Report of the key comparison CCQM-K58

Determination of nitrogen and trace elements in silicon nitride powder

(Final Report)

Akiharu Hioki and Yoshinori Uwamino (NMIJ),
Ralf Matschat (BAM)

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Abstract

The CCQM-K58 key comparison was organised by the Inorganic Analysis Working Group of CCQM to test the abilities of the national metrology institutes to measure the mass fractions of nitrogen and trace elements in silicon nitride powder. Elements to be analysed were Al, Fe, Ca, Ti, and N in silicon nitride powder. National Metrology Institute of Japan (NMIJ) and Federal Institute for Materials Research and Testing (BAM) acted as the coordinating laboratories. The number of participants was small, but they used various measurement methods. Comparability of measurement results as successfully demonstrated by the participating NMIs for the measurement of the mass fractions of Al, Fe, Ca, Ti and N in silicon nitride powder at the concentration levels of 824 mg/kg for Al, 351 mg/kg for Fe, 105 mg/kg for Ca, 13.8 mg/kg for Ti and 38.5 % for N within related expanded uncertainties.

It is expected that metals at the concentration level of more than several mg/kg in fine ceramics powder can be determined by each participant with the same technique(s) used for this key comparison within the similar uncertainties mentioned in the present report. It is also expected that nitrogen in silicon nitride powder can be measured by each participant with the same technique used for this key comparison within the similar uncertainty mentioned in the present report.

1 Introduction

Fine ceramics belong to one of the most important categories among advanced materials. Many fine ceramics have been widely used in different industries because of their excellent mechanical or thermophysical properties, and economic impact of chemical measurement is very large.

Following the pilot study CCQM-P74, NMIJ and BAM proposed a key comparison of "Determination of nitrogen and trace elements in silicon nitride powder" at the IAWG meeting held on April 4-5, 2006. At the CCQM meeting following the IAWG meeting, the proposal was agreed as CCQM-K58 and NMIJ and BAM were designated as coordinating laboratories. Elements to be analysed were N, Al, Fe, Ca, and Ti in the matrix silicon nitride powder at mass-fraction levels between 1000 mg/kg and 10 mg/kg except for N as a main constituent. All of these elements are related to characteristic properties of silicon nitride. Each participant could use any suitable method(s) of measurement. Each participant could decide the selected elements which he wanted to determine; however, these elements had to be declared at the registration of participation. Four measurements of each element had to be carried out by each participant. The homogeneity of the material used in this comparison had been investigated prior to the comparison. This is the first key comparison within CCQM in the field of fine ceramics analysis.

It was decided to conduct a parallel pilot study designated CCQM-P74.1, for which the same samples measured by the CCQM-K58 participants were also used.

2 List of Participants

Table 1 contains the full names of all participating NMI's.

Table 1 List of participating NMI's

No.	Participant	Country
1	**BAM** Federal Institute for Materials Research and Testing	Germany
2	**CENAM** National Center of Metrology	Mexico
3	**NIST** National Institute of Standards and Technology	USA
4	**NMIJ** National Metrology Institute of Japan	Japan

3 Samples

Each participant received one bottle containing about 25 g of silicon nitride powder. The homogeneity of the material, expressed as the relative standard deviation (RSD) of the mass fractions of analytes, was 1 %-2 % according to the results of Al, Fe, Ca, and Ti based on determination by ICP-OES and using a sample size of about 0.5 g. Moreover, the homogeneity of the material was 0.05 % (also expressed as RSD) according to the result of N based on determination by Kjeldahl method and using a sample size of about 0.15 g.

Benchmarks of the mass-fraction levels of the chosen elements in silicon nitride powder were about 40 % for N, 200 mg/kg to 1000 mg/kg for Al, 100 mg/kg to 500 mg/kg for Fe, 20 mg/kg to 200 mg/kg for Ca, and 1 mg/kg to 50 mg/kg for Ti. All these elements are of importance related to material properties of silicon nitride.

The samples were distributed to the participants from NMIJ by EMS mail on December, 2006. All samples reached their destinations safely. The contact persons are given in Table 2.

Table 2 List of contact persons of NMI's

Participant	Contact person
BAM	Ralf Matschat; Heinrich Kipphardt
CENAM	Antonio Salas
NIST	Robert R. Greenberg; Gregory Turk
NMIJ	Akiharu Hioki; Yoshinori Uwamino

4 Technical Protocol

The technical protocol attached as Annex A instructed participants concerning samples, methods of measurement, reporting and time schedule. The deadline for the reporting of results was originally March 15, 2007; it was, however, postponed to May 31, 2007.

5 Methods of Measurement

Participants were allowed to use any suitable method(s) of measurement. Any participant that chose to use multiple methods was required to report only one composite result (*e.g.*, an average value

from different methods) for each element. Several methods of measurement were employed for the determination of the metallic analytes: inductively coupled plasma optical emission spectrometry (ICP-OES), isotope-dilution inductively coupled plasma high-resolution mass spectrometry (ID-ICP-HRMS), inductively coupled plasma high-resolution mass spectrometry (ICP-HRMS), inductively coupled plasma quadrupole mass spectrometry (ICP-QMS), wavelength dispersive X-ray fluorescence spectrometry (XRF), instrumental neutron activation analysis (INAA). For the determination of nitrogen the following methods were used: neutron capture prompt gamma-ray activation analysis (PGAA), carrier gas hot extraction with thermal conductivity detection (Gas-ext-TC) as well as titrimetry (TIT). The number of results by each method is summarized in Table 3.

