

**METCHEM** Electrochemical Analysis WG

## **EUROMET Project 696**

**pH determination of a phthalate buffer**

### **Final report**

**Braunschweig, 30 June 2003**

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**Trilateral comparison on pH between LNE, France, VNIIFTRI, Russia and PTB,  
Germany**

**Field:**

Amount of substance

**Subject:**

pH determination of a phthalate buffer by Harned cell measurements

**Participants:**

PTB<sup>1</sup> (DE) LNE<sup>2</sup> (FR), VNIIFTRI<sup>3</sup> (RU)

**Organising body:**

METCHEM

## Abstract

The EUROMET project 696, a trilateral comparison between PTB, Germany, LNE, France and VNIIFTRI, Russia was performed in order to demonstrate and document the capability of the participants to measure the pH of a phthalate buffer by the primary measurement procedure for pH. Good agreement of the reported results was observed. The sample was very similar to the one used in the comparison CCQM-K17. PTB acts as pilot laboratory in CCQM-K17 and in EUROMET 696. This comparison allows to link the results obtained by LNE to CCQM-K17 key comparison through the degree of equivalence of PTB. On other hand, discrepancy between measured pH values at the VNIIFTRI and PTB for the same type of buffer solution decreased, as compared with bilateral comparison in 1997.

## Results

Temperature in °C	15		25		37	
Participants	pH	$U$ (pH)	pH	$U$ (pH)	pH	$U$ (pH)
LNE	3.9919	0.0024	4.0002	0.0038	4.0209	0.0046
VNIIFTRI	3.9961	0.0032	4.0036	0.0031	4.0201	0.0038
PTB	3.9985	0.0024	4.0052	0.0024	4.0225	0,0024

Summary of results of EUROMET 696.  $U$  is the expanded uncertainty with a coverage factor of  $k = 2$ .

## 1 Introduction

The purpose of the EUROMET comparison 696 was to assess the degree of equivalence of the pH measured at LNE, VNIIFTRI and PTB by the primary measurement procedure for pH. The primary measurement procedure for pH is based on the measurement of the potential difference between a platinum hydrogen electrode and a silver/silver chloride reference electrode of an electrochemical cell filled with a selected buffer solution, often called the Harned cell. A conventional procedure makes possible to relate the operation of the Harned cell to the definition of pH, very closely<sup>1</sup>.

The sample chosen for the EUROMET 696 was a phthalate buffer of approximately  $0.05 \text{ mol}\cdot\text{kg}^{-1}$  and ionic strength  $I = 0.0535 \text{ mol}\cdot\text{kg}^{-1}$ . The chemical composition of the sample was nominally the same as that of samples used in the CCQM-K17 key comparison<sup>2</sup> and in a bilateral comparison of 1997<sup>3</sup>.

The second key comparison on pH, CCQM-K17, on a phthalate buffer was organised in 2001 by the CCQM Working group on Electrochemical Analysis. Eleven national metrology institutes participated. The comparison was piloted by the PTB, Germany.

The Laboratoire National d'Essais (LNE), France only set-up a primary measuring system for pH in 2002. Therefore the LNE was not able to take part in a CCQM key comparison on pH. Evaluating the current EUROMET project it should be possible to link the measurement results obtained by LNE to the results of the CCQM-K17..

The results obtained by PTB and VNIIFTRI in the present comparison allow estimation of the progress in pH measurements on the primary level in both institutes.

## 2 Participants

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<sup>1</sup> R. P. Buck (CHAIRMAN), S. Rondinini (Secretary), A. K. Covington (Editor), F. G. K. Baucke, C. M. A. Brett, M. F. Camões, M. J. T. Milton, T. Mussini, R. Naumann, K. W. Pratt, P. Spitzer, and G. S. Wilson, Measurement of pH. Definition, standards, and procedures (IUPAC Recommendations 2002) Pure Appl. Chem., Vol. 74, No. 11, pp. 2169–2200, 2002.

<sup>2</sup> <http://kcdb.bipm.org/>, Report of CCQM-K17

<sup>3</sup> N.N. Zdorikov, O.V. Karpov, L.I. Kopaneva, I.I. Maximov, E.E. Seiku, V. V. Sobol and P. Spitzer, Comparison of the primary methods for pH measurement of the VNIIFTRI and the PTB, Metrologia, 1998, 35, 781-782

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### 3 Time schedule

Distribution of samples:	30 January 2003
Deadline for results:	15 April 2003
Draft report:	30 May 2003

### 4 Sample

The sample was a phthalate buffer, potassium hydrogen phthalate,  $0,05 \text{ mol}\cdot\text{kg}^{-1} \text{ KHC}_8\text{H}_4\text{O}_4$ ,  $\text{pH} \sim 4,01$  at  $25 \text{ }^\circ\text{C}$ . A batch of 10 kg solution was prepared from PTB CRM PHT 00/00 and distributed in 1L HDPE bottles by PTB. Each participant received three bottles of buffer solution together with the technical protocol and an Excel spreadsheet for reporting results. Only the total mass of the sample and the amount of water in the sample were given to the participants. The shipment of the samples was performed at the same time.

