National Institute of Metrology P.R.China

Report of the CCQM- K48.2014

(CCQM- K114)

Assay of Potassium Chloride

Final Report

Ma Liandi and Wu Bing

With participation of:
CENAM: José Luis Ortíz-Aparicio, Francisco Segoviano-Regalado, Aura Bibiana GarcíaAlcántara, Edith Valle-Moya, Griselda Rivera-Sánchez
GUM: Joanna Dumanska, Monika Pawlina, Anna Pietrzak, Wladyslaw Kozlowski
INMETRO: P. P. Borges, W. B. Silva Jr, C. S. Freitas, T. O. Araujo, M. D. Almeida
KRISS: Youngran Lim, Sung Woo Heo and Euijin Hwang
NIM: Ma Liandi, Wu Bing, Wang Qian
NIST: Jason F. Waters, John R. Sieber, Kenneth W. Pratt
NMIJ: Toshihiro Suzuki, Akiharu Hioki
SMU: Michal Mariassy, Zuzana Hankova
UNIIM: Alexandr Shimolin, Alena Sobina
VNIIFTRI: Vladimir Dobrovolsky, Sergey Prokunin, Aleksey Aprelev, Dmitry Frolov

Beijing，May 2016

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1. ABSTRACT

The CCQM-K114 key comparison for determination of the purity of potassium chloride was organized jointly by the inorganic analysis and electrochemical analysis working groups of CCQM to repeat a sub-set of comparisons to support CMC claims for all institutes in the relevant ranges with timely experimental data to measure the amount content of chloride in KCl. National Institute of Metrology P.R.China (NIM) acted as the coordinating laboratory of this comparison. Ten NMIs participated in this key comparison. All participants used coulometry and all of them analyzed the bromine impurity in the sample and made corrections. In general very good overlap of results was observed and also the results for bromide are consistent with one exception.

2. INTRODUTION

Potassium chloride is an often used reference material in precipitation titration methods, and is also used for pH, conductivity and mono-element standard solution. Pure materials are very important for traceability in chemical metrology, and pure material studies and comparisons are important activities in Electrochemical Analysis Working Group and Inorganic Analysis Working Group at all time. The EAWG with IAWG jointly organized a key comparison CCQM-K48 for assay of potassium chloride in 2007.

According to the EAWG strategy, “Periodically, it is necessary to repeat a sub-set of comparisons to support CMC claims for all institutes in the relevant ranges with timely experimental data. The repetition of measurements should be sufficiently frequent to enable NMIs with less well-established or newer facilities to benchmark their capabilities.”, so a repeat key comparison for determination the purity of KCl is necessary and CCQM had agreed to start a key comparison (CCQM-K114) for determination of the purity of potassium chloride, base on the CCQM new numbering scheme the repeat KC is also referenced as CCQM-K48.2014.

The objective of this key comparison “Assay of Potassium Chloride” was to determine the amount content of Cl in potassium chloride. The participants were free to choose the analytical procedure, but the coulometric method was recommended for this comparison. The comparison tested the capabilities for assay of high purity materials and underpinned the claimed calibration and measurement capabilities of the participating national metrology institutes.

3. LIST OF PARTICIPANTS

There were 10 NMIs registered in the key comparison. Table 1 contains the full names of all participating NMIs, countries and contact persons.

Table 1 List of participants

Institution	Country	Contact person
CENAM National Center of Metrology	Mexico	Judith Velina Lara Manzano
GUM Central Office of Measures	Poland	Wladyslaw Kozlowski
INMETRO Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brazil	Paulo Paschoal Borges
KRISS Korea Research Institute of Standards and Science	Korea	Euijin Hwang
NIM National Institute of Metrology	China	Ma Liandi
NIST National Institute of Standards and Technology	USA	Kenneth W. Pratt, Jason F. Waters
NMIJ AIST National Metrology Institute of Japan, AIST	Japan	Toshihiro Suzuki
SMU Slovak Institute of Metrology	Slovakia	Michal Mariassy
UNIIM Ural Scientific Research Institute for Metrology	Russia	Alexandr Shimolin, Gennady Terentiev
VNIIFTRI Russian Metrological Institute of Technical Physics and Radio Engineering	Russia	Dr. Vladimir Dobrovolskiy

4. TIME SCHEDULE

Deadline for registration: 10 May 2014
Dispatch of the samples: the end of May 2014
Deadline for result report: 31 December 2014
Discussing results: IA&EA meeting April, 2015
Draft A report: April 2015
Draft B (1) report: December 2015
Draft B (2) report: March 2016

5. SAMPLES

The source of the sample is a 20 kg batch of commercial pure potassium chloride material. After being homogenised, a 500 g portion was selected from the middle fraction of the batch, and was homogenised again in a large bottle. This homogenised portion was then transferred to 13 glass bottles closed with silicone lined plastic caps for the comparison, each containing about 15 g of the material. The impurities were determined by ICP-MS.

Twelve bottles were randomly selected from the set of 13 bottles. Two samples were sampled independently from each bottle. The content of chloride was determined by coulometry to check the homogeneity of the samples. No statistically significant heterogeneity was found based on F test, the RSD is 0.0033 % with each independent result and the RSD is 0.0012% with the average from each bottle, no statistically significant difference was found.

The samples were sent to the participants by DHL on the end of May 2014 (except INMETRO, where the sample was sent on June 3). All samples arrived to their destination without damage within two weeks. The dispatch dates and receipt dates are given in Table 2.

The deadline for reporting results was set to 31 December 2014, and all participants reported their results in time. A draft A report had been prepared and circulated on 1st, April 2015, and then which had been discussed at the CCQM WG meeting in April 2015.