Table 3 The number of results by each method for CCQM-K58 (*1)

	Al	Fe	Ca	Ti	N
ICP-OES	1+1/2	1+1/3	1+1/3	1+1/3	
ID-ICP-HRMS		1/3	1/3	1/3	
ICP-HRMS			1/3		
ICP-QMS	1/2	1/3		1/3	
XRF	1		1		
INAA	1	1	1		
PGAA					1
Gas-ext-TC					1
TIT					1
number of data reported	4	3	4	2	3

*1 The number for each method of the participants that chose to use two methods was counted as one half. The number for each method of the participants that chose to use three methods was counted as one third.

6 Results

The results are given in Tables 4-8 including information on the measurement methods and illustrated in Figures 1-5. The half of the bar of each data in the Figures indicates the expanded uncertainty reported (k = 2). Each Figure contains a solid, horizontal line representing the arithmetic mean of the submitted data for the set of laboratories shown in the Figure. The uncertainty of the arithmetic mean was based on the standard deviation of the mean. The dashed, horizontal lines indicate the range of the expanded uncertainty (k = 2) of the arithmetic mean. The arithmetic mean (mg/kg) and the expanded uncertainty (mg/kg) for all reported values are 824.4 and 15.6 for Al, 351.1 and 4.0 for Fe, 105.25 and 2.11 for Ca, and 13.830 and 0.060 for Ti. The arithmetic mean (mass fraction, %) and the expanded uncertainty (mass fraction (%)) for all reported values are 38.533 and 0.730 for N.

Regarding the previous pilot study CCQM-P74 on a different material, the median (mg/kg) and the expanded uncertainty (mg/kg) for all reported values were 727.8 and 16.7 for Al, 199.24 and 1.74 for Fe, 72.90 and 1.73 for Ca, and 8.03 and 0.51 for Ti, and the median (mass fraction, %) and the expanded uncertainty (mass fraction, %) for all reported values were 38.77 and 0.30 for N; therefore, the expanded uncertainty for each measurand in this key comparison is compared to that in the pilot study, except for Ti from only two key-comparison participants.

The median and the MMmedian of all results for each analyte are also represented in the Figures 1-5. The half of the bar of the median or the MMmedian indicates the expanded uncertainty (k = 2) based on the estimate according to median($|x_i$-median$|$)/0.6745, where x_i is each reported value.

Table 4a Results for aluminum of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration *1	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
BAM	ICP-OES (n=4), two point calibration/ Sc as internal standard/ matrix matching (Si)	HNO_3/HF digestion (10 h at 250 °C)	CSS traceable to NIST SRM *2	838	27
CENAM	WDXRF/ calibration by synthetic stds (reconstitution method)	borate fusion	CENAM CRM with metrological traceability (CENAM DMR 78b)	806.7	33.6
NIST	INAA (n=7)	pressed into pellets	NIST std soln from high-purity Al metal	816.0	19.4
NMIJ	weighted mean of two independent results by standard addition ICP-QMS (^{27}Al) (n=4) and by ICP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Al for ICP-QMS and CSS traceable to NMIJ for ICP-OES	837	11

*1 CSS: the calibration solutions were prepared from a commercial standard solution.
*2 The CSS was checked against self prepared BAM standard solution prepared from 5N Al, Alfa Johnson Matthey.

Table 4b NMIJ's individual results before weighted mean for aluminum of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration *1	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
NMIJ	standard addition ICP-QMS (^{27}Al) (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Al	844	21
	ICP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	CSS traceable to NMIJ	832	13

*1 CSS: the calibration solutions were prepared from a commercial standard solution.

Table 5a Results for iron of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration *1	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
BAM	ICP-OES (n=4), two point calibration/ Sc as internal standard/ matrix matching	HNO_3/HF digestion (10 h at 250 °C)	CSS traceable to NIST SRM *2	348	2.9
NIST	INAA (n=6)	encapsulated in polyethylene microcentrifuge tubes	Fe foil (99.995 % purity)	354.9	3.2
NMIJ	weighted mean of three independent results by ID-ICP-HRMS (^{56}Fe & ^{57}Fe) (n=3), by standard addition ICP-QMS with collision-reaction cell (^{56}Fe) (n=4), and by ICP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Fe for ID-ICP-HRMS and ICP-QMS, and CSS traceable to NMIJ for ICP-OES	350.5	3.5

*1 CSS: the calibration solutions were prepared from a commercial standard solution.
*2 The CSS was checked against self prepared BAM standard solution prepared from 3N Fe, Reacton Johnson Matthey.

Table 5b NMIJ's individual results before weighted mean for iron of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration *1	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
NMIJ	ID-ICP-HRMS (^{56}Fe & ^{57}Fe) (n=3)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Fe	354.1	4.4
	standard addition ICP-QMS with collision-reaction cell (^{56}Fe) (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Fe	345.9	12.4
	CP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	CSS traceable to NMIJ	348	5.5

*1 CSS: the calibration solutions were prepared from a commercial standard solution.