The electrolytic conductivity of the water for preparation was  $0.5 \text{ }\mu\text{S}\cdot\text{cm}^{-1}$ . The hydrochloric acid and the sodium chloride needed for the measurements was not provided but individual laboratory material of stated high quality was used in the comparison. The between bottle homogeneity of the batch was tested by PTB in measuring the pH of two randomly selected bottles. No significant difference was observed ( $\Delta\text{pH} < 0.0005$ ).

The sample arrived at LNE and at VNIIFTRI without damage. No significant mass deviation above 0,1 g was observed compared to the bottle mass reported by PTB.

In the EUROMET 696 comparison as well as in the CCQM-K17 and in the bilateral comparison PTB-VNIIFTRI the molality of the potassium hydrogen phthalate buffer was about  $0.05 \text{ mol}\cdot\text{kg}^{-1}$ . The ionic strength of the samples at all measurement temperatures was  $I = 0.0535 \text{ mol}\cdot\text{kg}^{-1}$ .

The NIST SRM K 84 used in the CCQM comparison has not been certified for pH but for titrimetry. The CRM PTB PHT 00/00 prepared from potassium hydrogen phthalate A112365 from Merck was certified for pH by PTB. For the bilateral comparison the potassium hydrogen phthalate was synthesised by the VNIIFTRI.

### 5 Principle of measurement

The primary method for pH has been described in the CCQM Working Document on  $\text{pH}^4$  and in the report of CCQM-K9<sup>5</sup>. The participants calculated the measurement uncertainty according to the GUM<sup>6</sup>. The measurements are carried out at  $15 \text{ }^\circ\text{C}$ ,  $25 \text{ }^\circ\text{C}$  and  $37 \text{ }^\circ\text{C}$ .

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<sup>4</sup> Working Documents of the 6<sup>th</sup> CCQM Meeting, BIPM, Paris, April 2000

<sup>5</sup> <http://kcdb.bipm.org/> Report of CCQM-K9

<sup>6</sup> Guide of Expression of Uncertainty in Measurement, 1993, ISO, Geneva

## 5.1. Values used for calculation

As recommended in the technical protocol all participants used the following values for the constants in their calculations.

Faraday constant,  $F = 96\,485.3415(39) \text{ C mol}^{-1}$

Gas constant,  $R = 8.314\,472(15) \text{ J}\cdot\text{mol}^{-1} \text{ K}^{-1}$

Source: 1998 CODATA recommended values<sup>7</sup>

Mean activity coefficient  $\gamma_{\pm}$  of hydrochloric acid at a molality of ( $m_{\text{HCl}} = 0.01 \text{ mol}\cdot\text{kg}^{-1}$ )<sup>8</sup>

15°C 0.9060

25°C 0.9042

37°C 0.9020 (interpolated from the values given at 35°C and 40°C)

Debye-Hückel constant  $A$ <sup>9</sup>

15°C 0.5026

25°C 0.5108

37°C 0.5215 (interpolated from the values given at 35°C and 38°C)

## 5.2. Experimental details

The experimental details are summarized in table 2.

The design of the Harned cell (cell I) was very similar for all participants of EUROMET 696. The vertical cell consisted of two connected chambers for the platinum hydrogen and the silver/silver chloride electrode and of a three-stage humidifier in which the hydrogen gas was saturated with water vapour.

For measuring in phthalate buffer platinized electrodes are not suitable as the phthalate is reduced on the platinum surface. Instead the platinum electrodes were coated with palladium black.

## 5.3. Date of measurement

The acronyms of the participants in the EUROMET project 696 are listed together with the date of measurement and the sample identification number in table 1.

Participant	Date of Measurement	Sample
LNE	11, 13, 18 February 03	5, 6, 7
VNIIFTRI	17 –21 March 03	8, 9,10
PTB	27 January 03	1, 2, 3

Table 1. Sample identification and date of measurement for EUROMET 696

<sup>7</sup> <http://physics.nist.gov/cuu/Constants/index.html>

<sup>8</sup> according to: Bates RG, Robinson RA (1980) J Solution Chem. 9:455

<sup>9</sup> according to: OIML Recommendation R 54 (1980)

Participant	HCl			NaCl, added to the buffer	Cell design
	Molality determined by	Molality, $m_{\text{HCl}}$ $\text{mol}\cdot\text{kg}^{-1}$	Standard uncertainty, $u$ $\text{mol}\cdot\text{kg}^{-1}$		
LNE	Argentometric titration / potentiometric endpoint determination of 0.1 $\text{mol}\cdot\text{kg}^{-1}$ , high-precision gravimetric method	0.01000	$3.75 \cdot 10^{-6}$	0.005, 0.01, 0.015, 0.02	150
VNIIFTRI	Coulometric ( $\text{H}^+$ ) titration.	0.01003	$1.3 \cdot 10^{-5}$	0.005, 0.01, 0.015, 0.02	150
PTB	Coulometric ( $\text{H}^+$ ) titration.	0.01005	$1 \cdot 10^{-5}$	0.005, 0.01, 0.015 (3)	90

