Report of the CCQM-K152 Assay of Potassium Iodate

Final report

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ABSTRACT

The CCQM-K152 key comparison in parallel with CCQM-P192 pilot comparison were organised jointly by the Inorganic Analysis (IAWG) and Electrochemical Analysis and Classical Chemical methods (EAWG) working groups of CCQM to test the abilities of the metrology institutes to measure the amount content of the non-metallic elements in high purity salts as well as assaying high purity salts to be used as primary standards.

Eight NMIs participated in the key comparison CCQM-K152. Ural Research Institute for Metrology (UNIIM) (since 2020 it has been called Affiliated Branch of D.I.Mendeleev Institute for Metrology (VNIIM-UNIIM)), Russian Federation, acted as the coordinating laboratory of the comparison. There were two measurands: the amount content of oxidants expressed as potassium iodate, mol/kg, and the mass fraction of iodine, kg/kg. The measurement methods used by participants for the amount content of oxidants expressed as potassium iodate were constant current coulometry and titrimetry. For the mass fraction of iodine results were provided by 5 NMIs, 3 of them used the direct approach (recalculation from coulometric or titrimetric results) and 2 NMIs implemented the indirect approach based on impurities assessment using combination of the instrumental methods (ion chromatography, ICP OES, ICP MS).

In general, good overlap of results was observed for both measurands. Direct and indirect approaches for purity determination of pure salt provide overlapping results when impurities are summarized in ionic form. The suitability of coulometry for assay of high purity materials was demonstrated again, and some possible technical problems were highlighted.

1 INTRODUCTION

The CCQM-K152 key comparison in parallel with CCQM-P192 pilot comparison were organised jointly by the Inorganic Analysis (IAWG) and Electrochemical Analysis and Classical Chemical methods (EAWG) working groups of CCQM. This CCQM-K152&P192 comparison is the next step in realization the long-term strategy of CCQM (IAWG+EAWG) on purity determination of the high pure substances (e.g. previously conducted comparisons are CCQM-P107 and CCQM-K72/P107.1, CCQM-P149; CCQM-K34, CCQM-K48.2014).

Pure materials are very important for traceability in chemical metrology. High purity metals are known as the best source for preparing element calibration solutions. But for a list of elements pure metals do not exist, are not convenient or are not readily available, and only compounds (salts, oxides) can be used, such as for iodine. Potassium iodate has a potential to be used as a source for preparing a calibration solution of iodine and a calibration standard of oxygen for elemental analyzers of oxygen. It is also widely used as a chemical standard for redox titrimetry in analytical chemistry.

The objective of the comparison was to determine the amount content of oxidants (mol/kg) expressed as KIO₃ and/or the mass fraction of iodine (kg/kg) in the sample of potassium iodate. Participants were free to choose the analytical procedure. It was welcomed to use both direct and indirect approaches for the mass fraction of iodine determination.

2 LIST OF PARTICIPANTS

There were 8 NMIs registered in the key comparison. Table 1 contains the full names of all participating NMIs, their countries, contact persons and measurand(-s) chosen, where (1) corresponds to the mass fraction of iodine and (2) to the amount content of oxidants expressed as potassium iodate.

Institution	Country	Contact person	Measurand
CENAM	Mexico	Judith Velina Lara	(2)
National Center of Metrology		Manzano	
INMETRO	Brazil	Paulo Paschoal Borges,	(1), (2)
Instituto Nacional de Metrologia,		Rodrigo Caciano de Sena	
Qualidade e Tecnologia			
INTI	Argentina	Hernan Lozano, Mabel	(1), (2)
Instituto Nacional de Tecnología Industrial		Puelles	
NIM	China	Ma Liandi,	(2)
National Institute of Metrology		Wu Bing	
NMIJ AIST	Japan	Toshiaki Asakai	(2)
National Metrology Institute of Japan,			
AIST			
SMU	Slovakia	Michal Mariassy	(1), (2)
Slovak Institute of Metrology			
TÜBİTAK UME	Turkey	Emrah Uysal	(1), (2)
TÜBİTAK Ulusal Metroloji Enstitüsü			
UNIIM	Russia	Alena Sobina	(1), (2)
Ural Scientific Research Institute for			
Metrology (since 2020 Affiliated Branch of			
the D.I.Mendeleev Institute for Metrology			
(VNIIM-UNIIM), in this report is indicated			
as UNIIM)			

Table 1 - List of participants

Time schedule

Deadline for registration: 30 June 2018 Dispatch of the samples: November 2018 Deadline for result report: 16 March 2019 Presenting results: IAWG&EAWG meeting April, 2019 Discussing results: IAWG meeting September, 2019 Draft A1 report: January 2020 Draft B report: October 2020

3 SAMPLES

4.1 Sample preparation

The source of the sample was a commercial pure potassium iodate (KIO_3). After being homogenised, a 500 g portion was taken from the middle fraction of the batch, and was homogenised again in a large bottle. This homogenised portion was transferred to 25 glass bottles. The impurities were determined by ICP-MS.

The mass fraction of iodine was in the range of 59,2 % to 59,7 %.

The assay was in the range of 99,5 % to 100,1 % of the theoretical value based on the amount content of oxidants.

4.2 Homogeneity test

Ten bottles were tested for homogeneity by analyzing two independent samples of each bottle by coulometry. The test portion was ~150 mg. Data was treated by ANOVA-analysis. Standard uncertainty of inhomogeneity was 0.0034 % which corresponded to the level of standard deviation of the mean.

The impurities were determined by ICP-MS and ion chromatography. Several major impurities were attempted to be investigated for inhomogeneity. No significant inhomogeneity has been found.

The material of potassium iodate has been considered as appropriate for the key/pilot comparison.

4.3 Distribution

Each participant received one numbered bottle containing about 20 g of material. UME requested two bottles of the sample as they implemented both direct and indirect approach for mass fraction of iodine determination where direct method was titrimetry demanding more sample. Shipment to all participants was performed at the same time. The bottles were shipped in a cardboard box by courier. Shipment of potassium iodate as a dangerous cargo (oxidizing solid) had some special requirements. There were difficulties in dispatching samples to four countries from Russia and NIST kindly assisted to send samples to the corresponding NMIs.

All participants confirmed the receipt of the samples without damage.

