

Determination of pH in Non-Aqueous Solutions

A simple extraction procedure using water is recommended for measuring the pH of non-aqueous solutions containing water-immiscible solvents. Water is added and mixed thoroughly with the sample. After reaching equilibrium, the solvent phase is separated and the pH of the water phase is then measured.



Introduction

Liquids can serve as solvents to dissolve solutes (i.e., solid, liquid or gaseous) to form solutions. The most common solvent is water. Solvents other than water are called non-aqueous solvents. Some examples of non-aqueous solvents are hexane, alcohol, oil, etc. These are often mixed with water or some other non-aqueous solvents to form mixed solvents appropriate for certain applications in chemical research or industrial processes. Non-aqueous solvents that tend to mix with water to form homogeneous mixture are called water-miscible (e.g., methanol, acetone) while those which separate or form a layer when mixed with water are water-immiscible (e.g., oil, hexane, toluene).

pH measurement in non-aqueous and mixed solutions poses a number of issues such as dissociation of the solvent, different pH scale, and liquid junction potential to name a few. The typical problems encountered during measurement with pH electrodes are slow response time, unstable readings, and erroneous results. According to Frant², the electrode should have an adequate outward flow from the junction and the junction design should permit easy cleaning for optimum performance. These two key features prevent memory effects at the junction and minimize liquid junction potential.

The Sleeve ToupH 9481-10C electrode (PN 3200611631) is our recommended product for pH measurement in non-aqueous and mixed solutions. It is a refillable, double-junction, glass-body, combination pH electrode. The cable length is 1m and the connector is BNC, compatible with any pH meter that has BNC input. The movable glass sleeve allows easy cleaning of the liquid junction

and prevents clogging. The applications include testing of non-aqueous solvents, viscous solutions, and samples containing non-aqueous solvent (e.g., cosmetics, paints, etc). If a combination pH electrode with built-in temperature sensor is desired, the Sleeve ToupH 9681S-10D electrode (PN 3200585463) meets this requirement. This electrode is compatible with HORIBA pH meters only.

Solvent Miscibility and Solubility

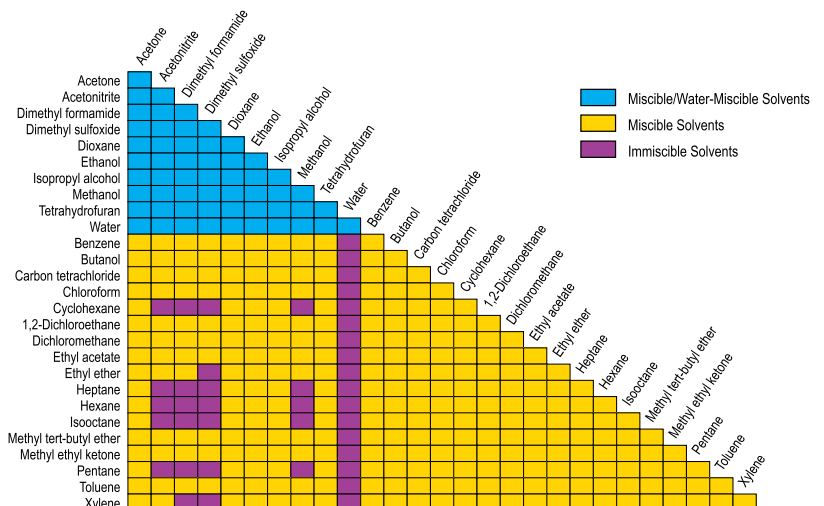


Figure 1: Solvent Miscibility and Solubility
(Source: Restek <http://www.restek.com/techtips/Solvent-Miscibility-and-Solubility>)

Continued at the back

Method

Calibrate the meter and electrode system according to manufacturer's instructions with at least two pH buffers that bracket the expected sample pH.

Sample Preparation And Measurement

The method described below is based on US EPA Method 9045D.

1. Add 20ml of water to 20g sample in a beaker or container. Cover and stir for 5 minutes.
2. Let the solution stand for 15 minutes or centrifuge it to allow the sample and water to separate.
3. Measure the pH of water phase. Record the pH value and the temperature.

To obtain accurate results, standard buffer solutions and samples should be measured at the same temperature. If the electrode is coated with oily material from a sample, clean it with detergent and warm water.

Results And Benefits

As non-aqueous solvents have very low conductivity and can dehydrate the glass membrane, it is difficult to use glass electrodes in measuring pH directly. There must be some electrical conductivity through the solution and glass membrane must be hydrated to function well.

