CCQM-K57

Chemical composition of clay

Final Report

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1. Summary

After the successful completion of the pilot study, CCQM-P65 [1], the Inorganic Analysis Working Group of CCQM agreed to conduct key comparison CCQM-K57, Chemical composition of clay, in Paris, April 2006. Five elements of Si, Ca, Fe, Al and Mg in natural mass fraction levels were measured and reported as oxides in clay. Six national metrology institutes participated in CCQM-K57, and CENAM (Queretaro, Mexico) coordinated.

The methods employed were isotope dilution mass spectrometry (IDMS), inductively coupled plasma-mass spectrometry (ICP-MS), inductively coupled plasma-optical emission spectrometry (ICP-OES) using dehydration method and condensation method, gravimetric analysis, neutron activation analysis (NAA), prompt gamma activation analysis (PGAA) and X-ray fluorescence spectrometry (XRF) with reconstitution method and external calibration.

This final report presents the capability of the participant institutes, based on the KCRV, which was approved in the IAWG spring meeting in 2008, and the equivalence statements regarding the KCRV, approved in its autumn meeting.

2. Introduction

To demonstrate the capability to conduct reliable measurements of elements at natural mass fraction levels (major and minor elements) in natural matrix is very important for many reasons, due to its impact on economy, environmental protection, production and quality control. In contrast to the notable works carried out on trace element analysis of matrix materials, no comparison has been done to evaluate the measurement capability of elements at the natural concentration level in natural matrix samples.

This comparison is organized to demonstrate and document the measurement capability of the participant laboratories in the determination of the mass fraction content of major and minor elements in clay, with the following concentration range:

SiO_2:	650 -	700	mg/g	CaO:	10 -	50	mg/g
Al_2O_3:	100 -	200	mg/g	MgO:	5 -	15	mg/g
Fe_2O_3:	20 -	100	mg/g				

This material, known as “Gold Clay”, was used to prepare candidate RM to be certified. Preparation, bottling and homogeneity studies were performed according to the procedure based on ISO Guide 34.

Participation in this key comparison was open to all NMIs and/or designated laboratories in accordance with the guidelines by the CIPM MRA. The use of potentially primary methods was recommended, but any analytical technique, suitable for the analyte and level of concentration, was allowed.

Some participants used more than one analytical method for each measurand; in this case, the participant was requested to provide results by each analytical method and the combined result together with their respective associated uncertainty.
Six national metrology institutes reported results; two of them reported combined result from several analytical methods. Reconstitution method with high performance borate fusion was employed by four institutes.

Some NMIs also reported results of potentially primary methods [IDMS or INAA (PGAA)] and reference methods were applied by other NMIs.

This comparison in natural matrix sample is characterized by the participation of several measurement methods with different principles and also the participation of several NMIs with the same measuring principles, which will give an indication of the reproducibility and accuracy achievable for the method.

3. Rationale of this comparison

- To demonstrate and document the measurement capability of the participant laboratories in determining the mass fraction content of major and minor elements in a natural sample of clay.
- To demonstrate the reliability of the reconstitution method, since their basis is the gravimetric preparation of standards for calibration, and provides direct link to the SI.
- To serve as evidence to support the CMCs in the Appendix C of the CIPM-MRA in the scope of this comparison.

4. Participants

Table 1 shows the participating institutes in the CCQM-K57. All institutes were registered to measure all the five elements.
Samples, measurement protocol and MSDS (Material safety data sheet) were shipped in March 15th, 2007 and received in their respective destinations by the end of March 2007.

Table 1. CCQM-K57 participants

INSTITUTE /ORGANIZATION	COUNTRY	CONTACT PERSON
BAM Federal Institute for Materials Research and Testing	Germany	Dr. Siegfried Noack
NIST National Institute of Standards and Technology	USA	Dr. Gregory C. Turk
NMIJ National Metrology Institute of Japan	Japan	Dr. Akiharu Hioki
SP Technical Research Institute of Sweden	Sweden	Dr. Bertil Magnusson
VNIIM All-Russia D.I. Mendeleyev Scientific and Research Institute for Metrology	Russia	Dr. L.A. Konopelko, Dr. Y.A. Kustikov
CENAM Centro Nacional de Metrologia	Mexico	Mr. J. Antonio Salas

5. Sample homogeneity

Homogeneity studies included determination of particle size distribution and chemical tests; in both cases, within and between bottles homogeneity tests were carried out according to the internationally accepted test for certification of reference materials [2].

For the particle size distribution measurements, low angle laser scattering in wet dispersion technique was used. Fifteen randomly selected bottles from the entire batch (250 bottles) were used. From each bottle, four sub-samples were taken employing a rotary sample splitter. F-test indicated that the result of the homogeneity by particle size distribution is insignificant ($F<F_{crit}$, the critical value of F for $\alpha = 5\%$).

Because XRF is a highly repeatable measurement method, it was used for the between bottle homogeneity study Si, Al, Fe, Ca and Mg were measured in samples prepared by duplicate from fifteen randomly selected bottles from the entire batch. In addition Ti, K, Zr, Sr, Rb, Zn, Mn, Cr and Ba were also measured. Sample preparation was very simple and no chemical transformation occurred. Tablets were prepared by compacting dry powder mixed with organic agglutinant in a 30 mm diameter dies, using a 23 ton pressure.

Given that the experiment design permits multiple sub-sampling in each bottle, one way analysis of variance (ANOVA-1 way) approach was used to estimate the between bottle variance , and it was used as an estimation of between bottle homogeneity, s_{bb}.
(ISO Guide 35 - section 7.8). In such way, s_{bb}^2 estimates u_{bb}^2.

The between bottle standard uncertainty estimations (u_{bb}) were calculated for each measurand and reported in relative terms with respect to the mean value. It was found that the relative uncertainty due to homogeneity is ranging from 0.2 to 1.5 % relative for the different measurands, being appropriate for the needs of this comparison.

The results given in table 2 indicate the relative uncertainty of homogeneity calculated for each measurand.

Table 2. Results for chemical homogeneity testing

	Si	Al	Fe	Ca	Mg
Uncertainty due to homogeneity (relative)	0.672 %	0.652 %	0.209 %	0.741 %	1.461 %

6. Technical protocol

The technical protocol distributed to participants is attached as Annex A.

7. Measurement and sample preparation methods

Table 3 summarizes the information regarding measurement and sample preparation methods, reported by the participants.

Table 3. Summary of the measurement and sample preparation methods

INSTITUTE		MEASURAND				
		Si	**Fe**	**Ca**	**Al**	**Mg**
BAM	MEASUREMENT METHOD	XRF Reconstitution				
	SAMPLE PREPARATION METHOD Sample aliquot Digest reagents	300 mg of clay and 6 g of lithium tetraborate ($Li_2B_4O_7$). Fusion.				
	CALIBRATION	Preparation of synthetic calibration samples with bracketing amounts of elements by the use of primary substances certified by BAM and VDEh (Steel and Iron Institute).				
NIST	MEASUREMENT METHOD	• HP-BF-XRF • PGAA	• HP-BF-XRF • INAA • PGAA	• HP-BF-XRF • INAA	• HP-BF-XRF • INAA	• HP-BF-XRF • INAA
	SAMPLE PREPARATION METHOD Sample aliquot Digest reagents	Not reported				
	CALIBRATION	Not reported				
NMIJ	MEASUREMENT METHOD	• Gravimetric dehydration for main Si. • ICP-OES for soluble Si	• IDMS • ICP-OES (condensation method)	• IDMS • ICP-OES (condensation method)	• ICP-MS • ICP-OES (Condensation method) • ICP-OES (Dehydration method)	• ICP-MS • ICP-OES (Condensation. method)
	SAMPLE PREPARATION METHOD Sample aliquot Digest reagents	0.5 g of sample + 3.0 g of sodium carbonate fusion and HCL dissolution	Acid digestion. 0.5 g of sample. 7 mL of 68% HNO_3 + 3 mL of 48 % HF + 5 mL of 96 % H_2SO_4, heat at 240 ºC for 16 hours. Moved into Pt plate and heated at 350 ºC until dryness. Add 5 mL of 48 % H2SO4 and then evaporated to dryness again. A 5 mL of 15 % HCl was added and heated at 80 ºC. Samples were diluted up to 50 g with 0.2 mol dm^{-3} HCl.			
	CALIBRATION	NIST SRM 3150 used in ICP-OES for soluble Si.	Isotope pairs ^{56}Fe and ^{57}Fe	Isotope pairs ^{42}Ca and ^{44}Ca	^{27}Al	^{25}Al
			ICP-OES: JCSS supplied by KANTO Chemicals (Al, Ca, Fe and Mg)			

