mL MnO calibration solutions: 0-0.516-1.033-2.582-5.165	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solution: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	MnO_2 99.99% from Johnson Matthey calibration samples: 106-117-126-135 mg/kg	XRF (after digestion by fusion)
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL.	10252 mg/L Mn m4N Mn in 12% HCl, self made from Alfa Johnson Matthey calibration solutions: 0.1-0.2-0.3-0.4 mg/L Mn addition calibration technique using a glass digestion solution	F AAS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solutions: 1.0 mg/L Mn	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1001 ± 2 mg/L Mn Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L)with and without matrix matching	ICP OES
21	M: 0.5 g; open digestion in Pt vessel with HF-$HClO_4$; Residue dissolved in 5% HCl	1000 mg/L Mn solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 5g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: 1 g/L Titrisol calibration solutions: 0.129-0.258-0.646 mg / 100 mL	F AAS

Element MoO_3

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 /5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Mo Dilution to 50 mg/L, 0-100-200 ppm weight (0-0.01-0.02 %) Mo in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL) +H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL + 2 mL HNO_3 spike with isotope 55	Spex Certiprep 1 g/L Mo Dilution to 10 ppm; Isotope 98 0-100-200 ppm weight (0-0.01-0.02 %) Ba in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Mo from $(NH_4)_2MoO_4$*H_2O traces NH_4OH It has certificate of analysis; traceable to SRM from NIST standard addition method	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 – 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	1 g/L MoO_3 from $(NH_4)_6Mo_7O_{24}$ calibration solution: 1 mg/L (CdO, CoO, CuO, CeO_2, MoO_3, V_2O_5)	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Mo from Mo-metal in 2% HNO_3 + 0.1% HF CPI PIN 4400-1000343 calibration solution: 0-0.50-1.00-1.50 mg/L Mo in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Mo from Mo-metal in 2% HNO_3 + 0.1% HF CPI PIN 4400-1000343 calibration solution: 0-0.50-1.00-1.50 mg/L Mo in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL	Alfa product Mo stock solution 1000 mg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Mo → 30.006 mg / 250 mL MoO_3 calibration solutions: 0-1.503-3.006-7.515-15.03	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L Mo Romil 1000 mg/L Mo CPI calibration solutions: 1.00-3.00-5.00 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
21	M: 1 g; open digestion in Pt vessel with HF-$HClO_4$; Residue dissolved in 5% HNO_3	1000 mg/L Mo solution supplied by BDH and Fisher calibration solutions: 1.0-2.0-5.0 mg/L Mo containing 0.1% w/v specpure sodium sulfate (anhydrous)	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF-HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4 mg/L plus matrix matching	ICP OES

Element NiO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-5) M: 0.1 g → 100 mL (6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g, Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Ni calibration solutions: 0-1 mg Ni / L	F AAS
	M: 0.1 g, Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Ni calibration solutions: 0-100 µg Ni / L	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certipur 1 g/L Ni preparation of a 50 ppm Ni standard solution; 0-100-200 ppm weight (0-0.01-0.02 %) Ni in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	F AAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certipur 1 g/L Ni dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Ni in glass matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Ni from Ni in 5% HNO_3 It has certificate of analysis; traceable to SRM from NIST standard addition method The analytical findings were checked with glass reference material NBS 610 and were found 444 mg/kg (certified 458.7 mg/kg)	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	1 g/L NiO from Ni-metal calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HCl and put in a 50 mL flask.	1 g/L Ni standard solution from Merck control is made with another standard from Fisher calibration solutions: 0-1-2-5-mg/L Ni addition method for one measurement	F AAS
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Ni from Ni-metal in 2% HNO_3 CPI P/N 4400-1000361 calibration solution: 0-0.10-0.20-0.30-0.40 mg/L Ni in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Ni from Ni-metal in 2% HNO_3 CPI P/N 4400-1000361 calibration solution: 0-0.10-0.20-0.30-0.40 mg/L Ni in 6% HNO_3	ICP OES
10	M: 2g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination with Furildioxim	Alfa product Ni stock solution 1000 mg/L; Ni standard solution I: 1 mL = 12.7 µg NiO Ni standard solution II: 1 mL = 1.27 µg NiO; Aliquot standard solutions: 0-1-3-5-mL	MAS
10	M: 2g; Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL (sample 1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 4-6)	Alfa product Ni stock solution 1000 mg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Ni → 10.1808 mg / 250 mL NiO calibration solutions: 0-0.509-1.018-2.545-5.090	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL; used ^{58}Ni	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck; 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab; 1000 mg/L Baker calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL.	10015mg/L Ni in 20% HNO_3, self made from 4N Ni calibration solutions: 5-10-15-20 µg/L Ni addition calibration technique using a glass digestion solution	ET AAS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solutions: 1.0 mg/L Ni	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1000 ± 2 mg/L Ni Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L)with and without matrix matching	ICP OES
21	M: 1.46-1.56 g; open digestion in Pt vessel with HF-HNO_3; Residue dissolved in 5% HCl	1000 mg/L Ni solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
22	M: 2 g; sample digestion with 2 times HF-HNO_3 (15-5); Residue dissolved in 10 mL HCl and diluted to 100 mL	100 mg/L Ni solution ready made from BDH and Reagecon calibration solutions: 0.5-1.0-1.5 mg/L	F AAS
23	M: 0.50-0.59 g; Decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 5g; Decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: 1 g/L Titrisol calibration solutions: 0.127-0.254-0.636 mg / 100 mL	F AAS

Element PbO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-3) M: 0.1 g → 100 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 5 100 mg/L Lot # 206616 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g, Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer 1000 mg/L Pb calibration solutions: 0-2.5 mg/L Pb	F AAS
	M: 0.1 g Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer 1000 mg/L Pb calibration solutions: 0-50 µg/L Pb	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Pb; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Pb in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5) dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask. 2) Aliquot of 1 mL in 50 mL + 2 mL HNO_3 spike with isotope 208	Spex Certiprep 1 g/L Pb; Dilution to 10 ppm, 0-100-200 ppm weight (0-0.01-0.02 %) Pb in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Pb from Pb in 5% HNO_3 It has certificate of analysis; traceable to SRM from NIST external calibration, standard addition method The analytical findings were checked with glass reference material CRM 664 and were found 54.4 mg/kg (certified 53.1 mg/kg).	ICP OES
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask.	Merck 1 g/L Pb calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HNO_3 and put in a 100 mL flask.	1 g/L Pb standard solution from Merck control is made with another standard from Fisher calibration solutions: 0-1-2-5-mg/L Pb; addition method for one measurement	F AAS
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Pb from Pb-metal in 2% HNO_3 CPI P/N 4400-1000281 calibration solution: 0.40-0.50-1.00-1.20 mg/L Pb in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Pb from Pb-metal in 2% HNO_3 CPI P/N 4400-1000281 calibration solution: 0.40-0.50-1.00-1.20 mg/L Pb in 6% HNO_3	ICP OES
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL	Alfa product Pb stock solution 1000 mg/L calibration solutions: 3-5-10-20 mg/L, matrix matching	F AAS
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Pb → 21.544 mg / 250 mL PbO calibration solutions: 0-1.077-2.154-5.386-10.772	ICP OES
12	M: 0.5 g; Decomposition in a Pt-dish with 2 mL $HClO_4$ and 5 mL HF and evaporate to dryness. Add 5 mL HF and evaporate to dryness. Dissolve with 2 mL HCl (1:1) and 2 mL H_2O. → 100 mL	High purity standard 1000 mg/l calibration solutions: 1 mg/L in 1% HCl and a blank in 1% HCl	F AAS
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck; 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab; 1000 mg/L Baker calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
16	M: 2.5 g of Pb^{207}-spike solution (evaporated to dryness) and 0.5 g of sample were decomposed with HF-HNO_3 (10mL-2mL) using a microwave oven for 33 min. at 220°C. The solution was transferred into a Pt dish and evaporated to dryness. The residue was dissolved twice with H_2O-HNO_3 (10mL-1mL) and evaporated to dryness. Then the residue was taken up with 10 mL water and 1 mL HNO_3 in order to get a nearly clear solution. 0.5 mL of $HClO_4$ were added to the solution and then the solution was evaporated until white fumes were observed. The residue was dissolved twice with 2 mL conc. HCl and 5 mL water and evaporated to dryness. Then the residue was taken up with 10 mL 0.2 mol/L HCl and the solution was transferred into a quartz-beaker. The analyte/matrix separation was carried out by a 3-steps-electrodeposition procedure.	Pb-207 spike solution (9.371 µg/g), back spike solution by using lead metal of highest purity, all solutions were prepared by weighing. stock solution was used, spiking was carried out before starting sample decomposition, the spiked analyte was separated from the matrix using an electrodeposition procedure only isotope ratios were measured (spiked samples, unspiked sample, 4 blanks, back-spike, spike) determination of the atomic weight of the sample-Pb using NBS 981	ID-TIMS
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	PbO, 99,99% from Johnson Matthey calibration samples: 181-195-210-219 mg/kg	XRF (after digestion by fusion)
18	M: 0,5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL	500 mg/L Pb in 2,5% HNO_3, self made from Alfa Johnson Matthey m5N5 Pb calibration solutions: 20-40-60-80 µg/L Pb addition calibration technique using a glass digestion solution	ET AAS
19	M: 0,1 g; pressure digestion in Parr bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1,0 mg/L Pb	ICP OES
20	M: 0,5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1001 ± 2 mg/L Pb Merck pure mono element calibration solutions: 0,1-0,5-1,00-3,00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
21	M: 0.50-0.58 g; open digestion in Pt-vessel with HF-HNO_3-$HClO_4$ (10-1-5); Method as described and recommended ICG/TC2.	1000 mg/L Pb solution supplied by BDH and Fisher calibration solutions: 0.5-1.0-2.0-5.0 mg/L MM: 2000 mg/L Na^+ and La^{3+}	F AAS
22	M: 2 g; sample digestion with 2 times HF-HNO_3 (15-5); Residue dissolved in 5 mL conc. HNO_3 and diluted to 100 mL	100 mg/L Pb solution ready made from BDH and Merck calibration solutions: 1-3-5 mg/L	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 5g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: 1 g/L Titrisol calibration solutions: 0.21-0.538-1.077 mg/100 mL	F AAS

Element Sb_2O_3

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-3) M: 0.1 g → 100 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 4 100 mg/L Lot # 123504 calibration solutions: 0.50-1.00-mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 0.1 – 0.2 g Decomposition with HF-$HClO_4$-HNO_3-$KMnO_4$ mixture in Pt-dishes on hot plate, then dissolved with hydrochloric + tartaric acid; pre-reduced with KI, ascorbic and hydrochloric acid; final reduction with $NaBH_4$	Merck, Perkin-Elmer 1000 mg/L Sb calibration solutions: 0-30 µg/L	FI-HG AAS
3	M: 0.1 g; Decomposition with HF-$HClO_4$-HNO_3 (5/3/3) + 2 mL $KMnO_4$ (0,1N); evaporated to 2 mL + 2mL $HClO_4$ fume again; + 5 mL HCl+H_2O → 50 mL vol. flask; sample aliquot (4 mL) + 10 mL HCl + 5 mL KI (10%); heating 10 min in boiling water.	Spex Certiprep 1 g/L Sb Dilution 1/1000 – 1 ppm 0-125-250 ppm weight (0-0.0125-0.0250 %) Sb in glass	HG AAS
	M: 0.5 g; Decomposition with HF-$HClO_4$-HNO_3; Residue dissolved in 5 mL HCl+H_2O → 100 mL vol. flask.	Spex Certiprep 1 g/L Sb Dilution 5/100 – 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Sb in glass	ICP OES
4	M: 0.1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3 and KMnO4 solution. It is evaporated to a small volume. The residue is dissolved in HCl and diluted with water in a 100 mL vol. flask. Pre-reduction with 10% KI and 1% ascorbic acid in 3% HCl.	1000 mg/L Sb from Sb in 8% HCl certified by the supplier; traceable to SRM from NIST calibration solutions: 50-100-200 ng Sb The analytical findings were checked with glass reference material CRM 664 (report EUR 18852 EN) and was found 26.1 mg/kg (certified value is 24.3 mg/kg)	FI-HG AAS
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask.	Merck 1 g/L Sb calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
7a	M: 0.25 g; pressure digestion acid with 10 mL HF, 3 mL HNO_3 at 140°C for 2 h; neutralisation with 5 g H_3BO_3 → with H_2O to 100 mL	1000 mg/L Sb from Sb – metal in 4% HNO_3-0.1% HF CPI P/N 4400-100023 calibration solution: 0-0.10-0.20-0.40-0.50 mg/L Sb with 10 mL HF-3 mL HNO_3 5 g H_3BO_3 pro 100 mL as matrix matching	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 4-6)	Alfa product Sb stock solution 1000 mg/L calibration solutions: 5-10-15-20 mg/L, matrix matching MM: CsCl for Varian system MM: CsCl/Butanol for Perkin-Elmer system	F AAS
	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 4-6)	Alfa product Sb stock solution 1000 µg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF ($KMnO_4$)-$HClO_4$ → 100 mL	Merck 1 g/L Sb → 11.16 mg / 250 mL Sb_2O_3 calibration solutions: 0-0.599-1.197-2.394-4.788	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL; used ^{121}Sb	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L; ^{115}In as an internal standard	ICP-MS
13	M: 0.5 g; Decomposition with HF-$HClO_4$-HNO_3-$KMnO_4$ Temp. < 140°C; Residue taken up with 10% HCl → 100 mL Reduction with KI in 10% HCl at 60°C	1000 mg/L Sb CPI checked with 1000 mg/L Sb Aldrich calibration solutions: 0.003-0.005-0.010 mg/L (Reduction with 10% KI)	HG AAS
14	M: 1 g; sample 1 – 5 Decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6 Decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L Sb ChemLab 1000 mg/L Sb Baker calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
15	M: 0.140 – 0.214 g weight in quartz ampoules; no sample digestion crushing of glass lump with a vice	2.0117 mg/g Sb self made from elemental Sb	INAA
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-HNO_3-$HClO_4$-H_2SO_4 (10/10/10/2) to a few mL at 160°C; after cooling addition of 5 mL $HClO_4$ and fuming off again to 2-3 mL; residue dissolved in 10 mL H_2O + 2mL HCl after heating transferred to 100 mL quartz flask, 20 mL HCl added and diluted with H_2O to 100 mL.	10194 mg/L Sb in 5 M HCl, self made from Alfa Johnson Matthey m6N Sb calibration solutions: 10-20-30-40 µg/L Sb addition calibration technique using a glass digestion solution	ET AAS
19	M: 0.1 g; pressure digestion in Parr bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Sb	ICP OES
21	M: 1.29-1.46 g; open digestion in PTFE dish with HF-HNO_3-$KMnO_4$ (13-10-2 (0.1 N)) Method as recommended by TC 2	1000 mg/L Sb solution supplied by BDH and Fisher calibration solutions: 1.0-2.0-5.0 mg/L	F AAS
24	M: 5g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: 1 g/L Titrisol calibration solutions: 0.5-1.0-2.0 mg / 100 mL	F AAS

Element Se

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	M: 0.1 – 0.2 g Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate; pre-reduced with HCl (7M); final reduction with $NaBH_4$	Merck, Perkin-Elmer 1000 mg/L Se calibration solutions: 0-40 µg/L	FI-HG AAS
3	M: 0.1 g,; Decomposition with HF-$HClO_4$-HNO_3 (5/3/2), fume $HClO_4$ on a sand bath low temperature + 2mL $HClO_4$ fume again; cool + 5 mL HCl+H_2O → 50 mL vol. flask; sample aliquot (10 mL) in 50 mL + 28 mL HCl (37%) → heating 10 min in boiling water.	Spex Certiprep 1 g/L Se Dilution 1/250 – 4 ppm 0-20-40 ppm weight (0-0.002-0.004 %) Se in glass	HG AAS
4	M: 0.5 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to a small volume and dissolved in HCl. → 100 mL flask. Pre-reduction in 7 mol/L HCl, hydride generation by $NaBH_4$/NaOH.	1000 mg/L Se from Se in 5% HNO_3 It has certificate of analysis; traceable to SRM from NIST calibration solutions: 5-10-15 µg/L Se The analytical findings were checked with glass reference material CRM 664 (Report EUR 18852 EN) and were found 8.6 mg/kg (certified 8.6 mg/kg)	FI-HG AAS
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask	Merck 1 g/L Se calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
8	M: 1 g; digestion with HF-HNO_3-$HClO_4$	1009 mg/LSe standard solution for AAS (Kanto Chemical Co. Inc.) calibration solution: 2 mg(/L Se in HCl (same concentration of sub-sample)	ICP OES
9	no sample preparation		K_0-INAA
11	M: 0.5 g; Digestion with HF ($KMnO_4$)-$HClO_4$ → 100 mL	Merck 1 g/L Se → 8mg / 250 mL Se calibration solutions: 0-0.50-1.0-2.0-4.0	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL used ^{82}Se	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 0.5 g; Decomposition with HF-HNO_3-$HClO_4$; Residue taken up with 7 M HCl → 100 mL	1000 mg/L Se CPI 1000 mg/L Se Carlo Erba calibration solutions: 0.005-0.010-0.015 mg/L (HCl 7 M)	HG AAS
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab 1000 mg/L Baker calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
15	M: 0.140 – 0.214 g weight in quartz ampoules; no sample digestion crushing of glass lump with a vice	0.9847 mg/g Se self made from elemental Se	INAA
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-HNO_3-$HClO_4$-H_2SO_4 (10/10/10/2) to a few mLs at 160°C; after cooling addition of 5 mL $HClO_4$ and fuming off again to 2-3 mL; residue dissolved in 10 mL H_2O + 2mL HCl after heating transferred to 100 mL quartz flask, 20 mL HCl added and diluted with H_2O to 100 mL	1001 mg/L Se in 5 M HCl, self made from 5N Se calibration solutions: 0.5-1.0-1.5-2.0 µg/L Se addition calibration technique using a glass digestion solution	FI-HG AAS
19	M: 0.1 g; pressure digestion in Parr bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Se	ICP OES
21	M: 0.10-0.14 g; open digestion in PTFE dish with HF-HNO_3-$HClO_4$ Method as recommended by TC 2	1000 mg/L Se solution supplied by BDH and Fisher calibration solutions: 25-50 µg/L Se	ET AAS

Element SnO_2

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: sample 1-5: 0.25 g → 50 mL and sample 6: 0.1 g → 100 mL Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, ICP Analytical Mixture 4 100 mg/L Lot # 123504 calibration solutions: 0.50-1.00-2.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 0.1 g Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Sn calibration solutions: 0-100 µg Sn / L	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3-$HClO_4$, Residue dissolved in 5 mL HCl +H_2O → 100 mL vol. flask.	Spex Certiprep 1 g/L Sn Dilution 5/100 – 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Sn in glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3-$HClO_4$, Residue dissolved in 5 mL HCl+H_2O → 100 mL vol. flask. Aliquot of 2 mL in 50 mL. spike with isotope 117	Spex Certiprep 1 g/L Sn Dilution 5/100 – 10 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Sn in glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Sn from Sn in 8% HCl It has certificate of analysis; traceable to SRM from NIST calibration solutions: standard addition method; external calibration	ICP OES
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask	Merck 1 g/L Sn Calibration solution: 4 mg/L (As, CdO, CoO, Cr2O3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Sn from Sn-metal in 40% HCl CPI P/N 4400-1000612 calibration solution: 0.10-0.20-0.30-0.40 mg/L Sn in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Sn from Sn-metal in 40% HCl CPI P/N 4400-1000612 calibration solution: 0.10-0.20-0.30-0.40 mg/L Sn in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 4-6)	Alfa product Sn stock solution 1000 mg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	ICP OES
12	M: 0.1 g; Digestion with 1 mL HF and 1 mL HNO_3 in a close Teflon vessel, Heat at 100°C for 12 hours. Add 50 µg/L Ga, In and Tb as internal standard → Dilute to 100 mL; used ^{118}Sn	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{115}In as an internal standard	ICP-MS
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab 1000 mg/L Baker calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O to 100 mL	8195 mg/L Sn in 5 M HCl, self made from Alfa Johnson Matthey 6N Sn calibration solutions: 10-20-30-40 µg/L Sn addition calibration technique using a glass digestion solution	ET AAS
21	M: 2.0-2.5 g; open digestion in Pt-vessel with HF-$HClO_4$; Residue dissolved in 5% HCl	1000 mg/L Sn solution supplied by BDH and Fisher calibration solutions: 2-5-10 mg/L Sn containing 2000 mg/L Na^+	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF-HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES

Element SO_3

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
2	M: 0.8-1 g Decomposition with HF-$HClO_4$ in Pt-dishes on hot plate, addition of $BaCl_2$	no stock and standard solution precipitate as $BaSO_4$	Gravimetry
3	M: 0.1 g; Decomposition with H_2O-$NaClO_3$ (100 mg)-HCl (5 mL)-HF (5 mL); evaporate to dryness; Residue dissolved into reducing mixture (H_2O-HCl-HI-H_3PO_2); H_2S formed fixed in KOH solution and titrated by 2 Hydroxymercuri benzoic acid in the presence of dithizone	2 Hydroxymercuri benzoic acid solution Standardize against standard S solution (Spex) 1 g/L	Titrimetry
4	The glass pieces were melted to form glass bead	SO_3 calibration was carried out by using internationally accepted glass reference materials, **No traceability**	XRF
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask	0.2 g / 100 mL HF-$HClO_4$ digestion of matrix reference material DGGI glass standard, **No traceability**	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L S from $(NH_4)_2SO_4$ in H_2O CPI P/N 4400-1000544 calibration solution: 0.50-1.00-4.00-5.00 mg/L S in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L S from $(NH_4)_2SO_4$ in H_2O CPI P/N 4400-1000544 calibration solution: 0.50-1.00-4.00-5.00 mg/L S in 6% HNO_3	ICP OES
8	M: 1 g; Digestion with HF-HNO_3-$HClO_4$	1000 mg/L Na_2SO_4 anhydrous (solid reagent) (Futaba Pure Chemicals Ltd.) calibration solutions: 2 mg/L in HCl (same concentration of sub-samples)	ICP OES
10	no dissolution	according to ICG/TC 2 protocol ICG/TC-2/02-1274, Jan.2002	IR-comb.
11	M: 0.15 g; no dissolution	Merck calibration solution: 2700 mg/l	IR-comb.
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L SO_4 BDH 1000 mg/L SO_4 Merck calibration solutions: addition method 2.00-5.00-10.00 mg/L, Y as internal standard	ICP OES
	M: 0.1 g	K_2SO_4 Aldrich parallel running of std. LECO and std. ELTRA	Comb.
14	M: 1 g; sample 1 – 5 open Decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6 Decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L S ChemLab calibration solutions: addition method, 3 solutions in the expected range of concentration.	ICP OES
21	M: 0.2 g; Combustion of sample; Inductive heating for 60 seconds under an oxygen atmosphere	BDH and Riedel-de Haen potassium sulphate (solid) calibration solutions: 0.25% SO_3 solution	Comb.-IR

Element SrO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-3) M: 0.1 g → 100 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	VHG Labs, Stock Multielement Standard 15 100 mg/L Lot #: SM1502/1 calibration solutions: 0.50-1.00-mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g, Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Sr calibration solutions: 0-2.5mg Sr / L	F AAS
	M: 0.1 g Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Sr calibration solutions: 0-25 µg Sr / L	ET AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL) +H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Sr; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Sr in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	F AAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL) +H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Sr; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Sr in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL) +H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL + 2 mL HNO_3 Spike with isotope 87	Spex Certiprep 1 g/L Sr; Dilution to 10 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Sr in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Sr from $Sr(NO_3)_2$ in 5% HNO_3 It has certificate of analysis; traceable to SRM from NIST calibration solutions: standard addition method, external calibration The analytical findings were checked with glass reference material NBS 610 and were found 509 mg/kg (certified value is 515.5 mg/kg)	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	1 g/L SrO from $Sr(NO_3)_2$ calibration solution: 5 mg/L (Cr_2O_3, MnO, P_2O_5, SrO, ZrO_2)	ICP OES
6	M: 2.5 g; Decomposition with HF-HNO_3-$HClO_4$ (15/1/10) in a Pt-crucible on a sand bath until evaporation then dissolution in a solution 5% HCl and put in a 50 mL flask.	dissolution of pure solid $SrCO_3$ (dried) calibration solutions: 0-1-2-5-mg/L SrO addition method for one measurement; addition of $LaCl_3$ in each solution	F AAS
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Sr from $SrCO_3$ in 2% HNO_3 CPI P/N 4400-1000531 calibration solution: 0-0.10-0.20-0.80-1.00 mg/L Sr in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Sr from $SrCO_3$ in 2% HNO_3 CPI P/N 4400-1000531 calibration solution: 0-0.10-0.20-0.80-1.00 mg/L Sr in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 4-6) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 1-6)	Alfa product Sr stock solution 1000 µg/L calibration solutions: 1-2-3-4 mg/L, matrix matching MM: CsCl/La for Varian system (N_2O/C_2H_2) MM: CsCl/La for Perkin-Elmer system (Air/C_2H_2) Alfa product Sr stock solution 1000 µg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	F AAS ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Sr → 9,4608mg / 250 mL SrO calibration solutions: 0-0.473-0.946-2.367-4.730	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solution: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck; 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	$SrCO_3$, 99.99% from Johnson Matthey calibration samples: 133-144-157-165 mg/kg	XRF (after digestion by fusion)
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Sr	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1000 ± 2 mg/L Sr Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
21	M: 0.7 g; open digestion in PTFE dish with HF-HNO_3; Residue dissolved in 5% HNO_3	1000 mg/L Sr solution supplied by BDH and Fisher calibration solutions: 0.5-1.0-2.0 mg/L MM: 2000 mg/L of Na^+ and La^{3+}	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 2g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: 1 g/L Titrisol calibration solutions: 0.1-0.2-0.5 mg/100 mL	F AAS

Element TiO_2

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-5); M: 0.1 g → 100 mL (6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	VHG Labs, Stock Multielement Standard 70A 100 mg/L Lot # SM70A11/01 calibration solutions: 0.50-1.00-mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 0.4 – 0.5 g Decomposition with HF-$HClO_4$ in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Ti calibration solutions: 0-0.1-0.2-0.3-0.4-0.5-mg Ti / L	MAS
3	M: 0.5 g; Decomposition with H_2SO_4-HF; 2. attack with H_2SO_4-H_3BO_3. Residue dissolved in H_2O-H_2SO_4. MAS with chromotropic acid (red complex with Ti4+ at 470 nm) in 100 mL vol. flask.	stock solution 1 g/l TiO_2 (prepared by attack of 500 mg TiO_2 Merck – fusion with $KHSO_4$); calibration solutions: 0-0.25-0.50 mg in 100 mL	MAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Ti; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Ti in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Ti from Ti in 5% HNO_3 + traces HF It has certificate of analysis; traceable to SRM from NIST standard addition method The analytical findings were checked with glass reference material Std. glass No. 5 (Soc. of glass Techn.) and were found 178 mg/kg (certified value is 204 mg/kg)	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	0.2 g / 100 mL HF-$HClO_4$ digestion of matrix reference material DGGI glass standard, **No traceability**	ICP OES
6	M: 1 g; Decomposition with HF-H_2SO_4 (15/1) in a Pt-crucible on a sand bath until evaporation then fusion of the residue with 4 g of $KHSO_4$ and then dissolution in a solution 5% HCl and put in a 100 mL flask. spectrocolorimetry with chromotropic acid (red-orange complex)	1 g/L Ti standard solution from Merck control is made with another standard solution from Fisher calibration solutions: 0-0.5-1-2 mg/L Ti	MAS
7b	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Ti from Ti-metal in 2% HNO_3-0.1%HF CPI P/N 4400-1000623 calibration solution: 0-0.10-0.20-0.60-0.70 mg/L Ti in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Ti from Ti-metal in 2% HNO_3-0.1%HF CPI P/N 4400-1000623 calibration solution: 0-0.10-0.20-0.60-0.70 mg/L Ti in 6% HNO_3	ICP OES
10	M: 2g;Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination with Tiron M: 2g;Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL (1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (4-6)	Alfa product Ti stock solution 1000 mg/L Ti standard solution I: 1 mL = 8.34 µg TiO_2 Aliquot standard solutions: 0-1-3-5-mL Alfa product Ti stock solution 1000 mg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	MAS ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Ti → 33.362mg / 250 mL TiO_2 calibration solutions: 0-1.668-3.336-8.341-16.681	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solution: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement CPI; 1000 mg/L Ti BDH calibration solutions: 0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method, 3 solutions in the expected range of concentration	ICP OES
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	TiO_2, 99.99% from Johnson Matthey calibration samples: 139-154-169-178 mg/kg	XRF (after digestion by fusion)
19	M: 0.1 g; pressure digestion in Parr bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Ti	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1006 ± 5 mg/L Ti Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
21	M: 0.5 g; open digestion in Pt vessel with HF-H_2SO_4; Residue dissolved in 10 mL HCl	1000 mg/L Ti solution supplied by BDH and Fisher calibration solutions: 20-40-60-80-100-150 µg	MAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 0.625 g; decomposition with HF-H_2SO_4, then fusion with $KHSO_4$ → 100 mL Complex: Ti-chromotropic acid in chloroacetic buffer (pH 2.9)	1 g/L Titrisol standard solution calibration solutions: 0-0.1-0.2-mg / 100 mL	MAS

Element V_2O_5

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.1 g → 100 mL Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	VHG Labs, Stock Multielement Standard 70A 99.4 mg/L Lot # SM70A11/01 calibration solutions: 0.50-1.00 mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L V; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) V in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL + 2 mL HNO_3 spike wit isotope 51	Spex Certiprep 1 g/L V; Dilution to 10 ppm 0-100-200-400 ppm weight (0-0.01-0.02-0.04 %) V in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L V from V_2O_5 in 5% HNO_3 It has certificate of analysis; traceable to SRM from NIST standard addition method; external calibration	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask.	1 g/L V_2O_5 from V_2O_5 Calibration solution: 1 mg/L (CdO, CoO, CuO, CeO_2, MoO_3, V_2O_5)	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O- and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L V from NH_4VO_3 in 2% HNO_3 CPI PIN 4400-1000651 calibration solution: 0.40-0.50-1.00-1.20 mg/L V in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O- and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L V from NH_4VO_3 in 2% HNO_3 CPI PIN 4400-1000651 calibration solution: 0.40-0.50-1.00-1.20 mg/L V in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL	Alfa product V stock solution 1000 mg/L calibration solutions: 0.5-1-5-10 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L V → 14.2816 mg / 250 mL V_2O_5 calibration solutions: 0-0.714-1.428-3.570-7.141	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solutions: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement CPI; 1000 mg/L V RDH calibration solutions: 1.00-2.00-3.00 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method, 3 solutions in the expected range of concentration	ICP OES
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	V_2O_5, 99.99% from Johnson Matthey calibration samples: 320-335-349-358 mg/kg	XRF (after digestion by fusion)
19	M: 0.1 g; pressure digestion in Parr bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solutions: 1.0 mg/L V	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1000 ± 2 mg/L V Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
21	M: 1.46-1.53 g; open digestion in Pt vessel with HF-HNO_3; Residue dissolved in 5% HCl	1000 mg/L V solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF-HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES

Element ZnO

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.1 g → 100 mL Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	VHG Labs, Stock Multielemental Standard 70A 103.4 mg/L Lot # SM70A11/01 calibration solutions: 0.50-1.00-mg/L in deionised water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 1 g;Decomposition with HF-$HClO_4$-HNO_3 in Pt-dishes on hot plate	Merck, Perkin-Elmer; 1000 mg/L Zn calibration solutions: 0-2.5 mg Zn / L	F AAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Zn; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Zn in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	FAAS
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Zn; Dilution to 50 ppm 0-100-200 ppm weight (0-0.01-0.02 %) Zn in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	1000 mg/L Zn from Zn in 5% HNO_3 It has certificate of analysis; traceable to SRM from NIST external calibration, standard addition method The analytical findings were checked with glass reference material NBS 610 and were found 423 mg/kg (certified value is 433 mg/kg)	ICP OES
5	M: 1 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 50 mL vol. flask.	1 g/L ZnO from Zn-metal calibration solution: 4 mg/L (As, CdO, CoO, Cr_2O_3, NiO, Pb, Sb, Se, Sn, ZnO)	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Zn from Zn-metal in 2% HNO_3 CPI P/N 4400-1000681 calibration solution: 0.40-0.50-1.00-1.20 mg/L Zn in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L V from NH_4VO_3 in 2% HNO_3 CPI PIN 4400-1000651 calibration solution: 0.40-0.50-1.00-1.20 mg/L V in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 1-3) M: 1 g; Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 4-6)	Alfa product Zn stock solution 1000 mg/L calibration solutions: 0.25-0.5-0.75-1 mg/L, matrix matching MM: Lanthanum – Varian, Perkin-Elmer system (Air/C_2H_2)	F AAS
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Zn → 9.9576 mg / 250 mL ZnO calibration solutions: 0-0.498-0.996-2.489-4.979	ICP OES
12	M: 0.1 g; Digestion with 5 mL HF, 2 mL HNO_3 and 2 mL 18 mΩ H_2O in a close Teflon vessel, Heat at 100°C for 2 hours. Uncap and evaporate to dryness. Add 5 mL 20% HNO_3 and heat for 1 hour with vessel tightly capped. Cool and dilute to 100 mL with H_2O; used ^{66}Zn	Perkin-Elmer multi-element ICP-MS calibration standard at 10 mg/L calibration solution: Create a 50 µg/L concentration of above solutions in 1% HF and 1% HNO_3 with 50 µg/L ^{71}Ga as an internal standard	ICP-MS
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement Merck; 1000 mg/L multielement CPI calibration solutions: 0.10-0.50-1.0-2.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
15	M: 0.140 – 0.214 g; weight in quartz ampoules; no sample digestion crushing of glass lump with a vice	1.0025 mg/g Zn self made from elemental Zn	INAA
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	ZnO, 99.99% from Johnson Matthey calibration samples: 178-196-208-222 mg/kg	XRF (after digestion by fusion)
18	M: 0.5 g; open acid digestion in Pt dishes on a graphite heating block; fuming off with a mixture of HF-$HClO_4$ (10/2) to dryness at 130°C; residue dissolved in 10 mL H_2O + 2mL HNO_3 after heating transferred to 100 mL quartz flask, 5 mL HNO_3 added and diluted with H_2O.	10046 mg/L Zn in 12% v/v HCl, self made from Alfa Johnson Matthey 6N Zn calibration solutions: 0.05-0.10-0.15-0.20 mg/L Zn addition calibration technique using a glass digestion solution	F AAS
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Zn	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1000 ± 2 mg/L Zn Merck pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
21	M: 0.5 g; open digestion in Pt-vessel with HF-$HClO_4$; Residue dissolved in 5% HCl	1000 mg/L Zn solution supplied by BDH and Fisher calibration solutions: 0.25-0.5-1.0-2.0-5.0 mg/L	F AAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES
24	M: 5g; decomposition with HF-$HClO_4$-HNO_3, after diluted in HCl (5%) to 100 mL	standard solution: **no information** calibration solutions: 0.5-1.0-2.0 mg/100 mL	F AAS

Element ZrO_2

Lab code	Sample Preparation (M = mass of sub-samples)	Calibration	Final Determination
1	M: 0.25 g → 50 mL (1-3) M: 0.1 g → 100 mL (4-6) Sample were weighed into Pt-crucible; 3 mL HCl and 4 mL $HClO_4$ were added; digestion to dryness, redissolved in 10 mL 1:1 HNO_3, to volume with H_2O	High Purity Standards, Zirconium 5, 100 mg/L Lot # 229525 calibration solutions: 0.50-1.00-2.00 mg/L in deion. water, 1.00 mg/L Y as internal standard	ICP OES
2	M: 0.3 g; Fusion with Na_2CO_3 + H_3BO_3 mixture (ratio: 5+2) t = 30 min , T = 950°C	Merck, Perkin-Elmer; 1000 mg/L Zr calibration solutions: 0-0.4-0.8-1.2-1.6-2.0 mg/L Zr	MAS
3	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask.	Spex Certiprep 1 g/L Zr Dilution 5/100 – 50 ppm 0-250-500 ppm weight (0-0.0250-0.0500 %) Zr in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP OES
	M: 0.5 g; Decomposition with HF-HNO_3 (10/5), Residue dissolved in HNO_3 (5 mL)+H_2O → 50 mL vol. flask. Aliquot of 1 mL in 50 mL + 2 mL HNO_3 spike with isotope 90	Spex Certiprep 1 g/L Zr Dilution to 10 mg/L 0-100-200 ppm weight (0-0.01-0.02 %) Zr in glass; matrix matching (addition of Al, Ca, Mg, Na) so that 25 mL of this solution is equivalent to 500 mg glass	ICP-MS
4	M: 1 g; The glass sample is decomposed with a mixture of HF-$HClO_4$-HNO_3. It is evaporated to dryness. The residue is dissolved in HNO_3 and diluted with water in a 100 mL vol. flask.	995 ± 6 mg/L Zr from Zr in HNO_3 + traces F^- standard addition method The analytical findings were checked with glass reference material NBS 621 and were found 41.3 mg/kg (certified value is 51.8 mg/kg)	ICP OES
5	M: 0.2 g; 3 mL HNO_3, 10 mL HF and 2 mL $HClO_4$ in glassy carbon crucible, heating to 105 - 110 °C in order to evaporate HNO_3 and HF. After 2 h the temperature is increased to 140 °C in order to evaporate the remaining $HClO_4$. Dissolution in water containing 0.5 mL HCl conc. per 100 mL vol. flask	1 g/L ZrO2 from $ZrOCl_2$ x 8 H_2O Calibration solutions: 5 mg/L (Cr_2O_3, P_2O_5, SrO, MnO, ZrO_2)	ICP OES
7b	M: 0.25 g; Decomposition with HF-$HClO_4$ (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL $HClO_4$ and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Zr from Zirconyl Nitrate in 1% HNO_3 CPI P/N 4400-1000691 calibration solution: 0.50-1.00-4.00-5.00 mg/L Zr in 6% HNO_3	ICP OES
7c	M: 0.25 g; Decomposition with HF-HNO_3 (10/2) Evaporate to a few millilitres on a sand bath. Add two times 5 mL H_2O-and 0.5 mL HNO_3 and evaporate to a few millilitres. Add 20 mL H_2O and 1 mL HNO_3 and cover. After digestion for 20 min transfer the solution into a 50 mL vol. flask. Clean the dish with 10 mL HNO_3 (1+4), then bring to volume with water.	1000 mg/L Zr from Zirconyl Nitrate in 1% HNO_3 CPI P/N 4400-1000691 calibration solution: 0.50-1.00-4.00-5.00 mg/L Zr in 6% HNO_3	ICP OES
9	no sample preparation		K_0-INAA
10	M: 2g;Dissolution with HF-H_2SO_4-$K_2S_2O_7$-H_2SO_4 → 100 mL Photometric determination with morin	Alfa product Zr stock solution 1000 mg/L Zr standard solution I: 1 mL = 13.5 µg ZrO_2 Zr standard solution II: 1 mL = 1.35 µg ZrO_2 Aliquot standard solution 0-1-2-3-4-5-mL	MAS
	M: 1 g; Dissolution with HF-$HClO_4$-HCl → 50 mL (sample 1-3) Dissolution with HF-$HClO_4$-HCl → 25 mL (sample 4-6)	Alfa product Zr stock solution 1000 mg/L calibration solutions: 0.5-1-5-10-20 mg/L, matrix matching	ICP OES
11	M: 0.5 g; Digestion with HF-HNO_3 → 100 mL	Merck 1 g/L Zr → 10.8064 mg / 250 mL ZrO_2 calibration solutions: 0-0.540-1.081-2.702-5.403	ICP OES
12	M: 0.1 g; in a Pt-dish. Decomposition with 2 mL $HClO_4$ and 5 mL HF, evaporate to dryness, add 5 mL HF and evaporate to dryness again. Dissolve in 4 mL HCl (1:1) and 10 mL H_2O. Dilute to 100 mL	Single Element High Purity Standard 1000 mg/L calibration solutions:: 2 mg/L single element standard in 2% HCl and 2% HCl as a blank	ICP OES
13	M: 1 g; Decomposition with HF-$HClO_4$ until dryness. Residue taken up with 10% HCl → 100 mL	1000 mg/L multielement CPI 1000 mg/L Zr CPI external calibration: 3.00-5.00-10.0 mg/L, matrix matching, Y as internal standard	ICP OES
14	M: 1 g; sample 1 – 5: open decomposition with HF-$HClO_4$-HNO_3; in Pt-crucible. sample 6: decomposition with HF-$HClO_4$-HNO_3; in close Teflon bomb	1000 mg/L ChemLab calibration solutions: standard addition method, 3 solutions in the expected range of concentration.	ICP OES
15	M: 0.140 – 0.214 g; weight in quartz ampoules; no sample digestion crushing of glass lump with a vice	0.7876 mg/g Zr self made from elemental Zr	INAA
17	M: 1 g fusion with 6 g $Li_2B_4O_7$ and 0.07% LiBr (A1000 from Merck) for 30 min in a Claisse-Fluxer.	ZrO_2 99.99% from Johnson Matthey calibration samples: 781-793-806-824 mg/kg	XRF (after digestion by fusion)
19	M: 0.1 g; pressure digestion in Paar bomb with HF-HNO_3 → 50 mL flask	Merck standard solution calibration solution: 1.0 mg/L Zr	ICP OES
20	M: 0.5 g; open digestion in a Pt vessel with HF-$HClO_4$-HNO_3 → 250 mL flask	1000 mg/L Zr Aldrich pure mono element calibration solutions: 0.1-0.5-1.00-3.00 mg/L checked against monitors made from 2 multel. std. sol. from Merck ICP solution IV, 23 El. (1000 mg/L) and Alfa Aesar 16 El. (100 mg/L) with and without matrix matching	ICP OES
21	M: 0.06 g; open digestion in Pt-vessel with HF-H_2SO_4; Residue evaporated to dryness again $HClO_4$-HNO_3. this operation repeated twice more. Residue dissolved in hot water	1000 mg/L Zr solution supplied by Alfa Aesar and Fisher calibration solutions: 10-20-30-40-50-60 µg	MAS
23	M: 0.50-0.59 g; decomposition in a microwave with HF- HNO_3 (10/2(1+1)) + 0.3 mL H_2O_2; evaporation during 45 min. The residue dissolved in HNO_3 10 mL (1+1) and dilution with H_2O to 100 mL.	1 g/L Titrisol stock solution calibration solutions: 0.25-0.5-1-2-3-4-mg/L plus matrix matching	ICP OES

7 Results and discussion

7.1 Presentation of the data; way of statistical evaluation

As soon as all results of the certification analysis had been submitted, they were summarized and checked by a statistical program of BCR for evaluation of results of interlaboratory comparisons for certification [4]. After this the data were technically discussed at four of the biannual meetings of ICG, TC2, at which more than half of the number of participants of the interlaboratory comparison for certification was present. Special discussion was concentrated to the statistically detected outliers and the question whether they should be excluded or not. In case that statistically outlying results came from participants of the ICG meetings, the question was discussed whether there were technical reasons to draw back the results. If technical reasons were found by the laboratories from where the outlying results came, these results were excluded from further runs of evaluation or from the final run of evaluation.