Table 2. Summary of experimental details of EUROMET 696

## 6 Results

The results at three different temperatures together with the associated expanded uncertainties  $U$  ( $k=2$ ) reported by the participants are reported in table 3. The individual results of the acidity function,  $p_a$ , at different chloride molalities are illustrated in figure 1 to 3. The pH values are shown in figures 4 to 6. For comparison figure 7 illustrating the results of CCQM-K17 at 25 °C is included in the report. All participants in EUROMET 696 supplied full uncertainty budgets. The standard uncertainties reported by the participants for the acidity function at the smallest amount of added chloride,  $u(p_a)$ , for the standard potential difference,  $u(E^0)$ , for the hydrochloric acid molality,  $u(m_{\text{HCl}})$ , and for the acidity function at zero molality,  $u(\text{intercept})$ , together with the values of the intercept and the slope are summarized in table 4.

The comparison demonstrates with one exception at 15 °C the comparability of measurement results within the uncertainties stated by the participants. The uniformity of the results is better at 25 °C and 37 °C than at 15 °C. At 15 °C only the uncertainties stated by VNIIFTRI and PTB and VNIIFTRI and LNE overlap.

Temperature in °C	15		25		37	
Participants	pH	$U$ (pH)	pH	$U$ (pH)	pH	$U$ (pH)
LNE	3.9919	0.0024	4.0002	0.0038	4.0209	0.0046
VNIIFTRI	3.9961	0.0032	4.0036	0.0031	4.0201	0.0038
PTB	3.9985	0.0024	4.0052	0.0024	4.0225	0,0024

Table 3. Summary of results of EUROMET 696.  $U$  is the expanded uncertainty with a coverage factor of  $k = 2$ .

Participant	$u(m_{\text{HCL}})$ , $\text{mol}\cdot\text{kg}^{-1}$	$u(E^0)$ , V	$u(\text{pa at } m_{\text{Cl}} = 0.005$ $\text{mol}\cdot\text{kg}^{-1})$	Intercept at $m_{\text{Cl}} = 0$	$u$ (intercept)	Slope
Measurement temperature $T = 15$ °C						
LNE	$3.8\cdot 10^{-6}$	$6.6\cdot 10^{-5}$	0.0011	4.0782	$3.8\cdot 10^{-4}$	-0.55
VNIIFTRI	$1.3\cdot 10^{-5}$	$6.8\cdot 10^{-5}$	0.0014	4.0824	$8.7\cdot 10^{-4}$	-0.61
PTB	$1.0\cdot 10^{-5}$	$5.2\cdot 10^{-5}$	0.0011	4.0848	$8.7\cdot 10^{-4}$	-0.74
Measurement temperature $T = 25$ °C						
LNE	$3.8\cdot 10^{-6}$	$8.6\cdot 10^{-5}$	0.0013	4.0881	$1.3\cdot 10^{-3}$	-0.66
VNIIFTRI	$1.3\cdot 10^{-5}$	$7.0\cdot 10^{-5}$	0.0013	4.0913	$7.9\cdot 10^{-4}$	-0.67
PTB	$1.0\cdot 10^{-5}$	$5.4\cdot 10^{-5}$	0.0011	4.0929	$3.3\cdot 10^{-4}$	-0.73
Measurement temperature $T = 37$ °C						
LNE	$3.8\cdot 10^{-6}$	$1.4\cdot 10^{-4}$	0.0018	4.1105	$1.4\cdot 10^{-3}$	-1.09
VNIIFTRI	$1.3\cdot 10^{-5}$	$7.3\cdot 10^{-5}$	0.0013	4.1112	$1.4\cdot 10^{-3}$	-0.72
PTB	$1.0\cdot 10^{-5}$	$5.6\cdot 10^{-5}$	0.0012	4.1120	$6.1\cdot 10^{-4}$	-0.75

Table 4. Intercept and slope of the acidity function  $\text{pa}$  corresponding to zero chloride molality determined by linear extrapolation of the acidity function as a function of the chloride molality; Uncertainties reported by the participants.

## 6.1. Link to CCQM-K17

Two of three participants in the EUROMET project 696, PTB and VNIIFTRI, also participated in the CCQM- K17 key comparison on pH. The PTB acts as pilot laboratory in both comparisons. To link the results obtained by LNE in the EUROMET comparison to CCQM-K17 the performance of PTB within its uncertainty is assumed to be similar in both cases. Therefore it is assumed that the bias between the PTB results and the key comparison reference value (KCRV) remains constant over both comparisons.

