National Institute of Metrology P.R.China

Report of the CCQM-K34.2016.1

Assay of potassium hydrogen phthalate

Final report

Ma Liandi and Wu Bing

With participation of:

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NIM: Ma Liandi,Wu Bing

NIST: Jason F. Waters

SMU: Michal Mariassy

Beijing, December 2020

Table of content

1. ABSTRACT

The CCQM-K34.2016.1was organized as a subsequent key comparison of CCQM-K34.2016 Assay of Potassium Hydrogen Phthalate to demonstrate the improved capability of the laboratories which did not perform well in the original CCQM-K34.2016. The key comparisons were organized jointly by the working groups of inorganic analysis and electrochemistry analysis. National Instituteof Metrology P. R. China(NIM) acted as the coordinating laboratory, and NIM and SMU (Slovak Institute of Metrology) served as linking laboratories to link to the CCQM-K34.2016 key comparison reference value (KCRV). CENAM, NIST and VNIIFTRI registered in K34.2016.1, however, VNIIFTRI gave up participating in the comparison due tofailure to get the samples through the customs clearance in Russia. All participants used constant current coulometry for measurement, and improved capabilities were demonstrated.

2. INTRODUTION

The subsequent key comparison was requested by CENAM and NIST after CCQM-K34.2016 “Assay of Potassium Hydrogen Phthalate” was completed. After discussion in the joint meeting of IAWG&EAWG it was approved by CCQM in April 2018 in Paris as CCQM-K34.2016.1.The purpose of the follow-up key comparison is to provide an opportunity for the laboratories which did not perform well and /or which did not participate in CCQM-K34.2016 to underpin their capabilities of assaying the purity or amount content of solid weak acids.

National Institute of Metrology P. R. China(NIM) acted as the coordinating laboratory, and NIM and SMU (Slovak Institute of Metrology) served as linking laboratories to the CCQM-K34.2016 key comparison reference value (KCRV). CENAM, NIST and VNIIFTRI registered in K34.2016.1.

Scope:

The scope is the same as in CCQM-K34.2016.The comparison tested the capabilities and methods used for assay of high purity materials and underpins the claimed calibration and measurement capabilities of the institutes.

The measurement results will indicate the performance and capability in assaying the amount content of solid weak acids.

3. LIST OF PARTICIPANTS

The participating NMIs and contact persons are given in Table 1.

Table 1 List of participants

Institution	Country	Contact person
CENAM National Center of Metrology	Mexico	Judith Velina Lara Manzano
NIM National Institute of Metrology	China	Ma Liandi, Wu Bing
NIST National Institute of Standards and Technology	USA	Jason F. Waters
SMU Slovak Institute of Metrology	Slovakia	Michal Mariassy
VNIIFTRI Russian Metrological Institute of Technical Physics and Radio Engineering	Russia	Sergey Prokunin, Vladimir Dobrovolskiy

4. TIME SCHEDULE

Call for participation: April 2019

Deadline for registration: 25 May 2019

Dispatch of the samples: In the end of May 2019

Deadline for result report: 18 October 2019

Discussing results: December 2019

Draft A report: IAWG&EAWG meeting April, 2020

Draft B report: November 2020

5. SAMPLES

A new batch of pure KHP material had been prepared. The source of the sample is from a 25kg 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 9 glass bottles closed with silicone lined plastic caps for the comparison.Six bottles randomly selected from the 9 bottles were tested for homogeneitybyanalyzing two independent samples from each bottle by coulometry. Nostatistically significant heterogeneity was found based on F test; between bottles homogeneity was found to be 0.0032% RSD and within bottle homogeneity 0.0012%; the sample is found to be adequate for the key comparison. The sample mass used for homogeneity testing at NIM was about 500 mg.

The samples were sent to the participants by DHL or EMS on the 31st of May 2019.The samples arrived to CENAM and SMU without damage within one month. When the sample was received by NIST，the Mylar bag had been cut open. Therefore, another sample was sent from NIM to NIST immediately, and NIST received it in July. After many attempts, the sample dispatched to VNIIFTRI arrived at Moscow on 15 August 2019, but it failed to pass the customs clearance and VNIIFTRI did not get the sample, so at last VNIIFTRI gave up the participation.

The dispatch dates and receipt dates are given in Table 2.
At the request of NIST and CENAM, the deadline was extended from the end of August to 18 October 2019. All participants observed the deadline.