NMI	Country	Date of shipping	Way of shipping	Date of sample receiving	Date of reporting results
CENAM	Mexico	16 November 2019	UNIIM – NIST - CENAM	11 January 2019	12 March 2019
INMETRO	Brazil	16 November 2019	UNIIM – NIST - INMETRO	17 January 2019	16 March 2019
INTI	Argentina	16 November 2019	UNIIM - NIST – INTI (by INTI's employee)	26 December 2018	14 March 2019

Table 2 – Information about sample delivery and report dates

NMI	Country	Date of shipping	Way of shipping	Date of sample receiving	Date of reporting results
NIM	China	16 November 2019	UNIIM - Shanghai airport (custom clearance by NIM)	19 December 2018	11 March 2019
NMIJ	Japan	16 November 2019	UNIIM - NIST - NMIJ	04 January 2019	02 February 2019
SMU	Slovakia	16 November 2019	UNIIM - SMU	27 November 2018	08 March 2019
UME	Turkey	16 November 2019	UNIIM – Istanbul (UME picked up by themselves)	28 November 2018	12 March 2019
UNIIM	Russia	-	-	-	06 March 2019

4 INSTRUCTIONS TO THE PARTICIPANTS

The instructions sent to the participants by e-mail consisted of technical protocol and results report form.

The technical protocol (appendix A) contained background information, timing of the comparison, information on sample homogeneity and sample preparation for measurements. Any method or combination of methods can be used. For the mass fraction of iodine determination the high precision instrumental methods such as GDMS, ICP-MS, ICP-OES etc. were expected to be used via impurities measurements. Calculation of the mass fraction of iodine was possible from the measurement results of the amount of oxidants expressed as potassium iodate after implementing corrections on the interfering components. For the amount of oxidants expressed as potassium iodate determination coulometric titration or titrimetry were recommended to be used.

Participants were requested for the results for one or both measurands, which are mass fraction of iodine [kg/kg] and/or the amount content of oxidants, expressed as potassium iodate [mol/kg], and to provide uncertainty evaluation according to Guide to the expression of uncertainty in measurement JCGM 100:2008.

The results report form contained entries relating to the measurement results, detailed uncertainty evaluation and description of the measurement procedures.

5 MEASUREMENT METHODS

Participants were free to choose any measurement method or combination of methods. The measurement methods used by the participants are shown in Table 3.

Measurand	NMI	Approach	Measurement method	Additional information
	CENAM		Weight potentiometric titrimetry	-
the amount	NIM		Coulometry	Mass fraction of 6 impurities using IC, GDMS
content of	INMETRO		Coulometry	-
oxidants expressed	INTI		Volumetric potentiometric titrimetry	-
as potassium	NMIJ		Coulometry + weight titrimetry	-
iodate,	SMU		Coulometry + weight titrimetry	mass fraction of 1 impurity using IC
mon/kg	TUBITAK UME		Volumetric potentiometric titrimetry	-
	UNIIM		Coulometry	mass fraction of 2 impurities using IC
	INMETRO	indirect	ICP OES, ICP MS (65 impurities)	direct approach result using coulometry
the mass	INTI	direct	Titrimetry	-
fraction of iodine,	SMU	direct	Coulometry + titrimetry, IC	mass fraction of 3 impurities using IC
kg/kg	UME	direct	Titrimetry	indirect approach result using ICP MS, IC (76 impurities)
	UNIIM	indirect	ICP MS, ICP OES, IC (70 impurities)	direct approach result using coulometry

Table 3 - Measurement methods and approaches used by the participants of CCQM-K152

Notes:

Coulometry here means constant current coulometry = coulometric titration.

ICP OES is inductively coupled plasma optical emission spectroscopy, ICP MS is inductively coupled plasma mass spectrometry, IC is ion chromatography.

The measurement methods used by participants for the amount content of oxidants expressed as potassium iodate were constant current coulometry and titrimetry. All participants reported more or less details on their coulometric and titrimetric procedures in their reports or additional information. Some details on measurement procedures from the reports as well as main uncertainty sources are given in Table 4 and Table 5.

According to the reported information, there are no two identical coulometric measurement procedures, but more or less similar ones are SMU + NMIJ and NIM + INMETRO + UNIIM.

SMU and NMIJ carried out firstly coulometric standardization of thiosulfate by electrogenerated iodine in pH neutral media and then weight titration of iodine (liberated from electrolyte (KI) by KIO₃) by standardized thiosulfate.

NIM, INMETRO and UNIIM executed firstly coulometric standardization of thiosulfate by electrogenerated iodine and then coulometric titration of an excess of thiosulfate remaining after reaction with iodine liberated from electrolyte by KIO₃. NIM and INMETRO carried out determination with cooling the cell to reduce iodine evaporation from the solution. UNIIM additionally implemented simultaneous adding of iodate and thiosulphate to prevent an excess of both reagents.

Parameter	NMIJ	NIM	SMU	INMETRO	UNIIM
Cell type	horizontal	horizontal	vertical	vertical	vertical
Vol., ml	80	150	250	180	100
Intermediate chamber	yes	yes	yes	yes	no
Working electrode surface, cm ²	20	6,28	94	50	80
The density of electric current, mA/cm ²	5	16,2	2,1	2	1,25
Inert gas purging	over the electrolyte	over the electrolyte	over the electrolyte	through the electrolyte	over the electrolyte
Faraday const., C/mol	96485,33289	96485,33289	96485,3383	96485,3365	96485,33289
Reported density of KIO ₃ , kg/m ³	3890	3890	3960	3480	3930
C(Na ₂ S ₂ O ₃), mol/kg	0,4	0,5	0,4	0,5	0,5
pH of thiosulfate standardization	~7	no information	~7	~ 4,5	~4,5
Mass of KIO ₃ , mg	160	160	190	150	150
Mass of Na ₂ S ₂ O ₃ at standardization, (at KIO ₃ , determ.), g	2,1 (10)	4 (8,2)	8,2 (13,6)	5,2 (8,9)	7,3 (7,8)
Thiosulfate solution added in standardisation	before I ₂	after I ₂	before I ₂	after I ₂	after I ₂
Charge of one impulse, mA·s, before (after) end-point	20	20	10	24	50(5)
The total charge of initial (final) titration, mA·s	50 (200) [0,3 %]	70 (560) [0,3%]	80 (175) [0,08%]	250 (500) [2,4%]	40 (150) [0,04%]

Table 4 – Some parameters of the coulometric measurement procedures

Parameter	NMIJ	NIM	SMU	INMETRO	UNIIM
[% of the main charge of thiosulfate standardization]					
pH of solution for iodate titration	~7	~4,5	~1	~4,5	~4,5
T, ℃	room	4	23	3	25
Protection from light during iodate determination	yes	yes	no (lights dimmed)	yes	yes
Major uncertainty sources	Na ₂ S ₂ O ₃ concentration, repeatability, balance for KIO ₃ , end point, vaporization	Na ₂ S ₂ O ₃ concentration, repeatability, end-point	Na ₂ S ₂ O ₃ concentration, air oxidation of Γ, blank	repeatability, Na ₂ S ₂ O ₃ concentration, impurities of electrolyte	repeatability, sample weighing, Na ₂ S ₂ O ₃ concentration, I ₂ elimination

