National Institute of Metrology P.R.China

Report of the CCQM-K34.2016

Assay of potassium hydrogen phthalate

Final Report

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1. ABSTRACT

The CCQM-K34.2016 key comparison for determination of the purity of potassium hydrogen phthalate was organized jointly by the inorganic analysis and electrochemical analysis working groups of CCQM to repeat CCQM-K34 for supporting CMC claims of participating metrology institutes in assaying the amount content of monoprotic weak acid. National Institute of Metrology P.R.China (NIM) acted as the coordinating laboratory of this comparison. Twelve NMIs participated in this key comparison. With the exception of one laboratory that used NaOH-titration, all participants used coulometry. In general good overlap of results was observed, the suitability of coulometry for assay of high purity materials was demonstrated again, and some possible technical problems were highlighted.

2. INTRODUTION

Assays of acids are made almost exclusively by titration methods. Potassium hydrogen phthalate (KHP) is the most used reference material for these measurements. 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 CCQM-K34 key comparison was organised jointly by the inorganic and electrochemistry working groups of CCQM as a follow-up to pilot study CCQM-P36 to test the abilities of the metrology institutes to measure the amount content of acid in solid weak acids. Slovak Institute of Metrology acted as the coordinating laboratory, in 2004. 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 repeat key comparison for assay of potassium hydrogen phthalate was proposed and discussed in the EAWG with IAWG joint meeting in April 2016, and it had been approved by CCQM to proceed to a key comparison which is numbered as CCQM-K34.2016, NIM (National Institute of Metrology P.R.China) is acting as the coordinating laboratory.

Scope:
The comparison tested the capabilities and methods used for assay of high purity materials and persistently underpin the claimed calibration and measurement capabilities of the institutes.
For coulometry or titrimetry, good results will indicate good performance in assaying the amount content of solid weak acid.

3. LIST OF PARTICIPANTS

There were 12 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
INM National Metrology Institute of Colombia	Colombia	Ronald Cristancho Amaya
INMETRO Instituto Nacional de Metrologia, Qualidade e Tecnologia	Brazil	Paulo Paschoal Borges
INTI Instituto Nacional de Tecnología Industrial	Argentina	Nadia Hatamleh, Mabel Puelles
KRISS Korea Research Institute of Standards and Science	Korea	Euijin Hwang
NIM National Institute of Metrology	China	Ma Liandi, Wu Bing
NIST National Institute of Standards and Technology	USA	Jason F. Waters
NMIJ National Metrology Institute of Japan	Japan	Toshiaki Asakai
SMU Slovak Institute of Metrology	Slovakia	Michal Mariassy
UNIIM Ural Scientific Research Institute for Metrology	Russian Federation	Alena Sobina
VNIIFTRI Russian Metrological Institute of Technical Physics and Radio Engineering	Russian	Sergey Prokunin, Vladimir Dobrovolskiy

4. TIME SCHEDULE

Call participations: March 2017
Deadline for registration: 10 May 2017
Dispatch of the samples: In the beginning of June 2017
Deadline for result report: 15 September 2017
Discussing results: September ~ December 2017
Draft A report: IAWG&EAWG meeting April, 2018
Draft B report: September 2018

5. SAMPLES

The source of the sample is from a 25 kg batch of commercial pure potassium hydrogen phthalate 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 15 glass bottles closed with silicone lined plastic caps for the comparison. The impurities were determined by ICP-MS. Ten bottles were tested for homogeneity by analysing two independent samples from each bottle by coulometry. No statistically significant heterogeneity was found based on F test; between bottles homogeneity was found to be 0.0031% RSD and within bottle homogeneity 0.0013%; the sample is found to be adequate for the key comparison. The sample mass used for homogeneity tests at NIM was about 500 mg.

The samples were sent to the participants by DHL on the 1st of June 2017 (shipment on 9th of June 2017 from Beijing). All samples arrived to their destination without damage within two weeks (except CENAM, where a new sample was sent on July 6). The dispatch dates and receipt dates are given in Table 2.

The deadline for reporting results was set to 15 September 2017 in order to prepare a presentation for discussion at the CCQM WG meeting in September 2017. All participants reported their results in time.

