

Sample 2 Key comparison CCQM-K9

MEASURAND : pH value of phosphate buffer
sample 2: 0.02 mol kg⁻¹ KH₂PO₄ + 0.02 mol kg⁻¹ Na₂HPO₄
 measurements at 15 °C, 25 °C and 37 °C

NOMINAL VALUE: pH = 6.9 at 25 °C

pH_i: result of measurement carried out by laboratory *i*

u_i: combined standard uncertainty (*k* = 1) of pH_i

Lab <i>i</i> ↓	Temperature / °C						Date of measurement
	15		25		37		
	pH _i	u _i	pH _i	u _i	pH _i	u _i	
NRCCRM	6.9232	0.0020	6.8886	0.0020	6.8635	0.0020	99-12
PTB	6.9259	0.0011	6.8914	0.0011	6.8673	0.0011	99-11
DPL	6.9265	0.0008	6.8923	0.0008	6.8695	0.0008	99-10
KRISS	6.9217	0.0008	6.8877	0.0008	6.8643	0.0008	99-11
NIMC	6.9352	0.0043	6.8933	0.0042	6.8655	0.0037	99-12
CENAM	6.9362	0.0055	6.9066	0.0065	6.8745	0.0055	99-11
GUM	6.9233	0.0009	6.8903	0.0008	6.8648	0.0011	99-12
VNIIFTRI	6.9272	0.0019	6.8936	0.0018	6.8665	0.0019	99-10
SMU	6.9192	0.0010	6.8846	0.0010	6.8605	0.0010	00-02
NIST	6.9295	0.0013	6.8941	0.0021	6.8707	0.0015	99-11
SMU discovered a calculation error. The erroneous result is used for computing the degrees of equivalence involving SMU. The result is corrected before it is used for evaluating the key comparison reference value.							
SMU corrected	6.9242	0.0009	6.8896	0.0009	6.8657	0.0009	00-02

Key comparison CCQM-K9

MEASURAND : pH value of phosphate buffer
sample 2: 0.02 mol kg⁻¹ KH₂PO₄ + 0.02 mol kg⁻¹ Na₂HPO₄
measurements at 5 °C, 10 °C, 20 °C, 30 °C, 40 °C, 45 °C and 50 °C

NOMINAL VALUE: pH = 6.9 at 25 °C

pH_i: result of measurement carried out by laboratory *i*

u_i: combined standard uncertainty (*k* = 1) of pH_i

Lab <i>i</i> ↓	Temperature / °C								Date of measurement
	5		10		20		30		
	pH _i	u _i	pH _i	u _i	pH _i	u _i	pH _i	u _i	
PTB	6.9770	0.0015	6.9490	0.0015	6.9068	0.0011	6.8790	0.0011	99-11
KRISS	6.9733	0.0008	6.9450	0.0008	6.9028	0.0008	6.8757	0.0008	99-11
GUM	6.9776	0.0010	6.9480	0.0008	6.9047	0.0011	6.8771	0.0008	99-12
VNIIFTRI	6.9787	0.0019	6.9509	0.0019	6.9074	0.0018	6.8797	0.0018	99-10

Lab <i>i</i> ↓	Temperature / °C						Date of measurement
	40		45		50		
	pH _i	u _i	pH _i	u _i	pH _i	u _i	
PTB	6.8631	0.0015	6.8605	0.0015	6.8596	0.0015	99-11
DPL			6.8629	0.0008			99-10
KRISS	6.8611	0.0008	6.8578	0.0008	6.8570	0.0008	99-11
GUM	6.8607	0.0011	6.8566	0.0009	6.8530	0.0011	99-12
VNIIFTRI	6.8619	0.0019	6.8559	0.0020	6.8569	0.0018	99-10

Key comparison CCQM-K9

MEASURAND : pH value of phosphate buffer
sample 2: 0.02 mol kg⁻¹ KH₂PO₄ + 0.02 mol kg⁻¹ Na₂HPO₄
all temperatures

NOMINAL VALUE: pH = 6.9 at 25 °C

The key comparison reference value, pH_R , is obtained as the variance-weighted mean of the results from the participants.
The standard uncertainty, u_R , of pH_R is calculated according to the external consistency concept (see page 11 of Final Report).

Temperature / °C	15	25	37
pH_R	6.9248	6.8905	6.8667
u_R	0.0009	0.0007	0.0008

Temperature / °C	5	10	20	30
pH_R	6.9756	6.9471	6.9046	6.8771
u_R	0.0013	0.0011	0.0010	0.0008

Temperature / °C	40	45	50
pH_R	6.8614	6.8592	6.8563
u_R	0.0009	0.0013	0.0013

The degree of equivalence of each laboratory with respect to the reference value is given by a pair of terms:

$$D_i = (pH_i - pH_R) \text{ and } U_i, \text{ its expanded uncertainty } (k = 2), U_i = 2(u_i^2 + u_R^2)^{1/2}.$$

Note: this gives a conservative estimate of U_i .