Table 2 Sample sent dates, receipt dates and report dates

Institute	Sample No.	Sample dispatch date	Sample receipt date	Date report sent
CENAM	01	30 May 2014	13 June 2014	31 December 2014
GUM	02	30 May 2014	5 June 2014	31 December 2014
INMETRO	03	3 June 2014	16 June 2014	22 December 2014
KRISS	04	30 May 2014	9 June 2014	31 December 2014
NIM	05	/	/	/

NIST	06	30 May 2014	10 June 2014	22 December 2014
NMIJ AIST	07	30 May 2014	4 June 2014	22 December 2014
SMU	08	30 May 2014	5 June 2014	25 December 2014
UNIIM	09	30 May 2014	6 June 2014	30 December 2014
VNIIFTRI	10	30 May 2014	2 July 2014	31 December 2014

Note：VNIIFTRI submitted coulometry results in time, but the Br impurity result and the corrected amount content of Cl in potassium chloride submitted on 13 March 2015.

6. INSTRUCTIONS TO PARTICIPANTS

The instructions sent to the participants by e-mail consisted of technical protocol, registration form, return receipt form 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 was given. Any method or combination of methods could be used, but the coulometric method was recommended for this comparison. Participants were requested to express the results as amount content of chloride in KCl [mol/kg] and/or mass fraction of chloride expressed as KCl [kg/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.

7. METHODS OF MEASUREMENT

All participants used coulometry for assay determination and reported more or less details on their procedure in their reports or additional information. Some details on measurements as derived from the reports are given in Table 3 and Table 4.

Table 3 Details on measurement methods used

Institute	*Approx. sample mass/g*	*Sample dried at 500 ℃ for 6h*	*Anolyte*	*How to add sample*
CENAM	5g~10g KCl (0.26 mol/kg) solution sample	yes	3.5 mol/L $HClO_4$	About 6 g of the KCl solution (0.26 mol/kg solution sample) is added to the electrolyte drop by drop
GUM	0.2	yes	3.5 mol/L $HClO_4$	The sample was dissolved in water and was added in portions before and during the main titration.
INMETRO	0.3	yes	3.5 mol/L $HClO_4$	The solid sample in a glass cup is added to the cell before the main titration.
KRISS	0.25	yes	1 mol/L $NaNO_3$, 1 mol/L acetic acid, 50 % methanol in volume	Solid sample is added in the cell after 99 % of main titration, and the solution is stirred very vigorously for 10 min.
NIM	0.15	yes	1 mol/L $NaNO_3$, 1 mol/L acetic acid, 60% ethanol in volume	The sample is dissolved in 2mL deionized water, and is added by portions during the main titration.
NIST	0.15~0.17	yes	the same concentration [1 mol/L] of both acetic acid and $NaNO_3$ in each	NIST added the sample in solid form after initial titration, the solution was stirred until the KCl had visibly dissolved
NMIJ AIST	0.2	yes	1 mol/L $NaNO_3$, 1 mol/L acetic acid, 65% ethanol in volume	The sample is added 0.7mL water before the measurement.
SMU	0.5	yes	A solution of $HClO_4$	two drops of deionized water were added to solid KCl in a glass cup; solid sample was dissolved before main titration
UNIIM	0.15	?	1 M $NaNO_3$ in 1 M CH_3COOH in 40% ethanol	A probe of KCl is diluted by deionized water and is added by portions during the main titration.
VNIIFTRI	0.15	yes	1.2 M solution of sodium nitrate	Approximately 150 mg of pre-treated KCl was put in the cell each time.

Table 4 Details on measurement methods used (continued)

Institute	*Details of coulometric procedures*				*EP estimation*	*Initial titration*	*Major unc. sources*	*Their contribution*
	Cell type	*IC rinse*	*Total volume （Analyte volume）/mL*	*Main current /mA*				
CENAM	vertical, 1 intermediate chamber (IC)	Yes	180 (100)	200	nonlinear regression	Yes	*Preparation of KCl soln* Mass of soln	96%
GUM	vertical,1 IC	Yes	250	150	nonlinear regression	Yes	weighing, End-point	99%
INMETRO	vertical, 1 IC	Yes	250	200	nonlinear regression.	Yes	u_A, End-point	99%
KRISS	horizontal, 2 IC	Yes	110	101.8	3rd order polynomial regr.	Yes	u_A,current efficiency, Measured total charge	99.8%
NIM	horizontal, 2 IC	Yes	250 (160-180)	101.8	3rd order polynomial regr.	Yes	u_A, End-point	93%
NIST	horizontal, 2 IC	Yes	180 (100)	101.8	3rd order polynomial regr.	Yes	u_A, occluded Ag+ in AgCl ppt, Cl- coprecipitation on AgCl, Ag+ gener. eff @ anode, msample	100%
NMIJ AIST	horizontal,2 IC	Yes	140	50	3rd order polynomial regr.	Yes	u_A, sample weighing	96%
SMU	vertical, 1 IC	Yes	500 （290）	200	nonlinear regression	Yes	u_A, adsorption on AgCl	98%
UNIIM	vertical, 1 IC	Yes	200	100	3rd order polynomial regr.	Yes	u_A, mass weighing	99.8%
VNIIFTRI	horizontal,2 IC	Yes	250	100	3rd order polynomial regr.	Yes	t, mass weighing	97%

8. RESULTS AND DISCUSSION

8.1 Sum of halides

The reported values and uncertainties of all results before correction are summarized in Table 5. Arithmetic mean, median and variance weighted mean of all results before Br correction in Table 6. The same results are displayed graphically in Figure 1.

