

VERSION 2
JAN 03, 2023

OPEN ACCESS

DOI:
dx.doi.org/10.17504/protocols.io.n92ld9dj8g5b/v2

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

Protocol Citation: Agnes Heering, Ivo Leito, Markus Lahe, Martin Vilbaste, John Paulo Samin 2023. Unified pH measurement v2.
protocols.io
<https://dx.doi.org/10.17504/protocols.io.n92ld9dj8g5b/v2> Version created by [Agnes Heering](#)

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Protocol status: Working
We use this protocol and it's working

Created: Jan 03, 2023

Last Modified: Jan 03, 2023

PROTOCOL integer ID:
74683

Keywords: unified acidity, pHabs, unified pH, pH

Unified pH measurement v2 V.2

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ABSTRACT

The purpose of this document is to present technical guidance of measuring $pH_{abs}^{H_2O}$ difference ($\Delta pH_{abs}^{H_2O}$ value) between two solutions by differential potentiometry in a cell with two compartments connected by a salt bridge filled with an ionic liquid.

MATERIALS TEXT

The ionic liquid triethylpentylammonium bis(trifluoromethylsulfonyl)imide $[N_{2225}][NTf_2]$ salt bridge has to be used.

BEFORE START INSTRUCTIONS

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

Software

- 1 Start Quick IV Measurement Software.

Note

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”.

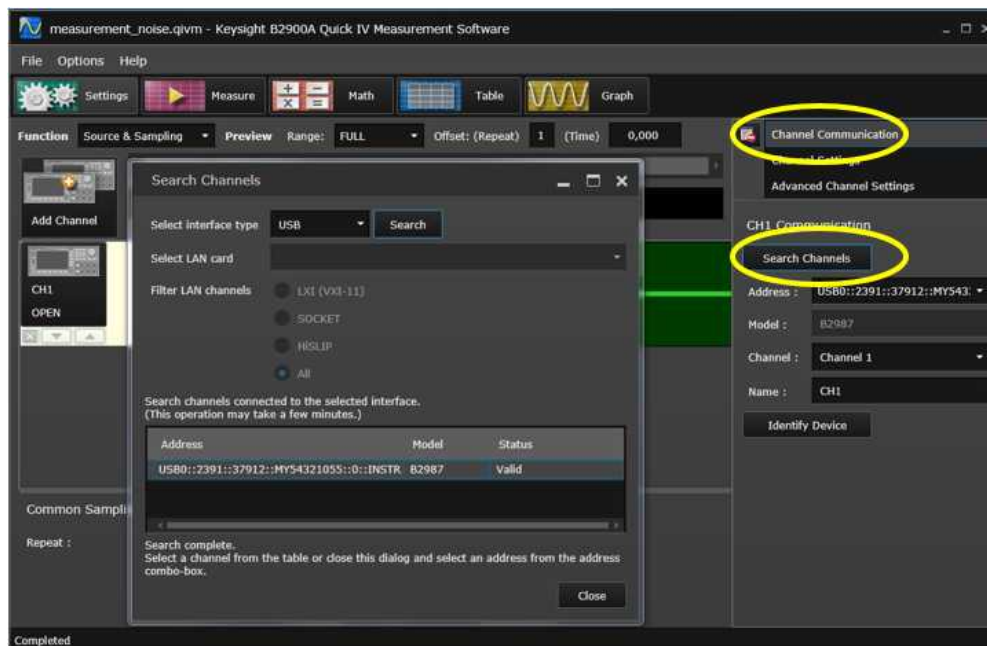


Position of the Function choice “Source & Sampling”.

Note

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.