The degree of equivalence for LNE,  $D_{\text{LNE}}$ , is calculated from the degree of equivalence of PTB in CCQM-K17,  $D_{\text{PTB(K17)}}$ , and from the degree of equivalence,  $D_{\text{PTB, LNE}}$ , between PTB and LNE in the EUROMET 696 comparison according to the equations (1) and (2):

$$D_{\text{LNE}} = D_{\text{PTB(K17)}} + D_{\text{PTB, LNE}} \quad (1)$$

$$D_{\text{PTB, LNE}} = \text{pH}_{\text{LNE(EUROMET)}} - \text{pH}_{\text{PTB(EUROMET)}} \quad (2)$$

The expanded uncertainties ( $k=2$ ) of the degree of equivalence of LNE,  $U_{\text{LNE(K17)}}$ , is calculated from key comparison reference value for CCQM-K17,  $u_{\text{R(K17)}}$ , and uncertainty of LNE in the EUROMET 696 (with additional uncertainty contribution  $u_{\text{PTB(EUROMET)}}$ ),  $u_{\text{LNE}}$ , according to the equations (3) and (4):

$$U_{\text{LNE(K17)}} = 2\sqrt{u_{\text{LNE}}^2 + u_{\text{R(K17)}}^2} \quad (3)$$

$$u_{\text{LNE}} = \sqrt{u_{\text{PTB(EUROMET)}}^2 + u_{\text{LNE(EUROMET)}}^2} \quad (4)$$

Summary of results of the degree of equivalence of LNE in the EUROMET 696 are presented in the table 5.

t, °C	$D_{\text{PTB(K17)}}$	$U_{\text{PTB(K17)}}$	$D_{\text{PTB,LNE}}$	$D_{\text{LNE}}$	$u_{\text{R(K17)}}$	$u_{\text{PTB}}$ (EUROMET)	$u_{\text{LNE}}$ (EUROMET)	$u_{\text{LNE}}$	$U_{\text{LNE(K17)}}$
15	0.0007	0.0028	-0.0066	-0.0059	0.00089	0.0012	0.0012	0.0017	0.0038
25	0.0012	0.0031	-0.0050	-0.0038	0.00109	0.0012	0.0019	0.0022	0.0049
37	0.0017	0.0039	-0.0016	0.0001	0.00125	0.0012	0.0024	0.0027	0.0059

Table 5. Summary of results for the degree of equivalence of LNE

Figure 8 illustrates the new line of data included for LNE in the graph of the equivalence statement of CCQM-K17 at 25 °C.

## 6.2. Link to the bilateral comparison PTB-VNIIFTRI

In 1997 for the phthalate buffer the deviation between the pH values measured at the VNIIFTRI and the PTB was  $\Delta\text{pH} = 0.005$  at 25°C. In the current EUROMET comparison the deviation at 25 °C is only  $\Delta\text{pH} = 0.002$ . As follow from table 6, this study illustrates also an improvement of reliability of parallel results of pH measurement at the same type of standard solution.

Temperature, °C	Bilateral comparison		CCQM-K17		EUROMET 696	
	PTB	VNIIFTRI	PTB	VNIIFTRI	PTB	VNIIFTRI
15	-	-	4.0100 ± 0.0022	4.0130 ± 0.0026	3.9985 ± 0.0024	3.9961 ± 0.0032
25	4.002 ± 0.003	4.008 ± 0.005	4.0168 ± 0.0022	4.0193 ± 0.0026	4.0052 ± 0.0024	4.0036 ± 0.0031
37	-	-	4.0360 ± 0.0030	4.0380 ± 0.0026	4.0225 ± 0.0024	4.0201 ± 0.0038

Table 6. Correlation of pH values for phthalate buffer solution measured by PTB and VNIIFTRI