The degree of equivalence between two laboratories is given by a pair of terms:

$$D_{ij} = D_i - D_j = pH_i - pH_j \text{ and } U_{ij}, \text{ its expanded uncertainty } (k = 2), U_{ij} = 2(u_i^2 + u_j^2)^{1/2}.$$

Key comparison CCQM-K9

MEASURAND : pH value of phosphate buffer, sample 2: 0.02 mol kg⁻¹ KH₂PO₄ + 0.02 mol kg⁻¹ Na₂HPO₄

NOMINAL VALUE: pH = 6.9 at 25 °C

Temperature: 15 °C Lab j →

Lab i ↓			NRCCRM		PTB		DPL		KRISS		NIMC		CENAM		GUM		VNIIFTRI		SMU		NIST	
	D _i	U _i	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}
NRCCRM	-0.0016	0.0044			-0.0027	0.0046	-0.0033	0.0043	0.0015	0.0043	-0.0120	0.0095	-0.0130	0.0117	-0.0001	0.0044	-0.0040	0.0055	0.0040	0.0045	-0.0063	0.0048
PTB	0.0011	0.0028	0.0027	0.0046			-0.0006	0.0027	0.0042	0.0027	-0.0093	0.0089	-0.0103	0.0112	0.0026	0.0028	-0.0013	0.0044	0.0067	0.0030	-0.0036	0.0034
DPL	0.0017	0.0023	0.0033	0.0043	0.0006	0.0027			0.0048	0.0023	-0.0087	0.0087	-0.0097	0.0111	0.0032	0.0024	-0.0007	0.0041	0.0073	0.0026	-0.0030	0.0031
KRISS	-0.0031	0.0023	-0.0015	0.0043	-0.0042	0.0027	-0.0048	0.0023			-0.0135	0.0087	-0.0145	0.0111	-0.0016	0.0024	-0.0055	0.0041	0.0025	0.0026	-0.0078	0.0031
NIMC	0.0104	0.0088	0.0120	0.0095	0.0093	0.0089	0.0087	0.0087	0.0135	0.0087			-0.0010	0.0140	0.0119	0.0088	0.0080	0.0094	0.0160	0.0088	0.0057	0.0090
CENAM	0.0114	0.0111	0.0130	0.0117	0.0103	0.0112	0.0097	0.0111	0.0145	0.0111	0.0010	0.0140			0.0129	0.0111	0.0090	0.0116	0.0170	0.0112	0.0067	0.0113
GUM	-0.0015	0.0025	0.0001	0.0044	-0.0026	0.0028	-0.0032	0.0024	0.0016	0.0024	-0.0119	0.0088	-0.0129	0.0111			-0.0039	0.0042	0.0041	0.0027	-0.0062	0.0032
VNIIFTRI	0.0024	0.0042	0.0040	0.0055	0.0013	0.0044	0.0007	0.0041	0.0055	0.0041	-0.0080	0.0094	-0.0090	0.0116	0.0039	0.0042			0.0080	0.0043	-0.0023	0.0046
SMU	-0.0056	0.0026	-0.0040	0.0045	-0.0067	0.0030	-0.0073	0.0026	-0.0025	0.0026	-0.0160	0.0088	-0.0170	0.0112	-0.0041	0.0027	-0.0080	0.0043			-0.0103	0.0033
NIST	0.0047	0.0031	0.0063	0.0048	0.0036	0.0034	0.0030	0.0031	0.0078	0.0031	-0.0057	0.0090	-0.0067	0.0113	0.0062	0.0032	0.0023	0.0046	0.0103	0.0033		

Temperature: 25 °C Lab j →

Lab i ↓			NRCCRM		PTB		DPL		KRISS		NIMC		CENAM		GUM		VNIIFTRI		SMU		NIST	
	D _i	U _i	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}	D _{ij}	U _{ij}
NRCCRM	-0.0019	0.0042			-0.0028	0.0046	-0.0037	0.0043	0.0009	0.0043	-0.0047	0.0093	-0.0180	0.0136	-0.0017	0.0043	-0.0050	0.0054	0.0040	0.0045	-0.0055	0.0058
PTB	0.0009	0.0026	0.0028	0.0046			-0.0009	0.0027	0.0037	0.0027	-0.0019	0.0087	-0.0152	0.0132	0.0011	0.0027	-0.0022	0.0042	0.0068	0.0030	-0.0027	0.0047
DPL	0.0018	0.0021	0.0037	0.0043	0.0009	0.0027			0.0046	0.0023	-0.0010	0.0086	-0.0143	0.0131	0.0020	0.0023	-0.0013	0.0039	0.0077	0.0026	-0.0018	0.0045
KRISS	-0.0028	0.0021	-0.0009	0.0043	-0.0037	0.0027	-0.0046	0.0023			-0.0056	0.0086	-0.0189	0.0131	-0.0026	0.0023	-0.0059	0.0039	0.0031	0.0026	-0.0064	0.0045
NIMC	0.0028	0.0085	0.0047	0.0093	0.0019	0.0087	0.0010	0.0086	0.0056	0.0086			-0.0133	0.0155	0.0030	0.0086	-0.0003	0.0091	0.0087	0.0086	-0.0008	0.0094
CENAM	0.0161	0.0131	0.0180	0.0136	0.0152	0.0132	0.0143	0.0131	0.0189	0.0131	0.0133	0.0155			0.0163	0.0131	0.0130	0.0135	0.0220	0.0132	0.0125	0.0137
GUM	-0.0002	0.0021	0.0017	0.0043	-0.0011	0.0027	-0.0020	0.0023	0.0026	0.0023	-0.0030	0.0086	-0.0163	0.0131			-0.0033	0.0039	0.0057	0.0026	-0.0038	0.0045
VNIIFTRI	0.0031	0.0039	0.0050	0.0054	0.0022	0.0042	0.0013	0.0039	0.0059	0.0039	0.0003	0.0091	-0.0130	0.0135	0.0033	0.0039			0.0090	0.0041	-0.0005	0.0055
SMU	-0.0059	0.0024	-0.0040	0.0045	-0.0068	0.0030	-0.0077	0.0026	-0.0031	0.0026	-0.0087	0.0086	-0.0220	0.0132	-0.0057	0.0026	-0.0090	0.0041			-0.0095	0.0047
NIST	0.0036	0.0044	0.0055	0.0058	0.0027	0.0047	0.0018	0.0045	0.0064	0.0045	0.0008	0.0094	-0.0125	0.0137	0.0038	0.0045	0.0005	0.0055	0.0095	0.0047		