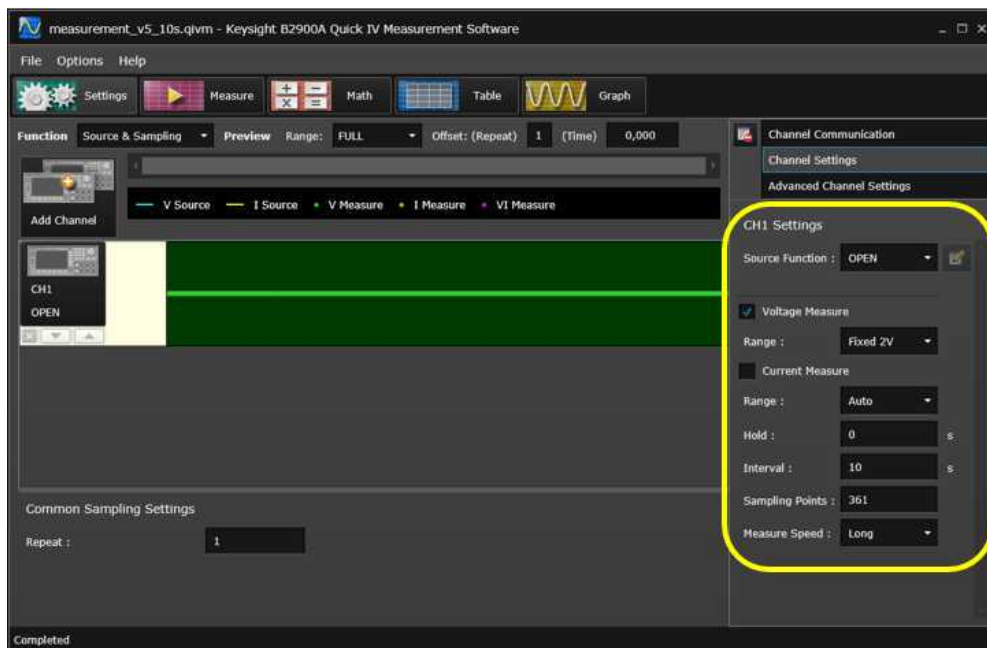


Position of the tabs “Channel Communication” and “Search Channels”.

Note

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



Cell from Gebr. Rettberg GmbH.

25.0 °C

Equipment

VistaShield	NAME
Faraday cage	TYPE
Gamry	BRAND
VistaShield	SKU

Equipment


UT cell	NAME
Special water-jacketed glass cell	TYPE
Rettberg	BRAND
Glass cell	SKU

Equipment

CORIO CD-200F	NAME
Refrigerated / heating circulator	TYPE
Corio	BRAND
9012701.03	SKU
https://www.julabo.com/en/products/refrigerated-circulators/refrigerated-heating-circulators/corio-cd-200f	LINK

Note


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 bottoms of the measurement compartments.  0.1 mL

2m

Note

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 synchronously.  20 mL both test solutions

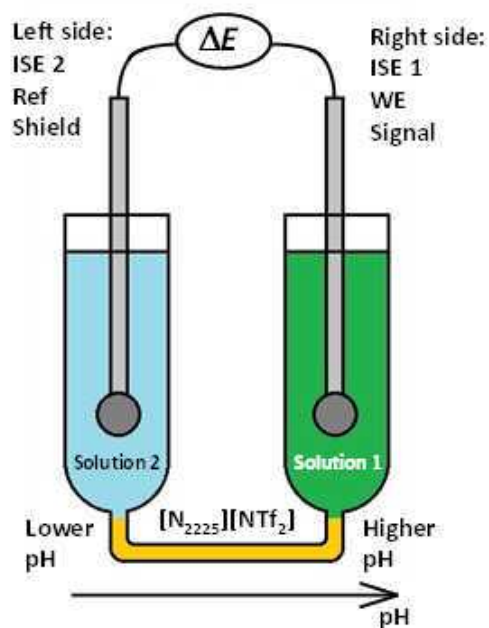
2m

Note

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.

Note

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

Equipment

EST-0601

NAME

Glass electrode half-cell

TYPE

Izmeritelnaya tekhnika

BRAND

EST-0601

SKU

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

10 Connect electrodes to the instrument.

Equipment

B2987A Electrometer / High Resistance Meter

NAME

Electrometer

TYPE

Keysight

BRAND

B2987A

SKU

<https://www.keysight.com/zz/en/home.html>

LINK

- 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.