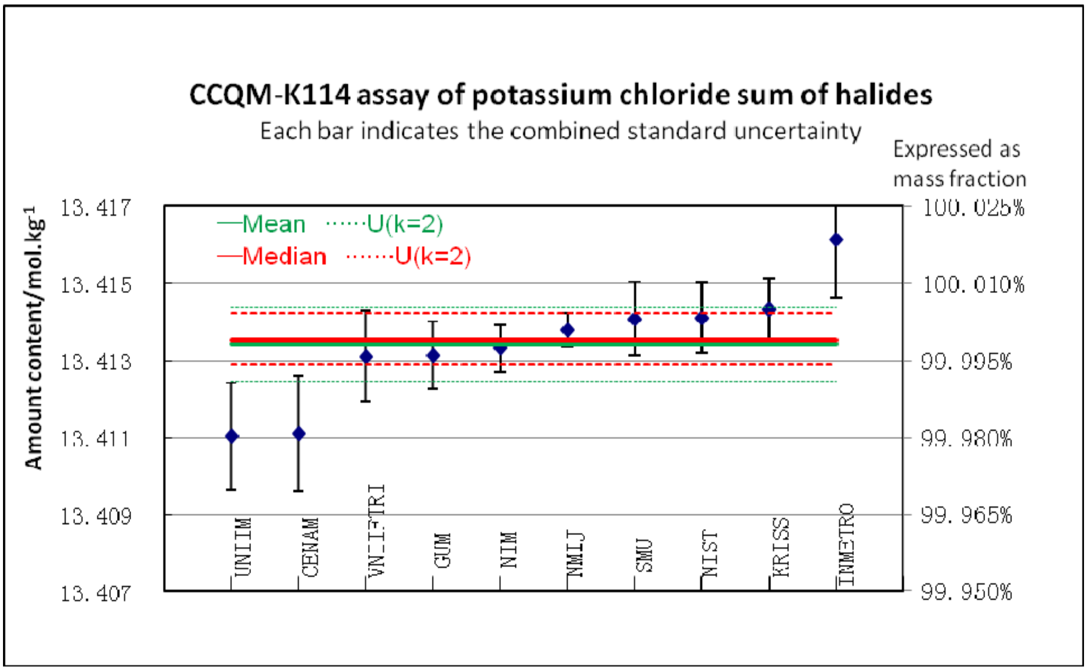
Table 5 Sum of halides expressed as KCl result (KCl result before Br correction)

Institute	***Measurement date***	***Result /mol.kg^{-1}***	***n***	***SD /mol.kg^{-1}***	***u_c /mol.kg^{-1}***	***U /mol.kg^{-1}***	***k***
UNIIM	Dec 9~Dec 19,14	13.4110	9	0.00311	0.00139	0.0028	2
CENAM	Oct 28~Oct30,14	13.4111	6	0.00125	0.00153	0.0031	2
VNIIFTRI	Dec 23~Dec 25,14	13.4131	6	0.00043	0.00117	0.0024	2
GUM	Dec 16~Dec 31,14	13.41312	6	0.00025	0.00087	0.0018	2
NIM	May 6~Dec 17,14	13.41331	13	0.00100	0.00061	0.0012	2
NMIJ	Dec 8~Dec 12,14	13.41379	10	0.00112	0.00044	0.0009	2
SMU	Dec 2~Dec 4,14	13.41408	5	0.00108	0.00095	0.0019	2
NIST	Sep 18~Dec 15,14	13.4141	12	0.00098	0.00091	0.0018	2
KRISS	Dec 23~Dec 29,14	13.41431	6	0.00044	0.00082	0.0017	2
INMETRO	Oct 10~Dec 15,14	13.41612	7	0.00344	0.00149	0.0030	2

Table 6 Arithmetic mean and Median of All Results before Br correction

	Value **(mol.kg^{-1})**	Standard uncertainty **(mol.kg^{-1})**	Expanded uncertainty **(mol.kg^{-1})**
Arithmetic mean （$\bar{x}$）	13.41340	0.00048	0.00096
Median	13.41355	0.00033	0.00067
Variance weighted mean	13.41361	0.00029	0.00066

Figure 1 The results of sum of halides



8.2 Chloride amount content

Based on little other halide impurities except Br that had been found in the sample, the results after Br correction are used as the final results (chloride amount content) of this KC. The reported values and uncertainties of all final results with Br correction are summarized in Table 7 . Arithmetic mean, median and variance weighted mean of all results with Br correction for possible KCRV in Table 8. The same results are displayed graphically in Figure 2.

Table 7 Results (amount content of chloride)