Key comparison CCQM-K9

MEASURAND : pH value of phosphate buffer, sample 2: 0.02 mol kg⁻¹ KH₂PO₄ + 0.02 mol kg⁻¹ Na₂HPO₄
 NOMINAL VALUE: pH = 6.9 at 25 °C

Temperature: 37 °C Lab j →

Lab i ↓			NRCCRM		PTB		DPL		KRISS		NIMC		CENAM		GUM		VNIIFTRI		SMU		NIST	
	<i>D_i</i>	<i>U_i</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
NRCCRM	-0.0032	0.0043			-0.0038	0.0046	-0.0060	0.0043	-0.0008	0.0043	-0.0020	0.0084	-0.0110	0.0117	-0.0013	0.0046	-0.0030	0.0055	0.0030	0.0045	-0.0072	0.0050
PTB	0.0006	0.0027	0.0038	0.0046			-0.0022	0.0027	0.0030	0.0027	0.0018	0.0077	-0.0072	0.0112	0.0025	0.0031	0.0008	0.0044	0.0068	0.0030	-0.0034	0.0037
DPL	0.0028	0.0022	0.0060	0.0043	0.0022	0.0027			0.0052	0.0023	0.0040	0.0076	-0.0050	0.0111	0.0047	0.0027	0.0030	0.0041	0.0090	0.0026	-0.0012	0.0034
KRISS	-0.0024	0.0022	0.0008	0.0043	-0.0030	0.0027	-0.0052	0.0023			-0.0012	0.0076	-0.0102	0.0111	-0.0005	0.0027	-0.0022	0.0041	0.0038	0.0026	-0.0064	0.0034
NIMC	-0.0012	0.0076	0.0020	0.0084	-0.0018	0.0077	-0.0040	0.0076	0.0012	0.0076			-0.0090	0.0133	0.0007	0.0077	-0.0010	0.0083	0.0050	0.0077	-0.0052	0.0080
CENAM	0.0078	0.0111	0.0110	0.0117	0.0072	0.0112	0.0050	0.0111	0.0102	0.0111	0.0090	0.0133			0.0097	0.0112	0.0080	0.0116	0.0140	0.0112	0.0038	0.0114
GUM	-0.0019	0.0027	0.0013	0.0046	-0.0025	0.0031	-0.0047	0.0027	0.0005	0.0027	-0.0007	0.0077	-0.0097	0.0112			-0.0017	0.0044	0.0043	0.0030	-0.0059	0.0037
VNIIFTRI	-0.0002	0.0041	0.0030	0.0055	-0.0008	0.0044	-0.0030	0.0041	0.0022	0.0041	0.0010	0.0083	-0.0080	0.0116	0.0017	0.0044			0.0060	0.0043	-0.0042	0.0048
SMU	-0.0062	0.0025	-0.0030	0.0045	-0.0068	0.0030	-0.0090	0.0026	-0.0038	0.0026	-0.0050	0.0077	-0.0140	0.0112	-0.0043	0.0030	-0.0060	0.0043			-0.0102	0.0036
NIST	0.0040	0.0034	0.0072	0.0050	0.0034	0.0037	0.0012	0.0034	0.0064	0.0034	0.0052	0.0080	-0.0038	0.0114	0.0059	0.0037	0.0042	0.0048	0.0102	0.0036		

Temperature: 5 °C Lab j →

Lab i ↓			PTB		KRISS		GUM		VNIIFTRI	
	<i>D_i</i>	<i>U_i</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
PTB	0.0014	0.0040			0.0037	0.0034	-0.0006	0.0036	-0.0017	0.0048
KRISS	-0.0023	0.0031	-0.0037	0.0034			-0.0043	0.0026	-0.0054	0.0041
GUM	0.0020	0.0033	0.0006	0.0036	0.0043	0.0026			-0.0011	0.0043
VNIIFTRI	0.0031	0.0046	0.0017	0.0048	0.0054	0.0041	0.0011	0.0043		

Key comparison CCQM-K9

MEASURAND : pH value of phosphate buffer, sample 2: 0.02 mol kg⁻¹ KH₂PO₄ + 0.02 mol kg⁻¹ Na₂HPO₄
 NOMINAL VALUE: pH = 6.9 at 25 °C