<table>
<tr><th rowspan="2" colspan="2">INSTITUTE</th><th colspan="5">MEASURAND</th></tr>
<tr><th>Si</th><th>Fe</th><th>Ca</th><th>Al</th><th>Mg</th></tr>
<tr><td rowspan="3">SP</td><td>MEASUREMENT METHOD</td><td colspan="5">XRF Reconstitution</td></tr>
<tr><td>SAMPLE PREPARATION METHOD
Sample aliquot
Digest reagents</td><td colspan="5">0.5 g of dried sample + 5 g of lithium tetraborate ($Li_2B_4O_7$) + 20 mg LiBr</td></tr>
<tr><td>CALIBRATION</td><td colspan="5">High purity standards of MgO (99.95 %), Al_2O_3 (99.999 %), KCO_3 (99.998 %), $CaCO_3$ (99.99 %), TiO (99.999 %), Fe_2O_3 (99.999 %). BSC 313 grinded in widi mill - SiO_2 (99.78 %), Teknolab A/S Mg^{2+}.</td></tr>
<tr><td rowspan="3">VNIIM</td><td>MEASUREMENT METHOD</td><td colspan="5">XRF</td></tr>
<tr><td>SAMPLE PREPARATION METHOD
Sample aliquot
Digest reagents</td><td colspan="5">0.6 g of sample and 7.2 g of combined borate flux. Fusion.</td></tr>
<tr><td>CALIBRATION</td><td colspan="5">Certified Reference Materials (different rocks).</td></tr>
<tr><td rowspan="3">CENAM</td><td>MEASUREMENT METHOD</td><td colspan="5">XRF Reconstitution</td></tr>
<tr><td>SAMPLE PREPARATION METHOD
Sample aliquot
Digest reagents</td><td colspan="5">1 g of dried sample + 9 g of lithium tetraborate ($Li_2B_4O_7$). Fusion.</td></tr>
<tr><td>CALIBRATION</td><td colspan="5">High purity metal Mg (99.99 %), Primary standards SRM 915a ($CaCO_3$), SRM 154c (TiO_2), High purity compounds Fe_2O_3 (99.998 %), Al_2O_3 (99.995 %), SiO_2 (99.999 %).</td></tr>
</table>

8. CCQM-K57 Results

The results sent by the participants in the form RESULTS REPORTING SHEET FOR CCQM-K57 and CCQM-P65.1, are presented in the tables 4 - 8 and figures 1 - 5, sorted by measurand. In the figures, for each institute, the central point is the reported result and the error bar corresponds to the expanded uncertainty. The red line in each figure indicates the median of all reported results. In the right side of each figure appear the results of individual methods for laboratories who reported combined results.

Table 4. Reported results for mass fraction of silicon as SiO_2

NMI	**MEASUREMENT METHOD**	**RESULT** mg/g	**EXPANDED UNCERTAINTY** mg/g	**COVERAGE FACTOR** (95 % confidence)	**RELATIVE UNCERTAINTY** %
BAM	XRF – Reconstitution	659.0	9.86	2	1.49
CENAM	XRF – Reconstitution	662.3	3.1	2.1	0.54
NIST	Combined value	665.6	13.2	2	1.98
	1) HP-BF-XRF	655.0	3.7	2.4	0.56
	2) PGAA	676.2	9.2	2	1.36
NMIJ	Gravimetric analysis	653.52	0.83	2	0.13
SP	XRF – Reconstitution	656.0	5.2	2	0.79
VNIIM	XRF - Fusion	657.08	3.81	2	0.58

Figure 1. Results for mass fraction of silicon as SiO_2

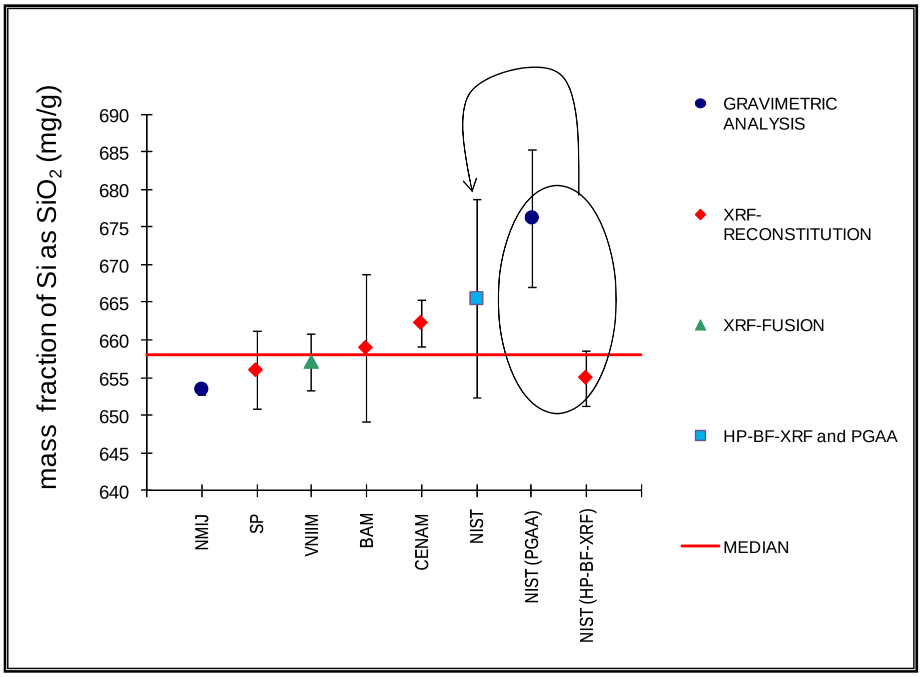


Table 5. Reported results for mass fraction of aluminum as Al_2O_3

NMI	**MEASUREMENT METHOD**	**RESULT** mg/g	**EXPANDED UNCERTAINTY** mg/g	**COVERAGE FACTOR** (95 % confidence)	**RELATIVE UNCERTAINTY** %
BAM	XRF – Reconstitution	147.3	1.3	2	0.88
CENAM	XRF – Reconstitution	150.22	1.29	2.1	0.86
NIST	Combined value	146.35	1.45	2	0.99
	1) HP-BF-XRF	146.49	0.81	2.4	0.55
	2) INAA	146.2	2.7	2	0.55
NMIJ	Combined value	148.34	2.74	2	1.85
	1) ICP-MS	148.5	11.5	2	7.74
	2) ICP-OES (Dehydration method)	148.21	2.7	2	1.82
	3) ICP-OES (Condensation method)	148.5	5.7	2	3.84
SP	XRF – Reconstitution	145.9	2.1	2	1.44
VNIIM	XRF - Fusion	149.22	2.66	2	1.78

Figure 2. Results for mass fraction of aluminum as Al_2O_3

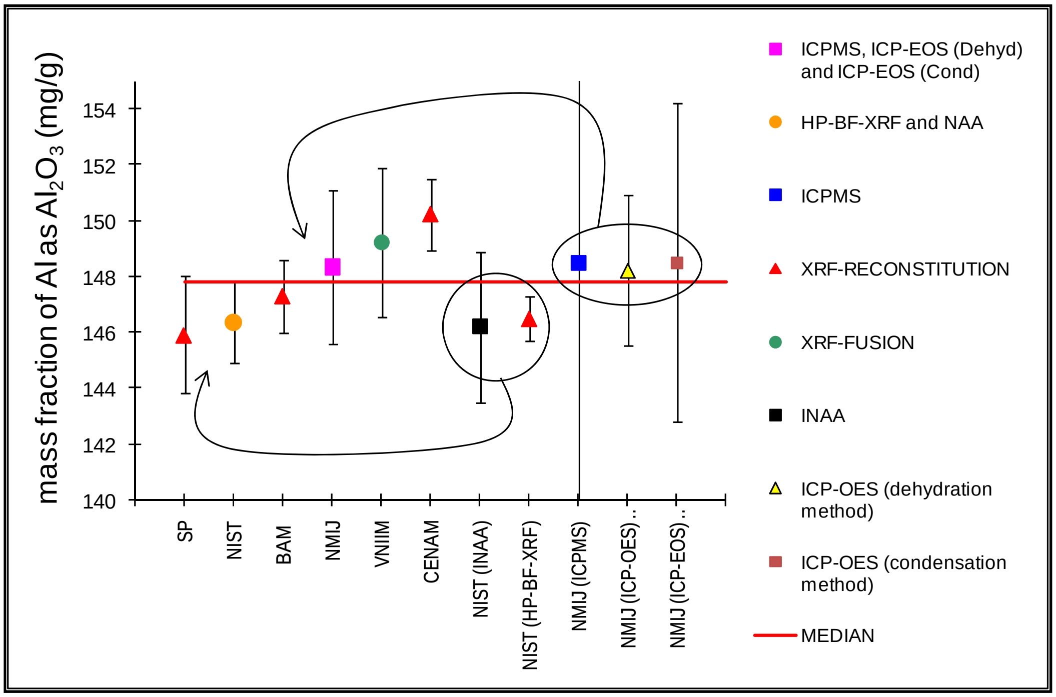


Table 6. Reported results for mass fraction of iron as Fe_2O_3

NMI	MEASUREMENT METHOD	RESULT mg/g	EXPANDED UNCERTAINTY mg/g	COVERAGE FACTOR (95 % confidence)	RELATIVE UNCERTAINTY %
BAM	XRF – Reconstitution	56.3	2.8	2	4.97
CENAM	XRF – Reconstitution	55.89	0.32	2.1	0.57
NIST	Combined HP-BF-XRF, NAA and PGAA	55.98	0.36	2	0.64
	1) HP-BF-XRF	55.98	0.90	3.2	1.61
	2) INAA	55.92	0.46	2	0.82
	3) PGAA	56.03	0.77	2	1.37
NMIJ	Combination of three methods	54.54	0.59	2	1.08
	1) IDMS	54.33	0.49	2	0.90
	2) ICP-OES (Condensation method)	55.74	2.81	2	5.04
SP	XRF – Reconstitution	56.6	1.2	2	2.12
VNIIM	XRF - Fusion	59.54	1.94	2	3.25

