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**Key comparison CCQM-K34**  
**Assay of potassium hydrogen phthalate**  
**Final report**

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With participation of:

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Kenneth W. Pratt (NIST); Akiharu Hioki and Toshihiro Suzuki (NMIJ); Ma Liandi, Wu Bing  
and Shen Yu (NRCCRM); Alena V. Skutina, Gennady I. Terentiev (UNIIM)

**Bratislava, October 2005**

## **Abstract**

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, seven NMIs expressed interest in participation. All participants used constant current coulometry at different sophistication level. In general very good agreement of the results was observed; some possible problems were highlighted.

## 1 INTRODUCTION

The CCQM-K34 key comparison “Assay of Potassium Hydrogen Phthalate” has been proposed and discussed at the October 2002 CCQM Inorganic and Electrochemical Analysis Working Group meetings in Ottawa as a follow-up for the pilot study P36. The aim of the comparison is to demonstrate and document the capability of interested National Metrology Institutes to measure the amount content of acid in a pure weak acid, in this case potassium hydrogen phthalate.

Assays of acids are made almost exclusively by titration methods. Potassium hydrogen phthalate (KHP) is the most used reference material for these measurements. The reliability of its assay is therefore of prime importance for chemical producers and analytical chemistry in general. It is also of interest regarding its use in pH standardisation, where the composition (specifically, the presence of trace phthalic acid or potassium phthalate) affects the pH value of the buffer solution. The main impurity present is usually water from mother liquor occluded in the crystals.

There are several producers, who offer this material as a reference material. In our previous experience, the assays can have a bias an order of magnitude higher than the declared uncertainties.

The objective of CCQM-K34 was to determine the total amount content ( $\text{mol}\cdot\text{kg}^{-1}$ ) of acid in a sample of potassium hydrogen phthalate. The participants were free to choose the analytical procedure.

## 2 LIST OF PARTICIPANTS

Five institutes originally indicated interest in participating in the comparison. At last, seven institutes took part. Table 1 contains the full names of all participating NMIs and contact persons.

*Table 1 List of participants*

<b>Institution</b>	<b>Country</b>	<b>Contact person</b>
<b>BAM</b> Bundesanstalt für Materialforschung und Prüfung	Germany	Martin Breitenbach
<b>KRISS</b> Korean Research Institute of Standards and Science	Korea	Euijin Hwang
<b>NIST</b> National Institute for Standards and Technology	USA	Kenneth W. Pratt
<b>NMIJ (AIST)</b> National Metrology Institute of Japan	Japan	Akiharu Hioki
<b>NRCCRM</b> National Research Center for Certified Reference Materials	China	Ma Liandi
<b>SMU</b> Slovak Institute of Metrology	Slovakia	Michal Máriássy
<b>UNIIM</b> Ural Scientific Research Institute of Metrology	Russia	Gennady I. Terentiev

### 3 SAMPLES

A batch of old commercial material was selected for comparison. The material was sieved through plastic sieves and the middle fraction was homogenised in a large bottle and filled into 10 glass bottles closed with silicone lined plastic caps. Four bottles were tested for homogeneity by analysing each bottle in triplicate by coulometry. Data were treated using ANOVA one-way analysis [1]. The results indicate that the between bottle variation is negligible compared to the repeatability of the measurement. The assay did not change on analysing fractions with small or large crystals nor crushed sample, thus it can be assumed that water content is below 0.005% (crushing is an effective means of releasing occluded water from KHP).

The samples were sent to the participants by Fedex on May 7, 2004 (except KRISS, where the sample was handed over personally, and UNIIM, where the sample was sent on May 10 by DHL due to import regulations). All samples arrived to their destination without damage. The receipt dates and the responsible persons are given in Table 2.

The deadline for reporting results was set to 31 August 2004 in order to prepare draft A report for discussion at the CCQM WG meeting in October 2004. All participants reported their results in time.

*Table 2 Sample receipt dates and report dates*

<i>Institute</i>	<i>Sample receipt date</i>	<i>Date report sent</i>
<b>BAM</b>	10 May 2004	July 15
<b>KRISS</b>	28 April 2004	August 27
<b>NIST</b>	11 May 2004	August 31
<b>NMIJ (AIST)</b>	10 May 2004	August 30
<b>NRCCRM</b>	11 May 2004	August 27
<b>SMU</b>	—	pilot
<b>UNIIM</b>	26 May 2004	August 31

### 4 INSTRUCTIONS TO 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, and information on the participating institutes. Information on sample homogeneity and sample preparation for measurements was given. The participants were free to choose the measurement procedure. Some possible problems with measurement were highlighted. Participants were requested the results as amount content of acid and to provide uncertainty evaluation according to ISO Guide [2].

