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Unified pH measurement

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1 Works for me

Share

dx.doi.org/10.17504/protocols.io.bybxpspnAgnes Heering
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ABSTRACT

The purpose of this document is to present technical guidance of measuring $\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ difference ($\Delta\text{pH}_{\text{abs}}^{\text{H}_2\text{O}}$ value) between two solutions by differential potentiometry in a cell with two compartments connected by a salt bridge filled with an ionic liquid.

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EXTERNAL LINK

<https://analytical.chem.ut.ee/>, uniphied.eu

PROTOCOL CITATION

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KEYWORDS

unified acidity, pHabs, unified pH, pH

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MATERIALS TEXT

The ionic liquid triethylpentylammonium bis(trifluoromethylsulfonyl)imide [N₂₂₂₅][NTf₂] salt bridge has to be used.

RECORD STARTING

Turn on the thermostat and electrometer at least half an hour before starting the work.

Software

- 1 Start Quick IV Measurement Software.

Computer cannot go to sleep during measurements or the communication between computer and instruments is lost and data collection stops.

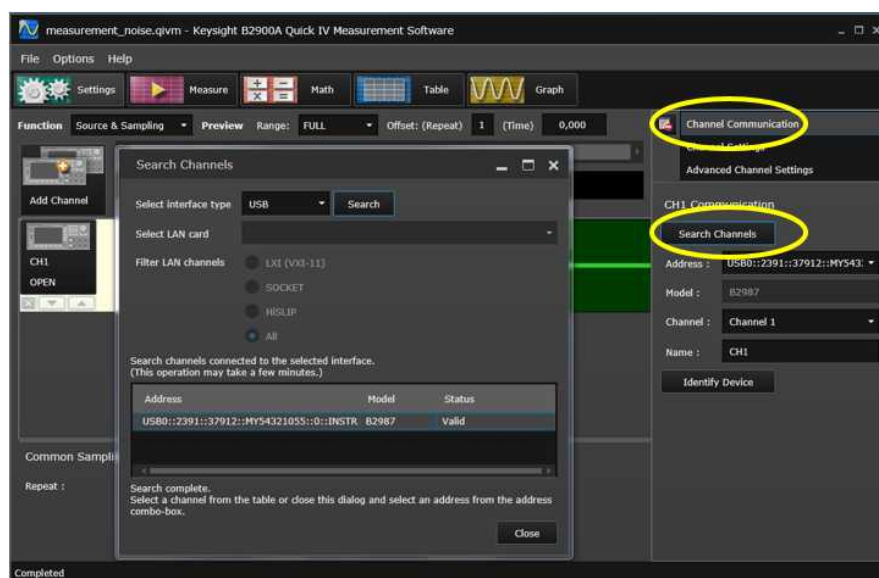
- 2 On the left hand pick Function "Source & Sampling".



Position of the Function choice "Source & Sampling".

Alternatively, open previously saved QIVM file with measurement settings.

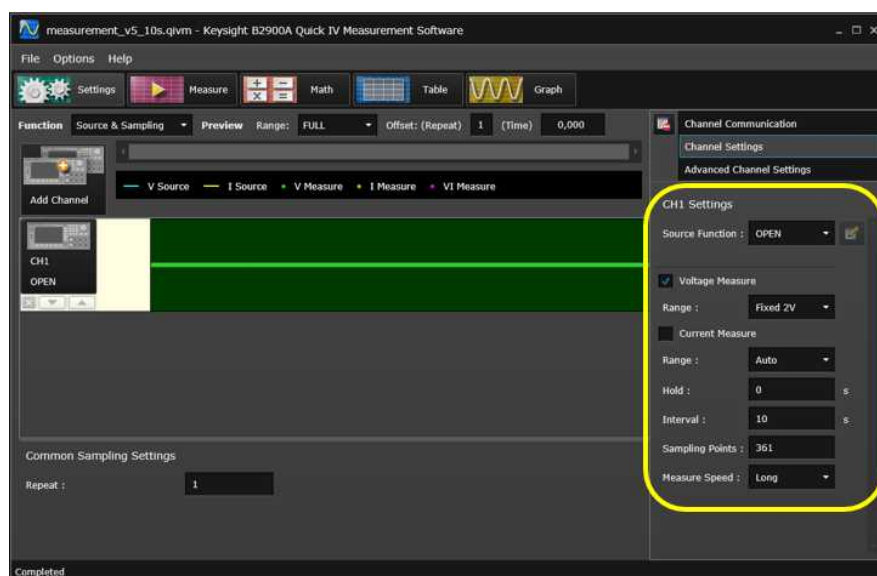
- 3 Right hand side click on tab "Channel Communication". Click on "Search Channels", which opens a new window. Select USB interface and search for the channel. After the search click on the channel name to choose the channel and close the window.



