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Measurements of pH under extreme conditions

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Abstract

pH is an important parameter of water solutions to determine in several studies, including the astrobiological ones. Large amount of reactions are controlled by this physical-chemical parameter, from biological reactions to redox processes involving transition metals. Its behaviour under standard condition is comprehended theoretically and experimentally, but not under certain extreme conditions: e.g. at high pressure that may exist at deep terrestrial ocean, or in the aqueous reservoirs within icy satellites. Here, we describe the testing analysis that we are carrying out concerning an instrument based on a spectrometric method to measure pH at high pressure (HPSpH, High Pressure Spectrometric pH-meter), which is selected among others due to its possibilities for future space exploration.

1. Introduction

Over time, a diverse set of methodologies to measure pH has been developed. Basically, these methodologies can be classified in electrometric and spectrometric methods.

As part of the electrometric methods, there are the potetiometric ones, which the most popular is the glass electrode. However, there are new types of probes such as solid-state electrodes [1] or ISFET sensors (Ion Sensitive Field Effect Transistor) [2]. Among the electrometric methods, it has been reported the use of conductimetric measurements to obtain the pH under conditions of high pressure [3].

Spectrometric/colorimietric methods avoid some interferences with metal ions that are often in electrometric methods and can be classified in two main groups depending on the type of the dye and the possibility of its immobilization: 1) Methods that has the dye immobilized. Examples are pH strips or other ones that immobilize the dye in a gel matrix. Both allow recovering the original sample after the pH of the sample is measured. 2) Methods that has the indicator in solution, such as the classical titration. Examples of dyes are the phosphorescent and fluorescent ones [4, 5]. There are several adaptations of these methods to high pressurized conditions [6].

As the water solution moves away from standard conditions, e.g. increasing pressure, the determination of pH becomes more complicate.

The chemical behaviour of water is not well understood at high pressure, specially the variation of the dissociation constant, which increases with pressure. Due to that, the pH of a neutral solution may be below 7, and then the reference for acidity and basicity changes [7].

A common technical difficulty is related to unavailable calibration buffers working far from the standard conditions. Consequently, an approximation to correct the pH value is used, being that a source of error. Potentiometric methods need stable reference electrodes, which may change their behaviour under extreme conditions. They also have problems with liquid junctions. Particularly, the glass electrode is not a valid technique due to glass fragility under pressure.

For our purposes, a colorimetric technique is chosen to be tested, although spectrometric methods may suffer displacement of the bands or/and in the equilibrium.

2. Methodology

Buffer solutions of pH from 1 to 12 are prepared using lab reagents and adjusted with HCl or KOH. A Crison GPL-21 pH-meter with a glass electrode is used to check the reference values of the pH.

Testing experiments are carried out in a high pressure chamber equipped with a sapphire window and surrounded by a rubber tube connected to a thermostating bath to maintain the temperature constant. High pressure is generated with a 7615 Ruska compressor, using water as the pressure transmitter fluid.

pH is measured using an Ocean Optics RF200-UV-VIS system with an optic fiber and a novel reflective patch attached to the sapphire window, which has the dye immobilized in a gel matrix. The tungsten halogen light probe is outside the chamber. The spectra is recorded in intensity (Fig. 1) and then transformed to absorbance taking the spectra of pH=1 as the initial intensity, I_0, (Fig. 2) by using the equation: $A=-\log(I/I_0)$ where A is absorbance. Testing is accomplished at both, atmospheric and high pressure.

3. Results

We confirm that the HPSpH may have some advantages for a space mission such as longer spaced recalibration times than other methods, low chemical and optical interferences (as turbid solutions), unnecessary sample pretreatment, it is not destructive, not contaminant, has small size and might share some of its components with other optical techniques. Some inconveniences that should be solved are: the equilibration time measured at 293K and 1 atm. is approximately 45 minutes. The precision decreases as long as the pH takes values farther from the pKa of the dye. Below, the spectra of a water solution buffered at several pH, which is used to make the calibration of a dye are shown. (theoretical pKa of 6.17)

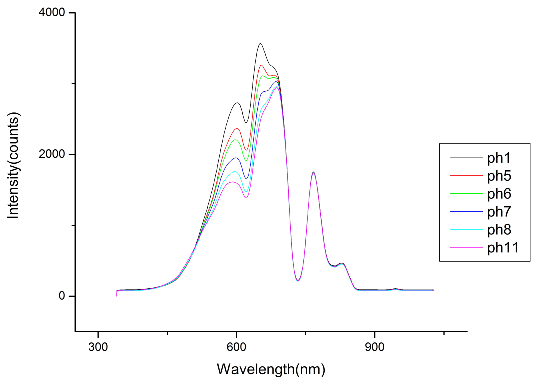

Figure 1: Intensity spectra of several pH-buffered water solutions

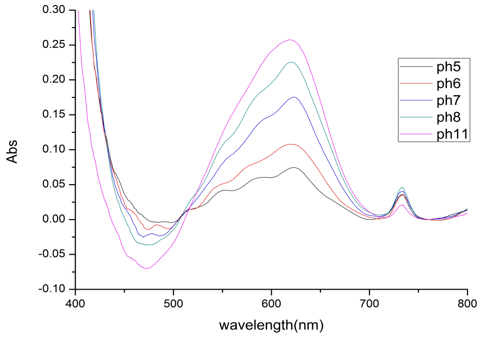

Figure 2: Absorbance spectra of several pH-buffered water solutions

4. Conclusions

An instrument to measure in situ the pH from liquid samples in water-rich planets is envisioned to be performed. HPSpH, a non-intrusive spectroscopic method to measure pH is helping to understand how extreme conditions affect the physical chemistry of planetary aqueous solutions. We are checking the feasibility of the instrument at high pressures measuring some samples of natural waters with interfering compounds, such as metal ions. Tests are being carried out at atmospheric and high pressure.

Acknowledgements

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