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

### 5 METHODS OF MEASUREMENT

The methods of measurement were left free to be selected by the participating institutes. The potential pitfalls for different methods were mentioned in the protocol. They included significant interference of carbon dioxide (the pH of the solution is alkaline during the final titration) for volumetric and coulometric titrations. For coulometric titration, there is in addition the possibility of electrochemical reduction yielding low results.

Indirect methods had to take into account the dependence of the assay on the H/K (or other metals) ratio and the water content. Probably in view of the difficulties associated with the indirect assay via impurities, no one of the institutes used this approach; some impurities were determined, however.

All participants used coulometric titration 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. Six participants introduced the solid samples directly into the coulometric cell, NMIJ used a special way to get the result for solid sample by extrapolation of the relationship of the result for solution versus inverse of the sample volume (with constant volume of liquid added). This procedure seems to minimise the influence of the gas and electrolyte impurities at the expense of more experimental work.

**Table 3** *Details on measurement methods used*

<i>Institute</i>	<i>Approx. sample mass /g</i>	<i>Procedure details</i>			
		<i>Cell type</i>	<i>IC rinse</i>	<i>Cell volume /mL</i>	<i>Main current /mA</i>
<b>BAM</b>	0.6	vertical, 1 intermediate chamber (IC)*	Yes	180	200
<b>KRISS</b>	0.5	horizontal, 2 IC	Yes	~100	100
<b>NIST</b>	0.4	horizontal, 2 IC	Yes	~80	100
<b>NMIJ</b>	0.05	horizontal, 2 IC	Yes	120	50
<b>NRCCRM</b>	0.5	horizontal, 2 IC	Yes	180	100
<b>SMU</b>	0.5	vertical, 1 IC*	Yes	250	200
<b>UNIIM</b>	0.5	vertical, 1 IC	No	400	100

\* - continuous flow into the working chamber during main titration

**Table 3** *Details on measurement methods used (continued)*

<i>Institute</i>	<i>EP estimation</i>	<i>Initial titration</i>	<i>CO<sub>2</sub> correction</i>
<b>BAM</b>	nonlinear regression	Yes	-
<b>KRISS</b>	max. slope	Yes	-
<b>NIST</b>	3 <sup>rd</sup> order polynomial regr.	Yes	-
<b>NMIJ</b>	3 <sup>rd</sup> order polynomial regr.	Yes	-
<b>NRCCRM</b>	3 <sup>rd</sup> order polynomial regr.	Yes	Yes
<b>SMU</b>	nonlinear regression	Yes	-
<b>UNIIM</b>	3 <sup>rd</sup> order polynomial regr.	No	-

## 6 RESULTS AND DISCUSSION

After receiving all the results, BAM and UNIIM were asked to check their results for numerical errors. No numerical errors were reported and thus the values are given as originally reported, but UNIIM indicated that a technical fault in the measurement could lead to errors as high as 0.2%.

The reason for higher result of BAM was not clear. In order to exclude material fault the sample was sent back to the coordinating laboratory; and a comparison with the original sample revealed a difference of about 0.023%, which indicates a change in the sample composition. This was confirmed by ion chromatography, which detected sample contamination with chlorides and another anion, presumably formate. As it is not exactly known whether the contamination occurred after BAM received the sample (BAM processed the whole sample), it was agreed to exclude BAM result from the comparison due to “travelling standard failure” and to do a subsequent bilateral comparison.

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

**Table 4** *Results (amount content of weak acid, relative standard deviation, relative combined standard uncertainty and number of measurements)*

<i>Institute</i>	<i>Measurement date</i>	<i>Result /mol.kg<sup>-1</sup></i>	<i>RSD</i>	<i>u<sub>C,r</sub></i>	<i>n</i>
AIST	June 7 - July 30	4.89192	0.0146%	0.0151%	2*
KRISS	Aug 18 - 25	4.89259	0.0017%	0.0034%	6
SMU	July 1 - 14	4.89269	0.0035%	0.0033%	6
NRCCRM	July 8 - Aug 19	4.89272	0.0057%	0.0056%	11
NIST	July 22 - 29	4.89298	0.0049%	0.0034%	10
UNIIM	Aug 9 - 26	4.89458	0.0213%	0.0155%	6