Table 5 – Some parameters of the titrimetric measurement procedures

Parameter	CENAM	TUBITAK UME	INTI
Electrolyte composition	1,5 g KI + 1M H ₂ SO ₄	1,5 g KI + 150 mL H ₂ O +10 mL 25% H ₂ SO ₄	3,5 g KI + 25 mL 25 % H ₂ SO ₄
Thiosulfate solution adding	After I ₂ formation immediately	After I ₂ formation	After I ₂ formation after 15 min
The thiosulfate standardization method	K ₂ Cr ₂ O ₇ (by coulometry)	KIO3 (CRM by BAM)	K ₂ Cr ₂ O ₇ (RM traceable to SRM 136f)
pH of thiosulfate standardization	no information	no information	acidic
End-point indication method	Potentiometric	Potentiometric	Potentiometric
C(Na ₂ S ₂ O ₃) for titration (at final titration)	0,42 mol/kg (0,04 mol/kg)	no information	0,5 M (0,5 M)
Mass of KIO ₃ , g (concentration, mol/kg) 6 (0,06)		0,3	10 g of 1,8g/100 g KIO ₃ solution
Major uncertainty sources	Na ₂ S ₂ O ₃ concentration, end-point, repeatability	repeatability, CRM, weighing	repeatability, titrant volume

All titrimetric determinations were carried out in acidic media using potentiometric endpoint indication. CENAM used gravimetric (weight) titrimetry and 10 times diluted solution of thiosulfate for the final titration, which helped to obtain smaller uncertainty than typically titrimetric results have. TUBITAK UME and INTI used volumetric titration.

The measurement methods for the mass fraction of iodine were dependent from the chosen direct or indirect approach. 3 NMIs (INTI, SMU, TUBITAK UME) used the direct approach based on recalculation from the amount content of oxidants expressed as potassium iodate and 2 NMIs (INMETRO and UNIIM) implemented the indirect approach based on impurities assessment using combination of the instrumental methods (ion chromatography, ICP OES, ICP MS). INMETRO, TUBITAK UME and UNIIM implemented both direct and indirect approaches, but choose the result from just one of them according to the rules for key comparison. The results from other approach are considered as additional data. Participants that used instrumental techniques reported conditions of the sample decomposition, treatment of the decomposed material (dilution, separation, etc.) and sources for traceability of the calibration materials.

6 RESULTS AND DISCUSSION

7.1 Results of the amount content of oxidants expressed as potassium iodate

The reported values and uncertainties of all results (by 8 NMIs) of the amount content of oxidants expressed as potassium iodate are summarized in Table 6. The same results are displayed graphically in Figure 1 in two scales.

Table 6 – Results for amount content of oxidants expressed as KIO₃ (as presented in the CCQM-K152 participants' protocols)

	1 1	,					
NMI/DIS	Amount content of oxidants expressed as KIO ₃ , mol/kg	u _A , mol/kg	n	Combined standard uncertainty, u _c , mol/kg	Expa uncer U(k mo	inded tainty, =2), l/kg	U _{relative,} %
INTI	4,65388103	0,005466	10	0,005466	0,010932		0,235
UME	4,664576	0,005466	6	0,007756	0,015511		0,333
INMETRO	4,6696	0,0023	6	0,0023	0,0045		0,097
UNIIM	4,67131	0,00016	11	0,00032	0,00	0064	0,014
NMIJ	4,671417	0,000162	9	0,000325	0,00	0651	0,014
NIM	4,672405	0,000219	13	0,000473	0,00	0946	0,020
SMU	4,67247	0,00007	6	0,00026	0,00	0052	0,011
CENAM	4,673848	0,000413	6	0,00105	0,00	0210	0,045
Consistency	χ^2_{obs}	$\chi^2_{0.05,\mathrm{m-1}}$	т			Con	clusion
test	27,70	14,70	8	$\chi^2_{obs} > \chi^2_{0.05,1}$	m—1	inco	nsistent

Generally, results of amount content of oxidants expressed as potassium iodate are in good agreement except INTI, which result is significantly lower. INTI suspects that a lack of appropriate certified reference materials could be a reason of the bias. The other possible reason for lower result is I_2 losses due to evaporation when determination is performed at the room temperature without cooling with delay before titration with thiosulfate as well as excessive acidity of electrolyte. Standardization procedure of thiosulfate solution and its stability are also points to pay attention.

During first results discussion some questionable issues concerning uncertainty evaluation were highlighted. INTI and INMETRO informed about inaccuracy in their calculations of type B standard uncertainty yielding to higher values.

For the reasons mentioned above, the result of INTI was excluded from the calculation of the KCRV. After that, several estimators for possible KCRV were considered according to [2]. Arithmetic mean, median and uncertainty-weighted mean of all results except INTI are given in Table 7. Formulas for possible KCRV estimators are given in 7.4. According to the consistency check (see Table 6) data are inconsistent. Uncertainties of results differ significantly due to using two methods (titrimetry and coulometric titration). Uncertainty weighted-mean (UWM) with correction for over-dispersion was agreed as KCRV because this estimator agrees better with the results having smaller uncertainties.



Fig.1 – The results of amount content of oxidants expressed as potassium iodate (figures a) and b) show the same results in different scales, bars correspond to the combined standard uncertainty (k=1)). Solid red line is KCRV (uncertainty-weighted mean with correction for overdispersion), dashed lines correspond to the standard uncertaity of KCRV.

uniount content of oxidants expressed as polassium fodate								
	Value,	Standard	Rel. standard					
Possible KCRV estimator	mol/kg	uncertainty, mol/kg	uncertainty, %					
Arithmetic mean	4,67080	0,00115	0,025					
Uncertainty-weighted								
mean	4,67194	0,00025	0,005					
Median	4,67142	0,00074	0,016					
Note: KCRV was agreed as uncertainty-weighted mean with correction for over-dispersion.								

Table 7 – Ariphmetic mean, median and uncertainty-weighted mean of the results for amount content of oxidants expressed as potassium iodate

7.2 Results of the mass fraction of iodine

The reported values and uncertainties of all results (by 5 NMIs) of the mass fraction of iodine in potassium iodate are summarized in Table 8. INTI, UME and SMU results were obtained by direct approach (i.e. by recalculating from the amount content of oxidants expressed as KIO₃); INMETRO and UNIIM implemented indirect approach (100 % minus sum of impurities). Additional data obtained by the same participants using second approach are provided in Table 9. The same results are displayed graphically in Figure 2.