Note

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

Equipment

N1415A Triax to Alligator Cable	NAME
Cable	TYPE
Keysight Technologies	BRAND
N1415A	SKU
https://www.keysight.com/zz/en/product/N1415A/triax-alligator-cable-200-v-1-5-m.html	LINK

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.

1h




- 13 Save data. Files are named as Date_ISE1_Solution1_vs_ISE2_solution2.

Note

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 most stable 15 min is used. The standard deviation of the points must be ≤ 1 mV and the drift ≤ 4 mV/h. Otherwise the measurement is left out from minimization.
- 21 Take the average of the chosen data points.

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

Protocol

 NAME
Calibration of glass electrode half-cells

CREATED BY
Agnes Heering

PREVIEW

22.1 Start Quick IV Measurement Software.

Note

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”.

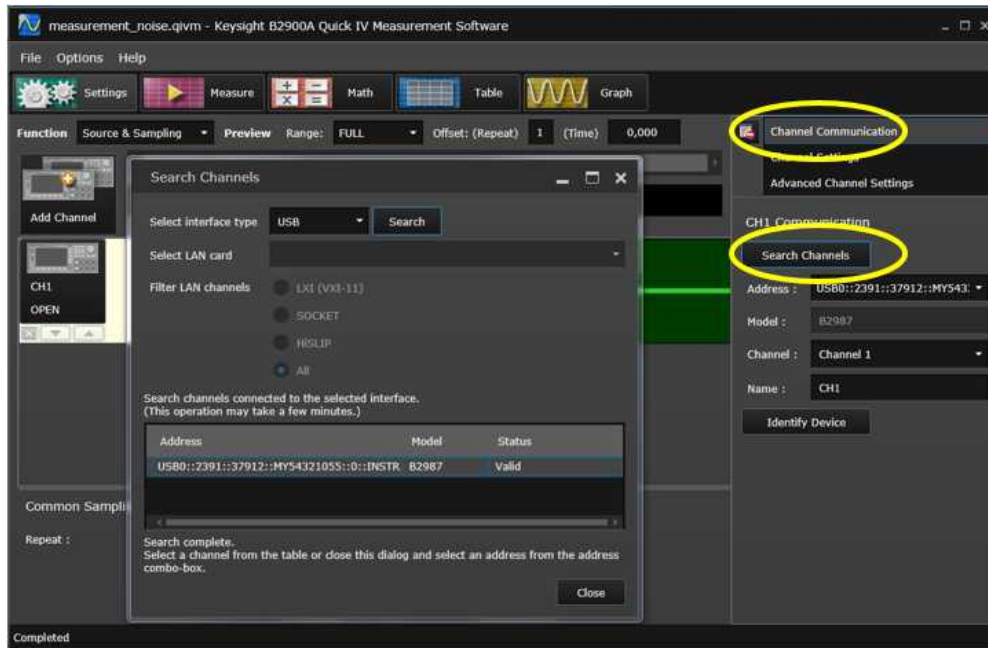


Position of the Function choice “Source & Sampling”.

Note

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.