Temperature: 10 °C

Lab <i>i</i>	<i>D_i</i>		<i>U_i</i>		PTB		KRISS		GUM		VNIIFTRI	
	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
PTB	0.0019	0.0037					0.0040	0.0034	0.0010	0.0034	-0.0019	0.0048
KRISS	-0.0021	0.0027	-0.0040	0.0034					-0.0030	0.0023	-0.0059	0.0041
GUM	0.0009	0.0027	-0.0010	0.0034	0.0030	0.0023					-0.0029	0.0041
VNIIFTRI	0.0038	0.0044	0.0019	0.0048	0.0059	0.0041	0.0029	0.0041				

Temperature: 20 °C

Lab <i>i</i>	<i>D_i</i>		<i>U_i</i>		PTB		KRISS		GUM		VNIIFTRI	
	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
PTB	0.0022	0.0030					0.0040	0.0027	0.0021	0.0031	-0.0006	0.0042
KRISS	-0.0018	0.0026	-0.0040	0.0027					-0.0019	0.0027	-0.0046	0.0039
GUM	0.0001	0.0030	-0.0021	0.0031	0.0019	0.0027					-0.0027	0.0042
VNIIFTRI	0.0028	0.0041	0.0006	0.0042	0.0046	0.0039	0.0027	0.0042				

Temperature: 30 °C

Lab <i>i</i>	<i>D_i</i>		<i>U_i</i>		PTB		KRISS		GUM		VNIIFTRI	
	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
PTB	0.0019	0.0027					0.0033	0.0027	0.0019	0.0027	-0.0007	0.0042
KRISS	-0.0014	0.0023	-0.0033	0.0027					-0.0014	0.0023	-0.0040	0.0039
GUM	0.0000	0.0023	-0.0019	0.0027	0.0014	0.0023					-0.0026	0.0039
VNIIFTRI	0.0026	0.0039	0.0007	0.0042	0.0040	0.0039	0.0026	0.0039				

Key comparison CCQM-K9

MEASURAND : pH value of phosphate buffer, **sample 2: 0.02 mol kg⁻¹ KH₂PO₄ + 0.02 mol kg⁻¹ Na₂HPO₄**
 NOMINAL VALUE: pH = 6.9 at 25 °C

Temperature: 40 °C

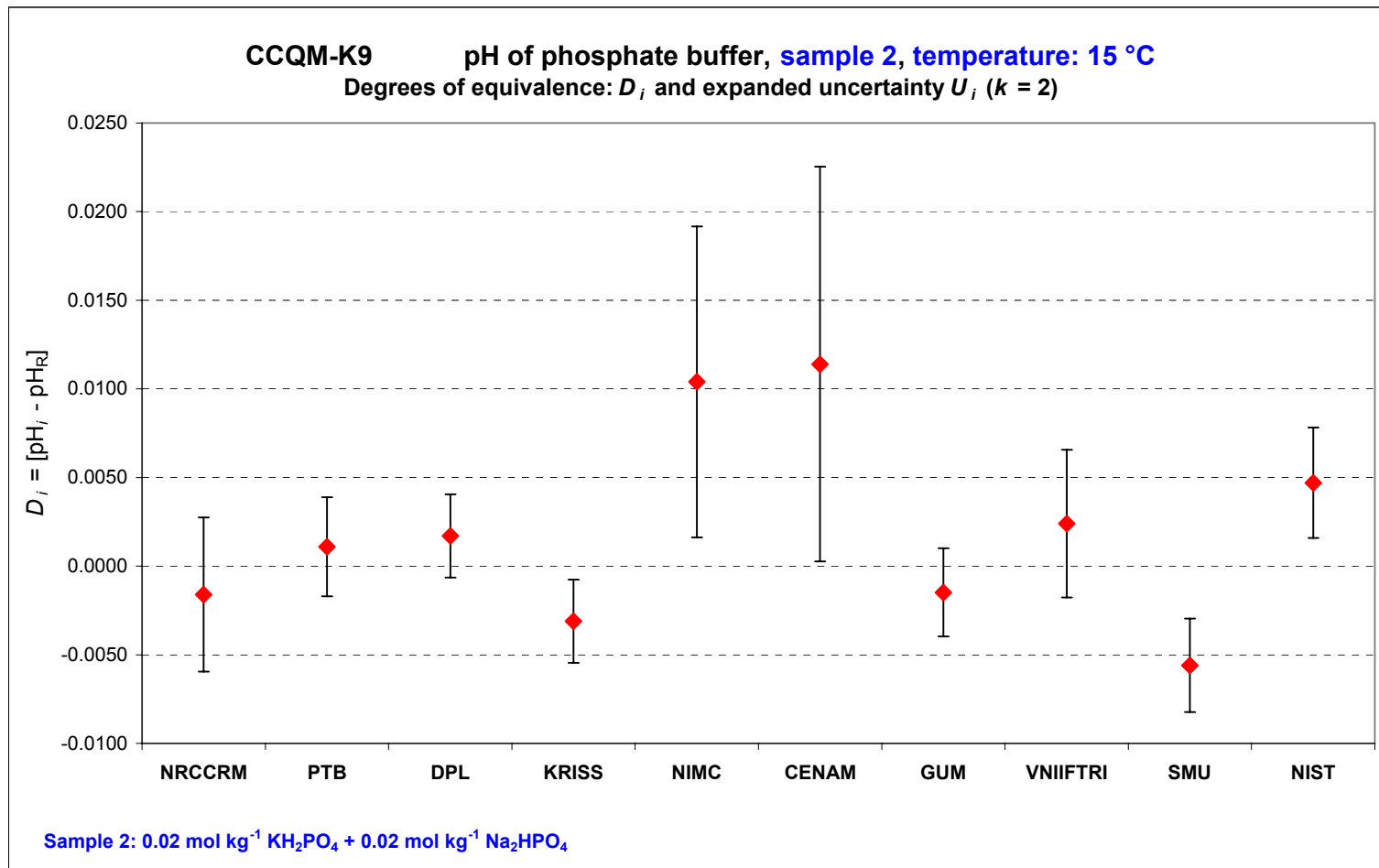
Lab <i>i</i>	<i>D_i</i>		<i>U_i</i>		PTB		KRISS		GUM		VNIIFTRI	
	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
PTB	0.0017	0.0035					0.0020	0.0034	0.0024	0.0037	0.0012	0.0048
KRISS	-0.0003	0.0024	-0.0020	0.0034					0.0004	0.0027	-0.0008	0.0041
GUM	-0.0007	0.0028	-0.0024	0.0037	-0.0004	0.0027					-0.0012	0.0044
VNIIFTRI	0.0005	0.0042	-0.0012	0.0048	0.0008	0.0041	0.0012	0.0044				

