TECHNICAL NOTE

Electrochemistry **October 2013**

Measuring a pH value is doing ultra-trace analysis

With a pH meter and pH electrode everybody can check the pH value of a solution. Whether the sample has a pH value of 1, 7 or 13 makes no difference for the measurement procedure. With actual measurement devises and sensors it is normal to have a resolution of the pH value of 0.01 or 0.001.

If a pH value of 12.0 is measured with a standard deviation of ±0.1 pH, it is seen as inaccurate measurement. But, what is really measured in such a solution?

The pH value is defined as negative logarithm (base 10) of the H^+ ion activity (a_{H+}), which can be simplified by H^+ ion concentration (C_{H+}):

$$pH = - \log a_{H+}$$

or easier as

$$pH = - \log C_{H+} .$$

Therefore a pH value of 12.0 is equal to a H^+ ion concentration of 10^{-12} mol/L.

pH = 12.0 -> $C_{H+} = 10^{-12}$ mol/L.

The concentration of 10^{-12} mol/L is equal to 0,000 000 000 001 mol/L or „pico mol/L“. With the atomic mass of 1 g/mol there is only 1 pico g/l H^+ ions in the sample.
From micro gram per liter (µg/L) trace analysis starts and after nano gram (ng/L) follows the ultra-trace analysis area (pico- and femto gram). For getting the lowest concentrations, complicated and expensive analysis systemts (e.g. MS, GC, ICP)* are necessary, for which extensive trainings are available to enable the handling and correct use of such high tech apparatus.

** MS = mass spectroscopy*
GC = gas chromatography
ICP = Inductively Coupled Plasma

With this said, the pH measurement gets into a new light. Which possibilities the pH glass sensor offers, will be clearer, if we consider the large measurement range of more than 10^{14} mol/l H^+ ions (1 mol/L H^+ down to 10^{-14} mol/L). Which other analysis method can cover such a measurement range without sample preparation and huge analytical and technical efforts?

A buffer solution of pH 7.0 contains µg/L H^+ ions (10^{-7}) and same amount of OH^- ions, the solution reacts „neutral“. An alkaline solution of pH 14 contains only 10^{-14} H^+ ions in a superior number of 1 mol/L OH^- ions.

The pH glass electrode is an excellent, very specific sensor for hydrogen ions. The handling is very easy and without specific knowledge, even untrained staff can do pH measurements.
However, it is important to know that the „simple“ electrode, which just measures in a water sample, is an high tech sensor.

10^{-3} milli (0,001)
10^{-6} micro (0,000 001)
10^{-9} nano (0,000 000 001)
10^{-12} pico (0,000 000 000 001)
10^{-15} femto (0,000 000 000 000 001)

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