Position of the tabs "Channel Communication" and "Search Channels".

This must be done every time the program is started.

- 4 Settings can be saved as QIVM file, which can be used for measurements. The saved file can be opened under tab "File". The settings will remain the same between the measurements if the program is not closed.



Program settings.

Filling the cell 8m

5



25.0 °C


Cell from Gebr. Rettberg GmbH.

VistaShield
Faraday cage
Gamry VistaShield


UT cell
Special water-jacketed glass cell
Rettberg Glass cell

U2c
Thermostat
MLW U2c

The side ports must be open.

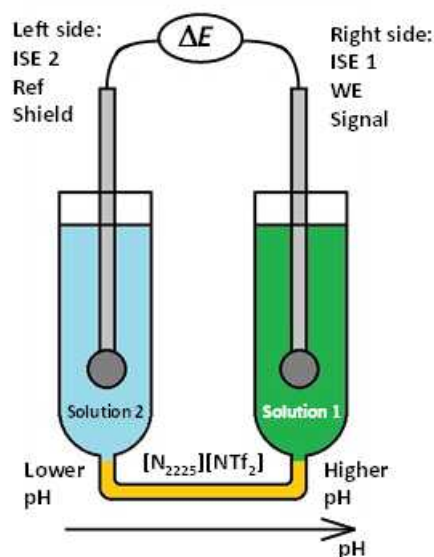
- 6 Fill capillary with a syringe or pipette with the ionic liquid, so that the level of ionic liquid is 1 mm to 2 mm below the ^{2m} bottoms of the measurement compartments.  **0.1 mL**

Ionic liquid has high viscosity, therefore flows very slowly, and can leave a film on the wall of the pipette tip or syringe during dispense.

- 7 The test solutions are added simultaneously to both compartments, raising solution levels in the compartments ^{2m} synchronously.  **20 mL both test solutions**

Equal amount by weight (not volume!) of solutions must be used. The volume of the lighter solution is calculated from the weight of the heavier solution using the densities of the two solutions in hand. This is especially important for solutions containing acetonitrile.

Minimum volume that can be used is 13 mL.



One option how to fill the cell. This configuration gives positive ΔpH values. Figure shows connections to a pH meter, a potentiostat and an electrometer.

8 After adding the test solutions, the air bubbles are removed from the capillary ends with a syringe or a pipette. 2m

9 Insert electrodes one-by-one. 1m

EST-0601
Glass electrode half-cell
Izmeritelnaya tekhnika EST-0601

9.1 Electrode is rinsed with water, gently dried, and then rinsed with solution to be measured. 1m

10 Connect electrodes to the instrument.

B2987A Electrometer / High Resistance
Meter
Electrometer
Keysight B2987A [↗](#)

10.1 Crocodile clips are as following:
red is signal and connects to ISE1,

black is shield and is connected to ISE2 and green is guard. Green stays unused.



Connections to electrodes.

Cable goes through the port in Faraday cage. Electrometer is not in the Faraday cage.

N1415A Triax to Alligator Cable
Cable
Keysight Technologies N1415A [↗](#)

Measurement 1h




- 11 Start the measurement by clicking on the "Measure" button on the upper panel.
- 12 Data collection. Point is taken at 10 s interval.
- 13 Save data. Files are named as Date_ISE1_Solution1_vs_ISE2_solution2.

1h

SAVE THE FILE BEFORE NEW MEASUREMENT! Otherwise, data is lost. Data is given in volts and seconds.

- 13.1 Go to table view, right click on the table, choose "Export as CSV..." and save the results. The data can be automatically imported into excel file while measuring or after (both under "Excel Navigation"), but this causes constant shift in the comma position.