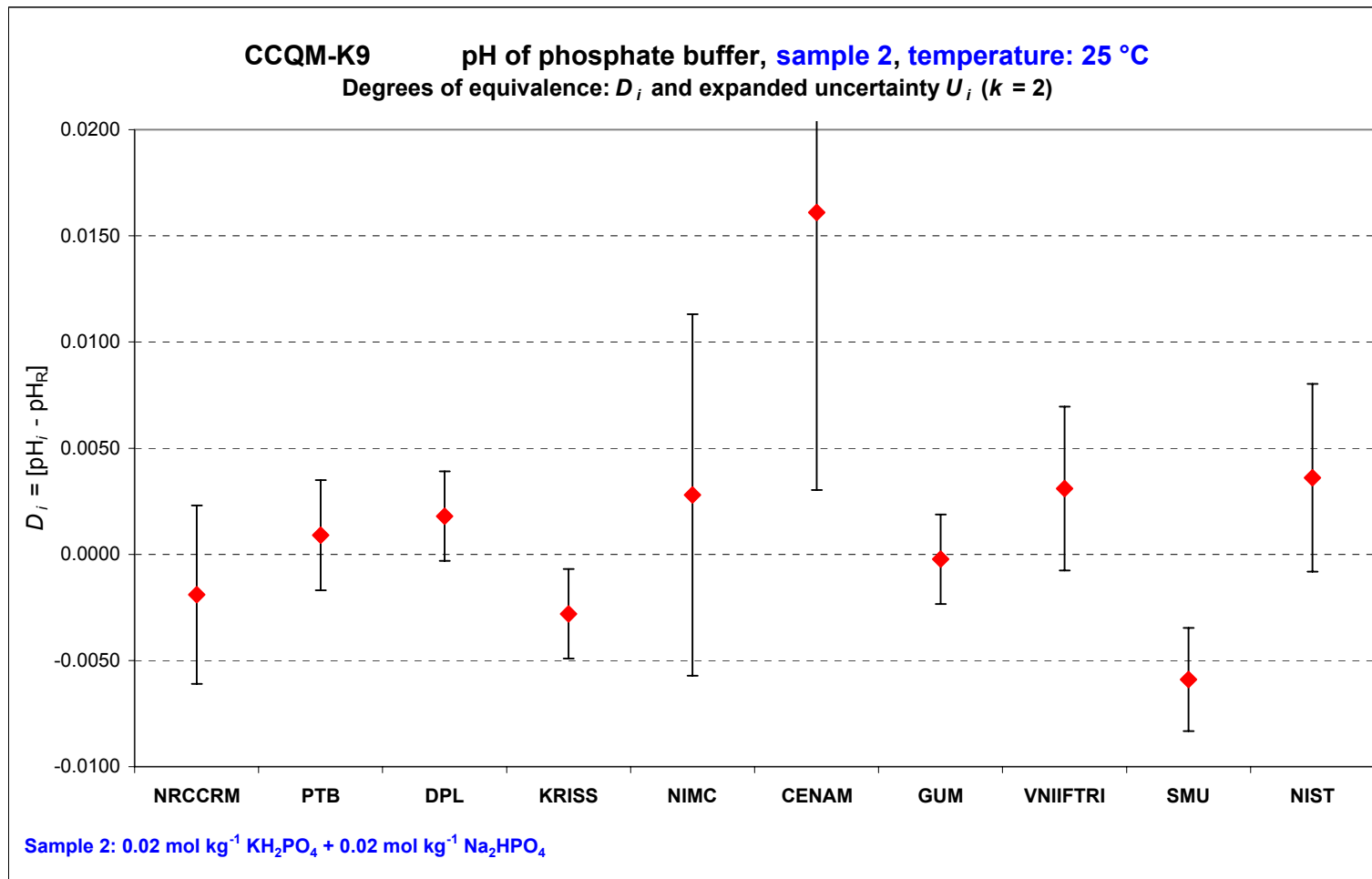
Temperature: 45 °C

Lab <i>i</i>	<i>D_i</i>		<i>U_i</i>		PTB		DPL		KRISS		GUM		VNIIFTRI	
	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
PTB	0.0013	0.0040					-0.0024	0.0034	0.0027	0.0034	0.0039	0.0035	0.0046	0.0050
DPL	0.0037	0.0031	0.0024	0.0034					0.0051	0.0023	0.0063	0.0024	0.0070	0.0043
KRISS	-0.0014	0.0031	-0.0027	0.0034	-0.0051	0.0023					0.0012	0.0024	0.0019	0.0043
GUM	-0.0026	0.0032	-0.0039	0.0035	-0.0063	0.0024	-0.0012	0.0024					0.0007	0.0044
VNIIFTRI	-0.0033	0.0048	-0.0046	0.0050	-0.0070	0.0043	-0.0019	0.0043	-0.0007	0.0044				

