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RESEARCH PAPERS

THE DETERMINATION OF THE LEVEL OF BICARBONATE, CARBONATE, OR CARBON DIOXIDE IN AQUEOUS SOLUTIONS

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ABSTRACT

A rapid and convenient method for the measurement of bicarbonate, carbonate, or carbon dioxide in water was developed using fourier transform infrared spectroscopy (FTIR). Bicarbonate and carbonate are converted to carbon dioxide by lowering the pH of the solution, then the absorbance of the dissolved carbon dioxide at 2345 wavenumbers is measured using a liquid sample cell. If the measurement of dissolved carbon dioxide is the objective, the pH is not adjusted, and the carbon dioxide in the free form can be measured without interference from low levels of carbonates. The method is linear from 10.48 ppm to a minimum of 366.8 ppm carbon dioxide (r squared = 0.9996). The coefficient of variation at 10.48 ppm (LOD @ 3x signal/noise), 52.4 ppm, and 262 ppm is 45.6, 4.0, and 3.9, respectively. The average percent recovery at 10.48 ppm, 52.4 ppm, and 262 ppm is 74.5, 104.2, and 104.0, respectively.

INTRODUCTION

The need to measure the level of bicarbonate, carbonate, or carbon dioxide in aqueous solutions spans many applications. Environmental issues require the measurement of the level of carbon dioxide in seawater[1,2]. The level of carbonate, bicarbonate, or carbon dioxide in detergents[3], effervescent bath tablets[4], and pharmaceutical preparations can be critical to the performance of the product. Carbon dioxide gas, which is generated by acidification of carbonates and bicarbonates, is used to disperse ingredients in cold tablets, antacids, and denture cleansers, as well as bath additives. In addition to dispersing ingredients, the dissolved carbon dioxide may have beneficial physiological properties[4].

Effervescence is produced from the neutralization of carbonate and bicarbonate by acid. The level of carbonate, bicarbonate, and carbon dioxide in effervescent solutions are related by pH as shown in Figure 1. Carbon dioxide can be dissolved into water up to the saturation level, which is 38.4 mM (1690 ppm) at 20 degrees C. The actual amount dissolved depends on factors such as water temperature[5] (see Figure 2), volume and depth, and bubble size[12].

Bicarbonate and carbonate are active ingredients in pharmaceutical preparations such as antacids. Techniques for the measurement of the level of these compounds are therefore required. Frequently the assay of the raw material or analysis of the finished product involves sample preparation followed by titration. These techniques can be time consuming and may involve the use of hazardous materials such as barium hydroxide.

Recently, methods for the analysis of carbon dioxide gas evolved from effervescent pharmaceutical preparations were reviewed and compared[6]. Gravimetric, volumetric, and gasometric methods were described, and precision and accuracy data were presented. In addition, approximate time of analysis was reported. In several cases, the methods were modified or expanded to determine the level of carbonates in the preparation. Several methods either lacked precision or accuracy requirements, or were too time consuming for routine use.

Although reported methods for the analysis of dissolved carbon dioxide can be sensitive, accurate, and precise, they are often time consuming and difficult to perform. Several articles have been published describing carbon dioxide gas selective electrodes[3,7]. This approach can yield satisfactory results, but the electrodes are often unreliable and difficult to maintain. Infrared gas analyzers[1] produce good results, but specialized and custom equipment is required to perform the analysis. Also, a variety of wet methods[2,8,9] are available, but they are time consuming and may lack the required sensitivity or precision for a particular application. An FTIR method for the analysis of carbon dioxide in water has been reported[10], but its use was not extended to bicarbonates or carbonates, and no accuracy or precision data were available.