Note: In spite of opinions of some experts, that the statistical procedure of evaluation of results should be carried out only one time for one element (= "in one run"), we used in some of the cases subsequent runs of evaluation as long until no significant outlier, necessary to remove, was found. For this decision whether a value was to remove or not, not only statistical criteria were used, but also hints from the society of experts of ICG TC2.

If no technical reasons for an outlying value could be found, it was discussed with the laboratory about its experience to determine the relative analyte in this kind of glass matrix. If the experience was not high, the laboratory was asked for its agreement that the value could be ignored for further/final statistical evaluation. In case that the laboratory had a high experience for the analytical problem and they had delivered a significantly deviating result, a discussion between members of ICG TC2 led to the decision whether the result was to accept or not for the further/final evaluation.

If the participating laboratory that had delivered the outlying result was not a member of ICG TC2, it was proceeded in an analogous way as described above. But all conversation with the participating laboratory had to be carried out via e-mail connection, - while the discussion and decision about this was performed at the subsequent meeting of members of ICG TC2.

In the following Tab. 6 all accepted laboratory mean values are summarized.

Tab. 6: Means of the series of measurements for the analytical procedure of one laboratory or of one method in one laboratory (laboratory means).
The results are arranged by increasing values of the laboratory means. **Mass fractions in mg/kg**

Part 1 of Tab. 6

Line No.	As_2O_3	BaO	CdO	CeO_2	Cl	CoO	Cr_2O_3	CuO	Fe_2O_3	MnO	MoO_3
1	-	-	47	90	198	39.3	11.4	98	373	105	302
2	-	106	48	92	212	40.3	13.2	99	386	107	315
3	103	106	54	99	234	43.4	13.5	100	394	109	327
4	111	107	55	100	238	43.8	13.5	101	395	110	332
5	119	108	57	101	239	44.5	13.6	103	408	110	332
6	122	108	58	102	250	44.7	14.7	105	411	112	333
7	128	111	59	102	253	46.2	15.0	107	411	113	339
8	131	112	60	104	255	47.2	15.0	107	412	115	344
9	132	113	61	108	270	47.7	15.1	110	412	119	354
10	133	115	63	110	272	49.0	15.3	112	414	120	354
11	135	116	63	112	291	49.2	15.3	113	416	123	355
12	135	117	65	113		49.7	15.4	114	418	124	362
13	142	118	65	113		50.0	15.9	114	423	124	368
14	144	118	66	119		50.8	16.0	114	423	127	385
15	146	118	66	-		51.8	16.2	114	426	128	
16	154	128	66			52.3	16.3	114	436	129	
17	-	129	67			52.7	16.5	114	439	129	
18		-	67			53.0	16.7	116	439	129	
19		-	67			54.0	16.8	116	447	131	
20			68			54.5	16.8	117	448	132	
21			69			54.9	16.9	117	450	132	
22			75			58.3	-	119	454	133	
23						58.8		120	460	136	
24								121	-	145	
25								122		149	
M:	132	115	62	105	247	49.4	15.2	112	422	124	343
s_M:	14	7	7	9	27	5.3	1.5	8	23	12	22

Note: Where a „ - “ appears in the table it indicates that an outlying value has been detected by a statistical test which was withdrawn or omitted after discussion in ICG-TC2 meetings. The line number should not be mistaken for the laboratory code number.
M: Arithmetic mean of the laboratory means
s_M: Standard deviation of the laboratory means
The laboratory means are based on 3 – 6 single values (in most cases 6 single values).

Part 2 of Tab. 6

Line No.	NiO	PbO	Sb_2O_3	Se	SnO_2	SO_3	SrO	TiO_2	V_2O_5	ZnO	ZrO_2
1	51.0	169	105	17.0	-	1834	128	126	279	-	-
2	52.7	175	116	17.4	76	1848	128	134	291	187	-
3	53.5	178.	121	18.7	85	1867	128	155	294	187	760
4	54.3	182	122	18.9	92	1883	132	157	312	188	772
5	55.5	185	123	19.3	94	1927	138	157	326	192	779
6	56.2	189	124	19.4	95	1933	140	157	328	193	792
7	56.3	192	126	19.6	95	1983	141	160	334	195	800
8	58.1	196	128	20.2	101	2001	144	163	335	198	800
9	58.1	197	128	20.6	101	2004	146	164	339	199	810
10	58.3	200	129	20.7	102	2012	148	164	341	199	820
11	58.6	200	132	20.8	103	2061	148	166	347	204	840
12	58.6	201	133	21.2	107		149	166	354	204	842
13	60.0	201	137	21.2	108		151	166	356	200	842
14	61.2	203	138	-	114		154	167	369	205	851
15	61.2	205	138		120		160	173	373	208	856
16	62.1	209	140				162	173	415	208	859
17	62.7	215	148				162	178	434	208	873
18	62.7	215	149				163	184	436	210	875
19	63.3	216	157				165	189		210	903
20	63.4	217					167	-		214	937
21	65.2	220					168			216	972
22	65.2	221					174			218	
23	-	221					175				
24		222									
25											
M:	59.0	202	132	19.6	100	1942	151	163	349	203	842
s_M:	4.1	16	13	1.4	12	76	15	15	46	10	56

Note: Where a „ - “ appears in the table it indicates that an outlying value has been detected by a statistical test which was withdrawn or omitted after discussion in ICG-TC2 meetings. The line number should not be mistaken for the laboratory code number.
M: Arithmetic mean of the laboratory means
s_M: Standard deviation of the laboratory means
The laboratory means are based on 3 – 6 single values (in most cases 6 single values).

7.2 Technical discussion

The results of table 6 are listed in more detail in Tab. 7 (Tables 7a1 ... 7v2). These tables are based on the statistical evaluation of the interlaboratory comparison using the BCR program [4], they are arranged alphabetically by different element symbols. Each table consists in the following three parts:

- upper part: a table containing 11 columns. #First column: current laboratory number (line number "L") in this special test; #second column: laboratory code number in this interlaboratory comparison together with the abbreviation of the analytical method used #third column: laboratory mean values arranged by increasing values; #fourth and fifth column: standard deviations of laboratory single values and half width of 95% confidence intervals of the laboratory mean values, respectively; #following 6 columns: all single values from different sub-samples;

- center-part: a table containing: range of all single values. And for the case of no pooling of all single values: mean of laboratory means, half width of 95% confidence interval and half width of 95%/95% tolerance interval. And below this: As well in case of pooling of all single values (but statistically not allowed in all current cases): mean of all single values and half width of 95% confidence interval and half width of 95%/95% tolerance interval. Further below the table: there are explanations to the abbreviations of statistical tests which were applied and which are indicated in the subsequent diagram of the lower part of the table.

- lower part: based on the specifications of the upper and center-parts of the table - a diagram showing the mean of all means of data sets (vertical line), the corresponding 95% confidence interval (C.I.) and tolerance interval (T.I.) and the means of data sets with their 95% confidence intervals (horizontal bars) arranged by increasing mean values. These bars are marked by abbreviations of four statistical tests, if results of one or more tests were positive at a level of 5% or even 1%. (Abbreviations are to find in the center part of the table).

7.2.1 Tables of evaluation

Tab. 7: Evaluation of all delivered results, arranged by elements (alphabetically by element symbols)

Table 7a1: Arsenic (III) oxide evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	14 ICP OES	79,983	5,221	5,479	73,900	87,500	80,400	83,800	79,600	74,700
L 2	1 ICP OES	81,733	9,063	9,511	88,500	90,200	91,200	73,100	73,600	73,800
L 3	21 F AAS	103,107	4,959	5,204	102,750	112,860	102,560	99,910	101,050	99,510
L 4	19 ICP OES	110,833	4,916	5,159	110,000	110,000	105,000	110,000	110,000	120,000
L 5	13 HG AAS	119,167	1,835	1,926	121,000	119,000	119,000	121,000	116,000	119,000
L 6	7a ICP OES	122,000	6,812	7,148	121,000	113,000	120,000	131,000	129,000	118,000
L 7	4 FI-HG AAS	128,000	1,095	1,150	128,000	127,000	128,000	130,000	128,000	127,000
L 8	11 ICP OES	130,783	4,147	4,352	133,300	137,500	128,000	125,700	130,000	130,200
L 9	2 FI-HG AAS	131,833	2,137	2,243	131,000	130,000	131,000	136,000	131,000	132,000
L 10	15 INAA	133,350	1,294	1,358	134,800	131,400	133,700	132,200	133,700	134,300
L 11	9 K_0-INAA	134,500	2,258	2,370	138,000	135,000	136,000	132,000	133,000	133,000
L 12	12 ICP-MS	135,000	3,347	3,512	140,000	137,000	130,000	134,000	135,000	134,000
L 13	3 ICP OES	142,200	6,252	6,561	130,940	141,020	146,040	141,680	144,450	149,070
L 14	10 MAS	143,833	13,106	13,754	151,000	148,000	164,000	139,000	132,000	129,000
L 15	10 ICP OES	146,167	12,400	13,013	151,000	154,000	164,000	134,000	142,000	132,000
L 16	3 HG AAS	153,602	2,906	3,049	155,900	152,980	156,530	148,530	152,800	154,870
L 17	5 ICP OES	173,000	1,732	4,303	175,000	172,000	172,000			

Range [min..max]	[73,100 .. 175,000]
	Case of No Pooling
Mean of means	127,594
95% H.W. Confidence Interval	12,246
95% H.W. Tolerance Interval	68,072
	Case of Pooling
Mean of All	126,218
95% H.W. Confidence Interval	4,559
95% H.W. Tolerance Interval	51,079

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

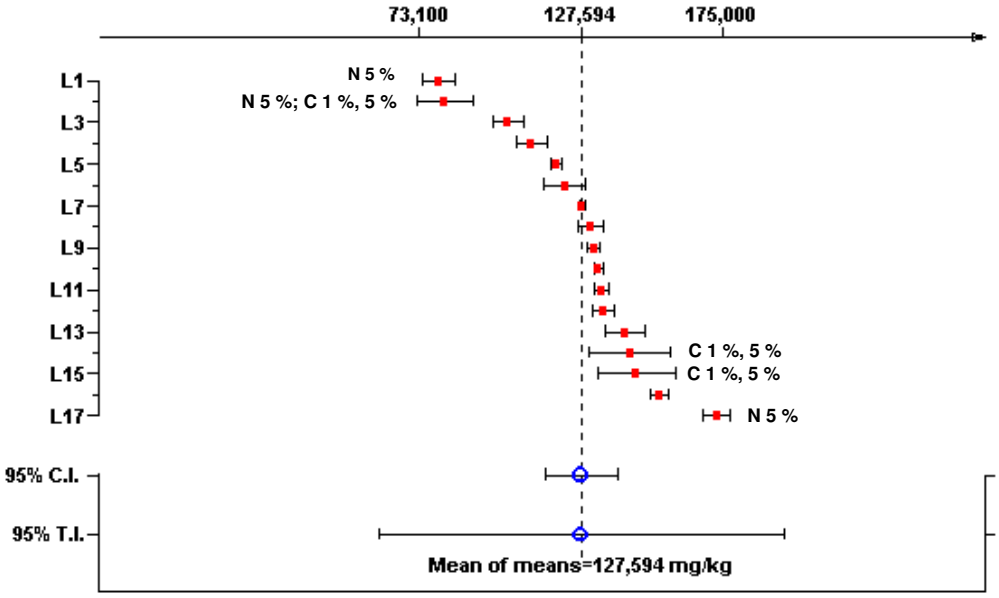


Table 7a2: Arsenic (III) oxide evaluation in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	21 F AAS	103,107	4,959	5,204	102,750	112,860	102,560	99,910	101,050	99,510
L 2	19 ICP OES	110,833	4,916	5,159	110,000	110,000	105,000	110,000	110,000	120,000
L 3	13 HG AAS	119,167	1,835	1,926	121,000	119,000	119,000	121,000	116,000	119,000
L 4	7a ICP OES	122,000	6,812	7,148	121,000	113,000	120,000	131,000	129,000	118,000
L 5	4 FI-HG AAS	128,000	1,095	1,150	128,000	127,000	128,000	130,000	128,000	127,000
L 6	11 ICP OES	130,783	4,147	4,352	133,300	137,500	128,000	125,700	130,000	130,200
L 7	2 FI-HG AAS	131,833	2,137	2,243	131,000	130,000	131,000	136,000	131,000	132,000
L 8	15 INAA	133,350	1,294	1,358	134,800	131,400	133,700	132,200	133,700	134,300
L 9	9 K_0-INAA	134,500	2,258	2,370	138,000	135,000	136,000	132,000	133,000	133,000
L 10	12 ICP-MS	135,000	3,347	3,512	140,000	137,000	130,000	134,000	135,000	134,000
L 11	3 ICP OES	142,200	6,252	6,561	130,940	141,020	146,040	141,680	144,450	149,070
L 12	10 MAS	143,833	13,106	13,754	151,000	148,000	164,000	139,000	132,000	129,000
L 13	10 ICP OES	146,167	12,400	13,013	151,000	154,000	164,000	134,000	142,000	132,000
L 14	3 HG AAS	153,602	2,906	3,049	155,900	152,980	156,530	148,530	152,800	154,870

Range [min..max]	[99,510 .. 164,000]
	Case of No Pooling
Mean of means	131,027
95% H.W. Confidence Interval	7,975
95% H.W. Tolerance Interval	41,604
	Case of Pooling
Mean of All	131,027
95% H.W. Confidence Interval	3,146
95% H.W. Tolerance Interval	32,810

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals (to Table X)

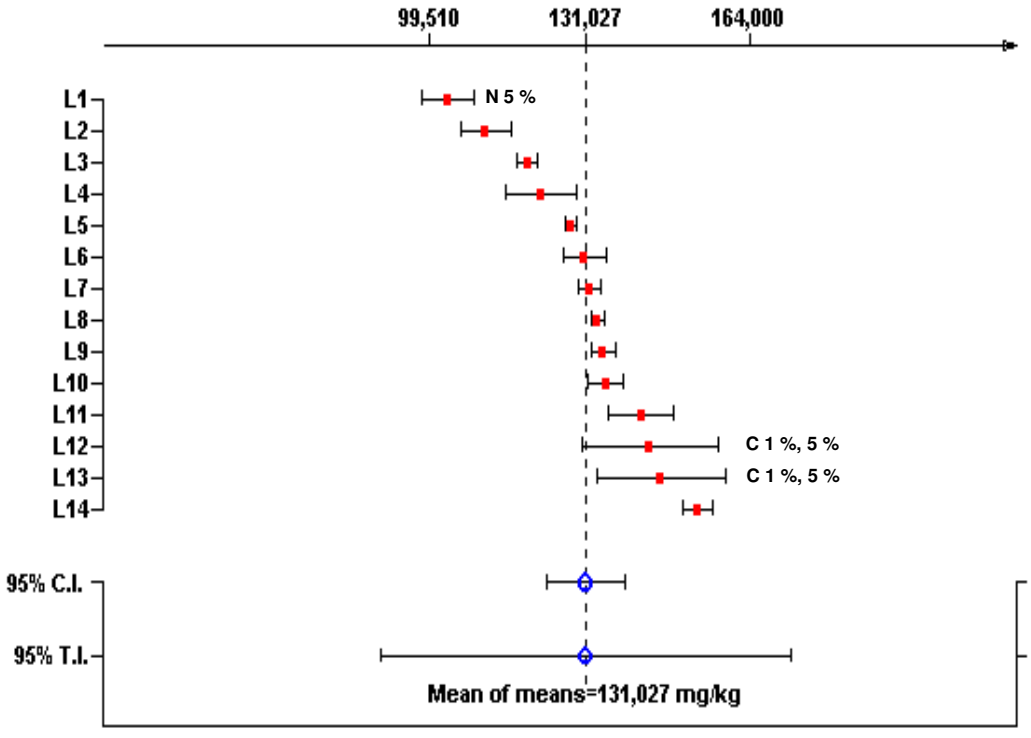


Table 7b1: Barium oxide evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES	60,000	4,082	6,496			60,000	60,000	65,000	55,000
L 2	9 K_0-INAA	105,833	1,472	1,545	107,000	105,000	105,000	106,000	108,000	104,000
L 3	7c ICP OES	105,833	4,070	4,271	113,000	106,000	107,000	104,000	104,000	101,000
L 4	7b ICP OES	107,333	4,502	4,724	111,000	113,000	110,000	104,000	103,000	103,000
L 5	10 ICP OES	108,333	3,983	4,180	109,000	110,000	113,000	111,000	103,000	104,000
L 6	20 ICP OES	108,447	3,091	3,243	107,680	103,790	108,600	108,530	113,490	108,590
L 7	14 ICP OES	110,917	3,590	3,768	116,800	110,100	112,100	111,700	108,500	106,300
L 8	4 ICP OES	112,333	5,502	5,773	119,000	108,000	119,000	106,000	111,000	111,000
L 9	3 ICP OES	113,177	3,690	3,872	111,600	115,280	119,640	112,270	109,950	110,320
L 10	13 ICP OES	114,833	2,994	3,142	118,000	118,000	114,000	114,000	115,000	110,000
L 11	17 XRF	116,167	5,584	5,860	113,600	119,000	110,700	117,600	125,200	110,900
L 12	1 ICP OES	116,500	1,871	1,963	114,000	118,000	119,000	117,000	116,000	115,000
L 13	12 ICP OES	117,500	1,871	1,963	117,000	115,000	116,000	118,000	119,000	120,000
L 14	3 ICP-MS	117,533	3,126	3,280	118,300	116,100	113,800	121,600	120,500	114,900
L 15	23 ICP OES	118,167	4,021	4,220	115,000	119,000	124,000	121,000	113,000	117,000
L 16	11 ICP OES	127,767	15,603	16,375	118,300	154,900	114,900	115,000	135,700	127,800
L 17	2 ET AAS	129,333	14,760	15,490	115,000	117,000	122,000	145,000	150,000	127,000
L 18	2 F AAS	143,500	6,348	6,662	135,000	148,000	150,000	138,000	149,000	141,000
L 19	10 F AAS	149,667	16,305	17,111	144,000	142,000	139,000	135,000	178,000	160,000

Range [min..max]	[55,000 .. 178,000]
	Case of No Pooling
Mean of means	114,904
95% H.W. Confidence Interval	8,633
95% H.W. Tolerance Interval	49,866
	Case of Pooling
Mean of All	115,884
95% H.W. Confidence Interval	3,247
95% H.W. Tolerance Interval	38,413

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

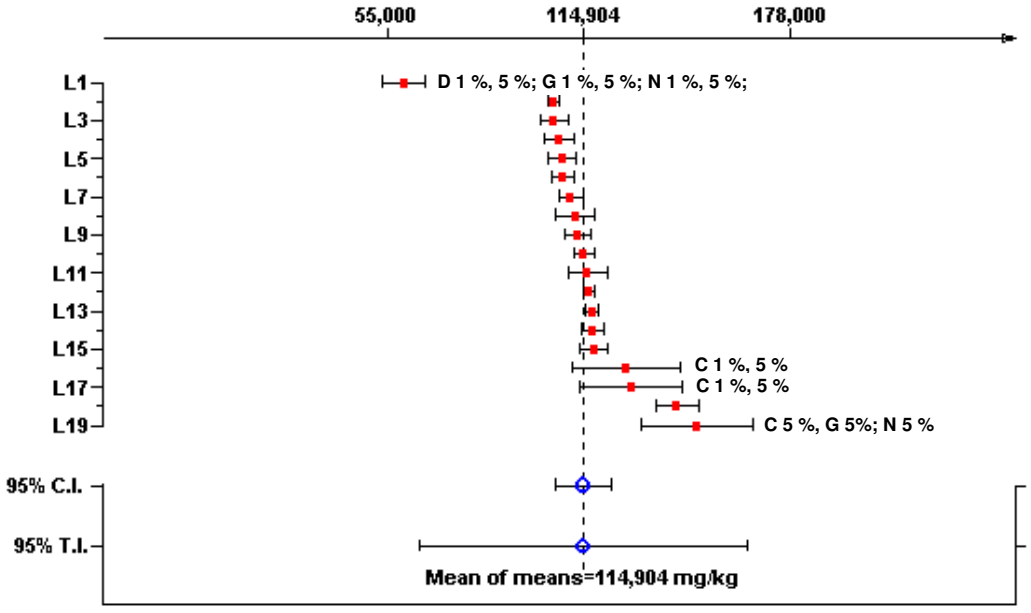


Table 7b2: Barium oxide evaluation in run 2 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	9 K_0-INAA	105,833	1,472	1,545	107,000	105,000	105,000	106,000	108,000	104,000
L 2	7c ICP OES	105,833	4,070	4,271	113,000	106,000	107,000	104,000	104,000	101,000
L 3	7b ICP OES	107,333	4,502	4,724	111,000	113,000	110,000	104,000	103,000	103,000
L 4	10 ICP OES	108,333	3,983	4,180	109,000	110,000	113,000	111,000	103,000	104,000
L 5	20 ICP OES	108,447	3,091	3,243	107,680	103,790	108,600	108,530	113,490	108,590
L 6	14 ICP OES	110,917	3,590	3,768	116,800	110,100	112,100	111,700	108,500	106,300
L 7	4 ICP OES	112,333	5,502	5,773	119,000	108,000	119,000	106,000	111,000	111,000
L 8	3 ICP OES	113,177	3,690	3,872	111,600	115,280	119,640	112,270	109,950	110,320
L 9	13 ICP OES	114,833	2,994	3,142	118,000	118,000	114,000	114,000	115,000	110,000
L 10	17 XRF	116,167	5,584	5,860	113,600	119,000	110,700	117,600	125,200	110,900
L 11	1 ICP OES	116,500	1,871	1,963	114,000	118,000	119,000	117,000	116,000	115,000
L 12	12 ICP OES	117,500	1,871	1,963	117,000	115,000	116,000	118,000	119,000	120,000
L 13	3 ICP-MS	117,533	3,126	3,280	118,300	116,100	113,800	121,600	120,500	114,900
L 14	23 ICP OES	118,167	4,021	4,220	115,000	119,000	124,000	121,000	113,000	117,000
L 15	11 ICP OES	127,767	15,603	16,375	118,300	154,900	114,900	115,000	135,700	127,800
L 16	2 ET AAS	129,333	14,760	15,490	115,000	117,000	122,000	145,000	150,000	127,000
L 17	2 F AAS	143,500	6,348	6,662	135,000	148,000	150,000	138,000	149,000	141,000
L 18	10 F AAS	149,667	16,305	17,111	144,000	142,000	139,000	135,000	178,000	160,000

Range [min..max]	[101,000 .. 178,000]
	Case of No Pooling
Mean of means	117,954
95% H.W. Confidence Interval	6,142
95% H.W. Tolerance Interval	34,816
	Case of Pooling
Mean of All	117,954
95% H.W. Confidence Interval	2,632
95% H.W. Tolerance Interval	30,642

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

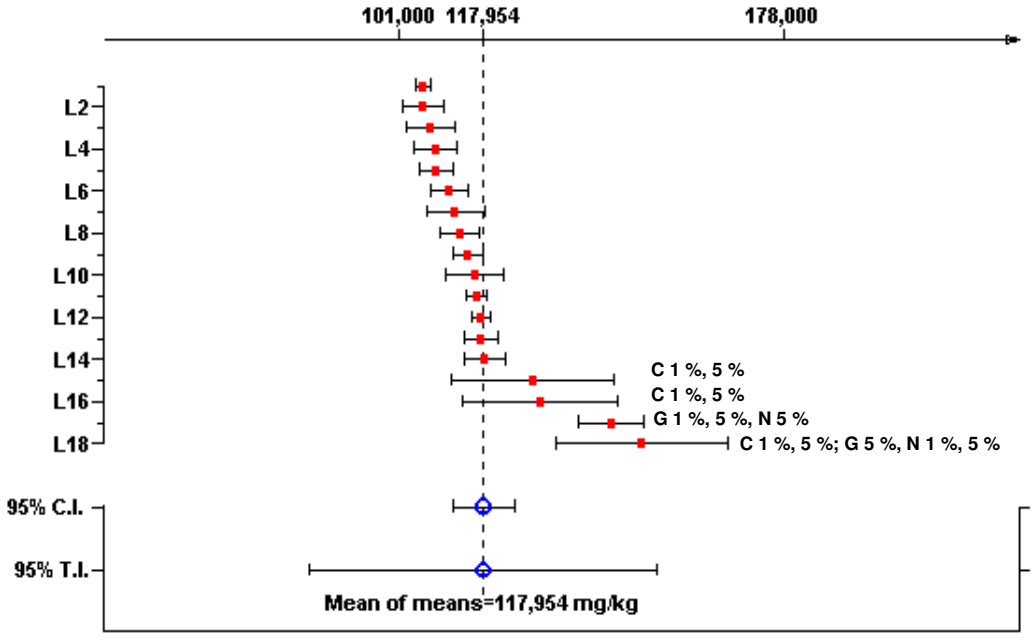


Table 7b3: Barium oxide run 3 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	9 K_0-INAA	105,833	1,472	1,545	107,000	105,000	105,000	106,000	108,000	104,000
L 2	7c ICP OES	105,833	4,070	4,271	113,000	106,000	107,000	104,000	104,000	101,000
L 3	7b ICP OES	107,333	4,502	4,724	111,000	113,000	110,000	104,000	103,000	103,000
L 4	10 ICP OES	108,333	3,983	4,180	109,000	110,000	113,000	111,000	103,000	104,000
L 5	20 ICP OES	108,447	3,091	3,243	107,680	103,790	108,600	108,530	113,490	108,590
L 6	14 ICP OES	110,917	3,590	3,768	116,800	110,100	112,100	111,700	108,500	106,300
L 7	4 ICP OES	112,333	5,502	5,773	119,000	108,000	119,000	106,000	111,000	111,000
L 8	3 ICP OES	113,177	3,690	3,872	111,600	115,280	119,640	112,270	109,950	110,320
L 9	13 ICP OES	114,833	2,994	3,142	118,000	118,000	114,000	114,000	115,000	110,000
L 10	17 XRF	116,167	5,584	5,860	113,600	119,000	110,700	117,600	125,200	110,900
L 11	1 ICP OES	116,500	1,871	1,963	114,000	118,000	119,000	117,000	116,000	115,000
L 12	12 ICP OES	117,500	1,871	1,963	117,000	115,000	116,000	118,000	119,000	120,000
L 13	3 ICP-MS	117,533	3,126	3,280	118,300	116,100	113,800	121,600	120,500	114,900
L 14	23 ICP OES	118,167	4,021	4,220	115,000	119,000	124,000	121,000	113,000	117,000
L 15	11 ICP OES	127,767	15,603	16,375	118,300	154,900	114,900	115,000	135,700	127,800
L 16	2 ET AAS	129,333	14,760	15,490	115,000	117,000	122,000	145,000	150,000	127,000

Range [min..max]	[101,000 .. 154,900]
	Case of No Pooling
Mean of means	114,375
95% H.W. Confidence Interval	3,717
95% H.W. Tolerance Interval	20,250
	Case of Pooling
Mean of All	114,375
95% H.W. Confidence Interval	1,819
95% H.W. Tolerance Interval	20,105

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

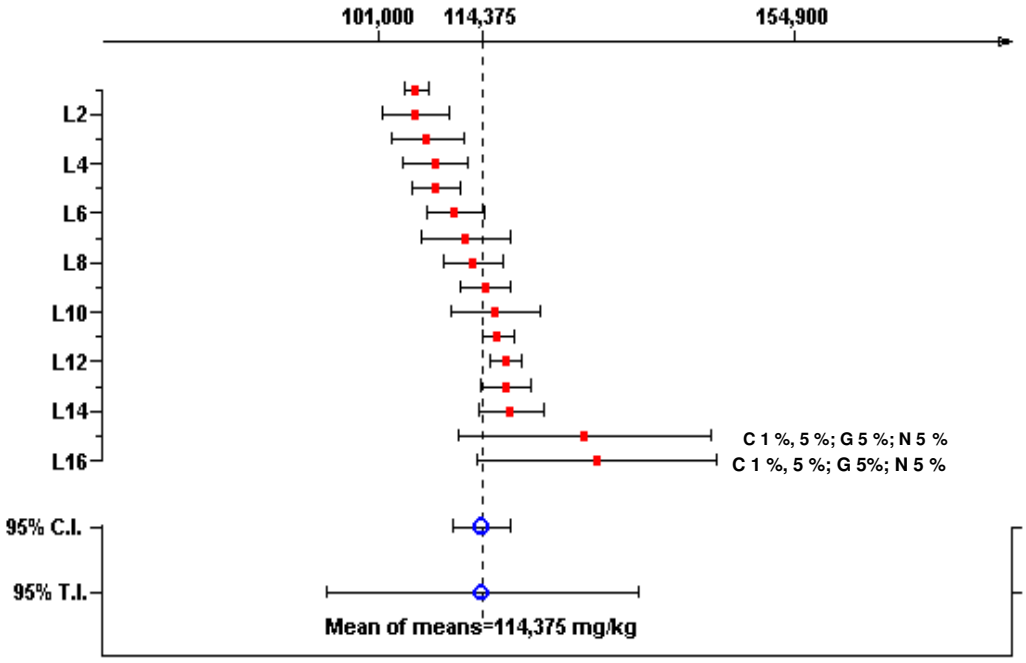


Table 7c1: Cadmium oxide run 1 in CRM BAM-S005 (values in mg/kg)

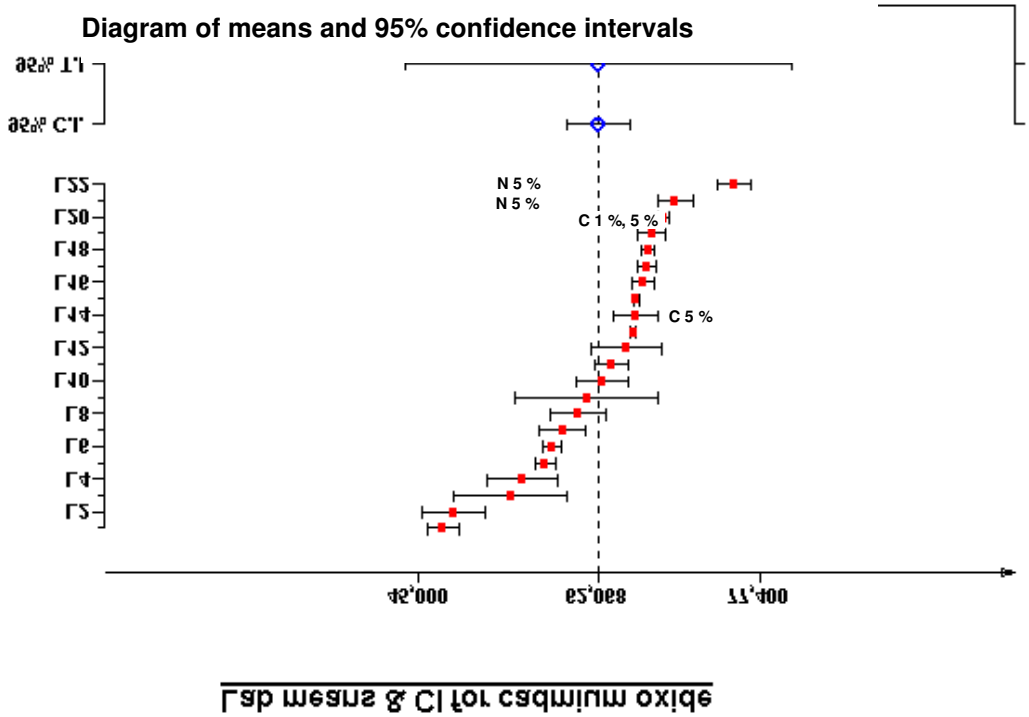
Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 ICP OES	47,333	0,577	1,434	47,000	48,000	47,000			
L 2	24 F AAS	48,333	2,875	3,017	52,000	50,000	50,000	45,000	45,000	48,000
L 3	2 ET AAS	53,767	5,137	5,391	52,000	52,400	51,100	64,200	51,100	51,800
L 4	10 ICP OES	54,833	3,189	3,346	57,000	58,000	58,000	51,000	52,000	53,000
L 5	20 ICP OES	57,008	0,928	0,974	57,190	56,750	57,240	58,610	55,980	56,280
L 6	7c ICP OES	57,667	0,816	0,857	57,000	58,000	57,000	57,000	59,000	58,000
L 7	7b ICP OES	58,667	2,066	2,168	56,000	58,000	57,000	59,000	61,000	61,000
L 8	22 F AAS	60,133	2,597	2,726	62,400	61,900	62,900	59,100	57,500	57,000
L 9	19 ICP OES	61,000	5,477	6,801	55,000	55,000	65,000	65,000		65,000
L 10	10 F AAS	62,500	2,345	2,461	66,000	63,000	63,000	59,000	63,000	61,000
L 11	13 ICP OES	63,333	1,506	1,580	63,000	62,000	64,000	62,000	66,000	63,000
L 12	23 ICP OES	64,667	3,204	3,363	66,000	65,000	64,000	70,000	61,000	62,000
L 13	18 ET AAS	65,417	0,264	0,277	65,300	65,500	65,900	65,200	65,400	65,200
L 14	14 ICP OES	65,583	1,986	2,085	65,700	66,400	63,400	66,400	63,200	68,400
L 15	2 F AAS	65,683	0,293	0,307	65,900	65,800	65,700	65,800	65,800	65,100
L 16	4 ICP OES	66,333	1,033	1,084	68,000	66,000	67,000	66,000	65,000	66,000
L 17	12 ICP-MS	66,667	0,816	0,857	67,000	68,000	67,000	66,000	66,000	66,000
L 18	21 F AAS	66,770	0,536	0,562	66,810	66,780	66,330	67,610	66,080	67,010
L 19	9 K_0-INAA	67,167	1,255	1,317	67,900	64,900	68,300	67,400	66,600	67,900
L 20	3 F AAS	68,233	0,516	0,542	68,600	68,100	68,600	67,800	68,800	67,500
L 21	3 ICP-MS	69,417	1,524	1,599	68,900	68,800	67,700	71,100	71,500	68,500
L 22	11 ICP OES	74,983	1,501	1,575	75,300	73,900	75,900	77,400	73,800	73,600

Range [min..max]	[45,000 .. 77,400]
	Case of No Pooling
Mean of means	62,068
95% H.W. Confidence Interval	3,029
95% H.W. Tolerance Interval	18,423
	Case of Pooling
Mean of All	62,422
95% H.W. Confidence Interval	1,179
95% H.W. Tolerance Interval	14,805

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**



Lab means & CI for cadmium oxide

Table7d1: Cerium (IV) oxide evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	7c ICP OES	90,333	1,033	1,084	92,000	90,000	90,000	91,000	89,000	90,000
L 2	7b ICP OES	92,333	1,751	1,838	90,000	91,000	92,000	95,000	93,000	93,000
L 3	10 ICP OES	99,167	4,875	5,116	101,000	106,000	103,000	96,000	94,000	95,000
L 4	11 ICP OES	99,600	5,697	5,979	97,700	90,600	107,800	102,500	98,500	100,500
L 5	23 ICP OES	101,000	2,757	2,893	99,000	99,000	101,000	106,000	99,000	102,000
L 6	9 K_0-INAA	101,500	1,049	1,101	103,000	100,000	102,000	101,000	102,000	101,000
L 7	20 ICP OES	101,727	3,028	3,178	102,520	105,730	103,190	102,280	96,990	99,650
L 8	3 ICP OES	103,867	1,680	1,763	105,100	101,900	101,900	104,700	103,700	105,900
L 9	4 ICP OES	107,833	0,753	0,790	107,000	109,000	108,000	108,000	107,000	108,000
L 10	12 ICP OES	109,500	0,837	0,878	110,000	108,000	110,000	110,000	109,000	110,000
L 11	13 ICP OES	111,500	3,017	3,166	113,000	114,000	115,000	110,000	107,000	110,000
L 12	3 ICP-MS	113,000	3,278	3,440	113,700	113,300	111,400	110,200	110,400	119,000
L 13	14 ICP OES	113,133	4,284	4,496	116,200	116,600	116,600	107,100	108,500	113,800
L 14	5 ICP OES	119,333	2,082	5,171	117,000	121,000	120,000			
L 15	1 ICP OES	165,833	1,169	1,227	167,000	167,000	165,000	166,000	166,000	164,000

Range [min..max]	[89,000 .. 167,000]
	Case of No Pooling
Mean of means	108,644
95% H.W. Confidence Interval	9,803
95% H.W. Tolerance Interval	52,289
	Case of Pooling
Mean of All	108,275
95% H.W. Confidence Interval	3,747
95% H.W. Tolerance Interval	39,681