Table 2 Sample sent dates, receipt dates and report dates

Institute	Sample No.	Sample dispatch date	Sample receipt date	Date report sent
CENAM	1, 13	1 June 2017, 6 July 2017	29 June 2017, 2 August 2017	18 September 2017
GUM	02	1 June 2017	19 June 2017	15 September 2017
INM	03	1 June 2017	5 July 2017	18 September 2017
INMETRO	04	1 June 2017	23 June 2017	15 September 2017
INTI	05	1 June 2017	30 June 2017	15 September 2017

KRISS	06	1 June 2017	21 June 2017	31 August 2017
NIM	07	-	-	31 August 2017
NIST	08	1 June 2017	19 June 2017	15 September 2017
NMIJ	09	1 June 2017	19 June 2017	1 September 2017
SMU	10	1 June 2017	21 June 2017	12 September 2017
UNIIM	11	1 June 2017	19 June 2017	16 September 2017
VNIIFTRI	12	1 June 2017	30 June 2017	20 September 2017

6. INSTRUCTIONS TO PARTICIPANTS

The instructions sent to the participants by e-mail consist of technical protocol, registration form, return receipt form and results report template.

The technical protocol (appendix A) contained background information, timing of the comparison. Information on sample homogeneity and sample preparation for measurements was given. The participants were free to choose the measurement procedure, but the coulometric method was recommended for this comparison.

Participants were requested to express the results as amount content of potassium hydrogen phthalate [mol/kg] and to provide uncertainty evaluation according to JCGM 100:2008[1].

The results report template 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 except INTI (which used NaOH titrimetry) 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, Table 4 and the main source of B type uncertainty in Table 5.

Table 3 Measurement methods

Institute	*Approx. sample mass/g*	*Sample dried at 110 ℃ for 2h*	*Corrected for buoyancy*	*Measurement method*	*Sampling*
CENAM	0.25~0.5 Solutions of KHP	yes	yes	Coulometry	solution
GUM	0.5~0.54	yes	yes	Coulometry	solid
INM	0.5	yes	yes	Coulometry (Potentiostat-Galvanostat Metrohm Autolab)	solid
INMETRO	0.5	yes	yes	Coulometry	solid
INTI	0.5~0.6	yes	yes	Titrametric	solid
KRISS	0.5~0.54	yes	yes	Coulometry	solid
NIM	0.5	yes	yes	Coulometry	solid
NIST	0.5~0.59	yes	yes	Coulometry	solid
NMIJ	0.45~0.52	yes	yes	Coulometry	solid
SMU	0.5	yes	yes	Coulometry	solid
UNIIM	0.5	yes	yes	Coulometry	solid
VNIIFTRI	0.095 Solutions of KHP	yes	yes	Coulometry	solution

Table 4 Details on measurement methods

Institute	*Details of coulometric procedures*				*EP estimation*	*Initial titration*	*Major unc. sources*	*Contribution*
	Cell type	*IC rinse*	*Cathodes cell (solution volume) /mL*	*Main current /mA*				
CENAM	vertical, 1 intermediate chamber (IC)	Yes	200	100	nonlinear regression	Yes	u_A , mass of salt weigthed to prepare solution, estimated of CO_2, Final titration voltage	97.1%

GUM	vertical,1 IC	Yes	300	200	nonlinear regression	Yes	u_A , current efficiency, CO_2 effect, impurities	93.5%
INM	vertical,1 IC	Yes	(250)	75	?	No	u_A	99.99%
INMETRO	vertical, 1 IC	Yes	250	200	nonlinear regression.	Yes	Current, Weighing, current efficiency, u_A	95.3%
INTI	/	/	/	/	/	/	NaOH mass for sample determination, Potassium Phtalate molar mass, NaOH mass for standardization	94.3%
KRISS	horizontal, 2 IC	Yes	160 (110)	101.8	3rd order polynomial regr.	Yes	u_A, end point estimation for the final titration, end point estimation for the pretitration	99.8%
NIM	horizontal, 2 IC	Yes	200 (160)	101.8	3rd order polynomial regr.	Yes	u_A, end-point, the influence of air and gas impurities	95.2%
NIST	horizontal, 2 IC	Yes	180 (100)	101.8	3rd order polynomial regr.	Yes	u_A, R_{std}, m_{sample} determination, CO_2 interference, E_{std}	97.6%
NMIJ	horizontal,2 IC	Yes	120	100	3rd order polynomial regr.	Yes	u_A, balance, Influence of air, Pulse efficiency	98.1%
SMU	vertical, 1 IC	Yes	400 （250）	200	nonlinear regression	Yes	u_A, gas impurities, Diffusion, voltage uncertainty	85.6%
UNIIM	vertical, 1 IC	Yes	200	100	3rd order polynomial regr.	Yes	u_A, m, Diffusion	99.7%
VNIIFTRI	horizontal,2 IC	Yes	250 (150)	49.7	3rd order polynomial regr.	Yes	u_A, t_1, I_2, t_4	98.2%

