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# NEAR INFRARED SPECTROSCOPY FOR pH MONITORING IN $CO_2 + H_2O$ SYSTEMS

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## Abstract

Oil production presents considerable technological challenges, especially due to the high concentration of carbon dioxide ($CO_2$). The decrease in solubility in the aqueous phase causes changes in the chemical properties of the water, resulting in an increase in pH. Furthermore, the presence of $CO_2$ in reservoirs can increase the risk of corrosion in equipment and pipes. Thus, pH monitoring helps maintain control in industrial processes. Near-infrared (NIR) spectroscopy is a promising method for measuring pH in aqueous systems. This approach enables real-time monitoring without the need for sampling systems in harsh environments, such as those subjected to high pressures and temperatures. In this context, this study investigated the influence of pH (acid) in a $CO_2 + H_2O$ system under different temperature conditions (313.15 to 333.15 K) using spectroscopic and electrometric techniques. These techniques were used as a reference for calibrating the data obtained via NIR. The results indicate that the variation in absorbance spectra is associated with changes in the pH of the system. This shows the sensitivity of the technique in detecting different levels of acidity in an aqueous solution, allowing better control of the dynamic mechanisms of the process.

## Keywords

NIR; pH; $CO_2 + H_2O$; Monitoring.

## Introduction

The pH in aqueous solutions decreases because of the dissolution of $CO_2$ and the formation of carbonic acid in the petroleum reservoir, especially due to $CO_2$ injection. This variation in pH can trigger corrosion in metallic materials in oil and gas wells and cause mineral dissolution or precipitation in saline systems, resulting in fouling in pipelines that transport water from oil fields [1-2].

Several studies have investigated the behavior of pH in aqueous systems containing $CO_2$ at different temperatures and pressures. Toews et al. (1995) [9] used UV-vis spectroscopy to determine the pH of the $CO_2 + H_2O$ system at pressures of up to 200 bar and temperatures of 343 K. Peng et al. (2013) [10] evaluated the behavior of pH in a $CO_2 + H_2O$ system at temperatures ranging from 308.15 to 423.15 K and pressures of up to 150 bar using pH electrodes coupled to a high-pressure equilibrium cell.

A promising alternative is the use of spectroscopic techniques in the near-infrared region for real-time monitoring of processes in flow systems [10]. This technique is based on the absorption of light in the visible range, which provides information on the identification and analysis of compounds and their molecular structures [3-7]. The information contained in an NIR spectrum can be used to monitor the concentration of a substance or to estimate a physical property, whenever these may result in changes in the intensity and/or wavelength of the spectral characteristics generated by the sample.

Therefore, this study proposes the development of a methodology that allows the evaluation of pH values in $CO_2 + H_2O$ systems at different temperatures (313.15 to 333.15 K) and ambient pressure using the NIR real-time monitoring technique.

Calibration studies of the spectrophotometer as a function of $CO_2$ concentration will be conducted using an acid-base indicator simultaneously with the pH probe.

# Methodology

## Experimental Setup

Experiments to evaluate the sensitivity of the NIR spectrophotometer to pH variations were conducted in a glass-jacketed reactor with an internal diameter of 10 cm, a height of 11 cm, and a useful volume of approximately 450 mL. The system temperature was monitored using an ultrathermostatic bath (Quimis, Q214M4) with an accuracy of ± 0.5 K. The measurement method was performed using a transfectant with an optical path of 1 mm, which combines transmission, scattering, and beam reflection signals because the emitted light crosses the sample twice. The NIR probe was connected to the spectrophotometer using optical fibers. The NIR equipment (*Thermo Fisher Scientific*, Antaris *MX Process Analyzer*) is specific for analysis in the spectral range of 14000 to 3800 $cm^{-1}$ (714 – 2631 nm).

## Experimental Procedure

The experiments were conducted in systems containing $CO_2$ + $H_2O$ at different temperatures.

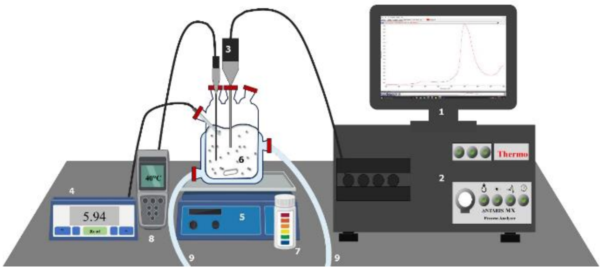

**Figure 01.** Schematic diagram of the unit for pH measurement: [1] Computer; [2] Near-infrared spectrophotometer; [3] Near-infrared spectrophotometer probe; [4] pH meter; [5] Magnetic stirring plate; [6] Reactor; [7] Indicator; [8] Thermocouple; [9] Thermostatic bath.

After reaching the desired temperature, the ultrapure water was continuously stirred at 240 rpm for approximately 5 min. The titrant agent (colorimetric indicator) was then added. The effects associated with the presence of the indicator on the absorption spectra, i.e. the location of the baseline, were normalized for the analyses. At the end of each stabilization period, 2 spectra per second were found by the spectrophotometer, with a resolution of 8 $cm^{-1}$. Each set of spectra consists of 1170 data points for each sample, obtained from the absorption values resulting from the variation of the pH of the medium. The NIR experiments were performed at temperatures of 313.15 K and 333.15 K, under ambient pressure. All tests were performed in duplicate.