Table 2 Sample sent dates, receipt dates and report dates

Institute	Sample No.	Sample dispatch date	Sample receipt date	Date report sent
CENAM	01	31 May 2019	27 June 2019	18 October 2019
NIM	02	-	-	-
NIST	03, 06,07	31 May 2019 24 June 2019	21 June 2019 13 July 2019	18 October 2019
SMU	04	31 May 2019	11 June 2019	15August 2019
VNIIFTRI	05	31 May 2019	-	-

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 template.

The technical protocol (appendix A) contained background information and timing of the comparison. Information on sample homogeneity and sample preparation for measurements was given. The participants were free to choose the measurement procedure, however, 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 related to the measurement results, a detailed uncertainty evaluation and a 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. Some details on measurements as derived from the reports are given in Table 3.

Table 3 Details on measurement methods

Institute	*Details of coulometric procedures*				*EP estimation*	*Initial titration*	*Major unc.sources*	*Contribution*
	Cell type	*IC rinse*	*Working cell(solution) volume /mL*	*Main current /mA*				
CENAM	vertical, 1 intermediate chamber (IC)	Yes	200	100	nonlinear regression	Yes	u_A voltage, end point, gas impurities	39% 23% 17% 18%
NIM	horizontal, 2 IC	Yes	200 (160)	101.8	3rd order polynomial regr.	Yes	u_A end-point, gas impurities	15% 64% 16%
NIST	horizontal, 2 IC	Yes	180 (100)	101.8	3rd order polynomial regr.	Yes	u_A migration/diffusion, sample mass	32% 37% 27%
SMU	vertical, 1 IC	Yes	400 （250）	200	nonlinear regression	Yes	u_A electrolyte impurities, gas impurities, diffusion, voltage	36% 20% 20% 10% 7%

Discussion:

As the constant current coulometry is an primary method, the sources of type B uncertainty should be paid more attention to, the major uncertainty sources and which contribution were given in table 3.

From table 3 we can find that the type A uncertainty is less than 40% for each result, and major type B uncertainties include end-point, gas impurities, voltage, migration/diffusion and sample mass, but each participant's estimation about type B uncertainty was different. We'd like to share the experiences from each participant, make fully consideration and improve the method in the future.

Note: CENAM also reported an information value obtained by NaOH titrimetry, traceable to reference material SRM-84L from NIST.

8. RESULTS AND DISCUSSION

The reported values and uncertainties are summarized in Table 4 and also displayed graphically in Figure 1.

Table 4 Results by Coulometry (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*
SMU	0.5	4.895475	5	0.000248	0.000186	0.00037	2
NIM	0.5	4.895524	14	0.000175	0.000122	0.00025	2
NIST	0.1~0.25	4.895775	13	0.000388	0.000192	0.00039	2
CENAM	0.4	4.896377	7	0.000306	0.000184	0.00037	2

Table 4a Additional Results by Titrimetry(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*
CENAM	0.3	4.897972	5	0.000303	0.000649	0.00130	2