Table 5 The main source of B type uncertainty

Institute	***The main source of uncertainty,*** mol/kg				***Contribution***
NIST	R_{std}: 3E-05	m_{sample} determination: 3E-05	CO_2 interference: 2E-05	E_{std}: 1E-05	34.4%
VNIIFTRI	t_1- time corresponding to the end point initial titration: 6E-05	I_2- value of direct current during first main titration: 4E-05	t_4- time corresponding to the end point of final titration: 6E-05		81.9%
NMIJ	Balance: 2.08 E-04	Influence of air: 1.23 E-04	Pulse efficiency: 5.87 E-05		91.7%
INTI	NaOH mass for sample determination: 9.51E-04	NaOH mass for standarization: 9.51E-04	Potassium Phtalate molar mass: 4.80 E-04		94.3%
GUM	Current efficiency: 5.00E-05	CO_2 effect, impurities: 5.00E-05	EP's determination impurities: 2.94E-05	Weighing: 3.51E-05	22.1%
KRISS	End point estimation for the final titration: 1.2E-04	End point estimation for the pretitration: 5.7E-05			74.5%
INMETRO	Weighing: 4E-05	Current: 8E-05	End-point det'n: 2E-05	Current efficiency: 4E-05	75.9%
NIM	the end-point: 1E-04	the influence of air and gas impurities: 5E-05			74.3%
UNIIM	m: 1.59E-04	Diffusion: 1.73E-04			89.1%
SMU	gas impurities: 1E-04	Diffusion: 6E-05	voltage uncertainty: 5E-05		77.8%
CENAM	Mass of salt weigthed to prepare solution:1E-04	Mass fraction estimated of carbon dioxide: 8E-05	Final titration voltage: 9E-05	Main titration voltage: 4E-05	24.8%
INM	Mass main-titration: 4.1E-04	Resistance: 2.2E-05	Potential main-titration: 2.3E-05		0.003%

8. RESULTS AND DISCUSSION

8.1 Amount content of potassium hydrogen phthalate

The reported values and uncertainties of all final results are summarized in Table 7 . Several approaches to estimate the key comparison reference value (KCRV) were considered. Arithmetic mean (all participants), Arithmetic mean (excluding INM), median and variance weighted mean for possible KCRV in Table 8. The same results are displayed graphically in Figure 1.

Table 7 Results (amount content of KHP)