Figure 3. Results for mass fraction of iron as Fe_2O_3

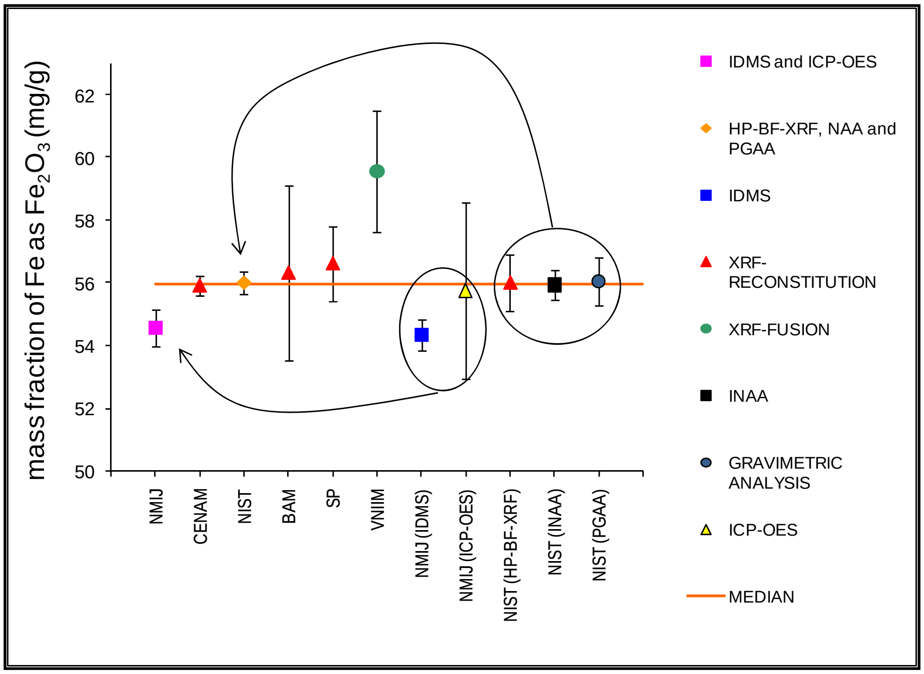


Table 7. Reported results for mass fraction of calcium as CaO

NMI	**MEASUREMENT METHOD**	**RESULT** mg/g	**EXPANDED UNCERTAINTY** mg/g	**COVERAGE FACTOR** (95 % confidence)	**RELATIVE UNCERTAINTY** %
BAM	XRF – Reconstitution	24.42	0.64	2	2.62
CENAM	XRF – Reconstitution	24.58	0.23	2.3	0.94
NIST	Combined HP-BF-XRF and NAA	24.19	0.69	2	2.85
	1) HP-BF-XRF	24.69	0.25	2.4	1.01
	2) INAA	23.68	0.73	2	3.08
NMIJ	Combination of three methods	24.23	1.37	2	5.65
	3) IDMS	24.09	2.82	2	11.71
	4) ICP-OES (Condensation method)	24.31	1.48	2	6.09
SP	XRF – Reconstitution	24.7	0.8	2	3.24
VNIIM	XRF – Fusion	23.138	0.926	2	4.0

Figure 4. Results for mass fraction of calcium as CaO

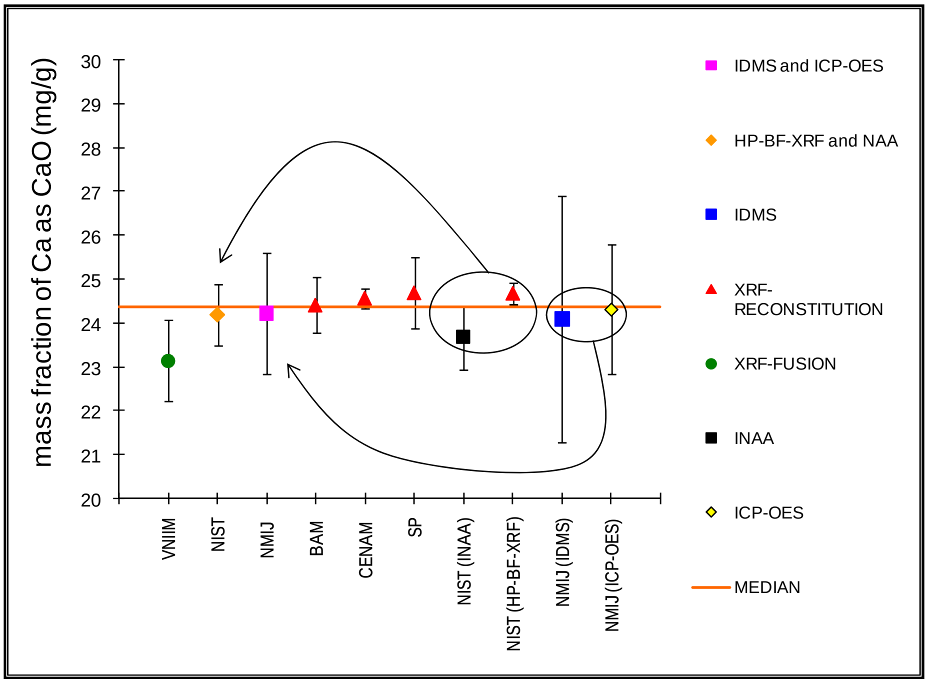
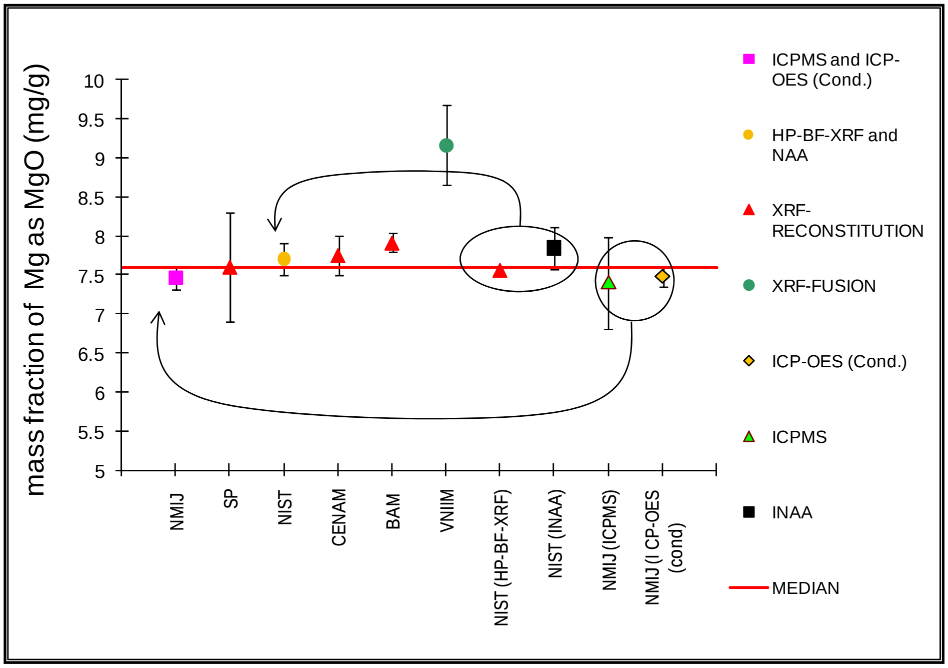


Table 8. Reported results for mass fraction of magnesium as MgO

NMI	**MEASUREMENT METHOD**	**RESULT** mg/g	**EXPANDED UNCERTAINTY** mg/g	**COVERAGE FACTOR** (95 % confidence**)**	**RELATIVE UNCERTAINTY** %
BAM	XRF – Reconstitution	7.91	0.12	2	1.52
CENAM	XRF – Reconstitution	7.75	0.24	2.8	3.1
NIST	Combined value	7.70	0.21	2	2.73
	1) HP-BF-XRF	7.560	0.047	2.4	0.62
	2) INAA	7.84	0.27	2	3.44
NMIJ	Combined value	7.460	0.145	2	1.94
	1) ICP-MS	7.40	0.59	2	7.97
	2) ICP-OES (Condensation method)	7.473	0.124	2	1.66
SP	XRF – Reconstitution	7.6	0.7	2	9.21
VNIIM	XRF – Fusion	9.157	0.513	2	5.6

Figure 5. Results for mass fraction of magnesium as MgO



9. KCRV Calculation

Several statistical parameters were calculated as candidates to KCRV and their values are shown in table 9.