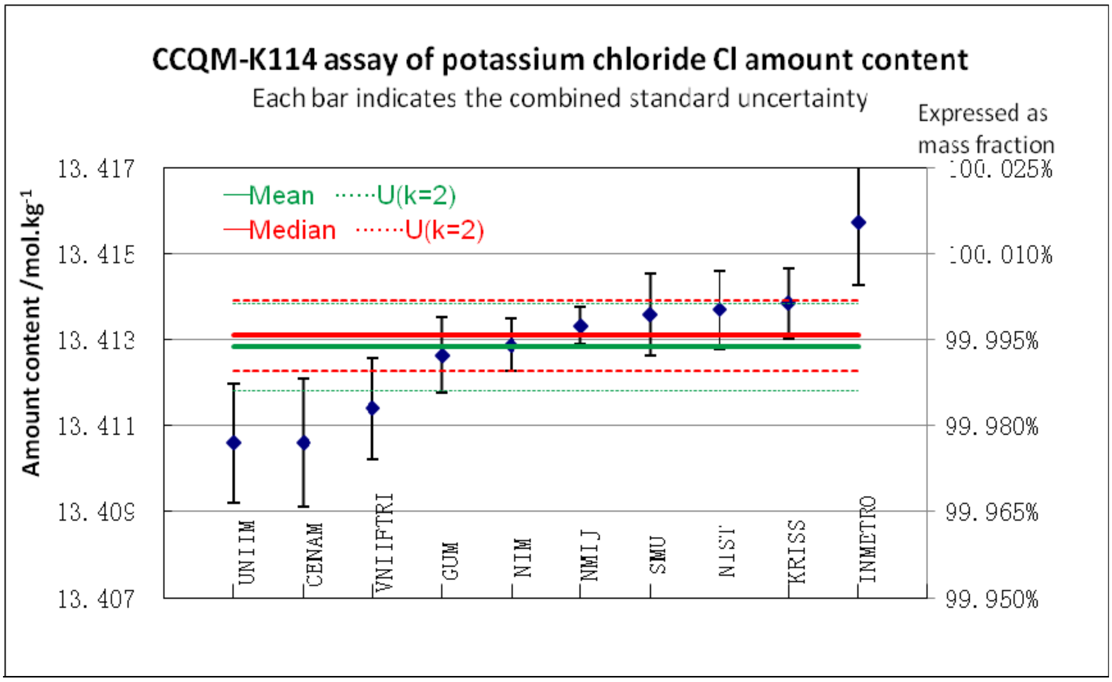
Institute	***Result /mol.kg^{-1}***	***n***	***SD /mol.kg^{-1}***	***u_c /mol.kg^{-1}***	***U /mol.kg^{-1}***	***k***
UNIIM	13.4106	9	0.00311	0.00139	0.0028	2
CENAM	13.4106	6	0.0012 5	0.00153	0.0031	2
VNIIFTRI	13.4114	6	0.00043	0.00117	0.0024	2
GUM	13.41265	6	0.00025	0.00087	0.0018	2
NIM	13.41288	13	0.00100	0.00061	0.0012	2
NMIJ	13.41333	10	0.00112	0.00044	0.0009	2
SMU	13.4136	5	0.00108	0.00095	0.0019	2
NIST	13.4137	12	0.00098	0.00091	0.0018	2
KRISS	13.41385	6	0.00044	0.00082	0.0017	2
INMETRO	13.41576	7	0.00344	0.00149	0.0030	2

Table 8 Possible estimators of KCRV

Potential KCRV	Amount content of Cl in KCl **(mol.kg^{-1})**	Mass fraction of Cl expressed as KCl **(kg.kg^{-1})**	Standard uncertainty **(mol.kg^{-1})**	Expanded uncertainty **(mol.kg^{-1})**
Arithmetic mean（$\bar{x}$）	13. 41284	0. 999941	0. 00051	0. 00102
Median* ***（KCRV）***	13. 41311	0. 999961	0. 00041	0. 00083
Variance weighted mean	13. 41310	0. 999960	0. 00032	0. 00072

Note：*It was agreed to use the median as the KCRV.

Figure 2 The results of Cl amount content



8.3 Formulas

Arithmetic mean

$$\bar{x} = \frac{\sum_{i=1}^{n} x_i}{n};$$

Expanded uncertainty of mean

$$\mathrm{U}_{KCRV(mean)} = 2 \times \sqrt{\frac{\sum_{i=1}^{n} (x_i - \bar{x})^2}{n \times (n-1)}}$$

Median

$median = average\left(x_{\frac{n}{2}} + x_{\frac{n}{2}+1}\right)$, n= even number; $median = x_{\frac{n+1}{2}}$, n=odd number

Expanded uncertainty of median [2]

$$\mathrm{U}_{KCRV(median)} = 2 \times \frac{1.858}{\sqrt{n-1}} \cdot median\left\{\left|x_i - KCRV\right|\right\}$$

Variance weighted mean [6]

$$\overline{\overline{x}} = \sum_{i=1}^{n} w_i \overline{x_i}\ , \quad w_i = \frac{\dfrac{1}{u^2\left(\overline{x_i}\right)}}{\sum_{i=1}^{n} \dfrac{1}{u^2\left(\overline{x_i}\right)}}$$

Expanded uncertainty of variance weighted mean

$$U = t_\alpha(n-1) \times \sqrt{\frac{\sum_{i=1}^{n} wi \cdot \left(\overline{x_i} - \overline{\overline{x}}\right)^2}{n-1}}$$

8.4 Impurity analysis

The impurity Br determined by all participants are summarized in Table 9, and other impurities detected by CENAM, GUM, UNIIM, NIM, NIST, NMIJ and VNIIFTRI are summarized in Table 10 and Table 11.

Table 9 The results of impurity Br determined

Institute	*Amount content / mol.kg^{-1}*	*Mass fraction /mg.kg^{-1}*	*Expanded uncertainty*	*Measurement method*
INMETRO	0.00036	29	48%	Ion Chromatography
NIST	0.00038	30	20%	XRF

UNIIM	0.00043	34	15%	ICP-MS
NIM	0.00043	34.	18%	ICP-MS
NMIJ	0.00046	37	7.8%	Ion Chromatography
KRISS	0.00046	37	139%	Ion Chromatography
SMU	0.00047	38	39%	Colorimetry
GUM	0.00047	38	11%	Ion Chromatography
CENAM	0.00047	38	51%	Ion Chromatography
VNIIFTRI*	0.00175	140	11%	ICP-MS
Average	0.00044	35	20%	/
RSD	9.8%	9.8%	15%	/

Note： * VNIIFTRI result was not used in the calculation of average value (see below).