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

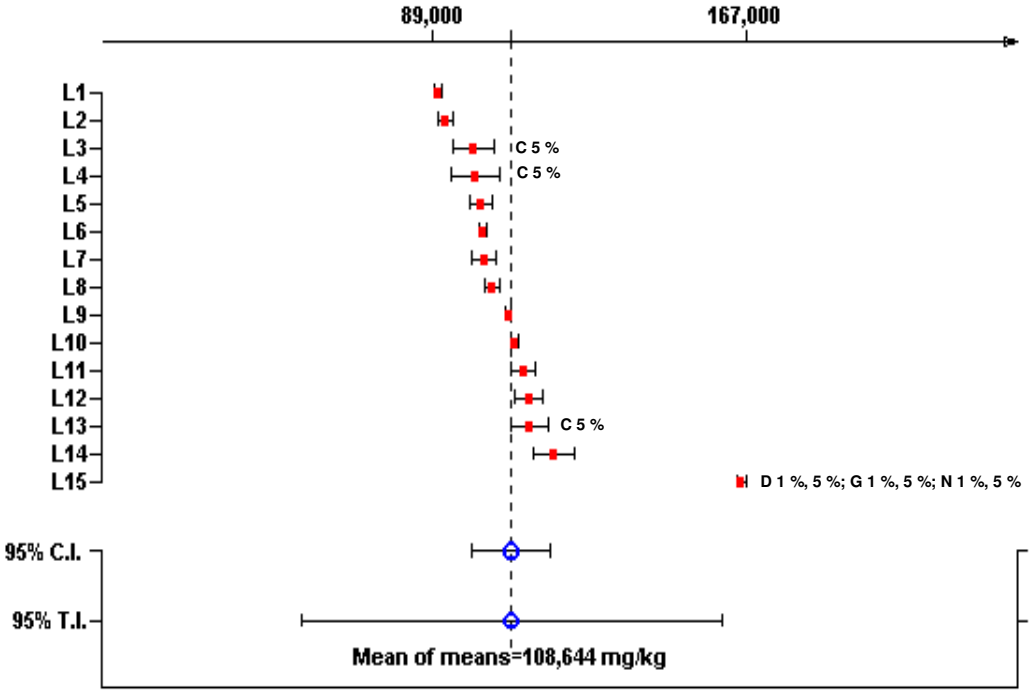


Table7d2: Cerium (IV) oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	7c ICP OES	90,333	1,033	1,084	92,000	90,000	90,000	91,000	89,000	90,000
L 2	7b ICP OES	92,333	1,751	1,838	90,000	91,000	92,000	95,000	93,000	93,000
L 3	10 ICP OES	99,167	4,875	5,116	101,000	106,000	103,000	96,000	94,000	95,000
L 4	11 ICP OES	99,600	5,697	5,979	97,700	90,600	107,800	102,500	98,500	100,500
L 5	23 ICP OES	101,000	2,757	2,893	99,000	99,000	101,000	106,000	99,000	102,000
L 6	9 K_0-INAA	101,500	1,049	1,101	103,000	100,000	102,000	101,000	102,000	101,000
L 7	20 ICP OES	101,727	3,028	3,178	102,520	105,730	103,190	102,280	96,990	99,650
L 8	3 ICP OES	103,867	1,680	1,763	105,100	101,900	101,900	104,700	103,700	105,900
L 9	4 ICP OES	107,833	0,753	0,790	107,000	109,000	108,000	108,000	107,000	108,000
L 10	12 ICP OES	109,500	0,837	0,878	110,000	108,000	110,000	110,000	109,000	110,000
L 11	13 ICP OES	111,500	3,017	3,166	113,000	114,000	115,000	110,000	107,000	110,000
L 12	3 ICP-MS	113,000	3,278	3,440	113,700	113,300	111,400	110,200	110,400	119,000
L 13	14 ICP OES	113,133	4,284	4,496	116,200	116,600	116,600	107,100	108,500	113,800
L 14	5 ICP OES	119,333	2,082	5,171	117,000	121,000	120,000			

Range [min..max]	[89,000 .. 121,000]
	Case of No Pooling
Mean of means	104,559
95% H.W. Confidence Interval	4,757
95% H.W. Tolerance Interval	24,815
	Case of Pooling
Mean of All	104,012
95% H.W. Confidence Interval	1,787
95% H.W. Tolerance Interval	18,346

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

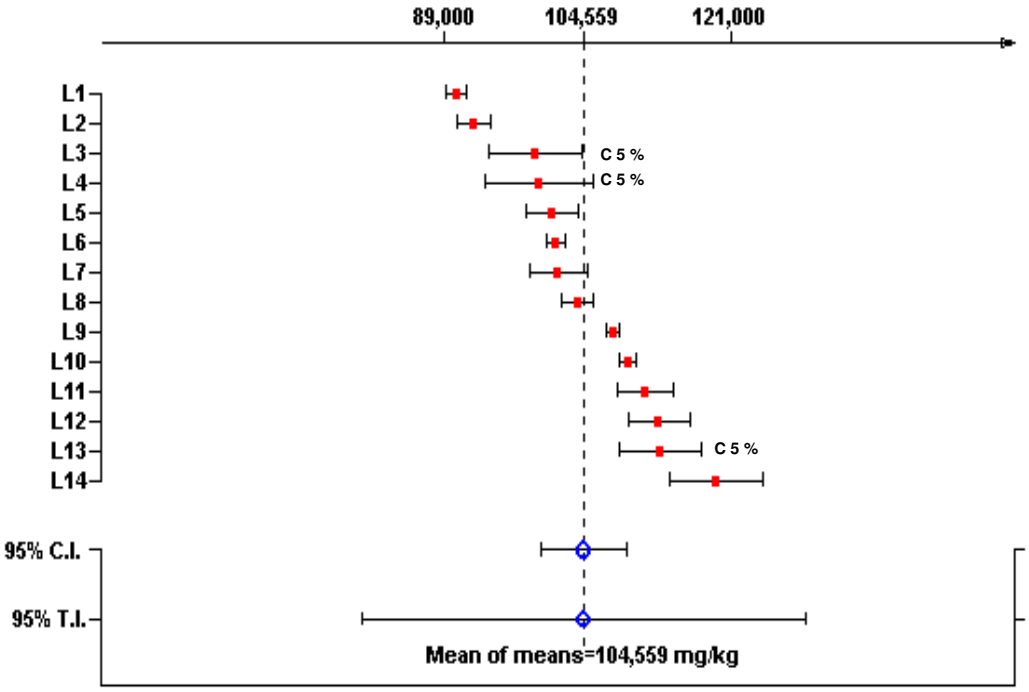


Table7e1: Chloride run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 POT	198,333	2,582	2,710	195,000	195,000	200,000	200,000	200,000	200,000
L 2	21 POT	212,140	17,355	18,213	222,120	218,610	234,610	191,160	214,540	191,800
L 3	3 POT	234,083	5,813	6,100	239,000	232,500	232,500	241,400	224,800	234,300
L 4	2 POT	237,500	10,784	11,317	248,000	239,000	220,000	237,000	249,000	232,000
L 5	22 POT	238,900	13,053	13,699	232,200	254,900	217,200	247,300	240,000	241,800
L 6	13 POT	249,667	13,337	13,996	266,000	231,000	255,000	248,000	260,000	238,000
L 7	24 POT	252,833	6,735	7,068	244,000	254,000	247,000	263,000	253,000	256,000
L 8	10 MAS	254,500	11,709	12,288	239,000	243,000	261,000	252,000	266,000	266,000
L 9	9 K_0-INAA	270,167	37,865	39,737	237,000	268,000	275,000	221,000	295,000	325,000
L 10	12 POT	272,000	5,020	5,268	276,000	280,000	270,000	271,000	267,000	268,000
L 11	23 POT	291,000	15,166	15,915	305,000	274,000	302,000	291,000	271,000	303,000

Range [min..max]	[191,160 .. 325,000]
	Case of No Pooling
Mean of means	246,466
95% H.W. Confidence Interval	17,899
95% H.W. Tolerance Interval	86,828
	Case of Pooling
Mean of All	246,466
95% H.W. Confidence Interval	7,214
95% H.W. Tolerance Interval	67,843

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

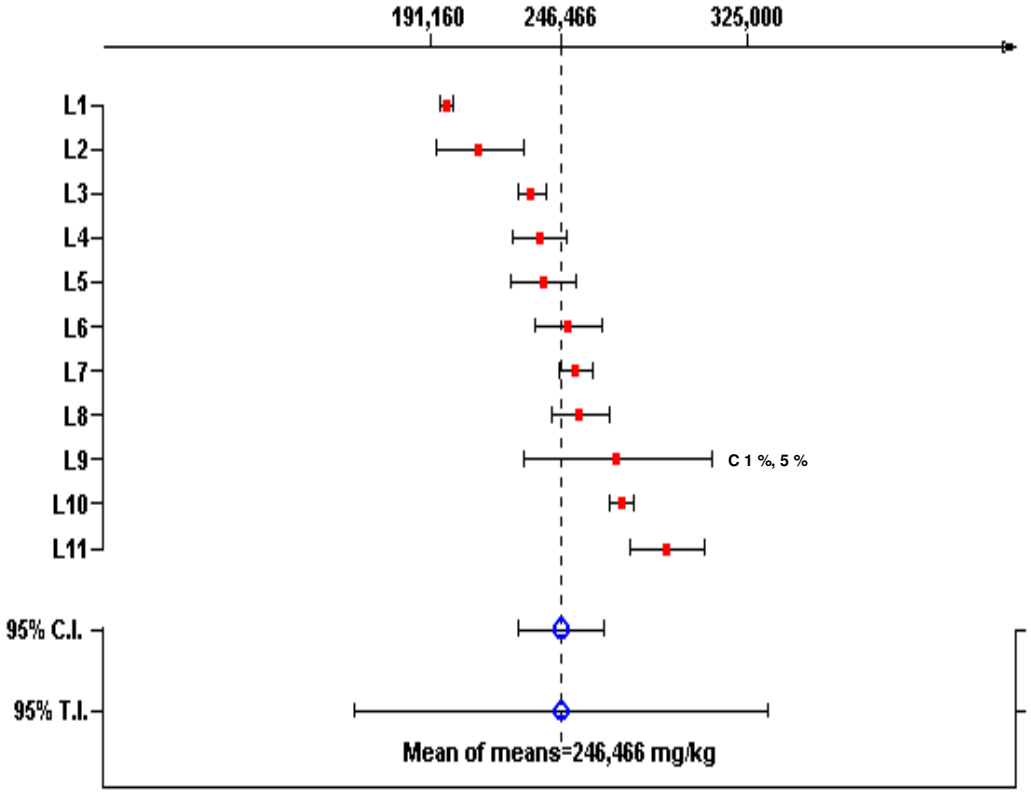


Table7f1: Cobalt (II) oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 ICP OES	39,333	0,577	1,434	39,000	40,000	39,000			
L 2	4 ICP OES	40,333	1,633	1,714	43,000	41,000	41,000	39,000	39,000	39,000
L 3	20 ICP OES	43,438	1,045	1,096	45,040	42,400	43,790	43,890	43,280	42,230
L 4	7b ICP OES	43,833	2,137	2,243	41,000	42,000	43,000	45,000	46,000	46,000
L 5	24 F AAS	44,500	0,837	0,878	46,000	44,000	44,000	44,000	44,000	45,000
L 6	7c ICP OES	44,667	1,211	1,271	43,000	46,000	46,000	44,000	45,000	44,000
L 7	1 ICP OES	46,233	0,703	0,738	45,700	45,900	45,400	46,400	46,700	47,300
L 8	6 F AAS	47,200	2,150	2,257	50,300	46,800	45,500	44,300	48,500	47,800
L 9	11 ICP OES	47,717	1,019	1,069	47,300	46,600	47,900	49,400	48,200	46,900
L 10	2 ET AAS	49,000	3,435	3,605	50,800	52,000	52,700	46,500	43,900	48,100
L 11	10 ICP OES	49,167	3,061	3,212	52,000	49,000	51,000	52,000	46,000	45,000
L 12	23 ICP OES	49,667	1,862	1,954	50,000	47,000	51,000	52,000	50,000	48,000
L 13	9 K_0-INAA	50,017	0,467	0,490	50,500	49,300	50,000	49,700	50,500	50,100
L 14	10 MAS	50,833	3,061	3,212	53,000	53,000	53,000	52,000	46,000	48,000
L 15	2 F AAS	51,800	0,978	1,026	50,600	51,400	51,300	51,700	53,400	52,400
L 16	21 F AAS	52,297	1,061	1,113	52,070	51,210	51,030	53,760	52,970	52,740
L 17	13 ICP OES	52,667	1,862	1,954	53,000	52,000	53,000	56,000	51,000	51,000
L 18	14 ICP OES	53,000	1,513	1,587	51,100	52,100	53,300	52,200	54,000	55,300
L 19	15 INAA	54,038	0,591	0,621	54,930	54,290	53,910	53,780	53,150	54,170
L 20	18 ET AAS	54,467	0,350	0,368	54,900	54,000	54,300	54,200	54,700	54,700
L 21	3 ICP-MS	54,917	0,674	0,707	54,000	55,100	55,400	55,100	55,700	54,200
L 22	12 ICP-MS	58,333	0,816	0,857	57,000	59,000	59,000	58,000	58,000	59,000
L 23	3 F AAS	58,782	1,087	1,141	58,780	57,980	58,040	59,270	57,910	60,710

Range [min..max]	[39,000 .. 60,710]
	Case of No Pooling
Mean of means	49,402
95% H.W. Confidence Interval	2,259
95% H.W. Tolerance Interval	13,961
	Case of Pooling
Mean of All	49,625
95% H.W. Confidence Interval	0,882
95% H.W. Tolerance Interval	11,343

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

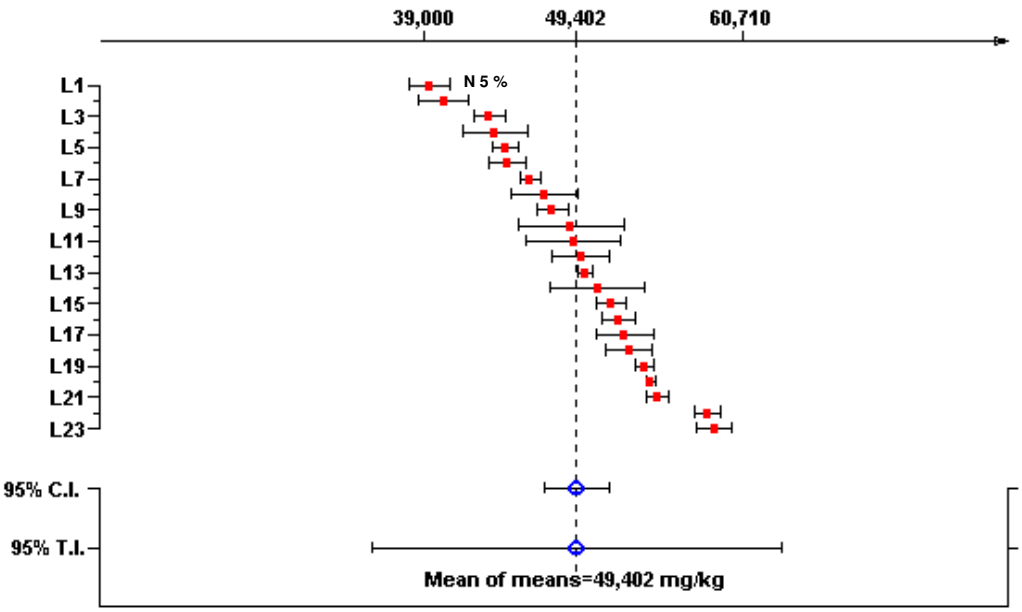


Table7g1: Chromium (III) oxide evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ICP OES	11,433	0,314	0,330	11,800	11,200	11,500	11,200	11,800	11,100
L 2	7c ICP OES	13,200	2,288	2,401	11,200	13,400	11,600	11,900	17,400	13,700
L 3	6 F AAS	13,450	1,241	1,302	13,000	15,700	13,000	13,000	12,100	13,900
L 4	22 F AAS	13,517	0,376	0,395	13,600	13,600	14,000	13,700	12,900	13,300
L 5	7b ICP OES	13,580	1,234	1,532	14,200	14,400	12,800		14,700	11,800
L 6	21 F AAS	14,683	0,968	1,016	16,290	15,430	14,020	14,180	13,820	14,360
L 7	1 ICP OES	14,983	3,652	3,832	18,700	17,400	18,300	13,000	9,800	12,700
L 8	19 ICP OES	15,000	0	0	15,000			15,000	15,000	15,000
L 9	9 K_0-INAA	15,117	0,560	0,588	15,400	14,300	15,100	14,700	15,900	15,300
L 10	5 ICP OES	15,333	0,577	1,434	16,000	15,000	15,000			
L 11	12 ICP-MS	15,333	0,816	0,857	14,000	16,000	16,000	15,000	15,000	16,000
L 12	2 ET AAS	15,400	0,460	0,483	14,800	15,900	15,400	14,900	15,800	15,600
L 13	13 ICP OES	15,867	0,961	1,008	14,800	17,400	15,900	15,100	15,500	16,500
L 14	14 ICP OES	16,000	0,583	0,612	16,500	15,600	15,500	16,800	16,200	15,400
L 15	15 INAA	16,152	0,344	0,361	16,220	16,520	15,930	15,640	16,080	16,520
L 16	10 ICP OES	16,333	2,944	3,089	19,000	19,000	19,000	14,000	13,000	14,000
L 17	16 ID-TIMS	16,498	0,514	0,540	16,250	17,120	16,040	17,190	16,230	16,160
L 18	10 MAS	16,667	1,862	1,954	15,000	15,000	15,000	18,000	18,000	19,000
L 19	3 ET AAS	16,830	1,042	1,093	16,810	16,510	16,810	18,410	15,200	17,240
L 20	23 ICP OES	16,833	2,994	3,142	15,000	15,000	22,000	19,000	15,000	15,000
L 21	11 ICP OES	16,867	1,707	1,792	16,600	16,100	15,700	19,000	18,900	14,900
L 22	20 ICP OES	21,442	2,920	3,064	20,590	24,660	23,550	23,550	18,850	17,450

Range [min..max]	[9,800 .. 24,660]
	Case of No Pooling
Mean of means	15,478
95% H.W. Confidence Interval	0,863
95% H.W. Tolerance Interval	5,251
	Case of Pooling
Mean of All	15,504
95% H.W. Confidence Interval	0,437
95% H.W. Tolerance Interval	5,453

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

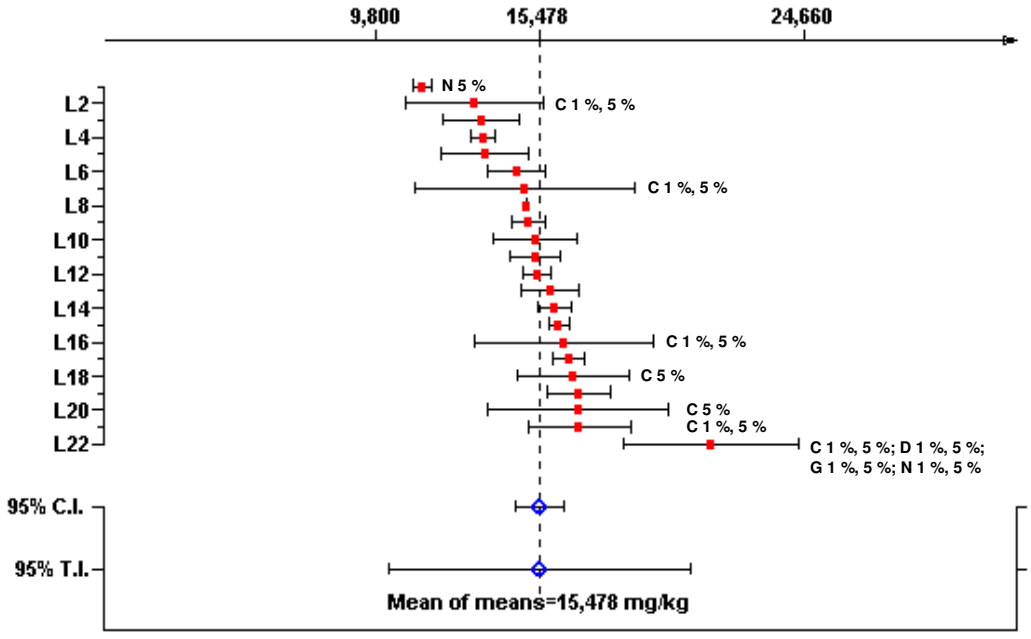


Table7g2: Chromium (III) oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ICP OES	11,433	0,314	0,330	11,800	11,200	11,500	11,200	11,800	11,100
L 2	7c ICP OES	13,200	2,288	2,401	11,200	13,400	11,600	11,900	17,400	13,700
L 3	6 F AAS	13,450	1,241	1,302	13,000	15,700	13,000	13,000	12,100	13,900
L 4	22 F AAS	13,517	0,376	0,395	13,600	13,600	14,000	13,700	12,900	13,300
L 5	7b ICP OES	13,580	1,234	1,532	14,200	14,400	12,800		14,700	11,800
L 6	21 F AAS	14,683	0,968	1,016	16,290	15,430	14,020	14,180	13,820	14,360
L 7	1 ICP OES	14,983	3,652	3,832	18,700	17,400	18,300	13,000	9,800	12,700
L 8	19 ICP OES	15,000	0	0	15,000			15,000	15,000	15,000
L 9	9 K_0-INAA	15,117	0,560	0,588	15,400	14,300	15,100	14,700	15,900	15,300
L 10	5 ICP OES	15,333	0,577	1,434	16,000	15,000	15,000			
L 11	12 ICP-MS	15,333	0,816	0,857	14,000	16,000	16,000	15,000	15,000	16,000
L 12	2 ET AAS	15,400	0,460	0,483	14,800	15,900	15,400	14,900	15,800	15,600
L 13	13 ICP OES	15,867	0,961	1,008	14,800	17,400	15,900	15,100	15,500	16,500
L 14	14 ICP OES	16,000	0,583	0,612	16,500	15,600	15,500	16,800	16,200	15,400
L 15	15 INAA	16,152	0,344	0,361	16,220	16,520	15,930	15,640	16,080	16,520
L 16	10 ICP OES	16,333	2,944	3,089	19,000	19,000	19,000	14,000	13,000	14,000
L 17	16 ID-TIMS	16,498	0,514	0,540	16,250	17,120	16,040	17,190	16,230	16,160
L 18	10 photometry	16,667	1,862	1,954	15,000	15,000	15,000	18,000	18,000	19,000
L 19	3 ET AAS	16,830	1,042	1,093	16,810	16,510	16,810	18,410	15,200	17,240
L 20	23 ICP OES	16,833	2,994	3,142	15,000	15,000	22,000	19,000	15,000	15,000
L 21	11 ICP OES	16,867	1,707	1,792	16,600	16,100	15,700	19,000	18,900	14,900

Range [min..max]	[9,800 .. 22,000]
	Case of No Pooling
Mean of means	15,194
95% H.W. Confidence Interval	0,662
95% H.W. Tolerance Interval	3,963
	Case of Pooling
Mean of All	15,207
95% H.W. Confidence Interval	0,372
95% H.W. Tolerance Interval	4,539

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

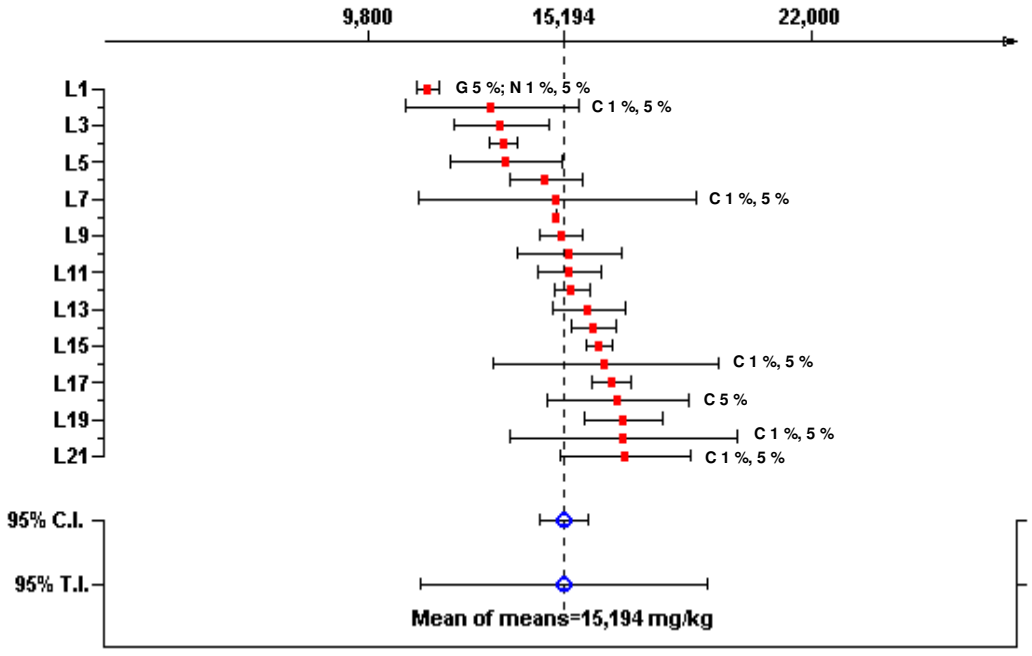


Table7h1: Copper (II) oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	7c ICP OES	98,000	1,549	1,626	98,000	99,000	99,000	99,000	95,000	98,000
L 2	7b ICP OES	98,833	1,602	1,681	99,000	100,000	101,000	99,000	97,000	97,000
L 3	20 ICP OES	99,728	2,711	2,845	98,900	96,050	97,780	100,850	101,120	103,670
L 4	24 F AAS	101,000	3,162	3,319	105,000	101,000	104,000	101,000	98,000	97,000
L 5	11 ICP OES	102,550	1,186	1,245	102,500	101,300	103,300	104,500	102,100	101,600
L 6	2 ET AAS	105,167	6,555	6,879	100,000	107,000	100,000	101,000	117,000	106,000
L 7	13 ICP OES	106,833	2,401	2,520	109,000	108,000	107,000	103,000	105,000	109,000
L 8	10 ICP OES	107,333	7,891	8,281	104,000	100,000	98,000	113,000	111,000	118,000
L 9	3 ICP OES	110,433	3,778	3,964	114,700	111,700	114,500	108,800	107,000	105,900
L 10	1 ICP OES	111,500	5,128	5,382	114,000	118,000	116,000	107,000	108,000	106,000
L 11	18 ET AAS	113,167	0,408	0,428	113,000	113,000	113,000	113,000	113,000	114,000
L 12	23 ICP OES	113,500	5,683	5,964	120,000	118,000	116,000	113,000	105,000	109,000
L 13	4 ICP OES	113,667	3,559	3,735	117,000	107,000	114,000	116,000	115,000	113,000
L 14	21 F AAS	113,685	1,560	1,637	115,700	115,000	111,550	113,590	113,910	112,360
L 15	19 ICP OES	113,750	6,292	10,011	105,000			120,000	115,000	115,000
L 16	14 ICP OES	113,950	4,682	4,913	113,900	110,500	120,900	118,300	109,900	110,200
L 17	6 F AAS	114,117	2,710	2,843	116,200	117,700	112,200	114,700	110,200	113,700
L 18	3 F AAS	115,503	1,184	1,243	114,310	114,380	116,290	116,790	116,630	114,620
L 19	2 F AAS	116,333	0,816	0,857	116,000	116,000	117,000	117,000	117,000	115,000
L 20	3 ICP-MS	116,967	4,452	4,672	118,400	118,500	122,700	111,800	111,400	119,000
L 21	16 ID-TIMS	117,308	0,312	0,328	117,490	116,900	117,650	117,510	116,950	117,350
L 22	22 F AAS	118,500	6,139	6,442	126,400	123,900	121,400	112,700	113,900	112,700
L 23	5 ICP OES	120,333	0,577	1,434	120,000	120,000	121,000			
L 24	10 MAS	120,667	1,633	1,714	122,000	119,000	119,000	121,000	120,000	123,000
L 25	12 ICP OES	122,000	2,683	2,816	121,000	119,000	121,000	122,000	122,000	127,000

Range [min..max]	[95,000 .. 127,000]
	Case of No Pooling
Mean of means	111,393
95% H.W. Confidence Interval	2,931
95% H.W. Tolerance Interval	18,683
	Case of Pooling
Mean of All	111,176
95% H.W. Confidence Interval	1,278
95% H.W. Tolerance Interval	16,971

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

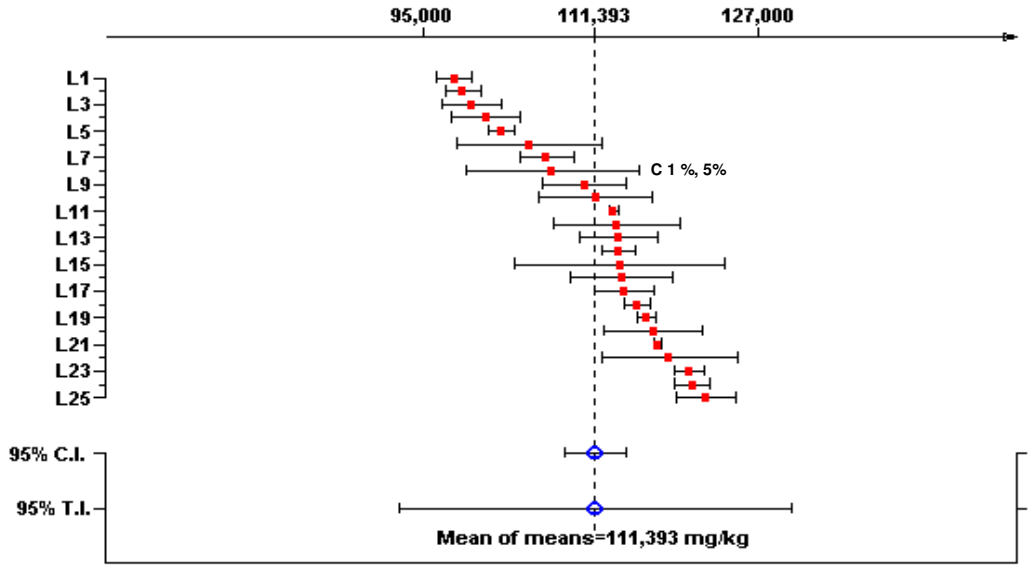


Table7i1: Iron (III) oxide evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	7b ICP OES	373,167	10,534	11,055	389,000	373,000	382,000	362,000	364,000	369,000
L 2	7c ICP OES	386,167	7,653	8,031	393,000	393,000	391,000	374,000	385,000	381,000
L 3	10 ICP OES	393,500	11,589	12,162	406,000	380,000	399,000	398,000	378,000	400,000
L 4	20 ICP OES	395,380	5,529	5,803	389,280	391,690	393,340	402,820	401,630	393,520
L 5	24 MAS	407,667	4,274	4,485	410,000	413,000	405,000	401,000	410,000	407,000
L 6	9 K_0-INAA	410,500	8,666	9,094	423,000	412,000	407,000	405,000	417,000	399,000
L 7	10 MAS	411,333	18,041	18,933	421,000	421,000	421,000	415,000	375,000	415,000
L 8	2 MAS	411,667	2,503	2,627	413,000	411,000	410,000	408,000	415,000	413,000
L 9	6 F AAS	411,883	21,524	22,588	413,500	442,100	400,300	407,200	427,800	380,400
L 10	14 ICP OES	414,167	9,415	9,881	406,200	405,400	428,600	411,100	422,800	410,900
L 11	10 F AAS	416,167	7,414	7,780	422,000	425,000	415,000	413,000	418,000	404,000
L 12	19 ICP OES	417,500	22,305	23,407	415,000	415,000	395,000	405,000	460,000	415,000
L 13	2 F AAS	422,667	3,141	3,296	427,000	421,000	418,000	425,000	423,000	422,000
L 14	4 ICP OES	423,333	5,645	5,924	426,000	415,000	424,000	432,000	421,000	422,000
L 15	3 F AAS	426,225	4,235	4,444	424,390	427,530	425,190	433,810	421,230	425,200
L 16	2 ET AAS	436,333	2,082	5,171	437,000	434,000	438,000			
L 17	21 F AAS	438,462	4,317	4,530	436,120	443,590	442,490	431,780	438,900	437,890
L 18	3 ICP OES	438,883	13,671	14,347	452,800	441,400	457,100	426,800	426,600	428,600
L 19	18 F AAS	447,333	5,428	5,697	450,000	452,000	454,000	442,000	445,000	441,000
L 20	11 ICP OES	448,033	14,832	15,565	462,000	435,400	430,500	440,800	467,200	452,300
L 21	13 ICP OES	450,167	15,728	16,505	424,000	464,000	450,000	462,000	461,000	440,000
L 22	23 ICP OES	453,667	21,049	22,090	448,000	435,000	489,000	469,000	439,000	442,000
L 23	12 ICP OES	460,000	6,325	6,637	460,000	460,000	450,000	460,000	470,000	460,000
L 24	1 ICP OES	495,500	53,817	56,478	501,000	444,000	549,000	546,000	515,000	418,000

Range [min..max]	[362,000 .. 549,000]
	Case of No Pooling
Mean of means	424,571
95% H.W. Confidence Interval	11,327
95% H.W. Tolerance Interval	71,114
	Case of Pooling
Mean of All	424,321
95% H.W. Confidence Interval	5,052
95% H.W. Tolerance Interval	66,246

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

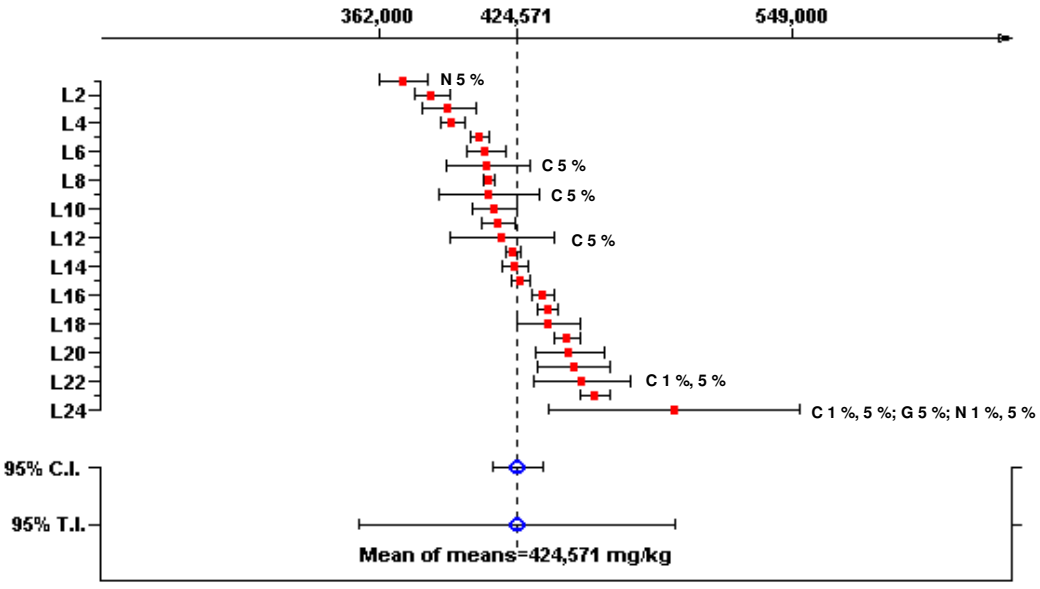


Table 7i2: Iron (III) oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	7b ICP OES	373,167	10,534	11,055	389,000	373,000	382,000	362,000	364,000	369,000
L 2	7c ICP OES	386,167	7,653	8,031	393,000	393,000	391,000	374,000	385,000	381,000
L 3	10 ICP OES	393,500	11,589	12,162	406,000	380,000	399,000	398,000	378,000	400,000
L 4	20 ICP OES	395,380	5,529	5,803	389,280	391,690	393,340	402,820	401,630	393,520
L 5	24 MAS	407,667	4,274	4,485	410,000	413,000	405,000	401,000	410,000	407,000
L 6	9 K_0-INAA	410,500	8,666	9,094	423,000	412,000	407,000	405,000	417,000	399,000
L 7	10 MAS	411,333	18,041	18,933	421,000	421,000	421,000	415,000	375,000	415,000
L 8	2 MAS	411,667	2,503	2,627	413,000	411,000	410,000	408,000	415,000	413,000
L 9	6 F AAS	411,883	21,524	22,588	413,500	442,100	400,300	407,200	427,800	380,400
L 10	14 ICP OES	414,167	9,415	9,881	406,200	405,400	428,600	411,100	422,800	410,900
L 11	10 F AAS	416,167	7,414	7,780	422,000	425,000	415,000	413,000	418,000	404,000
L 12	19 ICP OES	417,500	22,305	23,407	415,000	415,000	395,000	405,000	460,000	415,000
L 13	2 F AAS	422,667	3,141	3,296	427,000	421,000	418,000	425,000	423,000	422,000
L 14	4 ICP OES	423,333	5,645	5,924	426,000	415,000	424,000	432,000	421,000	422,000
L 15	3 F AAS	426,225	4,235	4,444	424,390	427,530	425,190	433,810	421,230	425,200
L 16	2 ET AAS	436,333	2,082	5,171	437,000	434,000	438,000			
L 17	21 F AAS	438,462	4,317	4,530	436,120	443,590	442,490	431,780	438,900	437,890
L 18	3 ICP OES	438,883	13,671	14,347	452,800	441,400	457,100	426,800	426,600	428,600
L 19	18 F AAS	447,333	5,428	5,697	450,000	452,000	454,000	442,000	445,000	441,000
L 20	11 ICP OES	448,033	14,832	15,565	462,000	435,400	430,500	440,800	467,200	452,300
L 21	13 ICP OES	450,167	15,728	16,505	424,000	464,000	450,000	462,000	461,000	440,000
L 22	23 ICP OES	453,667	21,049	22,090	448,000	435,000	489,000	469,000	439,000	442,000
L 23	12 ICP OES	460,000	6,325	6,637	460,000	460,000	450,000	460,000	470,000	460,000

Range [min..max]	[362,000 .. 489,000]
	Case of No Pooling
Mean of means	421,487
95% H.W. Confidence Interval	9,801
95% H.W. Tolerance Interval	60,582
	Case of Pooling
Mean of All	421,157
95% H.W. Confidence Interval	4,228
95% H.W. Tolerance Interval	54,375

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
nedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

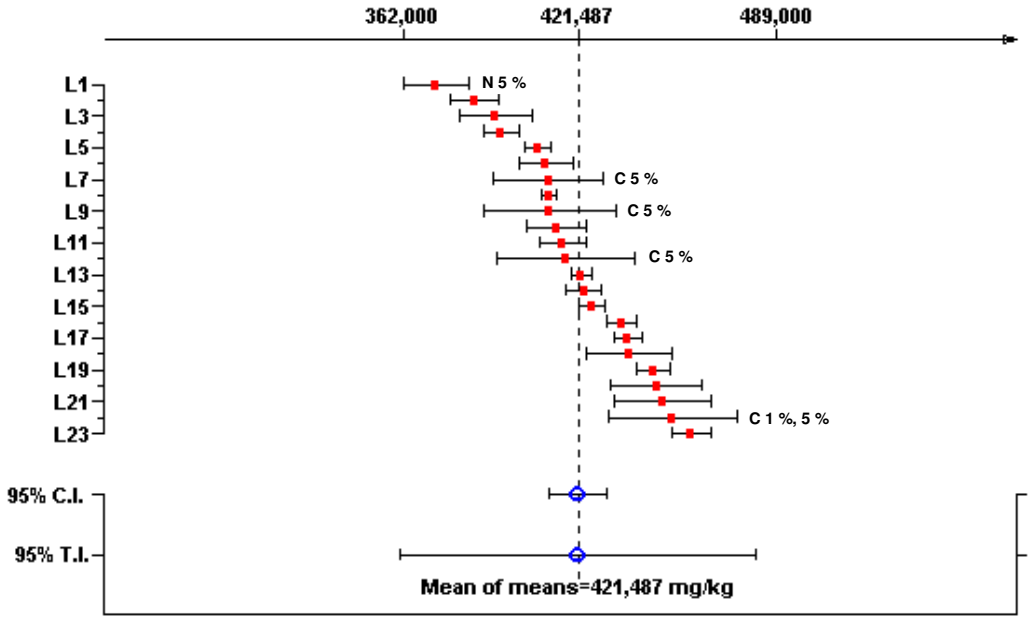


Table 7j1: Manganese (II) oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES	105,000	5,477	5,748	95,000	105,000	110,000	110,000	105,000	105,000
L 2	24 F AAS	107,167	5,269	5,530	109,000	101,000	111,000	100,000	110,000	112,000
L 3	7b ICP OES	108,500	1,871	1,963	106,000	107,000	108,000	109,000	110,000	111,000
L 4	10 ICP OES	109,500	1,871	1,963	112,000	111,000	108,000	107,000	109,000	110,000
L 5	7c ICP OES	110,167	1,835	1,926	109,000	113,000	111,000	108,000	109,000	111,000
L 6	10 MAS	111,667	10,270	10,777	119,000	119,000	116,000	119,000	98,000	99,000
L 7	5 ICP OES	113,000	1,000	2,484	112,000	114,000	113,000			
L 8	20 ICP OES	115,382	2,546	2,671	114,940	110,500	116,080	116,220	117,190	117,360
L 9	10 F AAS	118,500	3,271	3,433	118,000	116,000	114,000	119,000	123,000	121,000
L 10	2 ET AAS	120,167	7,935	8,327	112,000	113,000	116,000	131,000	121,000	128,000
L 11	23 ICP OES	122,833	1,941	2,037	121,000	120,000	124,000	125,000	123,000	124,000
L 12	11 ICP OES	123,517	14,785	15,516	115,200	113,100	110,700	143,800	140,900	117,400
L 13	13 ICP OES	124,000	3,347	3,512	121,000	121,000	129,000	122,000	127,000	124,000
L 14	4 ICP OES	127,167	1,941	2,037	130,000	125,000	128,000	128,000	125,000	127,000
L 15	17 XRF	127,567	8,110	8,511	123,100	131,600	118,800	135,300	137,100	119,500
L 16	21 F AAS	128,745	0,945	0,991	129,330	129,940	129,240	128,640	127,860	127,460
L 17	9 K_0-INAA	129,167	2,714	2,848	132,000	128,000	128,000	128,000	126,000	133,000
L 18	14 ICP OES	129,183	3,575	3,751	129,000	127,000	127,400	135,400	125,400	130,900
L 19	12 ICP OES	130,833	0,408	0,428	131,000	131,000	131,000	131,000	130,000	131,000
L 20	6 F AAS	132,250	3,804	3,992	131,500	133,000	136,800	136,100	128,500	127,600
L 21	2 F AAS	132,333	0,816	0,857	132,000	133,000	131,000	133,000	133,000	132,000
L 22	3 ICP-MS	133,217	1,728	1,813	130,400	133,000	133,000	134,300	135,600	133,000
L 23	18 F AAS	136,000	2,757	2,893	134,000	135,000	138,000	132,000	138,000	139,000
L 24	1 ICP OES	145,333	0,816	0,857	145,000	145,000	144,000	146,000	146,000	146,000
L 25	3 F AAS	148,678	5,339	5,603	153,270	153,830	153,480	144,050	144,510	142,930