Table 9. Some parameters calculated as candidates to KCRV for CCQM-K57

KCRV candidates	Silicon	Aluminum	Iron	Calcium	Magnesium
Mean	658.92	147.89	56.48	24.21	7.93
Weighted mean*	656.20	147.92	55.95	24.36	7.72
Median	658.04	147.82	56.14	24.32	7.72
Uncertainty estimations					
Expanded uncertainty of the mean $U = t \cdot u$ $u = {}^{s}/_{\sqrt{n}}$ *t: coverage factor*	4.63	1.76	1.74	0.59	0.65
Expanded uncertainty of the median** $U = t \cdot \left({}^{s(\tilde{m})}/_{\sqrt{n}} \right)$ *t: coverage factor*	4.90	2.23	0.55	0.30	0.24

* Weighted mean calculated using the following expression: $\overline{X_u} = \frac{\sum_n x_i \cdot \left(\frac{\bar{x}}{u_i}\right)}{\sum_n \left(\frac{\bar{x}}{u_i}\right)}$, where $\overline{X_u}$ is the weighted mean; x_i is the result of each NMI, $\bar{x}$ is the results average of all NMIs and u_i is the combined uncertainty reported for each NMI; $\left(\frac{\bar{x}}{u_i}\right)$ is used as simple weighing factor.

** Expanded Uncertainty of the median, where:
$s(\tilde{m})$ is the estimate of dispersion for the median [5], $MADe = median\{|x_i - \tilde{x}|\}/0.6745$
x_i is the result of each NMI
$\tilde{x}$ is the median of the results of the NMIs for each measurand.

Since the mean may be affected by extreme values, the most suitable way in this comparison is to work with robust statistics which suggest the median as KCRV value, since it has been recognized as useful tool to deal with suspected outliers [3], [4], [5]. Also, in this way, all participants will contribute to the reference value.
The uncertainty of the KCRV is based in the estimation of dispersion about the median.
The approved KCRV and its associated uncertainty for each element are summarized in table 10.
Figures 6 to 10 show the results of participants relative to the KCRV.

Table 10. Reference values and associated uncertainties for CCQM-K57

MEASURAND	**KCRV** mg/g	**EXPANDED UNCERTAINTY, U** mg/g	**RELATIVE UNCERTAINTY %**
Si as SiO_2	658.04	4.90	0.74
Al as Al_2O_3	147.82	2.23	1.51
Fe as Fe_2O_3	56.14	0.55	0.98
Ca as CaO	24.32	0.30	1.23
Mg as MgO	7.72	0.24	3.10

Since the uncertainties are based on five effective degrees of freedom, a coverage factor *t* =2.57 was used for all measurands.