## 7 Figures

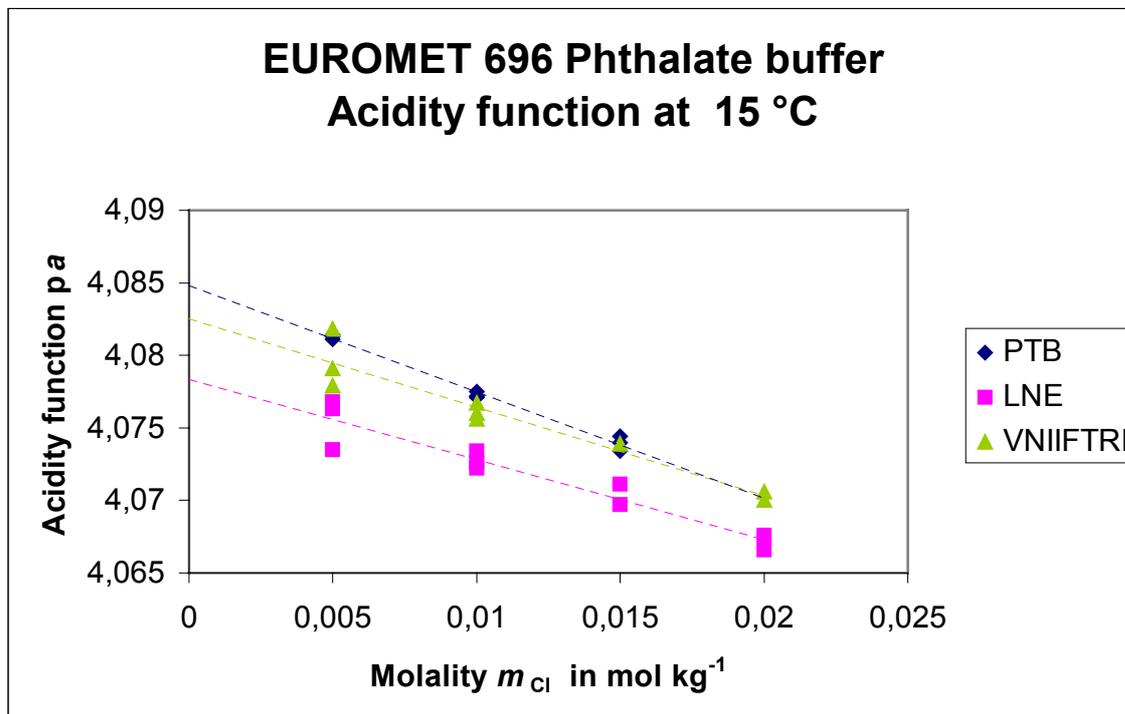


Figure 1. Individual results of the acidity function at different molalities of chloride. The dotted lines are the linear regression lines. Measurement temperature 15 °C.

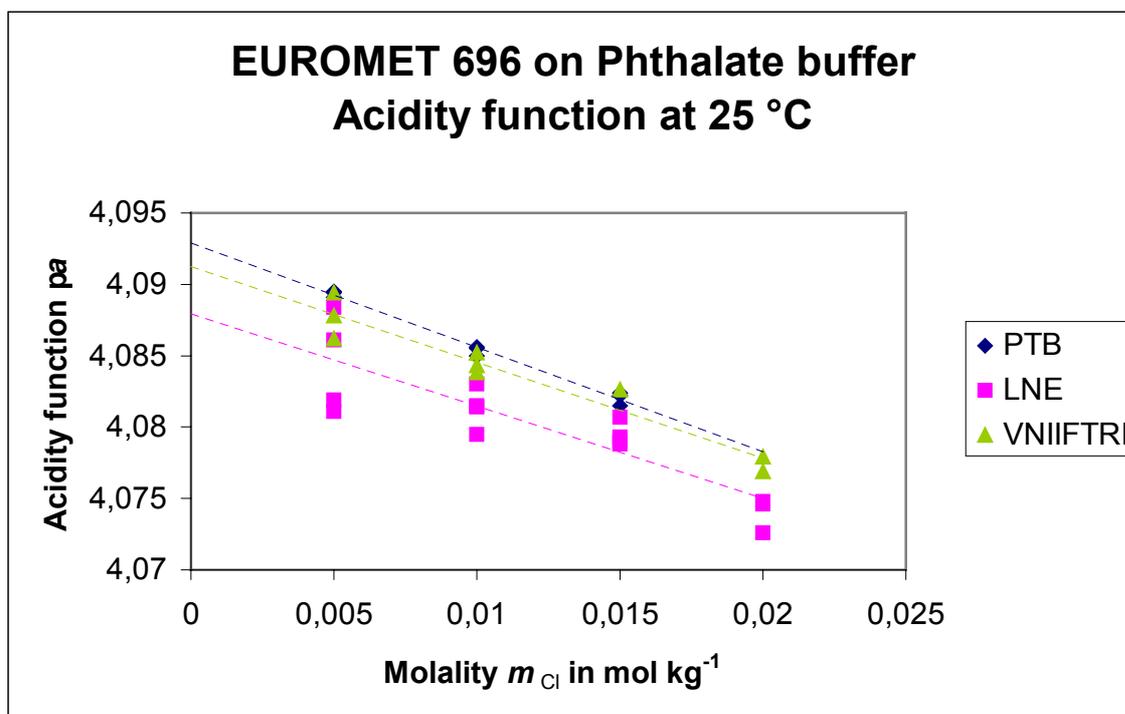


Figure 2. Individual results of the acidity function at different molalities of chloride. The dotted lines are the linear regression lines. Measurement temperature 25 °C.