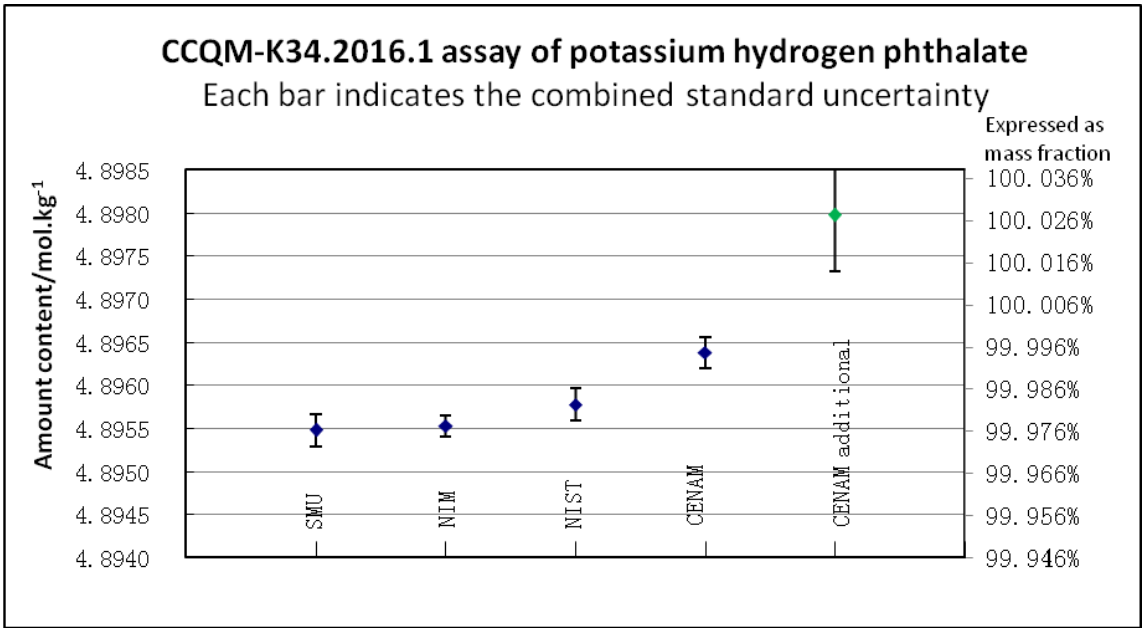

Figure 1 Results of K34.2016.1 (each bar indicates the combined standard uncertainty)

9. REFERENCE VALUE

The results from NIM and SMUmatch very well . The differences in both comparisons (K34.2016 and K34.2016.1) are less than 0.001%. Therefore, the average of NIM and SMU results is used as KCRV of CCQM-K34.2016.1, and it can be linked to original CCQM-K34.2016 very well.

The KCRV is calculated from the formula:

$$KCRV_{K34.2016.1} = average(v_{NIM,K34.2016.1}, v_{SMU,K34.2016.1}) \quad (1)$$

Where $KCRV_{K34.2016.1}$– the reference value of CCQM-K34.2016.1

$v_{NIM,\ K34.2016.1}$ – NIM result in CCQM-K34.2016.1

$v_{SMU,\ K34.2016.1}$ – SMU result in CCQM-K34.2016.1

The uncertainty of the *KCRV* in CCQM-K34.2016.1 (the standard uncertainty of the mean） is calculated from the formula:

$$u_{KCRV\,(K34.2016.1)} = \sqrt{\frac{1}{m}s^2(x)} = \sqrt{\frac{1}{m} \times \frac{1}{(m-1)}\sum_{i=1}^{m}(x_i - \bar{x})^2} \quad (2)$$

Where $u_{KCRV(K34.2016.1)}$– standard uncertainty of*KCRV* in CCQM-K34.2016.1

x_i– $v_{NIM,\ K34.2016.1}$or$v_{SMU,\ K34.2016.1}$

$\bar{x}$– arithmetic mean of NIM and SMU resultsin CCQM-K34.2016.1 that is$KCRV_{K34.2016.1}$.

The degree of equivalence for CENAM and NIST is calculated from the formula:

$$d_i = v_{i,K34.2016.1} - KCRV_{K34.2016.1} + average(d_{NIM\,(K34.2016)}, d_{SMU(K34.2016)}) \quad (3)$$

Where $v_{i,K34.2016.1}$ – CENAM or NIST result in CCQM-K34.2016.1

$KCRV_{K34.2016.1}$– the reference value of CCQM-K34.2016.1

$d_{NIM(K34.2016)}$– degree of equivalence of NIM in CCQM-K34.2016

$d_{SMU(K34.2016)}$– degree of equivalence of SMU in CCQM-K34.2016

The uncertainty of the degree of equivalence of CENAM and NIST, U_{di} will contain three contributions: the uncertainty of CENAM or NIST result, the uncertainty of reference value in CCQM-K34.2016.1 and the uncertainty of reference value in CCQM-K34.2016.

Therefore

$$U_{di} = 2 \cdot \sqrt{u^2_{i(K34.2016.1)} + u^2_{KCRV(K34.2016.1)} + u^2_{KCRV(K34.2016)}} \quad (4)$$

Where $u_{i(K34.2016.1)}$ – standard uncertainty of CENAM or NIST result in CCQM-K34.2016.1