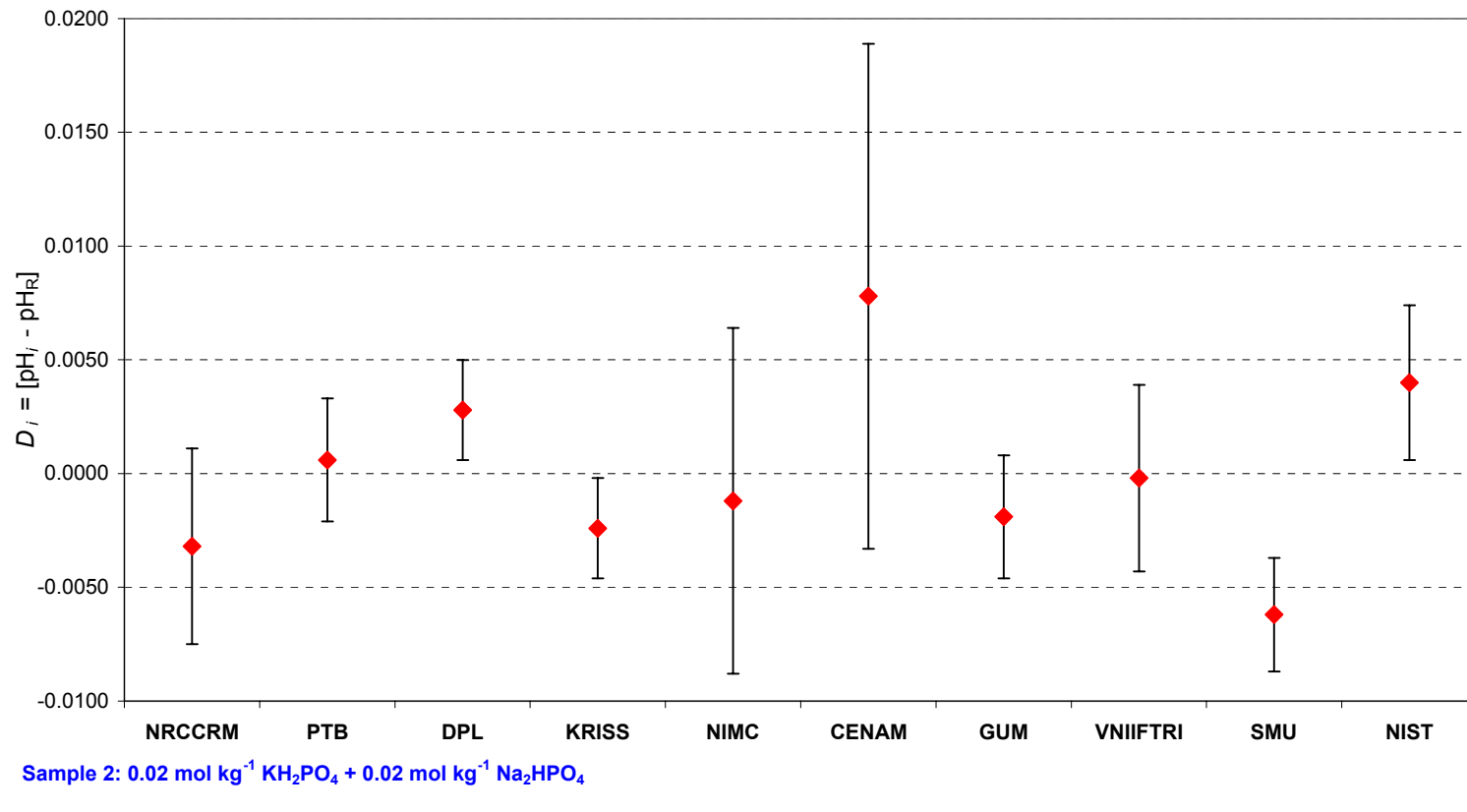
Temperature: 50 °C

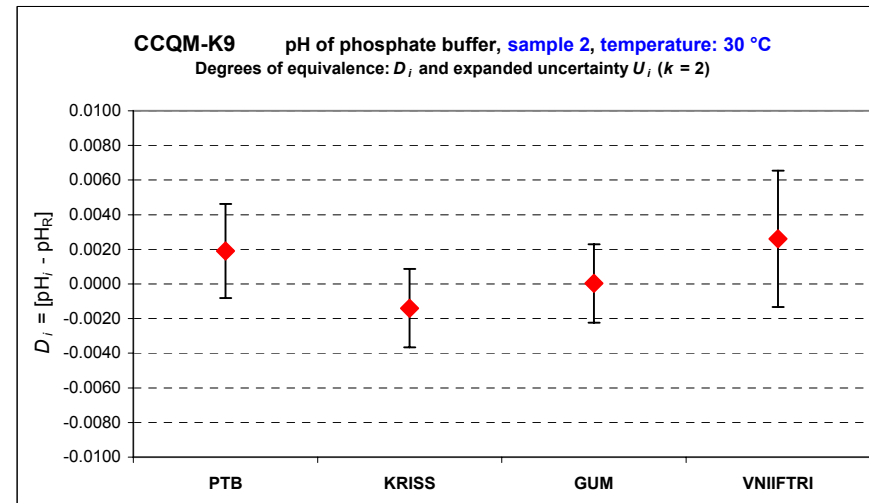
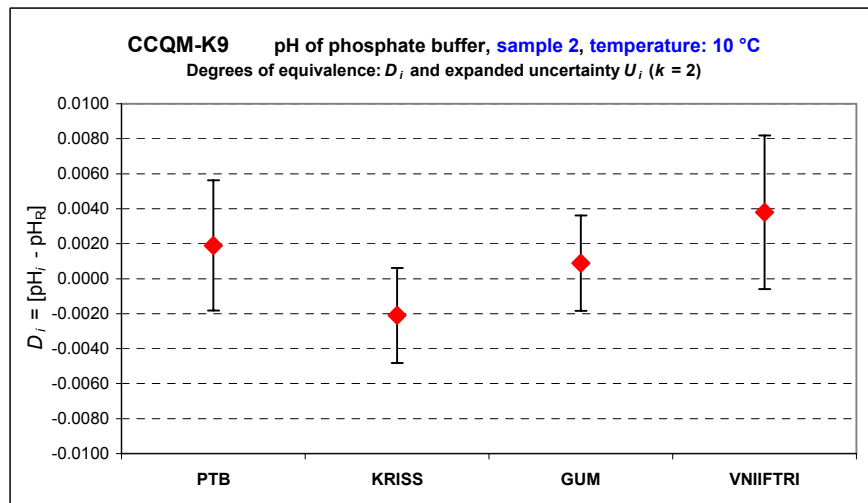
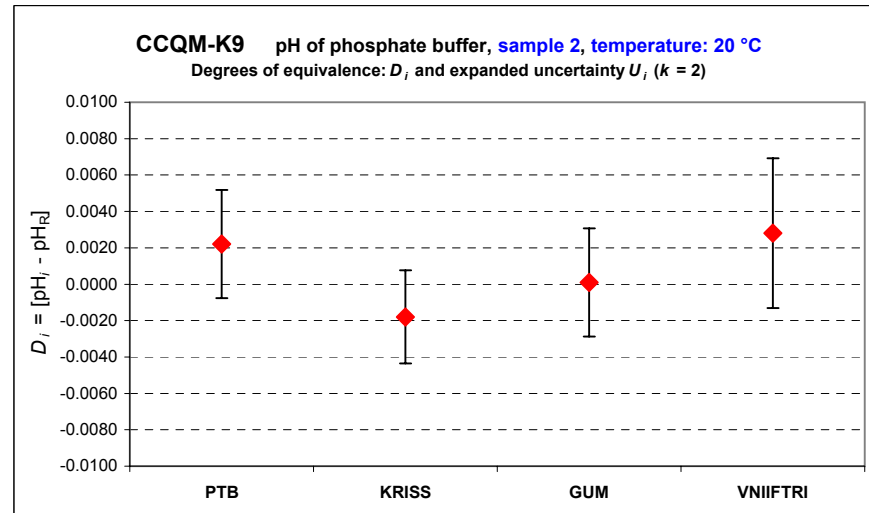
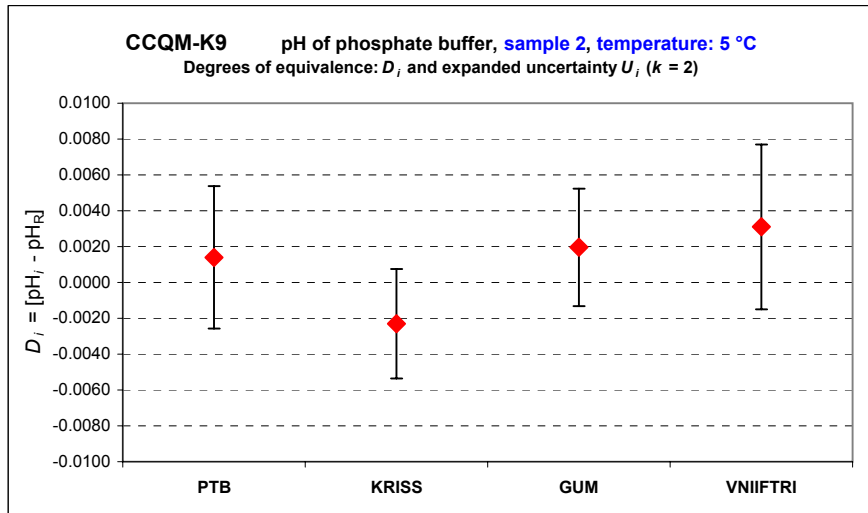
Lab <i>i</i>	<i>D_i</i>		<i>U_i</i>		PTB		KRISS		GUM		VNIIFTRI	
	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>	<i>D_{ij}</i>	<i>U_{ij}</i>
PTB	0.0033	0.0040					0.0026	0.0034	0.0066	0.0037	0.0027	0.0047
KRISS	0.0007	0.0031	-0.0026	0.0034					0.0040	0.0027	0.0001	0.0039
GUM	-0.0033	0.0034	-0.0066	0.0037	-0.0040	0.0027					-0.0039	0.0042
VNIIFTRI	0.0006	0.0044	-0.0027	0.0047	-0.0001	0.0039	0.0039	0.0042				