Figure 3 The results of Impurity Br determined

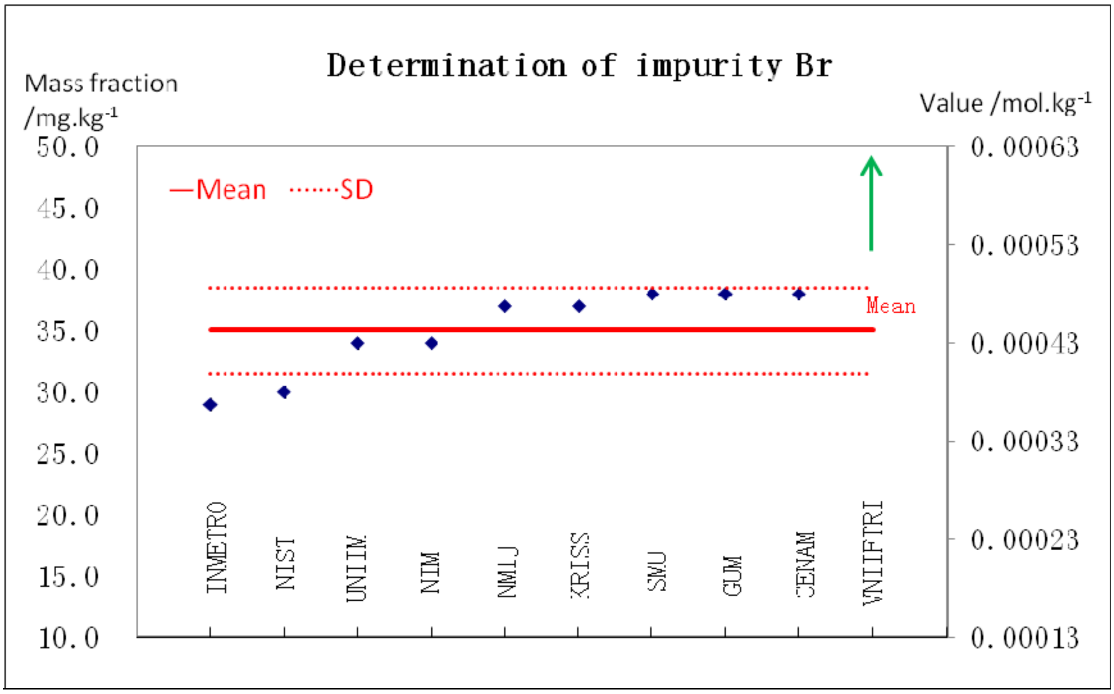


Table 10 Mass fraction of other impurities detected with relative uncertainties

Institute	NIM		*GUM*		CENAM		UNIIM		VNIIFTRI		NIST	
	value / mg.kg^{-1}	U_{rel}	*value /mg.kg^{-1}*	U_{rel}	*value / mg.kg^{-1}*	U_{rel}	*value / mg.kg^{-1}*	U_{rel}	*value / mg.kg^{-1}*	U_{rel}	*value / mg.kg^{-1}*	U_{rel}
method	ICP-MS		IC		ICP-SFMS		ICP-MS		ICP-MS		XRF	
Na	135.0	9%	83.6	18.6%	89	70%	149	9%	180	22%	/	/
Rb	20.3	14%	/	/	22.5	14%	31	8%	24	8%	/	/
Mg	/	/	24.4	42%	/	/	/	/	/	/	/	/
Ca	/	/	9.6	70.8%	/	/	/	/	/	/	/	/
Pb	/	/	/	/	/	/	0.74	21%	/	/	/	/
NO_3	/	/	2.8	19.1%	/	/	/	/	/	/	/	/
SO_4	/	/	1.6	49%	/	/	/	/	/	/	/	/
Sr	/	/	/	/	/	/	/	/	/	/	/	/
Be	/	/	/	/	/	/	/	/	/	/	/	/
I	/	/	/	/	/	/	/	/	/	/	/	/
S	/	/	/	/	/	/	/	/	1830	60%	10	40%
Mn	/	/	/	/	/	/	1.8	6%	/	/	/	/
Fe	/	/	/	/	/	/	7.4	22%	/	/	/	/
In	/	/	/	/	/	/	0.045	19%	/	/	/	/
Sn	/	/	/	/	/	/	0.055	27%	/	/	/	/
Ba	/	/	/	/	/	/	0.46	9%	0.5	/	/	/
Tl	/	/	/	/	/	/	0.0035	13%	/	/	/	/
Zn	/	/	/	/	/	/	/	/	26	4%	/	/

Table 11 Mass fraction of other impurities checked by semi-quantitative measurement method (in mg.kg^{-1})

Institutes(method) *Impurities*	*NIM (ICP-MS)*	*UNIIM (ICP-MS)*	VNIIFTRI *(ICP-MS)*	CENAM *(ICP-MS)*	*NMIJ (IC)*
Li	0.0079	<0.01	/	/	/
B	3.60	<0.05	/	/	/
Mg	<3.0E-3	<0.1	/	<32.4	/