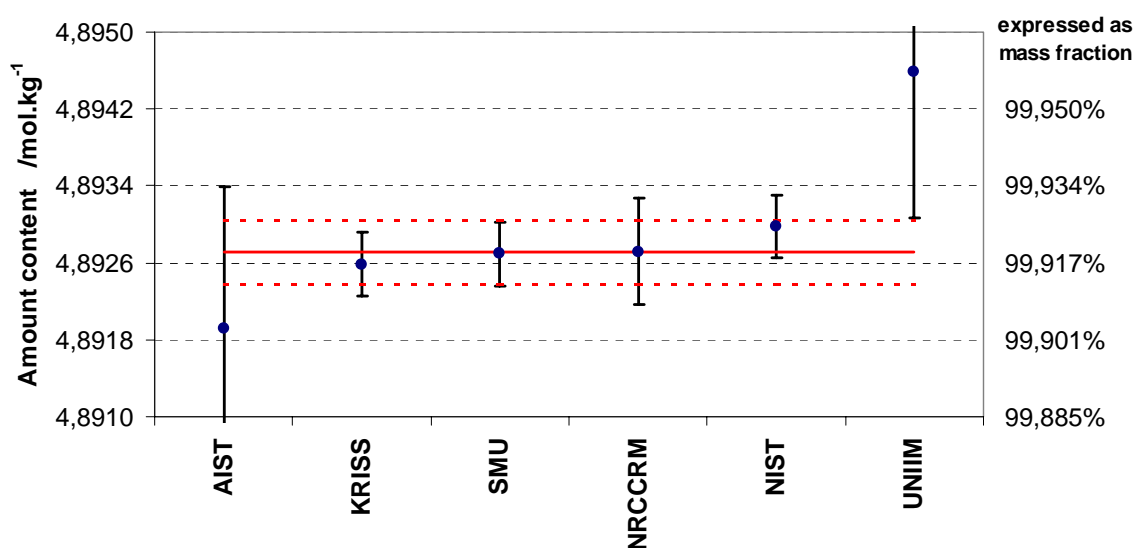
\* NMIJ used an extrapolation from several results with different solution sample sizes

Several approaches to estimate the key comparison reference value (KCRV) were considered. Except of arithmetic mean, all gave comparable values (table 5). The use of median and its uncertainty based on median of the absolute deviations (MAD) was agreed as the KCRV at the IAWG+EAWG meeting in October 2004. The formula used for calculation of the uncertainty of the median is as follows [3]:

$$u_{KCRV} = \frac{1.858 \cdot \text{MEDIAN}(x_i - KCRV)}{\sqrt{n-1}}$$

**Table 5** Arithmetic mean, MM-median, median and the weighted mean of the reported CCQM-K34 results

Possible KCRV	Value	Standard uncertainty	Rel. stand. uncertainty
Arithmetic mean	4,89291	0,00034	0.0069%
Variance weighted mean	4,89276	0,00013	0.0026%
MM-median	4,89275	0,00020	0.0042%
Median	4,89270	0,00016	0.0033%



**Figure 1** Results of CCQM-K34 (error bars correspond to expanded uncertainties ( $k=2$ ); median and its uncertainty are also given)

The higher uncertainty of NMIJ result is understandable in view of the about 10 times smaller samples used in the measurement, compared to the other participants.

The higher deviation of UNIIM result can be in part attributable to instrumentation and cell construction; the high uncertainty is dominated by a component attributed to endpoint determination.

Five of the six results are in excellent agreement. Most of the results overlap within the expanded uncertainty.

Significant differences can still be observed regarding the uncertainty evaluations, as summarised in Table 6. The chemical sources of uncertainty were in many cases not taken into account, thus leading to smaller uncertainty estimates. Some inconsistencies were also noted in uncertainty calculation.

Impurity determination (Table 7) and moisture (see above) do not explain the lower assay compared to the theoretical value. The lower assay therefore seems to be due to the presence of dipotassium phthalate impurity present in the sample.

**Table 6** *Summary of uncertainty evaluation*

<i>Institute</i>	<i>Major sources considered</i>	<i>chem. uncertainties considered</i>	<i>CO<sub>2</sub> influence</i>	<i>other impurities</i>	<i>phthalate reduction</i>
<b>BAM</b>	voltage, mass, current efficiency	Y	N	N	N
<b>KRISS</b>	EP determination	N	N	N	N
<b>NIST</b>	phthalate reduction, weighing	Y	Y	Y	Y
<b>NMIJ</b>	CO <sub>2</sub> correction	Y	Y		N
<b>NRCCRM</b>	CO <sub>2</sub> effect, EP determination	Y	Y	N	N
<b>SMU</b>	electrolyte&gas impurities, diffusion, voltage	Y	Y	Y	Y
<b>UNIIM</b>	EP detn., weighing	N	N	N	N

## **7 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 both strong and weak solid acids with  $pK_a < 7$ .



**Table 7 Impurities determined**

Institute (method)	UNIIM (ICP MS)		NIST (ICP MS)		BAM (ICP/OES)	
	value mg/kg	uncertainty	value mg/kg	uncertainty	value mg/kg	uncertainty
Ca	5.7 (AAS)	5%				
Na	35.1	3%			188	5%
Fe	6	47%				
Rb	8.5	1%	7.1	50%		
Al	1.9	53%				
Cu	1.05	114%	1.8	100%		
Zn	0.5	60%	9.1	100%		
Mn	0.2	50%				
Ni	0.13	46%				
Mg	0.22	45%				
Ba	0.14					
B	<1					
Si	<50					
Pb	<0.1		1.3	100%		
Cr, Co, Sr, Cd, Sn, Sb, Te, Bi	<0.1					

## 8 CONCLUSIONS

Good agreement between the participating laboratories for measurement of potassium hydrogen phthalate was observed. Median of the results was chosen as the reference value (amount content of acid 4,89270 mol/kg, associated expanded uncertainty 0.00032 mol/kg).