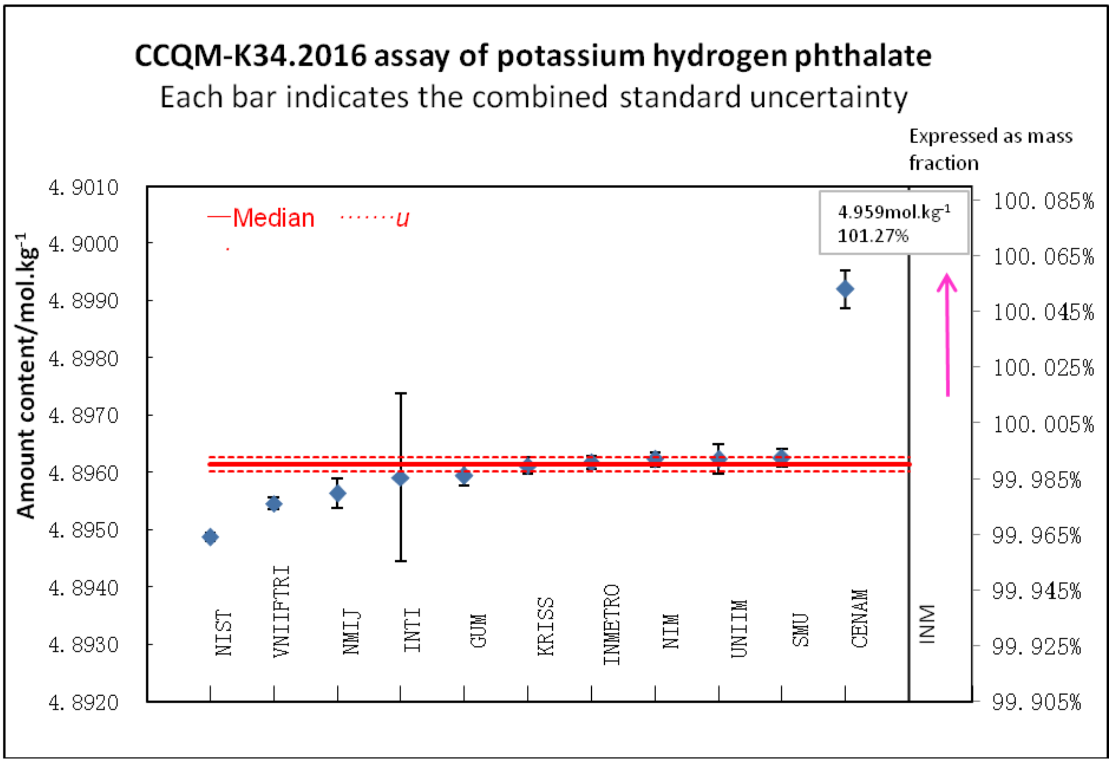
Institute	***Approx. Sample mass /g***	***Result*** $/mol.kg^{-1}$	***n***	***SD*** $/mol.kg^{-1}$	u_c $/mol.kg^{-1}$	***U*** $/mol.kg^{-1}$	***k***
NIST	0.5~0.59	4.89487	6	0.000153	0.000078	0.00016	2
VNIIFTRI	0.095 Solutions of KHP	4.89546	6	0.000072	0.000104	0.00021	2
NMIJ	0.45~0.52	4.89563	8	0.000185	0.000260	0.00052	2
INTI	0.5~0.6	4.8959	10	0.000924	0.001471	0.0030	2
GUM	0.5~0.54	4.89594	6	0.000386	0.000179	0.00036	2
KRISS	0.5~0.54	4.89612	6	0.000186	0.000151	0.00030	2
INMETRO	0.5	4.89617	7	0.000138	0.000118	0.00024	2
NIM	0.5	4.89623	12	0.000200	0.000127	0.00026	2
UNIIM	0.5	4.89624	7	0.000215	0.000249	0.00050	2
SMU	0.5	4.89625	8	0.000122	0.000154	0.00031	2
CENAM	0.25~0.5 Solutions of KHP	4.89920	14	0.001079	0.000335	0.00067	2
INM	0.5	4.959	8	0.078197	0.078199	0.157	2

Table 8 Possible estimators of KCRV

Potential KCRV	Amount content **(mol.kg^{-1})**	Mass fraction of H expressed as KHP (kg.kg^{-1})	Standard uncertainty **(mol.kg^{-1})**	Expanded uncertainty **(mol.kg^{-1})**
Arithmetic mean （$\bar{x}$）	4. 9014	1. 00097	0. 00523	0. 0105
Arithmetic mean (excluding INM)	4. 89618	0. 999905	0. 000327	0. 00066
Median*　(KCRV）	4. 89615	0. 999897	0. 000121	0. 00025
Variance weighted mean	4. 89569	0. 999804	0. 000218	0. 00048

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

Figure 1 The results of potassium hydrogen phthalate amount content



8.2 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 [5]

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

Expanded uncertainty of variance weighted mean

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

8.3 Impurity analysis

The impurities were analysed by NIM, GUM and UNIIM. Their results were summarized in Table 9.