This paper describes an FTIR method for the analysis of bicarbonate, carbonate, or carbon dioxide in water which requires a benchtop FTIR with a liquid cell and minimal sample preparation. The data

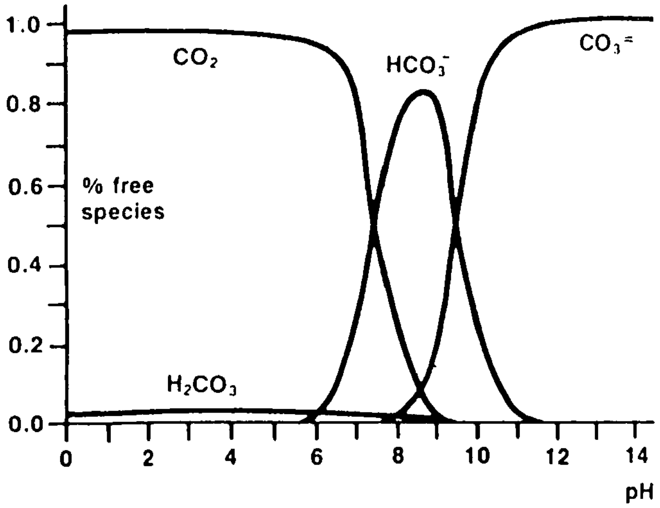


Figure 1
Fraction of Carbonate, Bicarbonate, and Carbon Dioxide as a Function of pH[11]

acquisition time per sample is about eight minutes, less than all of the methods referenced above. The method can be used to analyze for bicarbonate or carbonate in aqueous solutions by adjusting the pH (see Figure 1), or for free carbon dixoide without pH adjustment. Should more than one species be present, the sample can be analyzed for carbon dioxide prior to acidification to convert the bicarbonate and carbonate to carbon dioxide, then the amount of carbon dioxide and carbonate/bicarbonate determined by difference.

EXPERIMENTAL SECTION

Apparatus

All experiments were performed using a Mattson Galaxy Series 5000 FTIR with WinFirst data acquisition software. A Balston 75-62 FTIR purge gas generator was used to eliminate carbon dioxide interference from the air. A Spectra-Tech FTIR demountable liquid cell kit with barium flouride cell windows and a 0.2mm cell gasket was employed.

Instrument conditions:

# of scans = 250
resolution = 4 wavenumbers

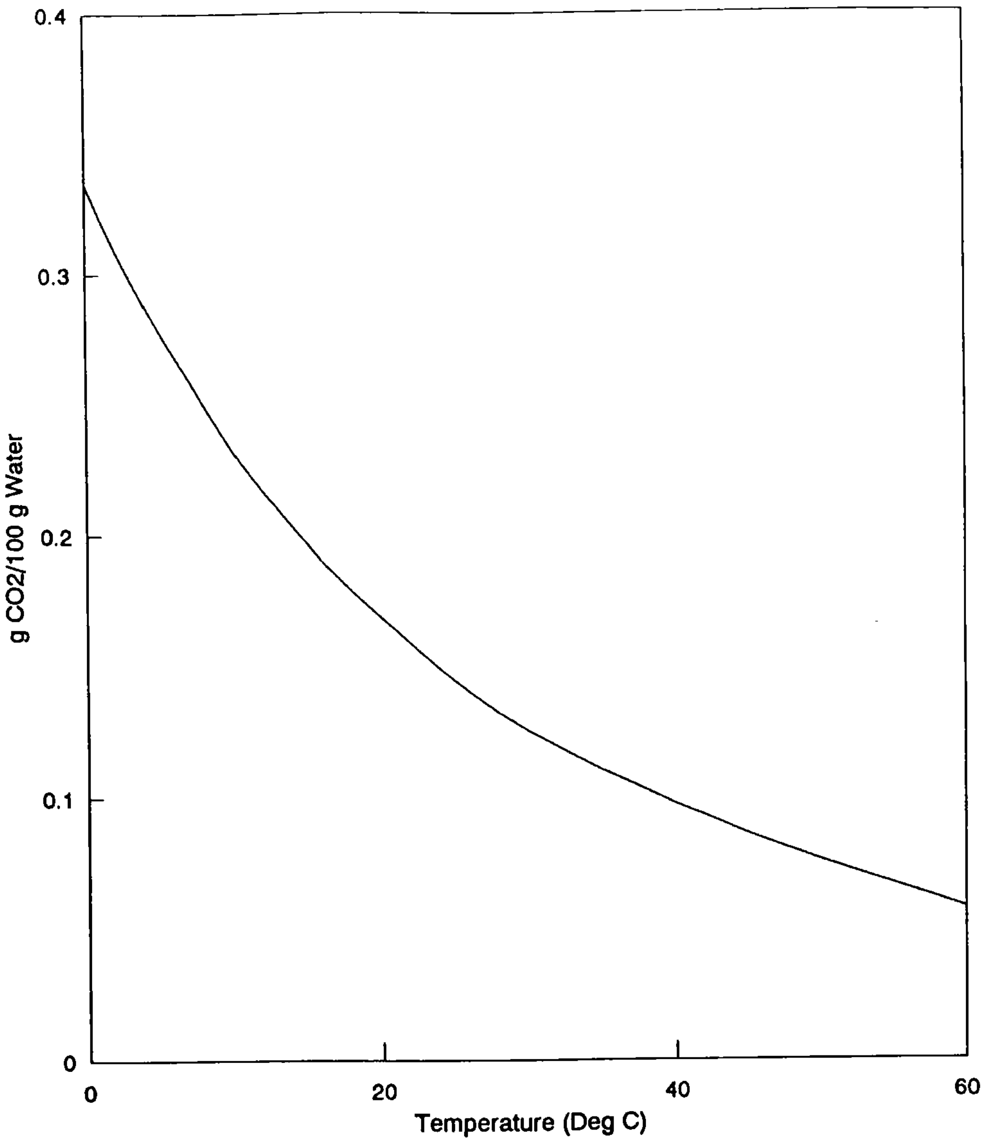


Figure 2
CO_2 Saturation Level vs. Water Temp.

signal gain = 10
spectra collected in absorbance mode
fwrd mirror velocity = 3.6 kHz
rev mirror velocity = 20.0 kHz
spectra collected in fwrd scan direction
starting frequency = 2200 wavenumbers
ending frequency = 2250 wavenumbers.

Reagents

Standards were prepared from analytical reagent grade anhydrous sodium bicarbonate purchased from Mallinckrodt. Sodium citrate/hydrochloric acid buffer (pH = 3) solution was prepared from USP/FCC grade citric acid received from Archer Daniels Midland, sodium hydroxide pellets purchased from Mallinckrodt, and 0.1N hydrochloric acid prepared from 37 percent acid purchased from Mallinckrodt. All solutions were prepared using helium sparged HPLC grade water (water).

Sodium citrate buffer solution (0.1M) was prepared by combining 9.605g of citric acid and 4.0g of sodium hydroxide into a 500 ml volumetric flask and diluting to volume with water. The final solution was prepared by combining 45 ml 0.1N hydrochloric acid and 55 ml of sodium citrate, and adjusting to pH 3 with either reagent as necessary.

Procedure

A sodium bicarbonate stock solution was prepared by weighing to 0.0001g approximately 0.1g of sodium bicarbonate into a 100 ml volumetric flask, and diluting to volume with water. To prepare working standards, the appropriate amount of sodium bicarbonate stock solution was pipetted into a 10 ml Class A volumetric flask, 1 ml of buffer solution was added, and the solution adjusted to 10 ml with water. Sample solutions for precision and accuracy determinations were prepared similarly to 100 ml.

A background spectrum was collected using water. The solution to be analyzed was transferred to a 10 ml luer-lok disposable syringe, and introduced into the liquid sample cell. The spectrum was obtained, and the net absorbance of the carbon dioxide asymmetric stretching band at 2345 wavenumbers was determined.