Range [min..max]	[95,000 .. 153,830]
	Case of No Pooling
Mean of means	123,595
95% H.W. Confidence Interval	4,805
95% H.W. Tolerance Interval	30,627
	Case of Pooling
Mean of All	123,811
95% H.W. Confidence Interval	2,016
95% H.W. Tolerance Interval	26,935

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

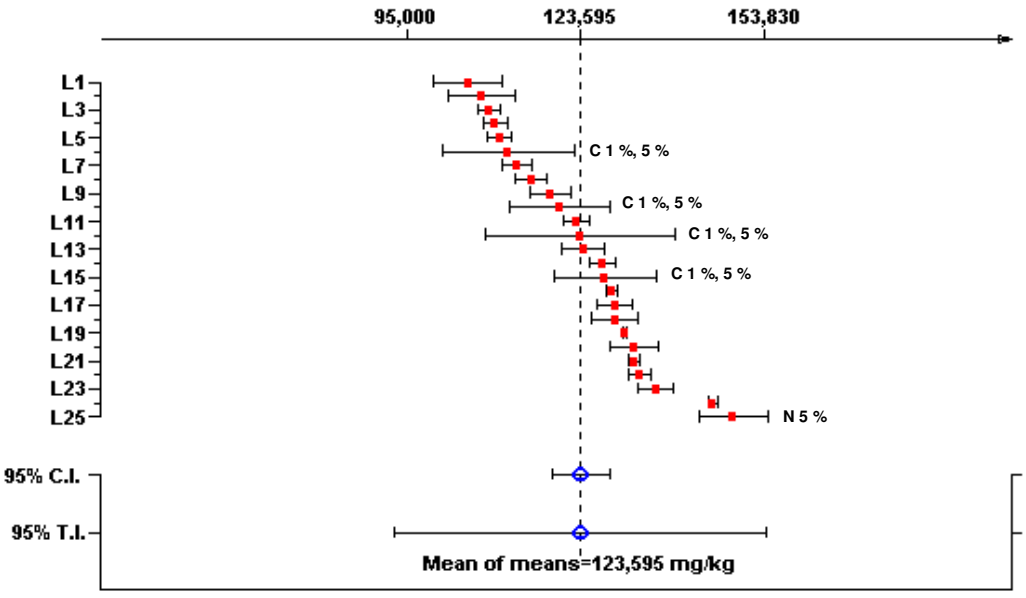


Table 7k1: Molybdenum (VI) oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	10 ICP OES	302,000	5,899	6,191	295,000	302,000	308,000	308,000	295,000	304,000
L 2	7b ICP OES	314,667	5,750	6,035	310,000	309,000	313,000	316,000	325,000	315,000
L 3	7c ICP OES	327,167	5,947	6,241	324,000	338,000	328,000	321,000	328,000	324,000
L 4	4 ICP OES	332,000	6,197	6,503	338,000	333,000	333,000	333,000	320,000	335,000
L 5	9 K_0-INAA	332,333	4,367	4,582	338,000	325,000	331,000	333,000	335,000	332,000
L 6	13 ICP OES	332,833	8,998	9,443	325,000	330,000	344,000	344,000	324,000	330,000
L 7	21 F AAS	337,830	5,554	5,829	347,720	336,830	332,290	336,490	333,590	340,060
L 8	23 ICP OES	344,167	9,867	10,355	342,000	332,000	341,000	360,000	339,000	351,000
L 9	14 ICP OES	353,800	6,920	7,262	343,600	354,200	348,200	355,200	359,400	362,200
L 10	5 ICP OES	354,000	1,732	4,303	353,000	353,000	356,000			
L 11	3 ICP-MS	354,600	9,327	9,788	351,100	346,600	345,100	366,100	366,100	352,600
L 12	3 ICP OES	361,667	10,637	11,163	350,400	352,700	359,200	363,500	364,000	380,200
L 13	11 ICP OES	367,483	7,997	8,392	368,600	360,000	356,000	377,400	372,100	370,800
L 14	12 ICP-MS	385,000	17,607	18,477	390,000	410,000	400,000	370,000	370,000	370,000

Range [min..max]	[295,000 .. 410,000]
	Case of No Pooling
Mean of means	342,825
95% H.W. Confidence Interval	12,593
95% H.W. Tolerance Interval	65,695
	Case of Pooling
Mean of All	342,411
95% H.W. Confidence Interval	5,047
95% H.W. Tolerance Interval	51,811

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

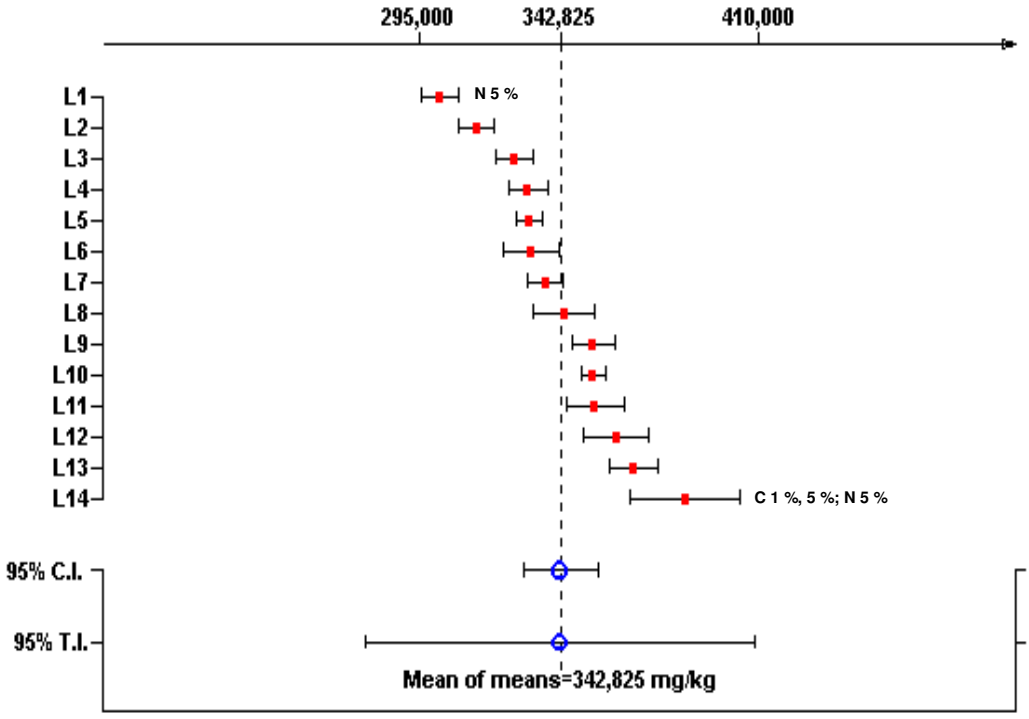


Table7l1: Nickel (II) oxide evaluation in run 1 (values in mg/kg)

Current Lab. number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	24 F AAS	51,000	2,966	3,113	48,000	50,000	49,000	50,000	53,000	56,000
L 2	7c ICP OES	52,667	1,211	1,271	54,000	53,000	52,000	51,000	52,000	54,000
L 3	7b ICP OES	53,500	1,517	1,592	51,000	53,000	53,000	54,000	55,000	55,000
L 4	10 MAS	54,333	2,875	3,017	50,000	55,000	52,000	55,000	56,000	58,000
L 5	10 ICP OES	55,500	1,975	2,072	59,000	56,000	53,000	55,000	55,000	55,000
L 6	20 ICP OES	56,155	1,754	1,841	54,290	53,830	57,200	56,810	56,430	58,370
L 7	23 ICP OES	56,333	3,559	3,735	55,000	53,000	56,000	59,000	62,000	53,000
L 8	3 ICP OES	58,050	3,200	3,359	55,200	55,400	54,900	61,800	60,700	60,300
L 9	22 F AAS	58,117	2,074	2,177	57,300	56,000	58,500	59,800	56,000	61,100
L 10	1 ICP OES	58,317	2,878	3,021	57,900	59,200	61,100	54,500	55,600	61,600
L 11	2 ET AAS	58,583	2,386	2,504	55,400	57,500	58,400	59,000	58,500	62,700
L 12	21 F AAS	58,647	0,700	0,735	58,670	58,390	57,400	59,270	58,880	59,270
L 13	5 ICP OES	60,000	1,000	2,484	61,000	60,000	59,000			
L 14	12 ICP-MS	61,167	0,753	0,790	61,000	62,000	62,000	61,000	60,000	61,000
L 15	3 F AAS	61,223	1,327	1,393	60,290	61,460	63,670	60,210	61,400	60,310
L 16	14 ICP OES	62,083	3,215	3,374	62,400	61,000	65,800	60,900	57,100	65,300
L 17	13 ICP OES	62,667	4,590	4,817	66,000	70,000	61,000	57,000	61,000	61,000
L 18	6 F AAS	62,683	3,213	3,372	63,600	67,200	63,600	63,100	61,100	57,500
L 19	4 ICP OES	63,333	1,211	1,271	64,000	63,000	64,000	64,000	61,000	64,000
L 20	11 ICP OES	63,350	6,012	6,309	63,800	74,600	62,700	57,400	62,400	59,200
L 21	18 ET AAS	65,200	0,358	0,375	65,000	65,700	64,900	65,100	65,600	64,900
L 22	2 F AAS	65,200	1,086	1,140	63,800	66,200	66,500	64,600	65,700	64,400
L 23	19 ICP OES	70,833	4,916	5,159	75,000	65,000	65,000	75,000	70,000	75,000

Range [min..max]	[48,000 .. 75,000]
	Case of No Pooling
Mean of means	59,519
95% H.W. Confidence Interval	2,023
95% H.W. Tolerance Interval	12,506
	Case of Pooling
Mean of All	59,509
95% H.W. Confidence Interval	0,903
95% H.W. Tolerance Interval	11,617

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

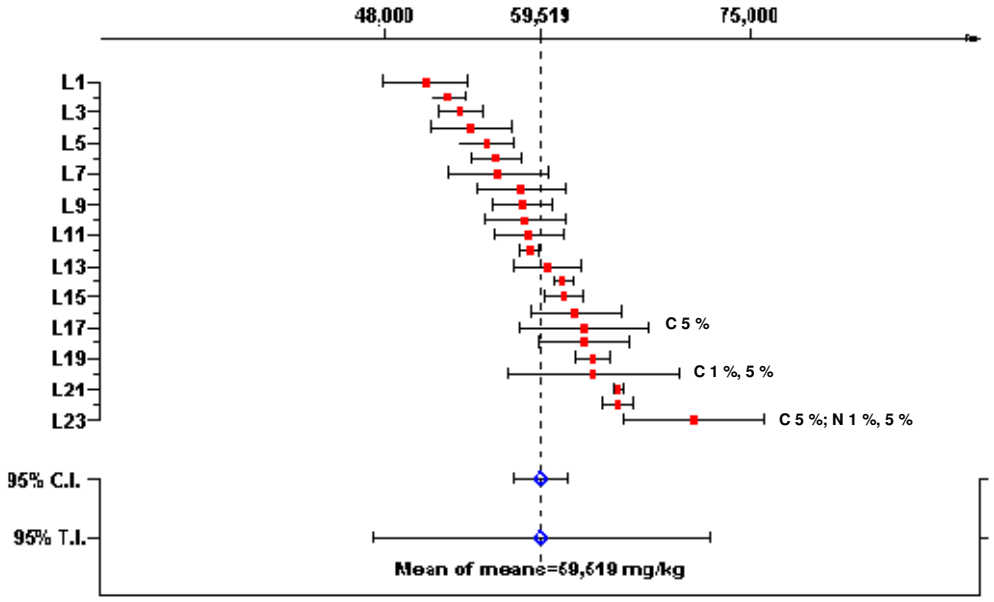


Table7l2: Nickel (II) oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	24 F AAS	51,000	2,966	3,113	48,000	50,000	49,000	50,000	53,000	56,000
L 2	7c ICP OES	52,667	1,211	1,271	54,000	53,000	52,000	51,000	52,000	54,000
L 3	7b ICP OES	53,500	1,517	1,592	51,000	53,000	53,000	54,000	55,000	55,000
L 4	10 MAS	54,333	2,875	3,017	50,000	55,000	52,000	55,000	56,000	58,000
L 5	10 ICP OES	55,500	1,975	2,072	59,000	56,000	53,000	55,000	55,000	55,000
L 6	20 ICP OES	56,155	1,754	1,841	54,290	53,830	57,200	56,810	56,430	58,370
L 7	23 ICP OES	56,333	3,559	3,735	55,000	53,000	56,000	59,000	62,000	53,000
L 8	3 ICP OES	58,050	3,200	3,359	55,200	55,400	54,900	61,800	60,700	60,300
L 9	22 F AAS	58,117	2,074	2,177	57,300	56,000	58,500	59,800	56,000	61,100
L 10	1 ICP OES	58,317	2,878	3,021	57,900	59,200	61,100	54,500	55,600	61,600
L 11	2 ET AAS	58,583	2,386	2,504	55,400	57,500	58,400	59,000	58,500	62,700
L 12	21 F AAS	58,647	0,700	0,735	58,670	58,390	57,400	59,270	58,880	59,270
L 13	5 ICP OES	60,000	1,000	2,484	61,000	60,000	59,000			
L 14	12 ICP-MS	61,167	0,753	0,790	61,000	62,000	62,000	61,000	60,000	61,000
L 15	3 F AAS	61,223	1,327	1,393	60,290	61,460	63,670	60,210	61,400	60,310
L 16	14 ICP OES	62,083	3,215	3,374	62,400	61,000	65,800	60,900	57,100	65,300
L 17	13 ICP OES	62,667	4,590	4,817	66,000	70,000	61,000	57,000	61,000	61,000
L 18	6 F AAS	62,683	3,213	3,372	63,600	67,200	63,600	63,100	61,100	57,500
L 19	4 ICP OES	63,333	1,211	1,271	64,000	63,000	64,000	64,000	61,000	64,000
L 20	11 ICP OES	63,350	6,012	6,309	63,800	74,600	62,700	57,400	62,400	59,200
L 21	18 ET AAS	65,200	0,358	0,375	65,000	65,700	64,900	65,100	65,600	64,900
L 22	2 F AAS	65,200	1,086	1,140	63,800	66,200	66,500	64,600	65,700	64,400

Range [min..max]	[48,000 .. 74,600]
	Case of No Pooling
Mean of means	59,005
95% H.W. Confidence Interval	1,804
95% H.W. Tolerance Interval	10,975
	Case of Pooling
Mean of All	58,982
95% H.W. Confidence Interval	0,822
95% H.W. Tolerance Interval	10,354

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

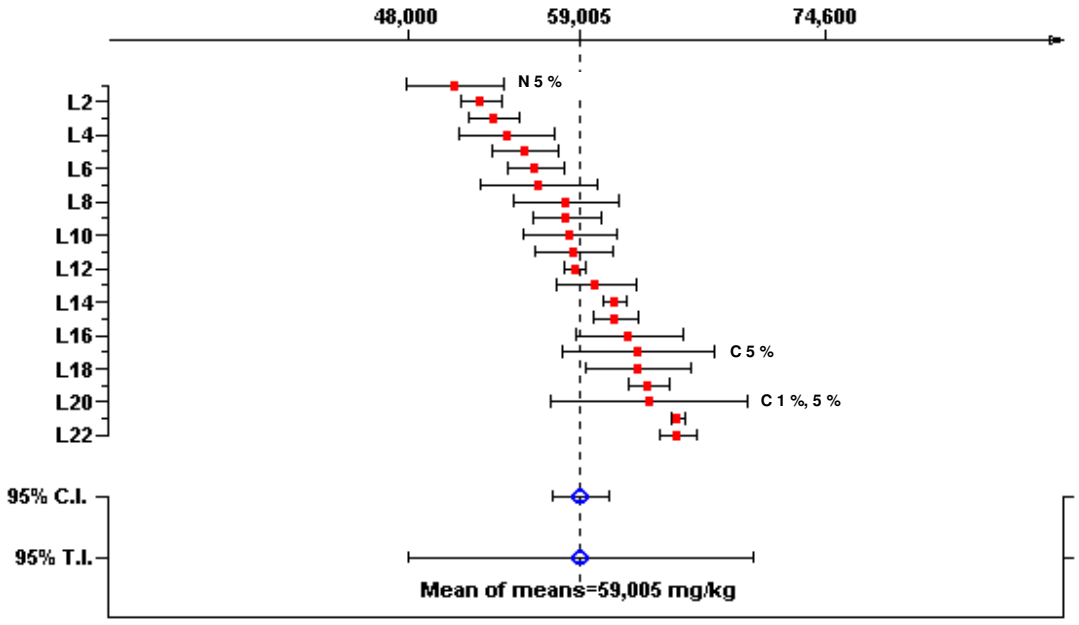


Table7m1: Lead (II) oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES	169,167	11,583	12,156	165,000	160,000	170,000	185,000	155,000	180,000
L 2	20 ICP OES	174,817	3,086	3,239	173,410	170,070	176,220	175,010	179,410	174,780
L 3	7c ICP OES	178,333	3,141	3,296	182,000	180,000	174,000	175,000	179,000	180,000
L 4	1 ICP OES	182,333	3,830	4,019	180,000	180,000	181,000	182,000	181,000	190,000
L 5	7b ICP OES	185,167	4,401	4,618	181,000	181,000	183,000	185,000	191,000	190,000
L 6	6 F AAS	189,400	3,866	4,057	185,900	187,900	185,500	192,400	189,300	195,400
L 7	11 ICP OES	192,317	1,957	2,054	193,900	193,200	194,700	191,000	191,600	189,500
L 8	24 F AAS	196,167	5,742	6,025	203,000	201,000	196,000	197,000	193,000	187,000
L 9	5 ICP OES	197,000	1,732	4,303	198,000	195,000	198,000			
L 10	23 ICP OES	199,833	12,254	12,860	212,000	208,000	211,000	193,000	182,000	193,000
L 11	18 ET AAS	200,333	0,516	0,542	200,000	200,000	201,000	200,000	200,000	201,000
L 12	22 F AAS	200,533	3,695	3,877	204,700	202,500	197,100	201,400	202,500	195,000
L 13	14 ICP OES	201,100	5,452	5,722	207,900	205,300	192,900	199,700	203,100	197,700
L 14	10 F AAS	202,500	8,385	8,799	219,000	197,000	199,000	197,000	200,000	203,000
L 15	4 ICP OES	204,833	2,041	2,142	205,000	206,000	204,000	208,000	204,000	202,000
L 16	13 ICP OES	209,167	8,280	8,690	215,000	214,000	203,000	195,000	214,000	214,000
L 17	16 ID-TIMS	214,533	0,431	0,453	214,530	214,230	214,690	215,290	214,060	214,400
L 18	3 ICP-MS	215,242	2,568	2,695	212,220	213,780	218,790	213,240	217,340	216,080
L 19	17 XRF	216,017	6,909	7,251	211,300	213,300	228,000	220,100	214,100	209,300
L 20	21 F AAS	217,205	1,538	1,614	216,870	219,200	218,220	218,000	215,320	215,620
L 21	2 ET AAS	219,500	26,387	27,692	199,000	197,000	202,000	248,000	214,000	257,000
L 22	12 F AAS	220,500	9,138	9,590	223,000	217,000	223,000	234,000	220,000	206,000
L 23	3 ICP OES	221,083	9,899	10,388	213,900	215,300	211,400	221,400	226,700	237,800
L 24	2 F AAS	222,000	3,225	3,384	220,000	221,000	219,000	228,000	221,000	223,000

Range [min..max]	[155,000 .. 257,000]
	Case of No Pooling
Mean of means	201,212
95% H.W. Confidence Interval	6,581
95% H.W. Tolerance Interval	41,316
	Case of Pooling
Mean of All	201,301
95% H.W. Confidence Interval	2,852
95% H.W. Tolerance Interval	37,395

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

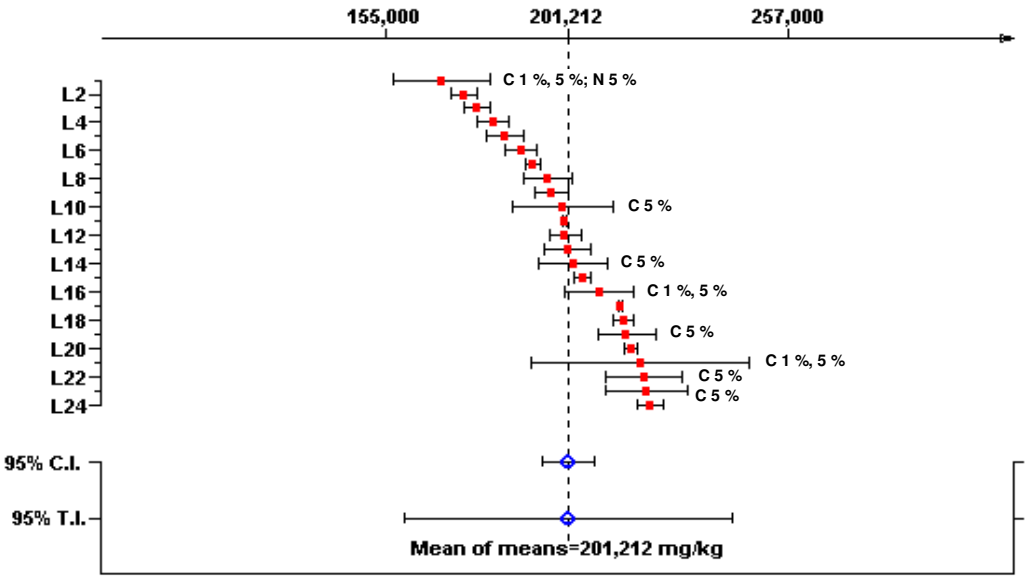


Table7n1: Antimony (III) oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	24 F AAS	105,000	8,626	9,052	114,000	101,000	90,000	110,000	110,000	105,000
L 2	19 ICP OES	115,833	5,845	6,134	110,000	115,000	115,000	125,000	110,000	120,000
L 3	5 ICP OES	121,333	1,528	3,795	121,000	123,000	120,000			
L 4	21 F AAS	121,458	4,927	5,170	116,950	116,690	118,110	127,340	127,040	122,620
L 5	10 ICP OES	123,333	2,251	2,362	122,000	123,000	122,000	127,000	121,000	125,000
L 6	11 ICP OES	123,550	4,070	4,271	121,200	120,100	120,000	128,800	128,500	122,700
L 7	10 F AAS	125,667	3,830	4,019	124,000	122,000	126,000	133,000	125,000	124,000
L 8	7a ICP OES	127,500	8,456	8,874	119,000	120,000	121,000	138,000	135,000	132,000
L 9	9 K_0-INAA	127,833	1,602	1,681	129,000	125,000	127,000	129,000	129,000	128,000
L 10	1 ICP OES	129,167	3,061	3,212	127,000	127,000	130,000	134,000	131,000	126,000
L 11	15 INAA	132,050	1,388	1,457	134,200	132,400	131,200	131,800	130,100	132,600
L 12	18 ET AAS	132,667	1,033	1,084	134,000	133,000	133,000	133,000	132,000	131,000
L 13	14 ICP OES	137,333	2,966	3,112	136,500	133,400	137,600	140,500	140,900	135,100
L 14	13 HG AAS	138,000	2,098	2,201	135,000	139,000	139,000	137,000	141,000	137,000
L 15	2 FI-HG AAS	138,333	5,125	5,378	137,000	134,000	138,000	147,000	133,000	141,000
L 16	3 HG AAS	140,080	1,582	1,660	141,810	137,510	141,550	140,250	140,130	139,230
L 17	4 FI-HG AAS	148,333	3,882	4,073	151,000	150,000	141,000	147,000	150,000	151,000
L 18	12 ICP-MS	148,833	1,835	1,926	148,000	148,000	146,000	150,000	150,000	151,000
L 19	3 ICP OES	157,042	8,166	8,570	146,410	149,400	156,220	158,260	165,800	166,160

Range [min..max]	[90,000 .. 166,160]
	Case of No Pooling
Mean of means	131,229
95% H.W. Confidence Interval	5,994
95% H.W. Tolerance Interval	34,622
	Case of Pooling
Mean of All	131,496
95% H.W. Confidence Interval	2,427
95% H.W. Tolerance Interval	28,606

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

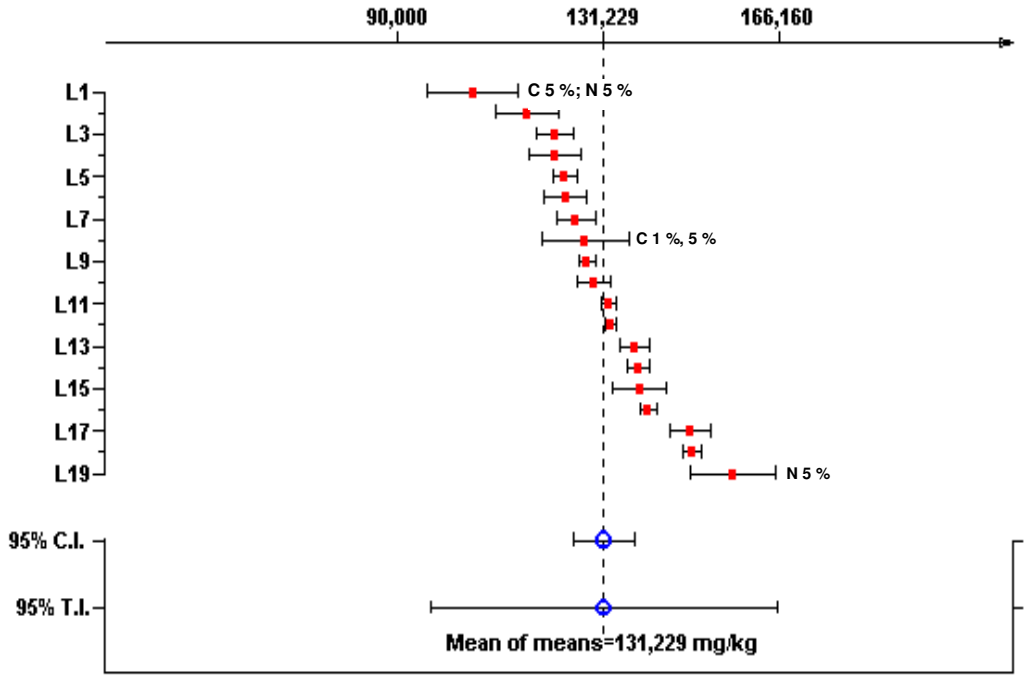


Table7o1: Selenium evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 ICP OES	17,000	2,000	4,968	15,000	19,000	17,000			
L 2	4 FI-HG AAS	17,433	0,137	0,143	17,400	17,500	17,200	17,600	17,400	17,500
L 3	12 ICP-MS	18,667	0,816	0,857	19,000	19,000	18,000	18,000	18,000	20,000
L 4	2 FI-HG AAS	18,850	1,751	1,838	22,200	17,700	19,100	17,400	18,600	18,100
L 5	18 FI-HG AAS	19,317	0,515	0,541	19,600	19,500	19,900	19,500	18,500	18,900
L 6	8 ICP OES	19,410	1,045	1,097	17,770	20,520	19,640	20,260	19,690	18,580
L 7	21 ET AAS	19,593	0,218	0,228	19,650	19,690	19,620	19,890	19,460	19,250
L 8	3 HG AAS	20,165	1,024	1,074	21,520	19,500	19,160	21,400	19,670	19,740
L 9	15 INAA	20,600	0,335	0,351	21,100	20,900	20,400	20,300	20,300	20,600
L 10	13 HG AAS	20,733	0,550	0,577	20,200	20,000	20,900	21,500	20,800	21,000
L 11	14 ICP OES	20,833	1,401	1,470	20,600	22,800	19,100	22,000	20,900	19,600
L 12	9 K_0-INAA	21,167	0,308	0,323	20,800	21,000	21,100	21,100	21,700	21,300
L 13	11 ICP OES	21,217	3,012	3,160	25,800	23,300	22,000	19,300	18,000	18,900
L 14	19 ICP OES	28,333	2,887	7,171		30,000	30,000		25,000	

Range [min..max]	[15,000 .. 30,000]
	Case of No Pooling
Mean of means	20,237
95% H.W. Confidence Interval	1,543
95% H.W. Tolerance Interval	8,047
	Case of Pooling
Mean of All	20,050
95% H.W. Confidence Interval	539
95% H.W. Tolerance Interval	5,439

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

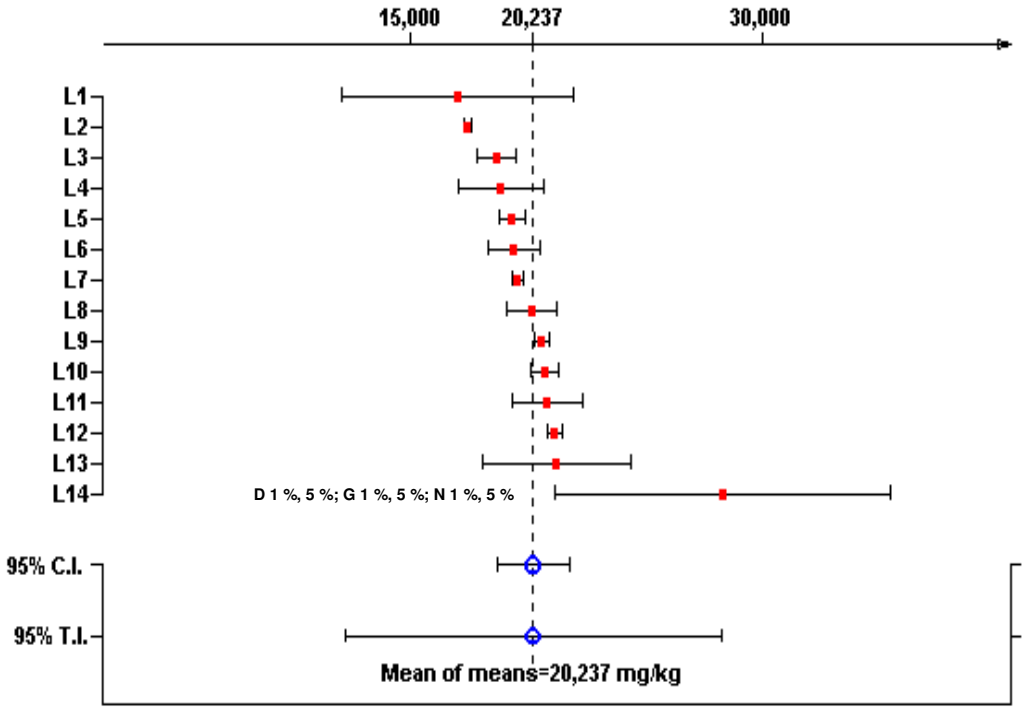


Table7o2: Selenium run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 ICP OES	17,000	2,000	4,968	15,000	19,000	17,000			
L 2	4 FI-HG AAS	17,433	0,137	0,143	17,400	17,500	17,200	17,600	17,400	17,500
L 3	12 ICP-MS	18,667	0,816	0,857	19,000	19,000	18,000	18,000	18,000	20,000
L 4	2 FI-HG AAS	18,850	1,751	1,838	22,200	17,700	19,100	17,400	18,600	18,100
L 5	18 FI-HG AAS	19,317	0,515	0,541	19,600	19,500	19,900	19,500	18,500	18,900
L 6	8 ICP OES	19,410	1,045	1,097	17,770	20,520	19,640	20,260	19,690	18,580
L 7	21 ET AAS	19,593	0,218	0,228	19,650	19,690	19,620	19,890	19,460	19,250
L 8	3 HG AAS	20,165	1,024	1,074	21,520	19,500	19,160	21,400	19,670	19,740
L 9	15 INAA	20,600	0,335	0,351	21,100	20,900	20,400	20,300	20,300	20,600
L 10	13 HG AAS	20,733	0,550	0,577	20,200	20,000	20,900	21,500	20,800	21,000
L 11	14 ICP OES	20,833	1,401	1,470	20,600	22,800	19,100	22,000	20,900	19,600
L 12	9 K_0-INAA	21,167	0,308	0,323	20,800	21,000	21,100	21,100	21,700	21,300
L 13	11 ICP OES	21,217	3,012	3,160	25,800	23,300	22,000	19,300	18,000	18,900

Range [min..max]	[15,000 .. 25,800]
	Case of No Pooling
Mean of means	19,614
95% H.W. Confidence Interval	0,822
95% H.W. Tolerance Interval	4,190
	Case of Pooling
Mean of All	19,719
95% H.W. Confidence Interval	0,386
95% H.W. Tolerance Interval	3,836

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

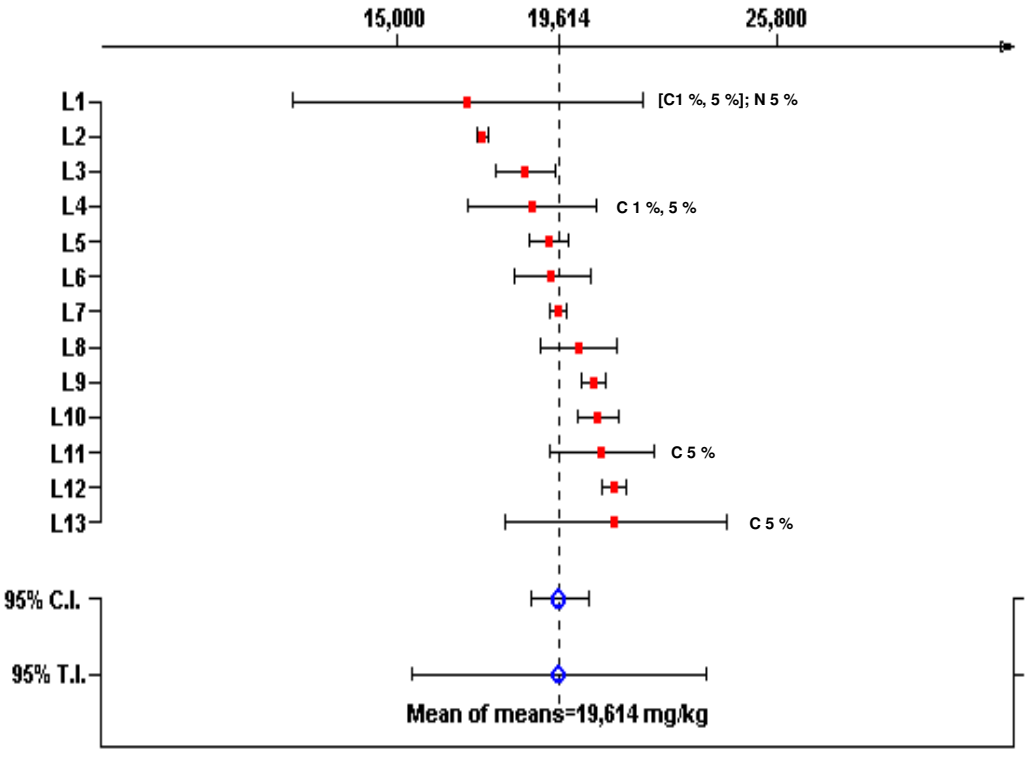


Table7p1: Tin (IV) oxide evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 ICP OES	64,000	6,083	15,110	68,000	67,000	57,000			
L 2	4 ICP OES	76,333	1,862	1,954	74,000	78,000	75,000	75,000	78,000	78,000
L 3	10 ICP OES	85,333	5,922	6,214	76,000	84,000	93,000	83,000	86,000	90,000
L 4	7b ICP OES	91,800	2,049	2,545	90,000	94,000	91,000		94,000	90,000
L 5	1 ICP OES	94,333	4,051	4,251	89,000	94,300	89,900	97,300	98,700	96,800
L 6	7c ICP OES	94,833	4,119	4,323	94,000	95,000	102,000	90,000	92,000	96,000
L 7	14 ICP OES	95,317	3,024	3,173	90,100	98,700	94,800	97,500	96,400	94,400
L 8	9 K_0-INAA	100,767	10,357	10,869	91,900	110,000	86,800	99,900	114,000	102,000
L 9	18 ET AAS	101,000	0,632	0,664	101,000	102,000	101,000	100,000	101,000	101,000
L 10	2 ET AAS	102,000	4,858	5,098	102,000	96,000	98,000	103,000	103,000	110,000
L 11	21 F AAS	102,967	1,234	1,295	102,380	102,590	101,060	104,070	104,450	103,250
L 12	12 ICP-MS	107,000	1,095	1,150	107,000	109,000	107,000	106,000	106,000	107,000
L 13	3 ICP-MS	107,777	3,826	4,015	103,750	108,230	102,500	109,460	111,810	110,910
L 14	3 ICP OES	113,835	5,629	5,907	104,710	111,480	114,950	113,590	116,690	121,590
L 15	23 ICP OES	120,000	9,381	9,845	112,000	131,000	114,000	127,000	127,000	109,000

Range [min..max]	[57,000 .. 131,000]
	Case of No Pooling
Mean of means	97,153
95% H.W. Confidence Interval	7,850
95% H.W. Tolerance Interval	41,872
	Case of Pooling
Mean of All	98,372
95% H.W. Confidence Interval	2,873
95% H.W. Tolerance Interval	30,269