The comparison demonstrated that great care must be taken if the assay of compounds is based only on 100%-impurities concept, as even the most important impurities may remain undetected.

## 9 ACKNOWLEDGEMENTS

The coordinating laboratory gratefully acknowledges the contributions of all participants and of David L. Duewer (NIST) for critical evaluation and provision of a copy of PDF\_maker macro spreadsheet to enable the calculation of the MM-median.

## 10 REFERENCES

- [1] Van der Veen A, Linsinger TPJ, Pauwels J, Uncertainty calculations in the certification of reference materials. 2. Homogeneity study. *Accred. Qual. Assur.* **6**, 26-30 (2001)
- [2] BIPM, ISO, IEC, OIML, Guide to the expression of Uncertainty in Measurement (1995) 1<sup>st</sup> ed., ISO, Geneva.
- [3] Müller J.W., Possible Advantages of a Robust Evaluation of Comparisons. *J. Res. Natl. Inst. Stand. Technol.* 105, 551-555 (2000)

## Appendix A – Technical Protocol

### CCQM-K34 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. The reliability of its assay is therefore of prime importance for chemical producers and analytical chemistry in general. It is also of interest regarding its use in pH standardisation, where the composition (specifically, the presence of trace phthalic acid or potassium phthalate) affects the pH value of the buffer solution. The main impurity present is usually water from crystallisation.

There are several producers, who offer this material as a reference material. In our previous experience, the assays can have a bias an order of magnitude higher than the declared uncertainties.

After the successful pilot study, CCQM approved a key comparison to underpin the claimed calibration and measurement capabilities of the institutes.

##### Scope:

The comparison will test the capabilities and methods used for assay of high purity materials. For titration or coulometric methods, good results will indicate good performance in assaying both strong and weak solid acids.

##### Time schedule

Dispatch of the samples:	beginning of May 2004
<b>Deadline for receipt of the report:</b>	<b>31 August 2004</b>
Distribution of Draft A for comments:	end of September 2004
Draft A discussion:	IAWG meeting in October 2004.

##### Samples

Each participant will receive one numbered bottle containing about 20 g of material. Shipment to all participants will be performed at the same time. The bottles are shipped in a cardboard box by courier and the airwaybill/consignment number<sup>1</sup> is reported by email to the contact person of the receiving laboratory for tracking purposes. The contents will be marked “potassium hydrogen phthalate” for research purposes and value 1 USD; please be attentive of possible customs delays, etc. The measurement protocol is sent by e-mail.

The homogeneity of the sample material was measured based on assay using sample size of about 500 mg and found to be adequate for the key comparison.

The assay is in the range of 99.9 – 100% of the theoretical value.

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<sup>1</sup> airwaybill/consignment number, the carrier identification of the shipment allowing detailed tracking of the shipment. If you have not received the shipment within 3 days of our notice, please use the tracking facility to monitor whether your shipment is being held up in customs or similar.

### Actions at receipt of samples

Please inspect the received bottles for damage. Please inform the contact person of receipt and report any mishaps to the coordinating laboratory. The sample should be stored 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.

### **Measurement method**

Any method or method combination can be used 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 four 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 August 31, 2004**, preferentially by e-mail. The coordinator will confirm the receipt of each report. If the confirmation does not arrive within one week, contact the coordinator to identify the problem.

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

Information requested:

1. Report the results as amount content [mol/kg] of weak monoprotic acid, 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 also: cell description, volume of electrolyte in working chamber, endpoint evaluation procedure, example titration curve for initial and final titration), and of the equipment used.
4. The complete measurement equation has to be given, as well as the values of the constants used and variables (raw data) for at least one measurement. The data should enable the recalculation of the result of this measurement.
5. State all the individual results, not only the final mean value.
6. The uncertainty budget has to include instrumental sources of uncertainty (mass, time, voltage, volume, ...) as well as chemical ones (endpoint estimation, equilibria, CO<sub>2</sub> interference, impurities, purity of calibration standards, ...). 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.
7. 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.
8. Report the details of the procedure used (a separate text file can be used).

## **Reference value**

The reference value will be agreed upon on the meeting of 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 at the autumn 2004 meeting of CCQM Working Groups on Electrochemical Analysis and on Inorganic Analysis. The individual reports will also be distributed among the participants.

## **Coordinating laboratory and contact person**

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