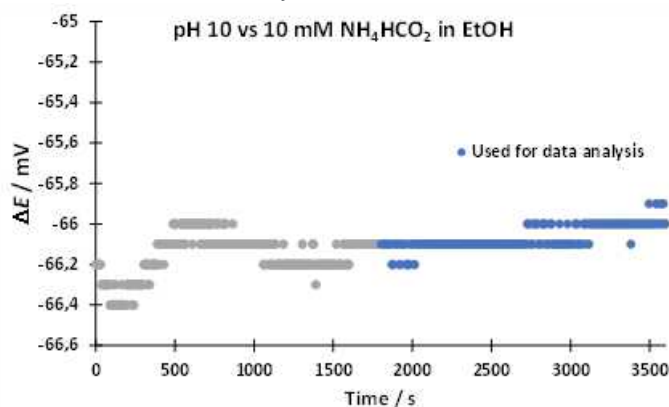
Washing

- | | | |
|----|--|-----|
| 14 | Remove the electrodes, rinse them and put them in storage solution. | 1m |
| 15 | Remove the solutions. | 3m |
| 16 | Rinse the cell with small amount of ethanol  5 mL | 2m |
| 17 | Rinse three times with plenty of water  20 mL each | 10m |
| 18 | Rinse once with acetone to ease the drying.  5 mL | 2m |
| 19 | Dry cell with compressed air. | 2m |

Data analysis

20m

- 20 Points from 30 min to 60 min are used for analysis. Points from 30 min to 60 min are used for analysis. Points from 30 min to 60 min are used for analysis.



Example of a good graph with non-aqueous system.

21 Take the average of the chosen data points.

22 $\Delta pH = \Delta E /$ average slope of the glass electrodes



Calibration of glass electrode half-cells

by Agnes Heering,

University of Tartu

PREVIEW

RUN

22.1 Start Quick IV Measurement Software.

Computer cannot go to sleep during measurements or the communication between computer and instruments is lost and data collection stops.

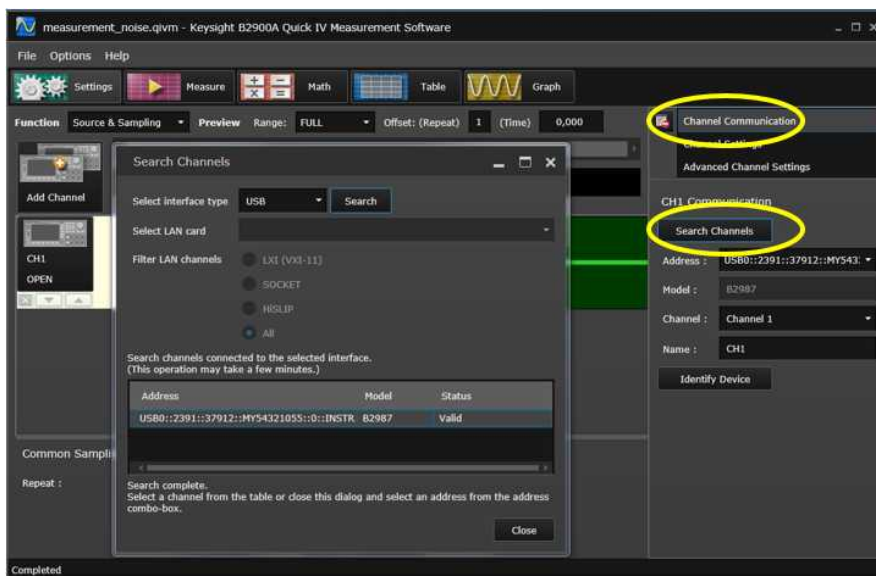
22.2 On the left hand pick Function "Source & Sampling".



Position of the Function choice "Source & Sampling".

Alternatively, open previously saved QIVM file with measurement settings.

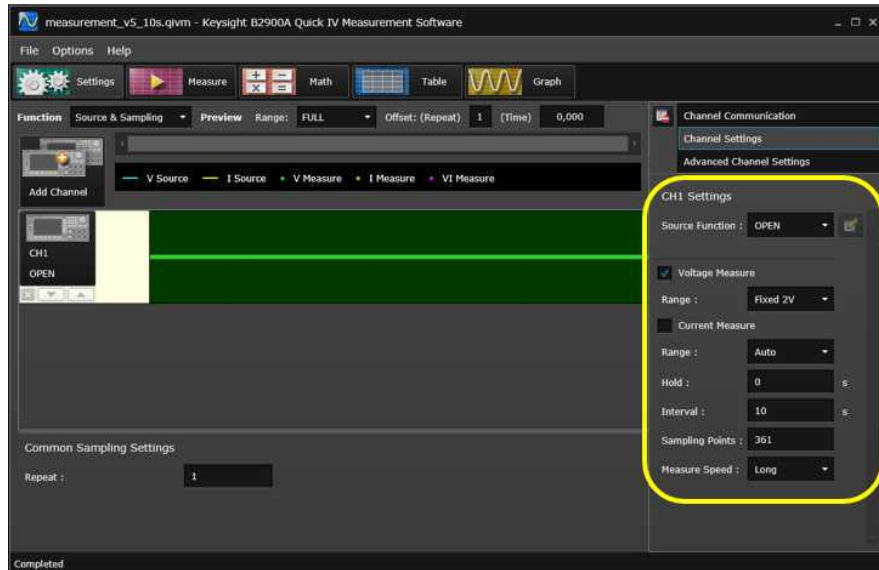
22.3 Right hand side click on tab "Channel Communication". Click on "Search Channels", which opens a new window. Select USB interface and search for the channel. After the search, click on the channel name to choose the channel and close the window.