Table 9 Mass fraction of impurities were checked by semi-quantitative measurement methods (in mg.kg^{-1})

Institutes(method) Impurities	***NIM (ICP-MS)***	***GUM (IC)***	***UNIIM (ICP-MS)***
Li	<0.23		<0.01
Be	<0.92		<0.01
B	<1.00		<0.05
Na	36	28.3	10.4
Mg	2.4	2.9	<0.05
Al	<0.14		<0.05
Si	<0.30		17.8
P	5.7		<5
Ca	35	7.4	4.2
Sc	<0.078		<0.5
Ti	2.8		<0.5
V	<0.085		<0.05
Cr	<0.09		0.10
Mn	0.66		0.19
Fe	6.1		<0.5
Co	<0.079		<0.01
Ni	<0.33		<0.01
Cu	<0.12		<0.1

Zn	2.9		<0.1
Ga	<0.067		<0.05
Ge	<0.22		<0.05
As	<0.37		<0.05
Se	<2.7		<0.05
Br	<2.22		/
Rb	8.4		/
Sr	0.16		<0.01
Y	<0.019		<0.01
Zr	<0.004		<0.01
Nb	<0.024		<0.01
Mo	0.17		<0.01
Ru	<0.13		<0.01
Rh	<0.024		<0.01
Pd	<0.11		<0.01
Ag	<0.059		<0.1
Cd	<0.26		<0.01
In	<0.025		<0.01
Sn	<0.1		<0.01
Sb	<0.089		<0.01
Te	<1.5		<0.01
I	<0.17		<0.1
Cs	<0.028		<0.01
Ba	<0.23		<0.01
La	<0.025		<0.01
Ce	<0.027		<0.01
Pr	<0.022		<0.01
Nd	<0.12		<0.01
Sm	<0.14		<0.01
Eu	<0.04		<0.01
Gd	<0.12		<0.01
Tb	<0.02		<0.01
Dy	<0.084		<0.01
Ho	<0.021		<0.01
Er	<0.062		<0.01
Tm	<0.02		<0.01
Yb	<0.09		<0.01
Lu	<0.02		<0.01
Hf	<0.073		<0.01
Ta	<0.022		<0.01

W	<0.086		<0.01
Re	<0.06		<0.01
Os	<0.12		<0.01
Ir	<0.044		<0.01
Pt	<0.11		<0.05
Au	<0.073		<0.05
Hg	<0.34		<0.05
Tl	<0.034		<0.01
Pb	<0.048		<0.01
Bi	<0.03		<0.01
Th	<0.026		<0.01
U	<0.026		<0.01

8.4 Discussion

The proposed median and its associate uncertainty (MAD) were agreed as the KCRV at both of the IAWG meeting in September 2017 and IAWG&EAWG joint meeting in April 2018. The KCRU 0.00025 mol/kg compares well with the original CCQM-K34 (KCRU: 0.00032 mol/kg).

CENAM, GUM, INM, INMETRO, INTI and VNIIFTRI are new comers for this key comparison they had not participated the original CCQM-K34, from the methodology and the facility used more or less problems had been found from most of them.

INTI had submitted satisfactory result by NaOH titration in time, but with larger uncertainties compare with results obtained with coulometry. INM reported a result with higher bias and larger uncertainties, and the 99.99% of uncertainty was from measurement (and RSD was used as uA), from their report and e-mail discussion the problem has been found that KHP was determined by “Potentiostat-Galvanostat Metrohm Autolab” instrument that it is a commercial instrument without good enough accuracy and precision. CNEAM and VNIIFTRI results did not overlap with the proposed KCRV, the potential problem is that they had taken the solid sample into solution and then weighed the solution perhaps introducing a large source of uncertainty that had not been fully calculated.

Based on the experience gained in the original CCQM-K34 and the results of this K34.2016, the coordinating laboratory NIM lists the potential possibilities for the bias and uncertainty on assay of potassium hydrogen phthalate as follows:

1. **Sample preparation before weighing.** Even most participated NMIs had dried sample before weighing according to the protocol (***dried at 110℃ for 2h*** without crushing or drying of the sample), most of the NMIs also considered the mass weighing as one of main uncertainty source （some-times it was considered as type A uncertainty）. The calibrations of balance and weights are certainly necessary.
2. **End-point calculation.** More than half of the participated NMIs regarded the uncertainty of End-point evaluation as one of the main uncertainty sources (some

times it was considered as type A uncertainty）. With at least 5 points after the largest pX change recorded, calculation of the end-point is more robust.