Table 6a Results for calcium of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration *1	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
BAM	ICP-OES (n=4), two point calibration/ Sc as internal standard/ matrix matching(Si)	HNO_3/HF digestion (10 h at 250 °C)	CSS traceable to NIST SRM *2	104.3	0.9
CENAM	WDXRF/ calibration by synthetic stds (reconstitution method)	borate fusion	NIST CRM with metrological traceability (NIST SRM 3109a)	103.3	6.5
NIST	INAA (n=7)	pressed into pellets	NIST std soln from $CaCO_3$ (NIST SRM 915) ($CaCO_3$ 99.99+ % purity)	108.2	3.5
NMIJ	weighted mean of three independent results by ID-ICP-HRMS (^{42}Ca & ^{44}Ca) (n=4), by matrix matching ICP-HRMS (^{44}Ca) (n=4), and by ICP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from $CaCO_3$ for ID-ICP-HRMS and ICP-HRMS, and CSS traceable to NMIJ for ICP-OES	105.2	1.4

*1 CSS: the calibration solutions were prepared from a commercial standard solution.
*2 The CSS was checked against self prepared BAM standard solution prepared from $CaCO_3$ powder specpure, 99.999%, Alfa Johnson Matthey.

Table 6b NMIJ's individual results before weighted mean for calcium of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration *1	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
NMIJ	ID-ICP-HRMS (^{42}Ca & ^{44}Ca) (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from $CaCO_3$	105.2	2.5
	matrix matching ICP-HRMS (^{44}Ca) (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from $CaCO_3$	103.0	8.5
	ICP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	CSS traceable to NMIJ	105.5	1.3

*1 CSS: the calibration solutions were prepared from a commercial standard solution.

Table 7a Results for titanium of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration *1	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
BAM	ICP-OES (n=4), seven point calibration/ Sc as internal standard/ matrix matching (SiO_2)	HNO_3/HF digestion (10 h at 250 °C)	CSS traceable to NIST SRM *2	13.86	0.05
NMIJ	weighted mean of three independent results by ID-ICP-HRMS (^{47}Ti & ^{49}Ti) (n=4), by matrix matching ICP-QMS with collision-reaction cell (^{47}Ti) (n=4), and by ICP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Ti for ID-ICP-HRMS and ICP-QMS, and NIST SRM 3162a for ICP-OES	13.80	0.24

*1 CSS: the calibration solutions were prepared from a commercial standard solution.
*2 The CSS was checked against self prepared BAM standard solution prepared from Ti crystal 99.99%, Alfa Johnson Matthey.

Table 7b NMIJ's individual results before weighted mean for titanium of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg) (k=2)
NMIJ	ID-ICP-HRMS (^{47}Ti & ^{49}Ti) (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Ti	13.79	0.61
	matrix matching ICP-QMS with collision-reaction cell (^{47}Ti) (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NMIJ std soln from Ti	13.59	0.48
	ICP-OES (n=4)	HNO_3/HF digestion + H_2SO_4 treatment + HCl dissolution (16 h at 160 °C)	NIST SRM 3162a	13.92	0.28

Table 8 Results for nitrogen of CCQM-K58

Participant	Measurement Method	Decomposition Method	Materials used for calibration	Reported value / mass fraction (%)	Expanded uncertainty / mass fraction (%) (k=2)
BAM	carrier gas hot extraction (n=8)/ thermal conductivity cell/ calibration with KNO_3	carrier gas hot extraction	KNO_3 (99.5%) from Merck	38.99	0.65
NIST	PGAA (n=5)	pressed into pellets	pressed pellets KNO_3 (NIST SRM 193)	38.80	0.80
NMIJ	Kjeldahl method/titrimetry (n=4) *1	H_2SO_4-HF digestion/ Kjeldahl distillation	Potassium hydrogen phthalate (NMIJ CRM 3001-a)	37.808	0.062

*1 The method was validated by using BAM S001: the results 38.021% (0.022%, standard deviation) was in good agreement with the certified value 38.1% (0.2%, a level of confidence of 95%).