RESULTS AND DISCUSSION

Samples are acidified and bicarbonate and carbonate converted to carbon dioxide because of the difficulty in analyzing specifically for bicarbonate and carbonate absorbances in the 1300-1400 cm^{-1}

region[10]. All units are expressed in terms of carbon dioxide, but they may be easily converted to the appropriate compound. Sodium bicarbonate was chosen for study because of high solubility in water and ready conversion to carbon dioxide upon acidification.

Method linearity was assessed by preparing standards over a range of 10.48 ppm to 366.8 ppm carbon dioxide. The results are shown in Table 1. Below 10.48 ppm, which is approximately 3x signal/noise, the net absorbance values become erratic. The r squared value obtained for measurements between 10.48 and 366.8 ppm is 0.9996.

Attempts were made to lower the limit of detection below 10.48 ppm by increasing the path length, but the strong absorbance of the O-H stretching band interfered with measurements at 2345 wavenumbers. To obtain the lowest detection limit, all sources of carbon dioxide must be removed during analysis. The FTIR should be equipped with a purge gas system, and all reagents must be prepared fresh using helium sparged HPLC grade water. Analysis of a water blank showed no detectable carbon dioxide. Example spectra are shown in Figure 3.

The precision of the method was determined by analyzing five replicate samples at 10.48, 52.40, and 262.0 ppm carbon dioxide. The samples were prepared in 100 ml flasks then transferred to 10 ml luer-lok syringes until analysis. As expected, the coefficient of variation (%CV) is large at the limit of detection. The %CV of the actual net absorbance measurements is 18.1, but after conversion to ppm carbon dioxide the %CV increases to 45. The first data point collected at the given concentration, plus a point at 26.20 ppm, was used for calibration purposes. The ppm carbon dioxide values were calculated based on the equation of this line. At 52.40 ppm the %CV is 4.0, and at 262.0 ppm the %CV is 3.9.

The results described were obtained with moderate cell cleaning between samples, and a single background spectrum acquired per day to maximize sample throughput. If necessary for a given application, the method precision could likely be improved with meticulous cell cleaning and more frequent background scans, perhaps every 5 samples.

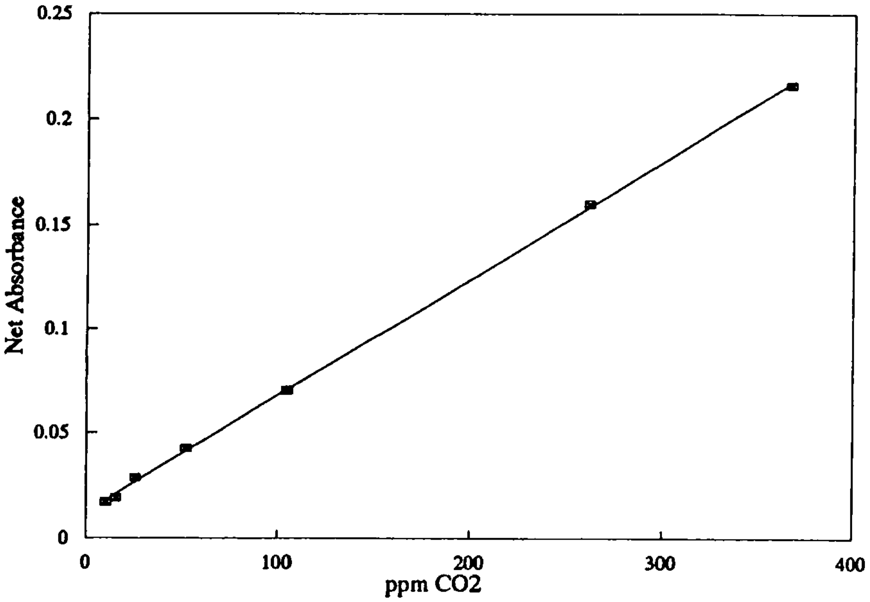
The calculated percent recovery based on least squares analysis of the calibration points ranged from 78.2 to 113.3 percent, with an average percent recovery over the linear range of 96.7 percent. The calculated recoveries of replicate analyses of samples at 10.48, 52.40, and 262.0 ppm are 74.5, 104.2, and 104.0, respectively. The percent recoveries can be improved if the expected level of carbon dioxide in water is