# Results and Discussion

The experimental results obtained through spectroscopic and electrometric techniques highlight the importance of NIR spectroscopy in monitoring pH variations different temperatures and under ambient pressure, as illustrated in Figure 02. During the pH variation tests using ultrapure water, the occurrence time ranged from 90 to 120 min, with longer test times being associated with higher temperatures (333.15 K). In fact, increasing the temperature reduced the solubility of $CO_2$ in the medium, which altered the balance of acid-base reactions. In addition, hydrogen ions ($H^+$) and hydroxyl ions ($OH^-$) are in equilibrium:

$$H_2O \rightleftharpoons H^+ + OH^-$$

The temperature can vary the balance constant of this, thus influencing the occurrence and pH of the solution. Absorption peaks in the range of 5900 to 7500 $cm^{-1}$ occur due to the O-H stretching of water molecules, originating from the presence of $CO_2$ in the medium [12]. This analysis is essential for interpreting the spectra and studying the effects of variables such as temperature, pressure, and pH on the molecular molecular interactions in the sample.

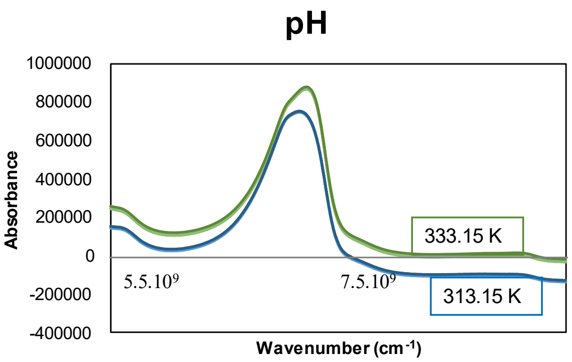

**Figure 02.** NIR spectra of the $CO_2$ + $H_2O$ system collected at different pH values (4 to 6), temperatures (313.15 and 333.15 K), and atmospheric pressures.

The higher absorption observed at 333.15 K curve compared to that at 313.15 K can be attributed to a greater attraction between water molecules and a higher concentration of $CO_2$, resulting in a greater energy absorption [14]. In addition, higher temperatures can increase the dissociation of carbonic acid into $H^+$ and $CO_3^-$ ions, further affecting absorption. Temperature can also influence the dynamics of intermolecular and intramolecular bonds in water, increasing the energy absorption in the NIR region [13]. This effect occurs because, with increasing temperature, there is an increase in the kinetic energy of water molecules, leading to a greater probability of vibrational transitions and molecular rotations that contribute to the absorption of energy.

An analysis of the spectra acquired in the acidic pH range using $CO_2$ to acififdiy the medium, revealed a significant influence on absorption. The structural changes of the $CO_2$ with pH variations, whether protonated at low pH or diprotonated at high pH, directly affect the observed peaks.

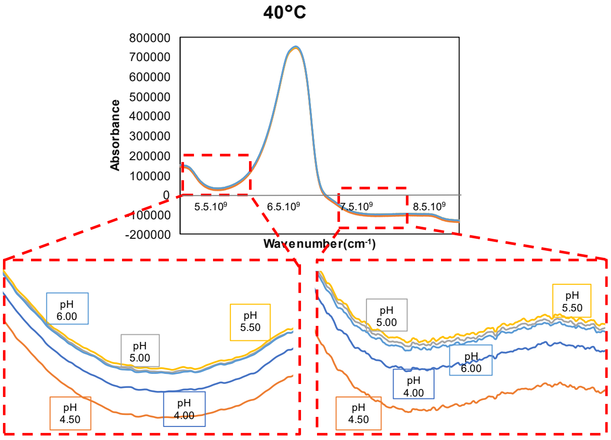

**Figure 03.** NIR Spectra of ultrapure water saturated with $CO_2$ at 313.15 K and atmospheric pressure: pH 4.00 (**-**), pH 4.50 (**-**), pH 5.00 (**-**), pH 5.50 (**-**) e pH 6.00 (**-**).

The nonlinearity in the results, which appeared between the data for pH 4.5 and pH 6, can be explained by the variation in the concentration of $CO_2$ in the medium and incomplete dissociation of carbonic acid, the presence of specific species, and the complexity of the spectral responses to pH changes.

The results revealed changes in pH values in response to $CO_2$ addition. It is important to note that all spectra were corrected to the baseline between the ranges of 5109 to 9109 $cm^{-1}$. These results confirm the solutions and efficiency of NIR spectroscopy as a robust analytical technique for real-time monitoring and prediction of pH variations in chemical responses under different temperatures and compositions of saline solutions. The proposed methodology has shown promise for the construction of spectral database for system limitation and is reliable for future analytical applications for monitoring and controlling corrosion processes in the oil industry.

## Conclusions

Given the results obtained in this investigation, the effectiveness of NIR spectroscopy stands out as a tool for monitoring and controlling pH variations in aqueous systems. NIR's sensitivity in capturing subtle changes in pH values, along with the ability to provide real-time measurements, highlights its usefulness in industrial applications, such as the petroleum industry, where accurate maintenance of pH is critical to avoid problems such as corrosion and incrustation. These results provide a solid foundation for the continued development of analytical techniques and process control strategies, contributing to significant advances in the efficiency and safety of industrial operations

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## Responsibility Notice

The authors are the only ones responsible for the content of this paper.

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