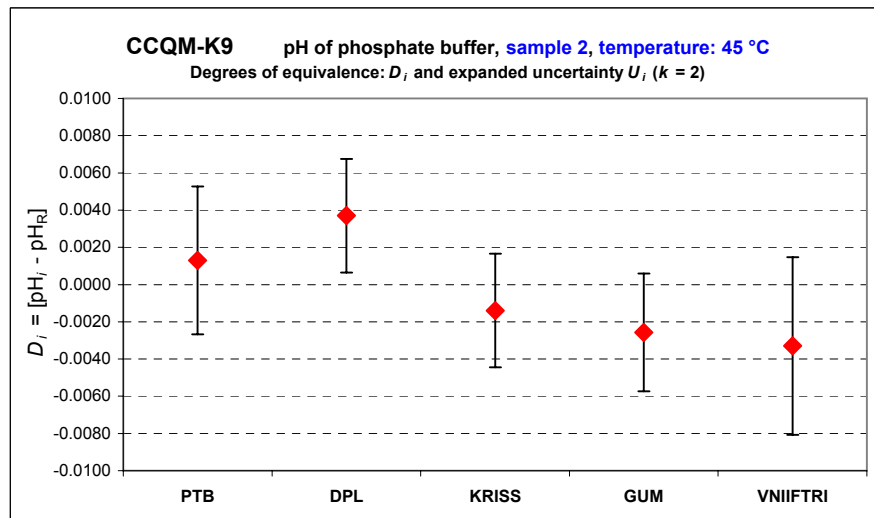
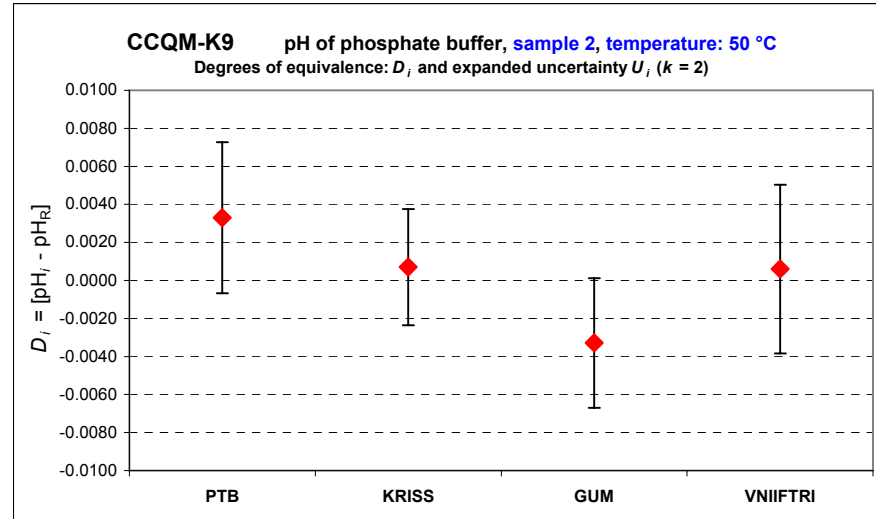
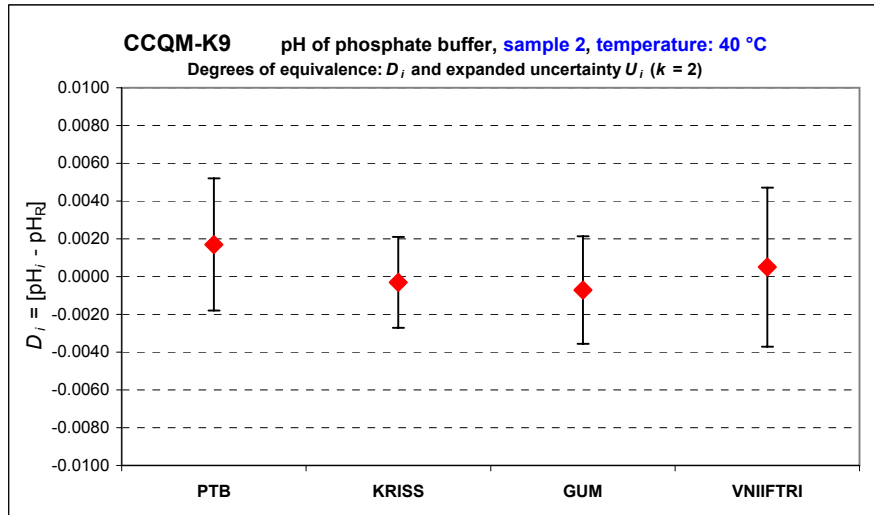


CCQM-K9 pH of phosphate buffer, **sample 2, temperature: 37 °C**
Degrees of equivalence: D_i and expanded uncertainty U_i ($k = 2$)





Sample 2: $0.02 \text{ mol kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{HPO}_4$



Sample 2: $0.02 \text{ mol kg}^{-1} \text{ KH}_2\text{PO}_4 + 0.02 \text{ mol kg}^{-1} \text{ Na}_2\text{HPO}_4$