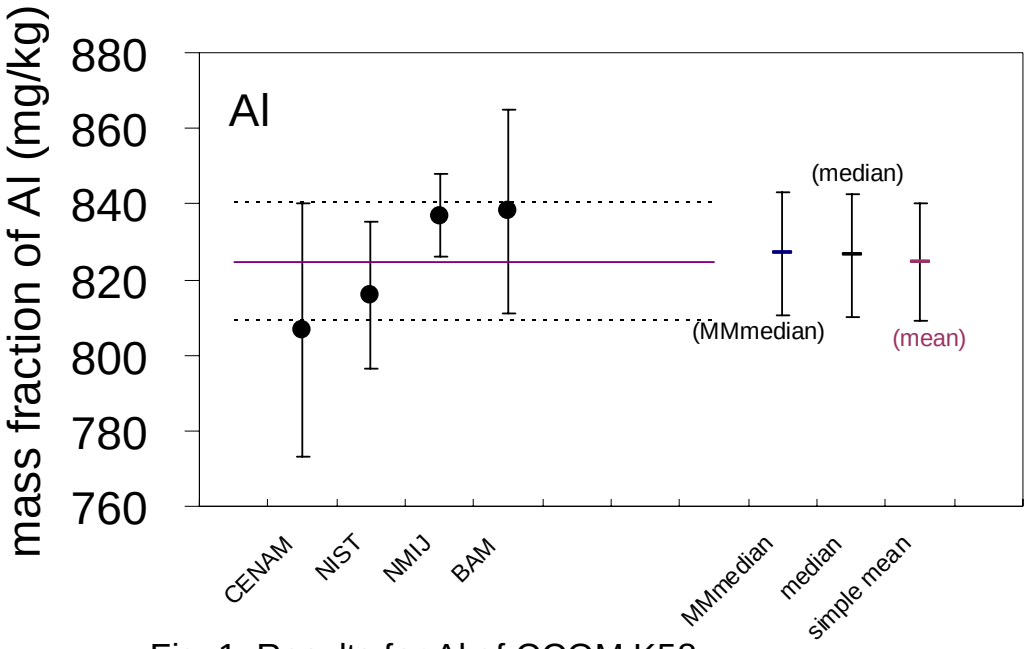

Fig. 1 Results for Al of CCQM-K58

The half of each bar indicates the expanded uncertainty (k =2).

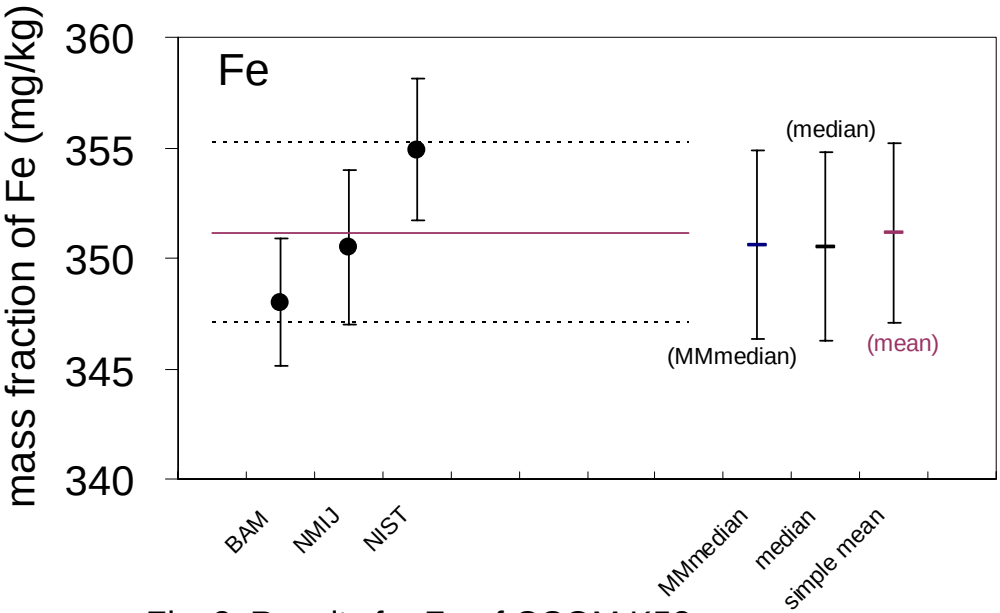

Fig. 2 Results for Fe of CCQM-K58

The half of each bar indicates the expanded uncertainty (k =2).

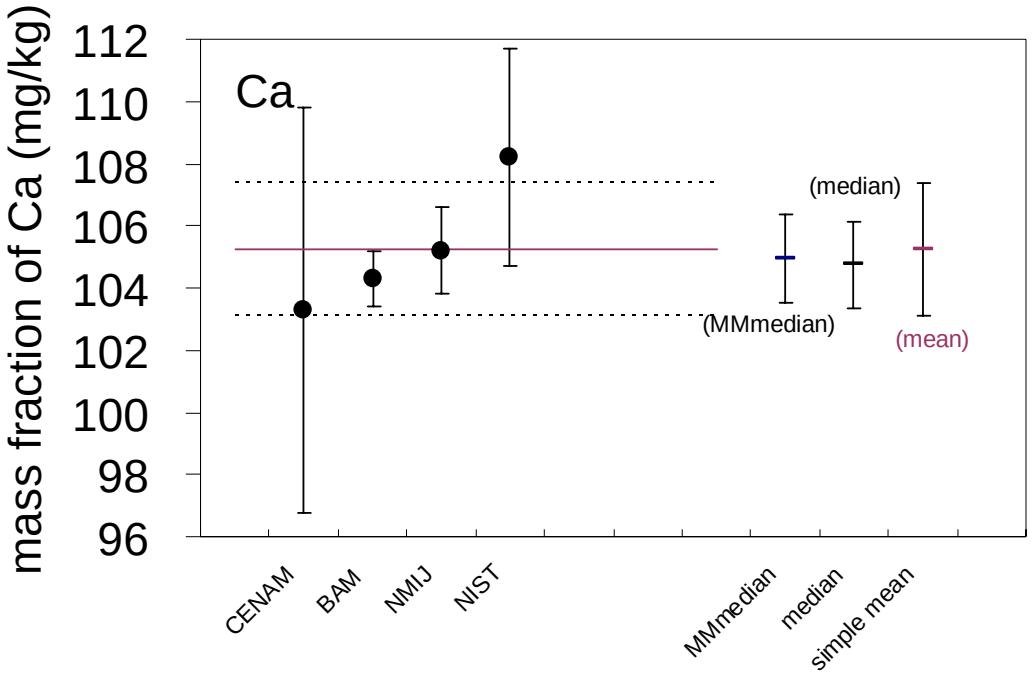

Fig. 3 Results for Ca of CCQM-K58

The half of each bar indicates the expanded uncertainty (k =2).