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

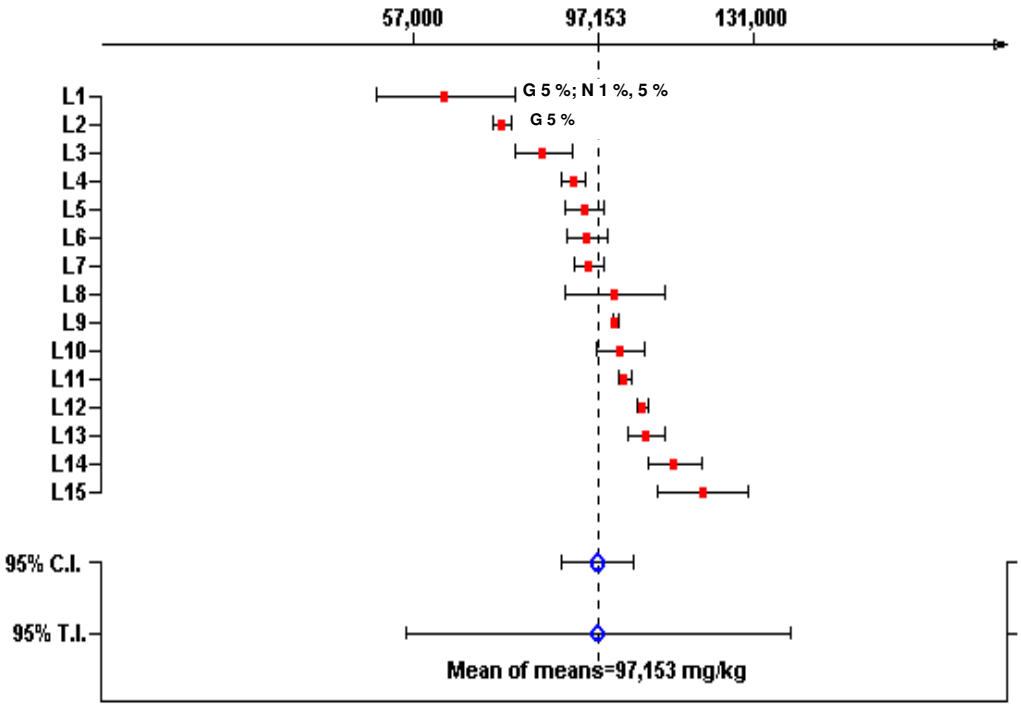


Table7p2: Tin (IV) oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	4 ICP OES	76,333	1,862	1,954	74,000	78,000	75,000	75,000	78,000	78,000
L 2	10 ICP OES	85,333	5,922	6,214	76,000	84,000	93,000	83,000	86,000	90,000
L 3	7b ICP OES	91,800	2,049	2,545	90,000	94,000	91,000		94,000	90,000
L 4	1 ICP OES	94,333	4,051	4,251	89,000	94,300	89,900	97,300	98,700	96,800
L 5	7c ICP OES	94,833	4,119	4,323	94,000	95,000	102,000	90,000	92,000	96,000
L 6	14 ICP OES	95,317	3,024	3,173	90,100	98,700	94,800	97,500	96,400	94,400
L 7	9 K_0-INAA	100,767	10,357	10,869	91,900	110,000	86,800	99,900	114,000	102,000
L 8	18 ET AAS	101,000	0,632	0,664	101,000	102,000	101,000	100,000	101,000	101,000
L 9	2 ET AAS	102,000	4,858	5,098	102,000	96,000	98,000	103,000	103,000	110,000
L 10	21 F AAS	102,967	1,234	1,295	102,380	102,590	101,060	104,070	104,450	103,250
L 11	12 ICP-MS	107,000	1,095	1,150	107,000	109,000	107,000	106,000	106,000	107,000
L 12	3 ICP-MS	107,777	3,826	4,015	103,750	108,230	102,500	109,460	111,810	110,910
L 13	3 ICP OES	113,835	5,629	5,907	104,710	111,480	114,950	113,590	116,690	121,590
L 14	23 ICP OES	120,000	9,381	9,845	112,000	131,000	114,000	127,000	127,000	109,000

Range [min..max]	[74,000 .. 131,000]
	Case of No Pooling
Mean of means	99,521
95% H.W. Confidence Interval	6,476
95% H.W. Tolerance Interval	33,781
	Case of Pooling
Mean of All	99,614
95% H.W. Confidence Interval	2,588
95% H.W. Tolerance Interval	26,845

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

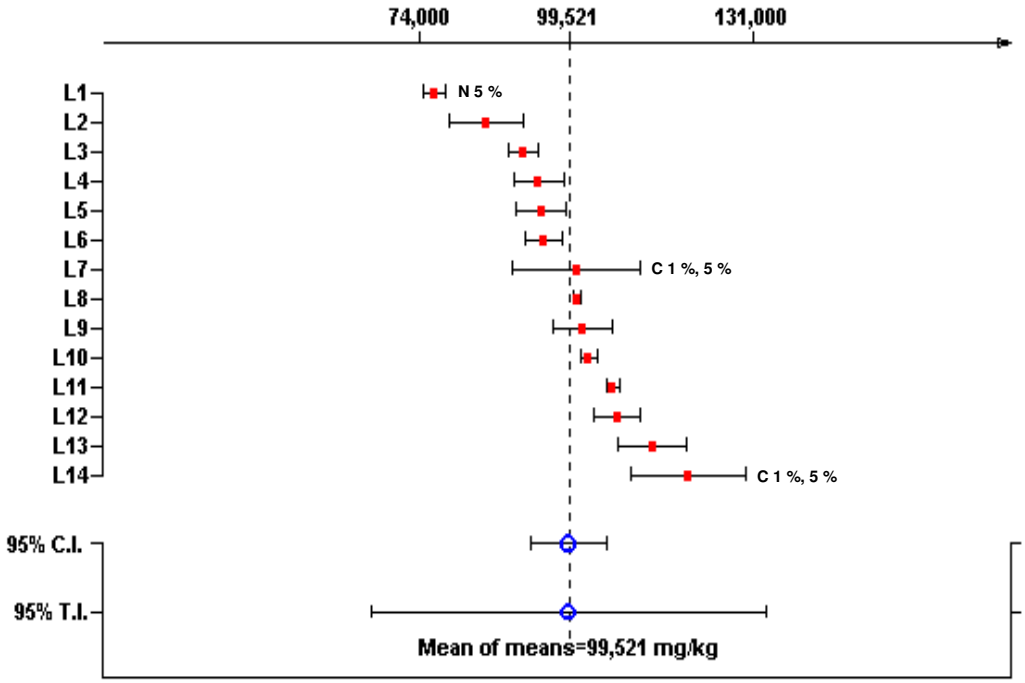


Table7q1: Sulfur trioxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	10 comb.-IR	1834	16	17	1853	1838	1813	1823	1849	1825
L 2	7c ICP OES	1848	7	17	1856	1843	1846			
L 3	11 comb.	1867	37	38	1824	1819	1897	1878	1903	1883
L 4	8 ICP OES	1883	77	81	1861	1754	1895	1978	1872	1940
L 5	21 comb.-IR	1927	12	12	1918	1916	1918	1942	1941	1929
L 6	7b ICP OES	1933	21	51	1953	1935	1912			
L 7	14 ICP OES	1983	94	99	1923	1907	1920	1941	2119	2086
L 8	3 titrimetry	2001	61	64	2095	1982	2045	1970	1920	1995
L 9	13 ICP OES	2004	79	83	1933	2075	1908	2058	1960	2090
L 10	2 gravimetry	2012	49	51	1966	2057	2027	1996	2073	1953
L 11	13 comb.	2061	39	41	2130	2040	2040	2030	2085	2038

Range [min..max]	[1754 .. 2130]
	Case of No Pooling
Mean of means	1941
95% H.W. Confidence Interval	51
95% H.W. Tolerance Interval	248
	Case of Pooling
Mean of All	1946
95% H.W. Confidence Interval	23
95% H.W. Tolerance Interval	209

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations:
C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

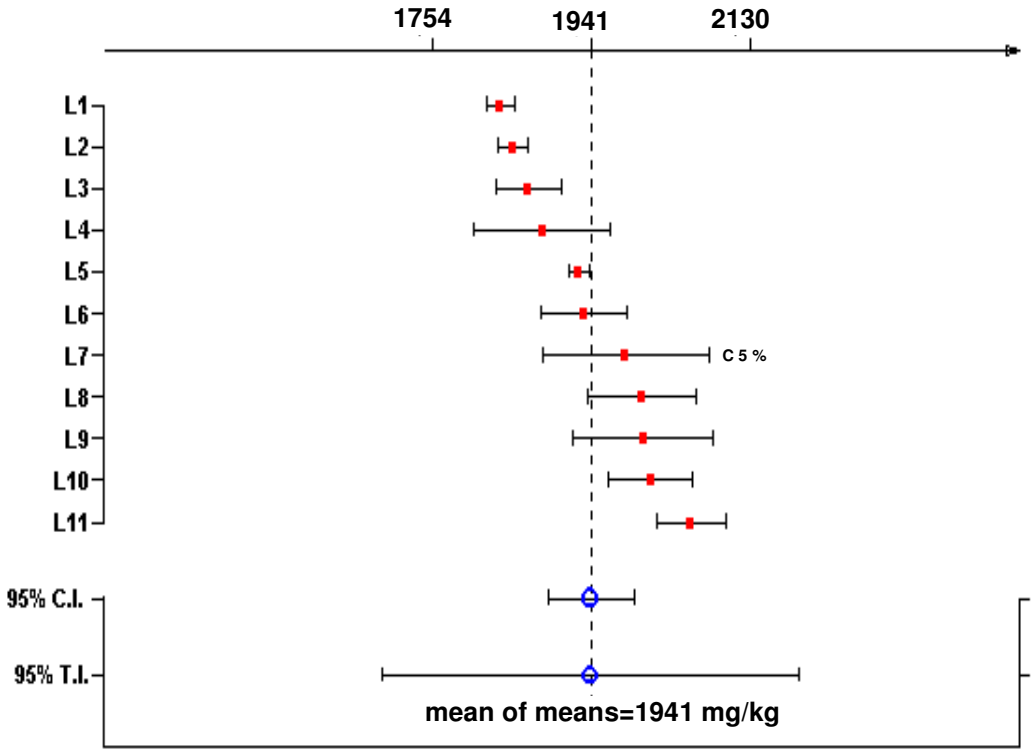


Table7r1: Strontium oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES	127,500	8,803	9,239	125,000	125,000	125,000	140,000	135,000	115,000
L 2	24 F AAS	127,667	3,445	3,615	126,000	126,000	124,000	132,000	132,000	126,000
L 3	3 F AAS	127,883	1,694	1,778	129,250	128,320	128,190	129,610	125,000	126,930
L 4	13 ICP OES	131,667	8,892	9,332	139,000	139,000	140,000	120,000	123,000	129,000
L 5	3 ICP OES	138,000	1,071	1,124	138,900	137,800	138,900	138,200	138,200	136,000
L 6	10 ICP OES	140,000	4,604	4,832	149,000	139,000	136,000	138,000	138,000	140,000
L 7	3 ICP-MS	140,533	2,740	2,875	138,400	139,500	137,200	143,100	144,300	140,700
L 8	10 F AAS	144,333	9,606	10,080	155,000	154,000	134,000	133,000	142,000	148,000
L 9	7c ICP OES	146,167	5,269	5,530	146,000	153,000	152,000	144,000	141,000	141,000
L 10	7b ICP OES	148,000	3,899	4,091	152,000	153,000	149,000	144,000	145,000	145,000
L 11	20 ICP OES	148,308	5,414	5,682	147,390	139,590	146,990	149,020	156,170	150,690
L 12	5 ICP OES	149,333	3,512	8,724	146,000	149,000	153,000			
L 13	11 ICP OES	150,900	3,808	3,997	154,800	151,000	145,000	155,100	150,800	148,700
L 14	1 ICP OES	153,833	1,941	2,037	155,000	157,000	154,000	152,000	153,000	152,000
L 15	14 ICP OES	159,750	2,563	2,690	158,700	163,800	159,200	158,100	156,900	161,800
L 16	17 XRF	161,550	1,773	1,860	164,600	160,200	162,200	160,000	162,000	160,300
L 17	6 F AAS	162,067	7,093	7,444	152,800	162,400	158,200	173,600	165,600	159,800
L 18	21 F AAS	162,525	0,951	0,998	163,520	162,320	162,460	160,800	163,110	162,940
L 19	9 K_0-INAA	164,833	7,026	7,373	158,000	163,000	169,000	177,000	160,000	162,000
L 20	4 ICP OES	166,500	2,074	2,176	166,000	163,000	168,000	169,000	166,000	167,000
L 21	12 ICP OES	168,000	1,265	1,327	168,000	167,000	167,000	167,000	169,000	170,000
L 22	2 ET AAS	174,333	8,454	8,872	172,000	172,000	176,000	165,000	190,000	171,000
L 23	2 F AAS	174,667	3,559	3,735	173,000	178,000	176,000	172,000	179,000	170,000

Range [min..max]	[115,000 .. 190,000]
	Case of No Pooling
Mean of means	150,798
95% H.W. Confidence Interval	6,365
95% H.W. Tolerance Interval	39,345
	Case of Pooling
Mean of All	150,830
95% H.W. Confidence Interval	2,612
95% H.W. Tolerance Interval	33,583

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

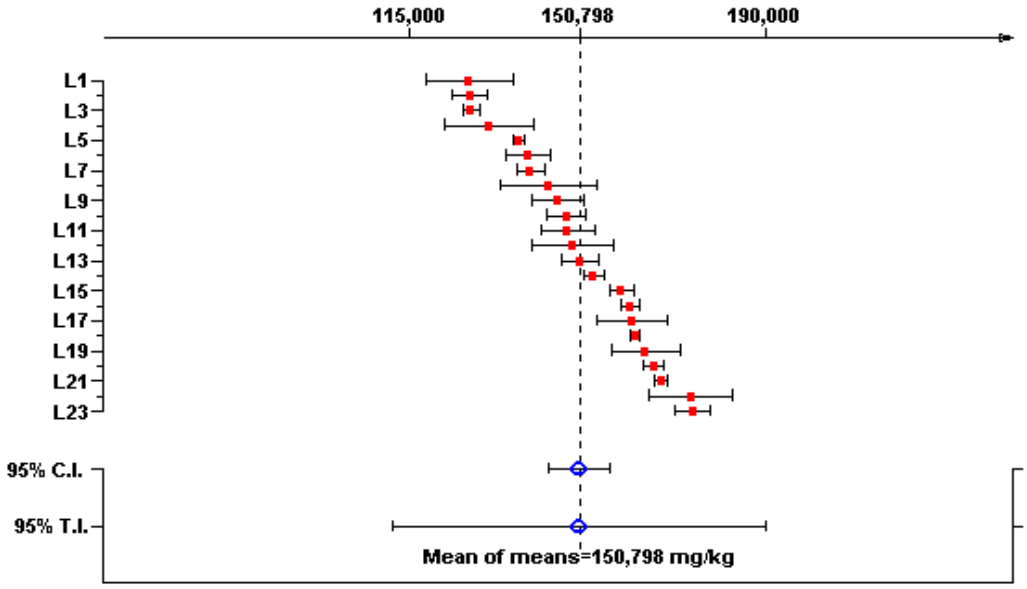


Table7s1: Titanium (IV) oxide evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES	125,833	10,206	10,711	115,000	125,000	140,000	135,000	115,000	125,000
L 2	3 MAS	133,833	6,023	6,321	134,200	123,800	131,200	139,900	134,000	139,900
L 3	2 MAS	154,667	3,141	3,296	159,000	155,000	157,000	154,000	153,000	150,000
L 4	7b ICP OES	156,500	0,837	0,878	157,000	157,000	157,000	157,000	155,000	156,000
L 5	24 MAS	156,500	5,010	5,258	161,000	162,000	158,000	150,000	157,000	151,000
L 6	6 MAS	156,633	4,756	4,991	161,500	162,200	152,500	150,800	154,500	158,300
L 7	1 ICP OES	160,333	2,251	2,362	159,000	158,000	162,000	163,000	162,000	158,000
L 8	12 ICP OES	163,333	8,165	8,569	180,000	160,000	160,000	160,000	160,000	160,000
L 9	4 ICP OES	163,833	2,137	2,243	163,000	165,000	165,000	166,000	160,000	164,000
L 10	14 ICP OES	163,900	4,300	4,513	162,400	167,100	170,500	164,100	160,000	159,300
L 11	7c ICP OES	165,500	4,278	4,489	174,000	162,000	165,000	164,000	164,000	164,000
L 12	10 ICP OES	165,833	4,119	4,323	159,000	167,000	163,000	169,000	167,000	170,000
L 13	20 ICP OES	165,965	3,932	4,127	168,930	158,360	167,200	168,930	166,560	165,810
L 14	17 XRF	166,517	2,745	2,880	167,300	167,600	167,100	165,000	170,100	162,000
L 15	10 MAS	172,500	11,005	11,549	163,000	168,000	158,000	179,000	184,000	183,000
L 16	3 ICP OES	172,650	6,344	6,658	177,100	173,400	178,400	160,600	172,200	174,200
L 17	21 MAS	177,707	2,929	3,074	182,090	177,490	180,380	175,440	174,750	176,090
L 18	13 ICP OES	183,667	10,231	10,736	171,000	196,000	179,000	195,000	176,000	185,000
L 19	23 ICP OES	188,667	10,764	11,296	187,000	178,000	202,000	198,000	175,000	192,000
L 20	11 ICP OES	252,333	35,223	36,964	245,400	323,100	228,900	244,700	237,200	234,700

Range [min..max]	[115,000 .. 323,100]
	Case of No Pooling
Mean of means	167,335
95% H.W. Confidence Interval	11,545
95% H.W. Tolerance Interval	67,884
	Case of Pooling
Mean of All	167,335
95% H.W. Confidence Interval	4,666
95% H.W. Tolerance Interval	56,913

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

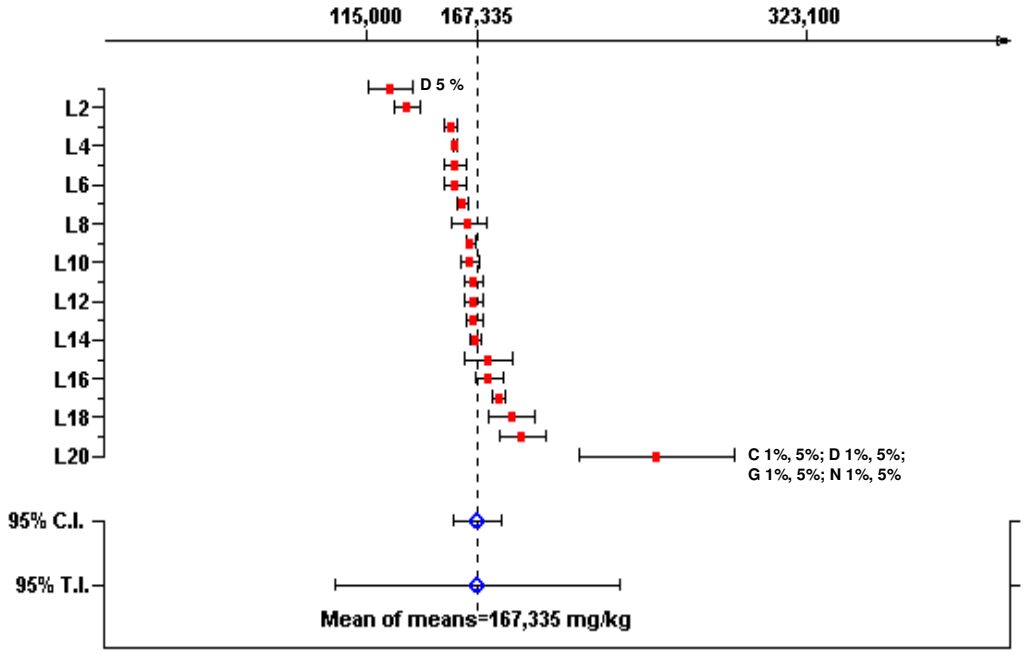


Table7s2: Titanium (IV) oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES	125,833	10,206	10,711	115,000	125,000	140,000	135,000	115,000	125,000
L 2	3 MAS	133,833	6,023	6,321	134,200	123,800	131,200	139,900	134,000	139,900
L 3	2 MAS	154,667	3,141	3,296	159,000	155,000	157,000	154,000	153,000	150,000
L 4	7b ICP OES	156,500	0,837	0,878	157,000	157,000	157,000	157,000	155,000	156,000
L 5	24 MAS	156,500	5,010	5,258	161,000	162,000	158,000	150,000	157,000	151,000
L 6	6 MAS	156,633	4,756	4,991	161,500	162,200	152,500	150,800	154,500	158,300
L 7	1 ICP OES	160,333	2,251	2,362	159,000	158,000	162,000	163,000	162,000	158,000
L 8	12 ICP OES	163,333	8,165	8,569	180,000	160,000	160,000	160,000	160,000	160,000
L 9	4 ICP OES	163,833	2,137	2,243	163,000	165,000	165,000	166,000	160,000	164,000
L 10	14 ICP OES	163,900	4,300	4,513	162,400	167,100	170,500	164,100	160,000	159,300
L 11	7c ICP OES	165,500	4,278	4,489	174,000	162,000	165,000	164,000	164,000	164,000
L 12	10 ICP OES	165,833	4,119	4,323	159,000	167,000	163,000	169,000	167,000	170,000
L 13	20 ICP OES	165,965	3,932	4,127	168,930	158,360	167,200	168,930	166,560	165,810
L 14	17 XRF	166,517	2,745	2,880	167,300	167,600	167,100	165,000	170,100	162,000
L 15	10 MAS	172,500	11,005	11,549	163,000	168,000	158,000	179,000	184,000	183,000
L 16	3 ICP OES	172,650	6,344	6,658	177,100	173,400	178,400	160,600	172,200	174,200
L 17	21 MAS	177,707	2,929	3,074	182,090	177,490	180,380	175,440	174,750	176,090
L 18	13 ICP OES	183,667	10,231	10,736	171,000	196,000	179,000	195,000	176,000	185,000
L 19	23 ICP OES	188,667	10,764	11,296	187,000	178,000	202,000	198,000	175,000	192,000

Range [min..max]	[115,000 .. 202,000]
	Case of No Pooling
Mean of means	162,862
95% H.W. Confidence Interval	7,145
95% H.W. Tolerance Interval	41,272
	Case of Pooling
Mean of All	162,862
95% H.W. Confidence Interval	2,892
95% H.W. Tolerance Interval	34,486

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

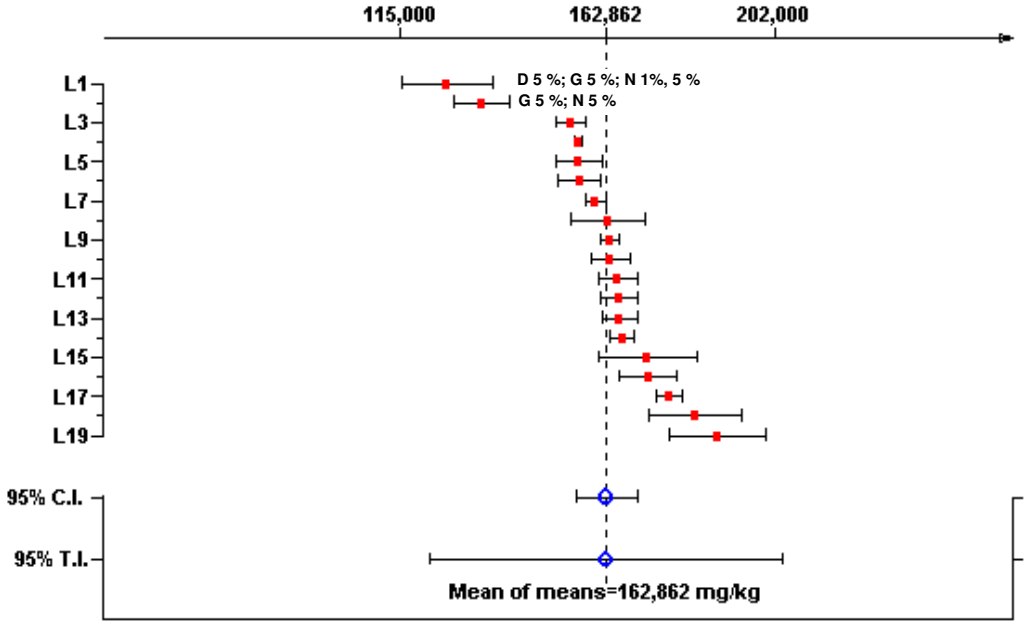


Table7t1: Vanadium (V) oxide run 1 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	19 ICP OES	279,167	10,685	11,213	270,000	270,000	285,000	295,000	270,000	285,000
L 2	11 ICP OES	290,633	6,314	6,626	294,500	287,700	282,400	299,500	286,100	293,600
L 3	7c ICP OES	294,333	15,832	16,615	299,000	311,000	311,000	275,000	277,000	293,000
L 4	10 ICP OES	311,833	4,070	4,271	308,000	310,000	309,000	314,000	311,000	319,000
L 5	7b ICP OES	326,000	6,261	6,570	315,000	325,000	326,000	334,000	327,000	329,000
L 6	4 ICP OES	328,000	9,274	9,732	324,000	346,000	327,000	326,000	319,000	326,000
L 7	3 ICP OES	334,400	7,275	7,635	330,100	330,300	324,600	337,900	339,200	344,300
L 8	23 ICP OES	334,500	16,634	17,457	348,000	345,000	352,000	312,000	332,000	318,000
L 9	13 ICP OES	339,333	5,955	6,250	330,000	347,000	341,000	335,000	341,000	342,000
L 10	3 ICP-MS	341,233	8,774	9,208	342,700	344,500	341,000	333,800	330,200	355,200
L 11	1 ICP OES	347,333	2,582	2,710	350,000	347,000	351,000	345,000	345,000	346,000
L 12	12 ICP OES	354,167	2,041	2,142	354,000	352,000	353,000	354,000	354,000	358,000
L 13	17 XRF	355,883	2,304	2,418	359,300	353,900	358,200	353,900	355,200	354,800
L 14	9 K_0-INAA	369,167	10,265	10,772	362,000	366,000	375,000	359,000	366,000	387,000
L 15	14 ICP OES	373,233	10,493	11,012	368,000	363,500	368,000	392,700	370,300	376,900
L 16	21 F AAS	414,877	6,465	6,785	421,570	414,550	406,600	421,590	416,890	408,060
L 17	5 ICP OES	434,333	8,505	21,127	431,000	428,000	444,000			
L 18	20 ICP OES	436,363	12,128	12,728	435,710	414,430	434,980	438,660	444,760	449,640

Range [min..max]	[270,000 .. 449,640]
	Case of No Pooling
Mean of means	348,044
95% H.W. Confidence Interval	22,405
95% H.W. Tolerance Interval	127,009
	Case of Pooling
Mean of All	345,578
95% H.W. Confidence Interval	8,299
95% H.W. Tolerance Interval	95,440

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

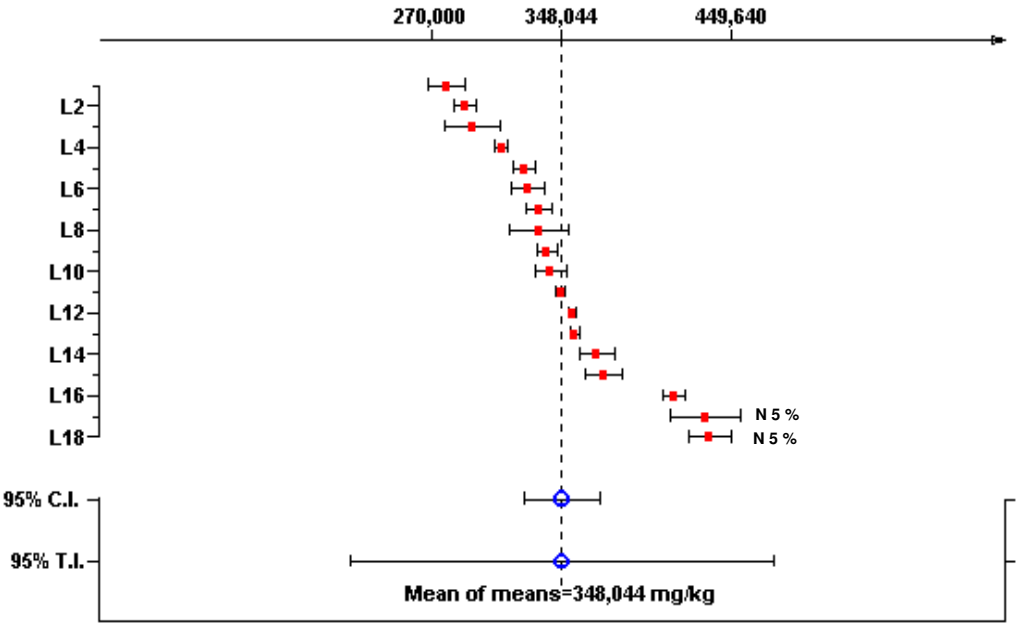


Table7u1: Zinc oxide evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	24 F AAS	171,667	5,610	5,887	172,000	180,000	165,000	170,000	167,000	176,000
L 2	7b ICP OES	187,000	9,798	10,282	174,000	181,000	180,000	195,000	196,000	196,000
L 3	7c ICP OES	187,333	5,574	5,849	188,000	182,000	179,000	191,000	192,000	192,000
L 4	20 ICP OES	188,115	3,502	3,675	191,600	184,880	190,780	191,020	186,970	183,440
L 5	12 ICP-MS	192,000	2,280	2,393	192,000	192,000	191,000	192,000	196,000	189,000
L 6	14 ICP OES	192,480	2,404	2,984		193,200	189,400	191,100	192,900	195,800
L 7	1 ICP OES	195,167	2,041	2,142	195,000	196,000	196,000	194,000	198,000	192,000
L 8	9 K_0-INAA	198,000	1,789	1,877	200,000	195,000	199,000	199,000	198,000	197,000
L 9	11 ICP OES	199,100	2,062	2,164	201,600	197,700	195,900	200,000	200,500	198,900
L 10	19 ICP OES	199,167	11,143	11,694	195,000	200,000	210,000	210,000	180,000	200,000
L 11	10 F AAS	203,500	5,822	6,110	202,000	199,000	195,000	207,000	210,000	208,000
L 12	15 INAA	203,967	3,478	3,650	209,200	205,400	205,400	201,700	199,200	202,900
L 13	3 ICP OES	204,000	2,008	2,107	205,000	204,000	207,100	204,100	202,500	201,300
L 14	23 ICP OES	204,500	12,534	13,154	202,000	197,000	225,000	205,000	188,000	210,000
L 15	2 F AAS	207,500	1,049	1,101	207,000	208,000	208,000	207,000	209,000	206,000
L 16	13 ICP OES	207,833	10,265	10,772	202,000	198,000	209,000	221,000	198,000	219,000
L 17	18 F AAS	208,167	6,401	6,717	203,000	199,000	207,000	211,000	213,000	216,000
L 18	21 F AAS	209,530	4,371	4,587	212,410	202,890	206,550	209,270	215,230	210,830
L 19	3 F AAS	210,050	1,427	1,497	211,300	210,900	211,200	210,000	209,300	207,600
L 20	4 ICP OES	213,667	14,610	15,333	211,000	196,000	224,000	237,000	209,000	205,000
L 21	5 ICP OES	215,667	15,503	38,511	216,000	231,000	200,000			
L 22	17 XRF	217,900	20,455	21,466	221,300	255,300	219,700	200,300	210,700	200,100

Range [min..max]	[165,000 .. 255,300]
	Case of No Pooling
Mean of means	200,741
95% H.W. Confidence Interval	4,937
95% H.W. Tolerance Interval	30,031
	Case of Pooling
Mean of All	200,456
95% H.W. Confidence Interval	2,301
95% H.W. Tolerance Interval	28,890

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

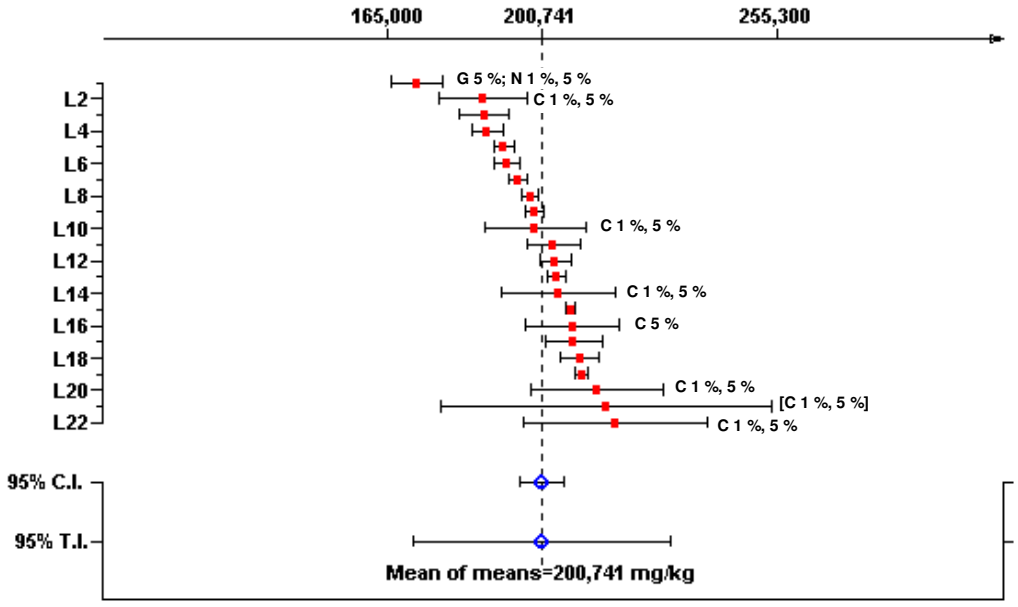


Table7u2: Zinc oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	7b ICP OES	187,000	9,798	10,282	174,000	181,000	180,000	195,000	196,000	196,000
L 2	7c ICP OES	187,333	5,574	5,849	188,000	182,000	179,000	191,000	192,000	192,000
L 3	20 ICP OES	188,115	3,502	3,675	191,600	184,880	190,780	191,020	186,970	183,440
L 4	12 ICP-MS	192,000	2,280	2,393	192,000	192,000	191,000	192,000	196,000	189,000
L 5	14 ICP OES	192,480	2,404	2,984		193,200	189,400	191,100	192,900	195,800
L 6	1 ICP OES	195,167	2,041	2,142	195,000	196,000	196,000	194,000	198,000	192,000
L 7	9 K_0-INAA	198,000	1,789	1,877	200,000	195,000	199,000	199,000	198,000	197,000
L 8	11 ICP OES	199,100	2,062	2,164	201,600	197,700	195,900	200,000	200,500	198,900
L 9	19 ICP OES	199,167	11,143	11,694	195,000	200,000	210,000	210,000	180,000	200,000
L 10	10 F AAS	203,500	5,822	6,110	202,000	199,000	195,000	207,000	210,000	208,000
L 11	15 INAA	203,967	3,478	3,650	209,200	205,400	205,400	201,700	199,200	202,900
L 12	3 ICP OES	204,000	2,008	2,107	205,000	204,000	207,100	204,100	202,500	201,300
L 13	23 ICP OES	204,500	12,534	13,154	202,000	197,000	225,000	205,000	188,000	210,000
L 14	2 F AAS	207,500	1,049	1,101	207,000	208,000	208,000	207,000	209,000	206,000
L 15	13 ICP OES	207,833	10,265	10,772	202,000	198,000	209,000	221,000	198,000	219,000
L 16	18 F AAS	208,167	6,401	6,717	203,000	199,000	207,000	211,000	213,000	216,000
L 17	21 F AAS	209,530	4,371	4,587	212,410	202,890	206,550	209,270	215,230	210,830
L 18	3 F AAS	210,050	1,427	1,497	211,300	210,900	211,200	210,000	209,300	207,600
L 19	4 ICP OES	213,667	14,610	15,333	211,000	196,000	224,000	237,000	209,000	205,000
L 20	5 ICP OES	215,667	15,503	38,511	216,000	231,000	200,000			
L 21	17 XRF	217,900	20,455	21,466	221,300	255,300	219,700	200,300	210,700	200,100

Range [min..max]	[174,000 .. 255,300]
	Case of No Pooling
Mean of means	202,126
95% H.W. Confidence Interval	4,219
95% H.W. Tolerance Interval	25,239
	Case of Pooling
Mean of All	201,872
95% H.W. Confidence Interval	2,099
95% H.W. Tolerance Interval	25,802

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

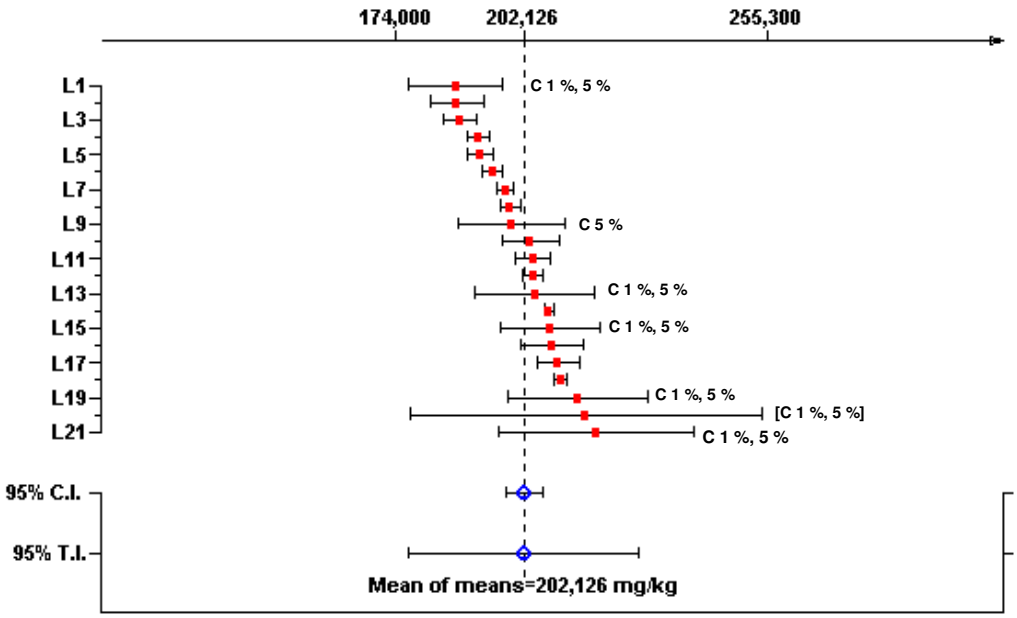


Table7v1: Zirconium (IV) oxide evaluation in run 1 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	5 ICP OES	633,667	9,609	23,870	625,000	632,000	644,000			
L 2	19 ICP OES	661,250	76,089	121,075	595,000			670,000	765,000	615,000
L 3	7b ICP OES	759,800	12,091	15,013	759,000	772,000	762,000		766,000	740,000
L 4	4 ICP OES	771,833	16,412	17,224	782,000	770,000	756,000	797,000	753,000	773,000
L 5	10 ICP OES	779,167	34,278	35,972	773,000	813,000	827,000	772,000	742,000	748,000
L 6	10 MAS	791,667	54,106	56,781	834,000	834,000	844,000	783,000	726,000	729,000
L 7	7c ICP OES	799,833	41,272	43,312	835,000	824,000	849,000	779,000	755,000	757,000
L 8	15 INAA	799,883	19,090	20,034	830,700	806,400	784,800	787,500	780,800	809,100
L 9	20 ICP OES	810,217	16,714	17,540	816,690	777,320	816,210	820,690	821,420	808,970
L 10	9 K_0-INAA	819,500	17,581	18,450	829,000	804,000	851,000	813,000	810,000	810,000
L 11	1 ICP OES	840,000	4,243	4,452	837,000	838,000	835,000	846,000	844,000	840,000
L 12	14 ICP OES	841,450	20,257	21,258	829,400	852,400	862,500	819,900	863,200	821,300
L 13	13 ICP OES	841,833	11,890	12,478	832,000	834,000	841,000	851,000	832,000	861,000
L 14	2 MAS	851,333	14,528	15,246	850,000	871,000	837,000	836,000	848,000	866,000
L 15	23 ICP OES	856,000	16,297	17,103	862,000	839,000	867,000	877,000	835,000	856,000
L 16	11 ICP OES	859,183	12,511	13,130	869,300	844,200	843,000	869,600	860,700	868,300
L 17	17 XRF	872,650	13,848	14,533	899,400	862,200	875,200	864,500	865,900	868,700
L 18	21 MAS	875,252	7,810	8,196	862,710	880,390	878,720	868,330	881,770	879,590
L 19	3 ICP OES	903,323	23,056	24,196	866,670	897,610	919,620	911,110	892,610	932,320
L 20	3 ICP-MS	937,018	15,202	15,953	943,070	944,540	954,330	941,670	911,850	926,650
L 21	12 ICP OES	971,667	13,292	13,949	960,000	960,000	990,000	980,000	960,000	980,000