$u_{KCRV(K34.2016.1)}$ –standard uncertainty of KCRV in CCQM-K34.2016.1

$u_{KCRV\ (K34.2016)}$– standard uncertainty of KCRV in CCQM-K34.2016

The d_i of NIM in CCQM-K34.2016 ($d_{NIM\ (K34.2016)}$) was 0.00008mol.kg^{-1}, the d_i of SMU in CCQM-K34.2016 ($d_{SMU\ (K34.2016)}$) was 0.00010 mol.kg^{-1},and the standard uncertainty of KCRV in CCQM-K34.2016 ($u_{KCRV(K34.2016)}$) was 0.000121mol.kg^{-1}.[1]

Table 5 Equivalence statements of KHP amount content for CCQM-K34.2016

Participant	Result (amount content of KHP)	u_c	$KCRV_{K34.2016}$	d_i	$u_{KCRV\ (K34.2016)}$
	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}
NIM	4.89623	0.00013	4.89615	0.00008	0.00012
SMU	4.89625	0.00015	4.89615	0.00010	0.00012

The average of NIM and SMU results is used as KCRV of CCQM-K34.2016.1. The reference value and uncertainty of the KCRV for CCQM-K34.2016.1 was given in table 6.

Table 6 KCRV and uncertainty of CCQM-K34.2016.1

$KCRV_{K34.2016.1}$	$u_{KCRV(K34.2016.1)}$	Expanded uncertainty
mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}（k = 2）
4.89550 (Average(NIM,SMU))	0.000025	0.00005

The d_i referred to the KCRV of CCQM-K34.2016 is given in Table 7and shown graphically in Figure 2 with the d_i from the original key comparison CCQM-K34.2016.

Table 7 Equivalence statements of KHP amount content for CCQM-K34.2016.1

Participant	Result (amount content of KHP)	$u_{i(K34.2016.1)}$	$u_{KCRV(K34.2016.1)}$	$u_{KCRV(K34.2016)}$	d_i	$U(d_i)$	$d_i / U(d_i)$
	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	mol.kg^{-1}	
NIST	4.89578	0.00019	0.000025	0.00012	0.00037	0.00046	0.81
CENAM	4.89638	0.00018	0.000025	0.00012	0.00097	0.00044	2.19