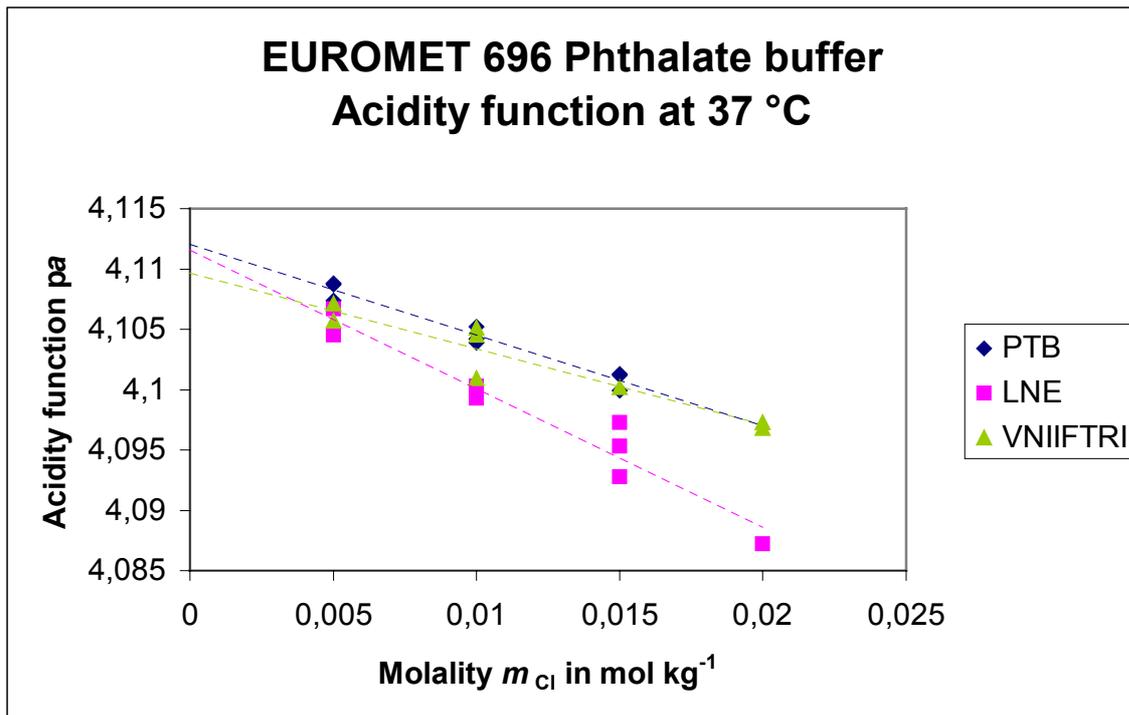


Figure 3. Individual results of the acidity function at different molalities of chloride. The dotted lines are the linear regression lines. Measurement temperature 37 °C.

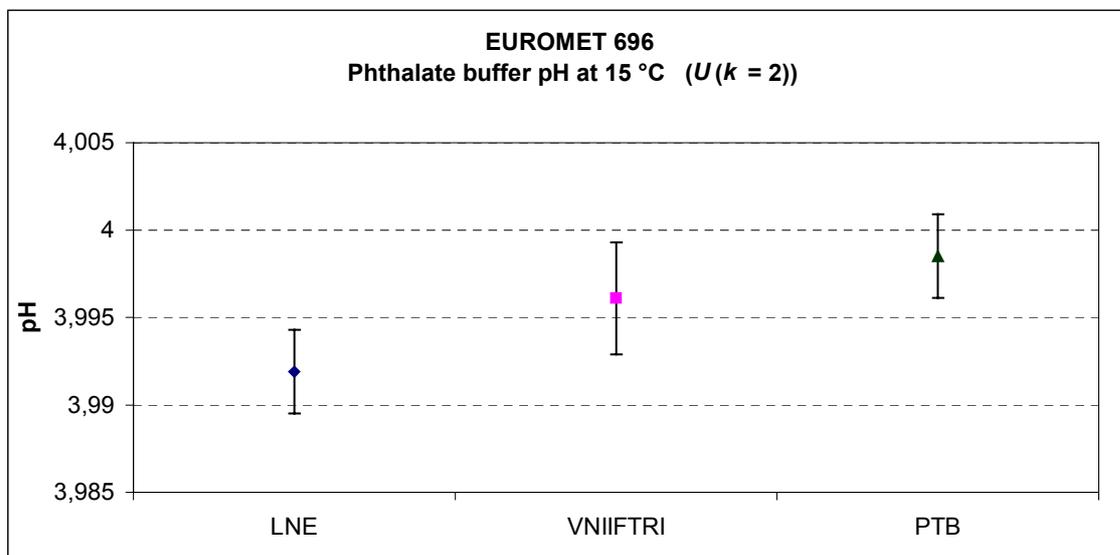


Figure 4. Individual results. pH of the phthalate buffer at 15 °C.