Al	0.16	<0.01	/	/	/
Si	11	<3	28	/	/
P	6.2	<50	/	/	/
Ca	<0.61	<0.5	/	<762	/
Sc	0.025	<0.1	/	/	/
Ti	0.21	<0.1	/	/	/
V	0.41	<0.05	/	/	/
Cr	1.9	<0.5	/	/	/
Mn	0.95	/	/	/	/
Fe	1.3	/	/	/	/
Co	0.0047	<0.01	/	/	/
Ni	0.016	<0.1	/	/	/
Cu	0.026	<0.1	/	/	/
Zn	1.5	<1	/	/	/
Ga	0.041	<0.05	/	/	/
Ge	0.1	<0.2	/	/	/
As	0.28	<2	/	/	/
Se	0.15	<0.2	/	/	/
Sr	<2.2E-3	<0.01	/	<1.84	/
Y	<1.7E-3	<0.01	/	/	/
Zr	0.089	<0.01	/	/	/
Nb	<2.1E-3	<0.01	/	/	/
Mo	0.24	<0.1	/	/	/
Ru	0.024	/	/	/	/
Rh	<2.0E-3	/	/	/	/
Pd	<9.2E-3	<0.1	/	/	/
Ag	<4.6E-3	<0.01	/	/	/
Cd	<0.020	<0.001	/	/	/
In	0.0097	/	/	/	/
Sn	<7.8E-3	/	/	/	/
Sb	0.0066	<0.01	/	/	/
I	0.054	/	/	/	<2
Pb	0.027	/	/	<6.1	/
Te	<0.11	<0.1	/	/	/
Cs	<1.9E-3	<0.01	/	/	/
La	<1.6E-3	<0.01	/	/	/
Ce	<1.7E-3	<0.02	/	/	/
Hg	/	<0.05	/	/	/
Bi	<1.9E-3	<0.01	/	/	/

Note: *Little iodine was not detected in the sample, so we considered the iodine had no effect on the results that means the sum of halides included Cl and Br only.*

8.5 Discussion

Compared with original CCQM-K48 (KCRV uncertainty: 0.00024 mol/kg), the KCRV uncertainty obtained in this comparison (0.00083 mol/kg) is somewhat larger, but considering the methodology (coulometric analysis on KCl), participants' expanded uncertainty ranging from 0.00088 mol/kg to 0.0031 mol/kg and participation of four new comers in the CCQM-K114, the KCRV 13.41311mol/kg with expanded uncertainty 0.00084 mol/kg is satisfactory. NIM, SMU and KRISS obtained good results in both K48 and K48.2014.

GUM, VNIIFTRI, CENAM and UNIIM are newcomers for the KC., GUM result is good and with smallest standard deviation; VNIIFTRI had submitted good coulometric result, but the Br impurity value determined by ICP-MS is too large (140mg/kg compared with the average 35mg/kg), influencing the final result; CENAM and UNIIM reported somewhat lower results with larger uncertainties.

Each relative degree of equivalence is within 0.02%, and overlaps within the expanded uncertainty of the degree of equivalence.

Based on the experiences of original CCQM-K48 and the results of this K114, the coordinating laboratory NIM highlights the potential possibilities for the bias and uncertainty on assay of KCl by coulometry as follows(for discussion):

1. **Sample preparation before weighing.** Even most participating NMIs had dried sample before weighing according to the protocol (***dried at 500 ℃ for 6h***), many of the NMIs also considered the mass weighing as one of main uncertainty source (sometimes it was considered as type A uncertainty). The calibrations of balance and weights are certainly important.

2. **End-point calculation.** Most of the participating NMIs regarded the uncertainty of End-point evaluation is one of main uncertainty source （some time it was considered as type A uncertainty）. Ag^+ or Cl^- diffusing into the SiO_2 gel plug would also cause biased results, all of the participated NMIs noticed diffusion problem and performed rinsing the cell carefully during the end-point recording process. Dr. Mariassy strongly adviced the number of points used for regression should be large enough (about 10) for robust end-point calculation.

3. **Occluded Ag^+ in AgCl and Cl^- adsorption on AgCl.** The occluded Ag+ in the precipitated AgCl may be the reason for high results, because the loss of Ag+ will prolong the time for electrolysis. On the other way Cl- co-precipitation/adsorption on AgCl may cause low results. NIST and SMU regarded the effects of occlude Ag+ in AgCl and/or adsorption on AgCl are the main uncertainty sources in their reports; for avoiding this type of effects NIM, NMIJ, CENAM and UNIIM performed the process that dissolved the solid KCl sample by pure water and then

added the solution into the anode compartment instead of adding the solid KCl sample into the anode cell directly at one time, the results from NMIJ and NIM were satisfactory with smallest uncertainty. If a a KCl solution is analyzed which had been prepared from the solid sample, there will be more uncertainties from solution preparation and weighing the mass of solution, that may be the main uncertainties sources as CENAM had considered in its report.

4. **Purity of Ag anode.** Metallic impurities in Ag anode and AgCl clinging on Ag anode may effect the efficiency of electric current to be less than 100%, causing a positive bias.
5. **Coulometric system calibration.** Almost all of the participated NMIs considered the uncertainties source from time, voltage, resistance and stability of current etc even they are not very big. The coulometric instruments must be calibrated before this determination to avoid the system errors
6. **Perform in dark place.** This reaction must be performed in the dark, because the light can cause the loss of Ag+ by reduction to Ag and leads to a positive bias.