Range [min..max]	[595,000 .. 990,000]
	Case of No Pooling
Mean of means	822,692
95% H.W. Confidence Interval	35,799
95% H.W. Tolerance Interval	214,154
	Case of Pooling
Mean of All	830,632
95% H.W. Confidence Interval	13,221
95% H.W. Tolerance Interval	161,281

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals

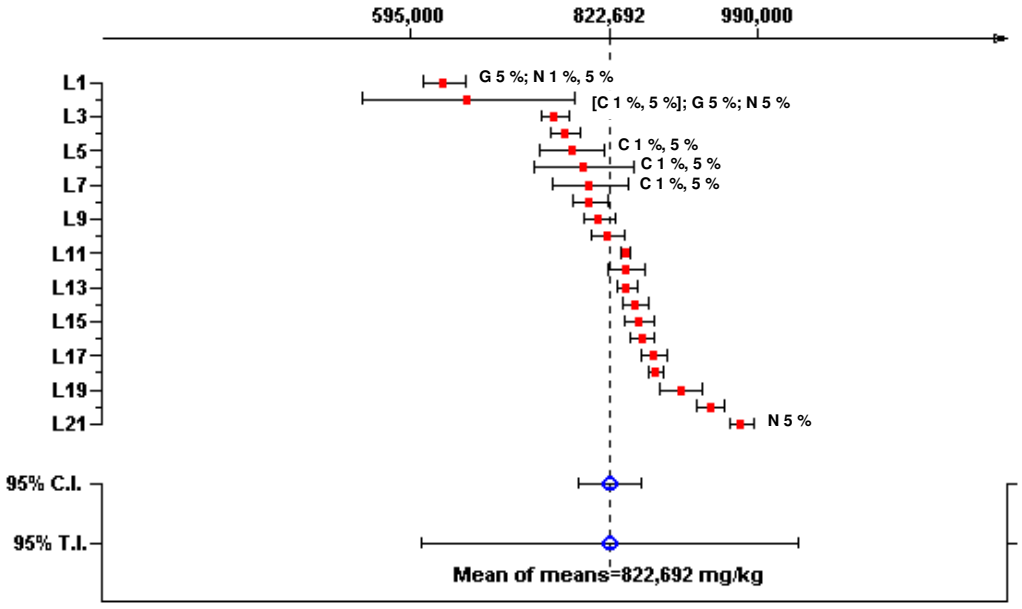


Table7v2: Zirconium (IV) oxide run 2 in CRM BAM-S005 (values in mg/kg)

Current Lab.number	Lab Abbreviation	Mean (mg/kg)	STDev	H.W. CI (95%)	Sample #1	Sample #2	Sample #3	Sample #4	Sample #5	Sample #6
L 1	7b ICP OES	759,800	12,091	15,013	759,000	772,000	762,000		766,000	740,000
L 2	4 ICP OES	771,833	16,412	17,224	782,000	770,000	756,000	797,000	753,000	773,000
L 3	10 ICP OES	779,167	34,278	35,972	773,000	813,000	827,000	772,000	742,000	748,000
L 4	10 MAS	791,667	54,106	56,781	834,000	834,000	844,000	783,000	726,000	729,000
L 5	7c ICP OES	799,833	41,272	43,312	835,000	824,000	849,000	779,000	755,000	757,000
L 6	15 INAA	799,883	19,090	20,034	830,700	806,400	784,800	787,500	780,800	809,100
L 7	20 ICP OES	810,217	16,714	17,540	816,690	777,320	816,210	820,690	821,420	808,970
L 8	9 K_0-INAA	819,500	17,581	18,450	829,000	804,000	851,000	813,000	810,000	810,000
L 9	1 ICP OES	840,000	4,243	4,452	837,000	838,000	835,000	846,000	844,000	840,000
L 10	14 ICP OES	841,450	20,257	21,258	829,400	852,400	862,500	819,900	863,200	821,300
L 11	13 ICP OES	841,833	11,890	12,478	832,000	834,000	841,000	851,000	832,000	861,000
L 12	2 MAS	851,333	14,528	15,246	850,000	871,000	837,000	836,000	848,000	866,000
L 13	23 ICP OES	856,000	16,297	17,103	862,000	839,000	867,000	877,000	835,000	856,000
L 14	11 ICP OES	859,183	12,511	13,130	869,300	844,200	843,000	869,600	860,700	868,300
L 15	17 XRF	872,650	13,848	14,533	899,400	862,200	875,200	864,500	865,900	868,700
L 16	21 MAS	875,252	7,810	8,196	862,710	880,390	878,720	868,330	881,770	879,590
L 17	3 ICP OES	903,323	23,056	24,196	866,670	897,610	919,620	911,110	892,610	932,320
L 18	3 ICP-MS	937,018	15,202	15,953	943,070	944,540	954,330	941,670	911,850	926,650
L 19	12 ICP OES	971,667	13,292	13,949	960,000	960,000	990,000	980,000	960,000	980,000

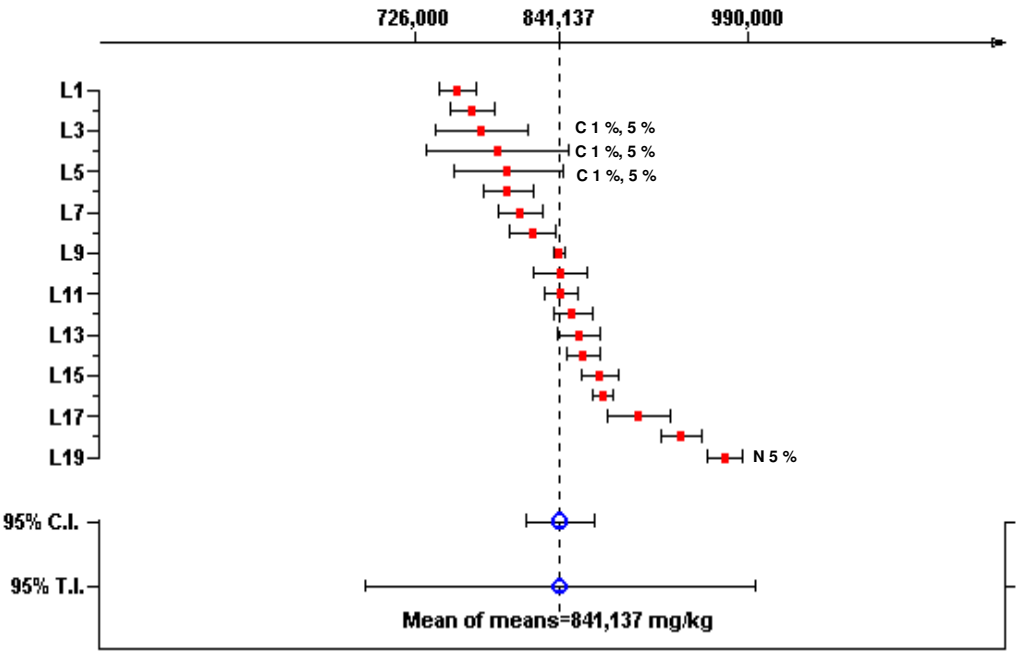
Range [min..max]	[726,000 .. 990,000]
	Case of No Pooling
Mean of means	841,137
95% H.W. Confidence Interval	26,751
95% H.W. Tolerance Interval	154,514
	Case of Pooling
Mean of All	841,857
95% H.W. Confidence Interval	10,767
95% H.W. Tolerance Interval	127,894

Outliers detected by different statistical tests at a = 1% level and at a = 5% level.

Abbreviations: C = Cochran test
D = Dixon test
G = Grubbs test (single and pair test)
N = Nalimov t - test

POSSIBILITY TO POOL THE DATA
Snedecor F-test and Bartlett test show that **pooling is: Not Allowed**

Diagram of means and 95% confidence intervals



Tab. 8: Applied Grubbs tests in detail (Supplement to Tab. 7)

Parameter	Evaluation	Test	Comments
As_2O_3	run 1	single and pair test	L1, L2 → outlier NOT detected L 16, L 17 → outlier NOT detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L 13, L 14 → outlier NOT detected
BaO	run 1	single test	L1 → 1%, 5% outlier detected
		pair test	L 18, L19 → outlier NOT detected
	run 2	single test	L18 → outlier detected 5% level
		pair test	L1, L2 → outlier NOT detected L17, L18 → outlier detected 1% und 5% level
	run 3	single test	L1, L16 → outlier NOT detected
		pair test	L1, L2 → outlier NOT detected L15, L16 → outlier 5% level
CdO	run 1	single and pair test	L1, L2 → outlier NOT detected L21, L22 → outlier NOT detected
CeO_2	run 1	single test	L15 → outlier detected 1%, 5% level
		pair test	L1, L2 → outlier NOT detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L13, L14 → outlier NOT detected
Cl	run 1	single and pair test	L1, L2 → outlier NOT detected L10, L11 → outlier NOT detected
CoO	run 1	single and pair test	L1, L2 → outlier NOT detected L22, L23 → outlier NOT detected
Cr_2O_3	run 1	single test	L22 → outlier detected 1%, 5% level
		pair test	L1, L2 → outlier NOT detected
	run 2	single test	L1 → outlier detected 5% level
		pair test	L1, L2 → outlier NOT detected L20, L21 outlier NOT detected
CuO	run 1	single and pair test	L1, L2 → outlier NOT detected L24, L25 → outlier NOT detected
Fe_2O_3	run 1	single test	L24 → outlier detected 5% level
		pair test	L1, L2 → outlier NOT detected L23, L24 → outlier NOT detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L22, L23 → outlier NOT detected
MnO	run 1	single and pair test	L1, L2 → outlier NOT detected L24, L25 → outlier NOT detected
MoO_3	run 1	single and pair test	L1, L2 → outlier NOT detected L13, L14 → outlier NOT detected
NiO	run 1	single and pair test	L1, L2 → outlier NOT detected L22, L23 → outlier NOT

			detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L21, L22 → outlier NOT detected
PbO	run 1	single and pair test	L1, L2 → outlier NOT detected L23, L24 → outlier NOT detected
Sb_2O_3	run 1	single and pair test	L1, L2 → outlier NOT detected L18, L19 → outlier NOT detected
Se	run 1	single test	L14 → outlier detected 1%, 5% level
		pair test	L1, L2 → outlier NOT detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L12, L13 → outlier NOT detected
SnO_2	run 1	single test	L1, L15 → outlier NOT detected
		pair test	L1, L2 → outlier detected 5 % level L14, L15 → outlier NOT detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L13, L14 → outlier NOT detected
SO_3	run 1	single and pair test	L1, L2 → outlier NOT detected L10, L11 → outlier NOT detected
SrO	run 1	single and pair test	L1, L2 → outlier NOT detected L22, L23 → outlier NOT detected
TiO_2	run 1	single test	L20 → outlier detected 1%, 5% level
		pair test	L1, L2 → outlier NOT detected
	run 2	single test	L1, L19 → outlier NOT detected
		pair test	L1, L2 → outlier detected 5 % level L18, L19 → outlier NOT detected
V_2O_5	run 1	single and pair test	L1, L2 → outlier NOT detected L17, L18 → outlier NOT detected
ZnO	run 1	single test	L1 → outlier detected 5 % level
		pair test	L1, L2 → outlier NOT detected L21, L22 → outlier NOT detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L20, L21 → outlier NOT detected
ZrO_2	run 1	single test	L1, L21 → outlier NOT detected
		pair test	L1, L2 → outlier detected 5 % level L20, L21 → outlier NOT detected
	run 2	single and pair test	L1, L2 → outlier NOT detected L18, L19 → outlier NOT detected

Tab. 9: Summary of results of statistical evaluation

	As_2O_3 run 1	As_2O_3 run 2	BaO run 1	BaO run 2	BaO run 3
Number of data sets	17	14	19	18	16
Number of replicate measurements	99	84	112	108	96
Mean of means (a)	127.594	131.027	114.904	117.954	114.375
St. Dev of means (a)	23.818	13.813	17.912	12.350	6.975
Outlying or straggling mean values					
▪ Dixon test	no	no	b, c	no	no
▪ Grubbs test (single and pair test)	no	no	b, c	b, c	c
▪ Nalimov t-test	c	c	b, c	b, c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	22.584	13.590	16.123	11.984	6.467
St. Dev. between laboratories (a)	6.164	6.051	7.228	7.310	6.401
Half-width of the 95% confidence interval (a)	12.246	7.975	8.633	6.142	3.717

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

	CdO run 1	CeO_2 run 1	CeO_2 run 2	Cl run 1	CoO run 1
Number of data sets	22	15	14	11	23
Number of replicate measurements	128	87	81	66	135
Mean of means (a)	62.068	108.644	104.559	246.466	49.402
St. Dev of means (a)	6.831	17.701	8.239	26.643	5.223
Outlying or straggling mean values					
▪ Dixon test	no	b, c	no	no	no
▪ Grubbs test (single and pair test)	no	b, c	no	no	no
▪ Nalimov t-test	c	b, c	no	no	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	c	c	b, c	no
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	6.463	17.851	7.737	25.870	5.002
St. Dev. between laboratories (a)	2.299	2.930	3.020	15.602	1.658
Half-width of the 95% confidence interval (a)	3.029	9.803	4.757	17.899	2.259

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

	Cr_2O_3 run 1	Cr_2O_3 run 2	CuO run 1	Fe_2O_3 run 1	Fe_2O_3 run 2
Number of data sets	22	21	25	24	23
Number of replicate measurements	126	120	145	141	135
Mean of means (a)	15.478	15.194	111.393	424.571	421.487
St. Dev of means (a)	1.947	1.455	7.101	26.825	22.665
Outlying or straggling mean values					
▪ Dixon test	b, c	no	no	no	no
▪ Grubbs test (single and pair test)	b, c	c	no	c	no
▪ Nalimov t-test	b, c	b, c	no	b, c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	b, c: Did not runned	b, c: Did not runned	no	no	no
St. Dev. within – laboratories (a)	1.856	1.324	6.918	26.237	22.281
St. Dev. between laboratories (a)	1.686	1.598	3.794	16.022	11.784
Half-width of the 95% confidence interval (a)	0.863	0.662	2.931	11.327	9.801

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

	MnO run 1	MoO_3 run 1	NiO run 1	NiO run 2	PbO run 1
Number of data sets	25	14	23	22	24
Number of replicate measurements	147	81	135	129	141
Mean of means (a)	123.595	342.825	59.519	59.005	201.212
St. Dev of means (a)	11.641	21.811	4.679	4.070	15.585
Outlying or straggling mean values					
▪ Dixon test	no	no	no	no	no
▪ Grubbs test (single and pair test)	no	no	no	no	no
▪ Nalimov t-test	c	c	b, c	c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	b, c	b, c	b, c	b, c
Variances homogeneous					
▪ Bartlett test	no	b, c	no	no	no
St. Dev. within – laboratories (a)	11.466	21.818	4.587	3.964	15.385
St. Dev. between laboratories (a)	5.095	8.609	2.811	2.673	8.066
Half-width of the 95% confidence interval (a)	4.805	12.593	2.023	1.804	6.581

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

	Sb_2O_3 run 1	Se run 1	Se run 2	SnO_2 run 1	SnO_2 run 2
Number of data sets	19	14	13	15	14
Number of replicate measurements	111	78	75	86	83
Mean of means (a)	131.229	20.237	19.614	97.153	99.521
St. Dev of means (a)	12.436	2.672	1.360	14.175	11.216
Outlying or straggling mean values					
▪ Dixon test	no	b, c	no	no	no
▪ Grubbs test (single and pair test)	no	b, c	no	c	no
▪ Nalimov t-test	c	b, c	c	b, c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	b, c	no	b, c	no	b, c
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	12.349	2.048	1.161	12.765	11.056
St. Dev. between laboratories (a)	4.566	1.331	1.249	5.087	5.056
Half-width of the 95% confidence interval (a)	5.994	1.543	0.822	7.850	6.476

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

	SO_3 run 1	SrO run 1	TiO_2 run 1	TiO_2 run 2	V_2O_5 run 1
Number of data sets	11	23	20	19	18
Number of replicate measurements	60	135	120	114	105
Mean of means (a)	1941	150.798	167.335	162.862	348.044
St. Dev of means (a)	76	14.720	24.667	14.825	45.055
Outlying or straggling mean values					
▪ Dixon test	no	no	b, c	c	no
▪ Grubbs test (single and pair test)	no	no	b, c	c	no
▪ Nalimov t-test	no	no	b, c	b, c	c
Differences between labs statistically significant?					
▪ Snedecor F-test	b, c	b, c	b, c	b, c	b, c
Outlying or straggling variances					
▪ Cochran test	c	no	b, c	no	no
Variances homogeneous					
▪ Bartlett test	no	no	no	no	no
St. Dev. within – laboratories (a)	73	14.733	24.330	14.603	42.937
St. Dev. between laboratories (a)	56	5.129	9.957	6.250	9.091
Half-width of the 95% confidence interval (a)	51	6.365	11.545	7.145	22.405

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

	ZnO run 1	ZnO run 2	ZrO_2 run 1	ZrO_2 run 2
Number of data sets	22	21	21	19
Number of replicate measurements	128	122	120	113
Mean of means (a)	200.741	202.126	822.692	841.137
St. Dev of means (a)	11.135	9.269	78.646	55.501
Outlying or straggling mean values				
▪ Dixon test	no	no	no	no
▪ Grubbs test (single and pair test)	c	no	c	no
▪ Nalimov t-test	b, c	no	b, c	c
Differences between labs statistically significant?				
▪ Snedecor F-test	b, c	b, c	b, c	b, c
Outlying or straggling variances				
▪ Cochran test	b, c	b, c	b, c	b, c
Variances homogeneous				
▪ Bartlett test	no	no	no	no
St. Dev. within – laboratories (a)	10.503	8.446	69.919	54.407
St. Dev. between laboratories (a)	8.185	8.291	25.673	22.527
Half-width of the 95% confidence interval (a)	4.937	4.219	35.799	26.751

Abbreviations:
(a) = Expressed in mg/kg; (b) = Outlier at 1% significance; (c) = Outlier at 5% significance

7.2.2 Explanations to the different analytes

7.2.2.1 Arsenic (III) oxide (Tab. 7a1 and 7a2)

17 laboratories delivered their results; with one exception all based on 6 separate determinations. 8 laboratories used ICP OES and 4 laboratories used FI-HG AAS or HG AAS. Other methods used were F AAS, INAA or K_0INAA and MAS. Both lowest results and the highest result, all based on ICP OES measurements, were discussed as outlying values because their lack of overlapping with the other values, though no serious outlier was indicated by one of the statistical tests. The values were removed after discussion. In the second run of the evaluation program carried out with the remaining 14 laboratories no further serious outlier was found. All remaining values lie within the tolerance interval.

7.2.2.2 Barium oxide (Tab. 7b1 to 7b3)

19 laboratories delivered their results; with one exception all based on 6 separate determinations. Most laboratories used ICP OES. Other methods used were F AAS, K_0INAA, ICP-MS, XRF and ET AAS. The lowest result, based on ICP OES and only 4 delivered single values, was discussed as outlying value because its lack of overlapping with the other values and indicated as a serious outlier by different statistical tests. The value was removed after discussion. After the second run of the evaluation program carried out with the remaining 18 laboratories, both highest values were discussed as statistically proven outliers. The values were removed after discussion. All mean values of the remaining values in the third run of the evaluation program carried out with 16 remaining laboratories lie within the tolerance interval.

7.2.2.3 Cadmium oxide (Tab. 7c1)

22 laboratories delivered their results; with two exceptions all based on 6 separate determinations. Half of the laboratories used ICP OES. Other methods used were F AAS, K_0INAA, ICP-MS and ET AAS. No result was discussed as outlying value or indicated as a serious outlier by a statistical test. Therefore no value was removed after first run. All values lie within the tolerance interval.

7.2.2.4 Cerium (IV) oxide (Tab. 7d1 and 7d2)

15 laboratories delivered their results; with one exception all based on 6 separate determinations. Most laboratories used ICP OES, one used K_0INAA and another one ICP-MS. The highest result, based on ICP OES, was discussed as outlying value because its lack of overlapping with the other values and an indication as a very serious outlier by different statistical tests. The value was removed. After the second run of the evaluation program carried out with the remaining 14 laboratories no further values were

indicated and discussed as outliers. All the remaining 14 values in the second run of the evaluation program lie within the tolerance interval.

7.2.2.5 Chloride (Tab. 7e1)

Only 11 laboratories delivered their results, all based on 6 separate determinations. Most laboratories used titrimetry with potentiometric end point determination, one laboratory used MAS, and another used K_0INAA. All results could be accepted. All the values lie within the tolerance interval. The results are trustable because very different procedures of sample preparation were used and because the values from MAS and from K_0INAA - which was used without chemical sample preparation – are in good agreement with the mean value of the interlaboratory comparison.

7.2.2.6 Cobalt (II) oxide (Tab. 7f1)

23 laboratories delivered their results, with one exception all based on 6 separate determinations. Most laboratories used ICP OES and F AAS, other laboratories used ET AAS, INAA, K_0INAA, ICP-MS and MAS. All results could be accepted. All the values lie within the tolerance interval. Though the relative wide distribution of the results of different laboratories, the mean value of all results is very trustable because very different procedures of sample preparation were used and because the values from K_0INAA - which was used without chemical sample preparation – are in good agreement with this mean value of the interlaboratory comparison.

7.2.2.7 Chromium (III) oxide (Tab. 7g1 and 7g2)

22 laboratories delivered their results; with three exceptions all based on 6 separate determinations. Most laboratories used ICP OES, one used K_0INAA, another INAA, and other laboratories used F AAS, ICP-MS, ET AAS, ID-TIMS or MAS. The highest result, based on ICP OES, was discussed as outlying value because it was proved as a serious outlier by different statistical tests. The value was removed. After the second run of the evaluation program carried out with the remaining 21 laboratories no further values were indicated and discussed as outliers. All the remaining 21 values in the second run of the evaluation program lie within the tolerance interval. The mean value of all results is trustable because very different procedures of sample preparation were used and because the values from ID TIMS, INAA and from K_0INAA are in agreement with the mean value of the interlaboratory comparison.

7.2.2.8 Copper (II) oxide (Tab. 7h1)

25 laboratories delivered their results, with two exceptions all based on 6 separate determinations. Most laboratories used ICP OES or F AAS, other laboratories used ET AAS, ICP-MS, ID-TIMS and MAS. All results could be accepted. All the values lie within the tolerance interval. The ID-TIMS value is somewhat higher than the mean value of all results and both values are not in fully statistical accordance. But the difference between them is small enough to tolerate this circumstance.

7.2.2.9 Iron (III) oxide (Tab. 7i1 and 7i2)

24 laboratories delivered their results, with one exception all based on 6 separate determinations. Most laboratories used ICP OES and some used F AAS, one used K_0INAA, and others used MAS, and ET AAS. The highest result, based on ICP OES, was discussed as outlying value because it was proved as an outlier by different statistical tests. The value was removed after discussion. After the second run of the evaluation program carried out with the remaining 23 laboratories no further values were indicated and discussed as outliers. All the remaining 23 values in the second run of the evaluation program lie within the tolerance interval. The result obtained with K_0INAA is in accordance with the mean value of the interlaboratory comparison.

7.2.2.10 Manganese (II) oxide (Tab. 7j1)

25 laboratories delivered their results; with one exception all based on 6 separate determinations. Most laboratories used ICP OES and some used F AAS, respectively, one used K_0INAA, and others used MAS, XRF, ICP-MS and ET AAS. Both highest results, based on ICP OES and F AAS, were discussed as outlying values because they do not overlap with the other values. But it was not decided to exclude them, because they were not proved to be serious outliers by any of the applied statistical tests. The

values were not removed after discussion. All the 25 values lie within the tolerance interval. The result obtained with K_0INAA is in accordance with the mean value of the interlaboratory comparison.

7.2.2.11 Molybdenum (VI) oxide (Tab. 7k1)

14 laboratories delivered their results; with one exception all based on 6 separate determinations. Most laboratories used ICP OES and one used K_0INAA, another used F AAS, and two used ICP-MS. All values could be accepted. They all lie within the tolerance interval. The result obtained with K_0INAA is in good accordance with the mean value of all laboratories.

7.2.2.12 Nickel (II) oxide (Tab. 7l1 and 7l2)

23 laboratories delivered their results; with one exception all based on 6 separate determinations. Most laboratories used ICP OES and some used F AAS, others usedICP-MS, MAS or ET AAS. The highest result, based on ICP OES, was discussed as outlying value because it was proved as an outlier by a statistical test. The value was removed after discussion. After the second run of the evaluation program carried out with the remaining 22 laboratories no further values were indicated and discussed as outliers. All the remaining 22 values in the second run of the evaluation program lie within the tolerance interval. The variety of methods and their distribution is satisfying and adequate.

7.2.2.13 Lead (II) oxide (Tab. 7m1)

24 laboratories delivered their results, with one exception all based on 6 separate determinations. Most laboratories used ICP OES some used F AAS, other laboratories used ET AAS, ICP-MS, ID-TIMS or XRF. All results could be accepted. All the values lie within the tolerance interval. The ID-TIMS value is somewhat higher than the mean value of all results and both values are not in fully statistical accordance. But the difference between them is small enough to tolerate this circumstance.

7.2.2.14 Antimony (III) oxide (Tab. 7n1)

19 laboratories delivered their results; with one exception all based on 6 separate determinations. Most laboratories used ICP OES and one used K_0INAA, others used F AAS, INAA, ET AAS, HG AAS, FI-HG AAS or ICP-MS. All values could be accepted. They all lie within the tolerance interval. The results obtained with K_0INAA and INAA are in good accordance with the mean value of all laboratories.

7.2.2.15 Selenium (Tab. 7o1 and 7o2)

14 laboratories delivered their results; with two exceptions based on 6 separate determinations. Fife laboratories used ICP OES, fife used FI-HG AAS or HG AAS and others used ICP-MS, ET AAS, K_0INAA or INAA. The highest value was indicated by statistical tests as an outlier and was removed after discussion. All other values could be accepted. They all lie after the second run within the tolerance interval. The result obtained with INAA is in accordance with the mean value of all laboratories; the result obtained with K_0INAA is higher, but the difference to the mean value is low enough to be accepted.

7.2.2.16 Tin (IV) oxide (Tab. 7p1 and 7p2)

15 laboratories delivered their results; with two exceptions all based on 6 separate determinations. Most laboratories used ICP OES, one used K_0INAA, and others used ET AAS, F AAS or ICP-MS. The lowest result, based on ICP OES, was discussed as outlying value because it was proved as a serious outlier by a statistical test. The value was removed after discussion. After the second run of the evaluation program carried out with the remaining 14 laboratories no further values were indicated and discussed as outliers. All the remaining 14 values in the second run of the evaluation program lie within the tolerance interval. The result obtained with K_0INAA is in very good accordance with the mean value of the interlaboratory comparison.

7.2.2.17 Sulfur trioxide (Tab. 7q1)

Only 11 laboratories delivered their results; with two exceptions all based on 6 separate determinations. Fife laboratories used ICP OES, four used combustion method, one laboratory used titrimetry and one gravimetry. All values could be accepted. They all lie within the tolerance interval. Gravimetric and titrimetric values are in accordance with the mean value of all laboratories.

7.2.2.18 Strontium oxide (Tab. 7r1)

23 laboratories delivered their results, with one exception all based on 6 separate determinations. Most laboratories used ICP OES and one used K_0INAA, others used F AAS, ET AAS, XRF or ICP-MS. All values could be accepted. They all lie within the tolerance interval. The results obtained with K_0INAA and XRF lie not too far from the mean value of all laboratories.

7.2.2.19 Titanium (IV) oxide (Tab. 7s1 and 7s2)

20 laboratories delivered their results; with no exception all based on 6 separate determinations. 13 laboratories used ICP OES, 6 laboratories used MAS and one used XRF. The lowest result, based on ICP OES, was discussed as outlying value because it was proved as a serious outlier by statistical tests. The value was removed after discussion. After the second run of the evaluation program carried out with the remaining 19 laboratories no further values were removed as outliers. All the remaining 19 mean values in the second run of the evaluation program lie within the tolerance interval. The result obtained with XRF is in very good accordance with the mean value of the interlaboratory comparison. The two lowest values had been discussed as outliers but they were not removed after discussion.

7.2.2.20 Vanadium (V) oxide (Tab. 7t1)

18 laboratories delivered their results; with one exception all based on 6 separate determinations. Almost all laboratories used ICP OES, one used K_0INAA, one used F AAS, one used XRF and one used ICP-MS. All values could be accepted. They all lie within the tolerance interval. The results obtained with K_0INAA and XRF are in accordance with the mean value of all laboratories. The three highest values were discussed as outliers but not removed after discussion.

7.2.2.21 Zinc oxide (Tab. 7u1 and 7u2)

22 laboratories delivered their results; with two exceptions all based on 6 separate determinations. Most laboratories used ICP OES, some used F AAS, one used K_0INAA, one used INAA and one used XRF. The lowest result, based on F AAS, was discussed as outlying value because it was proved as an outlier by a statistical test. The value was removed after discussion. After the second run of the evaluation program carried out with the remaining 21 laboratories no further values were indicated and discussed as outliers. All the remaining 21 mean values in the second run of the evaluation program lie within the tolerance interval. The results obtained with INAA and with K_0INAA are in good accordance with the mean value of the interlaboratory comparison.

7.2.2.22 Zirconium (IV) oxide (Tab. 7v1 and 7v2)

21 laboratories delivered their results; with three exceptions all based on 6 separate determinations. Most laboratories used ICP OES, one used K_0INAA and one used INAA, - others used MAS, ICP-MS or XRF. The two lowest results, based on ICP OES, were discussed as outlying value because of statistical tests. The values were removed after discussion. After the second run of the evaluation program carried out with the remaining 19 laboratories no further values were indicated and discussed as outliers. All the remaining 19 values in the second run of the evaluation program lie within the tolerance interval. The results obtained with INAA, K_0INAA and XRF are in accordance with the mean value of the interlaboratory comparison.

8 Calculation of certified values and their uncertainties

8.1 Mass fractions

8.1.1 Mass fractions of type B material

The certified values of mass fractions of certified analytes were calculated as the mean values "*M*" of all accepted means from the participating laboratories of the interlaboratory comparison (see 7.1, Tab. 6).

8.1.2 Mass fractions of type A material and statistical tests between type A and type B materials

The preparation of the type A material only differed from that of type B material in view of the point of time of taking samples from the (same) glass melt. Therefore, only one of both types (type B) was used in the interlaboratory comparison of certification. Subsequently, the contents of the material of type A were calculated on the basis of the certified values for type B material. In the homogeneity study samples of both materials were investigated. The analytical results were not only used to achieve information about the homogeneity of the materials, but also to compare the analyte contents of both and to compare their grade of homogeneity. Following calculations were performed to calculate the mass fractions of the type A material on the basis of the certified values of the type B material,

- On the basis of the measured mass fractions of both materials, as listed in the upper parts of Tabs. 10a – 10d, the mean values m_A and m_B and the related standard deviations s_A and s_B of both types of materials were calculated. Using a statistical t-test, differences between the both mean values were assessed as being significant or not. In this the value of test statistic was compared with the critical value at three different levels of significance (5%, 1% and 0.1%). Significant differences were found for mass fractions of SiO_2 (at 1%-level), of CaO (at 5% level), of V_2O_5 and TiO_2 (at 5%-level) and of Cr_2O_3 (at 0.1%-level).
- The differences in the contents of SiO_2 and of CaO, respectively, were without relevance, because they are only informative values. The mass fractions of V_2O_5, TiO_2 and Cr_2O_3 in the type A material were calculated by applying the factor m_A/m_B to the related mass fractions of type B material. Therefore one can find slightly increased mass fractions of these analytes in the certificate of type A compared with the values in the certificate of the material of type B.
- All the other mass fractions of the certified analytes were taken to the certificate of the material of type A as they had been calculated for type B material.

Besides the t-test mentioned above, an F-test was carried out basing on the same data of Tab. 10. In the lowest parts of Tab. 10a – 10c the calculated values of test statistic and the critical f-values at different levels of significance (5% and 1%) are listed. In the lowest lines of the tables the results of the test are classified by using “+”-signs. The test results indicate, that even the mass fractions of Al_2O_3, K_2O and CaO (as main constituents) are distributed in both types of materials with a different grade of uniformly. But, for our calculations this fact was without relevance, because the mass fractions of these analytes are only informative values. But significant differences in the variances between the samples were also found for some certified analytes by the f-test, in fact for: BaO, SO_3, Cl, CuO, MoO_3, ZrO_2, ZnO and Se. In the great majority of these cases, the variances of mass fractions of type B material was less (or much less) than the variances of mass fractions of type A material.

Tab. 10 Comparison between type A and type B material

Tab. 10a

	SiO_2	AL_2O_3	Na_2O	K_2O	CaO	MgO	BaO	CeO_2
	%	%	%	%	%	%	mg/kg	mg/kg
3A	71,304	1,142	13,734	0,682	10,485	2,2832	96,1	125,08
7A1	71,278	1,136	13,762	0,683	10,486	2,2882	98,7	124,69
11A	71,054	1,139	13,700	0,677	10,476	2,2920	96,5	127,07
15A	71,233	1,134	13,718	0,675	10,487	2,2941	92,6	125,19
19A	71,181	1,144	13,679	0,684	10,482	2,2961	97,3	125,15
23A	71,194	1,146	13,686	0,684	10,473	2,2853	99,9	127,79
27A	71,101	1,134	13,744	0,678	10,480	2,2874	96,0	126,80
31A1	71,257	1,152	13,656	0,692	10,480	2,2903	104,0	127,42
2B	71,177	1,136	13,738	0,683	10,490	2,2911	97,6	124,17
6B1	71,165	1,140	13,713	0,684	10,472	2,2942	98,9	130,16
10B	71,444	1,142	13,703	0,682	10,479	2,2948	101,1	125,32
14B	71,494	1,141	13,715	0,678	10,482	2,2920	96,0	126,13
18B	71,391	1,137	13,735	0,682	10,460	2,2959	98,9	126,65
22B	71,462	1,137	13,723	0,679	10,470	2,2920	96,8	125,01
26B	71,346	1,138	13,711	0,682	10,465	2,2996	99,0	124,98
30B	71,444	1,144	13,691	0,681	10,455	2,2903	98,3	127,63
34B	71,322	1,141	13,690	0,680	10,469	2,2929	97,1	126,35
38B1	71,313	1,138	13,640	0,682	10,464	2,2909	98,4	126,33
42B	71,369	1,144	13,711	0,680	10,449	2,2859	97,1	126,55
$mean_A$ (m_A)	71,20	1,141	13,710	0,682	10,48	2,290	97,6	126,1
s_A	0,087	0,0063	0,036	0,0053	0,005	0,0044	3,35	1,24
s_A rel. %	0,12	0,55	0,26	0,77	0,05	0,19	3,44	0,98
$mean_B$ (m_B)	71,36	1,140	13,706	0,681	10,47	2,293	98,1	126,3
s_B	0,109	0,0029	0,027	0,0018	0,012	0,0035	1,39	1,61
s_B rel. %	0,15	0,25	0,20	0,26	0,11	0,15	1,4	1,3
$mean_{A+B}$ (m_{A+B})	**71,29**	**1,140**	**13,71**	**0,681**	**10,47**	**2,291**	**97,9**	**126,2**
s_{A+B}	**0,126**	**0,0045**	**0,030**	**0,0036**	**0,011**	**0,0041**	**2,35**	**1,43**
s_{A+B} rel. %	**0,18**	**0,40**	**0,22**	**0,52**	**0,11**	**0,18**	**2,40**	**1,13**
Drift s rel. %	*0,20*	*0,080*	*0,22*	*0,086*	*0,065*	*0,15*	*0,98*	*1,1*
counting statistics %	0,069	0,23	0,12	0,14	0,058	0,16	0,43	0,43

s_D	0,10036	0,00461	0,03098	0,00365	0,00960	0,00390	2,40283	1,46728
test statistic (m_A/m_B)	**3,367**	**0,573**	**0,239**	**0,399**	**2,791**	**1,736**	**0,395**	**0,220**
critical value t(95%), f=17	2,110	2,110	2,110	2,110	2,110	2,110	2,110	2,110
critical value t(99%), f=17	2,898				2,898			
critical value t(99.9%), f=17	3,965							
	+	**-**	**-**	**-**	**(+)**	**-**	**-**	**-**

test statistic ($s_{A/B}$)	**1,576**	**4,740**	**1,825**	**8,513**	**6,159**	**1,562**	**5,810**	**1,680**
f_1 , f_2	10;7	7;10	7;10	7;10	10;7	7;10	7;10	10;7
critical value P=(95%)	3,64	3,14	3,14	3,14	3,64	3,14	3,14	3,64
critical value P=(99%)		5,20		5,20	6,62		5,20	
	-	**(+)**	**-**	**+**	**(+)**	**-**	**+**	**-**

Tab. 10b

	SO_3	Cl	Fe_2O_3	V_2O_5	TiO_2	CuO	MnO	MoO_3
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3A	1994,0	239,9	459,5	351,0	161,16	112,55	130,2	32,86
7A1	1962,6	240,0	462,7	351,7	161,71	111,33	129,5	32,76
11A	1972,6	234,7	460,4	351,4	161,05	113,15	130,1	33,07
15A	2009,1	243,7	461,0	350,6	159,05	114,12	130,2	32,30
19A	1977,9	230,1	458,7	351,7	160,57	112,59	130,4	33,54
23A	1944,7	228,0	460,5	351,0	161,13	112,85	130,3	33,78
27A	1973,9	239,9	460,2	353,3	160,52	113,14	129,6	32,89
31A1	1907,4	209,1	465,2	353,0	161,03	114,94	130,7	35,26
2B	1967,3	236,2	461,0	352,9	161,12	112,07	130,3	33,12
6B1	1956,2	234,7	460,2	351,2	161,02	112,78	130,3	33,48
10B	1947,2	232,5	461,1	350,5	159,49	113,03	130,6	33,45
14B	1967,5	236,3	458,5	352,1	159,73	112,76	130,0	32,96
18B	1978,3	234,5	459,2	349,9	160,20	112,33	129,7	33,45
22B	1974,2	233,9	458,1	349,9	160,27	113,08	129,6	33,02
26B	1975,0	235,1	458,9	347,9	159,12	111,92	130,0	33,29
30B	1975,1	235,3	460,4	348,9	160,18	112,90	129,4	33,22
34B	1982,8	237,8	458,2	351,1	158,75	112,88	130,1	32,96
38B1	1974,3	236,0	461,8	350,2	160,21	112,68	130,1	33,33
42B	1967,0	237,6	459,1	349,7	159,51	112,25	129,9	33,14
$mean_A$ (m_A)	1967,8	233,2	461,0	351,7	160,8	113,1	130,1	33,31
s_A	31,07	11,13	2,02	0,98	0,79	1,08	0,42	0,914
s_A rel. %	1,58	4,77	0,44	0,28	0,49	0,96	0,32	2,74
$mean_B$ (m_B)	1969,5	235,4	459,7	350,4	160,0	112,6	130,0	33,22
s_B	10,26	1,56	1,27	1,41	0,74	0,40	0,33	0,196
s_B rel. %	0,52	0,66	0,28	0,40	0,46	0,35	0,26	0,59
$mean_{A+B}$ (m_{A+B})	**1968,8**	**234,5**	**460,2**	**350,9**	**160,3**	**112,8**	**130,1**	**33,26**
s_{A+B}	**20,85**	**7,13**	**1,72**	**1,39**	**0,84**	**0,77**	**0,37**	**0,590**
s_{A+B} rel. %	**1,06**	**3,04**	**0,37**	**0,40**	**0,53**	**0,69**	**0,28**	**1,77**
Drift s rel. %	*0,38*	*0,49*	*0,27*	*0,25*	*0,32*	*0,22*	*0,20*	*0,19*
counting statistics %	0,23	0,33	0,22	0,26	0,29	0,28	0,33	0,22
test statistic (m_A/m_B)	**0,178**	**0,675**	**1,774**	**2,303**	**2,313**	**1,352**	**0,702**	**0,310**
critical value t(95%), f=17	2,11	2,11	2,11	2,11	2,11	2,11	2,11	2,11
critical value t(99%), f=17				2,898	2,898			
critical value t(99.9%), f=17								
	-	**-**	**-**	**(+)**	**(+)**	**-**	**-**	**-**
test statistic ($s_{A/B}$)	**9,166**	**50,770**	**2,523**	**2,070**	**1,154**	**7,327**	**1,606**	**21,800**
f_1 , f_2	7;10	7;10	7;10	10;7	7;10	7;10	7;10	7;10
critical value P=(95%)	3,14	3,14	3,14	3,64	3,14	3,14	3,14	3,14
critical value P=(99%)	5,20	5,20				5,20		5,20
	++	**++**	**-**	**-**	**-**	**+**	**-**	**++**

