CCQM WG on Electrochemical Analysis and Classical Chemical Methods
CCQM-K91.2022 Key Comparison on Phthalate Buffer
Technical Protocol

Purpose

This key comparison is being performed to evaluate the degree of equivalence of national standard measurement procedures for the measurement of pH of phthalate buffer solutions under the umbrella of the CIPM-MRA.

The comparison is a repetition of the key comparison CCQM-K91 from 2011.

The comparison is open to the National Metrology Institutes (NMI) or Designated Institutes (DI) of member or associate states of the Meter Convention. Only one result per institute (per temperature) is accepted. No measurement method is prescribed for the comparison, but it is expected that the highest-level method at each institute is used. Only independent results, obtained by the primary method, will be used to calculate the Key Comparison Reference Value (KCRV).

This comparison measurements of pH will be performed at 15 °C, 25 °C, 37 °C and optionally at 5 °C and 50 °C.

Time schedule

Oral invitation:	April 2022 at EAWG web meeting
Written invitation:	June 2022
Registration deadline:	15 July 2022
Dispatch of samples:	March 2023
Reporting deadline:	30 June 2023
Presentation of results:	EAWG autumn meeting 2023
Draft A report:	October 2023
Discussion of Draft A report:	via e-mail until December 2023
Draft B report:	January 2024
Approval of draft B report:	EAWG spring meeting 2024

Description of sample

The phthalate buffer solution with pH around ~ 4.01 at 25 °C will be prepared from deionized water and potassium hydrogen phthalate ($KHC_8H_4O_4$) dried at 110 °C for 2 h and then stored over a desiccant. The mass fraction of water in the solution will be given on the bottle label.

The homogeneity of the solution will be checked before shipment and the stability will be determined throughout the measurement period by Harned cell measurements

Each participant will receive 1 L high density polyethylene (HDPE) bottles which are numbered and sealed in aluminized plastic bags. The number of bottles received by each participant will be:

- For Participants using the primary (Harned cell) method: 2 bottles

- For Participants using a secondary method: 1 bottle

Shipment to all participants will be done at the same time by courier. The tracking information will be emailed to the contact people. The contents are described as “Non-hazardous aqueous solution” and the value is given as 1 EUR.

Hydrochloric acid and chloride ion sources will not be provided. It is recommended to dry the alkali chloride at no less than 400 °C for at least 2 hours and then store it over a desiccant prior to use.

Actions at receipt of the sample

- Inspect the received box, bags and bottles for visible damage or leakage.
- If damage is found, report the problems you have encountered to the coordinating laboratory, by email as soon as possible. If no damage is found, place the bottle in the bag and close the bag with tape. Store the bottle until the measurements at ambient conditions 25 °C ± 5 °C.
- Confirm the sample receipt by email to the coordinating laboratory.
- Report the weighing data to the coordinating laboratory as soon as the data are available.

    Allow the bottles to equilibrate in the weighing laboratory for two days before performing the weighing. Remove the aluminized plastic bag immediately before weighing. Do neither remove the tape nor the label from the bottles. Use 1000 kg m^{-3} for the density of the bottles filled with sample solution.

    Report the weighing result (balance reading) and bottle mass (corrected for air buoyancy) for each bottle in the measurement report (summary sheet). Also report the ambient atmospheric pressure, relative humidity and temperature at the time the bottle was weighed.

Instructions for measurements

- Inspect the bags and bottles and check the integrity again before measurements.

- Participants are requested to measure the buffer solution within four weeks after having received the solution.

- The measurements are performed at 15 °C, 25 °C, 37 °C and, optionally, at 5 °C and 50 °C.

- Recommended values of constants are:

  Molar gas constant, R = 8.314 4626 J mol^{-1} K^{-1}

  Faraday constant, F = 96 485.33212 C mol^{-1}

- The following conditions are used for primary measurements:

  The measurements must be evaluated using the standard pressure of 101 325 Pa.

  The standard potential of the Ag/AgCl electrodes should be determined using hydrochloric acid (aqueous HCl solution) having a molality value close to 0.01 mol kg^{-1}. The actual molality value must be traceable to the SI.

  Alkali chloride (sodium chloride or potassium chloride) should be added to prepare at least three different buffer solutions with molalities in the range of 0.005 mol kg^{-1} to 0.02 mol kg^{-1}.

Reporting

Please fill in the relevant reporting sheet and the relevant reporting form for the type of measurement you have done. These must be sent by email to the coordinating laboratory before the reporting deadline. The coordinating laboratory will confirm the receipt of the report by email to the contact person of the participant no later than two weeks after the receipt. If no confirmation is received, please contact the coordinating laboratory in order to identify the problem. The participants must report standard uncertainties calculated according to the Guide to the Expression of Uncertainty in Measurement (GUM).

The report must contain at least the following information:

  Name, acronym and address of the laboratory performing the measurements

  Name(s) of the analyst(s)

  Date of receipt of solutions

  Identification of the samples measured

  Results from weighing the bottles

  Date(s) of the measurement(s)

  Description of the method used

  Description of the instrumentation, the cell and the electrodes

  Measurement result and its standard uncertainty

  Technical details (depending on the procedure used):

- Primary measurements

  The participants are requested to report the value of the acidity function at zero chloride molality (which is determined from values of the acidity function from several measurements) and the associated standard uncertainties. Those values will be used further in the calculation

of the KCRV and evaluation of degree of equivalence of each participant.

The participants are requested to report also such numerical results as molalities, cell voltages, acidity functions and data for the extrapolation to zero chloride molality including a plot of the acidity function versus the chloride molality.

If several measurements are made, please make copies of the reporting form.

Please give detailed uncertainty budgets for the standard potential of the Ag/AgCl electrodes and for the buffer cell voltage.

Please give an example of the calculations you do to calculate the molality of chloride in the buffer, the corrected voltage in an HCl cell, the standard potential of the Ag/AgCl electrodes, and an individual acidity function value.

- Secondary measurements

Participants performing secondary pH measurements may adapt the template provided for the primary measurements. Alternatively, they might use their own report form. The secondary measurement report form must contain the fundamental information mentioned above.

If you have used the secondary differential potentiometric cell method, information the participants should include would be: an example plot of measured potential difference as a function of time, numerical values of potential difference and temperatures including the respective standard deviations. Please give a detailed uncertainty budget and the source of the traceability.

If you have used the secondary method with a glass electrode, information the participants should include would be: voltages and temperatures including the respective standard deviations for the measurements in standard buffers for calibrating the electrode, a table for reporting the calculated slope, intercept of the calibration function, and a plot of measured voltages as a function of pH for the calibration function. Please give a detailed uncertainty budget and the source of the traceability.

KCRV calculation

The final approval of the key comparison reference value will be agreed upon at the EAWG autumn meeting at the BIPM, Sèvres, presumably held in October 2023.

How Far the Light Shines statement

Phthalate reference buffer solutions are widely used as pH standards in acid range. Participants taking successfully part in the KC CCQM-K91.2022 will demonstrate their capability to measure the pH of primary buffer in the acid range of pH (25°C) = 3.8 to pH = 4.2.

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