Table 8 - Results for the mass fraction of iodine (as presented in the CCQM-K152 participants' protocols)

NMI	Approach	Mass fraction of iodine, kg/kg	Combined standard uncertainty, u _c , kg/kg	Expanded uncertainty, U(k=2), kg/kg	U _{relative,} %				
INTI	direct	0,59060	0,000690	0,001390	0,24				
UME	direct	0,591950	0,001040	0,002090	0,35				
UNIIM	indirect	0,592864	0,000030	0,000060	0,010				
SMU	direct	0,59296	0,00006	0,00012	0,020				
INMETRO	indirect	0,592982	0,0000062	0,000012	0,0020				
Consistency	χ^2_{obs}	$\chi^2_{0.05,\mathrm{m-1}}$	т	2 2	Conclusion				
test	27,8	9,49	5	$\chi^2_{obs} > \chi^2_{0.05,\mathrm{m-l}}$	inconsistent				
Note: "direct" m	Note: "direct" means that the result was obtained by recalculation from the amount content of oxidents								

Note: "direct" means that the result was obtained by recalculation from the amount content of oxidants expressed as potassium iodate; "indirect" means that the result was obtained as "100 % - sum of impurities".

Table 9 – Additional results for the mass fraction of iodine (as presented in the CCQM-K152 participants' protocols)

NMI	Approach	Mass fraction of iodine, kg/kg	Combined standard uncertainty, u _c , kg/kg	Expanded uncertainty, U(k=2), kg/kg	U _{relative,} %
INMETRO	direct	0,592600	0,000420	0,000830	0,14
UNIIM	direct	0,592810	0,000042	0,000083	0,014
TUBITAK					
UME	indirect	0,5929245	0,0000009	0,000002	0,0003



Fig.2 – The results of mass fraction of iodine. Figures a) and b) show the same results in different scales, bars correspond to the combined standard uncertainty (k=1).

INTI result was obtained by recalculation from the amount content of oxidants expressed as KIO_3 and, for the reasons mentioned above, the result of INTI was excluded from the calculation of the KCRV. The additional data were not used for KCRV estimation. Several estimators for possible KCRV were considered. Arithmetic mean, median and uncertaintyweighted mean of all results except INTI are given in Table 10. Formulas for possible KCRV estimators are given in 7.4 Arithmetic mean was not chosen here as it is shifted to the lower result with the highest uncertainty. Uncertainty-weighted mean is not recommended in this case as the smallest uncertainty seems to be underestimated. Median is also not ideal due to small number of results. But all estimators give the same verdict for all participants and there is no great difference. So median was proposed as KCRV estimator.

Table 10 - Ariphmetic mean, median and weighted mean of the results for mass fraction of iodine

		Standard uncertainty,	Rel. standard			
Possible KCRV estimator	Value, kg/kg	kg/kg	uncertainty, %			
Arithmetic mean	0,59269	0,00025	0,042			
Uncertainty-weighted mean	0,59298	0,00002	0,003			
Median	0,59291	0,00005	0,009			
Note: It was agreed to use the median as the KCRV.						

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7.3 Results for impurities

Mass fraction of impurities was not stated as a measurand in this comparison, however, the values are considered as very useful additional information.

The reported values and uncertainties for mass fraction of impurities are summarized in Table 11 (anions determined by ion chromatography) and Table 12 (elements determined by ICP MS, ICP OES, GDMS).

The results for the mass fraction of chloride-ions as the major impurity were graphically plotted displaying arithmetic mean value with the corresponding standard combined uncertainty (Fig. 3). Excellent agreement has been achieved between NMIs.



Fig. 3 – Mass fraction of chloride-ions in KIO_3 (bars correspond to the combined standard uncertainty (k=1))

NMI	NI	M	SN	ΛU	UN	1E	UN	IIIM
Anion	Mass fraction, mg/kg	U _{rel.} (k=2), %	Mass fraction, mg/kg	U, (k=2)	Mass fraction, mg/kg	U _{rel.} (k=2), %	Mass fraction, mg/kg	U _{rel.} (k=2), %
Cl	90,5	10	88	23 %	91,43	0,9	97	9,1
ClO ₃ ⁻	13,2	10	/	/	16,6	7,8	/	/
NO ₃ ⁻	10,3	10	/	/	/	/	/	/
NO ₂ ⁻	/	/	/	/	0,047	50	/	/
BrO ₃ ⁻	/	/	0	26 mg/kg	0,75	50	/	/
$C_2 O_4^{2-}$	/	/	/	/	0,21	50	/	/
Br⁻	/	/	/	/	0,088	50	/	/
SO4 ²⁻	/	/	/	/	/	/	1,3	30
I-	/	/	0	43 mg/kg	/	/	/	/
Note: IC	means ion chromato	ography						

Table 11 - Mass fraction of impurities (anions) in KIO₃ determined by ion chromatography and reported by participants

Table 12 - Mass fraction of impurities (elements) in KIO₃ reported by participants

NMI		INMETRO)	NIM				UME			UNIIM		
	Mass	U _{rel.}		Mass	U _{rel.}		Mass	U _{rel.}		Mass	U _{rel.}		
	fraction,	(k=2),	Meas.	fraction,	(k=2),	Meas.	fraction,	(k=2),	Meas.	fraction,	(k=2),	Meas.	
Element	mg/kg	%	method	mg/kg	%	method	mg/kg	%	method	mg/kg	%	method	
Br	15,6	24	ICP MS	/	/	/	/	/	/	<10	100	ICP MS	
Na	10,3	9	ICP OES	2,5	16	GDMS	1,77	4,5	ICP MS	4,1	30	ICP MS	
Rb	12,5	41	ICP-MS, ICP OES	48,8	15	GDMS	16,2	3,1	ICP MS	38,0	30	ICP MS	
Pb	<0,568	115	ICP OES	6,9	16	GDMS	0,0084	3,6	ICP MS	<0,05	100	ICP MS	
Si	/	/	/	/	/	/	1,15	2,6	ICP MS	<1	100	ICP MS	
Ca	<0,215	115	ICP OES	/	/	/	1,11	7,2	ICP MS	0,6	30	ICP MS	
Fe	<0,221	115	ICP OES	/	/	/	0,305	2,6	ICP MS	0,65	30	ICP MS	