Figure 6. KCRV and Uncertainty for SILICON

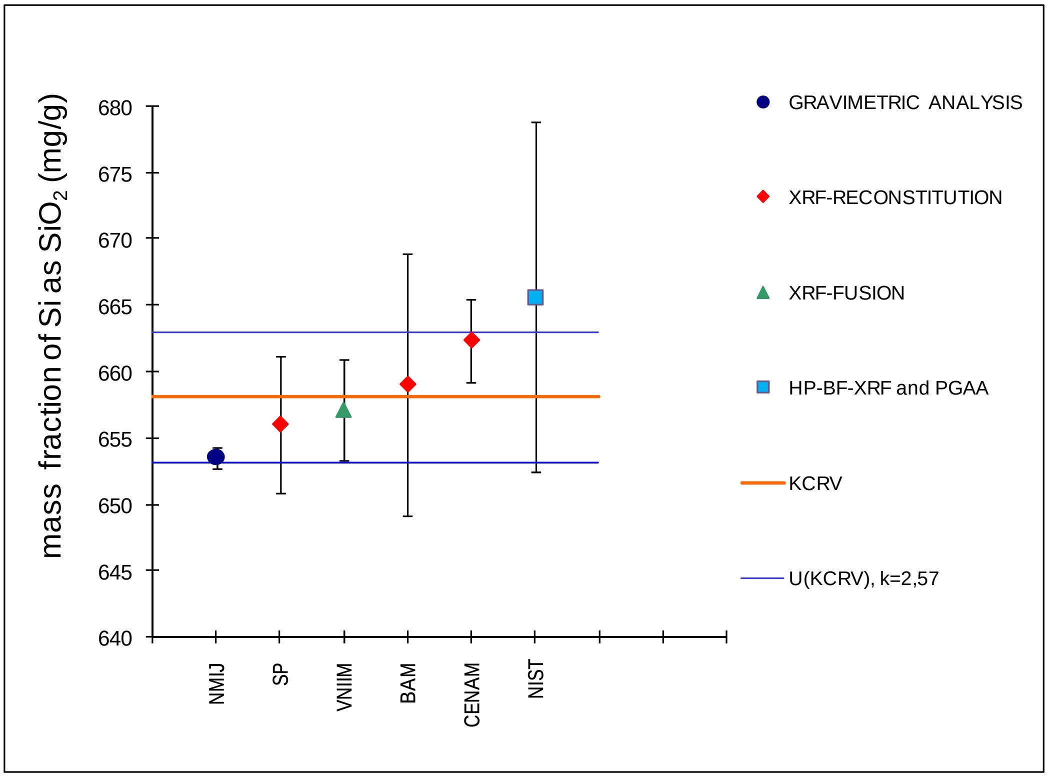


Figure 7. KCRV and Uncertainty for ALUMINUM

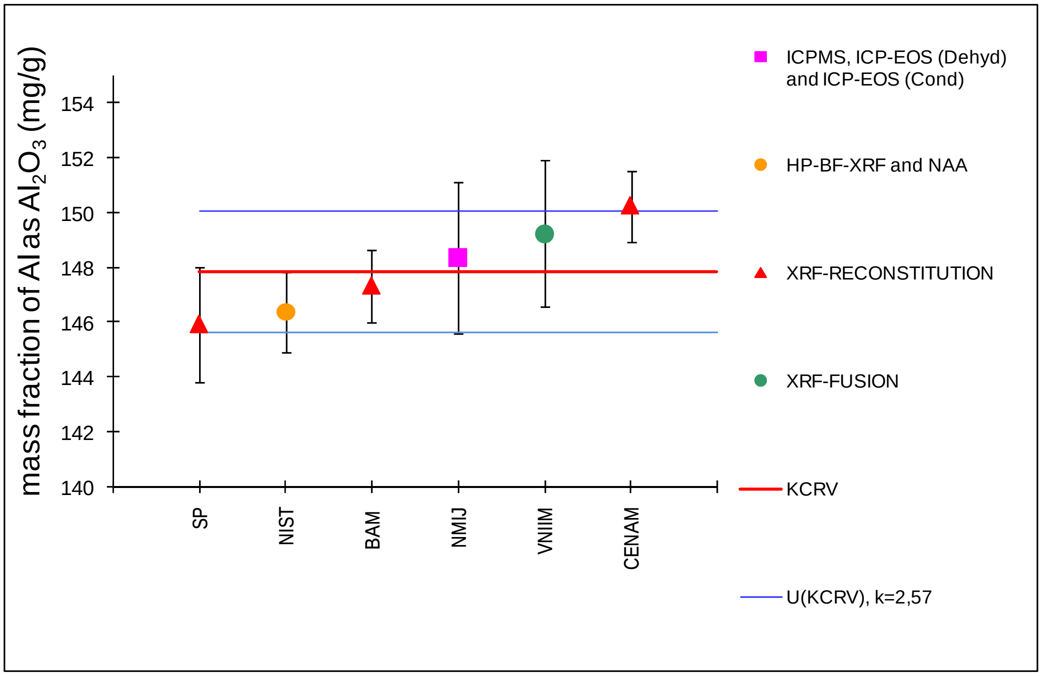


Figure 8. KCRV and Uncertainty for IRON

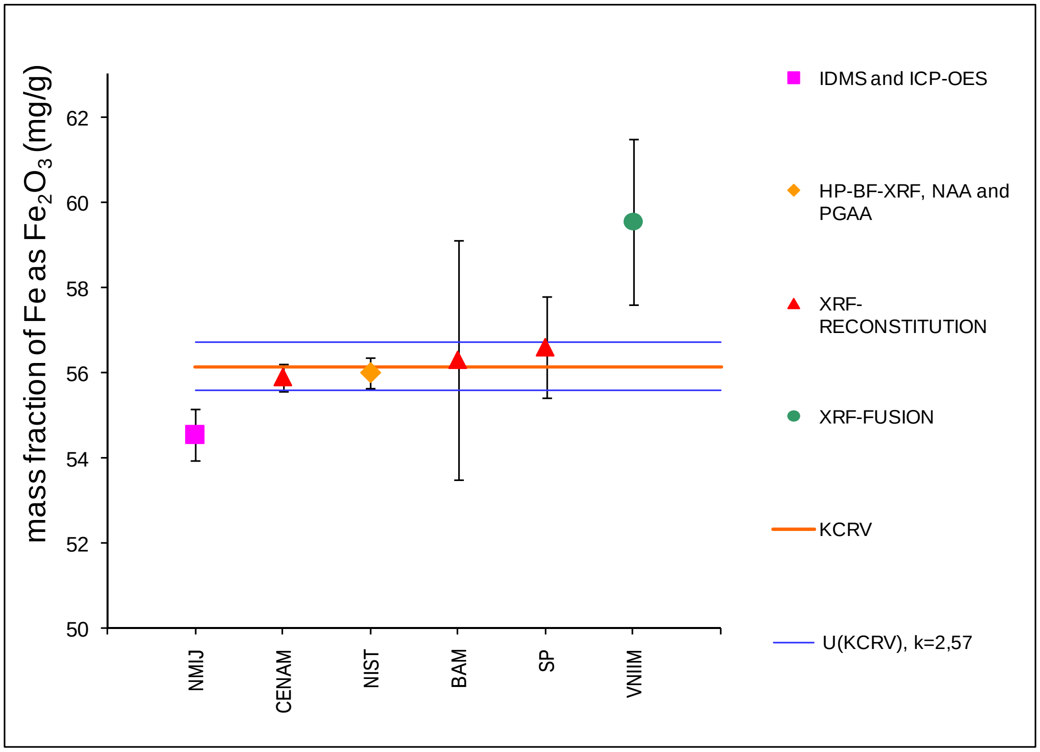


Figure 9. KCRV and Uncertainty for CALCIUM

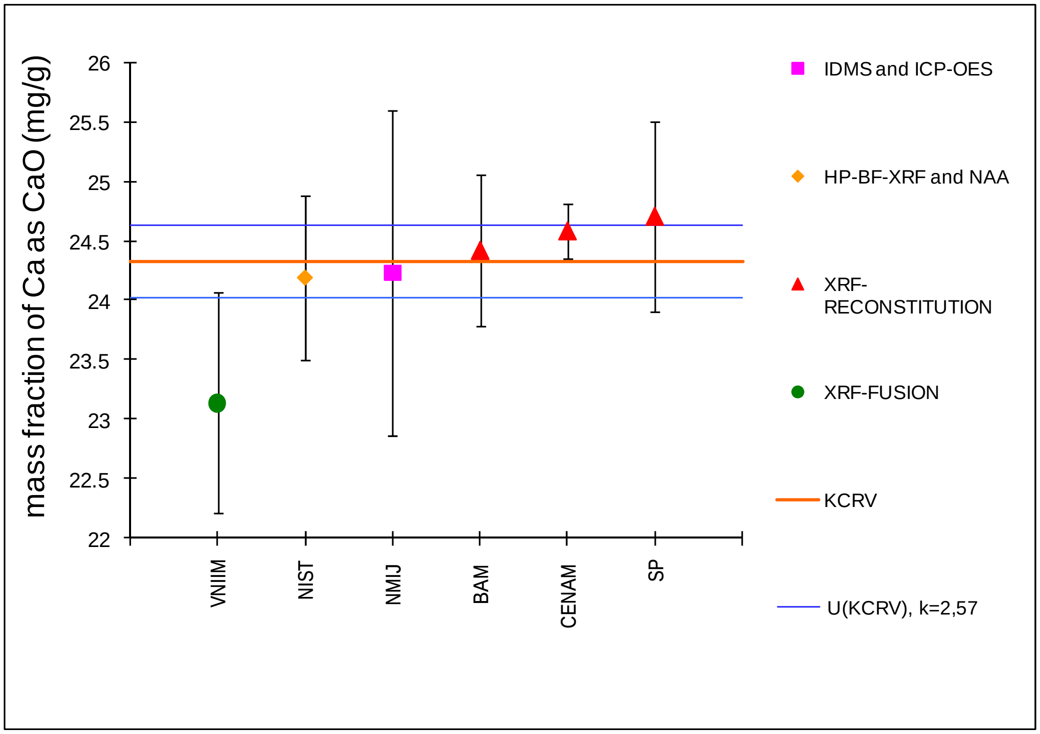
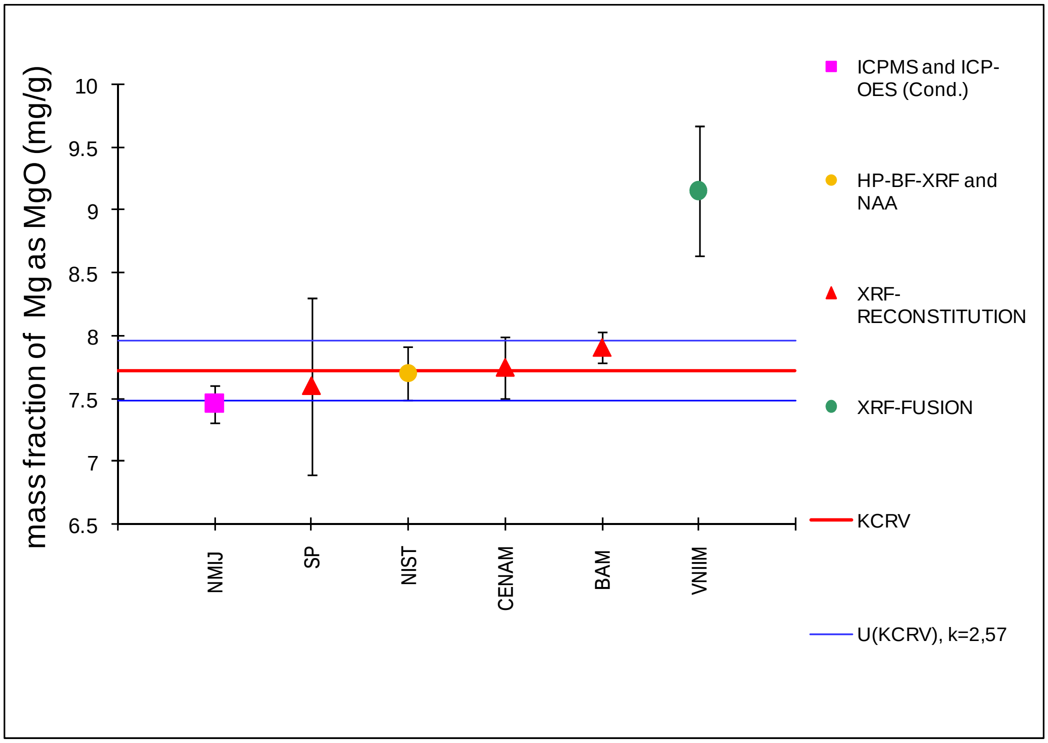


Figure 10. KCRV and Uncertainty for MAGNESIUM



10. Equivalence Statements

The degree of equivalence (DoE) for each NMI$_i$, regarding the key comparison reference value is calculated as follows:

$$d_i = x_i - x_{ref}$$

The combined uncertainty $u(d_i)$ of the degree of equivalence is estimated using the following expression:

$$u(d_i) = \sqrt{u^2(x_i) + u^2(x_{ref})}$$

The expanded uncertainty $U(d_i)$ for a 95 % level of confidence, with (k =2) is estimated as follows:

$$U(d_i) = 2 \cdot u(d_i)$$

Finally, in order to facilitate the graphical comparison, we calculate and plot the relative terms for degree of equivalence and its expanded uncertainty,

$$d_{i_{REL}}, \% = \frac{d_i}{x_{ref}} \cdot 100$$

$$U(d_i)_{REL}, \% = \frac{U(d_i)}{x_{ref}} \cdot 100$$

11. Degrees of equivalence

Arranged by measurand, tables 11-15, give the degrees of equivalence for each laboratory with respect to the KCRV, and figures 11-15 represent equivalence in relative terms.