Table 1

Linearity of Carbon Dioxide in Water Measurements

ppm CO_2	Net Absorbance	Calculated ppm CO_2	Percent Recovery
10.48	0.0168	8.54	81.5
15.72	0.0189	12.30	78.2
26.20	0.0286	29.67	113.3
52.40	0.0425	54.57	104.1
104.8	0.0700	103.8	99.1
262.0	0.1598	264.7	101.0
366.8	0.2157	364.8	99.5

Slope = 0.000558
Intercept = 0.0120
R Squared = 0.9996



above about 25 ppm, thus not requiring points at or near the limit of detection

All samples should be stored in tightly sealed containers with as little headspace as possible. Also, they should be analyzed as quickly as possible following preparation or sampling. Samples to be analyzed for carbon dioxide are stable for at least a period of eight hours stored at ambient temperature

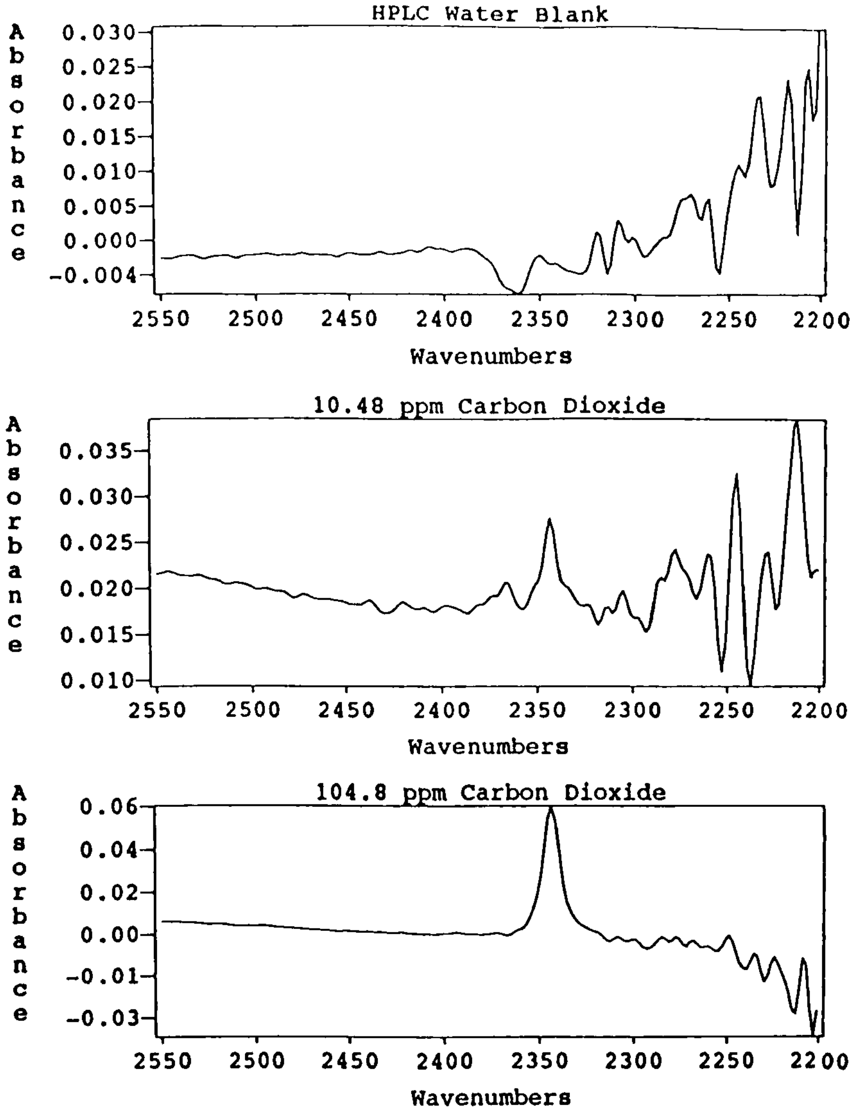


Figure 3
Example Spectra of Carbon Dioxide in Water

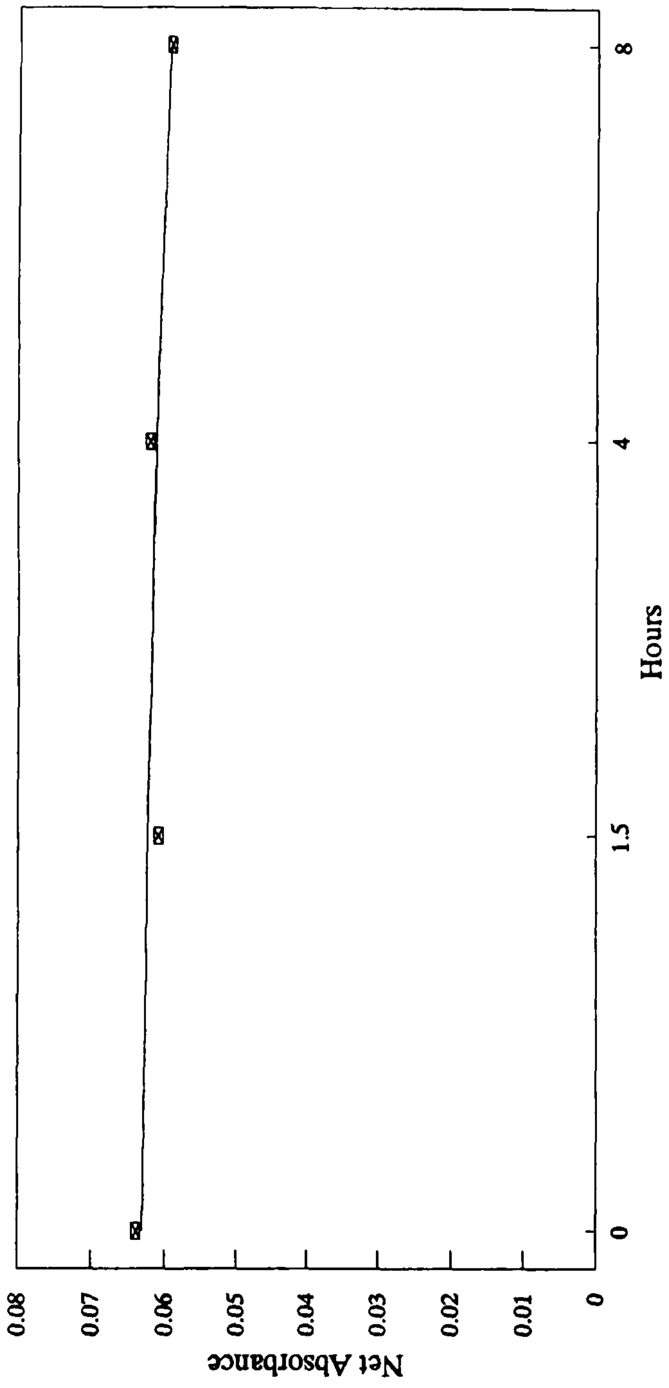


Figure 4
Stability of Carbon Dioxide in Water

under tightly sealed conditions (Figure 4). However, gas will evolve from samples, particularly those of higher concentration, after approximately 16 of storage or upon exposure to a large headspace. An absorbance band at 2370 wavenumbers, corresponding to the symmetric stretching frequency of gaseous carbon dioxide, will become more prevalent over time. Samples analyzed for bicarbonates and carbonates should be much more stable.

CONCLUSION

The FTIR method of analysis for bicarbonate, carbonate, or carbon dioxide is rapid and straightforward. Only a basic benchtop instrument, purge system, and a liquid cell are required. Some applications may require a lower limit of detection or improved precision, but for those in the capability range of this method, few methods are as convenient as the one described.

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