NMI		INMETRO)		NIM		UME			UNIIM		
Mg	<0,109	115	ICP OES	/	/	/	0,135	3,7	ICP MS	0,6	30	ICP MS
Sr	<0,098	115	ICP OES	/	/	/	0,13	2,3	ICP MS	1,4	30	ICP MS
Al	<0,224	115	ICP OES	/	/	/	0,12	8,3	ICP MS	1,4	30	ICP MS
Ba	<0,105	115	ICP OES	/	/	/	0,093	3,2	ICP MS	8,0	30	ICP MS
Te	<0,0353	115	ICP MS	/	/	/	0,09	5,6	ICP MS	<0,05	100	ICP MS
Р	<0,714	115	ICP MS	/	/	/	0,066	18,2	ICP MS	<1	100	ICP MS
Mn	<0,107	115	ICP OES	/	/	/	0,0258	3,5	ICP MS	<0,05	100	ICP MS
Ni	<0,442	115	ICP OES	/	/	/	0,024	8,3	ICP MS	0,1	30	ICP MS
Pr	<0,0066	115	ICP MS	/	/	/	0,015	2,7	ICP MS	<0,01	100	ICP MS
Cr	<0,109	115	ICP OES	/	/	/	0,013	3,8	ICP MS	<0,05	100	ICP MS
Li	<0,110	115	ICP OES	/	/	/	<0,001	50	ICP MS	<0,01	100	ICP MS
Be	<0,115	115	ICP OES	/	/	/	<0,0052	50	ICP MS	<0,01	100	ICP MS
В	<0,206	115	ICP OES	/	/	/	<0,09	50	ICP MS	<0,1	100	ICP MS
Y	<0,012	115	ICP MS	/	/	/	<0,0007	50	ICP MS	<0,01	100	ICP MS
Cd	<0,220	115	ICP OES	/	/	/	<0,02	50	ICP MS	0,18	30	ICP MS
In	<0,0109	115	ICP MS	/	/	/	<0,004	50	ICP MS	<0,01	100	ICP MS
Cs	<0,0066	115	ICP MS	/	/	/	<0,0006	50	ICP MS	<0,01	100	ICP MS
La	<0,0077	115	ICP MS	/	/	/	<0,0009	50	ICP MS	<0,01	100	ICP MS
Ce	<0,0074	115	ICP MS	/	/	/	<0,0009	50	ICP MS	<0,01	100	ICP MS
Nd	<0,0063	115	ICP MS	/	/	/	<0,006	50	ICP MS	<0,01	100	ICP MS
Sm	<0,0062	115	ICP MS	/	/	/	<0,0004	50	ICP MS	<0,01	100	ICP MS
Eu	<0,0060	115	ICP MS	/	/	/	<0,0003	50	ICP MS	<0,01	100	ICP MS
Gd	<0,0061	115	ICP MS	/	/	/	<0,0004	50	ICP MS	<0,05	100	ICP MS
Tb	<0,0060	115	ICP MS	/	/	/	<0,0003	50	ICP MS	<0,05	100	ICP MS
Dy	<0,0060	115	ICP MS	/	/	/	<0,0006	50	ICP MS	<0,01	100	ICP MS
Но	<0,0061	115	ICP MS	/	/	/	<0,0001	50	ICP MS	<0,01	100	ICP MS
Er	<0,0062	115	ICP MS	/	/	/	<0,0008	50	ICP MS	<0,01	100	ICP MS

NMI		INMETRO)		NIM		UME			UNIIM		
Tm	<0,0062	115	ICP MS	/	/	/	<0,00006	50	ICP MS	<0,01	100	ICP MS
Yb	<0,0062	115	ICP MS	/	/	/	<0,0003	50	ICP MS	<0,01	100	ICP MS
Lu	<0,0062	115	ICP MS	/	/	/	<0,00006	50	ICP MS	<0,01	100	ICP MS
Re	<0,0081	115	ICP MS	/	/	/	<0,0002	50	ICP MS	<0,01	100	ICP MS
Tl	<0,0069	115	ICP MS	/	/	/	<0,002	50	ICP MS	<0,01	100	ICP MS
Bi	<0,0099	115	ICP MS	/	/	/	<0,0001	50	ICP MS	0,42	30	ICP MS
Th	<0,0069	115	ICP MS	/	/	/	<0,0001	50	ICP MS	<0,01	100	ICP MS
U	<0,0081	115	ICP MS	/	/	/	<0,005	50	ICP MS	<0,01	100	ICP MS
Sc	<0,098	115	ICP OES	/	/	/	<0,0004	50	ICP MS	<0,05	100	ICP MS
V	<0,112	115	ICP OES	/	/	/	<0,003	50	ICP MS	<0,05	100	ICP MS
Со	<0,109	115	ICP OES	/	/	/	<0,0009	50	ICP MS	<0,01	100	ICP MS
Cu	<0,111	115	ICP OES	/	/	/	<0,012	50	ICP MS	0,129	30	ICP MS
Zn	<0,447	115	ICP OES	/	/	/	<0,046	50	ICP MS	0,186	30	ICP MS
Ga	<0,0089	115	ICP MS	/	/	/	<0,0003	50	ICP MS	<0,05	100	ICP MS
As	<0,182	115	ICP MS	/	/	/	<0,003	50	ICP MS	<0,05	100	ICP MS
Se	/	/	/	/	/	/	<0,04	50	ICP MS	<0,5	100	ICP MS
Sn	<0,0081	115	ICP MS	/	/	/	<0,078	50	ICP MS	<0,01	100	ICP MS
Hg	/	/	/	/	/	/	<0,003	50	ICP MS	<0,05	100	ICP MS
Zr	<0,013	115	ICP MS	/	/	/	<0,004	50	ICP MS	<0,05	100	ICP MS
Nb	<0,016	115	ICP MS	/	/	/	<0,0002	50	ICP MS	<0,01	100	ICP MS
Mo	<1,183	115	ICP OES	/	/	/	<0,008	50	ICP MS	<0,05	100	ICP MS
Ag	<0,0123	115	ICP MS	/	/	/	<0,004	50	ICP MS	<0,01	100	ICP MS
Sb	<0,0178	115	ICP MS	/	/	/	<0,003	50	ICP MS	<0,01	100	ICP MS
Hf	<0,0066	126	ICP MS	/	/	/	<0,001	50	ICP MS	<0,01	100	ICP MS
Та	<0,0071	126	ICP MS	/	/	/	<0,0001	50	ICP MS	<0,01	100	ICP MS
W	<0,0082	126	ICP MS	/	/	/	<0,001	50	ICP MS	<0,01	100	ICP MS
Ti	<0,118	115	ICP OES	/	/	/	<0,056	50	ICP MS	0,37	30	ICP MS

NMI		INMETRO)	NIM			UME			UNIIM		
Ge	<0,020	115	ICP MS	/	/	/	<0,01	50	ICP MS	<0,05	100	ICP MS
Ru	<0,0135	115	ICP MS	/	/	/	<0,002	50	ICP MS	<0,01	100	ICP MS
Rh	<0,0129	115	ICP MS	/	/	/	<0,0002	50	ICP MS	<0,01	100	ICP MS
Pd	<0,0125	115	ICP MS	/	/	/	<0,0005	50	ICP MS	<0,01	100	ICP MS
Os	/	/	/	/	/	/	<0,0002	50	ICP MS	<0,01	100	ICP MS
Ir	<0,0097	115	ICP MS	/	/	/	<0,0001	50	ICP MS	/	/	/
Pt	<0,0142	116	ICP MS	/	/	/	<0,002	50	ICP MS	<0,01	100	ICP MS
Au	<0,0393	117	ICP MS	/	/	/	<0,004	50	ICP MS	<0,01	100	ICP MS
S	/	/	/	/	/	/	<1,9	50	ICP MS	1,26	30	ICP MS
Note: ICP MS means inductively coupled plasma mass spectrometry, ICP OES – inductively coupled plasma optical emission spectrometry, GDMS – glow discharge												
mass spec	trometry											

7.4 Formulas

A consistency check was performed according to the CCQM guidance note [2] using the algorithm shown below

$$\overline{x}_{u} = \sum_{i=1}^{m} \frac{x_{i} / u(x_{i})^{2}}{\sum_{i=1}^{m} 1 / u(x_{i})^{2}},$$
(1)

$$\chi_{obs}^{2} = \sum_{i=1}^{m} \left(\frac{x_{i} - \overline{x}_{u}}{u(x_{i})} \right)^{2}, \qquad (2)$$

where x_i is the result of the value of *i* NMI, $u(\overline{x})$ is the standard uncertainty of \overline{x} , *m* is number of participants of the key comparison.