9. EQUIVALENCE STATEMENTS

The equivalence statements have been calculated according to the BIPM guidelines. The degree of equivalence (and its uncertainty) between a NMI result and the KCRV is calculated according to the following equations:

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

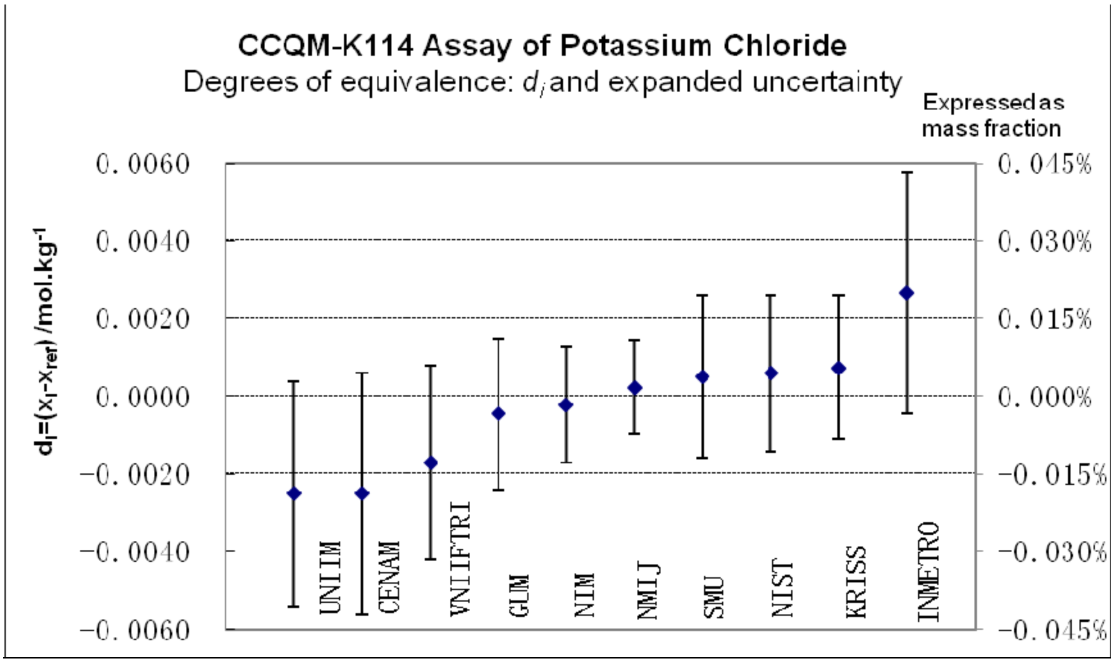
Where d$_i$ is the degree of equivalence between the NMI result x_i and the KCRV x_{ref}, and $U(d_i)$ is the expanded uncertainty *(k = 2)* of the d_i calculated by combining the standard uncertainty $u(d_i)$ of the NMI result x_i and the standard uncertainty $u(x_{ref})$ of the KCRV x_{ref}. The equivalence statements for CCQM-K114 are given in Table 12.

Table 12 Equivalence Statements of Cl amount content for CCQM-K114

Participant	Reported Value（x_i）/mol/kg	Standard uncertainty（$u(x_i)$）/mol/kg	d_i	$U(d_i)$
UNIIM	13.4106	0.00139	-0.0025	0.0029
CENAM	13.4106	0.00150	-0.0025	0.0032
VNIIFTRI	13.4114	0.00117	-0.0017	0.0025
GUM	13.4126	0.00087	-0.0005	0.0020
NIM	13.4129	0.00061	-0.0002	0.0015
NMIJ	13.4133	0.00044	0.0002	0.0013
SMU	13.4136	0.00095	0.0005	0.0021

NIST	13.4137	0.00091	0.0006	0.0020
KRISS	13.4138	0.00082	0.0007	0.0019
INMETRO	13.4158	0.00149	0.0026	0.0031

Figure 4 Degrees of equivalence d_i and expanded uncertainty U (d_i) (k=2)



10. SCOPE OF THE COMPARISON (How far the light shines)

The comparison tested the capabilities and methods used for assay of high purity materials. For coulometric methods, good results will indicate good performance in assaying chloride content in solid pure chlorides and chloride concentration in concentrated solutions.

11. CONCLUSIONS

The median of all results has been proposed for the KCRV (amount content of chloride in KCl 13.41311 mol/kg and associated expanded uncertainty 0.00083 mol/kg), and was agreed as the key comparison reference value at the IAWG and EAWG joint meeting in April 2015. In general very good agreement of the results between the participating laboratories was observed, and all of the results overlap within the expanded uncertainty. Moreover the results for bromide impurity are consistent very well with one exception. Some NMIs improved their coulometric method on KCl analysis, and each participant MNI's capability has been confirmed by this KC. The suitability of coulometry for assay of high purity materials was again demonstrated.

12.ACKNOWLEDGEMENTS

NIM gratefully acknowledges the helps and supports from Dr. Michal Máriássy - chairman of EAWG/CCQM, Dr. Mike Sargent - chairman of IAWG/CCQM and Dr. Kenneth W. Pratt from NIST, and thanks all of the analysts from the participant institutes for their contributions as well as the contact persons

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Appendix A – Technical Protocol

CCQM-K114 Assay of potassium chloride

Technical Protocol

Introduction

Potassium chloride is an often used reference material in precipitation titration methods, and it is also research foundation for pH, conductivity and mono-element standard solution. Pure materials are very important for traceability in chemical metrology, and pure material studies and comparisons are important activities in Electrochemical Analysis Working Group and Inorganic Analysis Working Group at all times. The EAWG with IAWG jointly organized a pilot study CCQM-P7 (CCQM 8) for determining the purity of KCl, NaCl and $K_2Cr_2O_7$ in 1998, and a key comparison CCQM-K48 for assay of potassium chloride in 2007. Seven NMIs participated in this key comparison, all participants used coulometry (except NMIJ which used gravimetry), and very good agreement between most of the participating laboratories for measurement of potassium chloride was observed. The median of all results was agreed as for the KCRV (amount content of chloride in KCl 13.41229 mol/kg, associated expanded uncertainty 0.00024 mol/kg). The suitability of coulometry for assay of high purity materials was again demonstrated.