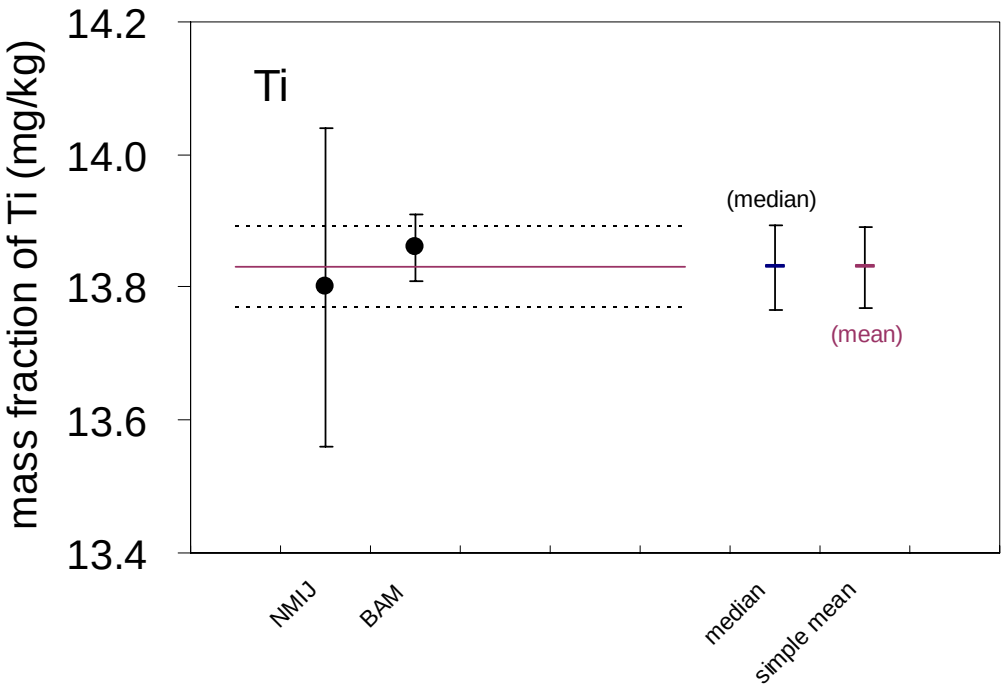

Fig. 4 Results for Ti of CCQM-K58

The half of each bar indicates the expanded uncertainty (k =2).

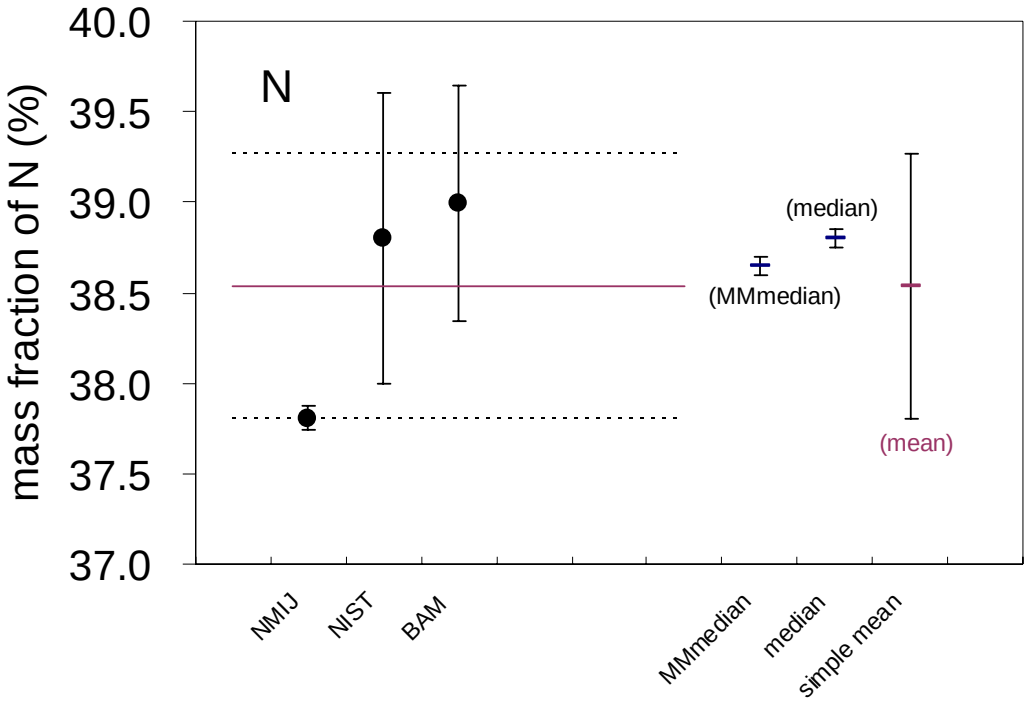

Fig. 5 Results for N of CCQM-K58
The half of each bar indicates the expanded uncertainty (k =2).