3. **The influence of air and gas impurities.** In the determination of weak acids, the influence of air（CO_2 and other acidic gases）can-not be ignored. In addition the impurities of protective gas maybe affect the measurement results.
4. **Current efficiency.** Although the current efficiency is almost 100% in the coulometric titration of inorganic acids, some participants have identified the influence of current efficiency as one of the main sources of uncertainty in the assessment.
5. **Coulometric system calibration.** Almost all of the participated NMIs noticed the uncertainties source from time, voltage, resistance and stability of current etc, even if they are not very large. The coulometric instruments should be calibrated before this determination to avoid system errors.

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:

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

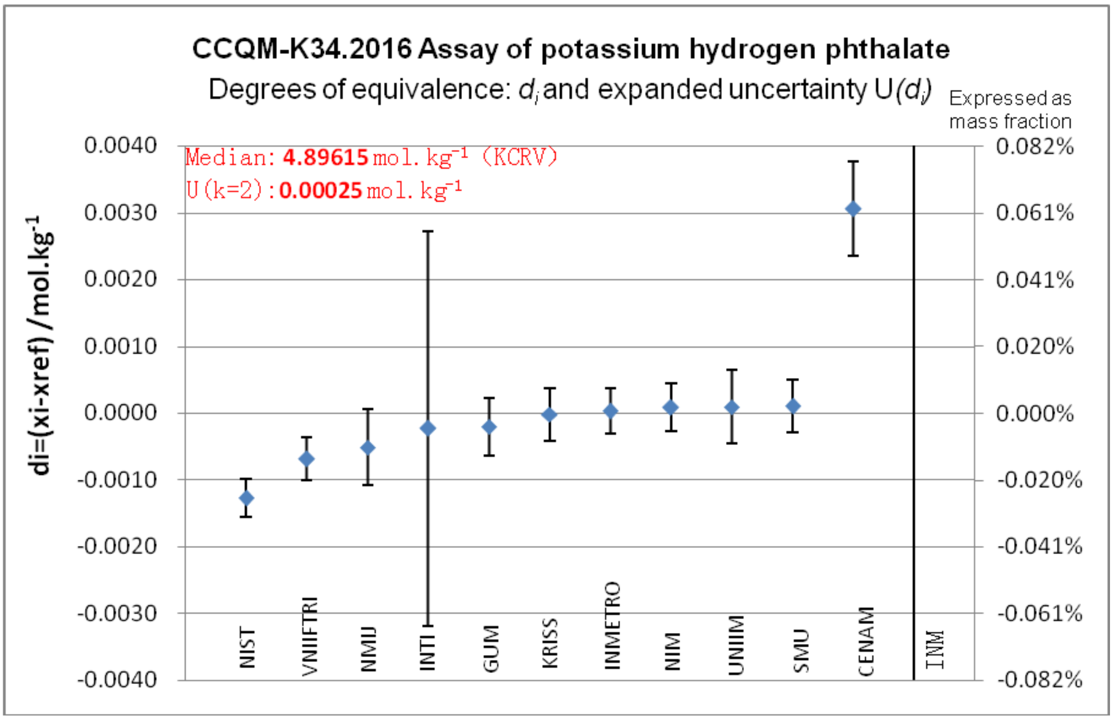
Where d$_i$ is the degree of equivalence between the NMI result x_i and the KCRV x_{ref}, and $U(d_i)$ is the expanded uncertainty *(k = 2)* of the d_i calculated by combining the standard uncertainty $u(d_i)$ of the NMI result x_i and the standard uncertainty $u\left(x_{ref}\right)$ of the KCRV x_{ref}. The equivalence statements for CCQM-K34.2016 are given in Table 12.

Table 12 Equivalence Statements of KHP amount content for CCQM-K34.2016

Participant	Reported Value （x_i）	Standard combined uncertainty （$u(x_i)$）	***d$_i$***	***U(d$_i$)***	***d$_i$/ U(d$_i$)***
	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	
NIST	4.89487	0.00008	-0.00127	0.00029	-4.42
VNIIFTRI	4.89546	0.00010	-0.00069	0.00032	-2.15
NMIJ	4.89563	0.00026	-0.00051	0.00058	-0.89
INTI	4.8959	0.00147	-0.00023	0.0030	-0.08
GUM	4.89594	0.00018	-0.00020	0.00044	-0.47
KRISS	4.89612	0.00015	-0.00002	0.00039	-0.06
INMETRO	4.89617	0.00012	0.00002	0.00034	0.07
NIM	4.89623	0.00013	0.00008	0.00036	0.24