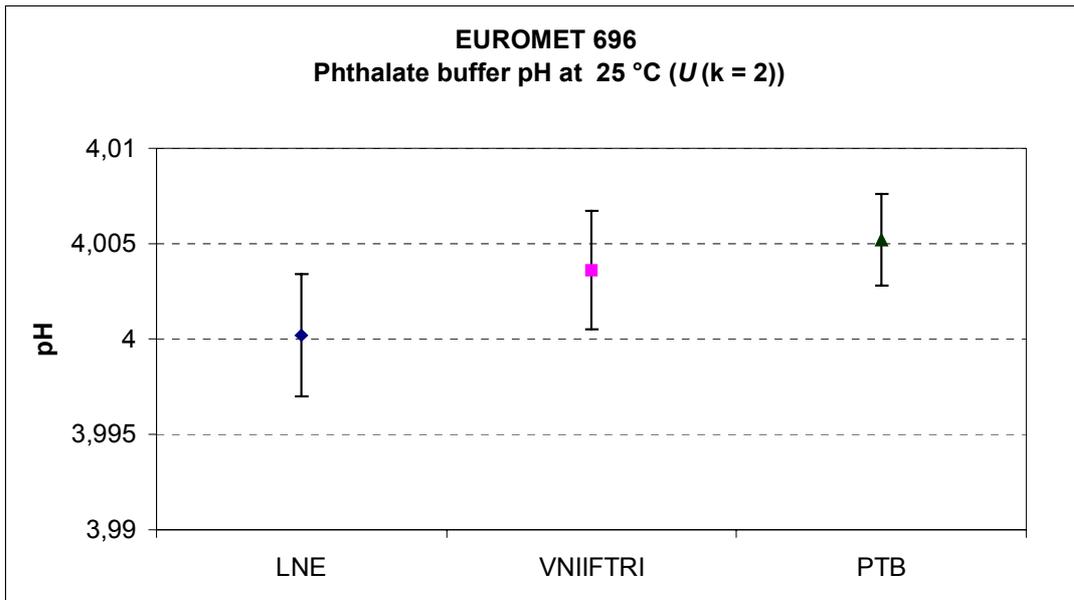


Figure 5. Individual results. pH of the phthalate buffer at 25 °C.

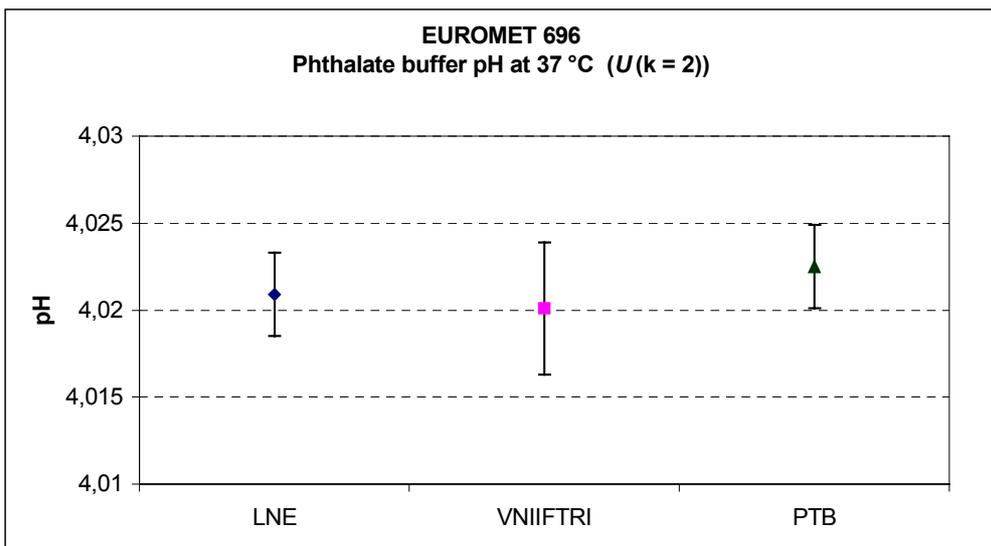


Figure 6. pH of the phthalate buffer at 37 °C.

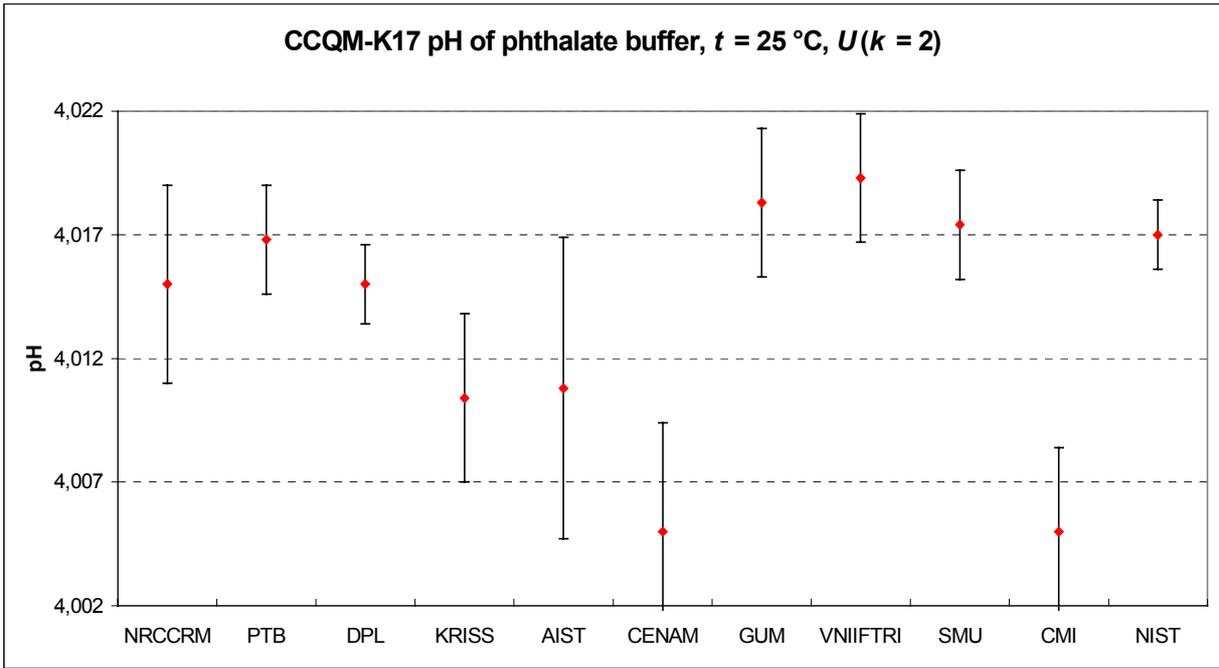


Figure 7. Results obtained by the participants in the key comparison CCQM-K17 on phthalate buffer at 25 °C. The scatter of the pH axis is the same as for figure 4 to 6 illustrating the results of the EUROMET comparison 696.