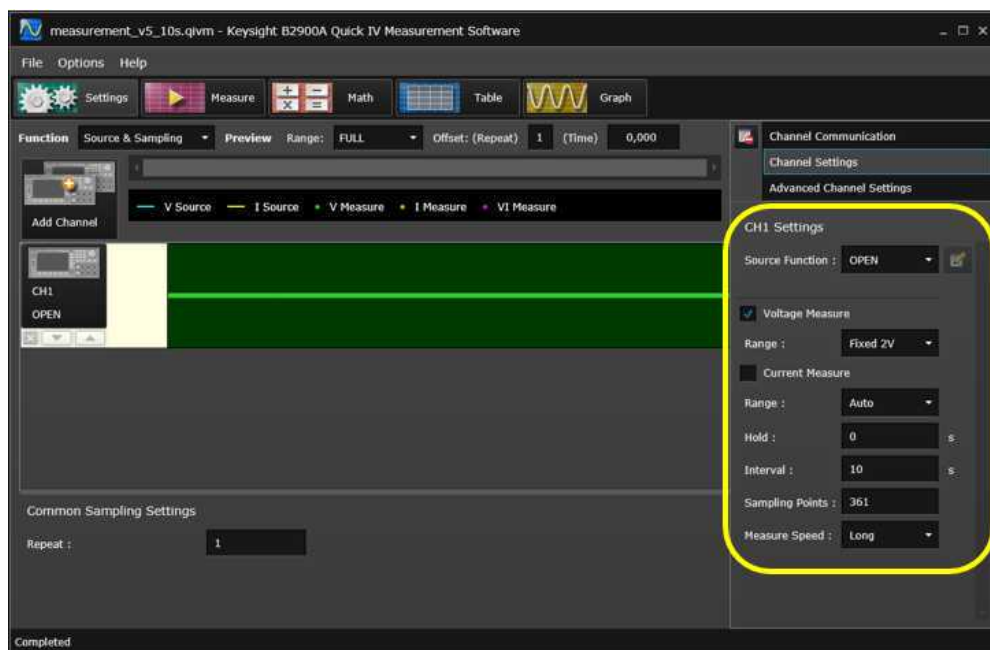


Position of the tabs “Channel Communication” and “Search Channels”.

Note

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.

Note

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



Special water-jacketed glass cell from Gebr. Rettberg.

🌡 25 °C

Equipment	
UT cell	NAME
Special water-jacketed glass cell	TYPE
Rettberg	BRAND
Glass cell	SKU

Equipment	
VistaShield	NAME
Faraday cage	TYPE
Gamry	BRAND
VistaShield	SKU


Equipment	
U2c	NAME
Thermostat	TYPE
MLW	BRAND
U2c	SKU

Note

The side ports must be open.

Note

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

Equipment	
K401	NAME
Calomel reference electrode	TYPE
Radiometer	BRAND
K401	SKU

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.

Equipment	
B2987A Electrometer / High Resistance Meter	NAME
Electrometer	TYPE
Keysight	BRAND
B2987A	SKU
https://www.keysight.com/zz/en/home.html	LINK

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.

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

Equipment	
N1415A Triax to Alligator Cable	NAME
Cable	TYPE
Keysight Technologies	BRAND
N1415A	SKU
https://www.keysight.com/zz/en/product/N1415A/triax-alligator-cable-200-v-1-5-m.html	LINK

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

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

1h

Note

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

22.11 Save data. Files are named as Date_GE_vs_ref_pHx.


Note


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.

22.12 Remove the electrodes.

22.13 Remove the solution.

22.14 Rinse three times with plenty of water  20 mL each

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

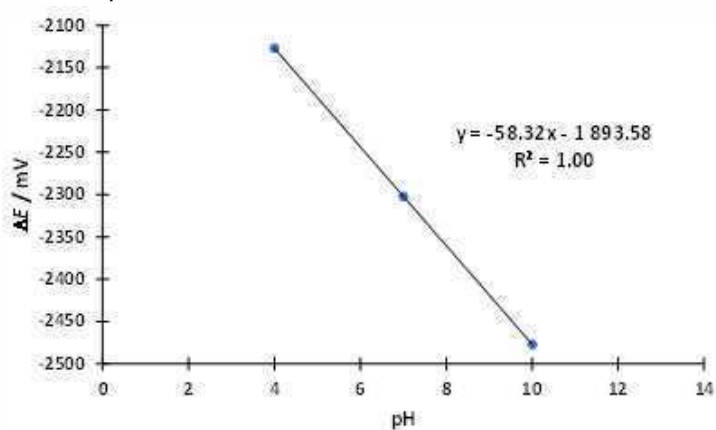
22.16 Dry cell with compressed air.

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

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

22.19 Take the average of the chosen data points.

22.20 Plot ΔE vs pH.



Calibration graph of a glass electrode half-cell.

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

23 Insert the ΔpH into the ladder.

Note

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.

Note

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.

Note

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