UNIIM	4.89624	0.00025	0.00009	0.00056	0.16
SMU	4.89625	0.00015	0.00010	0.00040	0.26
CENAM	4.89920	0.00034	0.00305	0.00072	4.29
INM	4.959	0.0782	0.0627	0.157	0.40

Figure 2 Degrees of equivalence



10. HOW FAR DOES THE LIGHT SHINE

The comparison tested the capabilities and methods used for assay of high purity materials. Good result indicates good performance in assaying the purity （amount content） of solid weak acids.

11. CONCLUSIONS

In general good agreement between most participating laboratories was observed for measurement of potassium hydrogen phthalate. The median of all results was agreed as the KCRV (amount content of potassium hydrogen phthalate 4.89615mol/kg and associated expanded uncertainty 0.00025mol/kg). The spread of results (as relative standard deviation) is comparable to that in previous comparisons on solid materials – potassium hydrogen phthalate in CCQM-K34[3]. The suitability of coulometry for assay of high purity materials was demonstrated again.

12. ACKNOWLEDGEMENTS

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National Institute of Metrology P.R.China

CCQM-K34.2016 Assay of potassium hydrogen phthalate

Technical Protocol

INTRODUCTION

Assays of acids are made almost exclusively by titration methods. Potassium hydrogen phthalate (KHP) is the most used reference material for these measurements. 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 CCQM-K34 key comparison was organised jointly by the inorganic and electrochemistry working groups of CCQM as a follow-up to pilot study CCQM-P36 to test the abilities of the metrology institutes to measure the amount content of acid in solid weak acids. Slovak Institute of Metrology acted as the coordinating laboratory, in 2004.

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 repeat key comparison for assay of potassium hydrogen phthalate was proposed again and discussed in the EAWG with IAWG joint meeting in April 2016, and it had been approved by CCQM to proceed to a key comparison which is numbered as CCQM-K34.2016, 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.

For coulometry or titrimetry, good results will indicate good performance in assaying acids.

Time schedule

Call participations: March 2017
Deadline for registration: 10 May 2017
Dispatch of the samples: In the beginning of June 2017
Deadline for result report: 15 September 2017
Discussing results: October ~ December 2017
Draft A report: IAWG&EAWG meeting April, 2018

Samples

Sample preparation:

The source of the sample is from a 25 kg batch of commercial pure potassium hydrogen phthalate 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 15 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 100.1% of the theoretical value based on the carboxylate hydrogen amount content.

Homogeneity test:

Ten bottles were tested for homogeneity by analysing each bottle in twice independence sampling by coulometry. No statistically significant heterogeneity was found based on F test; the RSD is 0.0031 % with each independent result and the RSD is 0.0013% 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 500 mg. Please pay attention that you do not use less than 500 mg in your analyses for the key 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 the same time. The bottles are shipped in a cardboard box by courier. The contents will be marked “**potassium hydrogen phthalate**” 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 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 density of the potassium chloride sample is 1.636 g/cm^3.
The quantity of sample to be used in the assay is not less than 500 mg.

Measurand and measurement method:

Any method or combination of methods can be used, but the coulometric method is recommended for this comparison. The results will be reported as amount content [mol/kg] of monoprotic weak acid, to be accompanied by a full uncertainty budget. Information on the assay dependence on sample mass is also welcome. At least six independent determinations should be performed (where applicable).
Indirect methods must take into account the dependence of the assay on the H/K(or other metals) ratio and the water content.

Reporting

The report should be sent to the coordinating laboratory before 30 September 2017, 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 [mol/kg] of monoprotic weak acid, to be accompanied by a full uncertainty budget. Information on impurities is welcome also from participants not using (100% - impurities) approach.
2. If the assay is determined from impurity analysis, results for all the elements/compounds sought must be included.
3. 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.

4. 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.
5. 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, CO_2 interference, 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
6. 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.
7. In order to further evaluate the effects of assay measurements, please report the details of the techniques used in the measurement procedure (the means of adding the sample, stirring, influence of CO_2...).A separate text file or official report may be used.

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

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