After calculations using formulas (1), (2) χ^2_{obs} with m-1 and with $\chi^2_{0.05,m-1}$ the 95 percentile of χ^2 with m-1 of freedom ($\chi^2_{0.05,m-1}$ - has been taken from Microsoft Excel) were compared,.

If $\chi^2_{obs} < m-1$ it is normally safe to proceed with the assumption that the results are mutually consistent and that the uncertainties account fully for the observed dispersion of values.

If $m-1 < \chi^2_{obs} < \chi^2_{0.05,m-1}$ the data does not provide strong evidence that the reported uncertainties are inappropriate, but it remains a risk that additional factors are contributing to the dispersion. Referring to the prior working group decision on presumptive consistency we proceed accordingly.

If $\chi^2_{obs} > \chi^2_{0.05,m-1}$ the data should be considered mutually inconsistent.

Candidates of the key comparison reference value (KCRV) were estimated following the CCQM guidance note [2] using different approaches. Results and uncertainties were taken from the participants' reports as they were. Formulas for calculation are shown below.

Arithmetic mean

$$\overline{x} = \frac{1}{m} \sum_{i=1}^{m} x_i, \qquad (3)$$

$$u^{2}(\bar{x}) = \frac{\sum_{i=1}^{m} (x_{i} - \bar{x})^{2}}{m(m-1)},$$
(4)

where x_i - is the result of the value of *i* NMI, $u(\overline{x})$ - is the standard uncertainty of \overline{x} .

Uncertainty-weighted mean

$$\overline{x}_{u} = \sum_{i=1}^{m} w_{i} x_{i} , \qquad (5)$$

$$w_{i} = \frac{1/u^{2}(x_{i})}{\sum_{i=1}^{m} 1/u^{2}(x_{i})},$$
(6)

$$\frac{1}{u^2\left(\overline{x}_u\right)} = \sum_{i=1}^m 1/u^2\left(x_i\right),\tag{7}$$

$$u_{corr}^{2}\left(\overline{x}_{u}\right) = \frac{\chi_{obs}^{2}}{m-1}u^{2}\left(\overline{x}_{u}\right) = \frac{\sum_{i=1}^{m} \left(\frac{x_{i}-\overline{x}_{u}}{u\left(x_{i}\right)}\right)^{2}}{m-1}u^{2}\left(\overline{x}_{u}\right), \quad (8)$$

where $u(x_i)$ - is the standard uncertainty of x_i .

Median

$$med(x) = \begin{cases} \frac{1}{2} (x'_{m/2} + x'_{m/2+1}), & m \ even \\ x'_{(m+1)/2}, & m \ odd \end{cases},$$
(9)

$$u^{2}\left(med\left(x\right)\right) = \frac{\pi}{2m}\hat{\sigma}^{2},$$
(10)

$$\hat{\sigma} = 1.483 med\left(\left|d_i\right|\right),\tag{11}$$

where $d_i = x_i - med(x)$.

7.5 Discussion

Potassium iodate was chosen as an object for the key comparison for the first time. For some participants it was a challenge to implement a new measurement procedure and to evaluate its uncertainty.

For direct approach based on constant current coulometry or titrimetry there were no two identical measurement procedures. Most participants try to reduce affecting of main chemical sources of bias summarized in Table 13. Coulometric results are in good agreement within the corresponding expanded uncertainties ($U_{rel.} \sim (0.01 \% - 0.02 \%)$) and titrimetric results showed higher discrepancy. Titrimetry is known to have larger uncertainty than coulometry, but some technics allow to reduce uncertainty, for example, using weight titrimetry instead of volumetric and implementing two-stage titration with lower concentration near the end-point, which was demonstrated by CENAM.

Sources of bias	Influencing factors
Thiosulfate decomposition in	pH (acidic is non-desirable)
acidic media	
Reaction rate (KIO ₃ assay)	pH (acidic media is desirable as there is no reaction at
	pH >6)
Thiosulfate solution instability	Temperature, time
during storage	(stabilization and/or control of concentration is necessary)
I ₂ losses due to evaporation	Temperature, time
	(low temperature of reaction media, no delays before
	titration are desirable)
Tetrathionate decomposition	Time, repeat using of electrolyte [3]
	(no delays before final titration, no repeated use of
	electrolyte are desirable)
Air oxidation of iodide in	pH, mass of KI in the solution [3], time, light
acidic media	(less acidic pH, less KI in electrolyte, no delays, no light are
	desirable)

Table 13 - Potential sources of bias in potassium iodate assay by coulometry or titrimetry

The additional challenge was to implement direct and indirect approaches for the purity of salt determination and compare obtained results. Potassium iodate used for comparison was of high purity (the main impurity was chloride-ion with mass fraction ~0,009 %, there were no significant content of other oxidants). This fact allows to calculate mass fraction of potassium iodate (purity) from the measurement results of both measurands. Participants' results were recalculated to purity and presented in Table 14 and Figure 4.

NMI/DIS	Mass fraction of potassium iodate, %	Combined standard uncertainty, u _c , %	Expanded uncertainty, U(k=2), %	d _i , %	U(d _i), %	Verdict	
INTI dir	99,5935	0,1170	0,2339	-0,3821	0,2343	-	
UME dir	99,8224	0,1660	0,3319	-0,1532	0,3322	+	
INMETRO dir	99,9299	0,0492	0,0963	-0,0457	0,0992	+	
UNIIM dir	99,9665	0,0068	0,0137	-0,0091	0,0186	+	
NMIJ dir	99,9688	0,00696	0,0139	-0,0067	0,0188	+	
UNIIM ind	99,9756	0,00506	0,01012	0,0000	0,0162	+	
UME ind	99,98578	0,0002	0,0003	0,0102	0,0126	+	
NIM dir	99,9899	0,0101	0,0202	0,0143	0,0239	+	
SMU dir	99,9913	0,0056	0,0111	0,0157	0,0168	+	
INMETRO ind	99,9955	0,0010	0,0021	0,0199	0,0128	-	
CENAM dir	100,0208	0,0225	0,0449	0,0452	0,0467	+	
purity1 ± U (recalculated from KCRV for amount content of oxidants)			99,9800±0,0	057			
purity2 ± U (recalculated from KCRV for mass fraction of iodine)	99,9837±0,0092						

Table 14 - Calculation results of potassium iodate purity



Fig. 4 - Participants' results obtained by direct and indirect approach and recalculated to mass fraction of potassium iodate.