For water-immiscible non-aqueous solvents and non-aqueous solutions with water-immiscible solvents, this measurement can be accomplished by adding water as described in the method above. Pure water with very low buffering capacity and no dissolved salts should be mixed thoroughly with the solvent. Once the two phases are in equilibrium with each other, the activity of any dissolved species should be the same in both phases. After separating the solvent phase, the pH of water phase is then measured.

For water-miscible non-aqueous solvents and mixed aqueous/water-miscible non-aqueous solutions (e.g., water

and methanol), a reproducible measurement process can be achieved if the solvent background is known and constant. To do this, it is important to describe the choice of pH electrode, calibration standards, sample preparation, and electrode conditioning.

1. pH electrode

A glass-body electrode resists chemical attack. A flowing reference should be used to eliminate or minimize liquid junction problem. An aqueous filling solution may be used, but most often develops a large or unstable junction potential. This can be reduced by changing the filling solution so that it is compatible with the sample (e.g., methanol saturated with KCl, 90% glacial acetic acid plus 10% saturated aqueous LiCl).

2. Calibration Standards

Ideally, the calibration standards should have the same background as the sample. A constant solvent background may be used in testing the measuring system. A "check" standard made with dry buffer and same solvent background can be measured after calibrating the electrode/meter system in aqueous pH buffers. Its reproducibility is a good test although the reading will be different from the aqueous values. In pH measurement of non-aqueous and mixed solutions, only relative readings can be obtained.

3. Sample Preparation

The ionic strength of non-aqueous solvents can be increased by adding a neutral electrolyte such as a quaternary ammonium salt.

4. Electrode Conditioning

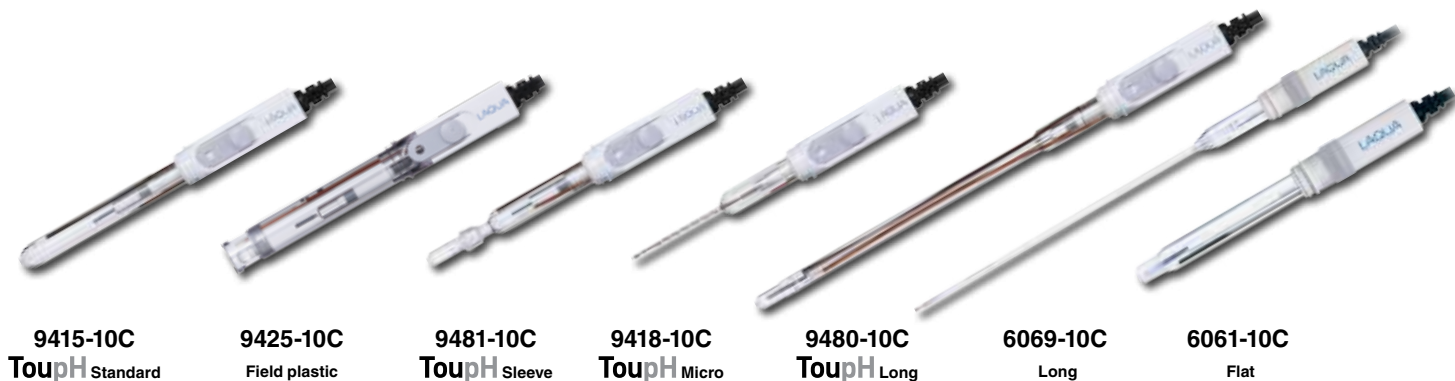
When measuring pure solvents or samples with less than 20% water, the contact time of the electrode to the sample should be kept to a minimum as solvents may dehydrate the glass membrane. Between measurements and after use, it should be soaked in buffer or KCl solution to hydrate the glass membrane. Dried electrodes can be drift and sluggish.

References And Suggested Readings

1. US Environmental Protection Agency Method 9045D Soil and Waste pH, Revision 4 November 2004
2. Frant, Martin. How to Measure pH in Mixed and Non-Aqueous Solutions. American Chemical Society, 1995
3. C. Westcott. pH Measurements. Academic Press Inc. New York, USA, 1978

REV 1.0, 9 September 2015

LAQUA pH Combination Electrodes Lineup



9415-10C
ToupH Standard

9425-10C
Field plastic

9481-10C
ToupH Sleeve

9418-10C
ToupH Micro

9480-10C
ToupH Long

6069-10C
Long

6061-10C
Flat



<http://www.horiba-laqua.com>

Horiba Instruments (Singapore) Pte Ltd
83 Science Park Drive, #02-02A,
The Curie, Singapore 118258
Tel. +65 6908 9660
E-mail: laqua@horiba.com

IMS

HORIBA Group is operating Integrated Management System (IMS)
ISO9001 JOA-0298 / ISO14001 JOA-E-90039 / ISO13485
JOA-MD0010 / OHSAS18001 JOA-OH0068