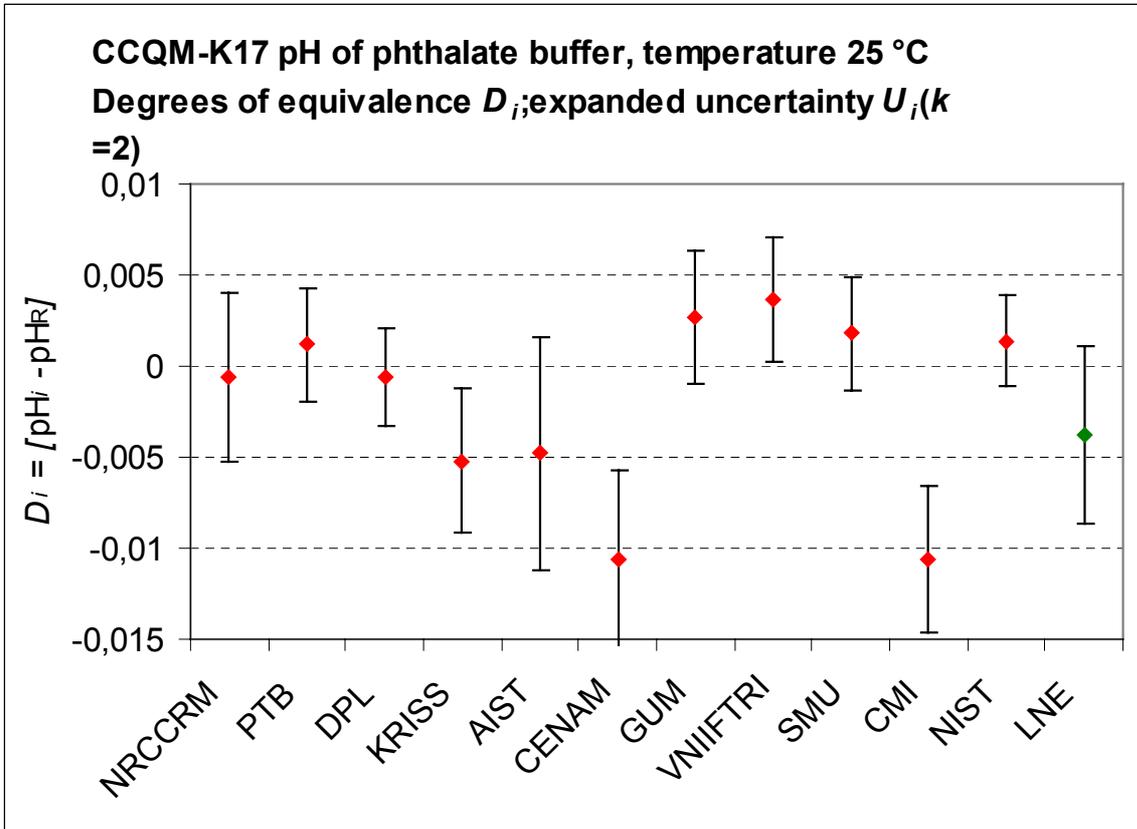


Figure 8. A new line of data included for LNE in the graph of equivalence of CCQM-K17.

## 7 Conclusion

The trilateral comparison between PTB, Germany, LNE, France and VNIIFTRI, Russia, the EUROMET project 696, has demonstrated the capability of the participants to measure the pH of a phthalate buffer by the primary measurement procedure for pH.

Good agreement of the reported results was observed. The sample was very similar to the one used in the comparison CCQM-K17 and in a bilateral comparison between PTB and VNIIFTRI in 1995. The pH values obtained in the EUROMET comparison overlap at the same order as observed for those participants in CCQM-K17 who have a long experience in pH measurement on the primary level.

The PTB was pilot laboratory in both comparisons. Therefore it should be possible to link the result obtained by LNE in the EUROMET project 696 to CCQM-K17. Assuming a similar performance of PTB within its uncertainty in both exercises the result of PTB in CCQM-K17 can act as a link between the comparisons. In this way it is possible to include a new line for LNE in the table of equivalence and in the graphs of CCQM-K17.

Compared to the results obtained in the 1997 bilateral comparison between PTB and VNIIFTRI the degree of equivalence of the pH values obtained is clearly improved from  $\Delta\text{pH} = 0.005$  in 1997 to  $\Delta\text{pH} = 0.002$  in 2003, both at 25 °C.

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