Tab. 10c

	ZrO_2	PbO	As_2O_3	CoO	CdO	ZnO	Se	SrO
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3A	831,3	210,36	156,64	46,05	60,37	184,4	21,15	160,86
7A1	823,1	210,12	157,87	45,51	60,51	185,7	21,21	160,39
11A	799,6	209,10	156,86	45,96	60,35	181,6	21,67	161,44
15A	739,4	211,84	157,41	46,54	59,93	177,3	22,34	161,59
19A	867,7	209,57	157,58	45,98	60,41	184,9	21,29	161,32
23A	856,0	211,33	157,42	46,05	60,44	184,7	21,03	160,96
27A	829,4	210,92	158,88	46,28	60,37	182,9	21,74	160,92
31A1	918,3	209,12	157,10	46,15	59,77	191,1	20,11	160,82
2B	840,4	211,37	159,31	45,60	59,81	184,3	21,39	161,94
6B1	854,4	210,60	155,46	45,92	60,25	185,8	21,25	161,27
10B	846,0	210,54	156,09	45,53	60,75	185,8	21,07	160,85
14B	813,0	210,61	156,45	46,12	60,21	182,4	21,68	160,98
18B	824,2	209,34	155,66	45,67	59,44	183,8	21,18	160,05
22B	813,1	208,20	157,89	45,72	59,96	182,2	21,42	160,04
26B	839,9	209,75	156,88	46,05	60,03	183,5	21,27	160,17
30B	828,2	210,33	157,74	46,26	60,81	183,5	21,40	160,85
34B	801,9	208,88	157,71	45,64	60,42	182,7	21,66	161,22
38B1	829,7	208,56	157,27	45,90	59,75	183,5	21,37	160,74
42B	829,8	209,43	156,66	46,11	60,72	184,4	21,22	160,68
$mean_A$ (m_A)	833,1	210,3	157,5	46,07	60,27	184,1	21,32	161,0
s_A	52,10	1,02	0,69	0,293	0,266	3,90	0,648	0,39
s_A rel. %	6,25	0,48	0,44	0,64	0,44	2,12	3,04	0,24
$mean_B$ (m_B)	829,1	209,8	157,0	45,87	60,20	183,8	21,36	160,8
s_B	15,65	0,99	1,13	0,246	0,449	1,21	0,189	0,57
s_B rel. %	1,89	0,47	0,72	0,54	0,75	0,66	0,88	0,36
$mean_{A+B}$ (m_{A+B})	**830,8**	**210,0**	**157,2**	**45,95**	**60,23**	**183,9**	**21,34**	**160,9**
s_{A+B}	**34,58**	**1,01**	**0,97**	**0,278**	**0,376**	**2,60**	**0,428**	**0,51**
s_{A+B} rel. %	**4,16**	**0,48**	**0,62**	**0,60**	**0,62**	**1,41**	**2,01**	**0,31**
Drift s rel. %	*0,38*	*0,45*	*0,53*	*0,59*	*0,57*	*0,15*	*0,62*	*0,23*
counting statistics %	0,23	0,28	0,33	0,37	0,37	0,29	0,29	0,24

test statistic (m_A/m_B)	**0,239**	**1,101**	**1,020**	**1,606**	**0,412**	**0,221**	**0,184**	**1,021**
critical value t(95%), f=17	2,11	2,11	2,11	2,11	2,11	2,11	2,11	2,11
critical value t(99%), f=17								
critical value t(99.9%), f=17								
	-	-	-	-	-	-	-	-

test statistic ($s_{A/B}$)	**11,083**	**1,045**	**2,632**	**1,420**	**2,845**	**10,436**	**11,778**	**2,165**
f_1 , f_2	7;10	7;10	10;7	7;10	10;7	7;10	7;10	10;7
critical value P=(95%)	3,14	3,14	3,64	3,14	3,64	3,14	3,14	3,64
critical value P=(99%)	5,20					5,20	5,20	
	++	-	**-**	-	**-**	**++**	**++**	**-**

Tab. 10d

	Cr_2O_3 mg/kg	SnO_2 mg/kg	Sb_2O_3 mg/kg
3A	28,87	70,81	208,41
7A1	30,26	69,99	208,92
11A	30,02	71,02	212,00
15A	29,14	69,32	206,65
19A	29,47	70,21	211,04
23A	29,42	69,87	210,02
27A	29,07	70,02	207,05
31A1	28,91	70,04	207,72
2B	28,99	70,51	206,98
6B1	29,42	70,22	208,37
10B	28,67	70,90	212,86
14B	28,52	71,37	211,21
18B	28,38	71,41	210,53
22B	28,30	69,80	209,05
26B	28,73	69,52	212,05
30B	28,70	70,44	208,73
34B	28,01	70,54	205,75
38B1	28,21	70,45	207,63
42B	28,17	70,26	206,84
$mean_A$ (m_A)	29,39	70,16	209,0
s_A	0,511	0,537	1,91
s_A rel. %	1,74	0,77	0,91
$mean_B$ (m_B)	28,55	70,49	209,1
s_B	0,408	0,578	2,30
s_B rel. %	1,43	0,82	1,10
$mean_{A+B}$ (m_{A+B})	28,91	70,35	209,0
s_{A+B}	0,613	0,571	2,09
s_{A+B} rel. %	2,12	0,81	1,00
Drift s rel. %	*1,6*	*1,4*	*1,1*
counting statistics %	0,8	0,7	0,7

test statistic (m_A/m_B)	**3,983**	**1,274**	**0,112**
critical value t(95%), f=17	2,110	2,110	2,110
critical value t(99%), f=17	2,898		
critical value t(99.9%), f=17	3,965		
critical	**++**	**-**	**-**

test statistic ($s_{A/B}$)	**1,572**	**1,155**	**1,458**
f_1, f_2	7;10	10;7	10;7
critical value P=(95%)	3,14	3,64	3,64
critical value P=(99%)			
critical	**-**	**-**	**-**

8.2 Uncertainties

8.2.1 Type B material

The combined uncertainties of the certified mass fractions of type A and B materials were calculated independent from the results of the homogeneity tests. But the basic values calculations carried out at later time (see below) had been calculated in the context of the homogeneity investigations as described in paragraph 4.2 and as documented in detail in the Appendix. These basic values are:

s_b = standard deviation of homogeneity investigation "between the bottles"
(note: it contains a contribution of the standard deviation of the analytical procedure used in homogeneity investigation)

s_w = standard deviation in homogeneity investigation "within the bottles"
(note: it contains a contribution of the standard deviation of the analytical procedure used in homogeneity investigation)

s_{HS} = standard deviation in homogeneity investigation of "homogeneous sample"
The value of s_{HS} is assumed to represent the standard deviation of the analytical procedure used for the homogeneity investigation.

Following symbols and abbreviations are used additionally:

u_c = combined uncertainty of certified mass fraction according to GUM [5] and ISO Guide 35 [6]

s_M = standard deviation of the accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 6)

n = number of accepted laboratory mean values of interlaboratory comparison for certification (see Tab. 6)

s_{inhom} = standard deviation resulting from inhomogeneity of the samples,

whereas

$$s_{inhom} = \sqrt{\left(s_b^2 - s_{HS}^2\right) + \left(s_w^2 - s_{HS}^2\right)} \qquad (1)$$

In equation (1) from each of the variances s^2_b (between the bottles) and s^2_w (within the bottles) the variance s^2_{HS} of the homogeneous sample (=the variance of the analytical procedure) was subtracted. Thus an effective contribution of the inhomogeneity (without the contribution of the analytical procedure) was calculated.

The combined uncertainty u_c is calculated as the sum of two contributions, - on the one hand resulting from the interlaboratory comparison for certification - and on the other hand from inhomogeneity of the sample:

$$u_c = \sqrt{\frac{s_M^2}{n} + s_{inhom}^2} \qquad (2)$$

Equation (2) was used in all cases in which the variance representing the contribution of the inhomogeneity s^2_{inhom} was not less than the variance u^2_{bb} , representing the blind part of the variances (see [6]) which could be “masked” by the variance of the analytical procedure s^2_{HS}, i. e. when

$$s^2_{inhom} > u^2_{bb} , \qquad (3)$$

whereas

$$u_{bb} = \sqrt{\frac{s_{HS}^2}{n_{HS}}} \bullet \sqrt[4]{\frac{2}{v_{s_{HS}^2}}} \qquad (4)$$

is valid, with

n_{HS} = number of parallel measurements at homogeneous sample,

$v_{s_{HS}^2}$ = degree of freedom for calculation of s^2_{HS}.

In cases when equation (3) was not valid, i. e. when

$$s^2_{inhom} \leq u^2_{bb}\ , \qquad (5)$$

the following equation was used instead of equation (2):

$$u_c = \sqrt{\frac{s_M^2}{n} + u_{bb}^2} \qquad (6)$$

In this case the combined uncertainty is consisting of the contribution of the interlaboratory comparison for certification and of a contribution (4) explained in the text below equation (2).

In the homogeneity testing at least two tables with calculations were made, one for the standard deviation between ("inter") and one for the standard deviation within ("intra") all samples of type A and type B material (for more explanation see 4.2 and APPENDIX). In cases, when neither the t-test indicated significant differences in the mean values between type A and type B materials, nor the F-test indicated significant differences (see 8.1.2) in the variances between both materials, the data of these tables were related to the totality of values from type A and type B materials together. In this case the statistical data (variances, degrees of freedom) from these tables were used for the calculations according to the equations (1) to (6). But, if one test or both tests (t-test, F-test) indicated significant differences between both types of materials, the statistical data of each of the materials were calculated additionally and separately. In this case they are to find in two additional tables of homogeneity testing (additionally to ".. AB inter" also: ".. A inter" as well as "..B inter"). In these cases the variances from these additional tables were used in the equations above, separately for both types of materials.

For following analytes the variances, based on the totality of values from type A and type B (A+B) were used in the equations (1) – (6): As_2O_3, CeO_2, CoO, Fe_2O_3, MnO, NiO, PbO, SnO_2, CdO, Sb_2O_3, SrO. The variances based on values from samples of type A or type B respectively, were used for the other analytes: BaO, Cl, Cr_2O_3, CuO, MoO_3, Se, SO_3, V_2O_5, ZnO, ZrO_2 and TiO_2.

u_c was calculatedfor most all analytes <u>of type B material</u> by using equations (1) and (2) with following exceptions: CdO, Sb_2O_3, SrO, TiO_2, for which u_c was calculated by using equations (4) and (6).

u_c, was calculated for most analytes <u>of type A material</u> by using equations (1) and (2) with TiO_2 as the only exception, for which u_c was calculated by using equations (4) and (6).

For NiO no homogeneity test could be carried out because of the composition of the anode material of the XRF tube used in the homogeneity study, which led to intolerable blank signals. But it is well known, that the distribution of Ni and Co in the soda-lime glass is correlated and similar. Therefore the variances

calculated for Co were taken for Ni, too, corrected by a factor calculated as the quotient of mass fractions of both analytes (see 5).

A contribution from an uncertainty caused by the possible aging of the material was not included, because no evidence was found, that a detectable aging of the material can occur before the date of expiry.

Finally, the expanded uncertainty "*U*" (coverage factor 2) of the certified mass fraction was calculated according to GUM as

$$U = 2\ u_c\ . \qquad (8)$$

8.2.2 Type A material

The combined uncertainties of the type A material were calculated in an analogous way as those of the type B material. But the following modifications were made:

- In case of several analytes (BaO, Cl, Cr_2O_3, CuO, MoO_3, Se, SO_3, TiO_2, V_2O_5, ZnO, ZrO_2) the s_b – values were separately calculated based on the results of the homogeneity study of type A material and of the type B material, respectively. Only the uncertainties for the other analytes are based on results of the homogeneity study of type A and type B materials together, as it was the case, when the F-test carried out (see 8.1.2) did not indicate significant differences between both groups of results.
- Considering this modification the uncertainties of the type A material were calculated in a first step in a totally analogous way as the uncertainty of the type B material. In a second step the following additional calculation was carried out for all analytes of type A material:

$$u'_c = \sqrt{u_c^2 + s_{HS}^2} \qquad (9)$$

- A third step of calculation was made, if the t-test indicated significant differences between the mean values m_A and m_B (for the analytes Cr_2O_3, TiO_2, V_2O_5, see Tabs. 10c, 10d). The additional calculation was carried out only for these analytes:

$$u''_c = \sqrt{u'^2_c + s_{HS}^2}\ . \qquad (10)$$

The expanded uncertainties were calculated according to GUM as:

$$U = 2\ u'_c \qquad (11)$$

or $$U = 2\ u''_c. \qquad (12)$$

The modifications were made because the tests had to be carried out to trace back the uncertainties of the type A material to those of the type B material.

8.3 Certified values

Basing on the calculations described in 8.1 and 8.2 the following values were certified (see Tab. 11)

Tab. 11: Certified and informative values

Tab. 11a: Certified values of BAM-S005A

Parameter	Mass fraction	
	Certified value [1] **in mg/kg**	**Uncertainty** [2] **in mg/kg**
Arsenic (III) oxide	132	8
Barium oxide	115	9
Cadmium oxide	62	4
Cerium (IV) oxide	105	6
Chloride	247	33
Cobalt oxide	49.4	2,4
Chromium (III) oxide	15.6	2,4
Copper (II) oxide	112	5
Iron (III) oxide	422	11
Manganese (II) oxide	124	5
Molybdenum (VI) oxide	343	12
Nickel (II) oxide	59.0	2
Lead (II) oxide	202	8
Antimony (III) oxide	132	7
Selenium	19.6	1,7
Tin (IV) oxide	100	7
Sulfur trioxide	1942	85
Strontium oxide	151	7
Titanium (IV) oxide	164	9
Vanadium (V) oxide	350	22
Zinc oxide	203	10
Zirconium (IV) oxide	842	125

1) The certified values are the means of 11-25 series of results (depending on the parameter) obtained by different laboratories. 3 up to 9 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of element mass fractions were calibrated using pure substances of definite stoichiometry or by solutions prepared from them, thus achieving traceability to SI unit.

2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$.

Tab. 11b: Certified values of BAM-S005B

Parameter	Mass fraction	
	Certified value [1] **in mg/kg**	**Uncertainty** [2] **in mg/kg**
Arsenic (III) oxide	132	8
Barium oxide	115	5
Cadmium oxide	62	3
Cerium (IV) oxide	105	5
Chloride	247	24
Cobalt oxide	49.4	2.3
Chromium (III) oxide	15.2	1.2
Copper (II) oxide	112	4
Iron (III) oxide	422	10
Manganese (II) oxide	124	5
Molybdenum (VI) oxide	343	12
Nickel (II) oxide	59.0	1.9
Lead (II) oxide	202	7
Antimony (III) oxide	132	6
Selenium	19.6	1.2
Tin (IV) oxide	100	7
Sulfur trioxide	1942	57
Strontium oxide	151	7
Titanium (IV) oxide	163	7
Vanadium (V) oxide	349	22
Zinc oxide	203	6
Zirconium (IV) oxide	842	76

1) The certified values are the means of 11-25 series of results (depending on the parameter) obtained by different laboratories. 3 up to 9 different analytical methods were used for the measurement of one parameter. The calibration of the methods applied for determination of element mass fractions were calibrated by pure substances of definite stoichiometry or by solutions prepared from them, thus achieving traceability to SI unit.

2) The certified uncertainty is the expanded uncertainty estimated in accordance with the Guide to the Expression of Uncertainty in Measurements (GUM) with a coverage factor $k = 2$.

Tab. 11c: not certified informative values; all mass fractions are given in %

Silicon (IV) oxide	71
Sodium oxide	13.7
Calcium oxide	10.5
Magnesium oxide	2.3
Aluminium oxide	1.1
Potassium oxide	0.7

9 Instructions for use

9.1 Area of application

The main area of application is checking the trueness of results of the determination and calibrating the determination of the certified analytes in soda-lime glass using direct sampling methods in combination with XRF. The direct use of the polished disc is preferred compared to XRF analysis by sample preparation in terms of crushing the glass and incorporating it into a pressed pellet with wax or fusing it with a flux (such as lithium tetraborate, $Li_2B_4O_7$) and casting the melt into a disc. The uncertainties given in the certificate are only valid in case of the direct XRF analysis of flat glass samples.
The polished disc guarantees very stable reference measurements over a very long period of time, at least several years. In contrast, pressed pellets and fused discs have the disadvantages that the measured samples are not stable over time and that their surface cannot be refreshed in a simple way. Such samples have to be re-prepared from time to time, whereas the polished disc needs only to be re-polished occasionally, as outlined below.
One important point is, that the CRM sample can be used to improve the results of semi-quantitative procedures by providing a one reliable point of calibration for each certified analyte.

9.2 Recommendations for correct sampling and sample preparation

At the first use it is recommended to take a CRM sample and abrade the surface to be measured by using, for example, aqueous slurry of Al_2O_3 powder on a flat surface. The latter might be a glass plate covered with the polishing slurry (for grinding and polishing manually), or the surface of the active part of a lapping machine. The surface of the sample is then polished, either manually or in a polishing machine, with polishing compounds of decreasing particle size. The final polishing with, for example, 1 µm diamond or ceria powder suspension leaves a mirror-like polished surface.

Note: ceria based polishing compounds should not be used if the intention is to determine cerium in the glass.

From time to time, depending on the frequency of use, the sample again has to be polished slightly by hand or in a polishing machine with the finest particle size polishing compound. In this way, a very thin surface layer is removed that contains absorbed atmospheric pollution, degradation products from X-ray irradiation and any surface corrosion layer of the glass itself. According to our experience no statistically significant shift occurs in the X-ray measurements over a period of about 4 weeks. However, the optimum interval between re-polishing procedures depends on the storage conditions of the sample.

9.3 Recommendations for correct storage

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

9.4 Possible line interferences

When using the CRM for XRF analysis it has to be taken into account that spectral overlapping may occur for some spectral lines and that the low thickness of the sample disc can influence the results.
No spectral interferences were observed for the Kα-lines of Ba, Ce, Co, Cu, Fe, Mn, Ni, Se, Sn, Sr and Zn.
If the thickness of the sample is too low, use the Ba-Lα or Ce-Lβ instead of K-lines of Ba and Ce, respectively.
The following table shows interferences which have been observed and possibilities to overcome these interferences.

Following interferences were observed: See Tab. 12, where also is explained, what is to do in case of interferences.

Tab. 12: Observed spectral interferences and their handling

Interfered element		Interfering element		What to do?
Element	Line	Element	Line	
As	Kα	Pb	Lα	Use the not interfered As- Kβ line
Cl	Kα	Mo	L	Interfering line with very low intensity, interference in CRM sample not relevant
Cr	Kα	V	Kβ	The intensity of Cr- Kβ line is too low, interference has to be corrected
Mo	Kα	Zr	Kβ	Use the not interfered Mo- Kβ line; a filter has to be used if a Rh tube is applied
Pb	Lα	As	Kα	Use the not interfered Pb-Lβ line
S	Kα	Mo	L	Interfering line with very low intensity, interference in CRM sample not relevant
Ti	Kα	Ba	L	Interfering line with very low intensity, interference in CRM sample not relevant
V	Kα	Ba	L	Interfering line with very low intensity, interference in CRM sample not relevant
Zr	Kα	Sr	Kβ	Interference has to be corrected
Zr	Kβ	Mo	Kα	Interference has to be corrected

9.5 Safety guidelines

1. The handling of the material does not require more safety precautions than the handling of any other glass material.
2. First aid measures
   In case of contamination of the eyes by dust (which may arise during dry polishing), rinse thoroughly with water with the eyelids held open. If product is swallowed, induce vomiting and consult a physician.
3. Handling
   Avoid formation and deposition of dust when polishing. Avoid braking of the sample.
4. Disposal considerations
   Unused material: reuse if possible.
   Or: may be disposed of in controlled landfills provided local regulations are respected.

9.6 Expiration of certification

Providing correct handling and storage of the material, this certification is valid within the specified uncertainty limits for ten years from the date of purchase. It is not excluded that the certified parameters will remain valid after this period.

10 References

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ICG-TC2

BAM

Federal Institute for Materials Research and Testing

and

International Commission on Glass – TC2

The Certification of the Mass Fractions of
Arsenic (III) oxide, Barium oxide, Cadmium oxide, Cerium (IV) oxide, Chloride, Cobalt oxide, Chromium (III) oxide, Copper (II) oxide,
Iron (III) oxide, Manganese (II) oxide, Molybdenum (VI) oxide,
Nickel (II) oxide, Lead (II) oxide, Antimony (III) oxide, Selenium,
Tin (IV) oxide, Sulfur trioxide, Strontium oxide, Titanium (IV) oxide,
Vanadium (V) oxide, Zinc oxide, and Zirconium (IV) oxide

in Soda Lime Glass

BAM-S005-A
and
BAM-S005-B

11. Appendix to the

Final certification report

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11.1 Appendix A to BAM S005

Explanation to homogeneity investigation

For data see Appendix B.

The homogeneity test was carried out at different samples (discs) which had been polished at one side. This side was measured for the test by XRF with the Siemens sequential spectrometer SRS303.
All samples had been produced from the same glass melt, but the melt had been casted two times as described in 4.1 of the certification report (for further sample preparation see also 4.1).

A representative number of analytical samples was taken from the entire number of samples by systematic selection for using in the homogeneity study.

From the type A material the following samples were taken for the test:

3A, 7A1, 7A2, 7A3, 7A4, 11A1, 15A, 19A, 23A, 27A, 31A1, 31A2, 31A3, 31A4,

From the type B material the following samples were taken for the test:

2B, 6B1, 6B2, 6B3, 6B4, 10B, 14B, 18B, 22B, 26B, 30B, 34B, 38B1, 38B2, 38B3, 38B4, 42B.

The numbering of the samples is explained by two examples:

- No. "38B1" stands for: "1st of the four prepared sample discs coming from the 38th raw sample (caky glass plate) of B series"
- No. "15A" stands for: "one of the four prepared sample discs coming from the 15th raw sample (caky glass plate) of A series".

All samples without a final digit and those samples with the final digit "1" were taken for the determination of standard deviations occurring between the samples of different raw sample plates ("between the samples", see Tab. A1 of Appendix B), whereas the standard deviations within the samples from the same raw sample plates ("within the samples") were determined using the samples 7A1-7A4, 31A1-31A4; 6B1-6B4 and 38B1-38B4 (see Tab. A3 of Appendix B).

The measurements were carried out at the cleaned samples, polished sides.

The trueness of results was for this study not of high interest, but the precision was very important. Therefore semi-quantitative calibration could be used.

The drift over the entire time of measurement was checked using sample 3A (see Tab A2 of Appendix B). The standard deviations of these measurements were treated like results from a homogeneous sample and were used for comparison.

The homogeneity test was carried out by F-tests and is documented in the tables of Tab. A4. For each analyte (all certified and informative ones, except Ni) there are at least two tables of homogeneity evaluation, one for the homogeneity test "between the samples" (A and B samples together) and one for the test "within the (raw) samples" (A and B samples together). In case of significant t- test or F-test results for the values between A- and B-groups of samples (see 8.1.2 of certification report), two tables were calculated additionally for the homogeneity test "between the samples", related to A- and to B-samples, separately.

For interpreting the tables of Tab. A4, the following explanations should be noticed.

- The "standard deviation within s_w" was calculated as the square root of the mean values of the standard deviations s_{1-4} of Tab. A3.
- As the "standard deviations between s_b" the related values from Tab. A1 were taken: s_A or s_B or s_{A+B}, depending, whether the values from materials of type A or B or of both types were considered, respectively.
- The "standard deviation for comparison s_{sc}" was taken from Tab: A2.
- The test values were calculated as shown in the tables of Tab. A4
- The F values (95%) are the tabulated value of F-distribution based on the corresponding degrees of freedom.
- The "characteristic number for the homogeneity …" is the quotient of test value and F-value. If this value is <1, no significant inhomogeneity was detected, otherwise the "grade of detected inhomogeneity" increases with this characteristic number.

By the tests the following results were achieved:

- Most test results do not indicate significant inhomogeneities "within".

Exceptions are following :
- Significant strong inhomogeneities "within" for Cl, CuO, MoO_3, ZrO_2 ;
- significant inhomogeneities "within" for K_2O, ZnO and Se ;
- significant weak inhomogeneities "within" for Al_2O_3, PbO.

Almost no significant inhomogeneities were found between the samples, - exceptions are weak inhomogeneities in type A material for Ba and Zn and in A+B Material for Cr.
This can be interpreted that way that most contents in the sample discs coming from different raw sample plates differ in the similar extent as those, coming from the same raw sample plate.

As the result of the homogeneity tests it was concluded, that the homogeneity of the material was sufficient to use it for the development of a CRM.

The contributions of the inhomogeneity (detected or maybe as not detected, i. e. "masked" contributions) of certified analytes were included into the total uncertainty of the certified values in a later stadium of evaluation (see 8.2 of certification report).

Note: The results of the homogeneity tests were only used to decide, whether the candidate material was appropriate to be used for the certification of a CRM, or not. The contribution of the inhomogeneity of the material to the uncertainty of the certified values was calculated independently from the results of the homogeneity tests (see 8.2 of the certification report), but the operands of the certification study were used for the calculation of the uncertainties of the certified values.

11.2 Appendix B: Tables of homogeneity investigation

11.2.1 Tab. A1: Between-data and tests between type A and type B materials

First (A) and second (B) casting

entstehen	SiO_2	AL_2O_3	Na_2O	K_2O	CaO	MgO	BaO	CeO_2
	%	%	%	%	%	%	mg/kg	mg/kg
3A	71,304	1,142	13,734	0,682	10,485	2,2832	96,1	125,08
7A1	71,278	1,136	13,762	0,683	10,486	2,2882	98,7	124,69
11A	71,054	1,139	13,700	0,677	10,476	2,2920	96,5	127,07
15A	71,233	1,134	13,718	0,675	10,487	2,2941	92,6	125,19
19A	71,181	1,144	13,679	0,684	10,482	2,2961	97,3	125,15
23A	71,194	1,146	13,686	0,684	10,473	2,2853	99,9	127,79
27A	71,101	1,134	13,744	0,678	10,480	2,2874	96,0	126,80
31A1	71,257	1,152	13,656	0,692	10,480	2,2903	104,0	127,42
2B	71,177	1,136	13,738	0,683	10,490	2,2911	97,6	124,17
6B1	71,165	1,140	13,713	0,684	10,472	2,2942	98,9	130,16
10B	71,444	1,142	13,703	0,682	10,479	2,2948	101,1	125,32
14B	71,494	1,141	13,715	0,678	10,482	2,2920	96,0	126,13
18B	71,391	1,137	13,735	0,682	10,460	2,2959	98,9	126,65
22B	71,462	1,137	13,723	0,679	10,470	2,2920	96,8	125,01
26B	71,346	1,138	13,711	0,682	10,465	2,2996	99,0	124,98
30B	71,444	1,144	13,691	0,681	10,455	2,2903	98,3	127,63
34B	71,322	1,141	13,690	0,680	10,469	2,2929	97,1	126,35
38B1	71,313	1,138	13,640	0,682	10,464	2,2909	98,4	126,33
42B	71,369	1,144	13,711	0,680	10,449	2,2859	97,1	126,55
$mean_A$ (m_A)	71,20	1,141	13,710	0,682	10,48	2,290	97,6	126,1
s_A	0,087	0,0063	0,036	0,0053	0,005	0,0044	3,35	1,24

s_A rel. %	0,12	0,55	0,26	0,77	0,05	0,19	3,44	0,98
mean$_B$ (m_B)	71,36	1,140	13,706	0,681	10,47	2,293	98,1	126,3
s_B	0,109	0,0029	0,027	0,0018	0,012	0,0035	1,39	1,61
s_B rel. %	0,15	0,25	0,20	0,26	0,11	0,15	1,4	1,3
mean$_{A+B}$ (m_{A+B})	**71,29**	**1,140**	**13,71**	**0,681**	**10,47**	**2,291**	**97,9**	**126,2**
s_{A+B}	**0,126**	**0,0045**	**0,030**	**0,0036**	**0,011**	**0,0041**	**2,35**	**1,43**
s_{A+B} rel. %	**0,18**	**0,40**	**0,22**	**0,52**	**0,11**	**0,18**	**2,40**	**1,13**
Drift s rel. %	*0,20*	*0,080*	*0,22*	*0,086*	*0,065*	*0,15*	*0,98*	*1,1*
counting statistics %	0,069	0,23	0,12	0,14	0,058	0,16	0,43	0,43

s_D	0,10036	0,00461	0,03098	0,00365	0,00960	0,00390	2,40283	1,46728
test statistic (m_A/m_B)	**3,367**	**0,573**	**0,239**	**0,399**	**2,791**	**1,736**	**0,395**	**0,220**
critical value t(95%), f=17	2,110	2,110	2,110	2,110	2,110	2,110	2,110	2,110
critical value t(99%), f=17	2,898				2,898			
critical value t(99.9%), f=17	3,965							
	+	**-**	**-**	**-**	**(+)**	**-**	**-**	**-**

test statistic ($s_{A/B}$)	**1,576**	**4,740**	**1,825**	**8,513**	**6,159**	**1,562**	**5,810**	**1,680**
f_1, f_2	10;7	7;10	7;10	7;10	10;7	7;10	7;10	10;7
critical value P=(95%)	3,64	3,14	3,14	3,14	3,64	3,14	3,14	3,64
critical value P=(99%)		5,20		5,20	6,62		5,20	
	-	**(+)**	**-**	**+**	**(+)**	**-**	**+**	**-**

	SO_3	Cl	Fe_2O_3	V_2O_5	TiO_2	CuO	MnO	MoO_3
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3A	1994,0	239,9	459,5	351,0	161,16	112,55	130,2	32,86
7A1	1962,6	240,0	462,7	351,7	161,71	111,33	129,5	32,76
11A	1972,6	234,7	460,4	351,4	161,05	113,15	130,1	33,07
15A	2009,1	243,7	461,0	350,6	159,05	114,12	130,2	32,30
19A	1977,9	230,1	458,7	351,7	160,57	112,59	130,4	33,54
23A	1944,7	228,0	460,5	351,0	161,13	112,85	130,3	33,78
27A	1973,9	239,9	460,2	353,3	160,52	113,14	129,6	32,89
31A1	1907,4	209,1	465,2	353,0	161,03	114,94	130,7	35,26
2B	1967,3	236,2	461,0	352,9	161,12	112,07	130,3	33,12
6B1	1956,2	234,7	460,2	351,2	161,02	112,78	130,3	33,48
10B	1947,2	232,5	461,1	350,5	159,49	113,03	130,6	33,45
14B	1967,5	236,3	458,5	352,1	159,73	112,76	130,0	32,96
18B	1978,3	234,5	459,2	349,9	160,20	112,33	129,7	33,45
22B	1974,2	233,9	458,1	349,9	160,27	113,08	129,6	33,02
26B	1975,0	235,1	458,9	347,9	159,12	111,92	130,0	33,29
30B	1975,1	235,3	460,4	348,9	160,18	112,90	129,4	33,22
34B	1982,8	237,8	458,2	351,1	158,75	112,88	130,1	32,96
38B1	1974,3	236,0	461,8	350,2	160,21	112,68	130,1	33,33
42B	1967,0	237,6	459,1	349,7	159,51	112,25	129,9	33,14
$mean_A$ (m_A)	1967,8	233,2	461,0	351,7	160,8	113,1	130,1	33,31
s_A	31,07	11,13	2,02	0,98	0,79	1,08	0,42	0,914
s_A rel. %	1,58	4,77	0,44	0,28	0,49	0,96	0,32	2,74
$mean_B$ (m_B)	1969,5	235,4	459,7	350,4	160,0	112,6	130,0	33,22
s_B	10,26	1,56	1,27	1,41	0,74	0,40	0,33	0,196
s_B rel. %	0,52	0,66	0,28	0,40	0,46	0,35	0,26	0,59

mean$_{A+B}$ (m_{A+B})	**1968,8**	**234,5**	**460,2**	**350,9**	**160,3**	**112,8**	**130,1**	**33,26**
s_{A+B}	**20,85**	**7,13**	**1,72**	**1,39**	**0,84**	**0,77**	**0,37**	**0,590**
s_{A+B} rel. %	**1,06**	**3,04**	**0,37**	**0,40**	**0,53**	**0,69**	**0,28**	**1,77**
Drift s rel. %	*0,38*	*0,49*	*0,27*	*0,25*	*0,32*	*0,22*	*0,20*	*0,19*
counting statistics %	0,23	0,33	0,22	0,26	0,29	0,28	0,33	0,22

test statistic (m_A/m_B)	**0,178**	**0,675**	**1,774**	**2,303**	**2,313**	**1,352**	**0,702**	**0,310**
critical value t(95%), f=17	2,11	2,11	2,11	2,11	2,11	2,11	2,11	2,11
critical value t(99%), f=17				2,898	2,898			
critical value t(99.9%), f=17								
	-	**-**	**-**	**(+)**	**(+)**	**-**	**-**	**-**

test statistic ($s_{A/B}$)	**9,166**	**50,770**	**2,523**	**2,070**	**1,154**	**7,327**	**1,606**	**21,800**
f_1, f_2	7;10	7;10	7;10	10;7	7;10	7;10	7;10	7;10
critical value P=(95%)	3,14	3,14	3,14	3,64	3,14	3,14	3,14	3,14
critical value P=(99%)	5,20	5,20				5,20		5,20
	++	**++**	**-**	**-**	**-**	**+**	**-**	**++**

	ZrO_2	PbO	As_2O_3	CoO	CdO	ZnO	Se	SrO
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3A	831,3	210,36	156,64	46,05	60,37	184,4	21,15	160,86
7A1	823,1	210,12	157,87	45,51	60,51	185,7	21,21	160,39
11A	799,6	209,10	156,86	45,96	60,35	181,6	21,67	161,44
15A	739,4	211,84	157,41	46,54	59,93	177,3	22,34	161,59
19A	867,7	209,57	157,58	45,98	60,41	184,9	21,29	161,32
23A	856,0	211,33	157,42	46,05	60,44	184,7	21,03	160,96
27A	829,4	210,92	158,88	46,28	60,37	182,9	21,74	160,92
31A1	918,3	209,12	157,10	46,15	59,77	191,1	20,11	160,82
2B	840,4	211,37	159,31	45,60	59,81	184,3	21,39	161,94
6B1	854,4	210,60	155,46	45,92	60,25	185,8	21,25	161,27
10B	846,0	210,54	156,09	45,53	60,75	185,8	21,07	160,85
14B	813,0	210,61	156,45	46,12	60,21	182,4	21,68	160,98
18B	824,2	209,34	155,66	45,67	59,44	183,8	21,18	160,05
22B	813,1	208,20	157,89	45,72	59,96	182,2	21,42	160,04
26B	839,9	209,75	156,88	46,05	60,03	183,5	21,27	160,17
30B	828,2	210,33	157,74	46,26	60,81	183,5	21,40	160,85
34B	801,9	208,88	157,71	45,64	60,42	182,7	21,66	161,22
38B1	829,7	208,56	157,27	45,90	59,75	183,5	21,37	160,74
42B	829,8	209,43	156,66	46,11	60,72	184,4	21,22	160,68
mean$_A$ (m_A)	833,1	210,3	157,5	46,07	60,27	184,1	21,32	161,0
s_A	52,10	1,02	0,69	0,293	0,266	3,90	0,648	0,39
s_A rel. %	6,25	0,48	0,44	0,64	0,44	2,12	3,04	0,24
mean$_B$ (m_B)	829,1	209,8	157,0	45,87	60,20	183,8	21,36	160,8
s_B	15,65	0,99	1,13	0,246	0,449	1,21	0,189	0,57
s_B rel. %	1,89	0,47	0,72	0,54	0,75	0,66	0,88	0,36
mean$_{A+B}$ (m_{A+B})	**830,8**	**210,0**	**157,2**	**45,95**	**60,23**	**183,9**	**21,34**	**160,9**
s_{A+B}	**34,58**	**1,01**	**0,97**	**0,278**	**0,376**	**2,60**	**0,428**	**0,51**

s_{A+B} rel. %	**4,16**	**0,48**	**0,62**	**0,60**	**0,62**	**1,41**	**2,01**	**0,31**
Drift s rel. %	*0,38*	*0,45*	*0,53*	*0,59*	*0,57*	*0,15*	*0,62*	*0,23*
counting statistics %	0,23	0,28	0,33	0,37	0,37	0,29	0,29	0,24

test statistic (m_A/m_B)	**0,239**	**1,101**	**1,020**	**1,606**	**0,412**	**0,221**	**0,184**	**1,021**
critical value t(95%), f=17	2,11	2,11	2,11	2,11	2,11	2,11	2,11	2,11
critical value t(99%), f=17								
critical value t(99.9%), f=17								
	-	-	-	-	-	-	-	-

test statistic ($s_{A/B}$)	**11,083**	**1,045**	**2,632**	**1,420**	**2,845**	**10,436**	**11,778**	**2,165**
f_1, f_2	7;10	7;10	10;7	7;10	10;7	7;10	7;10	10;7
critical value P=(95%)	3,14	3,14	3,64	3,14	3,64	3,14	3,14	3,64
critical value P=(99%)	5,20					5,20	5,20	
	++	-	**-**	-	**-**	**++**	**++**	**-**

	Cr_2O_3 mg/kg	SnO_2 mg/kg	Sb_2O_3 mg/kg
3A	28,87	70,81	208,41
7A1	30,26	69,99	208,92
11A	30,02	71,02	212,00
15A	29,14	69,32	206,65
19A	29,47	70,21	211,04
23A	29,42	69,87	210,02
27A	29,07	70,02	207,05
31A1	28,91	70,04	207,72
2B	28,99	70,51	206,98
6B1	29,42	70,22	208,37
10B	28,67	70,90	212,86
14B	28,52	71,37	211,21
18B	28,38	71,41	210,53
22B	28,30	69,80	209,05
26B	28,73	69,52	212,05
30B	28,70	70,44	208,73
34B	28,01	70,54	205,75
38B1	28,21	70,45	207,63
42B	28,17	70,26	206,84
$mean_A$ (m_A)	29,39	70,16	209,0
s_A	0,511	0,537	1,91
s_A rel. %	1,74	0,77	0,91
$mean_B$ (m_B)	28,55	70,49	209,1
s_B	0,408	0,578	2,30
s_B rel. %	1,43	0,82	1,10
$mean_{A+B}$ (m_{A+B})	28,91	70,35	209,0
s_{A+B}	0,613	0,571	2,09
s_{A+B} rel. %	2,12	0,81	1,00

Drift s rel. %	*1,6*	*1,4*	*1,1*
counting statistics %	0,8	0,7	0,7

s_D	0,45335	0,56145	2,14892
test statistic (m_A/m_B)	**3,983**	**1,274**	**0,112**
critical value t(95%), f=17	2,110	2,110	2,110
critical value t(99%), f=17	2,898		
critical value t(99.9%), f=17	3,965		
critical	**++**	**-**	**-**

test statistic ($s_{A/B}$)	**1,572**	**1,155**	**1,458**
f_1, f_2	7;10	10;7	10;7
critical value P=(95%)	3,14	3,64	3,64
critical value P=(99%)			
critical	**-**	**-**	**-**