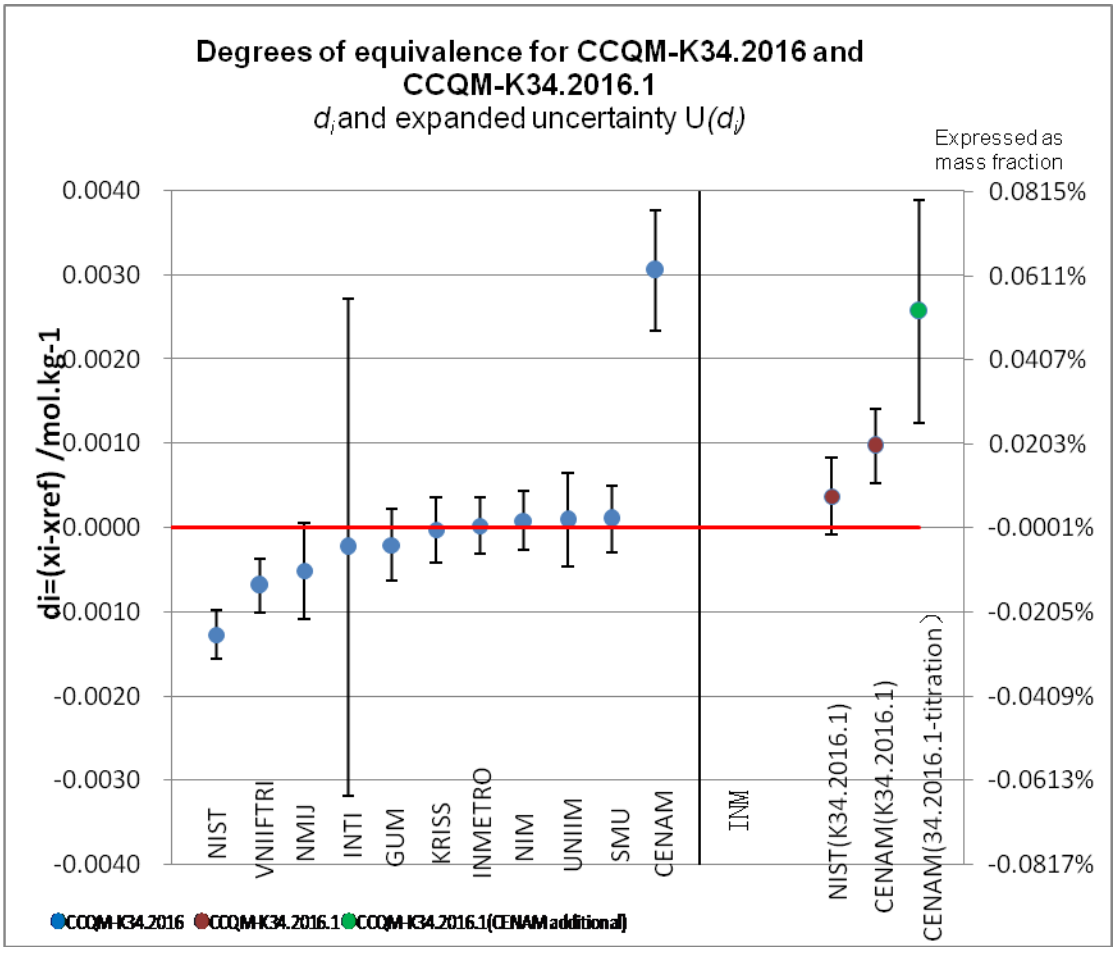

Figure2 Degrees of equivalence

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

The results from NIM and SMU are in excellent agreement in both comparisons, the original K34.2016 and the subsequent K34.2016.1, showing high quality and stable capabilities of the two NMIs, so they can support the link of the subsequent comparison to the original K34.2016 very well. The performances of NIST and CENAM confirmed their improved capabilities for assaying the purity (amount content）of solid weak acids.

12. ACKNOWLEDGEMENTS

The coordinating laboratory gratefully acknowledges the help and support from Dr. Michal Máriássy, the report review and DoE discussion from Dr. Steffen Seitz and Dr. Mike Winchester, and thanks all of the analysts from the participant institutes for their contributions as well as the contact persons.

13. REFERENCES

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National Institute of Metrology P.R.China

CCQM-K34.2016.1 Assay of Potassium Hydrogen Phthalate

Technical Protocol

Introduction

The CCQM-K34.2016.1 is a subsequent key comparison of the CCQM-K34.2016 Assay of Potassium Hydrogen Phthalate. The purpose of the comparison is to provide an opportunity for the laboratories which not performing well and /or which not participating in CCQM-K34.2016 to underpin their capabilities of assay the purity (amount content）of solid weak acids. National Institute of Metrology P. R. China (NIM) acts as the coordinating laboratory, NIM and SMU (Slovak Institute of Metrology) will serve as linking laboratories to link to the CCQM-K34.2016.

Time schedule

Call participation: April 2019

Deadline for registration: 25May 2019

Dispatch of the samples: In the end of May 2019

Deadline for result report: 18 October 2019

Discussing results: October~ December 2019

Draft A report: IAWG&EAWG meeting April, 2020

Samples

Sample preparation:

New batch of pure KHP material had been prepared. 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 6 glass bottles closed with silicone lined plastic caps for the comparison. 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:

Six bottles were tested for homogeneity by coulometry analyzing, each bottle in twice independence sampling. No statistically significant heterogeneity was found based on F test; the RSD is 0.0032 % 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 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 laboratorynumber.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 shouldbe dried at 110 ℃ 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 1.636g/cm^3.

The quantity of sample to be used in the assay is not less than 500mg.

Measurand and measurement method

All participants will use coulometry. The results will be reported as amount content [mol/kg] of potassium hydrogen phthalate, 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).

Reporting

The report should be sent to the coordinating laboratory before 31August 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.

Atemplate 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 ofstages 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 furtherevaluate the effects of assay measurements,please report the details of the techniques used in the measurementprocedure (the means of adding the sample, stirring, influence of CO_2...).A separate text file or official report may be used.

Link to CCQM-K34.2016

The results will have the linkage to the CCQM-K34.2016 (Assay of Potassium Hydrogen Phthalate), the average of the results of SMU and NIM will be used as the Key Comparison Reference Value (KCRV), and the degree of equivalence of each participant will be evaluated.

Participation

The subsequent comparison is organized based on the requirements from NIST and CENAM, as their results were not not performing very well. The participation will be open to the laboratories which not performing well and /or which not participating in CCQM-K34.2016 to underpin their capabilities of assay the purity (amount content） of solid weak acids.

Coordinating laboratory and contact persons

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