MEASURAND: Mass fraction of silicon as silicon oxide in common clay

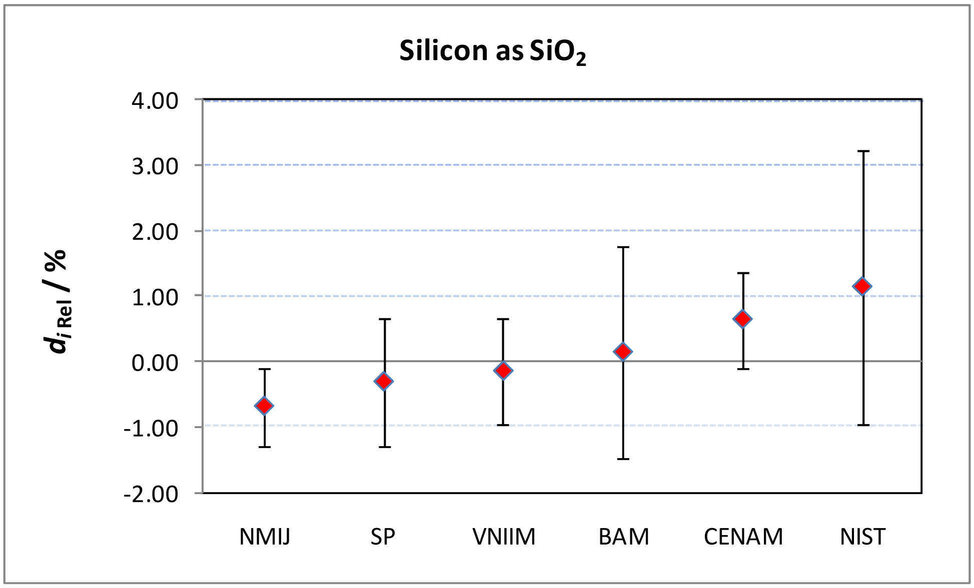
$x_{ref} = 658.04$ mg/g $u(x_{ref}) = 1.91$ mg/g

Table 11. Degrees of equivalence for silicon as silicon oxide in CCQM-K57

Lab i	d_i (mg/g)	$u(d_i)$ (mg/g)	$U(d_i)$ (mg/g)*	$d_{i_{REL}}$, %	$U(d_i)_{REL}$, %
NMIJ	-4.52	1.95	3.90	-0.69	0.59
SP	-2.04	3.22	6.45	-0.31	0.98
VNIIM	-0.96	2.70	5.40	-0.15	0.82
BAM	0.96	5.29	10.57	0.15	1.61
CENAM	4.26	2.41	4.83	0.65	0.73
NIST	7.56	6.87	13.74	1.15	2.09

*A coverage factor of k=2 is used for a 95 % of confidence

Figure 11. Relative degree of equivalence for Silicon as silicon oxide in CCQM-K57



MEASURAND: Mass fraction of aluminum as aluminum oxide in common clay

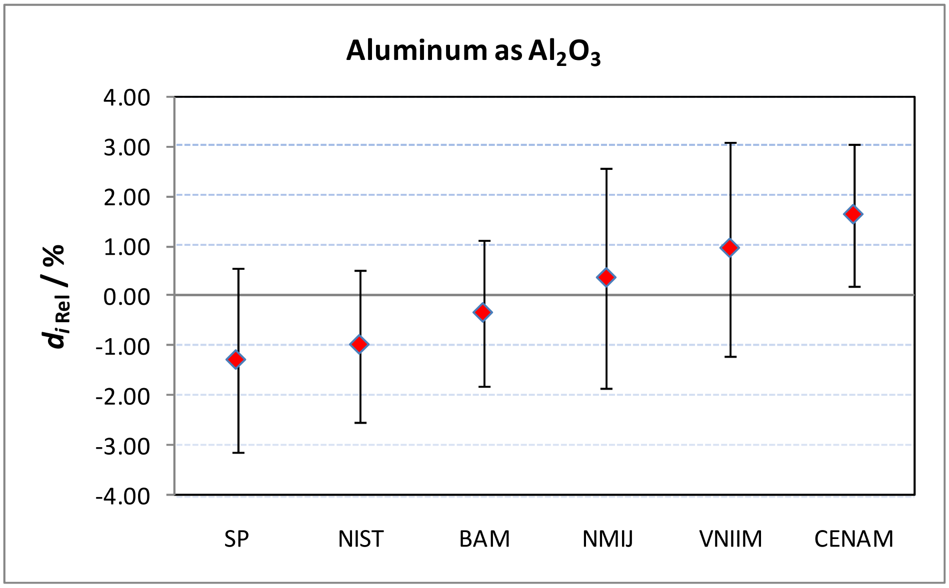
$x_{ref} = 147.82$ mg/g $u(x_{ref}) = 0.87$ mg/g

Table 12. Degrees of equivalence for aluminum as aluminum oxide in CCQM-K57

Lab i	d_i (mg/g)	$u(d_i)$ (mg/g)	$U(d_i)$(mg/g)*	$d_{i_{REL}}$, %	$U(d_i)_{REL}$, %
SP	-1.92	1.36	2.72	-1.30	1.84
NIST	-1.47	1.13	2.26	-0.99	1.53
BAM	-0.52	1.08	2.17	-0.35	1.47
NMIJ	0.52	1.62	3.24	0.35	2.19
VNIIM	1.40	1.59	3.18	0.95	2.15
CENAM	2.40	1.06	2.12	1.62	1.44

*A coverage factor of k=2 is used for a 95 % of confidence

Figure 12. Relative degree of equivalence for aluminum as aluminum oxide in CCQM-K57



MEASURAND: Mass fraction of iron as iron oxide in common clay

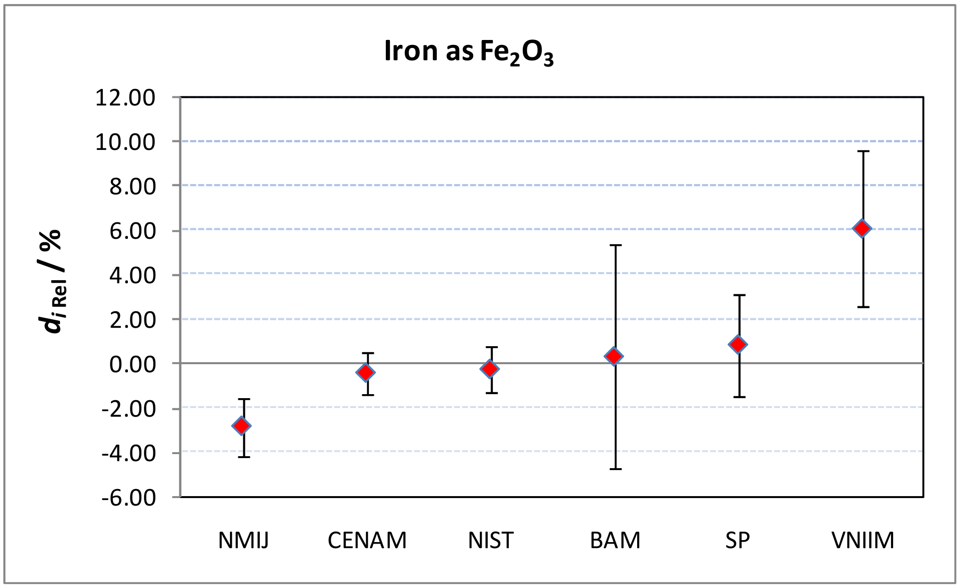
$x_{ref} = 56.14$ mg/g $u(x_{ref}) = 0.21$ mg/g

Table 13. Degrees of equivalence for iron as iron oxide in CCQM-K57

Lab ***i***	d_i (mg/g)	$u(d_i)$ (mg/g)	$U(d_i)$(mg/g)*	$d_{i_{REL}}$, %	$U(d_i)_{REL}$, %
NMIJ	-1.60	0.36	0.73	-2.85	1.30
CENAM	-0.25	0.26	0.52	-0.45	0.93
NIST	-0.16	0.28	0.56	-0.29	1.00
BAM	0.16	1.42	2.83	0.29	5.05
SP	0.46	0.64	1.27	0.82	2.27
VNIIM	3.40	0.99	1.99	6.06	3.54