Position of the tabs "Channel Communication" and "Search Channels".

This must be done every time the program is started.

- 22.4 Settings can be saved as QIVM file, which can be used for measurements. The saved file can be opened under tab "File". The settings will remain the same between the measurements if the program is not closed.



Program settings.

Range is "Fixed 20V" in case of EST-0601 calibration, otherwise it is "Fixed 2V".



25 °C

Special water-jacketed glass cell from Gebr. Rettberg.

UT cell
Special water-jacketed glass cell
Rettberg Glass cell

VistaShield
Faraday cage
Gamry VistaShield

U2c
Thermostat
MLW U2c

The side ports must be open.

A beaker can also be used if temperature is controlled.


22.6 Fill capillary with standard aqueous buffer with pH 7.00.  50 mL 2m

22.7 Insert a glass electrode and a reference electrode. 2m

K401
Calomel reference electrode
Radiometer K401


22.7.1 Electrode is rinsed with water, gently dried, and then rinsed with solution to be measured. 2m

22.8 Connect electrodes to the instrument.

B2987A Electrometer / High Resistance
Meter
Electrometer
Keysight B2987A 

22.8.1 Crocodile clips are as following:
red is signal and connects to the glass electrode,
black is shield and is connected to reference electrode and
green is guard. Green stays unused.

Cable goes through the port in Faraday cage. Electrometer is not in the Faraday cage.

N1415A Triax to Alligator Cable
Cable
Keysight Technologies N1415A 

22.9 Start the measurement by clicking on the "Measure" button on the upper panel.

2.10 Data collection. Point is taken at 10 s interval.

1h

Calibration duration must be the same as later used in pH measurements.

2.11 Save data. Files are named as Date_GE_vs_ref_pHx.

SAVE THE FILE BEFORE NEW MEASUREMENT! Otherwise, data is lost. Data is given in volts and seconds.

22.11.1 Go to table view, right click on the table, choose "Export as CSV..." and save the results. The data can be automatically imported into excel file while measuring or after (both under "Excel Navigation"), but this causes constant shift in the comma position.

2.12 Remove the electrodes.

2.13 Remove the solution.

2.14 Rinse three times with plenty of water  20 mL each

2.15 Rinse once with acetone to ease the drying.  5 mL

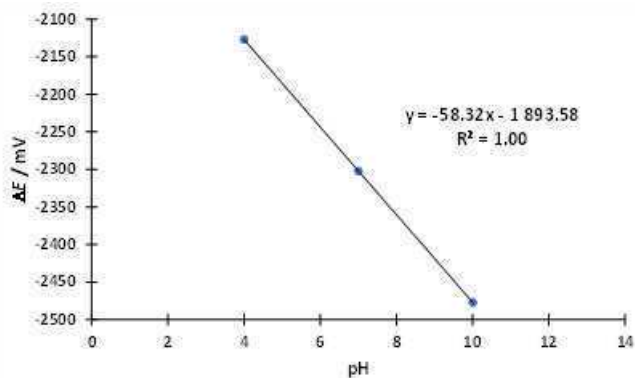
2.16 Dry cell with compressed air.

2.17 Repeat measurements with standard buffers pH 4 and pH 10.

2.18 Points from 30 min to 60 min are used for analysis.

2.19 Take the average of the chosen data points.

2.20 Plot ΔE vs pH.



Calibration graph of a glass electrode half-cell.

2.21 Obtain the slope and intercept of the glass electrode-half cell.

23 Insert the ΔpH into the ladder.

Symmetry **2020**, 12(7), 1150; <https://doi.org/10.3390/sym12071150>

Measurement

24 Repeat with a new pair of solutions.

Data analysis

20m

25 Repeat the data analysis with all the measured potentials.

26 Insert the data into the ladder.

27 Do the minimization process.

Symmetry **2020**, 12(7), 1150; <https://doi.org/10.3390/sym12071150>

28 Obtain the pH values for all the measured solutions from the minimization process.

29 Calculate uncertainty.

Analytica Chimica Acta, **2021**, 1182, 338923, doi.org/10.1016/j.aca.2021.338923