7 Discussion

The range of results reported for CCQM-K58 was not significantly different from the range of those reported by NMIs for CCQM-P74. For every element, most of the reported data were within ±2 % relative to the mean, and therefore, there were no clearly observed differences among the participants or among the measurement methods employed. Since there is some difference among the results for nitrogen by the participants, the methods and measurement uncertainties were reviewed; however, the reason for the difference was not obvious.

8 Estimation of KCRV

Some candidates for the key comparison reference value (KCRV) for each measurand are in Tables 9-13. At the IAWG meeting held on October, 2007 (NIST), the mean (arithmetic mean) for each measurand was chosen as the KCRV for CCQM-K58.

Table 9. Candidates of KCRV of Al for CCQM-K58

		Value mass fraction (mg/kg)	Expanded uncertainty (*k*=2) mass fraction (mg/kg)
Mean	*1	824.4	15.6
Median	*2	826.5	16.3
MMmedian	*3	827.0	16.3
Weighted mean (usual weight)	*4	830.8	8.7
Weighted mean (mild weight)	*5	827.7	9.6

Table 10. Candidates of KCRV of Fe for CCQM-K58

		Value mass fraction (mg/kg)	Expanded uncertainty (*k*=2) mass fraction (mg/kg)
Mean	*1	351.1	4.0
Median	*2	350.5	4.3
MMmedian	*3	350.6	4.3
Weighted mean (usual weight)	*4	350.9	1.8
Weighted mean (mild weight)	*5	351.0	1.8

Table 11. Candidates of KCRV of Ca for CCQM-K58

		Value mass fraction (mg/kg)	Expanded uncertainty (*k*=2) mass fraction (mg/kg)
Mean	*1	105.25	2.11
Median	*2	104.75	1.41
MMmedian	*3	104.94	1.41
Weighted mean (usual weight)	*4	104.71	0.74
Weighted mean (mild weight)	*5	105.01	0.88

Table 12. Candidates of KCRV of Ti for CCQM-K58

		Value mass fraction (mg/kg)	Expanded uncertainty (*k*=2) mass fraction (mg/kg)
Mean	*1	13.830	0.060
Median	*2	13.830	0.063
MMmedian	*3	13.850	0.063
Weighted mean (usual weight)	*4	13.858	0.049
Weighted mean (mild weight)	*5	13.850	0.059

Table 13. Candidates of KCRV of N for CCQM-K58

		Value mass fraction (%)	Expanded uncertainty (k=2) mass fraction (%)
Mean	*1	38.533	0.730
Median	*2	38.800	0.051
MMmedian	*3	38.649	0.051
Weighted mean (usual weight)	*4	37.824	0.062
Weighted mean (mild weight)	*5	37.970	0.092

*1 The expanded uncertainty was based on the standard deviation of the mean.
*2 The uncertainty of the median was based on the estimate from median($|x_i$-median$|$)/0.6745, where x_i is each reported value.
*3 The MMmedian was calculated according to the following:
David L. Duewer, "A robust approach for the determination of CCQM key comparison reference values and uncertainties", Working document CCQM/04-15, BIPM, 2004, (www.bipm.info/cc/CCQM/Allowed/10/CCQM04-15.pdf).
The uncertainty of the MMmedian was based on the estimate from median($|x_i$-median$|$)/0.6745, where x_i is each reported value.
*4 The square of reciprocal of reported uncertainty was used as a weight.
*5 The reciprocal of reported uncertainty was used as a weight.

9 Equivalence statements

The degree of equivalence and its uncertainty between an NMI result and the KCRV is calculated according to the following equations:
$D_i = (x_i - x_R)$
$U_i^2 = (k^2 u_i^2 + 2^2 u_R^2)$
where D_i is the degree of equivalence between the NMI result x_i and the KCRV x_R , and U_i is the expanded uncertainty (coverage factor: k = 2) of D_i calculated by both the combined standard uncertainty u_i of x_i and the standard uncertainty u_R of x_R . The calculation results are shown in Tables 14-18 and Figures 6-10. The half of each bar in the Figures indicates U_i .