*A coverage factor of k=2 is used for a 95 % of confidence

Figure 13. Relative degree of equivalence for iron as iron oxide in CCQM-K57



MEASURAND: Mass fraction of calcium as calcium oxide in common clay

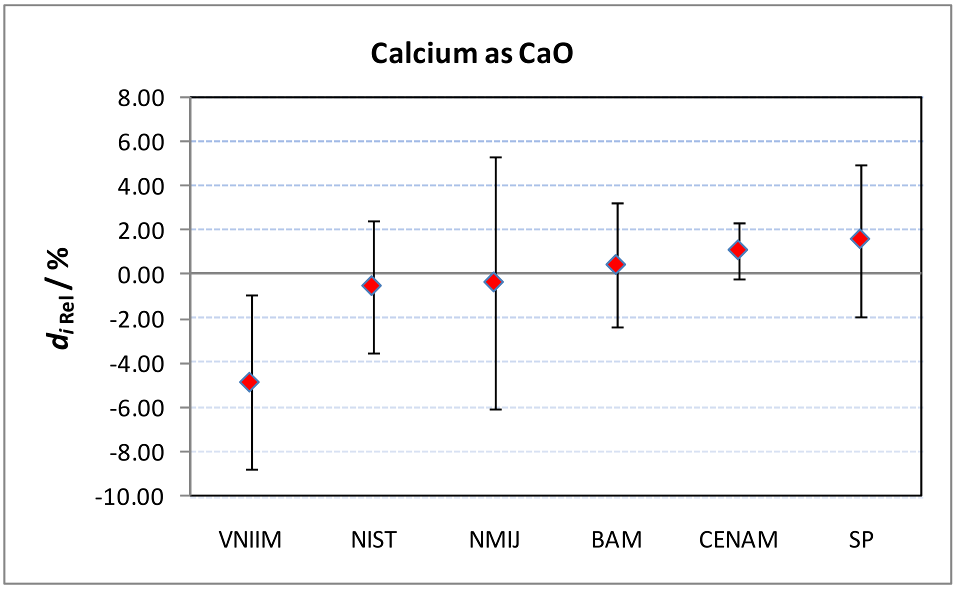
$x_{ref} = 24.32$ mg/g $u(x_{ref}) = 0.12$ mg/g

Table 14. Degrees of equivalence for calcium as calcium oxide in CCQM-K57

Lab *i*	d_i (mg/g)	$u(d_i)$ (mg/g)	$U(d_i)$(mg/g)*	$d_{i_{REL}}$, %	$U(d_i)_{REL}$, %
VNIIM	-1.19	0.48	0.96	-4.88	3.93
NIST	-0.13	0.36	0.73	-0.55	3.00
NMIJ	-0.095	0.70	1.39	-0.39	5.71
BAM	0.095	0.34	0.68	0.39	2.80
CENAM	0.25	0.16	0.31	1.05	1.28
SP	0.38	0.42	0.83	1.54	3.43

*A coverage factor of k=2 is used for a 95 % of confidence

Figure 14. Relative degree of equivalence for calcium as calcium oxide in CCQM-K57



MEASURAND: Mass fraction of magnesium as magnesium oxide in common clay

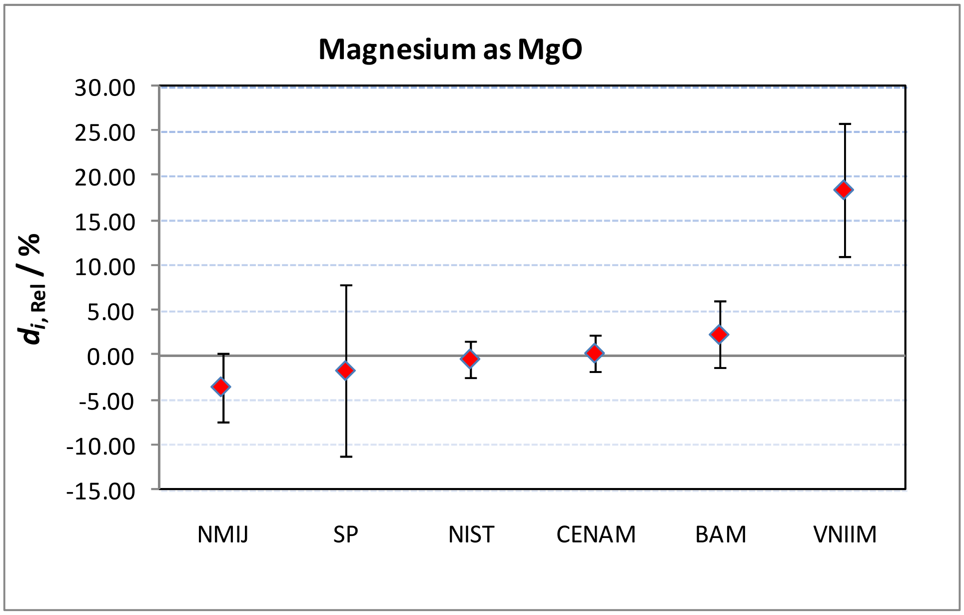
x_{ref} = 7.72 mg/g $u(x_{ref})$ = 0.09 mg/g

Table 15. Degrees of equivalence for magnesium as magnesium oxide in CCQM-K57

Lab i	d_i (mg/g)	$u(d_i)$ (mg/g)	$U(d_i)$(mg/g)*	$d_{i_{REL}}$, %	$U(d_i)_{REL}$, %
NMIJ	-0.26	0.12	0.24	-3.42	3.07
SP	-0.12	0.36	0.72	-1.61	9.38
NIST	-0.02	0.14	0.28	-0.31	3.65
CENAM	0.02	0.13	0.25	0.31	3.29
BAM	0.19	0.11	0.22	2.41	2.88
VNIIM	1.43	0.27	0.55	18.55	7.07

*A coverage factor of k=2 is used for a 95 % of confidence

Figure 15. Relative degree of equivalence for Magnesium as magnesium oxide in CCQM-K57



12. Observations

Six National Metrology Institutes reported results; NIST and NMIJ reported combined results from different analytical methods:

Potentially primary methods were applied by NMIJ (IDMS and Gravimetric analysis) and NIST (INNA and PGAA).

ICP-EOS and XRF calibrating with SRM were used by NMIJ and VNIIM respectively.
Reconstitution method and high performance borate fusion (HP-BF-XRF) were applied by four institutes: BAM, CENAM, NIST and SP. These results achieved a remarkable concordance.

13. Conclusions

CCQM-K57 comparison was completed and its results of equivalence statements are ready to be published.

The degree of equivalence achieved by the participants for this particular natural matrix is remarkable, in particular regarding that different measurement methods were used.

A diversity of methods with different physical principle was used and it was possible to verify that for clay and geological materials, reliable measurements of the highest metrological quality can be performed without method dependence problems.

Results obtained with reconstitution method are internally consistent and are comparable to results from primary methods. This method is both simpler and cheaper than some primary methods and less time consuming. All this advantages turn it into a method with significant metrological possibilities that remain to be explored.

Due to its proven performance, its direct link to SI and the possibility to carry out uncertainty evaluation in each step of the measurement, the reconstitution method should be considered a very reliable method of analysis for geological materials at the major and minor level of element concentrations.

14. How far the light shines statements

In order to discuss the applicability of the analytical capabilities demonstrated in the key comparison were prepared the following three sections:

1. Direct applicability
2. Other levels and matrices
3. Other analytes

1. Direct applicability

The analytical capability demonstrated in this key comparison is applicable straightforward to the analysis of Si, Al, Fe, Ca, Mg, K* and Ti* in geological materials silicon based, with the analytical methods and similar levels, (of concentration and uncertainty) handled in the key comparison.

*The analytes K and Ti, were measurands in CCQM-P65 but not in CCQM-K57; they were changed for aluminum and magnesium because the special industrial interest of those elements; however, CMC claims can be made in those analytes making reference to CCQM-P65.

Similar levels may be the established initially in the protocol of the comparisons, as it is shown in the table

MENSURAND	**KCRV** mg/g	**RANGE OF DIRECT APLICABILITY** mg/g	**RELATIVE UNCERTAINTY** (%)
SiO_2	658.04	650 – 700	0.74
Al_2O_3	147.82	100 – 200	1.51
Fe_2O_3	56.14	20 – 100	0.98
CaO	24.32	10 – 50	1.23
MgO	7.72	5 – 15	3.10
K_2O	25.6 (CCQM-P65 NMIs median)	20 – 50	1.2 (%RSD)
TiO_2	6.8 (CCQM-P65 NMIs median)	5 - 25	4.0 (%RSD)

2. How far the light shines for other levels and matrices

For silicon that was measured with gravimetric analysis and XRF with fusion and reconstitution methods, and the other analytes (Al, Fe, Ca, Mg, K and Ti) which were measured again with XRF, employing fusion and reconstitution, and with nuclear methods, it is not present complications extending the concentration range to up to 100 %, when the sample treatment and matrix matching process be adequately performed (when apply).
Additionally, for the mentioned methods, may be adequate to extend the applicability one order of magnitude lower.