11.2.2 Tab. A2: Data for “sample of comparison”

Tab. A2: Sample for comparison

						mass fraction								
	SiO_2	**AL_2O_3**	**Na_2O**	**K_2O**	**CaO**	**MgO**	**BaO**	**CeO_2**	**SO_3**	**Cl**	**Fe_2O_3**	**V_2O_5**	**TiO_2**	**CuO**
	%	%	%	%	%	%	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3A	71,32	1,139	13,67	0,684	10,50	2,281	99,0	125,3	1997,2	241,2	460,3	350,0	159,7	112,1
3A	71,19	1,142	13,67	0,682	10,49	2,282	99,9	124,4	1998,2	240,8	460,8	351,3	161,3	112,2
3A	71,19	1,141	13,65	0,684	10,48	2,295	96,6	126,7	2001,2	242,8	457,9	351,8	160,1	112,0
3A	71,23	1,145	13,69	0,683	10,49	2,285	97,7	123,9	2017,6	241,9	458,1	350,2	161,4	112,3
3A	71,21	1,142	13,66	0,683	10,48	2,285	97,5	126,4	2012,8	242,5	458,4	349,8	159,4	111,9
3A	71,06	1,146	13,65	0,683	10,49	2,280	98,1	124,1	2019,2	239,9	461,4	349,8	161,6	111,9
$Mean_{SC}$	**71,20**	**1,143**	**13,67**	**0,683**	**10,49**	**2,285**	**98,1**	**125,1**	**2007,7**	**241,5**	**459,5**	**350,5**	**160,6**	**112,1**
s_{SC}	**0,083**	**0,003**	**0,015**	**0,001**	**0,007**	**0,005**	**1,161**	**1,188**	**9,994**	**1,076**	**1,522**	**0,866**	**0,981**	**0,170**
s_{SC} (rel.%)	**0,12**	**0,22**	**0,11**	**0,09**	**0,07**	**0,23**	**1,18**	**0,95**	**0,50**	**0,45**	**0,33**	**0,25**	**0,61**	**0,15**
counting statistics %	0,069	0,23	0,12	0,14	0,058	0,16	0,43	0,43	0,23	0,33	0,22	0,26	0,29	0,28

	MnO	**MoO_3**	**ZrO_2**	**PbO**	**As_2O_3**	**CoO**	**CdO**	**ZnO**	**Se**	**SrO**	**Cr2O3**	**SnO2**	**Sb2O3**
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
3A	129,6	32,84	816,9	209,6	157,5	45,55	59,76	184,3	21,52	160,5	29,89	69,6	207,5
3A	129,9	32,74	819,8	209,5	158,5	46,23	59,58	184,1	21,30	160,0	29,71	69,8	203,3
3A	130,1	32,76	820,4	210,6	156,6	46,11	59,52	183,2	21,53	160,7	29,68	70,1	205,5
3A	129,7	32,84	819,0	210,5	158,2	45,83	60,81	183,9	21,38	160,7	29,38	70,7	208,5
3A	130,1	32,71	817,7	210,3	158,6	46,11	59,63	183,5	21,41	161,7	29,58	69,5	205,5
3A	129,3	32,73	821,8	209,7	158,0	45,91	60,53	184,1	21,39	160,8	29,38	69,2	204,9
$Mean_{SC}$	**129,8**	**32,77**	**819,3**	**210,0**	**157,9**	**45,96**	**59,97**	**183,8**	**21,42**	**160,7**	**29,60**	**69,83**	**205,86**
s_{SC}	**0,343**	**0,057**	**1,784**	**0,493**	**0,740**	**0,250**	**0,556**	**0,410**	**0,090**	**0,545**	**0,20**	**0,54**	**1,88**
s_{SC} (rel.%)	**0,26**	**0,17**	**0,22**	**0,23**	**0,47**	**0,54**	**0,93**	**0,22**	**0,42**	**0,34**	**0,67**	**0,77**	**0,91**
counting statistcs %	0,33	0,22	0,27	0,28	0,33	0,37	0,37	0,29	0,29	0,24	0,8	0,7	0,7

11.2.3 Tab. A3: Within-data (intra)

	SiO_2				Al_2O_3				Na_2O			
sample	%	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	%	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	%	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	71,388	71,295	0,095	0,134	1,142	1,141	0,002	0,206	13,726	13,733	0,023	0,171
7A2	71,360				1,143				13,704			
7A3	71,252				1,139				13,759			
7A4	71,182				1,138				13,742			
31A1	71,310	71,211	0,071	0,099	1,1549	1,147	0,010	0,849	13,619	13,670	0,043	0,314
31A2	71,166				1,1537				13,654			
31A3	71,213				1,1449				13,717			
31A4	71,154				1,1339				13,691			
6B1	71,433	71,304	0,104	0,145	1,1442	1,141	0,006	0,568	13,7103	13,706	0,005	0,037
6B2	71,261				1,1468				13,6993			
6B3	71,190				1,1411				13,7063			
6B4	71,332				1,1319				13,7097			
38B1	71,266	71,204	0,079	0,111	1,1392	1,145	0,005	0,412	13,686	13,678	0,020	0,150
38B2	71,181				1,1503				13,692			
38B3	71,268				1,1429				13,687			
38B4	71,102				1,1464				13,648			

Mean of the means	**71,254**	**1,143**	**13,697**
s (sample means)	0,0533641	0,0030343	0,0284927
s (sample means rel.%)	0,0748932	0,2654034	0,208022

	K_2O				CaO				MgO			
sample	%	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	%	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	%	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	0,6835	0,683	0,001	0,176	10,4937	10,493	0,008	0,072	2,2818	2,291	0,007	0,288
7A2	0,6841				10,5038				2,2959			
7A3	0,6817				10,4891				2,2958			
7A4	0,6818				10,4868				2,2907			
31A1	0,6884	0,687	0,004	0,579	10,4769	10,484	0,009	0,089	2,2888	2,290	0,003	0,123
31A2	0,6915				10,4975				2,2915			
31A3	0,6836				10,4819				2,2931			
31A4	0,6833				10,4788				2,2867			
6B1	0,6834	0,682	0,002	0,335	10,5053	10,496	0,007	0,071	2,2887	2,286	0,002	0,077
6B2	0,6850				10,4924				2,2860			
6B3	0,6803				10,4997				2,2845			
6B4	0,6805				10,4885				2,2855			
38B1	0,6823	0,682	0,001	0,183	10,4890	10,482	0,004	0,043	2,2943	2,292	0,003	0,110
38B2	0,6812				10,4813				2,2901			
38B3	0,6800				10,4809				2,2889			
38B4	0,6828				10,4787				2,2931			

Mean of the means	**0,683**	**10,489**	**2,290**
s (sample means)	0,002288	0,0069512	0,002446
s (sample means rel.%)	0,3348317	0,0662709	0,1068274

	BaO				CeO_2				SO_3			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	100,38	100,188	0,997	0,996	127,86	126,776	1,094	0,863	1963,5	1966,9	4,671	0,237
7A2	100,10				127,56				1962,2			
7A3	101,35				126,03				1970,9			
7A4	98,93				125,66				1970,9			
31A1	103,1	100,492	2,442	2,430	125,1	125,282	1,152	0,919	1906,4	1942,1	34,187	1,760
31A2	101,7				126,9				1920,2			
31A3	99,7				124,9				1963,8			
31A4	97,5				124,2				1977,9			
6B1	100,5	98,884	2,486	2,515	126,56	126,297	0,541	0,429	1957,1	1956,1	14,649	0,749
6B2	101,3				126,84				1935,0			
6B3	98,0				125,58				1965,5			
6B4	95,8				126,21				1966,6			
38B1	98,92	98,801	0,306	0,310	125,6	126,512	1,175	0,929	1969,4	1965,8	10,049	0,511
38B2	98,95				127,4				1952,3			
38B3	98,34				127,6				1976,1			
38B4	98,99				125,4				1965,3			

Mean of the means	**99,591**	**126,22**	**1957,7**
s (sample means)	0,874	0,653	11,494
s (sample means rel.%)	0,878	0,517	0,5871142

	Cl				Fe_2O_3				V_2O_5			
sample	mg/kg	m (1-4)	$s_{(1-4)}$	s (rel.%)	mg/kg	m (1-4)	$s_{(1-4)}$	s (rel.%)	mg/kg	m (1-4)	$s_{(1-4)}$	s (rel.%)
7A1	243,3	243,5	2,95	1,21	459,32	458,921	0,99	0,21	350,3	350,4	0,99	0,28
7A2	240,2				460,1				351,6			
7A3	247,3				458,2				350,4			
7A4	243,0				458,0				349,2			
31A1	213,8	230,8	15,68	6,79	465,4	461,6	3,09	0,67	349,3	350,1	0,98	0,28
31A2	221,2				462,9				349,3			
31A3	243,0				459,4				350,3			
31A4	245,2				458,8				351,3			
6B1	238,4	235,4	5,91	2,51	457,3	458,3	1,05	0,23	349,0	350,0	0,88	0,25
6B2	227,5				458,9				349,6			
6B3	234,7				459,5				350,8			
6B4	241,2				457,5				350,7			
38B1	234,2	238,4	3,11	1,30	459,8	458,7	1,61	0,35	350,9	350,7	0,75	0,21
38B2	239,3				460,3				351,7			
38B3	241,7				457,4				350,3			
38B4	238,5				457,2				350,0			

Mean of the means	**232,4**	**237,0**	**460,5**	**349,9**
s (sample means)	12,95	5,32	3,48	0,90
s (sample means rel.%)	5,57	2,24	0,76	0,26

	TiO_2				CuO				MnO			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	159,6	159,9	0,51	0,32	111,1	111,5	0,59	0,53	130,2	129,7	0,34	0,26
7A2	160,4				111,1				129,5			
7A3	159,3				111,3				129,5			
7A4	160,2				112,4				129,6			
31A1	161,1	160,1	0,82	0,51	114,4	112,9	1,80	1,59	130,5	130,1	0,35	0,27
31A2	160,4				114,4				130,3			
31A3	159,7				111,6				129,9			
31A4	159,3				111,1				129,7			
6B1	159,7	159,4	0,62	0,39	111,7	112,2	0,76	0,68	129,8	130,0	0,25	0,19
6B2	160,0				113,1				130,2			
6B3	158,8				112,6				129,8			
6B4	158,9				111,5				130,2			
38B1	159,1	159,0	0,39	0,25	113,1	112,9	0,28	0,25	129,5	129,4	0,42	0,32
38B2	159,5				113,0				129,5			
38B3	158,5				112,6				129,9			
38B4	158,8				112,7				128,9			

Mean of the means	**159,6**	**112,4**	**129,8**
s (sample means)	0,51	0,66	0,31
s (sample means rel.%)	0,32	0,59	0,24

	MoO_3				ZrO_2				PbO			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	32,57	32,59	0,068	0,210	827,2	823,3	4,21	0,51	211,3	210,1	0,90	0,43
7A2	32,68				826,0				210,0			
7A3	32,58				822,3				210,1			
7A4	32,52				817,8				209,1			
31A1	35,16	34,15	1,537	4,499	917,5	876,4	62,44	7,12	206,3	208,6	1,55	0,74
31A2	35,77				942,1				209,2			
31A3	32,84				822,1				209,8			
31A4	32,84				824,0				209,2			
6B1	33,47	33,45	0,266	0,795	841,9	840,8	11,11	1,32	208,8	210,2	1,60	0,76
6B2	33,82				855,2				209,6			
6B3	33,23				828,6				212,5			
6B4	33,29				837,3				210,0			
38B1	33,30	33,23	0,079	0,237	821,3	820,0	4,88	0,60	209,4	209,1	0,55	0,26
38B2	33,21				819,9				209,2			
38B3	33,29				825,2				208,3			
38B4	33,13				813,5				209,4			

Mean of the means	**33,36**	**840,1**	**209,5**
s (sample means)	0,646	25,87	0,78
s (sample means rel.%)	1,94	3,08	0,37

	As_2O_3				CoO				CdO			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	156,6	156,8	1,81	1,15	45,52	45,57	0,131	0,287	60,79	59,84	0,817	1,365
7A2	158,3				45,76				60,01			
7A3	158,0				45,57				58,82			
7A4	154,3				45,46				59,73			
31A1	158,0	157,0	1,25	0,80	46,34	45,72	0,586	1,281	59,95	59,55	0,500	0,840
31A2	155,2				45,71				59,82			
31A3	156,9				45,91				59,60			
31A4	157,7				44,94				58,83			
6B1	156,8	156,8	0,86	0,55	45,38	45,68	0,258	0,564	61,20	60,14	0,805	1,339
6B2	156,5				45,57				60,33			
6B3	158,0				45,99				59,59			
6B4	155,9				45,76				59,45			
38B1	158,9	157,2	1,41	0,90	45,34	45,87	0,367	0,801	59,47	59,58	0,383	0,643
38B2	157,6				46,19				59,25			
38B3	155,7				46,00				60,13			
38B4	156,5				45,97				59,45			

Mean of the means	**156,9**	**45,71**	**59,78**
s (sample means)	0,16	0,125	0,277
s (sample means rel.%)	0,10	0,27	0,46

	ZnO				Se				SrO			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	184,7	184,6	0,61	0,33	21,28	21,37	0,059	0,275	161,4	161,2	0,48	0,30
7A2	185,3				21,42				160,6			
7A3	184,5				21,38				161,7			
7A4	183,8				21,37				161,0			
31A1	189,9	187,2	3,63	1,94	19,97	20,79	0,782	3,764	161,5	161,1	0,24	0,15
31A2	190,7				20,27				160,9			
31A3	184,1				21,52				161,0			
31A4	183,9				21,39				161,1			
6B1	185,1	184,9	0,54	0,29	21,16	21,18	0,097	0,458	161,4	161,1	0,24	0,15
6B2	185,6				21,07				161,0			
6B3	184,4				21,18				161,3			
6B4	184,5				21,31				160,9			
38B1	182,2	182,9	0,71	0,39	21,61	21,34	0,185	0,866	161,2	161,4	0,50	0,31
38B2	183,7				21,20				162,2			
38B3	183,2				21,28				161,1			
38B4	182,4				21,28				161,3			

Mean of the means	**184,9**	**21,17**	**161,2**
s (sample means)	1,75	0,268	0,15
s (sample means rel.%)	0,95	1,27	0,09

	Cr_2O_3				SnO_2				Sb_2O_3			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	30,44	29,958	0,585	1,951	71,28	70,628	0,626	0,887	210,1	207,801	1,635	0,787
7A2	30,45				69,79				207,2			
7A3	29,28				70,62				206,3			
7A4	29,66				70,83				207,6			
31A1	29,81	30,042	0,162	0,538	70,5	70,920	0,647	0,913	210,2	210,211	0,926	0,440
31A2	30,17				71,4				209,3			
31A3	30,07				*)				209,9			
31A4	30,11				*)				211,5			
6B1	29,45	29,445	0,336	1,140	69,64	69,675	0,912	1,308	206,2	206,955	0,602	0,291
6B2	29,23				69,80				207,5			
6B3	29,18				68,51				207,3			
6B4	29,91				70,74				206,8			
38B1	29,16	29,520	0,291	0,985	70,53	70,557	0,654	0,927	206,9	207,923	2,371	1,140
38B2	29,66				70,54				205,4			
38B3	29,43				69,78				208,3			
38B4	29,83				71,38				211,0			
*) measurement failed by technical reasons												

Mean of the means	**29,741**	**70,445**	**208,223**
s (sample means)	0,3021996	0,5368475	1,3937673
s (sample means rel.%)	1,0160992	0,7620809	0,6693639

	TiO_2				CuO				MnO			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	159,6	159,9	0,51	0,32	111,1	111,5	0,59	0,53	130,2	129,7	0,34	0,26
7A2	160,4				111,1				129,5			
7A3	159,3				111,3				129,5			
7A4	160,2				112,4				129,6			
31A1	161,1	160,1	0,82	0,51	114,4	112,9	1,80	1,59	130,5	130,1	0,35	0,27
31A2	160,4				114,4				130,3			
31A3	159,7				111,6				129,9			
31A4	159,3				111,1				129,7			
6B1	159,7	159,4	0,62	0,39	111,7	112,2	0,76	0,68	129,8	130,0	0,25	0,19
6B2	160,0				113,1				130,2			
6B3	158,8				112,6				129,8			
6B4	158,9				111,5				130,2			
38B1	159,1	159,0	0,39	0,25	113,1	112,9	0,28	0,25	129,5	129,4	0,42	0,32
38B2	159,5				113,0				129,5			
38B3	158,5				112,6				129,9			
38B4	158,8				112,7				128,9			

Mean of the means	**159,6**	**112,4**	**129,8**
s (sample means)	0,51	0,66	0,31
s (sample means rel.%)	0,32	0,59	0,24

	MoO_3				ZrO_2				PbO			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	32,57	32,59	0,068	0,210	827,2	823,3	4,21	0,51	211,3	210,1	0,90	0,43
7A2	32,68				826,0				210,0			
7A3	32,58				822,3				210,1			
7A4	32,52				817,8				209,1			
31A1	35,16	34,15	1,537	4,499	917,5	876,4	62,44	7,12	206,3	208,6	1,55	0,74
31A2	35,77				942,1				209,2			
31A3	32,84				822,1				209,8			
31A4	32,84				824,0				209,2			
6B1	33,47	33,45	0,266	0,795	841,9	840,8	11,11	1,32	208,8	210,2	1,60	0,76
6B2	33,82				855,2				209,6			
6B3	33,23				828,6				212,5			
6B4	33,29				837,3				210,0			
38B1	33,30	33,23	0,079	0,237	821,3	820,0	4,88	0,60	209,4	209,1	0,55	0,26
38B2	33,21				819,9				209,2			
38B3	33,29				825,2				208,3			
38B4	33,13				813,5				209,4			

Mean of the means	**33,36**	**840,1**	**209,5**
s (sample means)	0,646	25,87	0,78
s (sample means rel.%)	1,94	3,08	0,37

	As_2O_3				CoO				CdO			
sample	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)	mg/kg	$m_{(1-4)}$	$s_{(1-4)}$	s (rel.%)
7A1	156,6	156,8	1,81	1,15	45,52	45,57	0,131	0,287	60,79	59,84	0,817	1,365
7A2	158,3				45,76				60,01			
7A3	158,0				45,57				58,82			
7A4	154,3				45,46				59,73			
31A1	158,0	157,0	1,25	0,80	46,34	45,72	0,586	1,281	59,95	59,55	0,500	0,840
31A2	155,2				45,71				59,82			
31A3	156,9				45,91				59,60			
31A4	157,7				44,94				58,83			
6B1	156,8	156,8	0,86	0,55	45,38	45,68	0,258	0,564	61,20	60,14	0,805	1,339
6B2	156,5				45,57				60,33			
6B3	158,0				45,99				59,59			
6B4	155,9				45,76				59,45			
38B1	158,9	157,2	1,41	0,90	45,34	45,87	0,367	0,801	59,47	59,58	0,383	0,643
38B2	157,6				46,19				59,25			
38B3	155,7				46,00				60,13			
38B4	156,5				45,97				59,45			

Mean of the means	**156,9**	**45,71**	**59,78**
s (sample means)	0,16	0,125	0,277
s (sample means rel.%)	0,10	0,27	0,46

11.2.4 Tab. A4 Homogeneity tests

SiO_2 - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,088	M_{total} 71,20	RSD % 0,12
standard deviation between the samples s_b	0,087	F-value	2,91
test value s_b^2/s_w^2	0,968	characteristic no. for homog. between the samples	0,333
Homogeneity between the samples: No significant inhomogeneity			

SiO_2 - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,088	M_{total} 71,36	RSD % 0,15
standard deviation between the samples s_b	0,109	F-value	2,75
test value s_b^2/s_w^2	1,526	characteristic no. for homog. between the samples	0,555
Homogeneity between the samples: No significant inhomogeneity			

SiO_2 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,088	M_{total} 71,29	RSD % 0,18
standard deviation between the samples s_b	0,126	F-value	2,572
test value s_b^2/s_w^2	2,041	characteristic no. for homog. between the samples	0,794
Homogeneity between the samples: No significant inhomogeneity			

SiO_2 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,083	M_{SC} 71,20	RSD_{SC}% 0,12
		F-value	4,68
test value s_w^2/s_{SC}^2	1,14	characteristic no. for homog. within the samples	0,243
Homogeneity within the samples: No significant inhomogeneity			

Al_2O_3 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,006	M_{total} 1,140	RSD % 0,40
standard deviation between the samples s_b	0,005	F-value	2,572
test value s_b^2/s_w^2	0,498	characteristic no. for homog. between the samples	0,194
Homogeneity between the samples: No significant inhomogeneity			

Al_2O_3 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,003	M_{SC} 1,143	RSD_{SC}% 0,20
		F-value	4,68
test value s_w^2/s_{SC}^2	6,581	characteristic no. for homog. within the samples	1,406
Homogeneity within the samples: Significant not very strong inhomogeneity			

Na_2O - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,027	M_{total} 13,71	RSD % 0,22
standard deviation between the samples s_b	0,030	F-value	2,572
test value s_b^2/s_w^2	1,281	characteristic no. for homog. between the samples	0,498
Homogeneity between the samples: No significant inhomogeneity			

Na_2O **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,015	M_{SC} 13,66563177	RSD_{SC}% 0,10
		F-value	4,68
test value s_w^2/s_{SC}^2	3,365	characteristic no. for homog. within the samples	0,719
Homogeneity within the samples: No significant inhomogeneity			

K_2O - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,0025	M_{total} 0,681	RSD % 0,52
standard deviation between the samples s_b	0,0036	F-value	2,572
test value s_b^2/s_w^2	2,110	characteristic no. for homog. between the samples	0,820
Homogeneity between the samples: No significant inhomogeneity			

K_2O **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,0006	M_{SC} 0,683	RSD_{SC}% 0,09
		F-value	4,68
test value s_w^2/s_{SC}^2	15,014	characteristic no. for homog. within the samples	3,208
Homogeneity within the samples: Significant inhomogeneity			

CaO - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,007	M_{total} 10,48	RSD % 0,05
standard deviation between the samples s_b	0,005	F-value	2,91
test value s_b^2/s_w^2	0,415	characteristic no. for homog. between the samples	0,143
Homogeneity between the samples: No significant inhomogeneity			

CaO - B

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,007	M_{total} 10,47	RSD % 0,11
standard deviation between the samples s_b	0,012	F-value	2,75
test value s_b^2/s_w^2	2,555	characteristic no. for homog. between the samples	0,929
Homogeneity between the samples: No significant inhomogeneity			

CaO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,007	M_{total} 10,47	RSD % 0,11
standard deviation between the samples s_b	0,011	F-value	2,572
test value s_b^2/s_w^2	2,305	characteristic no. for homog. between the samples	0,896
Homogeneity between the samples: No significant inhomogeneity			

CaO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,007	M_{SC} 10,49	RSD_{SC}% 0,07
		F-value	4,68
test value s_w^2/s_{SC}^2	1,108	characteristic no. for homog. within the samples	0,237
Homogeneity within the samples: No significant inhomogeneity			

MgO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,0039	M_{total} 2,291	RSD % 0,18
standard deviation between the samples s_b	0,0041	F-value	2,572
test value s_b^2/s_w^2	1,108	characteristic no. for homog. between the samples	0,431
Homogeneity between the samples: No significant inhomogeneity			

MgO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,0053	M_{SC} 2,285	RSD_{SC}% 0,23
		F-value	4,68
test value s_w^2/s_{SC}^2	0,541	characteristic no. for homog. within the samples	0,116
Homogeneity within the samples: No significant inhomogeneity			

BaO - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,82	M_{total} 97,6	RSD % 3,44
standard deviation between the samples s_b	3,35	F-value	2,91
test value s_b^2/s_w^2	3,401	characteristic no. for homog. between the samples	1,169
Homogeneity between the samples: Significant not very strong inhomogeneity			

BaO - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,82	M_{total} 98,1	RSD % 1,42
standard deviation between the samples s_b	1,39	F-value	2,75
test value s_b^2/s_w^2	0,585	characteristic no. for homog. between the samples	0,213
Homogeneity between the samples: No significant inhomogeneity			

BaO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,82	M_{total} 97,9	RSD % 2,40
standard deviation between the samples s_b	2,35	F-value	2,572
test value s_b^2/s_w^2	1,663	characteristic no. for homog. between the samples	0,647
Homogeneity between the samples: No significant inhomogeneity			

BaO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	1,16	M_{SC} 98,1	RSD_{SC}% 1,18
		F-value	4,68
test value s_w^2/s_{SC}^2	2,456	characteristic no. for homog. within the samples	0,525
Homogeneity within the samples: No significant inhomogeneity			

CeO_2 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,02	M_{total} 126,2	RSD % 1,13
standard deviation between the samples s_b	1,43	F-value	2,572
test value s_b^2/s_w^2	1,943	characteristic no. for homog. between the samples	0,755
Homogeneity between the samples: No significant inhomogeneity			

CeO_2 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	1,19	M_{SC} 125,1	RSD_{SC}% 0,95
		F-value	4,68
test value s_w^2/s_{SC}^2	0,743	characteristic no. for homog. within the samples	0,159
Homogeneity within the samples: No significant inhomogeneity			

SO_3 - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	19,40	M_{total} 1967,8	RSD % 1,58
standard deviation between the samples s_b	31,07	F-value	2,91
test value s_b^2/s_w^2	2,564	characteristic no. for homog. between the samples	0,881
Homogeneity between the samples: No significant inhomogeneity			

SO_3 - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	19,40	M_{total} 1969,5	RSD % 0,52
standard deviation between the samples s_b	10,26	F-value	2,75
test value s_b^2/s_w^2	0,280	characteristic no. for homog. between the samples	0,10
Homogeneity between the samples: No significant inhomogeneity			

SO_3 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	19,40	M_{total} 1968,8	RSD % 1,06
standard deviation between the samples s_b	20,85	F-value	2,572
test value s_b^2/s_w^2	1,154	characteristic no. for homog. between the samples	0,449
Homogeneity between the samples: No significant inhomogeneity			

SO_3 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	9,99	M_{SC} 2007,7	RSD_{SC}% 0,50
		F-value	4,68
test value s_w^2/s_{SC}^2	3,770	characteristic no. for homog. within the samples	0,806
Homogeneity within the samples: No significant inhomogeneity			

Cl - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	8,65	M_{total} 233,2	RSD % 4,77
standard deviation between the samples s_b	11,13	F-value	2,91
test value s_b^2/s_w^2	1,656	characteristic no. for homog. between the samples	0,569
Homogeneity between the samples: No significant inhomogeneity			

Cl - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	8,65	M_{total} 235,4	RSD % 0,66
standard deviation between the samples s_b	1,56	F-value	2,75
test value s_b^2/s_w^2	0,033	characteristic no. for homog. between the samples	0,012
Homogeneity between the samples: No significant inhomogeneity			

Cl - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	8,65	M_{total} 234,5	RSD % 3,04
standard deviation between the samples s_b	7,13	F-value	2,572
test value s_b^2/s_w^2	0,680	characteristic no. for homog. between the samples	0,264
Homogeneity between the samples: No significant inhomogeneity			

Cl **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	1,08	M_{SC} 241,5	RSD_{SC}% 0,45
		F-value	4,68
test value s_w^2/s_{SC}^2	64,627	characteristic no. for homog. within the samples	13,809
Homogeneity within the samples: Significant strong inhomogeneity			

Fe_2O_3 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,89	M_{total} 460,2	RSD % 0,37
standard deviation between the samples s_b	1,72	F-value	2,572
test value s_b^2/s_w^2	0,827	characteristic no. for homog. between the samples	0,321
Homogeneity between the samples: No significant inhomogeneity			

Fe_2O_3 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	1,52	M_{SC} 459,5	RSD_{SC}% 0,33
		F-value	4,68
test value s_w^2/s_{SC}^2	1,539	characteristic no. for homog. within the samples	0,329
Homogeneity within the samples: No significant inhomogeneity			

V_2O_5 - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,91	M_{total} 351,7	RSD % 0,28
standard deviation between the samples s_b	0,98	F-value	2,91
test value s_b^2/s_w^2	1,165	characteristic no. for homog. between the samples	0,400
Homogeneity between the samples: No significant inhomogeneity			

V_2O_5 - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,91	M_{total} 350,4	RSD % 0,40
standard deviation between the samples s_b	1,41	F-value	2,75
test value s_b^2/s_w^2	2,411	characteristic no. for homog. between the samples	0,877
Homogeneity between the samples: No significant inhomogeneity			

V_2O_5 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,91	M_{total} 350,9	RSD % 0,40
standard deviation between the samples s_b	1,39	F-value	2,572
test value s_b^2/s_w^2	2,351	characteristic no. for homog. between the samples	0,914
Homogeneity between the samples: No significant inhomogeneity			

V_2O_5 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,87	M_{SC} 350,5	RSD_{SC}% 0,25
		F-value	4,68
test value s_w^2/s_{SC}^2	1,094	characteristic no. for homog. within the samples	0,234
Homogeneity within the samples: No significant inhomogeneity			

TiO_2 - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,61	M_{total} 160,8	RSD % 0,49
standard deviation between the samples s_b	0,79	F-value	2,91
test value s_b^2/s_w^2	1,693	characteristic no. for homog. between the samples	0,582
Homogeneity between the samples: No significant inhomogeneity			

TiO_2 - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,61	M_{total} 160,0	RSD % 0,46
standard deviation between the samples s_b	0,74	F-value	2,75
test value s_b^2/s_w^2	1,467	characteristic no. for homog. between the samples	0,534
Homogeneity between the samples: No significant inhomogeneity			

TiO_2 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,61	M_{total} 160,3	RSD % 0,53
standard deviation between the samples s_b	0,84	F-value	2,572
test value s_b^2/s_w^2	1,937	characteristic no. for homog. between the samples	0,753
Homogeneity between the samples: No significant inhomogeneity			

TiO_2 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,98	M_{SC} 160,6	RSD_{SC}% 0,61
		F-value	4,68
test value s_w^2/s_{SC}^2	0,383	characteristic no. for homog. within the samples	0,082
Homogeneity within the samples: No significant inhomogeneity			

CuO - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,03	M_{total} 113,1	RSD % 0,96
standard deviation between the samples s_b	1,08	F-value	2,91
test value s_b^2/s_w^2	1,102	characteristic no. for homog. between the samples	0,379
Homogeneity between the samples: No significant inhomogeneity			

CuO - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,03	M_{total} 112,6	RSD % 0,35
standard deviation between the samples s_b	0,40	F-value	2,75
test value s_b^2/s_w^2	0,150	characteristic no. for homog. between the samples	0,055
Homogeneity between the samples: No significant inhomogeneity			

CuO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,03	M_{total} 112,8	RSD % 0,69
standard deviation between the samples s_b	0,77	F-value	2,572
test value s_b^2/s_w^2	0,567	characteristic no. for homog. between the samples	0,220
Homogeneity between the samples: No significant inhomogeneity			

CuO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,17	M_{SC} 112,1	RSD_{SC}% 0,15
		F-value	4,68
test value s_w^2/s_{SC}^2	36,508	characteristic no. for homog. within the samples	7,801
Homogeneity within the samples: Significant strong inhomogeneity			

MnO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,34	M_{total} 130,1	RSD % 0,28
standard deviation between the samples s_b	0,37	F-value	2,572
test value s_b^2/s_w^2	1,140	characteristic no. for homog. between the samples	0,443
Homogeneity between the samples: No significant inhomogeneity			

MnO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,34	M_{SC} 129,8	RSD_{SC}% 0,26
		F-value	4,68
test value s_w^2/s_{SC}^2	1,009	characteristic no. for homog. within the samples	0,216
Homogeneity within the samples: No significant inhomogeneity			

MoO_3 - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,781	M_{total} 33,31	RSD % 2,74
standard deviation between the samples s_b	0,914	F-value	2,91
test value s_b^2/s_w^2	1,367	characteristic no. for homog. between the samples	0,470
Homogeneity between the samples: No significant inhomogeneity			

MoO_3 - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,781	M_{total} 33,22	RSD % 0,59
standard deviation between the samples s_b	0,196	F-value	2,75
test value s_b^2/s_w^2	0,063	characteristic no. for homog. between the samples	0,023
Homogeneity between the samples: No significant inhomogeneity			

MoO_3 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,781	M_{total} 33,26	RSD % 1,77
standard deviation between the samples s_b	0,590	F-value	2,572
test value s_b^2/s_w^2	0,570	characteristic no. for homog. between the samples	0,222
Homogeneity between the samples: No significant inhomogeneity			

MoO_3 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,057	M_{SC} 32,77	RSD_{SC}% 0,17
		F-value	4,68
test value s_w^2/s_{SC}^2	187,819	characteristic no. for homog. within the samples	40,132
Homogeneity within the samples: Significant very strong inhomogeneity			

ZrO_2 - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	31,87	M_{total} 833,1	RSD % 6,25
standard deviation between the samples s_b	52,10	F-value	2,91
test value s_b^2/s_w^2	2,672	characteristic no. for homog. between the samples	0,918
Homogeneity between the samples: No significant inhomogeneity			

ZrO_2 - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	31,87	M_{total} 830,8	RSD % 4,16
standard deviation between the samples s_b	15,65	F-value	2,75
test value s_b^2/s_w^2	0,241	characteristic no. for homog. between the samples	0,088
Homogeneity between the samples: No significant inhomogeneity			

ZrO_2 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	31,87	M_{total} 830,8	RSD % 4,16
standard deviation between the samples s_b	34,58	F-value	2,572
test value s_b^2/s_w^2	1,177	characteristic no. for homog. between the samples	0,458
Homogeneity between the samples: No significant inhomogeneity			

ZrO_2 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	1,78	M_{SC} 819,3	RSD_{SC}% 0,22
		F-value	4,68
test value s_w^2/s_{SC}^2	319,089	characteristic no. for homog. within the samples	68,181
Homogeneity within the samples: Significant very strong inhomogeneity			

PbO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,23	M_{total} 210,0	RSD % 0,48
standard deviation between the samples s_b	1,01	F-value	2,572
test value s_b^2/s_w^2	0,670	characteristic no. for homog. between the samples	0,260
Homogeneity between the samples: No significant inhomogeneity			

PbO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,49	M_{SC} 210,0	RSD_{SC}% 0,23
		F-value	4,68
test value s_w^2/s_{SC}^2	6,259	characteristic no. for homog. within the samples	1,337
Homogeneity within the samples: Significant not very strong inhomogeneity			

As_2O_3 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,37	M_{total} 157,2	RSD % 0,62
standard deviation between the samples s_b	0,97	F-value	2,572
test value s_b^2/s_w^2	0,500	characteristic no. for homog. between the samples	0,195
Homogeneity between the samples: No significant inhomogeneity			

As_2O_3 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,74	M_{SC} 157,9	RSD_{SC}% 0,47
		F-value	4,68
test value s_w^2/s_{SC}^2	3,448	characteristic no. for homog. within the samples	0,737
Homogeneity within the samples: No significant inhomogeneity			

CoO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,375	M_{total} 45,95	RSD % 0,60
standard deviation between the samples s_b	0,278	F-value	2,572
test value s_b^2/s_w^2	0,549	characteristic no. for homog. between the samples	0,213
Homogeneity between the samples: No significant inhomogeneity			

CoO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,250	M_{SC} 45,96	RSD_{SC}% 0,54
		F-value	4,68
test value s_w^2/s_{SC}^2	2,238	characteristic no. for homog. within the samples	0,478
Homogeneity within the samples: No significant inhomogeneity			

CdO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,654	M_{total} 60,23	RSD % 0,62
standard deviation between the samples s_b	0,376	F-value	2,572
test value s_b^2/s_w^2	0,330	characteristic no. for homog. between the samples	0,128
Homogeneity between the samples: No significant inhomogeneity			

CdO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,556	M_{SC} 59,97	RSD_{SC}% 0,93
		F-value	4,68
test value s_w^2/s_{SC}^2	1,383	characteristic no. for homog. within the samples	0,295
Homogeneity within the samples: No significant inhomogeneity			

ZnO - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,89	M_{total} 184,1	RSD % 2,12
standard deviation between the samples s_b	3,90	F-value	2,91
test value s_b^2/s_w^2	4,246	characteristic no. for homog. between the samples	1,459
Homogeneity between the samples: Significant not very strong inhomogeneity			

ZnO - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,89	M_{total} 183,8	RSD % 0,66
standard deviation between the samples s_b	1,21	F-value	2,75
test value s_b^2/s_w^2	0,407	characteristic no. for homog. between the samples	0,148
Homogeneity between the samples: No significant inhomogeneity			

ZnO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,89	M_{total} 183,9	RSD % 1,41
standard deviation between the samples s_b	2,60	F-value	2,572
test value s_b^2/s_w^2	1,883	characteristic no. for homog. between the samples	0,732
Homogeneity between the samples: No significant inhomogeneity			

ZnO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,41	M_{SC} 183,8	RSD_{SC}% 0,22
		F-value	4,68
test value s_w^2/s_{SC}^2	21,351	characteristic no. for homog. within the samples	4,562
Homogeneity within the samples: Significant inhomogeneity			

Se - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,406	M_{total} 21,32	RSD % 3,04
standard deviation between the samples s_b	0,648	F-value	2,91
test value s_b^2/s_w^2	2,546	characteristic no. for homog. between the samples	0,875
Homogeneity between the samples: No significant inhomogeneity			

Se - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,406	M_{total} 21,36	RSD % 0,88
standard deviation between the samples s_b	0,189	F-value	2,75
test value s_b^2/s_w^2	0,216	characteristic no. for homog. between the samples	0,079
Homogeneity between the samples: No significant inhomogeneity			

Se - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,406	M_{total} 21,34	RSD % 2,01
standard deviation between the samples s_b	0,428	F-value	2,572
test value s_b^2/s_w^2	1,113	characteristic no. for homog. between the samples	0,433
Homogeneity between the samples: No significant inhomogeneity			

Se **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,090	M_{SC} 21,42	RSD_{SC}% 0,38
		F-value	4,68
test value s_w^2/s_{SC}^2	20,301	characteristic no. for homog. within the samples	4,338
Homogeneity within the samples: Significant inhomogeneity			

SrO - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,39	M_{total} 160,9	RSD % 0,31
standard deviation between the samples s_b	0,51	F-value	2,572
test value s_b^2/s_w^2	1,724	characteristic no. for homog. between the samples	0,670
Homogeneity between the samples: No significant inhomogeneity			

SrO **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,55	M_{SC} 160,7	RSD_{SC}% 0,34
		F-value	4,68
test value s_w^2/s_{SC}^2	0,499	characteristic no. for homog. within the samples	0,107
Homogeneity within the samples: No significant inhomogeneity			

Cr_2O_3 - A **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,376	M_{total} 29,39	RSD % 1,74
standard deviation between the samples s_b	0,511	F-value	2,91
test value s_b^2/s_w^2	1,851	characteristic no. for homog. between the samples	0,636
Homogeneity between the samples: No significant inhomogeneity			

Cr_2O_3 - B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,376	M_{total} 28,55	RSD % 1,43
standard deviation between the samples s_b	0,408	F-value	2,75
test value s_b^2/s_w^2	1,178	characteristic no. for homog. between the samples	0,428
Homogeneity between the samples: No significant inhomogeneity			

Cr_2O_3 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,376	M_{total} 28,91	RSD % 0,18
standard deviation between the samples s_b	0,613	F-value	2,572
test value s_b^2/s_w^2	2,657	characteristic no. for homog. between the samples	1,033
Homogeneity between the samples: (Almost) no significant inhomogeneity			

Cr_2O_3 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,199	M_{SC} 29,60	RSD_{SC}% 0,67
		F-value	4,68
test value s_w^2/s_{SC}^2	3,57	characteristic no. for homog. within the samples	0,762
Homogeneity within the samples: No significant inhomogeneity			

SnO_2 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	0,719	M_{total} 70,35	RSD % 0,81
standard deviation between the samples s_b	0,571	F-value	2,802
test value s_b^2/s_w^2	0,630	characteristic no. for homog. between the samples	0,225
Homogeneity between the samples: No significant inhomogeneity			

SnO_2 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	0,540	M_{SC} 69,83	RSD_{SC}% 0,77
		F-value	4,74
test value s_w^2/s_{SC}^2	1,773	characteristic no. for homog. within the samples	0,374
Homogeneity within the samples: No significant inhomogeneity			

Sb_2O_3 - A+B **inter**

Homogeneity between the samples			
Analysis of variance	**α = 0.05**		
standard deviation within the samples s_w	1,54	M_{total} 209,0	RSD % 1,00
standard deviation between the samples s_b	2,09	F-value	2,572
test value s_b^2/s_w^2	1,835	characteristic no. for homog. between the samples	0,713
Homogeneity between the samples: No significant inhomogeneity			

Sb_2O_3 **intra**

Homogeneity within the samples			
Analysis of variance	**α = 0.05**		
standard deviation of sample for comparison s_{SC}	1,88	M_{SC} 205,9	RSD_{SC}% 0,91
		F-value	4,68
test value s_w^2/s_{SC}^2	0,674	characteristic no. for homog. within the samples	0,144
Homogeneity within the samples: No significant inhomogeneity			