Table 14 Results for aluminum (CCQM-K58)

Participant	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg)		D_i / mass fraction (mg/kg)	U_i / mass fraction (mg/kg)
KCRV	824.4	15.6	k=2		
BAM	838	27	k=2	13.6	31.2
CENAM	806.7	33.6	k=2	-17.7	37.0
NIST	816	19.4	k=2	-8.4	24.9
NMIJ	837	11	k=2	12.6	19.1

Table 15 Results for iron (CCQM-K58)

Participant	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg)		D_i / mass fraction (mg/kg)	U_i / mass fraction (mg/kg)
KCRV	351.1	4.0	*k*=2		
BAM	348	2.9	*k*=2	-3.1	4.9
NIST	354.9	3.2	*k*=2	3.8	5.1
NMIJ	350.5	3.5	*k*=2	-0.6	5.3

Table 16 Results for calcium (CCQM-K58)

Participant	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg)		D_i / mass fraction (mg/kg)	U_i / mass fraction (mg/kg)
KCRV	105.25	2.11	*k*=2		
BAM	104.3	0.9	*k*=2	-1.0	2.3
CENAM	103.3	6.5	*k*=2	-2.0	6.8
NIST	108.2	3.5	*k*=2	3.0	4.1
NMIJ	105.2	1.4	*k*=2	0.0	2.5

Table 17 Results for titanium (CCQM-K58)

Participant	Reported value / mass fraction (mg/kg)	Expanded uncertainty / mass fraction (mg/kg)		D_i / mass fraction (mg/kg)	U_i / mass fraction (mg/kg)
KCRV	13.830	0.060	*k*=2		
BAM	13.86	0.05	*k*=2	0.03	0.08
NMIJ	13.80	0.24	*k*=2	-0.03	0.25

Table 18 Results for nitrogen (CCQM-K58)

Participant	Reported value / mass fraction (%)	Expanded uncertainty / mass fraction (%)		D_i / mass fraction (%)	U_i / mass fraction (%)
KCRV	38.533	0.730	*k*=2		
BAM	38.99	0.65	*k*=2	0.46	0.98
NIST	38.80	0.80	*k*=2	0.27	1.08
NMIJ	37.808	0.062	*k*=2	-0.73	0.73

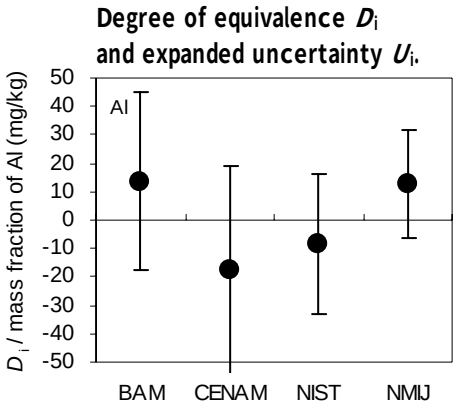

Fig. 6 Degree of equivalence for Al

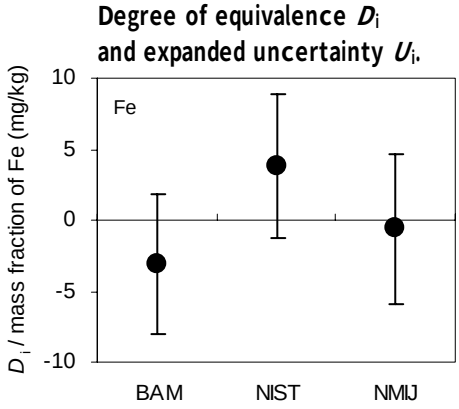

Fig. 7 Degree of equivalence for Fe

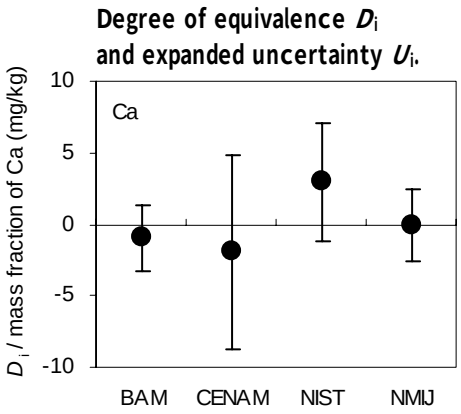

Fig. 8 Degree of equivalence for Ca

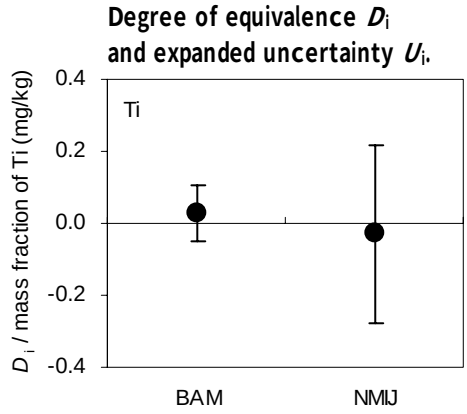

Fig. 9 Degree of equivalence for Ti

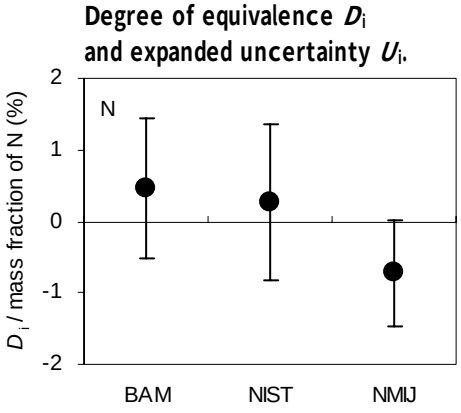

Fig. 10 Degree of equivalence for N

10 Conclusion

Comparability of measurement results was successfully demonstrated by the participating NMIs for the measurement of the mass fractions of Al, Fe, Ca, Ti and N in silicon nitride powder at the concentration levels of 824 mg/kg for Al, 351 mg/kg for Fe, 105 mg/kg for Ca, 13.8 mg/kg for Ti and 38.5 % for N within related expanded uncertainties.