For the analytes which were measured with instrumental spectrometric methods, as IDMS, ICP-MS and ICP-EOS, the light may extend to the low concentration range, since, the sample dissolution, already performed is considered between the most challenging competences, followed by the complex background or spectral interferences due to a natural complex matrix. The analytical methods previously mentioned, seem to work properly at low concentration levels, then, it may be appropriate to extend the applicability up to two orders of magnitude lower.

Geological natural samples whose major elements are oxides of Si, Al, Ca, Fe, Ti, K and Mg, such as clays, basalts, andesite, granites, quartz, silica, feldspars, anorthosites, caolinites, soils and some sediments, as well as minerals like limestone, dolomite, alumina, ilmenite, etc. can be considered examples of applicable matrices for this CMC claim.

3. Similar matrix and other analytes

For participants in the key comparison with consistently successful participation in all measurands, there is a purpose to extend the analytical capabilities to other elements in materials with similar matrix to K57, this, of course, should be judged individually for each case; however, the selection of elements would be based in the electronic nature, as their arrangement in periodic table:

CLASSIFICATION	**MEASURAND IN K57**
Alkaline earth metals	Calcium (IIA); Magnesium (IIA)
Transition elements	Iron (VIIIB)
Metalloids	Silicon (IV A)
Other metals	Aluminum (IIIA)

Additionally,

CLASSIFICATION	**MENSURAND IN P65 , non included in K57**
Alkali metals	Potassium (IA)
Transition elements	Titanium (IVB)

The extended analytes should have, under the consideration of difficulty of preparation and analysis, similar properties than the analytes in K57. The laboratory must present other evidences of its capability in analysis of the extended elements.

Finally, under those three considerations and within the Amount of Substance Categories, the light may shine to cover:

a) Part of category 9, as 9.4 Ceramics and 9.5 Others, as some composite materials.
b) Category 13 (Sediments, Soils, Ores, Particulates and Others (as refractories)), with the possible exception of Ores (13.3) based in non analytes of K57.
c) Category 14, with 14.1 Cements and 14.4 Glasses.

15. Acknowledgements

To the NMIs that participated in this CCQM-K57 Key comparison.
To Dr. Mike Sargent, chairman of the CCQM IAWG for his support during all stages of the comparison.
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To the analysts who performed the measurements from:

NMIJ: Dr. Yoshinori Uwamino, Dr. Akira Tsuge, Dr. Hisashi Morikawa, and Dr. Naoko Nonose.
VNIIM: Ms. Maksakova I.B.
NIST: John R. Sieber, PhD, Anthony F. Marlow, John L. Molloy, PhD, Robert R. Greenberg, Rick Paul, Rolf Zeisler and Rabia Spatz.
CENAM: Antonio Guardado, Fernando Rosas, Froylán Martínez, Edith Zapata, José M. Juárez, José L. Cabrera and Adrian Reyes.

16. References

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5. CCQM/04-15, Duewer L. David. - A Robust Approach for the Determination of CCQM Key Comparison Reference Values and Uncertainties.

Annex A

TECHNICAL PROTOCOL FOR CCQM-K57 and CCQM-P65.1
“CHEMICAL COMPOSITION OF CLAY”

I. GENERAL INFORMATION

Demonstration of measurement capabilities at trace level in natural matrices is very important but also it is at the level of concentration for matrix elements. For this reason, CCQM-K57 with CCQM-P65.1 completes the entire characterization of geological materials

All the reported results in CCQM-K57 and the equivalence statements will be included in the Appendix B of the CIPM MRA, which can support CMCs in the Appendix C. To support CMCs in the Appendix C of the BIPM MRA participation in the key comparison CCQM K57 is required. Results reported in the pilot study CCQM-P65.1 cannot be transferred to the key comparison on a later stage.

Following the international guide, only NMIs and official observers are allowed to participate in the CCQM-K57, however, a Pilot Study CCQM-P65.1 is running parallel to the key comparison in order to consider participation of other NMIs, national expert and industrial laboratories.

II. TIME SCHEDULE

Sample distribution:	February – March 2007
Deadline for receiving results	September 30, 2007
Draft A of KC report	December 2007
Draft B of KC report and pilot study report	March 2008

III. MEASURAND

The measurands are the mass fraction of silicon, aluminum, iron, calcium and magnesium in common clay. The results should be expressed as oxides.

Nominal values are in the following interval for each measurand:

SiO_2:	**650 - 700**	**mg/g**	**CaO:**	**10 - 50**	**mg/g**
Al_2O_3:	**100 - 200**	**mg/g**	**MgO**	**5 - 15**	**mg/g**
Fe_2O_3:	**20 - 100**	**mg/g**			

The results should be expressed on dry basis.
Dry instructions: 105 °C for two hours.

IV. SAMPLE

Description:

The test item is a sample of 40g of powdered material obtained from a natural deposit. Preparation and analysis of the material were performed by the Ceramic Materials Division of CENAM. Powdered material passes the sieve No. 325 ASTM.

Homogeneity testing: It was established on basis of two aspects: Particle size distribution measurements, done by laser diffraction technique, and Chemical measurements done by XRF Spectrometry for the following elements: Si, Ca, Fe, K, Ti, Al, Mg, Na, Mn and Cr.

Statistical evaluation of homogeneity: ANOVA analyses were carried out for particle size and chemical homogeneity results. No significant differences were observed between and within bottles of the entire batch with a 95 % confidence level.

Minimum sample size should be 0.5 g

Handling and storage of sample:
Sample is lightly hygroscopic; please follow the GLP for their correct handling.

Shipment:
You are receiving one glass bottle screw capped with plastic seal, together with the following documents: *"Results reporting sheet"* and *"Analysis report"*.

V. MEASUREMENT METHODS

Participants of the early pilot study and new participants in this key comparison CCQM-K57 and pilot study CCQM-P65.1 are encouraged to reduce their uncertainty levels, demonstrating their real capabilities analyzing geological matrix materials and, for participants in key comparison, establishing their equivalence degrees, using their particular analysis methods, where potentially primary methods are very welcomed as well as XRF with reconstitution method.
It is possible to use more than one analytical method for each analyte, in this case, the participant is requested to provide just one result for each analyte.

VI. REFERENCE VALUE

The KCRV (Key Comparison Reference Value) for each analyte will be the median of the results from the participants.

VII. REPORTING

Participants whom use one analytical method for each analyte are requested to submit six independent results for each analyte with the correspondent uncertainty estimation.
Participants whom use combined methods for each analyte, are requested to report in a separate sheet, the average results of each method together with a uncertainty estimation. Please report in the given form, the combined result of the methods and their combined uncertainty.
Please fill the **Part A** of the ***"Results reporting sheet"***. Specify in the head of each analyte if the correspondent result has to be considered in the Key Comparison or Pilot Study, indicate the bottle number and the method of methods used for each analyte.

VIII. UNCERTAINTY ESTIMATION

It is recommended to estimate uncertainty according to the Guide to Expression of Uncertainty in Measurement (GUM). Please fill the Part B of the *"Results reporting sheet"* as completely as possible.

IX. ANALYSIS REPORT

Please indicate the details of the analysis in the form *"Analysis Report"*.
Please describe on free format the stages of the analysis, Include all the relevant information. The following subjects are illustrative more than limitative.

MEASUREMENT METHODS: Description of the method or methods and analytical instrumentation used

SAMPLE PREPARATION METHOD: Sample preparation method (or methods): Sample size used, digestion methods, acids used, spike origin, etc.
For Reconstitution: Loss on ignition value, kind of flux or fluxes used, proportion sample-flux used, etc.

CALIBRATION: Materials used for calibration of the analytical instrumentation: origin, values and uncertainties, purity, etc. Please indicate the number of calibration points used for each analyte and indicate the traceability links.

DATA ANALYSIS: Description of the data reduction process including all equations and corrections (e.g. blanks, interferences, background, etc.)

UNCERTAINTY ESTIMATION: Including:

a. Complete specification of the measurand and mathematical model.
b. Identification and quantification of all sources of uncertainty.
c. Calculation of the combined standard uncertainty u_c (complete formula).
d. Information of the number of effective degrees of freedom, coverage factor and calculation of the expanded uncertainty, U.

X. MAILING OF RESULTS

- Please send by fax or e-mail (with signature) the Form*"Results reporting sheet"* before September 30, 2007 (deadline for receiving results).
- Please complete and send by e-mail The Form "Analysis report".

Address to send results:

To: Estela Ramírez
Metrología de Materiales
Fax: +52 442 2 11 05 69
e-mail: eramirez@cenam.mx

In unexpected event, you are requested to contact directly to the coordinating laboratory.

XI. COORDINATING LABORATORY

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Thank you very much for your participation!