Figure 5 shows the comparison of the results of mass fraction of iodine obtained by direct and indirect approaches.

Fig. 5 – Results of mass fraction of iodine obtained by direct and indirect approach

According to Figures 4 and 5 results obtained by indirect approach based on impurities assessment have a tendency to be higher than results from the direct one and to have smaller uncertainty. The smaller number of impurities was measured, the higher is the result. To obtain an appropriate measurement result by indirect approach it is necessary to measure a large number of impurities (close to 70). Taking into account ionic forms of the impurities when implementing indirect approach allow to obtain comparable results with results by direct approach.

The indirect method for determining the purity of salts is promising, since the indirect method is characterized by lower uncertainties. However, the determination of purity by indirect method is not sufficiently methodically developed, so all participants used different equations to determine the purity, as well as determined different number of impurities. This comparison showed that it is necessary to take into account the ionic form in which the element is present, as well as the non-stoichiometry of the salt based on the electroneutrality equation when implementing the indirect method in the equation.

7 THE EQUIVALENCE STATEMENTS

The degree of equivalence between a NMI result and the KCRV and corresponding uncertainty was calculated according to the following formulas:

$$d_i = \left(x_i - x_{ref}\right) \tag{15}$$

$$u^{2}(d_{i}) = u^{2}(x_{i}) + u^{2}(x_{ref})$$
(16)

$$U(d_i) = k \cdot u(d_i) \tag{17}$$

where d_i is the degree of equivalence between the NMI result x_i and the KCRV x_{ref} , and $U(d_i)$ is the expanded uncertainty (k = 2) of the d_i calculated by combining the standard uncertainty $u(d_i)$ of the NMI result x_i and the standard uncertainty $u(x_{ref})$ of the KCRV x_{ref} .

The equivalence statements for CCQM-K152 are given in Table 12 for amount content of oxidants expressed as potassium iodate and in Table 13 for mass fraction of iodine. The same data graphically are presented in Figures 6 and 7, respectively.

Table 12 - Equivalence Statements for amount content of oxidants expressed as potassium iodate for CCQM-K152

NMI	Result, mol/kg	u _c , mol/kg	U(k=2), mol/kg	d _i , mol/kg	U(d _i), mol/kg	Verdict
INTI	4,6539	0,0055	0,0109	-0,018	0,011	-
UME	4,6646	0,0078	0,0155	-0,0074	0,016	+
INMETRO	4,6696	0,0023	0,0045	-0,0023	0,0046	+
UNIIM	4,67131	0,00032	0,00064	-0,00063	0,00070	+
NMIJ	4,67142	0,00033	0,00065	-0,00052	0,00071	+
NIM	4,67241	0,00047	0,00095	0,00046	0,00099	+
SMU	4,67247	0,00026	0,00052	0,00053	0,00059	+
CENAM	4,6738	0,0011	0,0021	0,0019	0,0021	+



Figure 6 - Degrees of equivalence d_i and expanded uncertainty U (d_i) (k=2) for amount content of oxidants expressed as potassium iodate

Table 13 - Equivalence Statements for mass fraction of iodir	e for CCQM-K152
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NMI	Result, kg/kg	u _c , kg/kg	U(k=2), kg/kg	d _i , kg/kg	U(d _i), kg/kg	Verdict
INTI	0,59060	0,00069	0,00139	-0,00231	0,0014	-
UME	0,59195	0,0010	0,00209	-0,00096	0,0021	+
UNIIM	0,592864	0,000030	0,000060	-0,00005	0,0001	+
SMU	0,59296	0,00006	0,00012	0,00005	0,0002	+
INMETRO	0,592982	0,0000062	0,000012	0,00007	0,0001	+



Figure 7 - Degrees of equivalence d_i and expanded uncertainty U (d_i) (k=2) for mass fraction of iodine

9 SCOPE OF THE COMPARISON (How far the light shines)

The comparison tested the capabilities and methods used for assay of high purity salts and determination of non-metallic elements from their content.

For direct approach using coulometric and titrimetric methods, good results will indicate good performance in assaying purity of pure salts as iodate, chlorate and bromate as well as in measuring concentration of iodate, chlorate and bromate anions in solution (1 mmol/L and higher) and in determining other oxidizing agents by iodometry.

For indirect approach based on large number of impurities assessment good result will demonstrate capability of assaying purity of pure inorganic salts (mass fraction not less than 99.0 %) and determining constituent elements of these salts.

10 CONCLUSIONS

The measurement capabilities of NMIs for amount content of oxidants expressed as potassium iodate and measuring the mass fraction of iodine in high purity potassium iodate were demonstrated in this comparison. In general, good agreement was observed for the both measurands. The uncertainty-weighted mean and median were agreed as the reference values of the key comparison for the amount content of oxidants expressed as potassium iodate and the mass fraction of iodine, respectively.

The challenge of this comparison was comparing measurement results of mass fraction of iodine determined by direct approach (coulometry, titrimetry) and indirect approach based on impurities assessment. It was demonstrated that indirect approach has smaller uncertainty and its calculation is complicated. To unify approaches to determining the purity and basis elements in an indirect way, it is relevant to prepare an IAWG CCQM recommendation.

11 ACKNOWLEDGEMENT

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Dr. T. Asakai (NMIJ) for their contribution in discussing the results; participants of IAWG and EAWG, all analysts from participating institutions for their work, as well as contact persons.

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[1] JCGM, Evaluation of measurement data – Guide to the expression of uncertainty in measurement. JCGM 100:2008, <u>http://www.bipm.org/utils/common/documents/jcgm/JCGM 100 2008 E.pdf</u>

[2] CCQM Guidance note: Estimation of a consensus KCRV and associated Degrees of Equivalence, Version 10, 2013.

[3] M. Mariassy. Some experience with iodate assay using thiosulfate. EAWG, 8.04.2019

Appendix A CCQM-K152 and CCQM-P192 Assay of potassium iodate Technical Protocol

Introduction

Pure materials are very important for traceability in chemical metrology. High purity metals are known as the best source for preparing element calibration solutions. But for a list of elements pure metals do not exist, are not convenient or are not readily available, and only compounds (salts, oxides) can be used, such as for iodine.