It is expected that metals at the concentration level of more than several mg/kg in fine ceramics powder can be measured by each participant with the same technique(s) used for this key comparison within the

similar uncertainties mentioned in the present report. It is also expected that nitrogen in silicon nitride powder can be measured by each participant with the same technique used for this key comparison within the similar uncertainty mentioned in the present report.

11 Acknowledgement

The work of the key comparison was done by the contributions from many scientists as well as the contact persons: Estela Ramirez (CENAM); Rolf Zeisler, Rabia Spatz and Rick Paul (NIST); Naoko Nonose, Akira Tsuge and Hisashi Morikawa (NMIJ); Hans-Joachim Heinrich and Angelika Dette (BAM).

Annex A - Technical protocol

CCQM-K58 & P74.1 Key comparison and pilot study on determination of nitrogen and trace elements in silicon nitride powder

Technical protocol

Introduction

Fine ceramics are one of the most important categories among advanced materials. Many fine ceramics have been widely used in different industries because of their excellent mechanical or thermophysical properties, and because the economic impact of chemical measurement is very large. Selected elements in this key comparison or study are N, Al, Fe, Ca, and Ti in silicon nitride powder. All of these elements are related to characteristic properties of silicon nitride. Through this comparison, a participant's capability to analyse fine ceramics will be demonstrated, the decomposition of which is relatively difficult. This is the first CCQM key comparison in the field of fine ceramics analysis.

Samples

Each participant will receive one bottle containing about 25 g of silicon nitride powder. The homogeneity of the material, expressed as the relative standard deviation (RSD) of the mass fractions of analytes, was 0.5%-2% according to the results of Al, Fe, Ca and Ti based on determination by ICP-OES and using a sample size of about 0.5 g. Moreover, the homogeneity of the material was 0.05% (also expressed as RSD) according to the result of N based on determination by Kjeldahl method and using a sample size of about 0.15 g. The sample drying at 110 degree C for 2 hours before analysis is recommended. Each participant has to make sure that the drying temperature is really higher than 100 degree C.

Benchmarks of the mass-fraction levels of the chosen elements in silicon nitride powder are about 40% for N, 200 mg/kg to 1000 mg/kg for Al, 100 mg/kg to 500 mg/kg for Fe, 20 mg/kg to 200 mg/kg for Ca, and 1 mg/kg to 50 mg/kg for Ti. All these elements are of importance related to material properties of silicon nitride. The CCQM-P74.1 sample is the same as the sample for CCQM-K58.

Methods of Measurement

Each participant can use any suitable method(s) of measurement (using primary methods of measurement is preferred). NMIs or officially designated laboratories are welcome to participate in this comparison. Four measurements for each element which is declared at registration are to be carried out by each participant. The calibrations should be carried out by using standards with metrological traceability. It means that matrix materials, such as silicon nitride powders, are not allowed for using as calibration materials. But existing silicon nitride certified reference materials (such as BAM-S001, now ERM-ED101 for the determination of N, Al, Fe, Ca, or NIST RM 8983 for the determination of N) can be favorably used to check the accuracy of your own method prior to your analyses of this key comparison or study.

Reporting

The results should be reported as mass fractions of each measurand to NMIJ (Akiharu Hioki), accompanied by a full uncertainty budget. Reporting the details of the procedure (including details of sample preparation/digestion), traceability links, and the instrument(s) used is very desirable.

Time schedule

Deadline of registration of participation: October 27, 2006
Dispatch of the samples: November, 2006
Deadline for receiving the report: May 31, 2007

Participants

Participation is open to all interested NMIs or officially designated laboratories that can perform the determination. An NMI or an officially designated laboratory is recommended to participate in the key comparison rather than in the pilot study as far as possible. An NMI or an officially designated laboratory may nominate other institutes or laboratories to participate in the pilot study. Please inform NMIJ (Akiharu Hioki) of the contact person, the shipping address, and so on using the attached registration form. Even if you do not wish to participate, please inform NMIJ of it.

We would like to ask NMIs or officially designated laboratories to coordinate participation within their economies including inviting participants in the pilot study, shipping samples, and receiving the reports. The coordinating laboratories might invite some expert laboratories directly to participate in the pilot study.

Coordinating laboratories

Dr. Akiharu HIOKI / Dr. Yoshinori UWAMINO
National Metrology Institute of Japan (NMIJ),
AIST Tsukuba Central 3-9,
1-1-1, Umezono, Tsukuba, Ibaraki, 305-8563,
JAPAN
Tel : +81-29-861-9341 or +81-29-861-6881 Fax: +81-29-861-6890
E-mail: aki-hioki@aist.go.jp / y.uwamino@aist.go.jp

Dr. Ralf MATSCHAT
Division of Inorganic Analysis; Reference Materials
Bundesanstalt für Materialforschung und -prüfung (BAM),
Richard-Willstätter-Straße 11, D-12489 Berlin,
GERMANY
Tel: ++49 30 8104-1110 FAX: ++ 49 30 8104-1117
E-mail: ralf.matschat@bam.de