According to the EAWG strategy, “Periodically, it is necessary to repeat a sub-set of comparisons to support CMC claims for all institutes in the relevant ranges with timely experimental data. The repetition of measurements should be sufficiently frequent to enable NMIs with less well-established or newer facilities to benchmark their capabilities.”, a new key comparison for assay of potassium chloride was proposed again and discussed in the EAWG with IAWG joint meeting in April 2013, and it had been agreed by CCQM to proceed to a new key comparison which is numbered as CCQM-K114, NIM (National Institute of Metrology P.R.China,) is acting as the coordinating laboratory.

Scope:

The comparison will test the capabilities and methods used for assay of high purity materials and persistently underpin the claimed calibration and measurement capabilities of the institutes.

Time schedule

Deadline for registration: 10 May 2014
Dispatch of the samples: the end of May 2014
Deadline for result report: 31 December 2014
Discussing results: IA&EA meeting April, 2015
Draft A report: the end of June 2015

Samples

Sample preparation:

The source of the sample is from a 20 kg batch of commercial pure potassium chloride material. After being homogenised, a 500 g portion was selected from the middle fraction of the batch, and was homogenised again in a large bottle. This homogenised portion was then transferred to 13 glass bottles closed with silicone lined plastic caps for the comparison. The impurities were determined by ICP-MS. The assay is in the range of 99.9 % to 100 % of the theoretical value.

Homogeneity test:

Twelve bottles were randomly selected from the set of 13 bottles. Two samples were sampled independently from these seven bottles. The content of chloride was determined by coulometry to check the homogeneity of the samples. No statistically significant heterogeneity was found based on F test; the RSD is 0.0033 % with each independent result and the RSD is 0.0012% with the average from each bottle; the sample is found to be adequate for the key comparison.
The sample mass used for homogeneity tests at NIM was about 150 mg. Please pay attention that you do not use less than 150 mg in your analyses for the key comparison.

Distribution:

Each participant will receive one numbered bottle containing about 15g of material. The sample number will be the same as the laboratory number. Shipment to all participants will be performed at the same time. The bottles are shipped in a cardboard box by courier. The contents will be marked “**potassium chloride**” 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 NIM contact person by e-mail, fax or mail. If there is any damage, please contact us immediately, and NIM will mail out another bottle.

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 500 °C for 6 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 density of the potassium chloride sample is 1.984 g/cm^3.
The quantity of sample to be used in the assay is not less than 150 mg.

Measurand and measurement method:

Potassium chloride assay based on chloride content. The results will be reported as amount content of chloride in KCl [mol/kg] and/or mass fraction of chloride expressed as KCl [kg/kg]. The mass fraction of chloride expressed as KCl in the sample is in the range 0.999 to 1.000 (99.9 % to 100 %). Any method or combination of methods can be used, but the coulometric method is recommended for this comparison.

Reporting

The report should be sent to the coordinating laboratory before 31 December 2014, 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 will be reported as amount content of chloride in KCl [mol/kg] and/or mass fraction of chloride expressed as KCl [kg/kg], to be accompanied by a full uncertainty budget.

   For example:

If the chloride in KCl was determined by coulometry, the amount of Cl (after correction for Br and/or I) divided by the sample mass (corrected for air buoyancy) is the amount content of chloride [mol/kg] in the KCl sample. Such as: 13.4XXX mol/kg. In another way, the chloride content can also be expressed as mass fraction [kg/kg] of KCl, where the reported KCl mass fraction is based on the content of chloride in the sample (i.e."KCl" is the assumed form of the Cl present). Such as: 0.99XXX kg/kg. However, this alternate way includes a contribution to the uncertainty from the uncertainties of the molar masses of Cl and K.

2. Information on impurities determined (value, uncertainty, method), the correction included in the reported chloride content - value and uncertainty of this correction.
3. Participants using coulometry should also report, as an information value, the coulometric result uncorrected for impurities.
4. Participants using indirect assay (“100 % - trace components” approach) should also report, as an information value, the sum of the mass fractions of K and Cl.
5. A detailed description of the measurement procedure is to be given (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), and the equipment used.
6. The complete measurement equation has to be given, as well as the values of the constants (suggested Faraday constant: 96485.3365(21) 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.
7. At least six determinations should be performed. Please state all the individual results, not only the final mean value. The uncertainty budget must include instrumental sources of uncertainty (mass, time, voltage, volume ...) as well as chemical ones (endpoint estimation, equilibria, impurities, purity of calibration standards, ...) plus the relevant uncertainties for any trace element corrections. 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. The reported uncertainty should be expressed as a combined standard uncertainty and as an expanded uncertainty calculated using a coverage factor, *k*, of 2
8. In order to facilitate comparisons of your measured masses (for assay measurements), please also provide either (1) the air density used for each buoyancy correction, or (2) the air temperature, humidity and pressure in your laboratory at the time of each mass measurement.
9. In order to further evaluate the effects of assay measurements, please report the details of the techniques used in the measurement procedure (prevent lighted, the

means of adding the sample, stirring...), that a separate text file or official report may be used.

10. If the results are reported as mass fraction, state also the molar mass of KCl you used and the uncertainty in this molar mass.

Reference value

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

Participation

Participation is open to all institutes eligible for a key comparison in this field.

The Draft A Report based on the reported results will be prepared and sent to the participants for comments and will be discussed on the next joint meeting of the EAWG and IAWG.

Coordinating laboratory and contact persons

Ma Liandi and Wu Bing

National Institute of Metrology (NIM)

No. 18, Bei San Huan Dong Lu, Chaoyang District,

Beijing, 100013,

P.R.China

Tel.: +86 10 64223987 Fax: +86 10 64225471

E-mail: mald@nim.ac.cn; wubing@nim.ac.cn