Potassium iodate is used as a source for preparing a calibration solution of iodine. It is also widely used as a chemical standard for redox titrimetry in analytical chemistry. Purity of potassium iodate and its measurement uncertainty contribute to the uncertainty of iodine calibration solution and furthermore to the uncertainty of iodine routine measurement results.

The CCQM-K152 key comparison in parallel with CCQM-P192 pilot comparison are organised jointly by the Inorganic Analysis (IAWG) and Electrochemical Analysis (EAWG) working groups of CCQM to test the abilities of the metrology institutes to measure the amount content of the non-metallic elements in high purity salts as well as assaying high purity salts to be used as primary standards. This CCQM-K152&P192 comparison is the next step in realization the long-term strategy of CCQM (IAWG+EAWG) on purity determination of the high pure substances (e.g. previously conducted comparisons are CCQM-P107 and CCQM-K72/P107.1, CCQM-P149; CCQM-K48.2014).

Scope

The comparison will test the capabilities and methods used for assay of high purity salts. CCQM-K152 will support CMC claims. CCQM-P192 will not support CMC claims.

Time schedule

April 2018
30 June 2018 (changed from 31 May 2018)
November 2018
16 March 2019 (changed from 28 February 2019)
April 2019
April ~ July 2019
September 2019

Samples

Sample preparation

The source of the sample is a commercial pure potassium iodate. After being homogenised, a 500 g portion is to be selected from the middle fraction of the batch, and to be homogenised again in a large bottle. This homogenised portion is to be transferred to 25 glass bottles. The impurities are to be determined by ICP-MS.

The mass fraction of iodine is in the range of 59,2 % to 59,7 %.

The assay is in the range of 99,5 % to 100,1 % of the theoretical value based on the amount content of oxidants.

Homogeneity test

Ten bottles will be tested for homogeneity by analysing each bottle in twice independence sampling by coulometry. Preliminary homogeneity tests before bottling were carried out by coulometric titration. Standard uncertainty of inhomogeneity was 0.003 %.

Please pay attention that you do not use less than 150 mg in your analyses for the key or pilot comparison.

Distribution

Each participant will receive one numbered bottle containing about 20 g of material. The sample number will be the same as the laboratory number. Shipment to all participants will be performed at approximately the same time. The bottles are shipped in a cardboard box by courier. The contents will be marked "potassium iodate" for research purposes; please be attentive of possible customs delays, etc. The measurement protocol is sent by e-mail.

The participants will be informed of the date of dispatching of the samples. Participants must confirm the receipt of the sealed samples, by filling in the return receipt table and sending it to the UNIIM contact person by e-mail, fax or mail. If there is any damage, please contact us immediately.

Handling and storing instructions

The sample should be stored in a dark, dry place at laboratory temperature in the original container until used.

Sample preparation for measurement

The material should be dried at 110°C for 2 h without crushing or grinding the material. After drying, it should be placed in a desiccator with silica gel or other desiccant, and cooled to room temperature before weighing.

The mass of the samples should be corrected for buoyancy.

The quantity of sample to be used in the assay is not less than 150 mg.

Measurands and measurement methods

Measurands are:

- the mass fraction of iodine, kg/kg,
- the amount of oxidants expressed as potassium iodate, mol/kg.

Any method or combination of methods can be used by participants.

For the mass fraction of iodine determination the high precision instrumental methods such as GDMS, ICP-MS, ICP-OES etc. are expected to be used via impurities measurements. Calculation of the mass fraction of iodine is possible from the measurement results of the amount of oxidants expressed as potassium iodate after implementing corrections on the interfering components.

For the amount of oxidants expressed as potassium iodate determination coulometric titration or titrimetry are recommended to be used.

At least six independent determinations should be performed.

Non-stoichiometry and ion forms of the elements determined in the sample must be taken into account.

Reporting

The report should be sent to the coordinating laboratory before 16 March 2019, preferentially by e-mail. The coordinator will confirm the receipt of each report to the participant. If the confirmation does not arrive within one week, please contact the coordinator to identify the problem.

A template for the report will be enclosed (Excel spreadsheet). If possible, the requested data should be entered into the corresponding boxes. If this is not possible, the format can be modified or the data can be reported in another form.

Information requested:

- 1. The results are to be reported as:
- the mass fraction of iodine, kg/kg,
- the amount of oxidants expressed as potassium iodate, mol/kg.

The measurement results are to be accompanied by a full uncertainty budget.

If the value of the measurand was determined from impurity analysis, results for <u>all the elements/compounds sought must be given</u>. Participants using multiple methods for the measurement of an individual impurity are obliged to report only one composite result (e.g. an average value from different methods) for each impurity.

Information on impurities is welcome also from participants not using (100 % -impurities) approach.

Information on the measurands dependence on sample mass is also welcome.

2. A detailed description of the equipment used and the measurement procedure is to be given. If several methods were used, please provide the detailed information about each measurement method, equipment used and procedure.

For (100 % - impurities) approach this should include the following: information about reference materials used for calibration (origin, certified value, standard uncertainty, and isotopic ratio if necessary) or other materials used in the measurement procedure, the complete measurement equation for the measurand including corrections if applied.

For coulometry this should include the following: cell description, volume of electrolyte in working chamber, the number of stages used in the titration and the current used for each stage, evaluation procedure for the endpoint, examples of the titration curve for initial and final endpoint determination. The complete measurement equation has to be given, as well as the values of the constants (suggested Faraday constant: 96485.33289(59) C mol⁻¹) used and variables (raw data) for at least one measurement. The data should enable the recalculation of the result of this measurement. If trace element correction is used, the relevant data must be included here also.

3. Please also provide the air temperature, humidity and pressure in your laboratory at the time of each mass measurement as well as the air density used for each buoyancy correction.

4. The uncertainty calculations should conform to the ISO document: *Guide to the Expression of Uncertainty in Measurement* (1995) 1st ed., ISO, Geneva. Both Type A and Type B uncertainty components and a summary of how they are calculated have to be included. Please identify and quantify all the uncertainty components. The reported uncertainty should be expressed as a combined standard uncertainty and as an expanded uncertainty calculated using a coverage factor, k, of 2.

For coulometry the uncertainty budget must include instrumental sources of uncertainty (mass, time, voltage, volume, ...) as well as chemical ones (endpoint estimation, equilibria, migration, O_2 interference, impurities, ...) plus the relevant uncertainties for any trace element corrections.

Reference value

The reference values will be agreed upon on the joint meeting of the EAWG and IAWG.

Participation

National metrological institutes (NMIs) and designated institutes (DIs) in accordance with the CIPM MRA are welcome to take part in the CCQM-K152 or CCQM-P192. Any proposed participation in CCQM-P192 by an expert laboratory should first be discussed with the coordinating laboratory and the EAWG and IAWG Chairs and finally approved by CCQM President.

Coordinating laboratory and contact persons

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