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Key comparison CCQM-K34.1
Assay of potassium hydrogen phthalate

Final report

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With participation of:
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Abstract

The CCQM-K34.1 subsequent key comparison was organised as a subsequent comparison to CCQM-K34 Assay of Potassium Hydrogen Phthalate to demonstrate the capability of BAM to measure the amount content of acid in potassium hydrogen phthalate. The BAM sample was contaminated in CCQM-K34 and therefore the result of BAM was not taken into account. Both key comparisons and the previous pilot study CCQM-P36 were organised jointly by the working groups of inorganic analysis and electrochemistry analysis. Both participants used high-accuracy constant current coulometry for measurement. The agreement of the results was very good. Slovak Institute of Metrology acted as the coordinating laboratory and served as a link to the reference value of CCQM-K34.

1 INTRODUCTION

The CCQM-K34.1 bilateral comparison “Assay of Potassium Hydrogen Phthalate” has been proposed at the October 2004 CCQM Inorganic and Electrochemical Analysis Working Group meetings in Ottawa as a follow-up for the CCQM-K34, where problems with sample contamination were observed for BAM measurement. It was later found that the magnesium perchlorate drying agent used in the desiccator released acetic acid, which contaminated the sample. BAM therefore requested a supplementary bilateral comparison in order to confirm its measurement capability.

Scope of the comparison:
The scope is the same as in CCQM-K34 The comparison tested the capabilities and methods used for assay of high purity materials. For coulometric methods, good results indicate good performance in assaying both strong and weak solid acids.

2 LIST OF PARTICIPANTS

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

Table 1 List of participants

Institution	Country	Contact person
BAM Bundesanstalt für Materialforschung und Prüfung	Germany	Martin Breitenbach
SMU Slovak Institute of Metrology	Slovakia	Michal Máriássy

3 SAMPLES

A SMU reference material (with different treatment compared to the certificate) was used for comparison. The material was sieved through plastic sieves and the middle fraction was homogenised in a large bottle and filled into 4 glass bottles closed with silicone lined plastic caps. The 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. It is assumed that water content is about 0.03% (based on comparison with crushed sample – crushing is an effective means of releasing occluded water from KHP).

The sample was sent to BAM by TNT on April 1, 2005. The sample arrived to its destination without damage on April 4.
The deadline for reporting results was set to 30 June 2005 in order to prepare draft A report for discussion at the CCQM WG meeting in October 2005. Both participants reported their results in time.

4 INSTRUCTIONS TO PARTICIPANTS

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

The technical protocol 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.

Both participants used the same method as in CCQM-K34 (coulometric titration) for assay determination. Some details on measurements are given in Table 3 of the report of CCQM-K34.

6 RESULTS AND DISCUSSION

The reported values and uncertainties are summarised in Table 2 and also displayed graphically in Figure 1.

Table 2 Results (amount content of weak acid, relative standard deviation, relative combined standard uncertainty and number of measurements)

Institute	***Measurement date***	***Result /mol.kg^{-1}***	***$u_{C,}$ /mol.kg^{-1}***	***$u_{C,r}$***	***RSD***	***n***
BAM	May 26 – June 18, 2005	4.89530	0,00016	0.0033%	0.0015%	6
SMU	May 27 – June 3, 2005	4.89520	0,00018	0.0037%	0.0035%	5

The agreement of both results is very good.

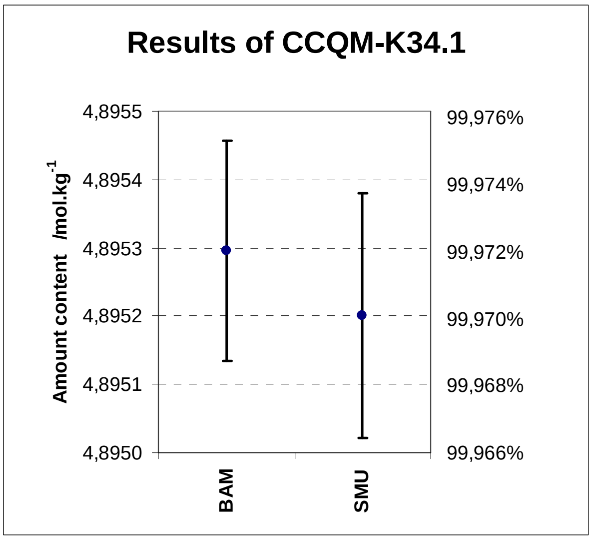

Figure 1 *Results of CCQM-K34.1 (standard uncertainties (k=1 are given))*

7 REFERENCE VALUE

SMU result is used as a link to KCRV from CCQM-K34. The results in both comparisons differ by about 0,05%, so the degrees of equivalence are directly comparable. The degree of equivalence for BAM is calculated from the formula:

$D_{\mathrm{BAM}} = D_{\mathrm{SMU(K34)}} + v_{\mathrm{BAM(s)}} - v_{\mathrm{SMU(s)}}$

where $D_{\mathrm{SMU(K34)}}$ – degree of equivalence of SMU in CCQM-K34
$v_{\mathrm{BAM(s)}}$ – BAM result in CCQM-K34.1
$v_{\mathrm{SMU(s)}}$ – SMU result in CCQM-K34.1

The uncertainty of degree of equivalence of BAM, $U_{Di,BAM}$ will contain three contributions: the uncertainty of reference value in CCQM-K34, the uncertainty of BAM result and the uncertainty arising from the link provided by SMU. The latter uncertainty is assumed to be equal to uncertainty of the SMU result in the bilateral comparison.
Therefore

$$U_{Di,\,BAM} = 2 \cdot \sqrt{u_{SMU,s}^2 + u_{BAM,s}^2 + u_{KCRV,K34}^2}$$

where $u_{\mathrm{KCRV,K34}}$ – standard uncertainty of KCRV in CCQM-K34
$u_{\mathrm{BAM,s}}$ – standard uncertainty of BAM result in CCQM-K34.1
$u_{\mathrm{SMU,s}}$ – standard uncertainty of SMU result in CCQM-K34.1

The degree of equivalence between BAM and other laboratory j is calculated from the respective degrees of equivalence:

$$D_{BAM,\,j} = D_{BAM} - D_j$$

The uncertainty of degree of equivalence between BAM and other laboratories is calculated according to the formula:

$$U_{DBAM,\,j} = 2 \cdot \sqrt{u_{SMU,s}^2 + u_{BAM,s}^2 + u_j^2}$$

The BAM result linked to the original CCQM-K34 reference value is presented in Figure 2.

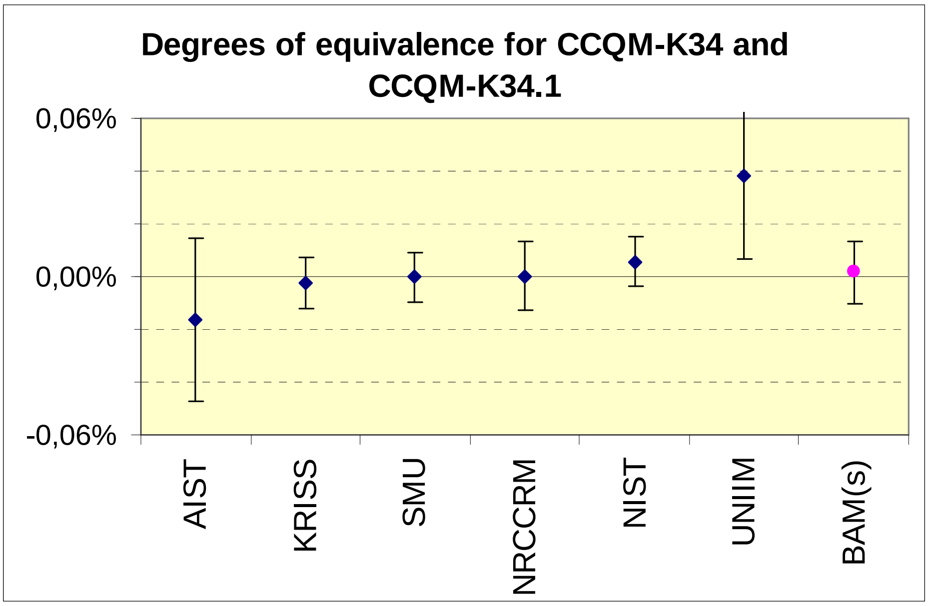

Figure 2 *Results of CCQM-K34.1 (expanded (k=2) uncertainties are given)*

8 CONCLUSIONS

The agreement of the results of SMU and BAM was excellent. The SMU provided the necessary link for calculation of BAM degree of equivalence for CCQM-K34.
It was shown again that in the high accuracy work the necessary care is to be given to the sample preparation step, as it may invalidate the entire result.

References

[1] Van der Veen A, Linsinger TPJ, Pauwels J, Accred. Qual. Assur. **6**, 26-30 (2001)
[2] BIPM, ISO, IEC, OIML, Guide to the expression of Uncertainty in Measurement (1995) 1st ed., ISO, Geneva.